SIMULTANEOUS PRODUCTION OF PAPER-MAKING FIBERS AND POTENTIAL BIO-PRODUCTS FROM SUGARCANE BAGASSE

by

Ericka Figueiredo Alves

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Approved: Department of Paper and Bioprocess Engineering

_____	_____
Raymond C. Francis, Major Professor	Christopher A. Nowak, Chair Examining Committee
_____	_____
Gary Scott, Department Chair	S. Scott Shannon, Dean The Graduate School

_____

Gary Scott, Director, Division of
Environmental Resources Engineering

TO MY LOVED FAMILY

(PARA MINHA FAMÍLIA QUE TANTO AMO)

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List of Abreviattions

AFEX- Amonia Fiber Explosion

AGX- Arabino(glucurono)xylans

AHQ- Anthrahydroquinone

AQ- Anthraquinone

ARP- Ammonia Recycle Percolation

ASL- Acid Soluble Lignin

AX- Arabinoxylans

CA- Coniferyl Alcohol

CC- Crushed Cane

CDB-Carb- Chemically Depithed Bagasse with Sodium Carbonate

CSF- Canadian Standard Freeness

DHP- Dehydrogenation Polymers

EG- Ethylguaiacol

FA- Ferulic Acid

FT-IR- Fourier Transform Spectroscopy- Infrared Spectroscopy

GC- Gas Chromatography

HPLC- High-Performance Liquid Chromatography

HSQC- Heteronuclear Single Quantum Coherence

HW- Hot Water Pretreatment

IE- Isoeugenol

K/NAQ- Potassium Hydroxide (KOH) + Ammonium Hydroxide (NH_4OH) + AQ Pulping

KAQ- Potassium Hydroxide (KOH) +AQ Pulping

LCC- Lignin-Carbohydrate Complex

LSC- Light Scattering Coefficient

ML- Milled Lignin

MW- Molecular Weight

MWL- Milled Wood Lignin

N→KAQ- Pre-treatment with NH_4OH followed by KAQ Pulping

NBO- Nitrobenzene Oxidation

NMR- Nuclear Magnetic Resonance

p-CMA- Coumaryl Alcohol

p-CMAc- Coumaric Acid

PhOH- Phenolic Hydroxyl Group

QM- Quinone Methide

SA- Sinapyl Alcohol

SAQ- Soda Anthraquinone Pulping

UV- Ultraviolet

VG- Vinylguaiacol

VP- Vinylphenol

WDB- Water Depithed Bagasse

Abstract

E.F.ALVES. Simultaneous Production of Paper-Making and Potential Bio-Products from Sugarcane Bagasse, 192 pages, 33 tables, 88 figures, 2011.

The aim of this research project was to investigate the scientific and technical feasibility of making unbleached pulp by cooking bagasse with anthraquinone (AQ) in conjunction with KOH or KOH and NH_4OH. The NH_4OH could be used as a pretreatment or in the cooking stage. The design called for recovery of some NH_4OH by distillation but no recovery of KOH. Bagasse was delignified much more rapidly by KAQ (KOH + AQ) or SAQ (NaOH +AQ) cooking as compared to most hardwoods. When 15 mesh, solvent extracted bagasse and sugar maple were treated to SAQ delignification to a H factor of 441, bagasse pulp was obtained with kappa number 10.1 as compared to 44.5 for sugar maple. The non-syringyl fraction of bagasse lignin was found to contain 67% more uncondensed β-O-4' dimeric units compared to sugar maple. It was observed that if 23% KOH on depithed bagasse was used at 12:1 liquor to biomass ratio, a pulp with unbleached kappa number of 12.6 and excellent bleachability was obtained. Pretreatments were investigated and an A→N→KAQ sequence merits further investigation (A=acid treatment to end pH 4.0→4.5; N= NH_4OH). The preliminary results obtained indicated that the A stage could be used to extract xylan (M_W ~10,000), Ca and Mg. The xylan could be converted to bio-products in the future while Ca and Mg removal should decrease the scaling problems associated with alkaline silica. Strength and drainage data were minimally affected when bagasse KAQ pulp was mixed into eucalyptus kraft pulp at 10 wt% but significantly affected at 20% substitution.

Key Words: Bagasse, Hardwoods, Alkaline Pulping, Anthraquinone, Lignin Condensation, Pretreatments

Ericka Figueiredo Alves
Candidate for the degree of Doctor of Philosophy, August 2011
Raymond C. Francis, Ph.D
State University of New York College of Environmental Science and Forestry, Syracuse, NY

Raymond C. Francis, Ph.D _____

1.0 INTRODUCTION

The total world production of wood pulp in 2009 was approximately 160 Million tons, and only 17.8 Million tons of pulp was produced from other fibers. Even though pulp produced from non-woody biomass corresponds for only 10% of the total world production, this value has doubled in the past two decades. Some countries do not have an adequate supply of wood, but they have available non-woody plants with fiber properties that allow their use in papermaking. China has been traditionally using non-woody fibers for pulp and paper production because of their abundant agricultural waste supply but lack of wood. Whereas in 2009 the total wood pulp production in that country was 5.4 Million tons, more than 12 Million tons of pulp fibers were produced from non-woody biomass. In the same period, India produced approximately equivalent amounts of pulp from wood (2.3 Million tons) and non-woods (~ 2.0 Million tons). Other countries such as the USA and Brazil have mainly focused their pulp production on wood. These countries produced in 2009 only ~ 245 thousand and ~ 58 thousand tons of non-woody pulp fibers, respectively (FAO Stat, 2011).

The most important non-woody fibers used for papermaking are wheat and rice straw, sugarcane bagasse, reed and bamboo. Although some paper grades can be produced with 100% non-wood fibers, small proportions of those fibers may be blended into wood pulps. China Paper Association (CPA) and collaborators (2006) reported that in 2004, the total non-woody pulp production in China was 11.6 Million tons which were used to produce several paper grades. Eighty percent (80%) of non-woody fibers plus 20% wood fibers is typically used in uncoated printing and writing (P&W) grades, 40% non-woody fiber substitution in corrugate medium, 15% in tissue, 10% in coated P&W, and less than 5% substitution was used in other grades such as packing/wrap, linerboard, specialties and others. It has been predicted that by 2020 the total production of non-woody fibers in that country will be approximately 14.0 Million tons (CPA et al., 2006).

Countries, such as Brazil, which are predominantly located in the tropical and sub-tropical zone, between the Tropic of Cancer (30^{o}N) and Tropic of Capricorn (30^{o}S), receive adequate solar radiation during the entire year and this makes it an ideal region for biomass production. Although Brazil has a large fraction of its land mass under agricultural production it still has an ample reserve of arable land available for increased agricultural production. There is

no need for infringement on natural forest lands. The major agricultural crops in Brazil are soybeans, corn, rice and sugarcane, which represent 90% of the planted area. Brazil produces a large amount of agricultural residues and a significant fraction of these residues is converted to energy via combustion. The majority of the agro-industry residues (> 70%) come from the sugarcane processing (EPE, 2007). Like petroleum, biomass has a complex composition that after a primary separation is converted into a wide range of products. This fractionation scheme is called biorefinery due to its similarity with the approaches used in a petroleum refinery. An example of the "Lignocellulosic Feedstock Biorefinery" is illustrated in **Figure 1. 1**.

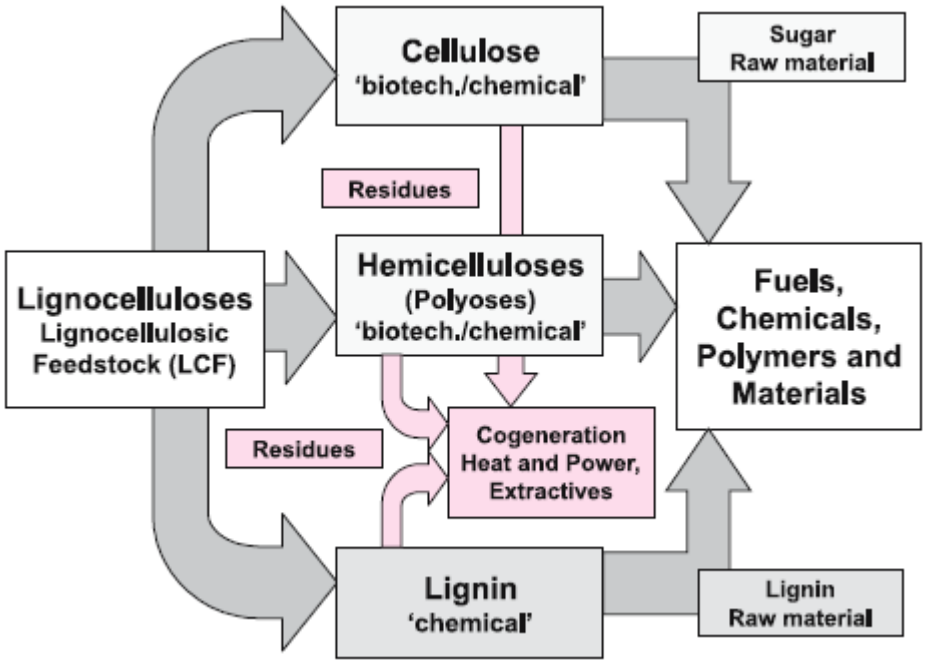


Figure 1. 1 Lignocellulosic feedstock biorefinery. Source: Kamm and Kamm (2007).

According to FAO Stat (2010), the top sugarcane producers in the year of 2008 were Brazil, India and China. Sugar factories can be considered as a biorefinery since several products can be generated **(Figure 1. 2**). After being harvested, the sugarcane (*Saccharum officinarum*) is brought to the mill and it is crushed to extract the juice. In the Brazilian factories, half of the juice is used for sugar production and the other half is fermented and distilled for ethanol production. The bagasse generated in the crushing process is burnt for its fuel value to produce steam and electricity. In addition to that, bagasse has properties suitable for a myriad of value-

added renewable products such as pulp and paper, fibreboard, building materials and renewable fuels.

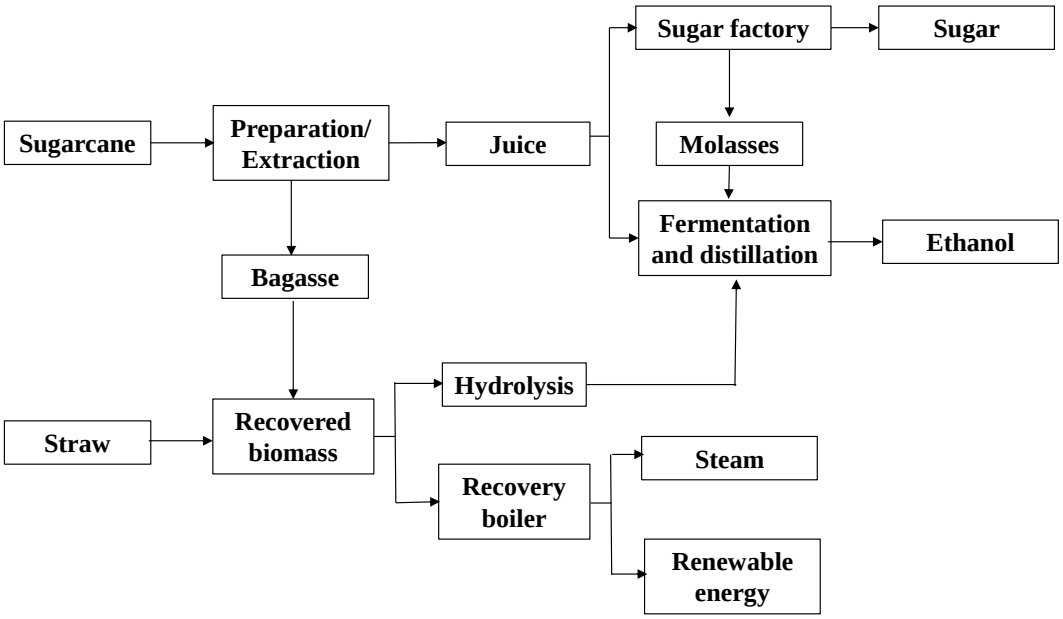


Figure 1. 2 Schematic of sugarcane processing.

In the Report elaborated by EPE (2007), it was predicted that of 516 Million tons of sugarcane and 142 Million tons of biomass, including bagasse and straw, would be produced in Brazil in 2010. Bagasse is currently burnt to generate steam and electricity most of which are used in the mills with the excess usually being sold to the regional electrical grid. However, the mill boilers that are currently in use have low pressure and efficiency. For instance, 8.1 TWh of electricity was produced from sugarcane production in Brazil during 2004/05 (EPE, 2007). If more efficient boilers were to be used, it was estimated that 24.3 TWh could have been produced (EPE, 2007). No credible projections regarding the use of bagasse for papermaking in Brazil has been made as yet. Currently, only one company (GCE Papéis) has been using 50% of sugarcane bagasse pulp blended with 50% of post-consumer recovered fibers for the production of one of their paper grades.

Bagasse fiber dimensions are fairly similar to those of hardwoods fibers such as eucalyptus (Sanjuán et al., 2001). The abundance of bagasse fibers in Brazil stimulated our interest in investigating the possibility of mixing pulp from bagasse with unbleached eucalyptus kraft pulp and bleaching the mixture at an existing eucalyptus mill. However, some features of

bagasse such as high contents of pith and silica require that its pulping process be different than that for eucalyptus chips. In the sugar factories, sucrose is extracted from the parenchyma cells mainly located in the pith. Some of the processing difficulties associated with bagasse pulps are attributed to these short pith materials (length < 0.3 mm) which can block the holes in the paper mat, thus decreasing drainage, production rate and paper quality (Rainey, 2009). Moreover, if the pith is retained in the pulp, it reduces the strength, opacity, and brightness. It also excessively consumes pulping chemicals. As a result, removing these short materials by depithing is an essential step for papermaking. Usually, pith and also some fibers that are removed in this process are burnt in the mill boilers (Young, 1997). These materials could be removed from the crushed cane by a pretreatment that could be beneficial to the subsequent pulping and bleaching processes. In addition to that, the extracted pith fraction which is rich in holocelluloses (75%) could be used for ethanol production.

Bagasse when compared to other non-woody fibers has a low amount of silica (SiO_2), but it is still twenty times higher than eucalyptus. Silica is present in black liquor in the form of Na_2SiO_3 which create operational problems in the recovery system. Black liquor burning behavior can be improved after desilication (Dixit et al., 2010). Conventional kraft, soda and soda-anthraquinone (soda-AQ or SAQ) pulping of non-woody fibers have been reported in the literature. In most cases, the bulk delignification occurs during the heating-up period and most of the lignin is dissolved in this initial stage. One of the advantages of using soda or SAQ pulping over kraft pulping is the elimination of the unpleasant odor related to reduced sulfur compounds. Unlike with softwoods and hardwoods, soda pulping of bagasse can produce a low kappa number pulp.

On the other hand, the bleachability of soda and SAQ bagasse pulps appear to be poorer than for kraft and SAQ pulps from hardwoods. Results are in the literature for CEHD bleaching comparison of woody and non-woody kraft pulps (C= chlorine at pH<3.0; E= alkaline extraction with NaOH; H= sodium hypochlorite and D= chlorine dioxide at end pH 3.5 – 5.5). When 5 – 8% equivalent Cl_2 on pulp was used the typical final brightness was in the range of 80 – 83% for bagasse while when 6 – 8% equivalent Cl_2 were used on hardwood pulps with higher lignin contents, the final brightness was in the range of 85 – 90% (Young, 1997). The results of Mohta et al. (1998) on delignification by soda or soda-AQ (SAQ) cooking followed by oxygen

bleaching appear to be typical for bagasse. They observed that with a NaOH dose of 12% Na_2O and 0.1% AQ on bagasse, a pulp with kappa number of 13.3 could be produced after an H-factor of 720 in batch cooking. The net effect of both cooking time and temperature can be expressed by means of a single variable. The rate at 100°C is chosen as unity and rates at all other temperatures are related to this standard. When using a value of 134 kJ/mole for E_a (activation energy) the rates at any other temperatures can then be expressed as the H factor (Sjöström, 1993). It is the time integral of the relative reaction rate and can be expressed by the following equation:

$$H = \int_0^t \exp\,(43.2 - \frac{16{,}113}{T})\,dt \qquad (1)$$

where *t* is time and T is absolute temperature in Kelvin.

The H Factor for 1.0 h of alkaline cooking at 100°C is 1.0 while the corresponding values for 150°C, 160°C and 170°C are 165, 401 and 927 respectively (Vroom, 1957). These factors are very accurate for the pulping of hardwoods and softwoods in the practical temperature range of 150°C - 175°C. Therefore, using the same cooking liquor one would obtain nearly identical kappa number and pulp yield for 1.0 h of cooking at 170°C and 2.31 h at 160°C (2.31 x 401 = 927). When 2.5% NaOH on pulp was used in O_2 delignification at 10% consistency the kappa number fell from 13.3 to 6.8 but the pulp brightness increased from only 37.2% ISO to 49.9% ISO (the O_2 brightness was even lower for the soda pulp). Compared to hardwoods it appears that bagasse is much more responsive to SAQ cooking but the brightness development in O_2 bleaching is much less than for hardwood SAQ pulps. When 14.0% Na_2O and 0.1% AQ were used in batch cooking of sugar maple (*Acer saccharum*) a kappa number of ~ 20 was attained after H-factor = 1297 (Bose et al., 2009a; Kanungo et al., 2011). However, brightness development in O_2 delignification appears to be higher for hardwoods as compared to bagasse. Francis et al. (2008a) reported on a poplar SAQ pulps that achieved kappa number 7.3 after the O_2 delignification (O stage). Although not reported, the pulp had a brightness of ~59% ISO. Schild et al. (2010) used oxygen to delignify a eucalyptus SAQ pulp from kappa number 15.5 to 10.3 and observed a brightness increase from 39.7% ISO to 54.4% ISO.

The societal outcome that was the aim of this research project was to demonstrate the economic and environmental accurals that would be associated with mixing 10% of unbleached SAQ bagasse pulp into unbleached eucalyptus kraft pulp in regions of Brazil where sugar cane farms, sugar refineries and pulp mills are in close proximity. The only major drawback that could be envisioned is that the bagasse pulp would not respond well to bleaching reagents used for hardwood kraft or SAQ pulps. If this pulp substitution process were to be commercialized the plan would be to avoid chemical recovery from bagasse pulping. Ammonia (NH_4OH) would be used in a possible pretreatment and KOH with or without ammonia used in the cooking stage.If this pulp substitution process were to be commercialized the plan would be to avoid chemical recovery of KOH from bagasse pulping effluents. The effluent containing potassium and nitrogen would be used to fertilize growing sugar cane in nearby fields. Some NH_4OH would be recovered by distillation. One possibility would be to start the pulping process with an hot water (HW) extraction of the bagasse, then neutralize the fibers with NH_4OH followed by KOH+ AQ (KAQ) cooking. The HW treatment may provide a xylan rich stream and also increase the rate of subsequent delignification in the KAQ stage. These HW treatments when applied to hardwood chips are known to dramatically improve the rate of kraft and SAQ delignification (Francis et al., 2008a, b; Duarte, 2010; Colodette et al., 2011; Duarte et al., 2011) and produce pulps that are much easier to bleach by the OD_0EpD_1 sequence (Francis et al., 2008a, b; Colodette et al., 2011; Nicholson et al., 2011). In the OD_0EpD_1 sequence, the acronym O is for a pressurized alkaline O_2 stage; D_0 is for chlorine dioxide delignification with an end pH of 2.5-3.0; Ep is for alkaline extraction with sodium hydroxide and hydrogen peroxide for incremental delignification; while D_1 is for chlorine dioxide brightening with an end pH of 3.7-4.5.

Research was performed on chemical composition of bagasse fibers after wet or water depithing to ~85% yield based on the starting crushed cane (CC) or chemical pretreatment/depithing to 55 – 65% yield; comparison of SAQ delignification rate between bagasse and sugar maple; comparison of native lignin structures between bagasse and sugar maple; optimization of KAQ cooking of bagasse; bleaching optimization of KAQ bagasse pulps; and strength and drainage properties of bagasse KAQ/Kraft eucalyptus pulp mixtures.

2.0 OBJECTIVES

The idea to be investigated was a more efficient utilization of sugar cane bagasse as compared to burning for energy. An approach that appeared feasible for regions in Brazil such as Sao Paulo State, where sugar plantations, sugar and pulp mills are in close proximity, was to use the bagasse for the production of unbleached chemical pulp. The pulping process should produce an effluent (black liquor) with significant market value and as such it could be disposed of thus avoiding chemical recovery. The processes associated with chemical recovery from black liquor are normally quite expensive in terms of capital cost. Small bagasse pulp mills would produce unbleached pulp that would be mixed with unbleached eucalyptus kraft pulp and bleached at an existing kraft mill. Bagasse pulp would constitute only 10-20% of furnish entering the bleaching process.

The only major drawback that could be envisioned was that the bagasse pulp would not respond well to the bleaching reagents normally used for hardwood kraft or SAQ pulps. If this pulp substitution process were to be commercialized the plan would be to avoid KOH recovery from the bagasse black liquor. Ammonia (NH_4OH) would be used in a possible pretreatment and KOH, with or without ammonia, used in the cooking stage. Some NH_4OH would be recovered by distillation. The effluent containing potassium and nitrogen would be used to fertilize growing sugar cane in nearby fields. The following topics were investigated:

- ✓ Refinements to analytical techniques developed at SUNY-ESF for the carbohydrate fraction of hardwoods in order to obtain excellent chemical composition data for bagasse.
- ✓ Investigation into the effects of water or wet depithing of bagasse and chemical depithing in a pretreatment stage on KAQ pulping and bleaching.
- ✓ Analysis of native bagasse and hardwood lignin to try and discover why bagasse is much more responsive to SAQ or KAQ cooking than are hardwoods but appears more difficult to bleach.
- ✓ Investigation of physical properties and drainage of eucalyptus kraft/bagasse KAQ pulp mixtures.
- ✓ Perform preliminary research on techniques to produce low silica bagasse SAQ pulps.

3.0 LITERATURE REVIEW

3.1 Anatomy of Nonwoody *vs.* Woody

There are two categories of seed plants: gymnosperms (from the Greek for "naked seed") and angiosperms (from the Greek for "vessel seed" or seeds contained in a vessel). The largest group of gymnosperms is the conifers ("cone-bearers") which include softwood species such as pine, fir, spruce and redwood. Angiosperms are flowering plants that include monocotyledons and dicotyledons. When seeds germinate in monocotyledons, it has one seed leaf and lack tissues that form secondary growth in thickness (vascular cambium). This group of plants includes grasses, grains (rice, wheat, maize, etc), sugarcane and bamboos. Dicotyledons have two seed leaves and, like conifers, have the ability to grow in thickness through their vascular cambium. They include plants such as the hardwoods sugar maple and eucalyptus (Carpita, 2000).

Many monocotyledons are herbaceous plants that can be used as raw material for the pulp and paper (P&P) industry such as agricultural residues like cereal straw, sugarcane and corn stalks, natural and planted bamboos, and some wild growing grasses. The major source of fibers for the P&P industry comes from the stem of woody and non-woody plants. The main anatomical difference between mono-and dicotyledon plants is the cambium tissue. Whereas a woody stem has a continuous growth in the diameter due to the presence of the vascular cambium (**Figure 3.1. 1**), monocots lack this tissue. They have instead, a stem structure with numerous vascular bundles scattered in a tissue of parenchymatic storing cells, surrounded by a string and dense epidermis (Tillich, 1998; Scott, 1996). The transport of water and solutes in monocotyledons occur inside the vascular bundle. The vascular system of monocots is composed of two major complex tissues: xylem which faces inward and phloem which faces outward. Since there is no cambium in monocots, phloem and xylem are in contact with each other (Scott, 1996). The xylem tissues have a strengthening and conducting role and they transport water and solutes from the roots upward through the plant. Phloem transports a solution of metabolites (mainly sugars, amino acids, and some ions) from "sources" of production, such as leaves to for instance, developing leaves and roots (Barclay, 2007).

A cross section of the internode of sugarcane stem with numerous vascular bundles is illustrated in **Figure 3.1. 2**. The parenchyma constitutes the filler between the bundles which are

scattered throughout the section. The vascular tissue of the bundle has xylem and phloem disposed collaterally in relation to each other.

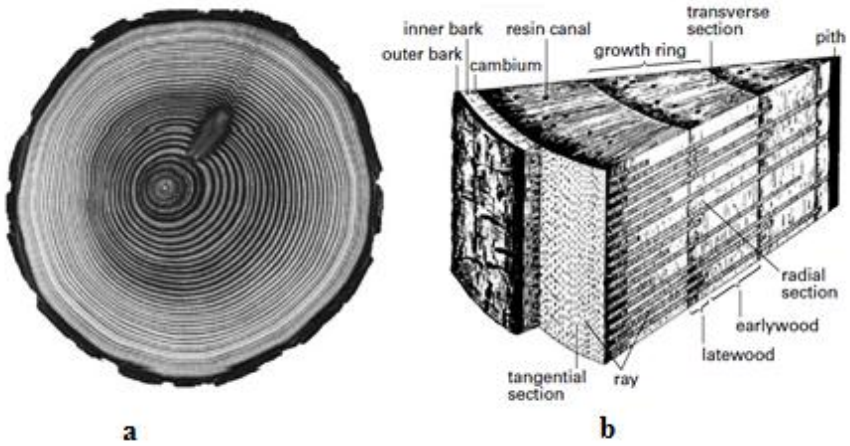


Figure 3.1. 1 a) Transverse section of pine trunk showing the bark, sap-and heartwood regions, and the annual rings composed of early-and latewood. b) Detailed sectional view of a young pine stem showing its axial and radial organization and location of the major types. Note that both the wood structure and its cell types can be viewed in transverse (TS), tangential longitudinal (TLS) and radial longitudinal (RLS) views. Source: Daniel (2009).

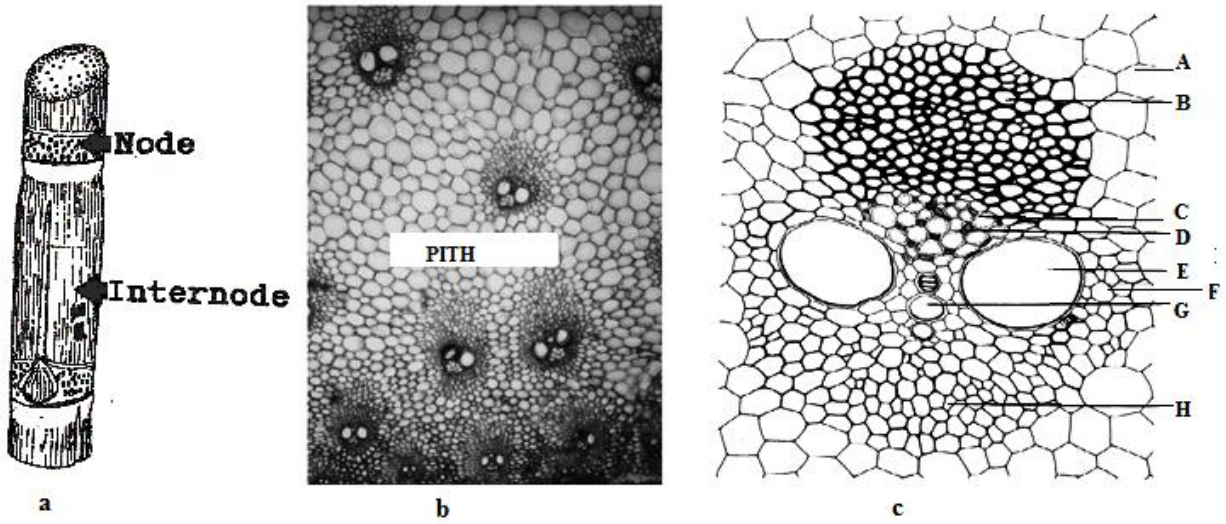


Figure 3.1. 2 a) Longitudinal view of the grass steam; b) Transversal view of vascular bundle of sugarcane bagasse (70X magnitude) and c) 290X magnitude. A, outer bundle parenchyma, B, sclerenchyma, C, sieve tube, D, companion cell, E, large pitted vessel, F, bundle sheath; G, protoxylem, H, sclerenchyma cap of xylem pole bundle. Source: Artschwager (1925).

Similar to wood tracheids, the wheat straw and reed fibers consist of middle lamellae (ML), primary wall (P) and secondary wall (S1, S2 and S3), as shown in **Figure 3.1. 3** and **Table 3.1. 1**. However, the thickness of each layer differs among woody and non-woody plants. The percentage volume fraction (PVF) of ML and CC of wheat straw is greater than that of spruce tracheid. On the other hand, the cell wall of reed is basically made of primary and secondary wall. However, this secondary wall have abnormal S2 layer made up by S2-1, S2-2, and S2-3 from outer and inner layer. Similar to reed, sugarcane bagasse fiber contains primary and secondary wall which is alternatively arranged by broad layer and narrow layer, or build up by number of layers. In bamboo, the number of layers varies among species and, a maximum of 18 is found (Xu, 2010).

A model for the thick-walled bamboo is illustrated in **Figure 3.1. 3** along with a classical representation of the woody cell wall. The orientation of the cellulose microfibrils are represented by the arrows in the woody cell wall. For bamboo, the affixes *l* and *t* used in this illustration stands for almost longitudinal and transversal orientation (Xu, 2010).

Table 3.1. 1 Distribution of morphological layers in wheat straw fiber, spruce tracheid and reed fiber

Morphological Layers	***Wheat Straw (Thick Fiber)***		***Spruce tracheid***		***Reed fiber***	
	Thickness (µm)	***PVF (%)***	***Thickness (µm)***	***PVF (%)***	***Thickness (µm)***	***PVF (%)***
ML + P	0.1-0.2	9.3	0.05-0.1	10.2	0.07	11.9
S1	0.1-0.3	83.5	0.15-0.2	9.9	0.3-0.5	31.2
S2	1.8-2.5		0.7-2.0	75.9	0.7-1.0	48.2
S3	0.15-0.3		0.1	4.0	0.2-0.3	8.7
CC	-	5.4	-	-	-	-

Source: Xu (2010).

Non-wood fibers can be divided into three groups based on fiber length: a) fiber length > 4.0 mm, represented by cotton lint, abaca and hemp; b) fibers length varying from 1.5 to 4.0 mm, represented by bamboo, bagasse, kenaf and reed; and c) fiber length < 1.5 mm, represented by all kinds of straw pulps (Sixta, 2006). Typical fiber dimensions of wood and non-wood fibers are presented in **Table 3.1. 2**. It is clear that non-wood fibers are usually shorter than softwood

fibers, but similar in length to hardwood fibers. Another import feature of non-wood fibers is that they contain more fine cells (less wide) than those found in wood plants. However, sugarcane bagasse presents fibers with similar features to hardwoods.

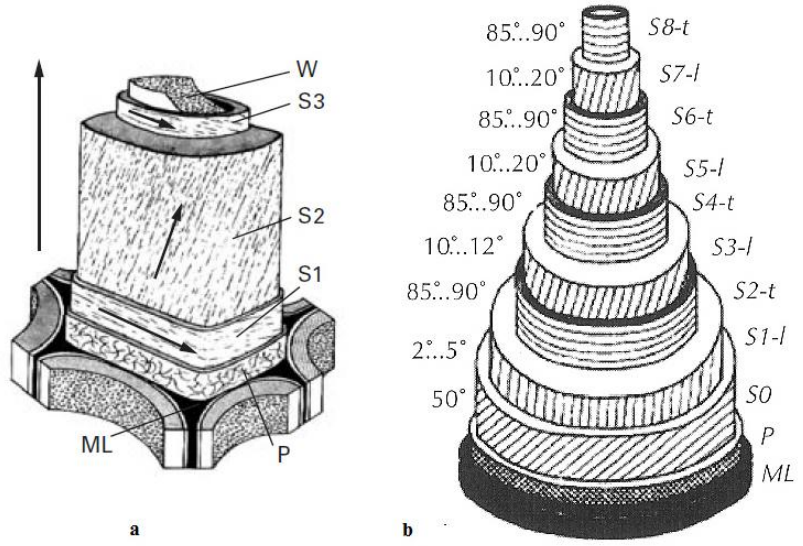


Figure 3.1. 3 Simplified structure of woody cell wall (a) and bamboo (b). Source: Sjöström (1993); Xu (2010).

Sugarcane stalk can be basically divided into two sections: a) the fibre, which consists of vascular bundles and give the stalk its strength, and b) the soft pith section which consist of cells such as vessels, parenchyma and epithelial cells and contain the juice (Barker and Wesley-Smith, 2008). During sugarcane processing the stalk is crushed to remove the juice. The crushed cane is then called bagasse. Updahyaya et al. (1991) reported the composition of the bagasse after the juice extraction which consisted of 30% pith. Even after dry and wet depithing, 15.5% pith is still associated with sugarcane bagasse fibers, while useful fibers are 71.4% (Agnihotri et al., 2010). Sanjuán et al. (2001) determined the differences on cell wall dimensions of the fiber bundle and pith fraction of sugarcane bagasse (**Table 3.1. 3**).The main elements of the pith fraction have wider lumen, thinner cell walls and higher diameter compared to the fibers in the bundle fraction. These cells with smaller dimensions and thin walls are easily collapsed and form a very dense sheet with few pores which results in a poor drainage on filters and on the papermachine.

Table 3.1. 2 Average length and diameter and length/diameter ratio of various pulp fibers

	Length (mm)	***Diameter (μm)***	***Ratio***
Woods			
Coniferous (softwood)	3.0	40	75
Deciduous (hardwood)	1.0	22	45
Straws and Grasses			
Rice	0.5	9	60
Cereal (wheat, rye)	1.5	13	120
Cane and Reeds			
Bagasse (sugarcane)	1.7	20	80
Miscellaneous	1.2	12	100
Bamboos			
Several varieties	2.8	1.5	180
Bast fibers			
Linen	55	20	2600
Leaf fibers			
Abaca	6	24	250
Seed Fibers			
Cotton linters	20	20	1000

Source: Smook (1992).

Table 3.1. 3 Dimensional characteristics of both fractions of sugarcane bagasse

Fraction	***Cell types***	***Length (mm)***	***Lumen width (μm)***	***Wall thickess (μm)***	***Cell diameter (μm)***
Fiber bundle	Fiber	1.1	12	4.0	20
Pith	Vessels	1.2	75	2.7	80
	Parenchyma	0.3	57	1.7	60

Source: Sanjuán et al. (2001).

3.2 Chemical Composition of Nonwoody *vs.* Woody

Non-woody feedstocks include agricultural residues such as crop residues (sugarcane bagasse, corn stover, corn stalks, rice straw, wheat straw and others), and perennial grasses (bamboo, elephant grass, reeds and others). These feedstocks can be used for pulping and they differ from woody materials in regards to chemical, physical and mechanical properties. A comparison on the chemical composition of woody and non-woody plants used for papermaking is shown in **Table 3.2. 1**. As can be seen, higher contents of inorganics (mainly silicon dioxide), proteins and extractives are found on non-woody plants. One of disadvantages of using these materials for papermaking is a higher rate of scale formation, due in a larger part to their higher

silica content (Stenius, 2000). Due to the higher concentration of extractives, another problem may occur during the papermaking of non-woody feedstock is pitch deposition on equipment and also on the paper sheets. Carbohydrates are the major components in both woody and non-woody plants. It is interestingly to notice that non-woody feedstock typically contain a higher content of hemicelluloses and lower content of lignin as compared to woody materials.

Table 3.2. 1 Comparison between the typical chemical composition of woody and non-woody feedstocks used for pulping (% of the feedstock dry solids)

Component	***Woody feedstock***	***Non-woody feedstock***
Carbohydrates	65-80	60-80
Cellulose	40-45	30-45
Hemicelluloses	25-35	30-45
Lignin	20-30	10-25
Extractives	2-5	5-15
Proteins	<0.5	5-10
Inorganics	0.1-1.0	0.5-10
SiO_2	<0.1	0.5-7

Source: Stenius (2000).

Significant compositional differences between grass and dicot cell walls can be seen in **Table 3.2. 2.** The types and relative abundance of non-cellulosic polysaccharides and abundance of proteins and phenolic compounds are the main difference between grasses and dicotyledonous plants.

3.2.1 Hemicelluloses of Non-woody *vs.* Woody Plants

Hemicelluloses are one of the main constituents of lignocellulosic materials and along with cellulose and lignin they have structural function in the cell wall. Cellulose is a homopolysaccharide with a higher degree of polymerization, while hemicelluloses are heteropolysaccharides formed by myriads of monomeric units with much lower degree of polymerization (~ 200). These building blocks which are released by acid hydrolysis are following: hexoses (D-glucose, D-mannose and D-galactose); pentoses (D-xylose and L-arabinose); small amounts of deoxyhexoses (L-rhamnose and L-fucose) and few uronic acids (4-O-methyl-D-glucuronic acid, D-galacturonic acid and D-glucuronic acid). These monomers are

illustrated in **Figure 3.2. 1**. Additionally, hemicelluloses are generally acetylated with acetyl groups (-$COCH_3$) (Sjöström, 1993).

Table 3.2. 2 Approximate composition (% dry weight) of typical dicot and grass primary and secondary cell walls

Component	***Primary Wall***		***Secondary Wall***	
	Grass	***Dicot***	***Grass***	***Dicot***
Cellulose	20-30	15-30	35-45	45-50
Hemicelluloses				
Xylans	20-40	5	40-50	20-30
Mixed linkage glucans	10-30	Absent	Minor	Absent
Xyloglucan	1-5	20-25	Minor	Minor
Mannans and Glucomannans	Minor	5-10	Minor	3-5
Pectins	5	20-35	0.1	0.1
Structural Proteins	1	10	Minor	Minor
Phenolics				
Ferulic and *p*- coumaric acid	1-5	Minor	05-1.5	Minor
Lignin	Minor	Minor	20	7-10
Silica			5-15	Variable

Source: Vogel (2008).

Due to the complexity of the hemicellulose structure some abbreviations for the type of monosaccharide residue are usually used (**Figure 3.2. 2**). Moreover, in the hemicellulose nomenclature, the order of importance is related to the highest content of the monosaccharide residue. It is written by citing the lower content towards the left and the highest content to the right. For instance, in galactoglucomannans the order of relative importance is galactose < glucose < mannose.

Hemicellulose structure and chemical composition varies among plant material, type of tissue, growth stage, growth conditions and storage (Teleman, 2009). **Table 3.2. 3** summarizes the major hemicellulose type in softwoods, hardwoods and some non-woods.

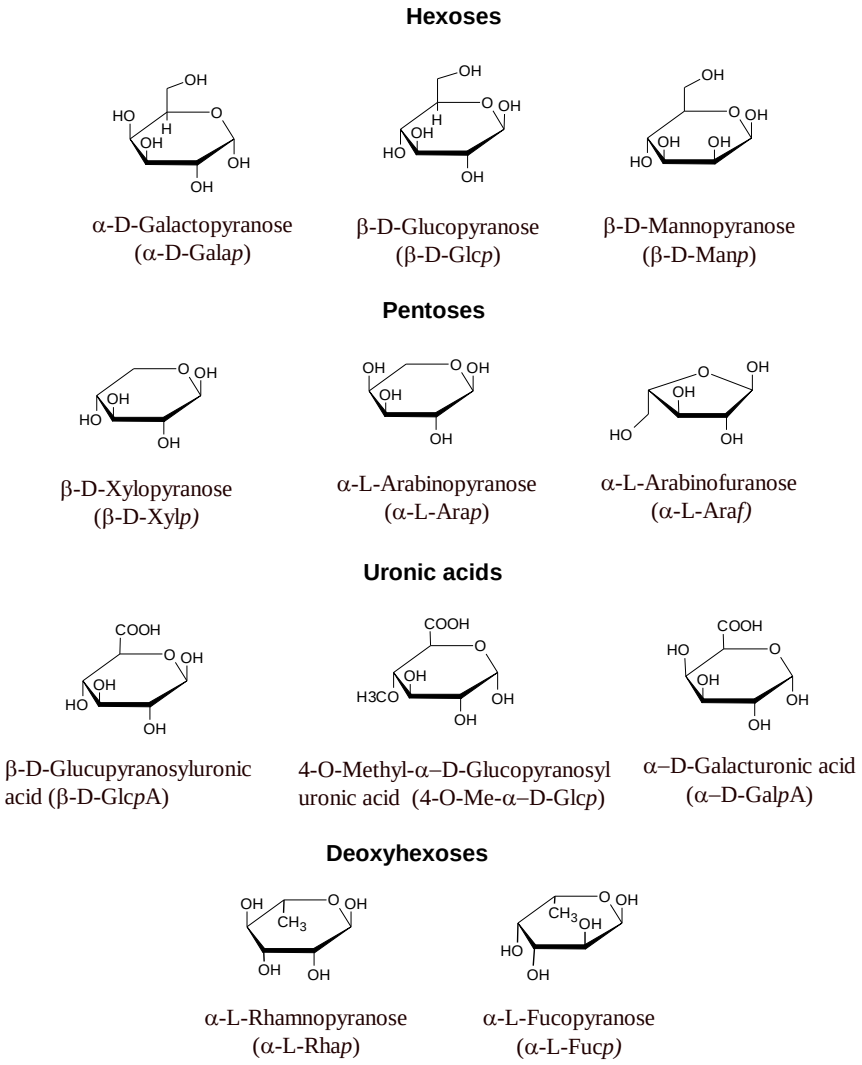


Figure 3.2. 1 Main monosaccharides constituents of hemicelluloses. Adapted from Xu (2010).

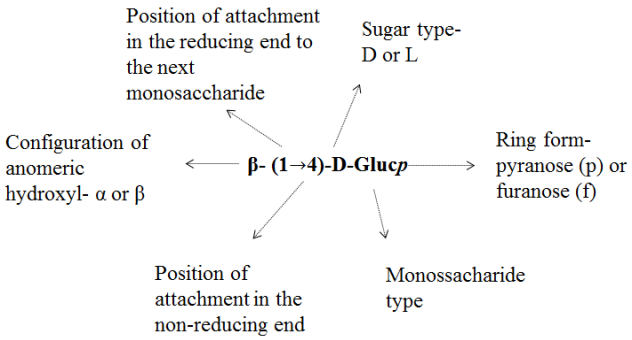


Figure 3.2. 2 Nomenclature of the monosaccharide residue in the chain.

Table 3.2. 3 Major hemicelluloses on softwoods, hardwoods and wheat straw

Raw Material	***Hemicellulose type***	***Molar ratios***
Softwoods[a]	Glucomannan	β-D-Man*p*: β-D-Glc*p*:α-D-Gal*p*:O-acetyl= 3-4:1:0.1:1
	Arabinoglucuronoxylan	β-D-Xyl*p*: 4-O-Me-α-D-Glc*p*A:α-L-Ara*f*= 10:2:1.3
	Galactoglucomannan	β-D-Man*p*: β-D-Glc*p*: α-D-Gal*p*: O-acetyl= 3-4:1:1:1
Hardwoods[a]	Glucuronoxylan	β-D-Xyl*p*: 4-O-Me-α-D-Glc*p*A: O-acetyl = 10:1:7
	Glucomannan	β-D-Man*p*: β-D-Glc*p*: O-acetyl= 1-2:1:1
Wheat straw[b]	Arabinoglucuronoxylan	β-D-Xyl*p*: 4-O-Me-α-D-Glc*p*A:α-L-Ara*f*= 12:1:1
Sugarcane bagasse[c]	L-arabino-4-O-methyl-D-glucurono-D-xylan	Acetylated at unkown ratios

Where: Glucose (Glu), Mannose (Man), Xylose (Xyl), Galactose (Gal), Arabinose (Ara), Rhamnose (Rha), Glucuronic acid (GlcUA), Galacturonic acid (GalUA) and 4-O-methyl-D-glucuronic acid (GlcUA)

[a]Adapted from Teleman (2009); [b]Sun, R.-C. et al. (1996); [c]Sun, J.-X. et al. (2004a)

In softwoods and hardwoods, the hemicellulose content varies from a low value of 20-25% to a high value of ~35% (Sjöström, 1993). Both mannans and xylans are found in softwoods and hardwoods, but the type and proportion differs significantly. In softwoods, the main hemicelluloses constituents are glucomannans (10-15%), arabinoglucuronoxylan (7-15%) and galactoglucomannans (5-8%). Meanwhile, in hardwoods the main hemicelluloses are glucuronoxylan (15-35%) and glucomannans (2-5%) (Sjöström, 1993).

Softwoods hemicelluloses are more diversified than those in hardwoods. In softwood glucomannans, the main backbone is formed by β-(1→ 4)-D-Man*p* and β-(1→ 4)-D-Glc*p* units with side branches of α-(1→ 6)-D-Gal*p*. It has also been observed O-acetyl groups linked to the side chain at C-2 and C-3. The approximate molar ratios are 3-4:1:0.1:1 of β-D-Man*p*; β-D-Glc*p*; α-D-Gal*p*: O-acetyl, respectively. Another important hemicelluloses found in softwood is arabinoglucuronoxylans. The main backbone is formed by β-(1→ 4)-D-Xyl*p* with side chains composed of 4-O-Me-α-(1→ 2)-D-Glc*p*A and α-(1→ 3)-L-Ara*f*. Acetyl groups have not been found. The molar ratios are as following 10:2:1.3 of β-D-Xyl*p*, 4-O-Me-α-D-Glc*p*A, α-L-Ara*f*, respectively (Sjöström, 1993; de O. Buanafina, 2009). Another class of hemicelluloses in softwood is galactoglucomannan. The main backbone is formed by β-(1→ 4)-D-Man*p* and β-(1→ 4)-D-Glc*p* units with side chains of α-(1→ 6)-D-Gal. It has also found to be acetylated at

C-2 and C-3 and the molar ratios are 3-4:1:1:1 of β-D-Man*p*; β-D-Glc*p*; α-D-Gal*p*: O-acetyl, respectively.

The most important hemicelluloses found in hardwoods are glucuronoxylans which has a structure highly acetylated at C-2 and C-3. The main backbone is β-(1→ 4)-D-Xyl*p* with side chains of 4-O-Me-α-(1→ 2)-D-Glc*p*A. The molar ratio of β-D-Xyl*p*: 4-O-Me-α-D-Glc*p*A varies from 4:1 to 16:1. However, on average the ratios are 10:1:7, for β-D-Xyl*p*, 4-O-Me-α-D-Glc*p*A, O-acetyl, respectively. On the other hand, glucomannans, a minor content in hardwoods, glucomannan, has also been found to be acetylated at C-2 and C-3. The main backbone is composed of β-(1→ 4)-D-Man*p* and β-(1→ 4)-D-Glc*p*. The molar ratios are 1-2:1:1 of β-D-Man*p*; β-D-Glc*p*, O-acetyl, respectively (Sjöström, 1993; de O. Buanafina, 2009).

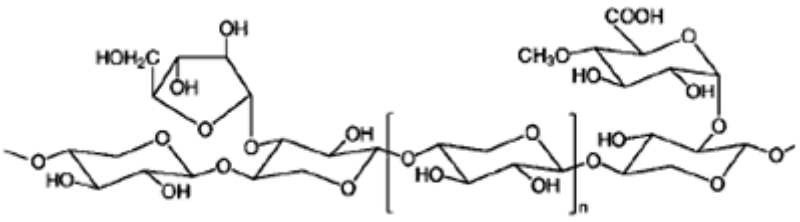
Arabino(glucurono)xylans (AGX) were found to be the dominant hemicellulose in cell walls of lignified supporting tissues of grasses and cereals. These are present into two forms in corncobs: water-insoluble xylans (wis-AGX) which have~95% of their backbone unsubstituted and water-soluble xylan (ws-AGX) which has more than 15% of their backbone substituted. Higher content of uronic acids (~ 9%) were found in ws-AGX compared to wis-AGX (~ 4%). Another form of hemicelluloses that have been found in commercial cereals is arabinoxylans (AX) which can be either monosubstituited or disubstituited at O-2 and/or O-3 by α-L-Ara*f*. Moreover, esterification of O-5 at α-L-Ara*f* by phenolic acids (ferulic and coumaric acids) can occur (Ebringerová et al., 2005). In monocots, ferulic acid (FA) are linked by either ester bonds between the carboxylic acid group on FA and the C-5 hydroxyl group of α-L-Ara*f* or linked by ether bond between the phenolic hydroxyl groups on FA and the sidechain of another phenylpropane (C_9) unit. On the other hand, in dicots FA are associated with pectic polysaccharides via esterification to the C-2 of the α-L-Ara*f* or C-6 hydroxyl group of α-D-Gal*p* (de O. Buanafina, 2009).

Arabino(glucorono)xylan (AGX) is found on lignified tissues of grasses and annual plants (**Figure 3.2. 3**a). However, neutral arabinoxylans (AX) substituted at C-2 and C-3 by α-L-Ara*f* on β-(1→ 4)-D-Xyl*p* backbone are the main component of cereal grain (**Figure 3.2. 3**b). (Ebringerová and Heinze, 2000). For instance, the hemicellulose fraction of wheat straw isolated with 0.5M NaOH at 35^{o}C for 2 hours consists of L-arabinofuranosyl and D-xylopyranosyl attached at C-3 and D-glucopyranosyluronic acid and 4-O-methyl-D-glucopyranosyluronic acid

groups attached at C-2. A significant portion of the xylopyranosyl units on cereal straw was found to be acetylated at mainly C-2 and also C-3. Acetyl contents of native bagasse were found to be 3.2% on the dry weight (Atsushi et al., 1984).

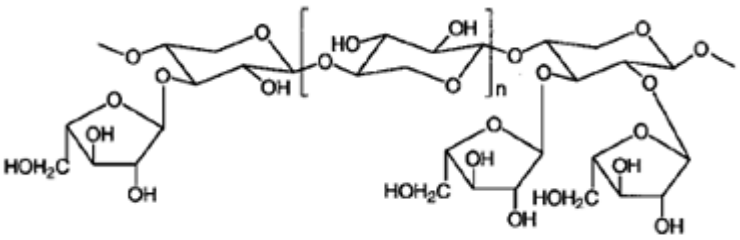
Water-soluble (ws-) and water-insoluble (wis-) arabinoxylans are usually found in several commercialized cereal grains such as wheat, barley, rye and oat. The former has lower content of Ara*f* residues which are mono-substituted on Xyl*p* (**Figure 3.2. 3**c). On the other hand, ws-xylan has a more branched chain composed of β-D-Xyl*p* residues and disaccharide side chains containing 2-O- β-D-Xyl- α-L-Ara*f* next to the single Ara*f* and 4-O-Me-α-D-Glc*p*A side chains (**Figure 3.2. 3**d).

Arabinoglucuronoxylan (AGX)



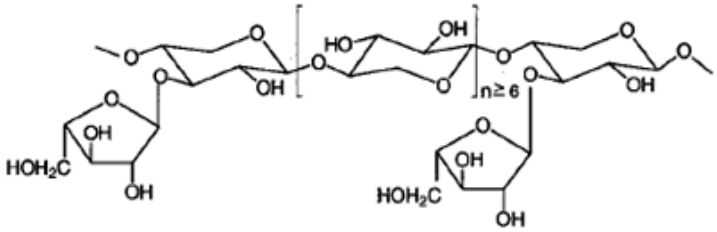
a

Neutral arabinoxylans (AX)



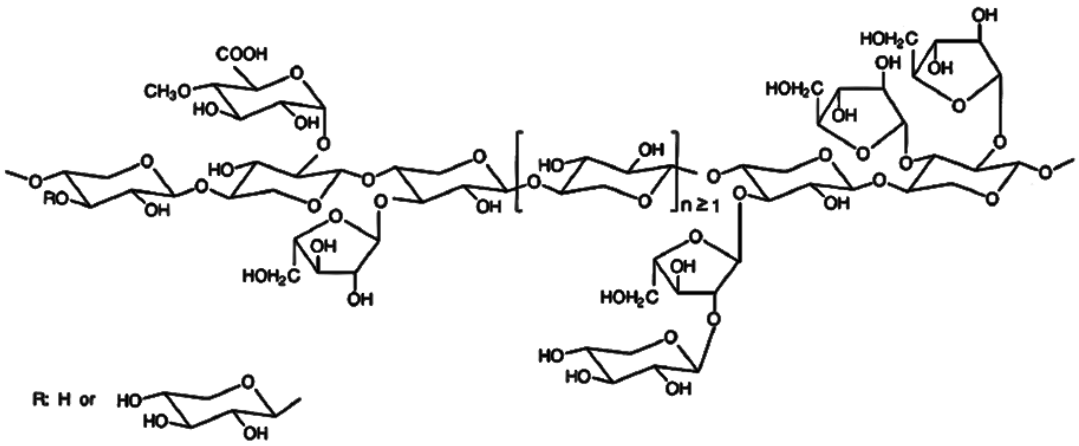
b

Water-insoluble (Wis)-AX



c

Water-soluble (Ws)-AGX



d

Figure 3.2. 3 Common xylans in grasses. Source: Ebringerová and Heinze (2000).

3.2.2 Lignin of Non-woody *vs.* Woody Plants

Lignins are complex racemic aromatic heteropolymer of phenylpropane units. They are mainly derived from three hydroxycinnamyl alcohol monomers which differ in their degree of methoxylation. No methoxylation is found in *p*-coumaryl alcohol, while coniferyl alcohol has one methoxyl group at C-3 and sinapyl alcohol has two methoxyl groups at C-3 and C-5. These three monolignols produce, respectively, *p*-hydroxyphenyl, guaiacyl and syringyl units or also simply called H, G and S units (Boerjan et al., 2003). These compounds which are incorporated into the lignin polymers are illustrated in **Figure 3.2. 4**.

Not only does the lignin content vary amongst softwoods, hardwoods and grasses, but also the distribution of H, G and S units. Hardwood lignins consist of G and S units and traces of H units, whereas softwoods are basically composed of G units. On the other hand, grasses incorporate much higher amounts of H units (**Table 3.2. 4**).

Fernandez and Suty (1981) determined the distribution of H, G and S units in bagasse lignin by nitrobenzene oxidation and the molar ratios were 1.2:1:0.8 of vanillin, syringaldehyde and *p*-hydroxybenzaldehyde, respectively. The approximate 1:1:1 ratio was corroborated by Chen et al. (1998). On the other hand, lignin characterization of wheat straw has shown a much lower concentration of H units. The molar ratios determined by nitrobenzene oxidation were 1:6.9:6.7 of H, G and S units, respectively (Sun, R.-C et al., 1995).

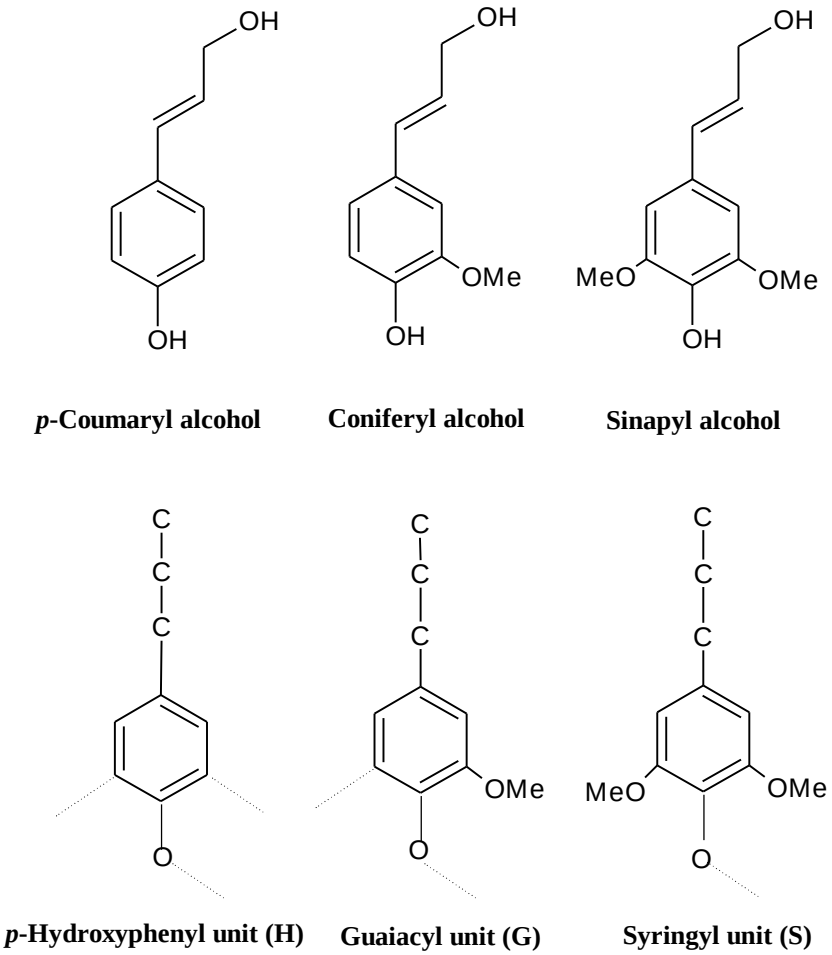


Figure 3.2. 4 The three primary lignin monomers and it's respectively lignin units. Adapted from Lu and Ralph (2010).

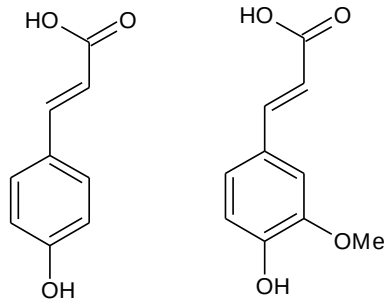
Table 3.2. 4 Composition of monolignols in softwood, hardwood and grass

Plant	***p-Coumaryl alcohol (%)***	***Coniferyl alcohol (%)***	***Sinapyl alcohol (%)***
Coniferous-Softwood	5<	>95	None or traces
Dicotyledonous hardwood	0-8	25-50	46-75
Monocotyledonous grass	5-33	33-80	20-54

Source: Henriksson (2009).

Other cell wall components of non-woody feedstocks are for instance ferulic acid (4-hydroxy-3-methoxy-cinnamic acid) and *p*-coumaric acid (4-hydroxy-cinnamic acid) (**Figure 3.2.**

5). Xu et al. (2005) used a combination of acid and alkaline treatments to hydrolyze *p*-coumaric (1.76%) and ferulic (1.29%) acid from bagasse. The lignin content of the sample was 18.1%. Higuchi et al. (1967) determined the ferulic acid (FA) and *p*-coumaric acid (*p*-CMAc) contents on several species of grasses and monocotyledons. The content of ferulic acid varied from 0 to 0.98% of grass milled wood lignin (MWL) which was much lower compared to *p*-coumaric acid (0-9.75%). The highest content of *p*-coumaric acid (9.75% on biomass) was found in *Miscanthus sacchariflorus* which is a type of grass native to Asia.



***p*-Coumaric acid** **Ferulic acid**

Figure 3.2. 5 Other cell wall components in grasses. Source: Lu and Ralph (2010).

A comprehensive study on sugarcane bagasse lignin indicated that β-O-4' ether bonds are the majority of linkages between structural lignin with other common bonds such as β- β', 5-5' and β-5' carbon-carbon linkages (Sun, J.-X. et al., 2003). **Figure 3.2. 6** shows partial HSQC spectra of eucalyptus and bagasse milled lignin (ML) samples, in which C-H correlations of lignin side chains from the major linkages (left) and aromatic C-H lignin unit correlations (right). The three major linkages, β-O-4', β-5' and β-β' are colored in blue, green and purple, respectively. Whereas all the three types of bonds are easily identified in eucalyptus the predominant type of linkage in bagasse is β-O-4'. Another significant difference between these two samples is the evident signal for *p*-coumarates on bagasse ML (Lu and Ralph, 2010).

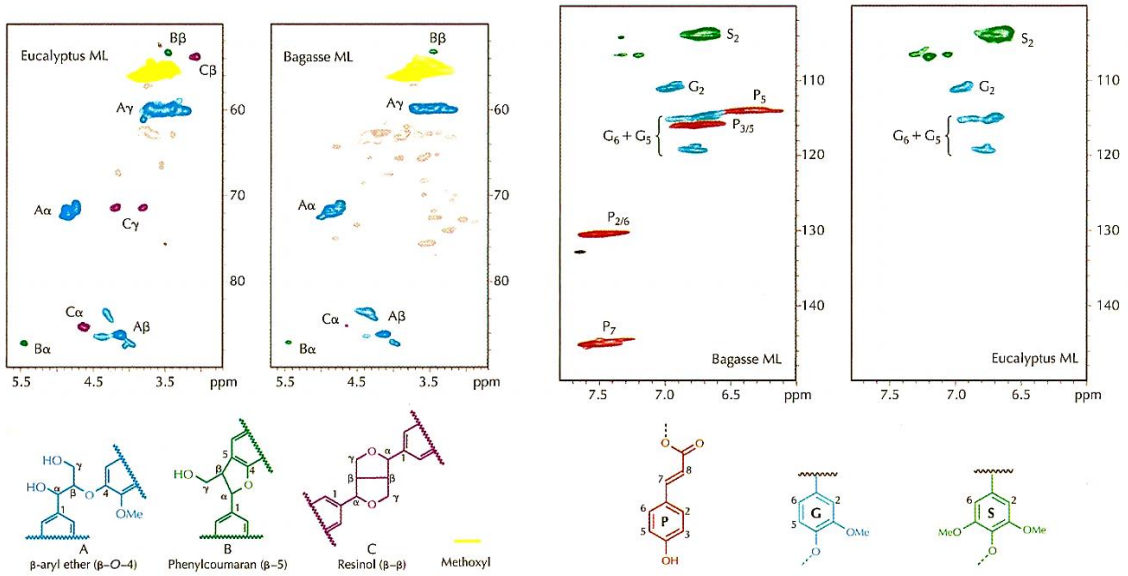


Figure 3.2. 6 Partial HSQC NMR spectra of milled lignin (ML) from eucalyptus and bagasse. Source: Lu and Ralph (2010).

Naturally acetylated, coumarylated and/or *p*-hydroxybenzoylated lignin in non-woody plants is usually found. These structures are shown in **Figure 3.2. 7** (Buranov and Mazza, 2008). Highly acylated lignin is found in kenaf. Moreover, all grasses have lignin that is acylated by *p*-coumaric acid (Ralph, 1999). Crestini and Argyropoulos (1997) determined by quantitative ^{31}P and 2D NMR spectroscopy that milled straw lignin contains about 12 ester units per 100 C-9 units. Of that, 77% of the carboxyl fraction of these ester bonds was composed of *p*-coumaric acid (III) mainly at γ position of lignin side chains. The remaining portion was found to be aromatic acids bound to lignin via intra-and/or intermolecular ester bounds (**Figure 3.2. 7**).

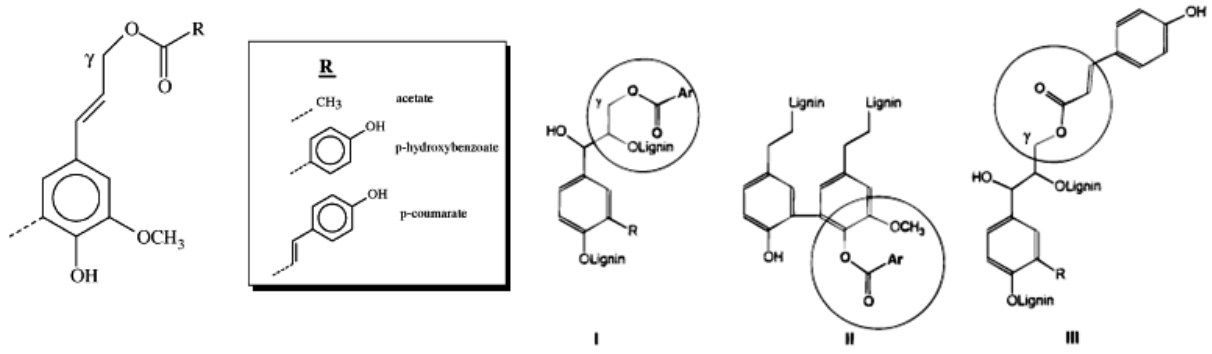


Figure 3.2. 7 Acylated lignin in Kenaf. Source: Buranov and Mazza (2008). I-Intra-and/or intermolecular ester bonds of wheat straw lignin side chain; II- Phenolic groups in C-5 condensed esterified; III- Ester bonds in terminal units with *p*-coumaric acid. Source: Crestini and Argyropoulos (1997).

Advanced analytical tools have been recently used in studies on biosynthesis of lignin monomers. It has become clear that lignin is composed of more monomeric units in addition to *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Lu and Ralph, 2010). **Figure 3.2. 8** illustrate some of those compounds that can be incorporated into lignins via free radical coupling reactions. After their synthesis, the monolignols precursors are transported to the cell where they are polymerized.

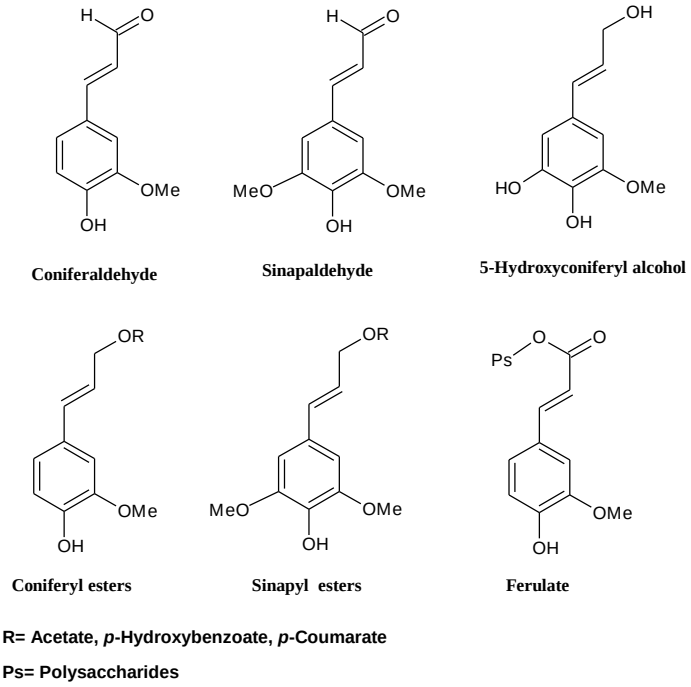


Figure 3.2. 8 Additional lignin precursors. Source: Lu and Ralph (2010).

3.2.3 Lignification Process of Woody *vs.* Non-Woody Plants

Peroxidases, laccases, polyphenol oxidases and coniferyl alcohol oxidase are believed to participate in the dehydrogenation of the monolignols to radicals. For instance, peroxidases use hydrogen peroxide (H_2O_2) to oxidizes their substrates, while laccases (*p*-diphenol: O_2 oxidoreductases) consume O_2 in its oxidation of the monolignols. The unpaired electron can be localized either at 4-O-, 3-, 5-, 1- or β-position. Two radicals (each with an unpaired electron) can form covalent bonds (Henriksson, 2009).

Lignification is the process by which the units are linked together via radical coupling reactions. A new monomer is coupled to the growing polymer during the "end-wise" reaction. (Ralph, 1999). **Table 3.2. 5** summaries the type and frequency of bonds found in softwood and hardwoods. As can be seen, the main bonds are β-O-4', β-5', 5-5' and 4-O-5'. Cross-coupling of coniferyl alcohol with S units yields only β-O-4'. This explains why S lignins have elevated β-ether linkages. Moreover, the most frequent linkage is β-O-4' which it is also the one cleaved to the highest degree during chemical pulping.

Table 3.2. 5 Bonds between monolignols and lignin functional groups

Name	***Bonds***	***Frequency softwood (%)***	***Frequency hardwood (%)***
Ether Bonds			
B-aryl ether	β-O-4'	35-60	50-70
Diaryl ether	4-O-5'	<4	7 (?)
	1-O-4'	low	low
Glyceraldehyde aryl ether	β-O-4'	<1	<1
Carbon-Carbon bonds (Condensed)			
Dihydroxybiphenyl	5-5'	10	~ 5
Phenyl Coumarate	β-5'	11-12	4-9
Pinoresinol	β-β'	2-3	3-4
Secoisolariciresinol		1-2	1
Spirodienon	β-1'	1-3	2-3
Dibenzodioxocin		4-5	trace
End groups			
Coniferyl alcohols		1-6	trace-6
Dihydroconiferyl alcohol		2	none
Free phenol		11	9 (?)

Source: Henriksson (2009).

In 1960's a novel structure was found in lignins, 1,2-diarylpropane or β-1' unit. Higher content of this structure have been found as a product of acidolysis and thiacidolysis (Brunow et al., 1998). For instance, Sjöström (1993) reports values of 7% β-1' (percentage of total linkages) for both hardwood and softwood. However, determination of the frequencies of such structures by NMR spectroscopy has revealed only small amounts in both softwood and hardwood. Some clarification occurred when Gellerstedt and Zhang (1991) isolated β-1' type compounds from wood by mild acidolysis (**Figure 3.2. 9**). The intermediary spirocyclohexadienone undergoes acid-catalyzed hydrolytic cleavage of the α-O bond to form 1,2-diarylpropane. This reaction explain why the quantification of the β-1' by acidolysis yields higher content of the 1,2-diarylpropane, thus overestimating this type of compound in the native wood (Brunow et al., 1998).

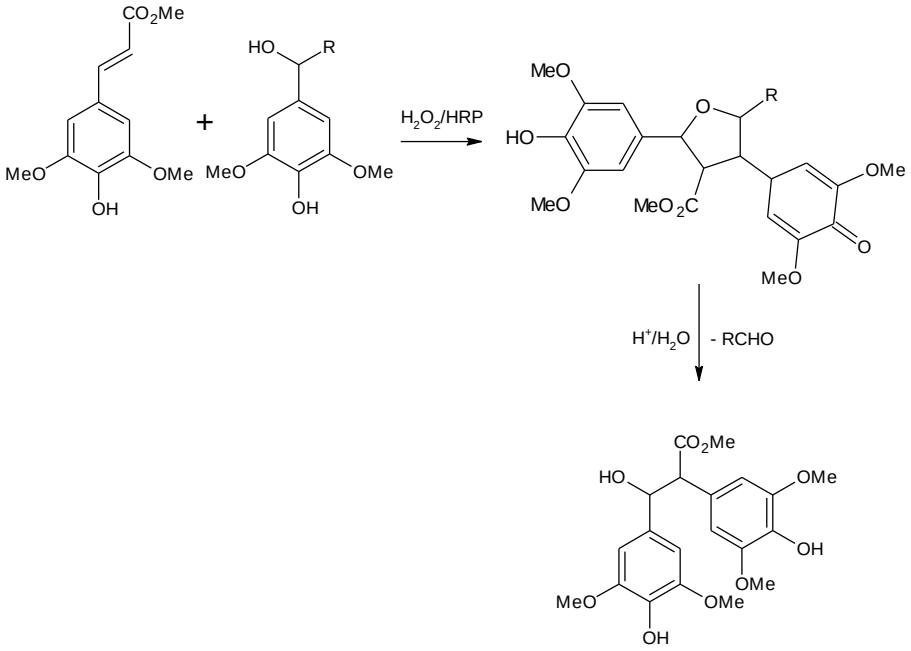


Figure 3.2. 9 Spirocyclodienone undergoing acid-catalysis cleavage to form 1,2-diarylpropane. Source: Gellerstedt and Zhang (1991).

According to Ralph (1999), the advance in techniques such as NMR have discovered novel lignin structure and clarified some mechanisms. Recently, the most important discovery in lignin was dibenzodioxocins (5-5', β-O-4', α-O-4'). This compound is readily apparently in NMR spectra, particularly 2D ^{13}C-^{1}H-correlation (HMQC or HSQC) experiments. Although it have been found in all lignin class (SW, HW and grasses), this structure is more abundant in

softwood (4-5%) (Henriksson, 2009). The arylglycerol-β-aryl ether and dibenzodioxocins (DBDO) structure were detected in bagasse lignin by ^{13}P-NMR and Derivatization Followed by Reductive Cleavage (DFRC Method) (Shu-bin et al., 2006). The DBDO structure is shown in **Figure 3.2. 10**.

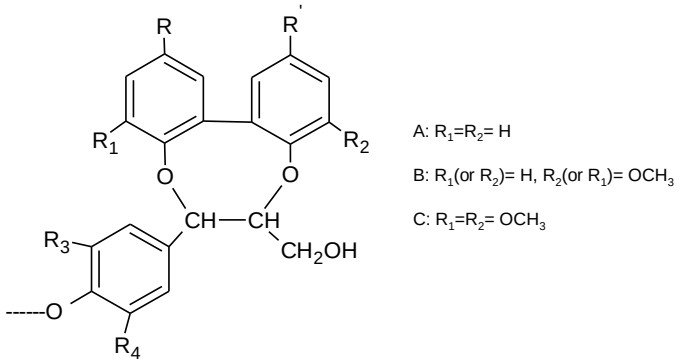


Figure 3.2. 10 - Possible structures of dibenzodioxocins in bagasse lignin. Source: Shu-bin et al. (2006).

A new structural scheme for softwood lignin has been proposed by Brunow et al. (1998) and it is illustrated in **Figure 3.2. 11**. A combination of data from oxidative coupling experiments and 2D NMR spectroscopic studies were taken into consideration. A new feature such as dibenzodioxocin has also been included into this structure. A similar model for the lignin structure in wheat straw has been proposed and it is illustrated in **Figure 3.2. 12**. This model illustrates the types of linkages between the lignin units and also lignin and carbohydrates.

Lignification differs from dimerization of monolignols. Only three dimers (β-β', β-O-4' and β-5') are produced during dimerization of coniferyl alcohol (**Figure 3.2. 13**). The differences in these two processes are very important since it explains why lignification in vivo occurs endwise, while dimerization or bulk polymerization is observed in vitro (Brunow et al., 1998). Lapierre (1993) has clearly shown that synthetic DHP (Dehydrogenation Polymers) differs significantly from spruce in-situ lignin. The relative frequencies (molar % of G unit) involved in 5-5', β-5', β-1', 4-O-5', and β-β' linkages were 35, 33, 26, 6, traces in the in-situ case and 17, 53, 6, 2, 22, in the synthetic DHP case. It has been observed that the end-wise polymerization is favored at low concentrations of coniferyl alcohol, while high concentrations of it favor dimerization (Brunow et al., 1998).

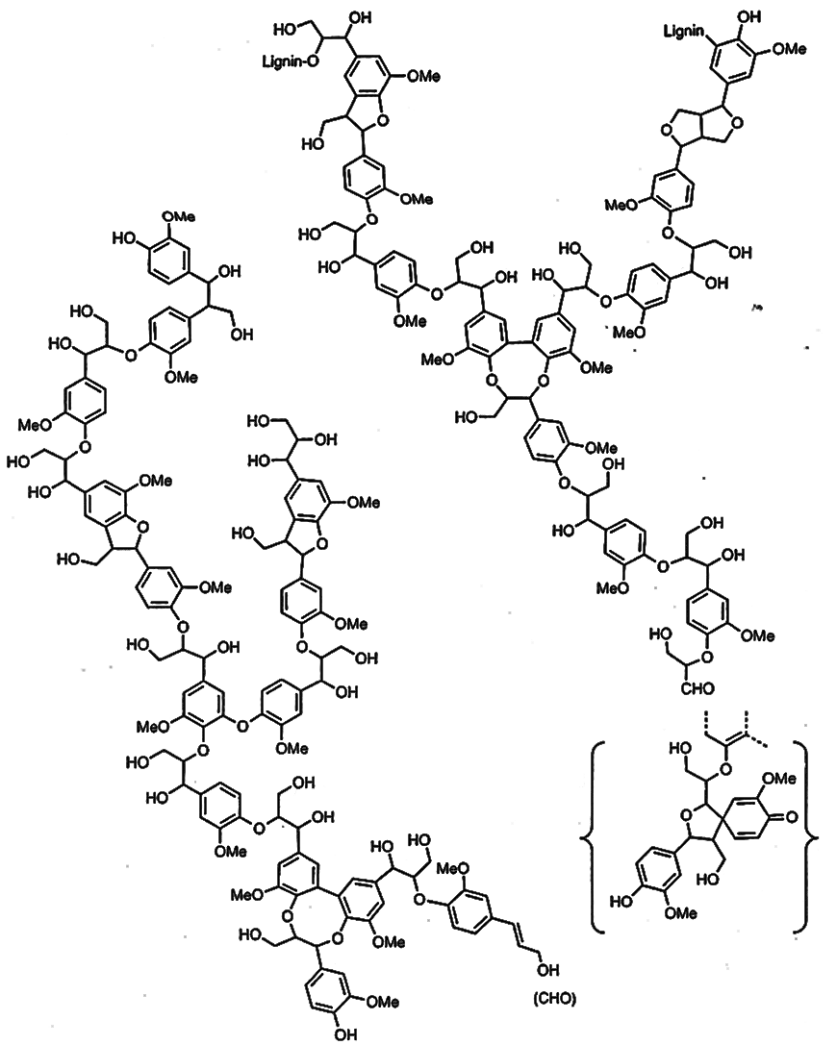


Figure 3.2. 11 Softwood lignin by Brunow et al. (1998).

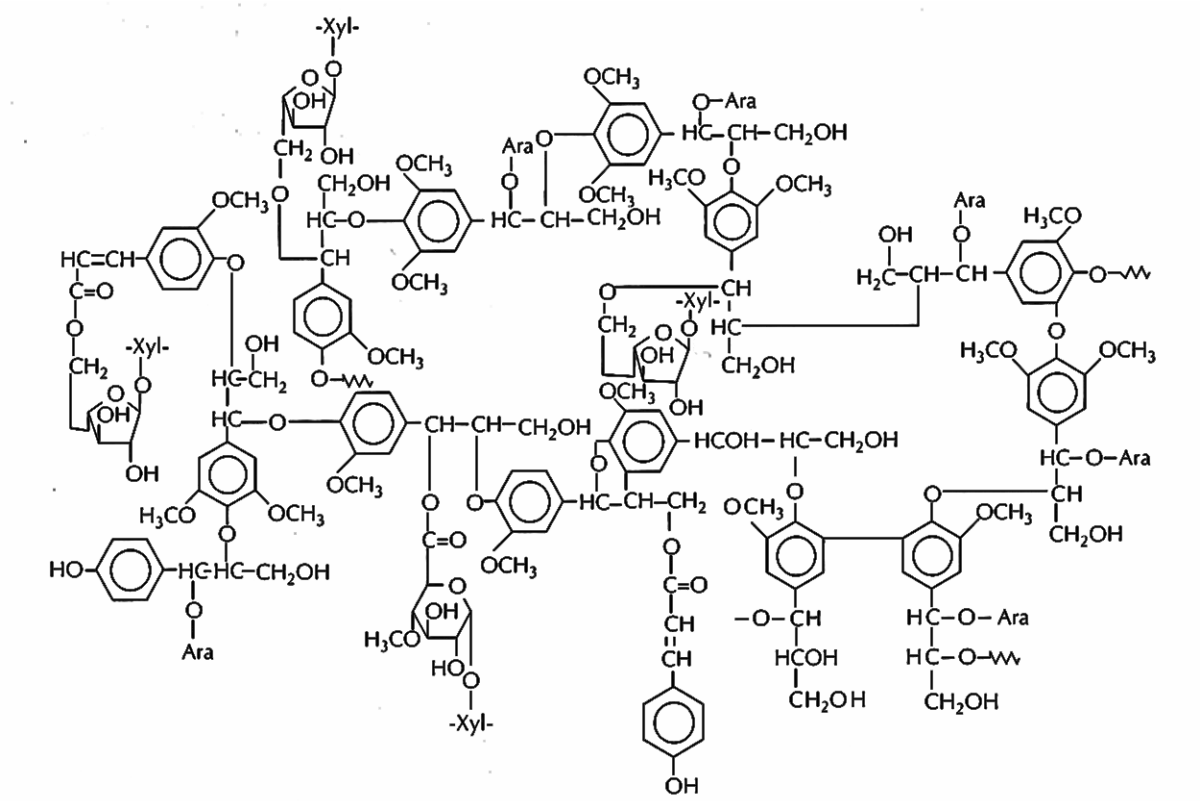


Figure 3.2. 12. Structural model of wheat straw lignin. Source: Xu (2010).

The reasons behind the distribution of different bonds are unknown. It is known however that the β-position is the most reactive. This final distribution of bonding types may be influenced by irreversible hydrolytic reactions. For instance, the formation of the final product in β-O-4' coupling involves the addition of water (external nucleophile) to a quinone methide intermediate. The formation of the *erythro* and *threo* forms of β-O-4' structures from two coniferyl alcohol radicals are illustrated in **Figure 3.2. 14**. On the other hand, no water is required for the formation of final product in β-5' and β-β' structures (Brunow et al., 1998).

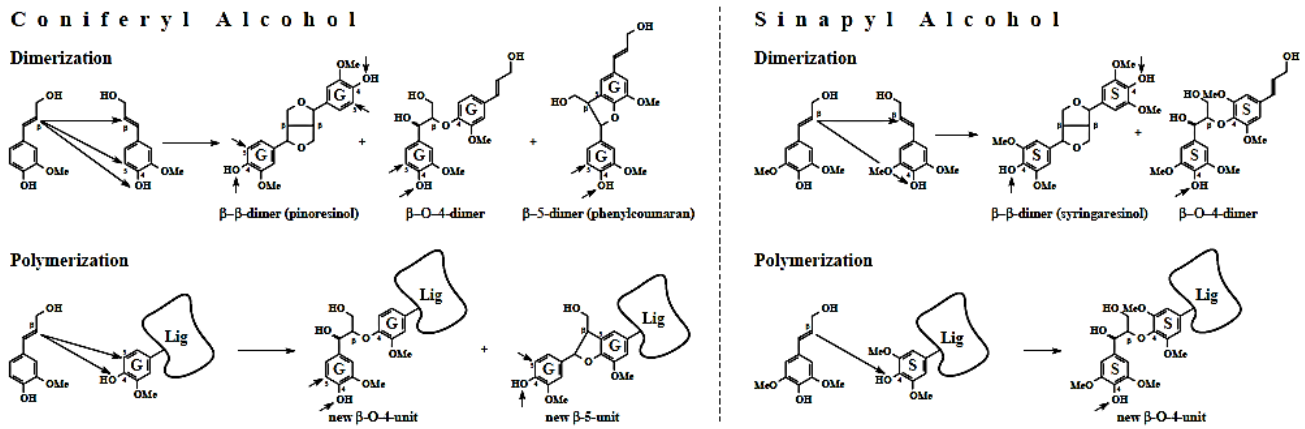


Figure 3.2. 13 Differences between lignification and dimerization. Source: Ralph (1999).

Dimerization is controlled by the reactivities and the concentration of the radicals. In order for cross coupling to occur, those parameters have to favor the process. One parameter is redox potential of the phenolic hydroxyl group (PhOH). Lower redox potential results in higher cross coupling at equimolar concentrations with the rate of coupling of sinapyl alcohol>>coniferyl alcohol>*p*-coumaryl alcohol. Therefore, a phenol with higher redox potential such as one derived from *p*-coumaryl alcohol has to be present at a higher concentration for coupling to occur (Brunow et al., 1998).

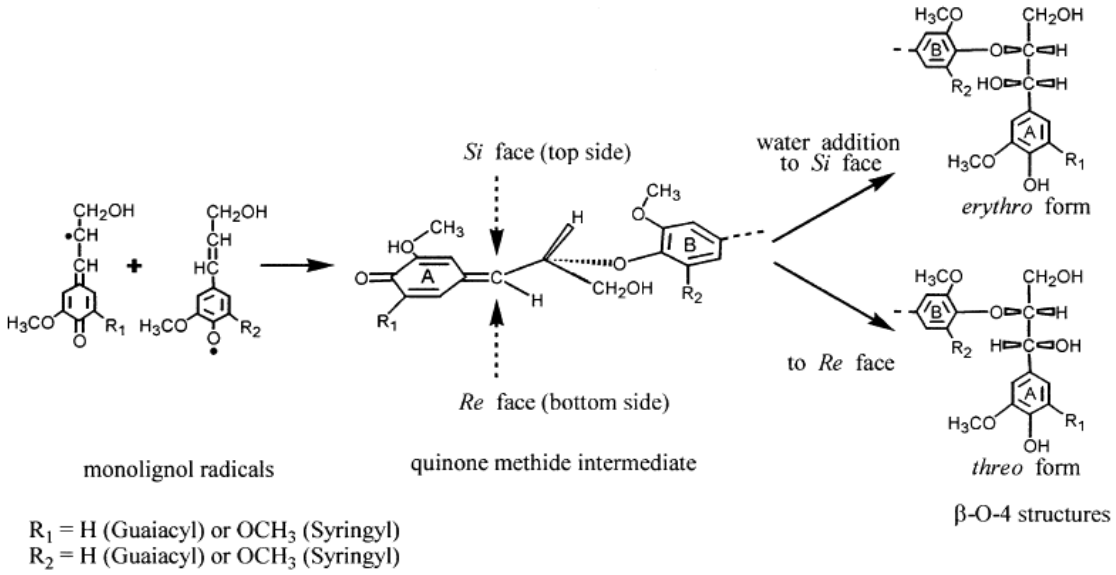


Figure 3.2. 14 Formation of erythro and threo forms of β-O-4' structures by the addition of water to the quinone methide intermediates. Source: Akiyama et al. (2003).

The cell wall formation in graminaceous plants differ significantly from woody plants. Since there is an intercalate meristem and differentiation zone in each internode, no thickening growth occurs in the culm. Also, the lignification patterns in the culm and internodes are different (Terashima et al., 1993). He and Terashima (1991) studied the formation and structure of lignin in cell wall of sugarcane and rice. According to the authors, lignification starts on the protoxylem vessels, proceeds in the compound middle lamellae of fibers and the cell wall of metaxylem vessels, and finally in the secondary walls of the fibers. Secondary walls of fiber and metaxylem vessels have lower lignin content than secondary wall of protoxylem and cell corners. Secondary walls of protoxylem vessel lignin are mainly composed of G units and a small amount of hydroxycinnamic acid moieties; small amount of S units are deposited at later stages of lignification. The lignin in cell wall corners of fibers and the secondary walls of metaxylem vessels consists of G and S units; the proportion of G and S units increase with the progress of lignification. Lastly, in the secondary walls of fibers lignin are composed of S and G units which are deposit throughout the entire lignification process (He and Terashima, 1991).

Phenolic acids (*p*-coumaric and ferulic acids) contents vary with the progress of lignification. Ferulic acid deposits in the cell walls at the early stages of lignification, subsequently *p*-coumaric acid deposits continuously throughout the mid and late stages of lignification, thus becoming the predominant hydroxycinnamic acid. Parenchyma cell wall incorporates more phenolic acids than vascular bundle; in both young and mature tissue (He and Terashima, 1991).

3.3 Lignin-Carbohydrates Complexes in Woody *vs.* Non-Woody Plants

In plant tissue, lignin is associated to other polymers, cellulose and hemicelluloses, which forms a complex structure. The nature of the different bonds between lignin and carbohydrates is highly complex. The term “Lignin-Carbohydrate Complex” or LCC are generally used to describe the covalently bonded aggregates between lignin and hemicelluloses. The most suggested bonds in LCC include benzyl ether and ester, glycosidic and acetal bonds (Stenius, 2000; Koshijima and Watanabe, 2003). However, the benzyl ether and ester types have been

considered to be the most probable mode of linkage (Koshijima and Watanabe, 2003). These bonds are illustrated in **Figure 3.3. 1.**

Atsuhi et al. (1984) reported that *p*-coumaric and ferulic acid are esterified to polysaccharide and lignin moieties in the cell wall of sugarcane bagasse. ^{13}C NMR study on lignin bagasse suggested that *p*-coumaric acid, in *trans*-configuration, is linked to lignin via ester bonds (Fernandez, 1990). Ferulic and *p*-coumaric acids were found in xyloglucan and arabinoxylan preparations of bamboo shoot cell walls. These structures were also found in *trans*-configuration (Ishii and Hiroi, 1990). Ishii (1991) reported for the first time that arabinoxylans are covalently cross-linked via di-ferulic acid in bamboo shoot cell walls. Sun, J.-X. et al. (2004a,b) confirmed the association of esterified hydroxycinnamic acids to L-arabino-(4-O-methyl-D-glucurono)-D-xylan in sugarcane bagasse. ^{13}C NMR spectrum of acid-insoluble lignin indicated that *p*-coumaric acid is linked to lignin by ester bonds, whereas ferulic acid is linked to lignin by both ether and ester bonds (Sun, J.-X. et. al., 2003). Further studies on the cell wall of sugarcane bagasse by a combination of methods (UV and FT-IR spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy) confirmed that a predominant amount of *p*-coumaric acid (69.5-76.4%) is ester linked to mainly lignin. About half of the ferulic acid (44.0-55.0%) is esterified to hemicelluloses. The other half remaining of the ferulic acid is etherified thought the phenolic oxygen to lignin (Xu et al., 2005).

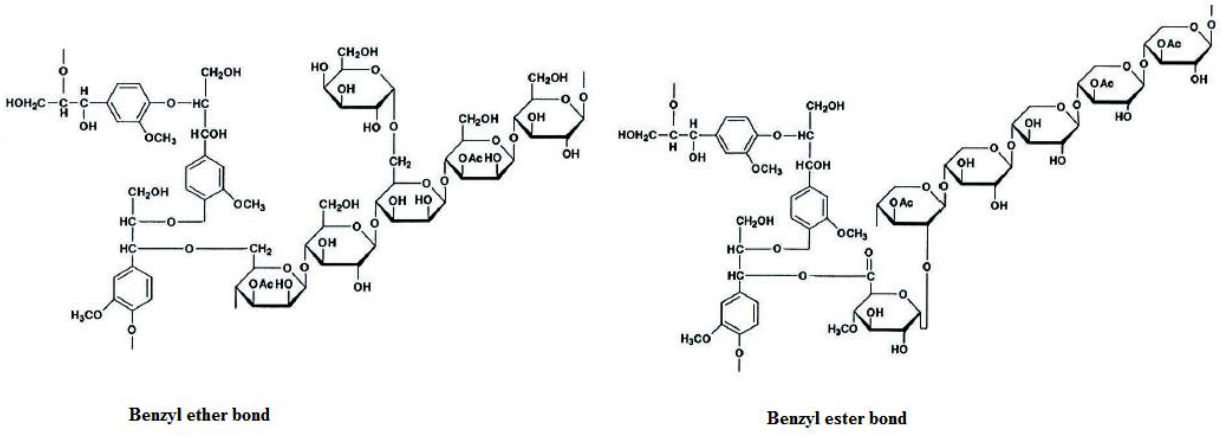


Figure 3.3. 1 Most probable linkages between lignin and hemicelluloses. Source: Koshijima and Watanabe (2003).

The LCCs from herbaceous crops are different from those found in wood. It has been reported in the literature that ferulic acid are esterified to arabinoxylan through the arabinose residues. Three types of arrangements have been identified and they were summarized by Ralph et al. (1998): a) FAXX= *O*-[5-*O*-*trans*-feruloyl)-α-L-arabinofuranosyl]-(1→ 3)-*O*-β-D-xylopyranosyl-(1→ 4)-D-xylopyranose; b) FAXXX= *O*-β-D-xylopyranosyl-(1→ 4)-*O*-[5-*O*-*trans*-feruloyl-α-L-arabinofuranosyl-(1→ 3)]-*O*-β-D-xylopyranosyl-(1→ 4)-D-xylopyranose and c) X-(F)A= 2-*O*-β-D-xylopyranosyl-(5-*O*-*trans*-feruloyl)-L-arabinose (**Figure 3.3. 2**). This association between ferulic acid with polysaccharides are called ferulates (de O. Buanafina, 2009). It has been identified in barley straw cell walls not only feruloyl but also *p*-coumaroyl groups bound to carbohydrates. These associations were type FAXX and PAXX (*O*-[5-*O*-*trans*-*p*-coumaroyl)-α-L-arabinofuranosyl]-(1→ 3)-*O*-β-D-xylopyranosyl-(1→ 4)-D-xylopyranose (Mueller-Harvey et al., 1986).

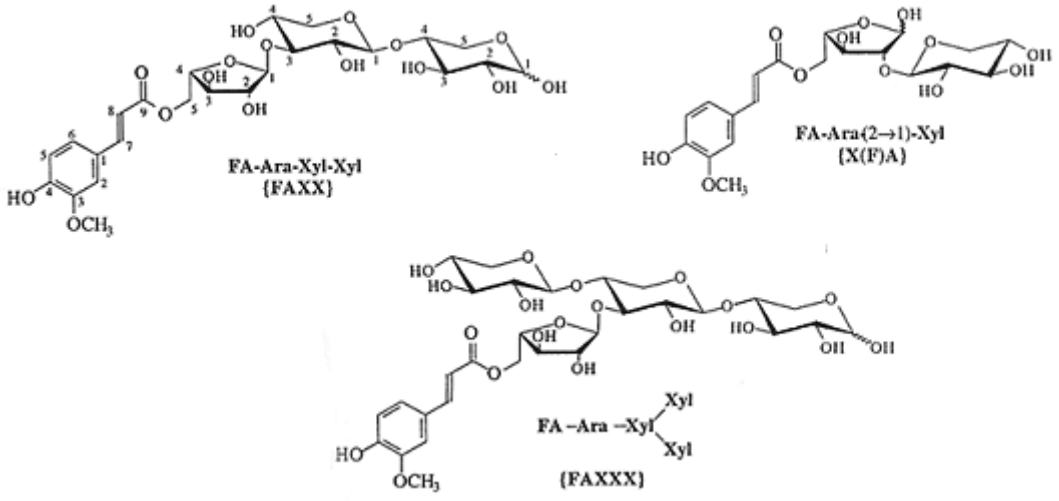


Figure 3.3. 2 Ferulate-Oligosaccharide esters isolated from grass cell wall following dissolution by mild acid or enzyme hydrolyzates. Source: Ralph et al. (1998).

Ferulate-polysaccharide esters, arabinoxylans feruloylated at C-5 of α-L-Ara*f* moiety, "attach" to lignin during cell wall development (Ralph et al., 1995). Two different mechanisms have been proposed for this attachment. They are called active and passive (or opportunistic) (**Figure 3.3. 3**). In the active mechanism, the ferulate is incorporated into lignin via oxidative

coupling process. In the passive mechanism, the ferulate nucleophile (1) "opportunistically" reacts with the quinone methide intermediates (13) to form benzyl aryl ethers (Ralph et al., 1995). The nucleation sites for lignification for ferulic acids and similarly for di-ferulates are summarized in **Figure 3.3. 4** (Buranov and Mazza, 2008). It is believed that ferulates are functioning as initiation sites or nucleation sites for lignification process. Not only ferulates, but also ferulate dimers are incorporated into the newly forming lignins via radical coupling (Hatfield et al., 1999).

Ferulic acid (FA) and *p*-coumaric acid (*p*-CMAc) are synthesized by the phenylpropanoid pathway. Although, they are structurally related, it is believed that these compounds have different functional roles within the cell wall. As already discussed, ferulates have a critical role in cross-linking between structural polysaccharides and links between lignin and polysaccharides. The role of *p*-coumarates in plant cell walls is not fully understood (Hatfield and Marita, 2010). However, Hatfield et al. (2008) proposed a possible role of *p*-coumarates as an oxidation shuttle. The *p*-CMAc component of a sinapyl alcohol-*p*-coumaric acid conjugate (SA- *p*-CMAc) can be readily oxidized and will subsequently transfer its oxidation state to a suitable acceptor molecule such as sinapyl alcohol. The authors suggest that even though the oxidized ferulate could also exchange its oxidative state with sinapyl alcohol, this role would be limited due to the attachment of ferulates to arabinoxylans. It could limit their mobility in the grass cell wall. On the other hand, SA- *p*-CMAc conjugates could diffuse into the wall along with sinapyl alcohol residues. The oxidized *p*-coumarate units remain largely uncoupled; it does not radically couple with sinapyl alcohol or syringyl units in lignin. This idea has proved to work in vitro but it remains to determine if this process indeed occurs within the cell wall matrices. Hatfield and Chaptman (2009) observed a positive relationship between the amount of the *p*-CMAc and the amount of lignin within a specific tissue of a given corn type. They suggest that there are some relationships between *p*-coumaroylation and lignin accumulation in grass cell wall.

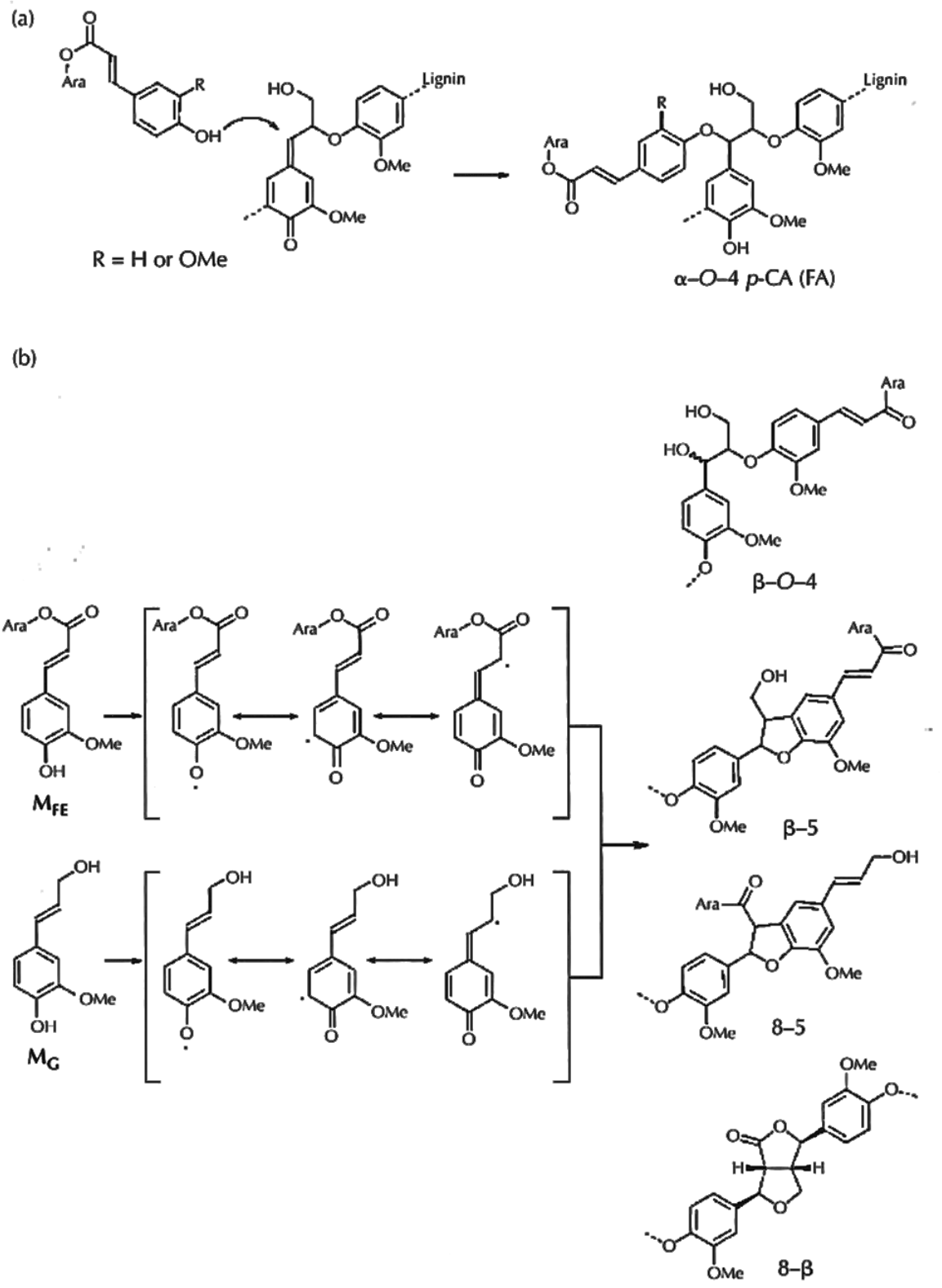


Figure 3.3. 3 Mechanism for incorporatation of ferulates into lignins: a) "Passive" mechanism, b) "Active" Mechanism. Source: Lu and Ralph (2010).

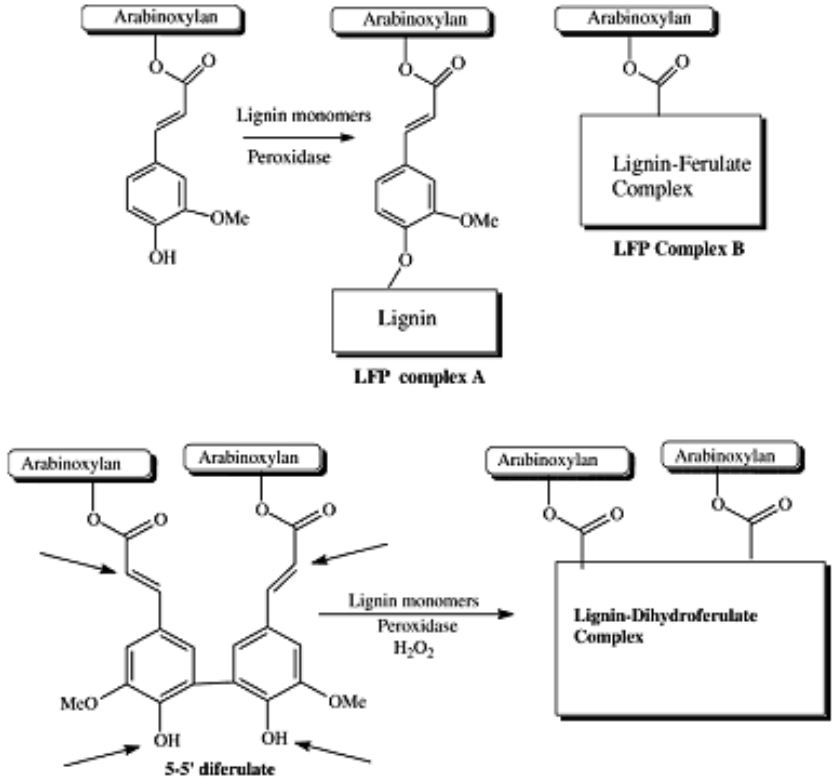


Figure 3.3. 4. a) Lignification mechanisms involving ferulates; b) Incorporation of 5-5’ –di-ferulates into lignins. Source: Buranov and Mazza (2008).

In summary, several types of linkages may occur in cell wall grasses (**Figure 3.3. 5**). Acetylation of xylan is shown in (1). Ester linkages occur between α-L-Ara*f* branch in the xylan chain and FA (2). Arabinofuranose can also be directly linked with lignin (3). Cross-linking between arabinoxylan chains occurs by 5-5’-ester linked FA dimer (4). FA simultaneously links α-L-Ara*f* by ester bonds (2) and lignin by ether bond (5) (de O. Buanafina, 2009).

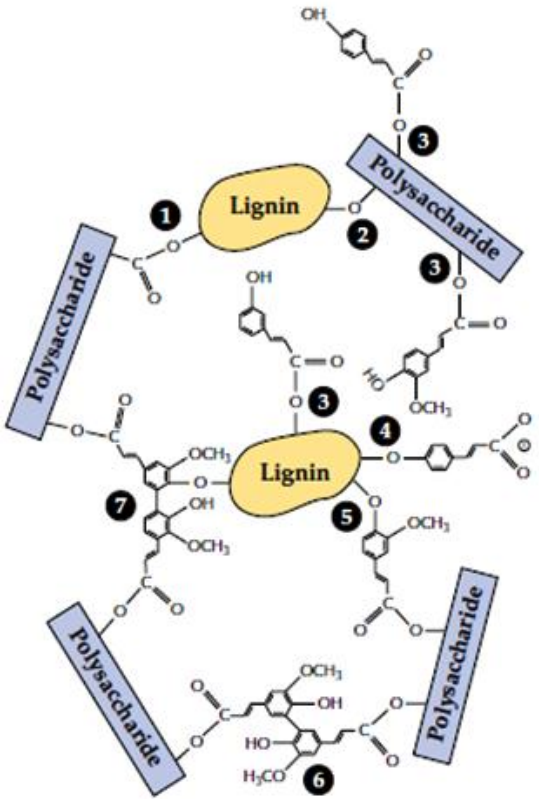


Figure 3.3. 5 Lignin carbohydrate network in non-woody ; 1) direct ester linkage; 2) direct ether linkage; 3) hydroxycinnamic acid ester; 4) hydroxycinnamic acid ether; 5) ferulic acid bridge; 6) dehydro di-ferulic diester bridge and 7) dehydro di-ferulic diester-ether bridge and 8) dehydro di-ferulic di-ester-ether bridge. Source: Carpita (2000).

3.4 Fractionation of Lignin/Phenolic-Carbohydrate Complex

Plant carbohydrates are mainly built by glycosidic bonds. Acetyl groups in hemicelluloses are linked to the pentoses by ester bonds, while for lignin, in addition to ether bonds, C-C-bonds also occur between phenylpropane units (Bobleter, 1994). Hydrolysis leads to cleavage of ether and ester bonds with addition of one molecule of water for every broken linkage. Experimental reaction rate results have shown that the cleavage of glycosidic bonds in water-soluble carbohydrates is the highest. Generally, hemicelluloses are much less resistant to hydrolysis than cellulose due to the higher accessibility of their branched chains. The good thermal stability of lignins requires elevated temperature for hydrothermal reactions (Bobleter, 1994).

Although lignocelluloses materials can be hydrolyzed by water (Jacobs et al., 2002); acid (Nigam, 2001; Aguilar et al., 2002; Lavarack et al., 2002; Gámez et al., 2006; Cheng et al., 2007;

Canettieri et al., 2007); alkali (Xu et al., 2006); enzymes (Badger, 2002; Gáspár et al., 2005; Mazumder et al., 2005; Öhgren et al., 2007; Gáspár et al., 2007), and combinations of these methodologies (Lloyd and Wyman, 2005), acid hydrolysis is the one most widely used. The typical goals of these pretreatments include: 1) Production of digestible solids that enhances sugar yields during enzyme hydrolysis, 2) Avoiding the degradation of sugars (mainly pentoses) including those derived from hemicellulose, 3) Minimizing the formation of inhibitors for subsequent fermentation steps, and 4) Recovery of lignin for conversion into valuable co-products (Brodeur et al., 2011).

The Consortium for Applied Fundamentals and Innovation (CAFI) formed in early 2000 has compared leading pretreatment technologies. The pretreatments investigated in this research used dilute acid, sulfur dioxide, ammonia and lime over a wide range of pH. Whereas low pH acidic treatments tend to remove and recover significant fraction of hemicelluloses, high pH pretreatments typically remove lignin (Yang and Wyman, 2008). **Table 3.4. 1** presents the key features that differentiate amongst the pretreatments. As can be seen, steam explosion, hot water and acidic treatments basically remove hemicelluloses with minor to major alterations in lignin structure. On the other hand, alkaline treatments remove lignin and hemicellulose to some extension. Additionally, all those treatments are believed to increase surface area/porosity (Thompson et al., 1992; Chang et al., 1998; Kim et al., 2003; Lloyd and Wyman, 2005; Mosier et al., 2005; Teymouri et al., 2005; Kim et al., 2008; Karunanithy and Muthukumarappan, 2011)

The effect of pretreatment on the grass cell wall is illustrated in **Figure 3.4. 1**. As can be seen, the main effects of pretreatment are the cleavage of LCC, hemicellulose solubilization, coalescing of lignin, some cellulose decrystallization and increase in porosity (Chundawat et al., 2011).

There are three general chemical categories of hemicellulose extraction: alkaline, acidic, and solvent. Some of these methods have been used prior to making paper products; others have been developed for facilitating total conversion of lignocellulose to fuels and chemicals. However, not many of these treatments have been investigated regarding them offering benefits to pulping, bleaching and/or papermaking (Kenealy et al., 2007). For ethanol production, the purpose of pretreatment is to remove lignin and hemicellulose, reduce crystallinity, and increase the porosity of the materials. In addition to that, it has to improve the yield of sugar monomers in

subsequent enzymatic hydrolysis, minimize carbohydrate loss and formation of byproducts that could be inhibitory to subsequent hydrolyses and fermentation process and be cost-effective (Sun and Cheng, 2002).

Table 3.4. 1 Effect of various pretreatment methods on the chemical and chemical/physical structure of lignocellulosic biomass

Pretreatment	***Removes hemicellulose***	***Removes lignin***	***Alters lignin structure***	***Increases accessible surface area***
Uncatalyzed steam explosion	++		+	++
Liquid hot water	++		+	++
pH controlled hot water	++			++
Flow-through liquid hot water	++	+	+	++
Dilute acid	++		++	++
Flow-through acid	++	+	++	++
AFEX	+	++	++	++
ARP	+	++	++	++
Lime	+	++	++	++

++: Major effect; +: Minor effect
Source: Mosier et al. (2005).

For the pulp and paper industry, the objective of pretreatment is to utilize materials that are difficult to retain in the fibers during the cooking and bleaching process. Since these material will dissolve during processing, using a pretreatment to remove them without significant modification is a good idea (Kenealy et al., 2007). For instance, hemicelluloses are underutilized in the kraft pulping process as they are degraded into low molecular weight compounds during cooking and end up in the black liquor along with the degraded lignin. Therefore, the degraded hemicelluloses in the black liquor are combusted in the recovery boiler. However, the heating value of wood carbohydrates ($\sim$ 13.6 MJ/kg) is only approximately half of the lignin. Extracting the hemicelluloses before pulping for generation of high value products would be a more economical approach (Amidon et al., 2006; Tunc and van Heiningen, 2008; Al-Dajani and Tschirner, 2008).

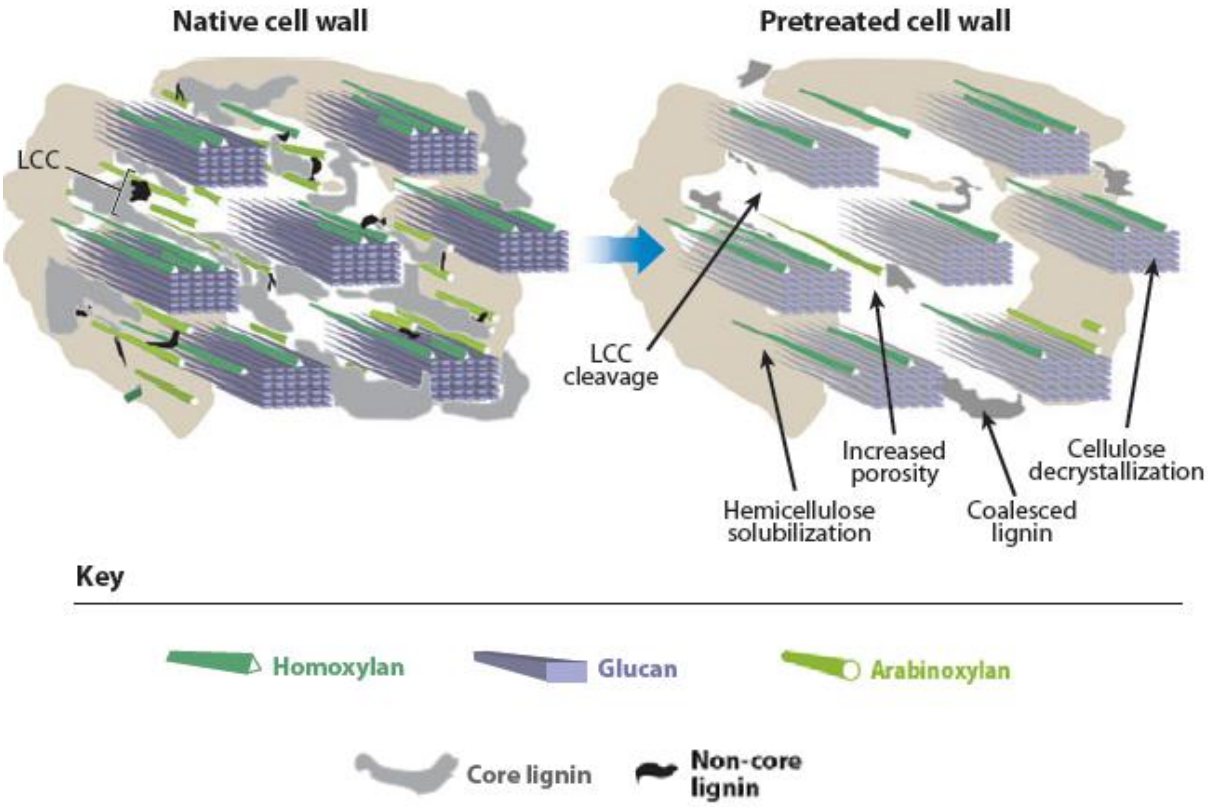


Figure 3.4. 1 Effect of pretreatment on the cell wall of monocot grass. Source: Chundawat et al. (2011).

Fractionation technologies used for corn stover can be divided into two major groups alkaline and acidic (Buranov and Mazza, 2008). Alkaline treatments are used to break the ester bonds between arabinoxylan and hydroxycinnamic acids. Those treatment include aqueous ammonia fiber explosion (AFEX), ammonia recycle percolation (ARP) and over-liming ($Ca(OH)_2$) approaches. For the cleavage of the ether bonds between lignin and hydroxycinnamic acids, treatments with steam (steam explosion), hot water, dilute acid, aqueous ammonia and lime are considered the most promising. The acid and alkali-labile bonds are shown in **Figure 3.4. 2**.

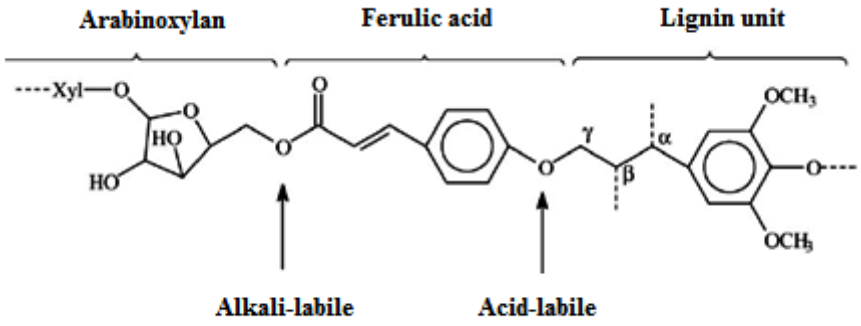


Figure 3.4. 2 The cleavage sites of lignin/phenolics–carbohydrate complexes during acid and alkali pretreatments. Source: Buranov and Mazza (2008).

3.4.1 Hydrothermolysis Pretreatment

Water pretreatments use pressure to maintain the water in the liquid state at elevated temperature. This water, at elevated temperature, is passed through the lignocellulosic biomass in the flow-through processes. This type of pretreatment has been termed hydrothermolysis, aqueous or steam/aqueous fractionation, uncatalyzed solvolysis and aquasolv (Mosier et al., 2005).

In order to remove pith from bagasse and recover hemicelluloses, Jahan et al. (2009) pre-extracted bagasse with water at 150^{o}C for 60 min. After extraction the pH of the hydrolyzate was 3.57 and the total weight loss was 26.7% on bagasse. Under those conditions, 16.11% of sugars (based on initial bagasse), 6% of lignin, 0.38% of acetic acid and 0.32% of furfural were recovered in the hydrolyzate. Hydrothermolysis was used to treat switchgrass in order to disrupt lignin, dissolve hemicellulose, and increase accessibility of cellulose to cellulase enzymes. Amongst the temperatures (190, 200 and 210°C) and hold times (10, 15, and 20 min.), the greatest recovery of xylan in the hydrolyzate was at 190°C for 10 min. At those conditions, less than 1g/L of furfural and hydroxymethylfurfural were measured in the hydrolyzate. Additionally, acetic acid formation increased with increasing temperature. The highest concentration of acetic acid was 5.1 g/L at 210°C for 10 min (Suryawati et al., 2009). Hydrothermal pretreatment was also used in wheat straw and the separation of cellulose and hemicellulose was achieved at relatively short residence time (10-20 min.) and moderate temperature (~ 200°C). Delignification values between 44.4% and 58.0% were observed with the highest value being

obtained at 195°C with fiber recovery of 61.5%. The authors suggested that this pretreatment allows a subsequent utilization of the cellulosic residue for the production of pulp and paper (Kubikova et al., 1996).

3.4.2 Alkaline Pretreatments of Non-Woody Materials

3.4.2.1 Pretreatment with Sodium Hydroxide

When agricultural residues such as wheat straw and corn stover were treated at room temperature (25°C) in alkaline solution of hydrogen peroxide, approximately one-half of the lignin and most of hemicelluloses were solubilized. The delignification efficiency was highly dependent on the pH. The maximum delignification was at pH 11.5. This was explained by the formation of the highly reactive hydroxyl radical ($OH^{\bullet}$) formed during the decomposition of H_2O_2 (Gould, 1984; Gould and Freer, 1984).

Hydroxycinnamic acids in ester and α-aryl ether linkages from wheat internodes have been released at room temperature and alkaline treatment at 170^{o}C. The ester linkages joining phenolic acids in the cell walls are easily saponified by dilute alkali at room temperature. While phenolic benzyl aryl ether is cleaved only at high temperature (170^{o}C), non-phenolic benzyl aryl ethers are only partially cleaved under these conditions (Iyama et al., 1990). **Figure 3.4. 3** illustrates these different compounds released in the cleavage of lignin/phenolic-carbohydrates by alkali treatment. According to Jung and Shalita-Jones (1990), different preparation conditions and alkali concentration yield different molar ratio of *p*-coumaric to ferulic acids extracted from forage samples.

Buranov and Mazza (2009) used non-pressurized and pressurized alkaline hydrolysis and pressurized solvent extraction procedures in order to extract phenolic compounds from flax shives, wheat and corn bran. In the extraction with 0.5M NaOH at 50^{o}C for 4 hours the yield of ferulic acid were 25, 391 and 2510mg/100g and *p*-coumaric acid were 61, 20, 350mg/100g obtained from flax, wheat and corn, respectively. Some degradation of the bound-ferulic acid in the biomass into vanillic acid, vanillin and acetovanillone was observed under the pressurized conditions of water and ethanol. Moreover, the authors suggested a commercially production of ferulic acid by easily precipitating it with 30% aqueous ethanol.

Successive alkali and hydrogen peroxide treatments on rice straw were also able to cleave the α-benzyl linkages between lignin and hemicelluloses fractions. However, the hydroxycinnamic acids such as ferulic and *p*-coumaric acids in the hemicelluloses fractions or lignin in the rice straw have shown to be strongly bound to that fraction. These results were confirmed by nitrobenzene oxidation which ferulic and *p*-coumaric acids were further oxidized to vanillin and *p*-hydroxybenzaldehyde, respectively (Sun, R.-C. et al., 2000a). Alkaline peroxide treatment of wheat straw indicated lower lignin content (3.8%) bounded to the solubilized hemicellulose fractions. However, an extended treatment with 0.05% AQ in H_2O_2 solution resulted in an increase of associated lignin (6.5%), presumably due to condensation (Sun, R.-C. et al., 2000b).

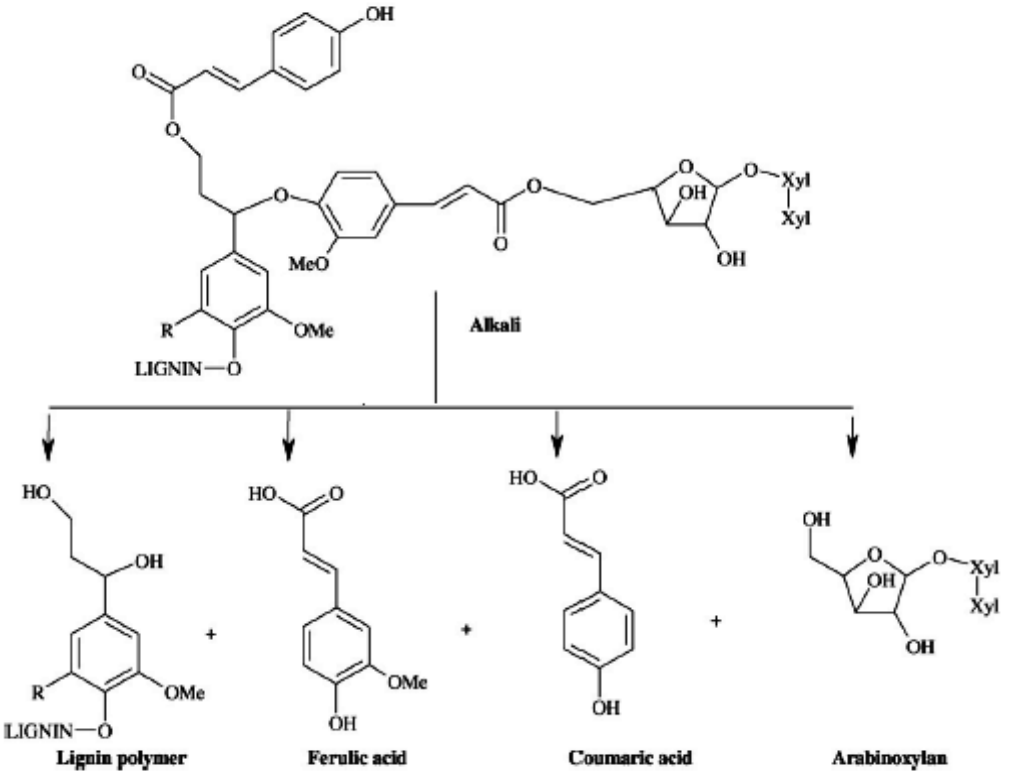


Figure 3.4. 3 Lignin/phenolic-carbohydrate complex from corn cob cell walls and its cleavage with alkali. Source: Buranov and Mazza (2008).

The influence of different alkaline pretreatments in wheat straw on loss of dry matter, lignin and hemicellulose were studied by Sun, R.-C. et al. (1995). There was an 11%

solubilization of the hemicelluloses with minimal loss of lignin when the wheat straw was treated with a 1.5% $Ca(OH)_2$ solution for 6h at 20^oC. On the other hand, 1.5% H_2O_2 on biomass at the same conditions dissolved more than 7% of lignin, while no hemicellulose solubilization occurred. The pretreatment with 0.1g $Ca(OH)_2$/g dry biomass for 2 hours at 120^oC removed large amounts of lignin, xylan and crude proteins in switchgrass. Lime (calcium hydroxide) is a very inexpensive and safe to handle. However, it is a weak alkali which is minimally soluble in water. Therefore, lime pretreatment is put at disadvantage compared to sodium hydroxide, ammonia and potassium hydroxide (Chang et al., 1997). The authors suggested that the removal of both lignin and hemicelluloses contributed to the increase of the biomass digestibility. Similar conditions but shorter time (1h) was used in the pretreatment of bagasse. At these conditions, no removal of ash, xylan and glucan was observed but 14% of lignin and 23% of crude proteins were released during the lime pretreatment. Since the lime pretreatment was mild, the biomass yield was high (93.6%) (Chang et al., 1998).

When sugarcane bagasse was pretreated with lime and lime plus hydrogen peroxide, peroxide addition led to higher glucose yield at a lower temperature and in less time. At the optimal conditions, the bagasse pretreated with peroxide presented lower total mass compared to the pretreated with lime which had lower removals of lignin and hemicelluloses (Rabelo et al., 2011).

3.4.2.2 Ammonia Pretreatments

Ammonia pretreatment has been currently studied specially on low lignin content material such as agricultural residues and herbaceous feedstock. It has successfully demonstrated a good delignification without affecting the carbohydrate content. Furthermore, the lignin generated is sulfur and sodium-free. Two different approaches based on aqueous ammonia have been used. They are Ammonia Fiber Explosion (AFEX) and Ammonia Recycle Percolation (ARP).

Ammonia Fiber Explosion (AFEX) utilizes the same techniques as steam explosion but uses ammonia as the chemical reagent. In a pressure vessel, the biomass is placed with ammonia (2kg/kg of dry biomass) and treated with temperatures below 100°C and high pressures (above 3 MPa) for a period varying from 10 to 60 min. After treatment, the pressure is released and the

fibrous biomass is exploded and the ammonia is then recovered for reuse. Because of the high volatility of ammonia, the unbounded ammonia can be easily recovery by distillation and recycled (Kim et al., 2009).

Ammonia-Recycled Percolation (ARP) also uses ammonia as the treatment reagent but in this process the reactor is a packed-bed flow-through-type (percolation reactor) used in a recirculation mode. The biomass is placed into the reactor and the preheated liquid ammonia (10-15% wt) is passed through the substrate. The reaction occurs at elevated temperatures (150-180°C and, after the pretreatment, ammonia is also recovered. Both AFEX and ARP are more effective with agricultural residues than with woody materials (Gong et al., 1999; Galbe and Zacchi, 2007).

The lignocellulosic material is treated with high-pressure liquid ammonia in the AFEX pretreatment, and then an explosion occurs during the pressure release. The lignocellulosic materials improved response to the post enzymatic treatment is due to a combination of chemical changes such as cellulose decrystallization and physical changes such as increase in surface area. The process parameters conditions are ammonia and water loading, temperature, time and blowdown pressure (Holtzapple et al., 1991). Those authors (Holtzapple et al., 1991) optimized the AFEX conditions of three lignocellulosic materials: coastal Bermuda grass, bagasse and newspaper. The difficulties in treating the materials increased with the increase in lignin content (Bermuda grass< bagasse< newspaper). The reactivity of the biomass was more dependent on the temperature than ammonia and water loading. Several studies have shown improvements in the enzymatic hydrolysis of corn stover (Moniruzzaman et al., 1997; Teymouri et al., 2004; Teymouri et al., 2005) and switchgrass (Alizadeh et al., 2005), forage and sweet sorghum (Li et al., 2010) by AFEX treatment.

Prior and Day (2008) investigated the degree of hydrolysis of sugarcane bagasse by AFEX process and NH_4OH pretreatments with enzymatic hydrolysis with combinations of cellulase, β-glucosidase, and hemicellulase enzymes. The conditions used for AFEX were 2.0g NH_3/g bagasse, 100°C, and residence time of 30 minutes. While the NH_4OH pretreatment was with 0.5 g NH_4OH of a 28% [v/v] per gram of dry bagasse at 160°C for 60 min. Both pre-treatments seemed to increase the glucan content from 38.4% for the starting bagasse to 41.7% for AFEX and to 56.6% for NH_4OH. Better delignification was obtained with NH_4OH

pretreatment (15.6% on bagasse lignin removal) than AFEX pretreatment (9.6%). On the other hand, when Teixeira et al. (1999) used 2.63% and 5.25% ammonium hydroxide (on biomass) in the pre-treatment of bagasse, little improvement on the sugar conversions was observed. Better conversion was then achieved when higher ammonium hydroxide solution (14% on biomass) was used. The treatments were performed at room temperature for 24 hours.

Some limitations of the ammonia-based pretreatments were pointed out by Kim et al., (2009). Although the high volatility of the ammonia makes the recovery process easier, it also requires high pressure to keep it into solution and also, even higher pressure can be developed during the process. However, an upper limit of pressure about 30kg/cm^2 or 450 psi was found for a reaction conditions range of 60-180°C and 5-15% NH_3 on dry biomass.

3.5 Alkaline Pulping of Woody and Non-woody Biomass

3.5.1 Mechanisms to Explain Depolymerization During Kraft and SAQ Cooking

The main fragmentation reactions of lignin in alkaline media are the cleavages of α-aryl ether bonds in phenolic units and of β-aryl ether bonds in phenolic and non-phenolic units (Gierer, 1985). The chemistry of cleavage of phenolic β-O-4' structures is shown in **Figure 3.5. 1**. The phenolate rearranges to a quinone methide (QM) in an equilibrium reaction. The sulfide and hydrosulfide anions add to the QM to generate a benzyl thiol group that dissociates to the thiolate. This thiolate anion adds to the β-carbon atom in a neighboring group nucleophilic reaction with the formation of a thiirane (episufide) and a new phenolic end group. Because the episulphide structure is not stable, some desulfurization does occur resulting in the formation of some coniferyl alcohol (CA). The formation of CA during both kraft and kraft-anthraquinone (AQ) pulping has been monitored by Mortimer (1982) (**Figure 3.5. 2**a). The formations of coniferyl and sinapyl alcohol (SA) have been also monitored by Venica et al. (2008) in soda and SAQ pulping of hardwood (**Figure 3.5. 2**b).

A significant increase in the formation of coniferyl alcohol (CA) is obtained when anthraquinone is added in both kraft and soda pulping (**Figure 3.5. 2**a, b). Typically CA generation is four to five times higher in SAQ than in kraft pulping. Mortimer (1982) attributes

the decreases of the CA concentrations, after reaching a maximum at 140°C, as being due to its decomposition/transformation into vinylguaiacol (VG), isoeugenol (IE) and other products.

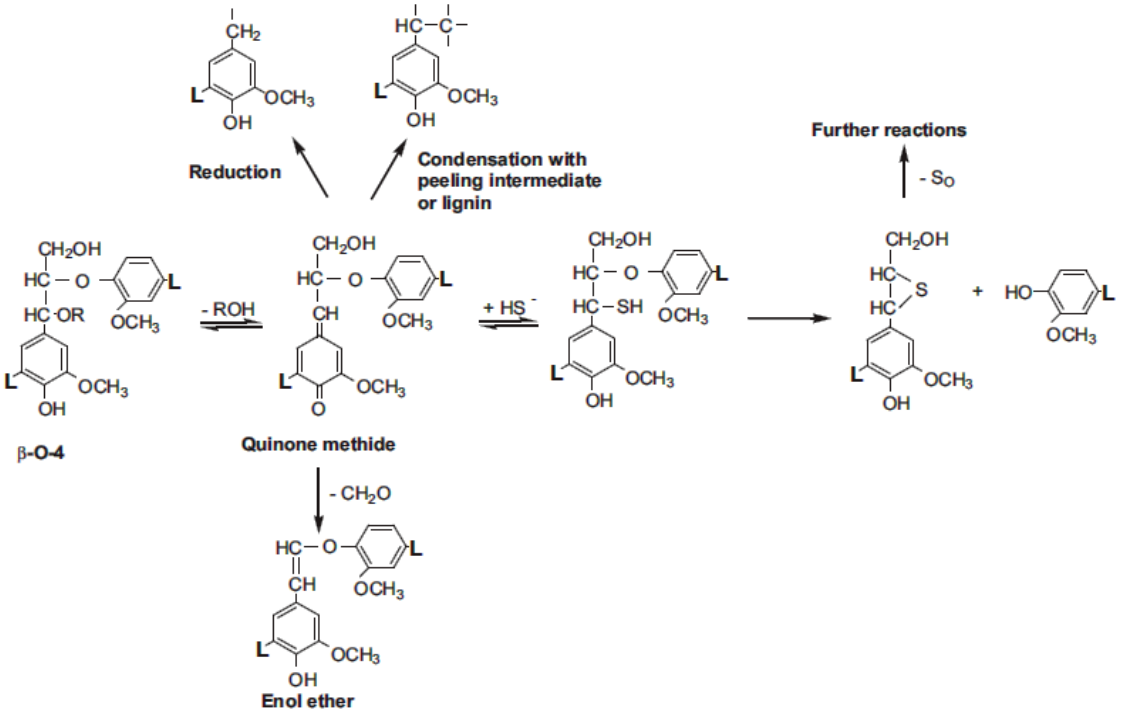


Figure 3.5. 1 Reaction scheme for the cleavage of phenolic β-O-4' structures in lignin kraft pulping conditions. L denotes a lignin residue. Source: Gellerstedt (2009).

The ionic mechanism that explains the high yield of CA, SA and *p*-coumaryl alcohol (*p*-CMA) from SAQ delignification of biomass is shown in **Figure 3.5. 3** (Gierer et al., 1979; Landucci, 1980; Venica et al., 2008). However a credible free radical mechanism is also supported by substantial data (Dimmel, 1985; Smith and Dimmel, 1994). The transformation of CA to VG and IE can be explained by the reactions in **Figure 3.5. 4**.

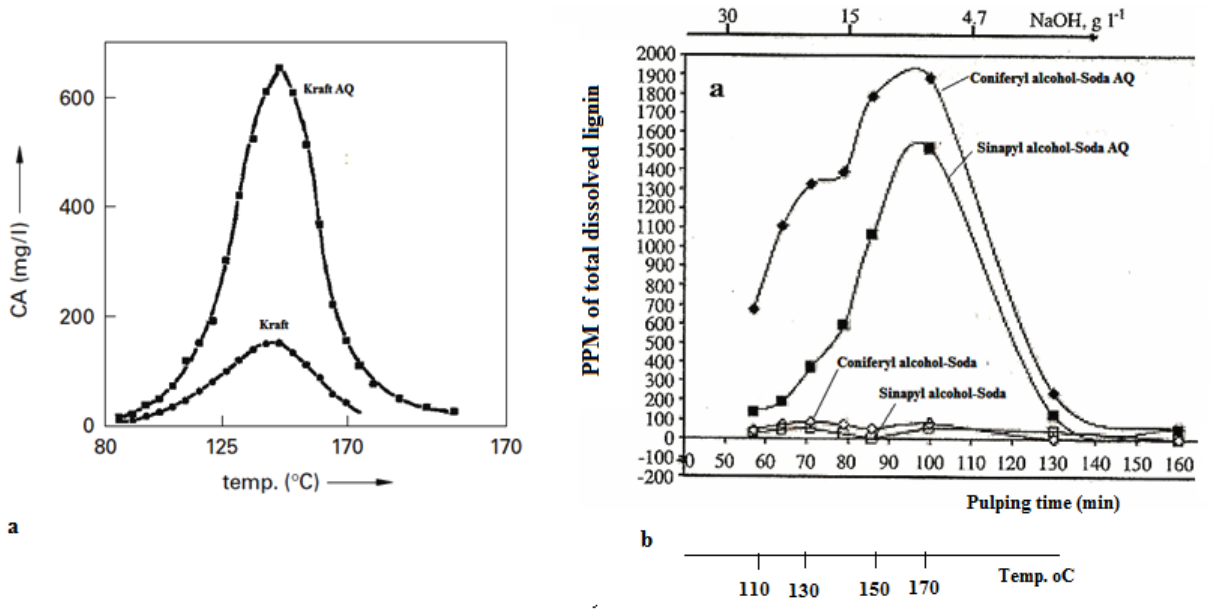


Figure 3.5. 2 a) The presence of coniferyl alcohol (CA) in the pulping liquor of softwood. Source: Mortimer (1982); b) Formation of coniferyl and sinapyl alcohol during soda and soda-AQ (SAQ) pulping. Source: Venica et al. (2008).

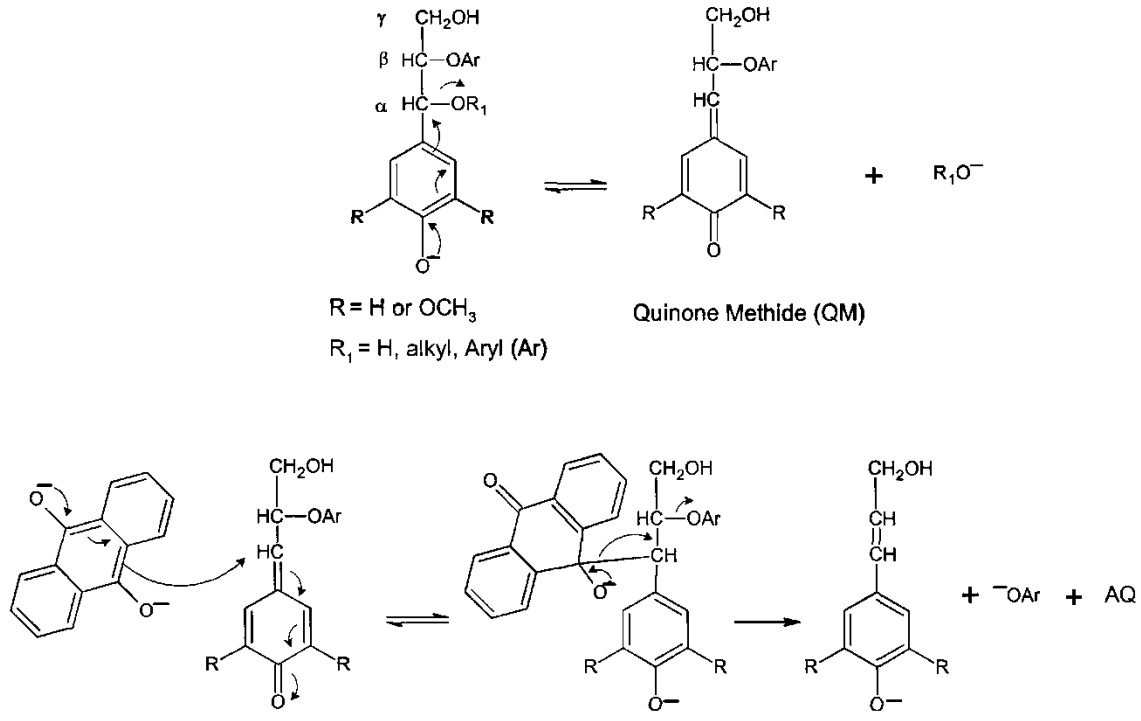


Figure 3.5. 3 SAQ depolymerization of lignin to generate *p*-coumaryl, coniferyl and sinapyl alcohols (Gierer et al., 1979; Landucci, 1980; Venica et al., 2008).

3.5.2 Condensation Reactions in Alkaline Pulping

It is known that a variety of condensation reactions occurs during alkaline pulping and, because of that, lignin dissolution is retarded. It has been suggested that the majority of condensation process occurs at the unoccupied C-5 position of phenolic units. As a result, syringyl units cannot undergo condensation of this type (Sjöström, 1993). During pulping, external nucleophiles, present in the cooking liquor and responsible for the rate and extent of delignification, have to compete with internal nucleophiles in reactions with quinone methide intermediates. These internal nucleophiles are carbanions from phenolic and enolic structures (Gierer, 1980; Gierer, 1985). In both types of condensation, the reversible addition of carbanions is followed by an irreversible proton or formaldehyde elimination, thus resulting in rearomatization of the quinone methide. Examples of primary and secondary condensation occurring during alkaline pulping are shown in **Figure 3.5. 5**. In addition, these carbanions may also condense with formaldehyde liberated from the γ-carbon in the sidechain (Figure 3.5.1) to form the diaryl methane type structures (Gierer, 1980; Gierer, 1985).

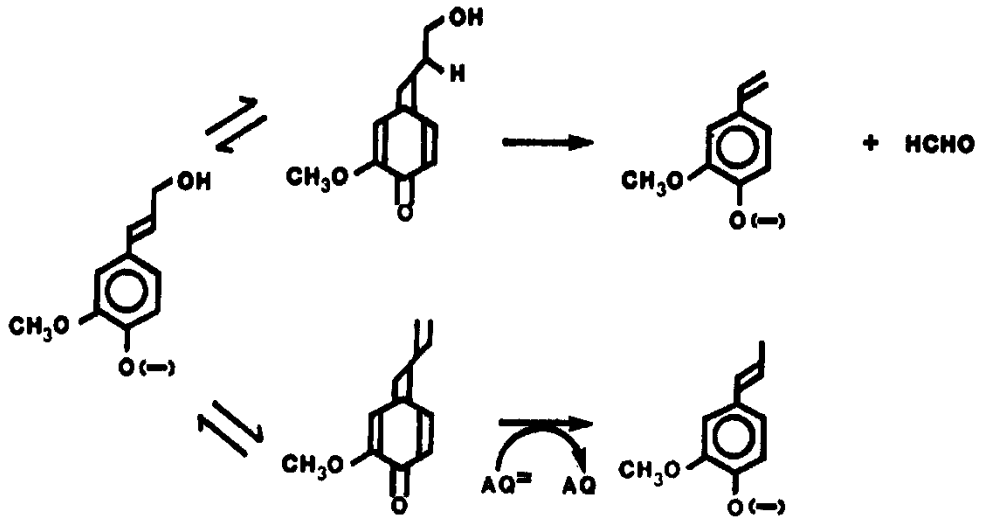


Figure 3.5. 4 Transformation of coniferyl alcohol to vinylguaiacol (top) and isoeugenol (bottom) Source: Mortimer (1982).

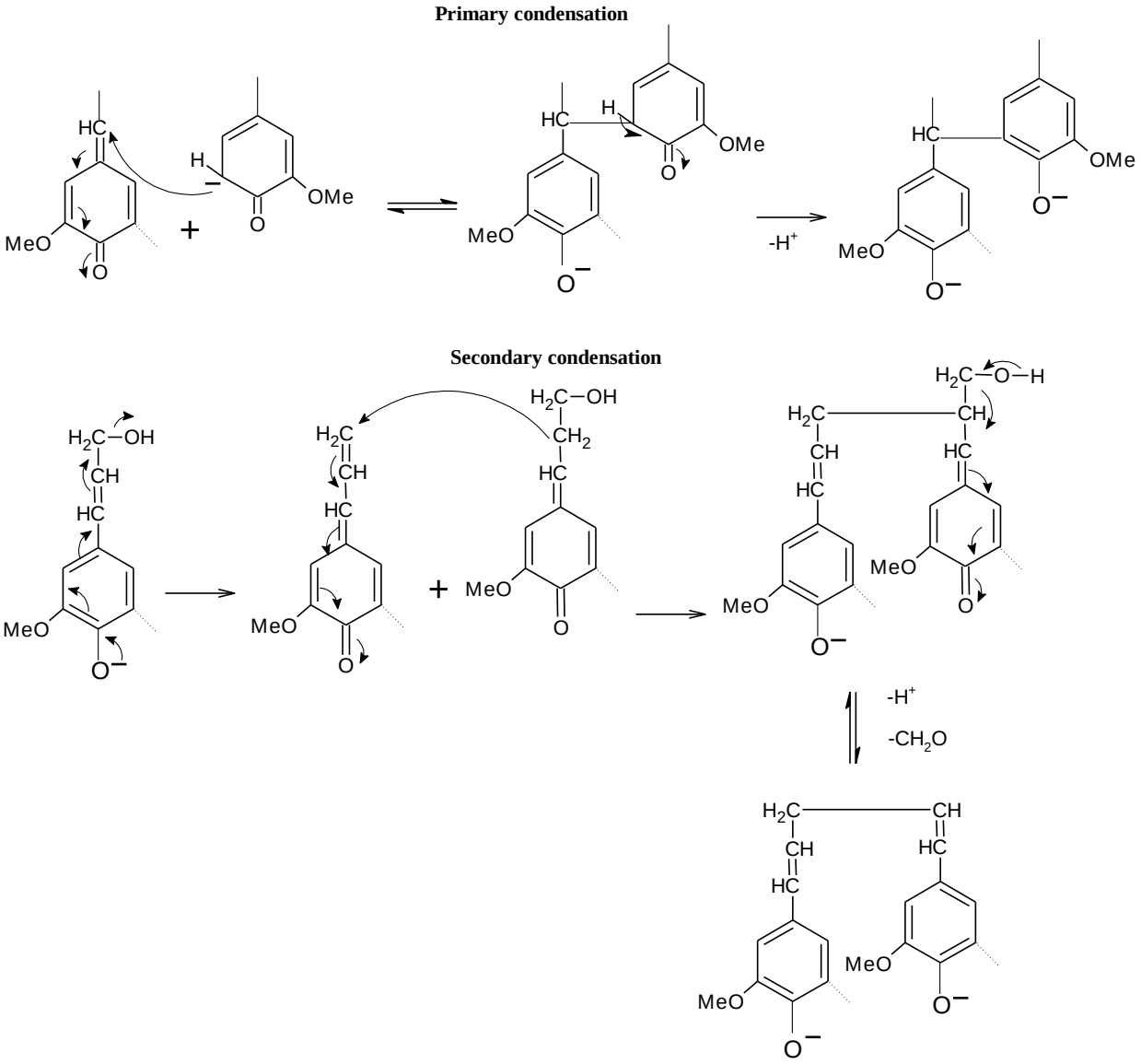


Figure 3.5. 5 Examples of condensation reactions occurring during alkaline pulping. Source: Gierer (1985).

Formation of covalent ether bonds between lignin and carbohydrate may occur during alkaline pulping due to the cleavage of β-aryl ether bonds in non-phenolic units. These bonds may prevent residual lignin fractions from being dissolved in the residual phase of the cook. The formation of the LC-ether bonds involves addition of ionized hydroxyl groups in carbohydrates to oxirane intermediates which are formed during the cleavage of β-aryl ether bonds (Gierer and Wännström, 1986).

3.5.3 Additional Data on SAQ Pulping of Wood

Funaoka and Abe (1985) have presented results showing similarities between SAQ and kraft lignins. Their results indicated that the condensation degree of lignin from cooking with anthraquinone was slightly higher than those without AQ, if α-vinylic protons are neglected (**Table 3.5. 1**). This was the case for either kraft or soda pulping.

Francis et al. (2006) observed that SAQ cooking of hardwoods did not achieve as low a kappa number as kraft cooking at equivalent temperature, time, and effective alkali applications. However, pulps equivalent to the kraft pulps in terms of kappa number, yield, and tear strength were obtained by SAQ when the maximum temperature was increased from 165°C to 170°C. Moreover, when kraft and SAQ pulps were bleached by a D_0EpD_1, slightly lower brightness, but no significant difference in yield loss was obtained for the SAQ pulp as compared to the kraft pulp. In addition to that, the SAQ pulp was equivalent in strength to the kraft pulp as demonstrated in **Figure 3.5. 6** (Francis et al., 2006).

Table 3.5. 1 Functional groups and condensed units of *Pinus thunbergii* Parl. lignins after different pulping processes

	Soda	***Soda/AQ***	***Kraft***	***Kraft/AQ***
Total OH, mol/C9	1.25	1.24	1.29	1.23
Phenolic OH, mol/C9	0.32	0.36	0.39	0.39
Aliphatic OH, mol/C9	0.93	0.88	0.90	0.84
Phenolic α-CO, mol/C9	0.051	0.050	0.053	0.055
Condensed unit, %	56	59	52	54
OCH_3, %	15.0	15.4	14.7	15.1

Pulping conditions: 0.5% AQ, 20% AA, as Na_2O, 5:1 liquor:wood ratio, 90 min at 170°C, 25% Sulphidity (Kraft). Source: Funaoka and Abe (1985).

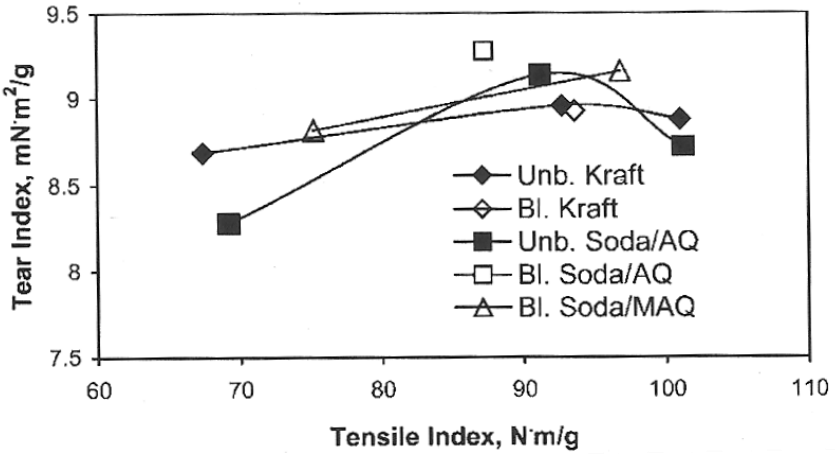


Figure 3.5. 6 Tensile-tear plots for kraft, soda/AQ, and soda/MAQ pulps from sugar maple. Source: Francis et al. (2006).

3.5.4 Alkaline Pulping of Non-Woody Biomass

Different delignification behavior has been reported in conventional kraft and soda-pulping of some non-wood species compared to that woody feedstock. The dissolution of carbohydrates and lignin from wood during kraft cooking proceeds in three distinct phases with hemicellulose loss being quite significant in the initial phase. At the end of the bulk phase (second), more than 85% of all lignin has been dissolved and, during the final phase, the removal of lignin is difficult and occurs at expense of large loss of carbohydrates (Gellerstedt, 2009). The most significant difference during the non-wood pulping is that in most cases the bulk delignification occurs during the heating-up period. For instance, straw, grass, and bagasse pulping can take place at a temperature as low as 80-100°C (Feng, 2001).

The delignification phases and kinetics of soda pulping of bagasse was investigated by Sabatier et al. (1993). There were only two distinct phases identified during the delignification process. The "bulk" delignification normally comes to an end after an H factor of ~400 for soda, SAQ or kraft pulping of bagasse as compared to ~800 for kraft pulping of hardwoods. During the "residual" phase, delignification is much less selective with significant yield loss associated with a minor amount of lignin removal. The kinetic model developed by Sabatier et al. (1993) is described below:

$$W_g = \sum_{i=1}^{2} a_i e^{-k_i t} = a_1 e^{-k_1 t} + a_2 e^{-k_2 t} \quad (2)$$

where W_g is the weight fraction of the insoluble residual lignin. a_1 is the maximum fraction of lignin removal achievable in the "bulk" phase and k_1 is the corresponding reaction rate constant for the bulk phase. Meanwhile, and a_2 and and k_2 are the corresponding parameters for the "residual" phase.

El-Ashmawy et al. (1984) compared soda, SAQ and kraft pulping of bagasse at 140°C and 160°C. Anthraquinone was shown to be an effective catalyst for delignification not only at 160°C but also at lower temperature (140°C). The optimum AQ concentration was between 0.05-0.1% on bagasse, for both kraft and soda pulping. The authors suggested that the SAQ pulping can replace kraft pulping in bagasse since comparable results of yield and kappa number were obtained. A further study on the optimization of SAQ pulping of bagasse was conducted by Saad et al. (1988). The authors confirmed that the AQ concentration up to 0.1% on bagasse decreases significantly the lignin content, while maximizing fiber (pulp) yield. This 0.1% AQ dose was also noticed to be optimum for chlorine requirement during the bleaching process and for mechanical properties.

Alkaline pulping methods (conventional soda, soda-AQ, and sulphite-anthaquinone) for the depithed bagasse and totally chlorine free bleaching of the resulting pulps were evaluated for papermaking (Khristova et al., 2006). Once again the SAQ pulping (0.1% AQ) was proven to be more selective than soda pulping. This pulping resulted in a kappa number of 12.2 at a screened yield of 55.5% while the corresponding values for soda pulping were kappa number 13.9 at 53.2% screened yield. Alkaline sulphite-anthaquinone (AS-AQ) pulping of bagasse afforded even better effects, thus resulting in pulps with lower kappa numbers at higher yields (Khristova et al., 2006). However, the AS-AQ process is not sulfur free and sulfur can posed difficulties when the pulping effluent (black liquor) has to be processed.

3.5.5 Modified Alkaline Pulping of Non-Woody

3.5.5.1 Bases Other than Sodium Hydroxide

A pulping technology for wheat straw using mixtures of NH_4OH and KOH as cooking liquor was investigated by Huang et al. (2002). The effects of the KOH and NH_3 concentrations in the cooking liquor, liquor to wood ratio, maximum temperature, time to maximum temperature and time at maximum temperature were studied. At 25% NH_3 on biomass, the highest delignification (85.5%) was achieved when 5% KOH on biomass was used. When the KOH concentration was higher (6-7%) the pulp yield continuously dropped, due to carbohydrates degradation. The optimized conditions for temperature, time to temperature and time at temperature was 155°C, 60 min, 45 min, respectively. Similar results for pulping of wheat straw were obtained for NaOH-AQ, NH_4OH - KOH and $(NH_4)_2SO_3$ - NH_4OH processes. However, NH_4OH - KOH and ammonia sulfite pulping presented higher yield than the conventional SAQ pulping. Additionally, the black liquor from NH_4OH - KOH pulping was rich in nitrogen, potassium, phosphorous and other organic substance and had the potential to be used as fertilizer.

Huang et al. (2006) further studied wheat straw pulping with NH_4OH and KOH. The optimized conditions were previously determined in Huang et al. (2002). The change in chemical composition during pulping is shown in **Figure 3.5. 7**. Three delignification stages were identified. The first phase, from the beginning of the cook until 100°C, resulted in about 65% lignin removal. In the second phase, from 100°C to 155°C in 45 min., approximately 21% of lignin was removed. In the last phase (residual phase) that goes until the end of the cook, little additional delignification occurred (from 86% to 91.6%) while a considerable amount of carbohydrate degradation occurred. This was shown by the loss of yield from 48% to 40%. Therefore, it was recommended that the pulping be terminated after the 45 min ramp to 155°C.

Since the cooking liquor in NH_4OH-KOH pulping is mixture of a weak strong and a strong alkali, the kinetics of delignification must be different from the conventional alkaline pulping. According to Huang et al. (2006), delignification rate could be expressed by:

$$-\frac{dL}{dt} = kL^n\left[OH^-\right]^m \qquad (3)$$

The differential equation thus became:

$$\ln\left(-\frac{\Delta L}{\Delta t}\right) = \ln k + n\ln L + m\ln\left[OH^{-}\right] \quad (4)$$

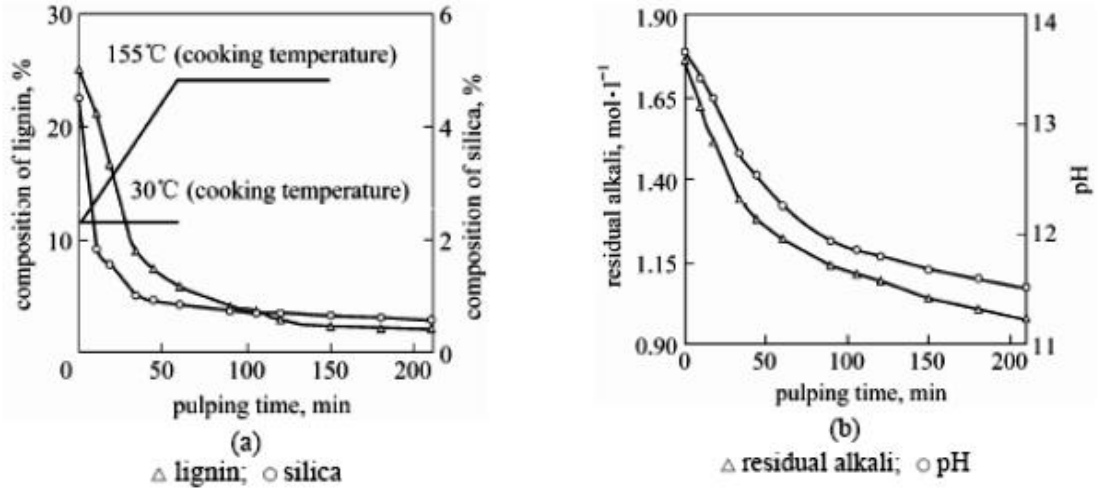


Figure 3.5. 7 Change in chemical composition during NH_4OH and KOH pulping of wheat straw. Source: Huang et al. (2006).

From their experimental data the order of reaction for the residual lignin varied from 0.8477 to 1.089 (first order) and for [OH^-] it varied from 0.2823 to 0.4006 (0.34 order).

Huang et al. (2007a) further studied the black liquor originated in the NH_4OH-KOH pulping and proposed schemes for chemical and lignin recovery. In this work, 98% of the free NH_3 in the black liquor was recovered by distillation. The black liquor free of NH_3 was treated with different coagulants such as chitosan, polyacrylamide (PAM), aluminum polychloride (PAC), ferric polysulfate and PAC-PAM and lignin precipitation as high as 90.3% was obtained for 8 mg/L of PAC + 12 mg/L of PAM at pH 9.1. The supernatant was recycled up to four times and used as cooking liquor with some make-up of NH_4OH and KOH while the coagulated residues were further processed as solid fertilizer. However, this lignin could be burnt for energy with the K_2CO_3 containing ash used in the formulation of fertilizers.

NH_4OH-KOH pulping mechanisms and kinetic of rice straw was also studied by Huang et al. (2007b). The pulping conditions used in this work were the same as for wheat straw in Huang et al. (2002). The delignification process of rice straw presented the same trend as wheat

straw with three distinct phases. Although the overall delignification of rice straw was approximately the same as wheat straw, 92%, the overall yield was much lower, 31.8%. This could be explained by the low cellulose content (35.4%) and high silica content (11.2%) found in the rice straw. Most of the silica was solubilized during alkaline pulping. The reaction order for both residual lignin and [OH^-] were shown to be the same as those found in wheat straw pulping.

NH_4OH-KOH pulping was modified by AQ addition for depithed bagasse and the optimum pulping conditions were evaluated (Huang et al., 2008). The authors stated that the most suitable pulping conditions are: 5% KOH, 35% NH_3, 0.1% AQ on bagasse, 6:1 liquor to bagasse ratio, 165°C maximum temperature for 60 minutes. At these conditions, the kappa number was 11.3 and the unscreened yield was 65%.

3.5.5.2 Effect of Oxygen during Alkaline Pulping

Gaschke et al. (1966) obtained a patent on a process for pulping bagasse with ammonium hydroxide and oxygen. Bagasse pulps with good yield and bleachability were obtained under relatively mild pulping conditions; 100psig of O_2, temperature ranging 130-150°C, pH> 9.0 for 0.5-1.5 hours. The authors suggested that the pulping liquor could be treated with calcium hydroxide to release ammonia from ammonium salts, subjected to distillation to recover ammonia, and then discharged onto agricultural lands.

Results on soda-oxygen pulping of bagasse and rice straw were reported by El-Ashmawy et al. (1977). For all conditions studied with bagasse, temperature of 100 and 120°C and 10 and 12% NaOH, increasing oxygen pressure from 0 to 5 kg/cm^2 increased the pulp yield by 4-8% and decreased lignin content considerably. Optimum strength properties were obtained at 5 kg/cm^2 oxygen pressure. The results for the rice straw showed the same trend with higher pulp yields when oxygen pressure was increased. Yilmaz (1995a) performed lime/soda ($Ca(OH)_2$/NaOH) pulping of wheat straw with and without oxygen. The inclusion of oxygen gave the lime-soda-oxygen (LSO) pulping process. Oxygen addition increased pulp brightness, allowed for shorter cooking times and gave slightly lower kappa number but lowered the pulp viscosity. Further studies in the LSO process showed that increasing the oxygen pressure from 0 to 10 kg/cm^2

improves the optical properties but lowers the breaking length and burst index of papers (Yilmaz, 1995b).

On the other hand, the presence of oxygen in the digester at the beginning of SAQ cooking led to significant retardation in the delignification of both wood and non-woods (Basta and Samuelson, 1978; Samuelson and Wennergren, 1979; Fullerton, 1979; Nada et al., 1986). When a softwood was SAQ delignified at 170°C, the inclusion of 0.41 g mole of O_2 or 13.1 g/kg of chips at the start of the cook increased kappa number of the resulting pulp from 48.4 to 51.6 and total yield from 47.7% to 49.4%. The amount of rejects (not fully cooked fiber bundles) was 0.6% without oxygen and 2.5% when it was included. The retardation in delignification can be explained by analyzing the proposed reaction scheme of AQ functioning as a redox catalyst (**Figure 3.5. 8**). The main catalytic effect of AQ on the delignification depends on lignin reactions with anthrahydroquinone (AHQ) that is formed from the reduction of AQ. Oxygen would oxidize AHQ to AQ and retard the process (Basta and Samuelson, 1978; Samuelson and Wennergren, 1979; Fullerton, 1979).

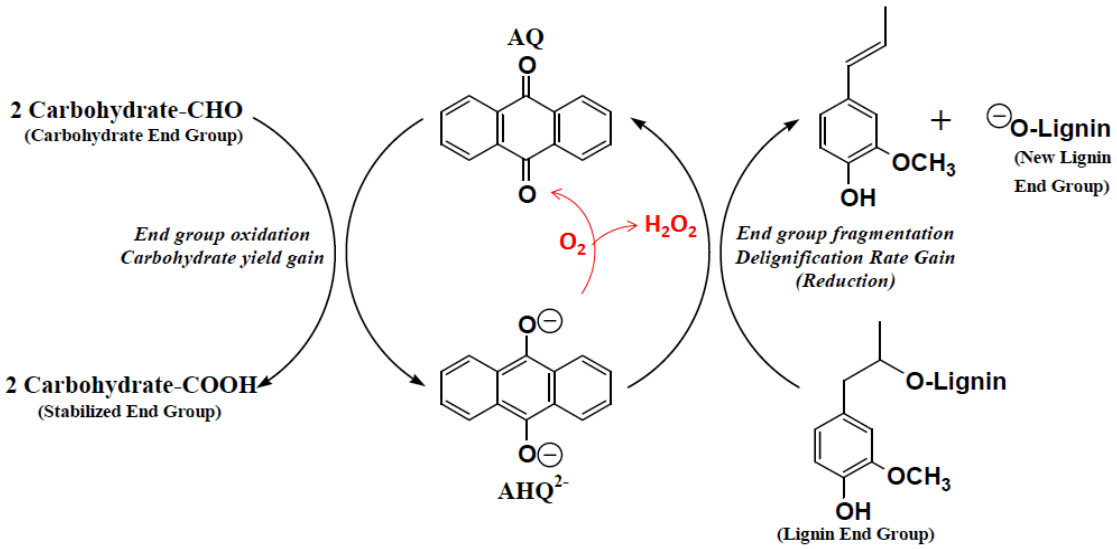


Figure 3.5. 8 Redox mechanism of anthraquinone during alkaline pulping. Adapted from Dimmel (1985).

Oxygen addition in the late stage of SAQ pulping of southern pine was investigated by Tsai et al. (1984) and Shin (1988). Lower kappa number and higher pulp yield were observed when oxygen was added to SAQ cooking at kappa number ~50. At that stage almost all of the β-

O-4’ bonds were already cleaved and AHQ was no longer needed. Oxygen addition basically converted the SAQ cooking system to an oxygen delignification stage which is a more selective process performed at a lower alkalinity. Oxygen addition apparently resulted in the rapid oxidation of organics in the reactor to generate a sizeable amount of carboxylic acid (COOH) groups. Neutralization of these COOH groups lowered the pH of the system to a value high enough for oxygenation reactions but low enough to retard the rate of cellulose depolymerization thus slowing yield loss.

3.6 Principles of Pulp Bleaching

3.6.1 Bleaching of Wood Pulps

Bleaching is a chemical process applied to cellulosic materials to increase their brightness. The term “brightness” describes a number used to indicate reflectance of visible blue light (457 nm, blue green) from a pad of pulp sheets or an opaque stack of paper or paperboard. It has been used to monitor effectiveness of bleaching. Unbleached paper appears brown because blue light is absorbed by chemical constituents called “chromophores”. On the other hand, bleached paper has a lighter or whiter hue because it reflects more blue light than it did before the bleaching process. The objective in the bleaching of (chemi)-mechanical pulps is to selectively remove these chromophores (color-contributing groups) while preserving pulp yield. The basic chromophores units in lignin are carbonyl and ethylenic groups and aromatic rings (Dence and Reeve, 1996). In order to reach an acceptable brightness, the residual lignin should either be removed from the pulp (chemical pulp situation) or, alternatively, the concentration of chromophores should be decreased while the lignin is retained in the pulp (mechanical pulp situation) (Sjöström, 1993).

Single stage treatment is normally used if the brightness gain required is low or the material to be bleached is already rather clear or bright, and responds well to chemical addition. This is not the case for chemical pulps which requires a multi-step treatment to oxidize and solubilize most of the lignin and simultaneously brighten the trace amounts left in the pulp. Normally, electrophilic oxidation takes place under acidic conditions and, as a result, generates carboxylic acids. Since the solubility of these acids is not high in water, an alkaline extraction (E

stage) follows the electrophilic oxidation stage and converts COOH to carboxylates (COO^{-}) which are more soluble (Suess, 2010). The general mechanism for these alternate oxidation and extraction treatment can be represented by the simplified scheme shown in **Figure 3.6. 1** (Gellerstedt, 2009).

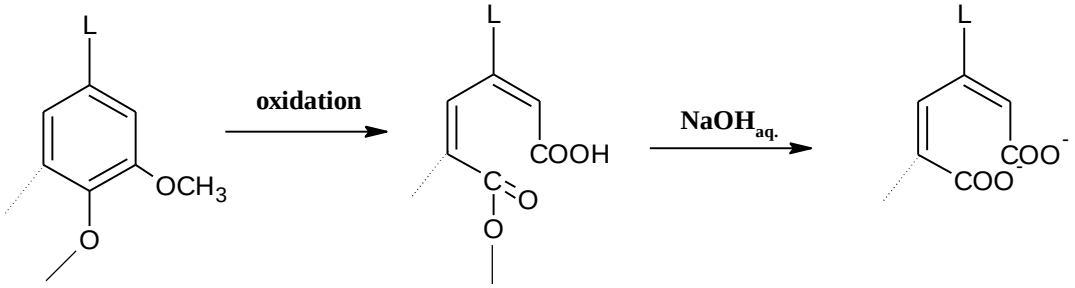


Figure 3.6. 1 - General mechanism for alternation of oxidation and extraction treatment in bleaching process. Source: Gellerstedt (2009).

The abbreviations used in bleaching process are listed in **Table 3.6. 1**. Bleaching sequences are described by combining these letters, for instance: ODED. In this case, since the washing procedure is not explicit mentioned, it is assumed that it occurs after each stage (Suess, 2010). Treatment of the pulp with aqueous elemental chlorine (C) followed by alkaline extraction was used as the predominant delignification stage before 1970s. During the 1970s, oxygen delignification (O stage) was introduced ahead of the C stage and chlorine use was decreased by ~50%. The O stages was first commercially implemented in the early 1970s when it was discovered that small amounts of magnesium salts added to an O stage protected to a large extent the carbohydrates from being degraded. More than 50% of the lignin remaining in the pulp after pulping could be removed by the oxygen stage. The effluent generated in this stage could be incorporated in the chemical recovery cycle of a kraft mill. Therefore, the amount of of dissolved materials in the bleaching effluent was dramatically reduced. The environmental situation was further improved with gradual replacement of some of the chlorine (C-stage) with chlorine dioxide (D). By the late 1990s, the use of elemental chlorine had declined to essentially zero and the modern bleaching sequences of today became established with (O), chlorine dioxide (D) and hydrogen peroxide (P) as the predominant oxidizing agents. Some mills have also installed ozone (Z) and peracetic acid (Paa) stages. Elemental chlorine free (ECF) and totally

chlorine free (TCF) are the bleaching technologies currently used. Nowadays, the typical sequences are OD(OP)DD and OQ(OP)Q(PO) (Gellerstedt, 2009).

Table 3.6. 1 Bleaching stages abbreviations, conditions and effects

Bleaching Stage	***Usual Conditions and Effect Achieved***
O	Oxygen stage for oxidation of lignin, using molecular oxygen under alkaline conditions at 90°C to 100°C
A	Acid stage to remove transition metals (at 40 °C to 60 °C) or (at >90 °C) hexenuronic acid by hydrolysis, the acid typically used is sulfuric acid
Q	Acidic stage (pH 5 to pH 6.5) with chelating agents (such as EDTA or DTPA) for removal of transition metals
D	Chlorine dioxide stage using a solution of ClO_2 at pH <5 in water for lignin oxidation
E	Extraction stage using caustic soda for solubilization of oxidized lignin (pH 9.5 to 11)
Eo	Extraction with addition of oxygen gas for improved lignin removal by oxidation
Eop	Extraction reinforced with oxygen and hydrogen peroxide for improved lignin removal by oxidation and brightening.
P	Alkaline bleaching stage with hydrogen peroxide, (pH >10 to 11, 60 °C to 90 °C)
OP	Pressurized peroxide stage with addition of oxygen, potentially operated above 100 °C with up to 0.3MPa pressure
Z	Delignification stage with gaseous ozone
Paa	Weakly acidic stage (pH 5) with peracetic acid for lignin oxidation and activation of a subsequent P stage.
X	Enzyme treatment stage with xylanase or other hemicellulases to improve lignin accessibility by removal of precipitated carbohydrates
Y	reductive treatment with dithionite
N	Neutralization.

Source: Suess (2010).

3.6.2 Pulp Bleaching of Non-Wood Pulps

Bleaching processes are applied to cellulosic textiles, woven articles made from cotton, and cellulosic pulp, in the form of aqueous slurries of individual fibers separated from both woody and non-woody materials such as straw, reed, jute, sugarcane bagasse, and bamboo. Non-wood fibers are a major source in some parts of the world, notably in much of Asia where wood

resources are limited. In general, the bleachability of non-wood pulps is similar to that sulfite or hardwood kraft pulps (Dence and Reeve, 1996).

Optimum oxygen bleaching conditions for wheat straw have been determined by Eroğlu and Utsa (1989). According to the author, the most important parameter was alkali charge. In principle, higher alkali charge has detrimental effect on physical properties and decrease bleaching yield. The best conditions, for pulp brightness and physical properties, were 4% alkali, 10 kg/cm^2 O_2, 12.5% consistency at 110°C for 20 min. The results of Mohta et al. (1998) for oxygen bleaching of bagasse were previously described in the Introduction. A good alternative for oxygen and peroxide bleaching of bagasse and kenaf pulps (chemical or mechanical pulp) is to use phosphonic acid analog of DTPA, i.e. DTPMPA (diethylene triamine penta methylene phosphonic acid). This chelant affords a higher degree of transition metal deactivation than DTPA and affords a lower kappa number, less carbohydrate damage and a higher brightness (Suess, 2010).

It was noted in the Introduction that Mohta et al. (1998) observed that an O stage with 2.5% NaOH on pulp (10% consistency, 30 min at 115°C) lowered the kappa number of a SAQ pulp from 13.3 to 6.8 but only increased the pulp brightness from37.2% to 49.9% ISO. Khristova et al. (2006) used only 2.0% NaOH on pulp in a 90°C O_2 delignification stage but added 1.0% H_2O_2 on pulp (O/P stage). A brightness increase from 33.6% to 59.1% ISO was observed for a 13.9 kappa number soda pulp from bagasse. Even higher O/P brightness was observed for the SAQ and AS-AQ pulps that were previously described (Khristova et al., 2006).

4.0 RESULTS AND DISCUSSION

The societal outcome that was the aim of this research project was to demonstrate the economic and environmental accurals that would be associated with mixing 10% of unbleached KOH-AQ (KAQ) bagasse pulp into unbleached eucalyptus kraft pulp in regions of Brazil where sugarcane farms, sugar refineries and pulp mills are in close proximity. The only major drawback that could be envisioned is that the bagasse pulp would not respond well to bleaching reagents used for hardwood kraft or SAQ pulps. Some preliminary research was performed and much emphasis was placed on the response of unbleached KAQ and K/NAQ (KOH-NH_4OH-AQ) bagasse pulps to the OD_0EpD_1 bleaching sequence that is normally used for hardwood kraft. Those results will be presented starting in Section 4.2 but the research program initiated with refinements to analytical techniques developed at SUNY-ESF for compositional analysis of biomass (Kiemle et al., 2004; Mittal et al., 2009, Bose et al., 2009b). All of the prior results were obtained with temperate hardwoods. The research was extended to eucalyptus, bagasse and bamboo, another non-wood with high growth rates in Brazil.

4.1 Carbohydrate Composition of Eucalyptus, Bagasse and Bamboo by a Combination of Methods

4.1.1 Introduction to the Section

Most quantification of carbohydrate monomers from biomass samples start with a hydrolysis procedure close to the one first reported by Saeman et al. (1954). That protocol calls for 1h of primary hydrolysis (PH) in 72% H_2SO_4 at 30°C followed by dilution to 4% H_2SO_4 and secondary hydrolysis (SH) for 1h at 121°C. In an earlier paper it was demonstrated that SH treatment in 40% H_2SO_4 at 80°C for 50-70 min afforded higher xylose yields for temperate hardwoods and with a much lower standard deviation than is typically reported for the Saeman et al. method (Bose et al., 2009b). Similar to data cited in the Bose et al. paper for sugar maple (*Acer saccharum*) and aspen *(Populus tremuloides)*, the literature contains a relatively wide variation in xylan content (calculated from xylose yield) for depithed sugarcane bagasse when protocols close to that of Saeman et al. were used. Rabelo et al. (2008) obtained glucan and xylan contents of 39.6% and 19.7%, respectively while Aguilar et al. (2002) obtained values of 38.9%

and 20.6% and Neureiter et al. (2002) obtained values of 40.2% and 22.5%. While the highest of the three glucan contents is only 3.3% greater than the lowest, the corresponding value for xylan content is 14.2% (22.5/19.7 = 1.142).

One of the primary objectives of this research was to see if consistently high xylan contents would be obtained for depithed bagasse when SH is performed in 40% H_2SO_4 at 80°C. A second objective was to compare the results obtained with this hydrolysis protocol plus sugar analysis by ^{1}H NMR to the Saeman et al. hydrolysis protocol coupled with sugar analysis by HPLC. A third objective was to see if summative analyses close to 100% could be achieved for depithed bagasse, bamboo and *E. grandis*. In the earlier research (Bose et al., 2009b), uronic acid contents were estimated but they were determined by acidic methanolysis in this investigation. The research program was conducted in the laboratories of three universities in the USA, Brazil and Finland.

4.1.2 Materials and Methods

4.1.2.1 Biomass Samples

Eucalyptus grandis (Mogi Guaçu, São Paulo, Brazil) and *Bambusa vulgaris* (Coelho Neto, Rio de Janeiro, Brazil) chips were obtained from Brazilian pulp manufacturing facilities. Nodal sections of the *Bambusa vulgaris* were removed before chipping. Depithed sugarcane *(Saccharum officinarum)* bagasse (Sample A) was obtained from a pulp mill located in Jujuy Province, Argentina. Sugarcane *(Saccharum officinarum)* bagasse Sample B, already depithed, was obtained from a sugar factory in KwaZulu-Natal, South Africa. All four samples meals (15 mesh) were extracted with ethanol/toluene in accordance with Tappi Method T 204 om-88 (Tappi 1988) before all analyses were initiated.

4.1.2.2 Hydrolysis of Milled Biomass Followed by ^{1}H NMR analysis

Extractive-free biomass meal (0.50 g, oven dried or OD basis) was added to a 50 ml centrifuge tube and placed in a water bath at 25^{o}C. Then 16 ml of 72% H_2SO_4 (specific gravity 1.634) was added and carefully kneaded into the particles using a glass rod. The slurry was allowed to sit in the water bath at 25 ± 1.0^{o}C for 2 h with mixing every 15 min. After primary

hydrolysis, water (21 ml) was added to the slurry and the tubes sealed (now 40 wt% H_2SO_4), shaken, and placed in a water bath at 80 ± 1.0^oC for 60 min. The tubes were shaken occasionally to homogenize the slurry. After 60 min of hydrolysis treatment, the tubes were removed from the water bath and chilled in an ice bath. They were stored overnight in a refrigerator (4^oC) and lignin precipitation occurred. A recorded mass of the supernatant was taken and the internal standards were added. The solution was then analyzed by ^1H NMR spectroscopy as soon as possible. All the detailed information about the quantification of the relative molar concentration of sugars and other compounds resulting from wood hydrolysis is described by Bose et al. (2009b). The use of glucosamine (GluN) as a back-up internal standard was not recorded in the earlier paper (Bose et al. 2009b). Trimethylamine hydrochloride (TMA) was the primary internal standard but its concentration decreased when there was a long delay (>24 h) between sample preparation and ^1H NMR analysis. In such cases GluN (added at 1.9 x 10^{-4} mol/g) was used as an internal standard to determine the TMA concentration at the time of analysis. This research was performed at SUNY College of Environmental Science and Forestry, Syracuse, NY.

4.1.2.3 Hydrolysis of Milled Biomass Followed by HPLC analysis

Extractive-free biomass meal (300 mg, OD basis) was quantitatively transferred to a test tube (60mm x 1.5mm) and 3 ml of 72% H_2SO_4 were added and kneaded into the particles. The slurry was allowed to sit in the water bath at 30^oC for 1 h with occasional mixing. The slurry was then transferred into a penicillin bottle containing 84 ml of deionized water and the flask was sealed with a rubber stopper and aluminum seal. The bottle was placed in an autoclave calibrated at 118 ºC for 1h. The slurry was then filtered through a regenerated cellulose membrane (0.45 μm) and the filtrate quantitatively transferred to a 250 ml volumetric flask and subsequently analyzed for sugars.

The sugar solution (50ml) and 1 ml of erythrol (1.0 g/l) were added to a beaker and the pH was adjusted to 5.3 with a saturated solution of barium hydroxide. The mixture was then centrifuged at 5000 rpm for 2.5 min then analyzed by HPLC using instrument model SCL-10A, equipped with a refractive index detector, RID-10A, and columns HPX 87P (7.8 mm x 300 mm) and SCR 101P (7.9 mm x 300 mm) coupled at 80°C. The samples were analyzed with deionized water as eluent at a flow rate of 0.4 ml/min for 70 min. Correlations between peak areas and concentrations were determined for authentic samples of glucose, xylose, galactose, arabinose,

mannose, etc. These correlations were used to determine the concentration of sugars in the hydrolyzates. This research was performed at the University of Viçosa, Minas Gerais, Brazil.

4.1.2.4 Acidic (HCl) Methanolysis followed by Gas Chromatographic (GC) Analysis

A known mass close to 10 mg of the dry biomass was transferred to a pear shaped vessel and dried in a vacuum oven (40°C, 70 mbar for 1 h). Two (2) ml of the methanolysis reagent (2M HCl in methanol, prepared by adding acetyl chloride to anhydrous methanol) was added and the vessel was tightly closed and put into an oven (100°C for 5 h). The vessels were shaken every 1 h to ensure uniform hydrolysis. After cooling to room temperature the vessels were opened and 200 μL of pyridine were added to neutralize the excess of HCl followed by addition of 1 ml of the standard solution (0.1 mg/mL sorbitol in methanol). The methanol was then evaporated in a stream of nitrogen. After that the vessels were put in the vacuum oven (40°C, 70 mbar for 30 min) to obtain dried samples. The samples were then dissolved in 0.5 mL anhydrous pyridine (10 min in ultrasonic bath) and silylated by adding 250 μL of the silylating mixture (BSFTA + 5% TMC). The silylation was done overnight (10-15 h). The samples were then centrifuged and transferred to the GC vials. The analysis was done with a Shimadzu GC-17A gas chromatograph using NB-30 capillary column (length 30 m, internal diameter 0.32 mm). The temperature program: 2 min at 100°C, 4°C/min to 220°C, 2 min at 220°C. The sample (1 μL) was introduced via split injector (290°C). The carrier gas was hydrogen and FID detection (290°C) was used. A typical chromatogram is shown in **Figure 4.1. 1**. These analytical protocols are similar to those of Sundberg et al. (1996) and Bertaud et al. (2002) but with some minor modifications. This research was performed at Helsinki University of Technology (now Aalto University), Espoo, Finland.

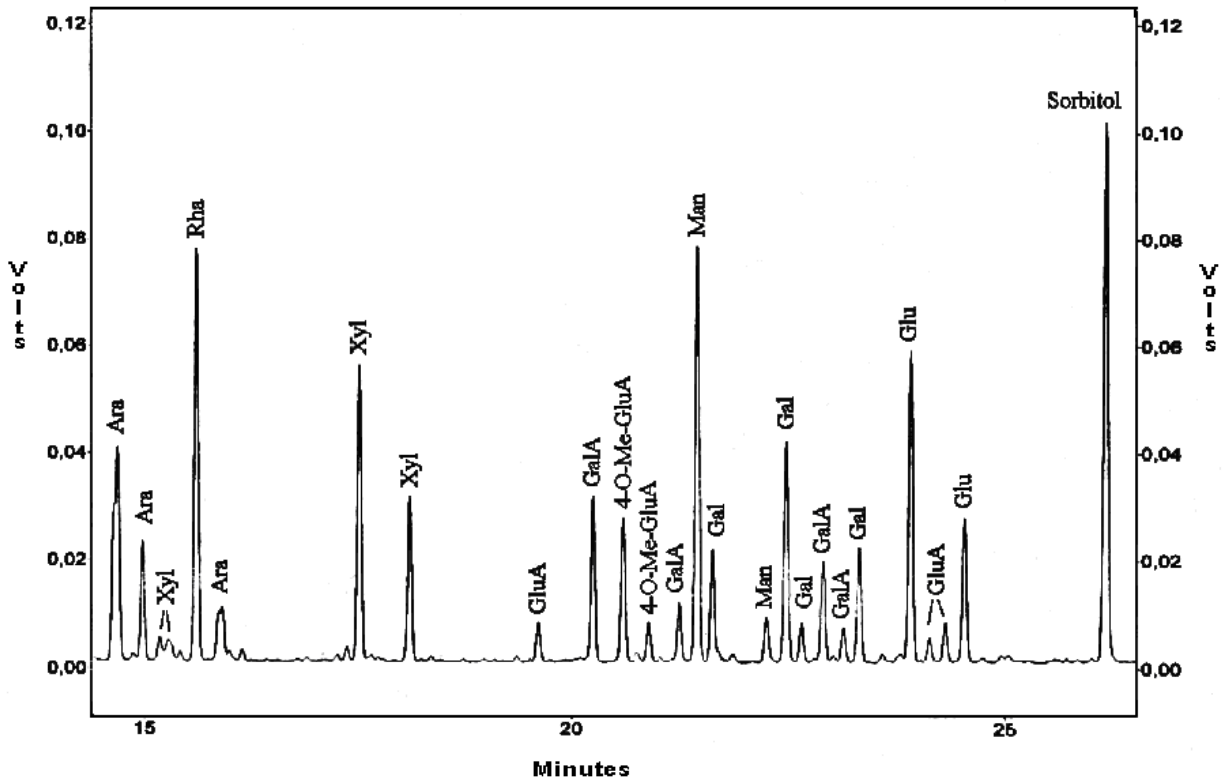


Figure 4.1. 1 A typical chromatogram of methylated products for acidic methanolysis of hardwoods.

4.1.2.5 Other analyses

Lignin content was determined as previously described (Bose et al., 2009c) while ash content was determined by Tappi Method T 211 om-93 (Tappi 1993).

4.1.3 Data and Data Analyses

4.1.3.1 Brief Descriptions of the Methodologies

Descriptions of the HPLC technique and examples of typical chromatograms for biomass hydrolyzates can easily be found in the literature. However, an excellent description of the technique is provided by Kaar et al. (1991) who used it to determine the carbohydrate composition of nine common North American wood species in a later publication (Kaar and Brink, 1991). Excellent and detailed results on polysaccharide characterization using the HPLC method were also reported by Wallis et al. (1996).

A typical spectrum resulting from ^{1}H NMR analysis of biomass hydrolyzate (20 – 40 wt% H_2SO_4) is shown in **Figure 4.1. 2**. It can be seen that the sugar peaks are well resolved and that the peaks for glucose and xylose are dominant. As previously discussed (Bose et al., 2009b), the peaks between 4.60 and 5.05 ppm are for the C1-β protons while those between 5.15 and 5.55 ppm are for the C1-α protons. The peaks for other detectable compounds and internal standards fall outside the range of that shown in Figure **Figure 4.1. 2**. However, the approximate locations of those peaks are already reported (Bose et al., 2009b).

The peaks assigned as GluU were observed with an authentic sample of glucuronic acid. However, they do not show up consistently when hydrolyzates are analyzed and as such we do not use these peaks to estimate the uronic acid content of biomass samples. The acid-catalyzed cleavage of the glucuronosyl linkage between 4-O-methylglucuronic acid (Me-GluU) and a xylose trimer (Me-GluU(1→2)α-xylose) as well as the stability of released monomers was previously investigated (Bertaud et al., 2002). When the HCl concentration was maintained close to 2M (in methanol) for 3h at 100°C there was a high rate of hydrolysis of Me-GluU but ~75% of it degraded (Bertaud et al., 2002). It is possible that our PH and SH conditions afforded almost complete hydrolysis of GluU and Me-GluU but degraded a majority of the uronic acid monomers generated. In the new protocol, PH is performed for 2 h in 72% H_2SO_4 instead of the 1.0 h suggested by Saeman et al. (1954) and this is followed by a 60 min treatment in 40% H_2SO_4 instead of 4.0% H_2SO_4 recommended by Saeman et al. (1954). A sample to sample variation in the rate of degradation of uronic acids would explain the variation in the uronic acids to xylose that is observed in our ^{1}H NMR spectra. On many occasions the uronic acid peaks are not observed. Also, the reproducibility of arabinose, mannose, galactose and rhamnose concentrations ranges from poor to average for hardwoods (Bose et al., 2009b).

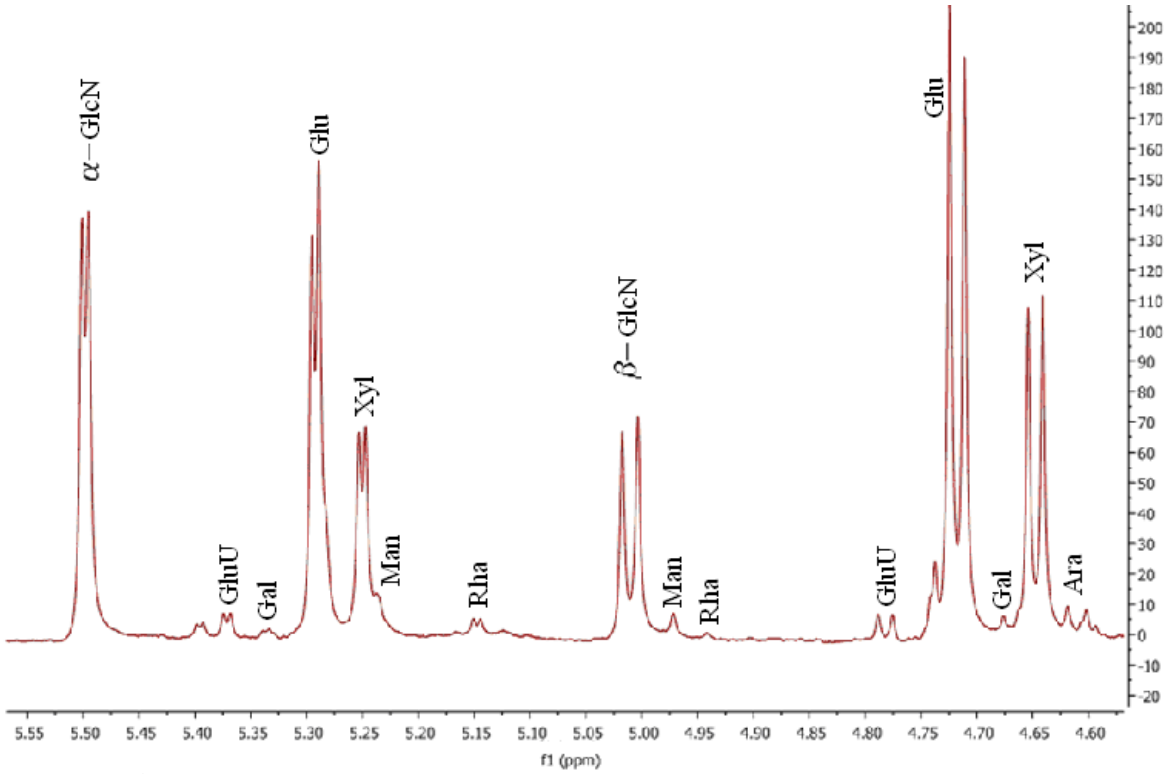


Figure 4.1. 2 [1]H NMR spectrum for sugars in the hydrolyzate of a hardwood; this spectrum is typical for biomass containing a high concentration of xylan (>10 wt%). Acronym GlcN stands for glucosamine an internal standard.

4.1.3.2 Xylan Content of Bagasse by NMR, HPLC and Methanolysis

The [1]H NMR results for Sample A (South America) and Sample B (South Africa) are presented first in **Table 4.1. 1**. The [1]H NMR sugar results along with lignin, ash and uronic anhydride contents afforded summative analyses of 99.2% and 99.1% for the two samples. The samples were almost equal in glucan content at 41.3% and 41.4%, respectively. The content of lignin, glucan and xylan for the two samples are close to 23.1% lignin, 41.7% glucan and 24.7% xylan reported for the U.S. National Institute of Standards and Technology (NIST) bagasse standard reference material #8491 (Scurlock et al., 2000). Although both of our xylan contents are higher than the three values reported in the Introduction, the value for Sample A (24.9%) was approximately equal to the 23.8% value obtained by the HPLC method (**Table 4.1. 1**). The HPLC results did not include xylose dehydrated to furfural. The furfural yield for the Saeman et al. (1954) hydrolysis protocol is estimated at ~0.05 mole/mole xylose (to be discussed later) and multiplication of the 23.8% xylan content by 1.05 results in a value of 25.0%. The 95%

confidence interval data in Tables 4.1.1 and 4.1.2 were estimated based on extensive data collected in the SUNY and University of Viçosa laboratories plus data in the published literature where many replicates were used for glucan, xylan and lignin analyses (Tappi Method T 222 om-88, 1988; Kaar et al., 1991; Bose et al., 2009b). A significant difference between the HPLC and ^{1}H NMR methods was not expected with bagasse for two reasons. First, the researchers at the University of Viçosa who performed the HPLC analysis are highly skilled and have many years of experience with the analytical protocols. Second, bagasse contains a low number of uronic acids groups. The 1→2 linkage between Me-GluU and xylose units in xylan are known to be resistant to mild acid hydrolysis (Whistler and Richards, 1958; Bertaud et al., 2002). While temperate hardwoods contain ~0.15 uronic acids per xylose unit (Kaar and Brink, 1991) and some eucalypti contain >0.20 (Wallis et al., 1996; Magaton, 2008), the reported value for sugarcane bagasse is only ~0.05 uronic acids per xylose unit (Brienzo et al., 2009). When the Saeman et al. (1954) hydrolysis protocol is used, lower than expected xylose yields are frequently reported for hardwoods as discussed by Bose et al. (2009b). Incomplete cleavage of the glucuronosyl linkages between uronic acids and xylose is a probable cause.

Table 4.1. 1 Chemical composition (wt%) of extractive-free sugarcane bagasse by different techniques; Bagasse-A (South American), -B (South African)

	Bagasse-A NMR	***Bagasse-B NMR***	***Bagasse-A HPLC***	***Bagasse-A Methanol***
% Glucan	41.3 ± 0.4[a]	41.4 ± 0.4[a]	43.1 ± 0.3[a]	
% Xylan	24.9 ± 0.2[a]	23.9 ± 0.2[a]	23.8 ± 0.3[a] 25.0 [b]	20.1[c]
% Galactan	0.6	0.6	0.4	
% Mannan	-	-	0.3	
%Arabinan	1.7	2.4	1.5	
% Lignin[g]	23.2 ± 0.3[a]	23.9 ± 0.3[a]	23.2 ± 0.3[a]	
% Acetyl	3.0	2.8	3.0 [d]	
% Uronics [e]	1.2[f]	1.2[f]	1.2[f]	1.2
% Me-GluU	0.8[f]	0.8[f]	0.8[f]	0.8
% Ash	2.5	2.1	2.5	
% Total	***99.2***	***99.1***	***99.8, 101.0[b]***	

[a] Average for 2-4 samples plus estimated 95% confidence interval (see text)
[b] Corrected for xylose dehydrated to furfural (see text)
[c] Excluding xylose converted to furfural
[d] NMR value
[e] Glucuronic and galacturonic acids
[f] Methanolysis value; calculated as anhydrides
[g] Klason Lignin + Acid Soluble Lignin

The methanolysis method gave a xylose yield that was ~19% lower than that obtained by ^{1}H NMR for Sample A (**Table 4.1. 1**). However, once again the xylose converted to furfural was not quantified by methanolysis. If the uronic acids by methanolysis is correlated with xylan from ^{1}H NMR an uronic acids to xylose ratio of 0.06 is obtained. This value is close to the 0.05 ratio reported by Brienzo et al. (2009). The molecular weights for xylose, galacturonic acid (Ga1U), GluU and Me-GluU as anhydro sugars or anhydrides are 132, 176, 176 and 190, respectively.

4.1.3.3 Xylan Content of *E. grandis* and Bamboo

The results are presented in **Table 4.1. 2** and those for *E. grandis* will be discussed first. The repeatability for glucose and xylose yields was excellent for both the ^{1}H NMR and HPLC methods. The ^{1}H NMR method afforded duplicate glucan contents of 46.4% and 46.6% while the corresponding values were 46.6% and 46.8% for the HPLC method. The repeatability was also excellent for xylan content with values of 13.1% and 13.2% for ^{1}H NMR and 11.3% and 11.6% by HPLC. If the uronic acids content from methanolysis is combined with the xylan content from ^{1}H NMR then an uronic acids to xylose ratio of 0.20 is obtained. This ratio is close to the 0.22 value obtained by Magaton (2008) who isolated O-acetyl-4-O-methylglucuronoxylan (AMX) from *E. grandis* and analyzed it by acidic methanolysis. The xylan yield determined by methanolysis was 10.4% in the present study. As noted by Bertrand et al. (2002) the methanolysis method underestimates the true uronic acid content of biomass due to incomplete hydrolysis of the glucuronosyl linkage and partial degradation of the uronic acid generated. Magaton (2008) isolated AMX by extraction of *E. grandis* with 24% KOH. The sample was soluble in D_2O and it was analyzed by ^{1}H NMR without being hydrolyzed by a mineral acid solution. The ^{1}H NMR results indicated an uronic acids to xylose ratio of 0.28. Five other eucalypti (*E. dunni, E. globulus, E. nitens, E. urograndis and E. urophylla*) were analyzed by ^{1}H NMR and their uronic acids to xylose ratio varied from 0.19 to 0.26 with an average of 0.23 (Magaton, 2008).

A probable explanation for the higher xylose yield using the ^{1}H NMR method in the present study is that its hydrolysis protocol afforded a more complete hydrolysis of the glucuronosyl linkages than the Saeman et al. protocol that was used with the HPLC method. The

harsher conditions used in the ^{1}H NMR hydrolysis protocol (2 h of PH in 72% H_2SO_4 at 25°C followed by SH in 40% H_2SO_4 for 1 h at 80°C) probably degraded most of the liberated uronic acids.

Table 4.1. 2 Chemical composition (wt%) of extractive-free E. *grandis* and bamboo by NMR and HPLC; Samples from South America

	Eucalyptus NMR	***Eucalyptus HPLC***	***Bamboo NMR***	***Bamboo HPLC***
% Glucan	46.5 ± 0.4[a]	46.7 ± 0.3[a]	49.4 ± 0.4[a]	50.4 ± 0.3[a]
% Xylan	13.2 ± 0.2[a]	11.5 ± 0.3[a] 12.1[b]	18.7 ± 0.2[a]	18.7 ± 0.3[a] 19.6[b]
% Galactan	1.4	1.2	0.4	0.4
% Mannan	0.9	1.0	0.5	0.3
% Arabinan	1.5	0.5	1.1	1.2
% Lignin[g]	29.2 ± 0.3[a]	29.2 ± 0.3[a]	23.4 ± 0.3[a]	23.4 ± 0.3[a]
% Acetyl	2.8	2.8[c]	2.4	2.4[c]
% Uronics	2.1[d]	2.1[d]	0.5[d]	0.5[d]
% Me-GluU	1.6[d]	1.6[d]	0.7[d]	0.7[d]
% Ash	0.3	0.3	1.5	1.5
% Total	***99.5***	***96.9*** ***97.5[b]***	***98.6***	***99.5*** ***100.4[b]***

[a] Average for 2-4 samples plus estimated 95% confidence interval
[b] Corrected for xylose dehydrated to furfural (see text)
[c] NMR value
[d] Methanolysis value; calculated as anhydrides
[g] Klason Lignin + Acid Soluble Lignin

When the Saeman et al. hydrolysis protocol was used for sugar maple and aspen the ratio of furfural to xylose in the hydrolyzates were 0.07 and 0.01, respectively (Mittal et al., 2009). If an average of 0.05 is assumed then the HPLC xylose yield can be increased by 5% from 11.5% to 12.1%. In light of nearly identical results for bagasse Sample A, it is unlikely that the 9% higher xylose yield (13.2% *vs.* 12.1%) for the new hydrolysis protocol was due to a difference in quantification methodologies, i.e. ^{1}H NMR versus HPLC.

Very similar results were obtained by the ^{1}H NMR and HPLC methods for the bamboo another biomass with a low uronic acids content (**Table 4.1. 2**). The xylan content by HPLC was actually 5% higher than by ^{1}H NMR. The uronic acids to xylose ratio was 0.05 when the uronic acids determined by methanolysis was correlated with xylan by ^{1}H NMR. The xylan content determined by methanolysis was 15.5%.

4.1.4 Summary of the Section

A new hydrolysis protocol has been developed to convert carbohydrate polymers in biomass to their monomeric constituents. However, results have only been reported for temperate hardwoods so far (Bose et al., 2009b). This research investigated three different biomass samples that are usually associated with tropical and sub-tropical regions, i.e. sugarcane bagasse, eucalyptus, and bamboo. The new hydrolysis protocol that consists of 2 h of primary hydrolysis in 72% H_2SO_4 at 25°C followed by 1 h SH in 40% H_2SO_4 at 80°C gave nearly identical results to the well established hydrolysis protocol of Saeman et al. (1954) for bagasse and bamboo. The new protocol was coupled with ^{1}H NMR analysis of monomers while the traditional hydrolysis protocol was coupled with HPLC analysis. The two analytical techniques (^{1}H NMR and HPLC) appear to give very similar values for glucose and xylose. When the *E. grandis* was analyzed, the new hydrolysis protocol gave a xylan content that was 9% (13.2 wt% *vs.* 12.1 wt%) higher than for the Saeman et al. (1954) method. Unlike the bagasse and bamboo that had uronic acids to xylose ratios <0.10, the *E. grandis* had a ratio >0.20. The 1→2 linkages of Me-GluU to xylose units in xylan are known to be resistant to acidolysis (Whistler and Richards, 1958; Bertaud et al., 2002). It appears as if the new hydrolysis protocol is more efficient at cleaving those glucuronosyl linkages thus affording a higher yield of xylose monomers. The new hydrolysis protocol coupled with ^{1}H NMR analysis afforded summative analyses that fell in a narrow range (98.6% to 99.5%) for the two bagasse samples plus *E. grandis* and bamboo. The Saeman protocol coupled with HPLC afforded values of 101.0% for one of the bagasse samples and 100.4% for the bamboo. However, a summative analysis of only 97.5% was obtained for the *E. grandis.*

4.2 Pulping and Bleaching Characteristics - Bagasse versus Hardwood

4.2.1 Introduction to the Section

The results of Mohta et al. (1998) on delignification by soda-AQ (SAQ) cooking followed by oxygen bleaching appear to be typical for sugarcane bagasse (*Saccharum officinarum*). They observed that with a NaOH dose of 12% Na_2O and 0.1% AQ on bagasse, a pulp with kappa number of 13.3 could be produced after an H-factor of 720 in batch cooking. When 2.5% NaOH on pulp was used in O_2 delignification at 10% consistency the kappa number fell from 13.3 to 6.8 but the pulp brightness increased from only 37.2% ISO to 49.9% ISO. Compared to hardwoods it appears that bagasse is much more responsive to SAQ cooking but the brightness development in O_2 bleaching is much less than for hardwood SAQ pulps. When 14.0% Na_2O and 0.1% AQ were used in batch cooking of sugar maple (*Acer saccharum*) a kappa number of ~ 20 was attained after H-factor = 1297 (2h at 165°C) (Bose et al., 2009a; Kanungo et al., 2011). The xylan content of bagasse (~24%, Section 4.1) is usually much higher than the 18.6% reported for sugar maple (Bose et al., 2009b) and a significant fraction of the applied alkali is consumed in xylan extraction and degradation during SAQ cooking. It is therefore remarkable that a bagasse SAQ pulp achieved a much lower kappa number than maple SAQ pulp when a significantly lower alkali dose and H-factor are used. However, brightness development in O_2 delignification appears to be higher for hardwoods as compared to bagasse. Francis et al. (2008a) reported on a poplar SAQ pulps that achieved kappa number 7.3 after the O_2 delignification (O stage). Although not reported, the pulp had a brightness of ~59% ISO. Schild et al. (2010) used oxygen to delignify a eucalyptus SAQ pulp from kappa number 15.5 to 10.3 and observed a brightness increase from 39.7% ISO to 54.4% ISO.

The objective of this research was to see if bagasse was much more responsive to SAQ/KAQ delignification because its lignin contained a much higher concentration of uncondensed β-O-4’ structures than hardwood lignin but less responsive in O_2 delignification because of condensation reactions in SAQ that are significant with bagasse but minimal with hardwoods.

4.2.2 Materials and Methods

4.2.2.1 Bagasse Samples

A water depithed bagasse (WDB) sample was donated by the Bangladesh Forest Research Institute (BFRI). Crushed cane (CC) was agitated in water to dissolve water soluble extractives and convert some of the pith material to fines. When the slurry was filtered the WDB was recovered at ~85% yield (OD basis). The fibers were air-dried and shipped from BFRI to SUNY ESF, Syracuse, New York.

CC was procured from a Brazilian sugar factory and cooked with Na_2CO_3 (4.0% Na_2O on CC) in an M&K digester in the SUNY ESF laboratory. The temperature profile was 60 min to 160°C and 60 min at 160°C and a 14:1 liquor to bagasse (L to B) ratio was used. The liquor pH was 6.0 and 4.8 after 0 min and 60 min at 160°C, respectively. The chip basket of the digester was lined with a cloth made of coarse mesh cotton. The fiber recovery from this treatment was 62.3% based on CC and the sample is identified as chemically depithed bagasse (CDB-Carb).

4.2.2.2 KAQ and SAQ Pulping

Both WDB and CDB-Carb were delignified in M & K digesters at 160°C. The time to temperature was 60 min and time at temperature either 60 min or 90 min. A 12:1 L to B ratio was used for the CDB-Carb (no cloth lining) while a 10:1 ratio with the cloth lining was used for WDB. The strong alkali was either potassium or sodium hydroxide and the solvent media was either water or 1.0 M NH_4OH. The AQ dose was always 0.1% on bagasse when M&K digesters were used. When NH_4OH was used in pretreatment of the WDB, the fibers were treated with 1.0 M NH_4OH at 10:1 L to B (the ramp time to 160°C was 60 min and retention at that temperature was 30 min). The NH_4OH liquor was drained off through a condenser and an equal volume of KOH solution added to the digester. The temperature was increased from 80°C back to 160°C in ~30 min. A Wiley mill was used to produce sugar maple and bagasse (WDB) meals (15 mesh) that were toluene/ethanol extracted in accordance with Tappi Method T 204 om-88. These solvent extracted meals were also delignified in small stainless steel autoclaves at 12:1 liquor to biomass ratio. The AQ dose was always 23 mg in 60 ml. The biomass and chemicals were added to the autoclaves that were sealed, shaken vigorously, and then placed in a 165°C oil bath. Finally, 15 mesh WDB and CDB-Carb were delignified in a PARR pressure vessel at 50:1 L to B

ratio. The AQ dose was always 63 mg in 250 ml. A flow sheet for the reactor system is shown in **Figure 4.2. 1**.

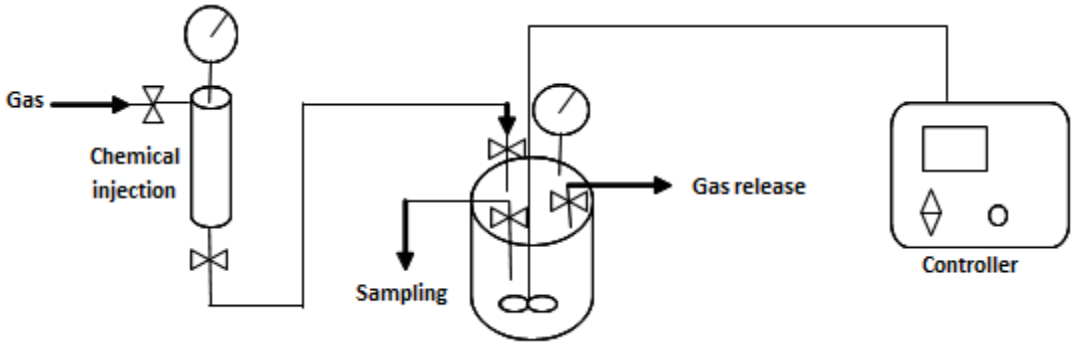


Figure 4.2. 1 Schematic of a reactor system, including a PARR pressure vessel, that was used for SAQ delignification of bagasse meal.

4.2.2.3 SAQ Delignification in the Presence of Ethylguaiacol (EG)

The following substrates were added to 60 ml of 0.4 M NaOH in stainless steel autoclaves; 5.0 g (OD basis) of sugar maple (24.8% lignin content) or bagasse (23.7% lignin content), 250 mg of EG (1.64 mmoles) and 23 mg of AQ. Solvent extracted meals were used. The slurries were shaken vigorously to ensure good mixing and the autoclaves heated for 60 minutes at 165°C. Based on accurate vapor pressure measurements with deionized water only, the internal temperature profile in the autoclaves that were used was estimated to be 14 minutes to 163°C and 46 minutes at that temperature (H-factor 441). The increase in product yields was statistically insignificant when treatment time was increased to 75 min. After 60 minutes, the autoclaves were cooled and the product mixture was acidified and extracted in dichloromethane (DCM). The DCM extract was reduced to a low volume by evaporation and the internal standard, benzhydrol, added. A fraction of the DCM solution (100 µl) was added to another vial along with 100 µl of BSTFA [N,O-bis(trimethylflouromethyl-silylacetamide)] and a drop of pyridine. The mixture was allowed to sit at room temperature overnight or for ca. 30 minutes at 40°C before being analyzed by gas chromatography - mass spectrometry (GC/MS). Similar procedures were used when condensation between *p*-coumaric acid (*p*-CMAc) and EG or self-condensation of *p*-CMAc was investigated but the 5.0 g of meal was replaced by 1.64 mmoles of *p*-CMAc and 300 mg of d-glucose was added.

4.2.2.4 Chelation Treatment and Bleaching Conditions

- **Chelation or Q-stage:** 0.2% Na_5DTPA and 3.0% SO_2 on pulp (from $NaHSO_3$), 3% consistency, 80°C for at least 30 min. with end pH~6.0.

- **O-Stage:** Conducted in a Quantum Mark IV reactor at 10% consistency, 0.72 MPa of O_2, 2.0% NaOH, and 0.5% $MgSO_4.7H_2O$ on pulp at 90°C for 1 h.

- **P-Stage:** In plastic bags at 12% consistency, 80°C, 2h and with 0.5% $MgSO_4.7H_2O$ on pulp. Three different doses of H_2O_2 and NaOH were used: 2.0% H_2O_2 and 3.0% NaOH on pulp; 3.0% H_2O_2 and 4.0% NaOH on pulp; and 4.0% H_2O_2 and 5.0% NaOH on pulp. The chemicals were mixed into the fibers at room temperature, heated to approximately 80°C in a 1.1 kW microwave oven and then placed in a water bath.

- **D_0-Stage:** In plastic bags at 10% consistency, 70°C, 2h with initial pH approximately 4.0 (before the addition of $C1O_2$) and end pH 2.0-2.8. A ClO_2 dose factor of either 0.076 or 0.114 (%$C1O_2$/incoming kappa number) was used. These ClO_2 dose factors correspond to kappa factors (% equiv. Cl_2/incoming kappa number) of 0.20 and 0.30

- **Ep-Stage:** In plastic bags at 12% consistency, 80°C, 2h with 2.0% NaOH, 0.25% H_2O_2 and 0.1% $MgSO_4.7H_2O$ on pulp. The chemicals were mixed into the fibers at room temperature, heated to approximately 80°C in a 1.1 kW microwave oven and then placed in a water bath. The end pH was always greater than 11.5 – 12.0.

- **D_1-Stage:** In plastic bags at 10% consistency, 70°C, 3h, and 0.5% or 0.8% $C1O_2$ on pulp. Enough sodium hydroxide was mixed into the fibers before $C1O_2$ addition in order to ensure an end pH of approximately 3.5 to 4.5. The chemicals were mixed into the fibers at room temperature, heated to approximately 70°C in a 1.1 kW microwave oven then placed in a water bath. One-half of the pulp was bleached in this final stage and the treatment was repeated with the other half if the end pH was outside of the range mentioned above.

All the conditions described above were similar to those previously reported by (Francis et al., 2008a) but with some minor modifications.

4.2.2.5 GC/MS and Other Analyses

GC-MS analyses were performed using a Thermo Scientific Finnigan Trace GC Ultra GC coupled to Thermo MAT95XP double focus magnetic sector mass spectrometer. The column used was a 30 m x 0.25 mm ID., Rtx®-5MS (5% diphenyl/95% dimethylpolysiloxane) capillary column (film thickness 0.25 μm). Helium at a flow rate of 1 ml/min was used as the carrier gas. About 1 μL sample were injected and analyzed using a split ratio of 20:1. The injector temperature was 240°C and the column temperature profile was initial temperature 110°C (hold for 4 min); a ramp from 110°C to 260°C at 5°C/min. followed by a 5 min hold; then a second ramp at 5°C/min to 300°C and a hold at this maximum temperature for 20 minutes. Ionization was carried out at a 70 eV impact voltage in an ion chamber heated at 280°C. The MS range scanned was 45-800 m/z at a rate of 0.6 scan/second. Peak identification was carried out on the basis of mass fragmentation patterns, and by comparing the MS data with those in the Pfleger-Mauer-Weber, Wiley and NIST libraries.

Lignin content and S:G ratio by nitrobenzene oxidation were determined by the method of Bose et al. (2009c) while carbohydrate composition was by the ^{1}H NMR techniques described in Section 4.1.

4.2.3 Data and Data Analyses

4.2.3.1 Chemical Composition of WDB and CDB-Carb

The WDB was analyzed using the procedures described in Section 4.1 and it was found to contain 41.5% glucan, 25.3% xylan and 23.7% lignin. Interestingly, two other depithed bagasse samples from South America and South Africa were previously analyzed (Section 4.1) and their respective composition were 41.3% glucan, 24.9% xylan and 23.2% lignin for the South American one and 41.4%, 23.9% and 23.9% for the South African one. The fiber content of CC is typically in the range of 60 wt% with pith and other extraneous substances making up the remaining 40% (Sanjuán et al., 2001). If one assumes that the extent of depithing would have varied amongst samples prepared in three different regions of the World then the likely reason why nearly identical compositions were observed is that the glucan, xylan and lignin contents of the fibers and pith are nearly equal. This has been reported in the literature. Actually, when the 8-10 wt% of hot water soluble extractives are removed from CC, the glucan, xylan and lignin

contents of the fibers and pith are reported to be nearly equal (Sanjuán et al., 2001; Jahan et al., 2009).

The compositions of the WDB and CDB-Carb are compared in **Table 4.2. 1**. There is enrichment in glucan but not xylan and lignin as the depithed yield is decreased from ~85% (WDB) to 62.3% (CDB-Carb). The glucan enrichment from 41.5% to 47.1% appears to come at the expense of minor components chemically hydrolyzed or extracted from the crushed cane. The total yield of glucan, xylan, arabinan and lignin for the extractive-free WDB in **Table 4.2. 1** is 91.7% while the value for CDB-Carb was 97.8%. Minor components that could have been partially removed during carbonate treatment include acetyls, uronic anhydrides and ash.

Table 4.2. 1 Chemical Composition of CDB and WDB

	***CDB-Carb*[1]**	***WDB*[2]**
Glucan, % on Sample	47.1	41.5
Xylan, % on Sample	25.2	25.3
Arabinan, % on Sample	1.6	1.2
Lignin, % on Sample	23.9	23.7

[1] Fibers recovered at 62.3% yield based on CC
[2] Fibers recovered at ~85% yield based on CC

4.2.3.2 Preliminary Pulping Trials

The CDB-Carb meal was delignified in 0.2M KOH + AQ (KAQ) at 140°C, 150°C, 155°C and 160°C in the PARR reactor (**Figure 4.2. 1**). The time to maximum temperature was ~30 min for 140°C; ~35 min for 150°C; ~40 min for 155°C and ~45 min for 160°C. The temperature-time profiles from which H-factors were calculated are shown in **Figure 4.2. 2** and the H-factor to achieve maximum temperature was 4 for 140°C; 10 for 150°C; 16 for 155°C and 27 for 160°C.

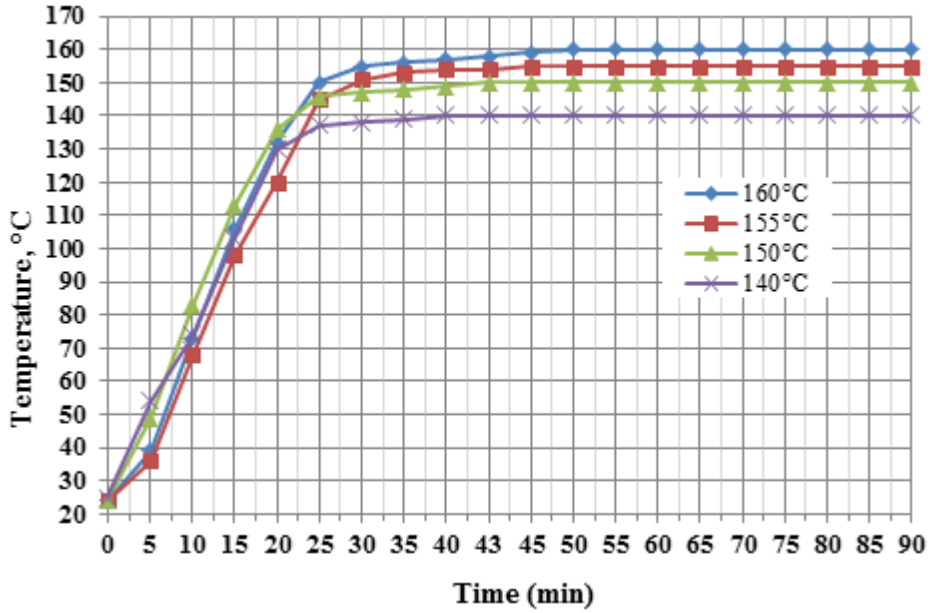


Figure 4.2. 2 Temperature-Time profile for the PARR Reactor.

The kappa numbers versus cooking time results are presented in **Figure 4.2. 3**. A kappa number of 13.3 was obtained after and H-factor of only 70 at 140°C; kappa number 14.3 after an H-factor of only 79 at 150°C; kappa number of 12.3 after H-factor 103 at 155°C and kappa number 11.9 after an H-factor of 97 at 160°C. The unscreened pulp yield after 90 min was 62.8% for 140°C; 57.7% for 150°C; 53.2% for 155°C and 52.6% for 160°C. It appears as if pulp yield declines quite dramatically below a kappa number of ~10 (57.7% yield was obtained for kappa number 9.9 at 150°C).

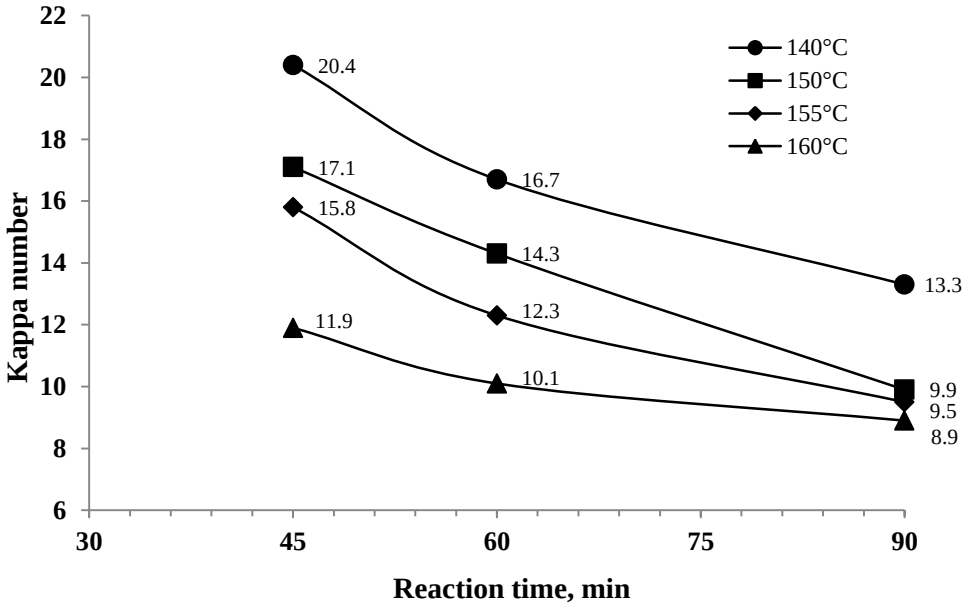


Figure 4.2. 3 Cooking of CDB-Carb in 0.2M KOH + AQ (KAQ) at various temperatures.

The kinetics for SAQ delignification of WDB (solvent extracted) and CDB-Carb are compared in **Figure 4.2. 4** and not much difference can be seen. The cooking temperature was 160°C and 0.2M KOH was used. It can also be seen that adding 1.0 M NH_4OH to the cooking liquor (K/NAQ cooking) had only a minimal or no effect (**Figure 4.2. 4**). A kappa number of 12.6 after 45 min corresponds to 94.3% delignification while kappa number 10.6 corresponds to 95.2%.

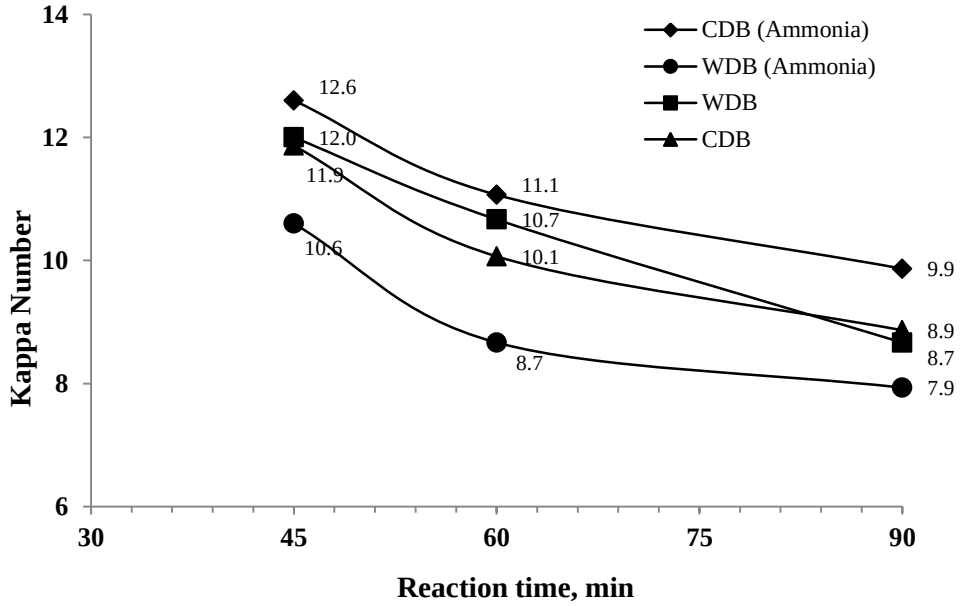


Figure 4.2. 4 Kinetics for KAQ and K/NAQ delignification of WDB and CDB-Carb at 160°C.

When 15 mesh sugar maple meal (solvent extracted) was SAQ delignified to H-factor 441 in 0.4M NaOH at a 12:1 liquor to wood ratio, the resulting pulp had a kappa number > 40. The WDB and sugar maple meals were delignified under identical conditions (to be discussed later) and a much higher delignification rate was confirmed for the bagasse. An investigation of the two native lignins was initiated. The sugar maple contained 24.8% lignin while the WDB contained 23.7%, both an extractives-free basis.

4.2.3.3 Comparison of Native Lignins in Sugar Maple and Bagasse, some Basic Lignin Chemistry

High yields of *p*-coumaryl, coniferyl and sinapyl alcohols are obtained when uncondensed β-O-4' structures are treated with SAQ liquor at elevated temperatures. The mechanism in **Figure 3.5. 3** is frequently cited as an explanation (Gierer et al., 1979; Landucci, 1980; Venica et al., 2008) but a credible free radical mechanism is also supported by substantial data (Dimmel, 1985; Smith and Dimmel, 1994). A concern in SAQ pulping is the possibility that these three lignin monomers rearrange to quinone methides (QMs) and become involved in condensation reactions with lignin and carbohydrate moieties. The rearrangement of a phenolate

containing an α-β double bond to a QM is shown in **Figure 4.2. 5**. It was recently observed that ethylguaicol (EG) is quite effective at condensing with monomeric QMs and the dimers generated react only slowly in further condensation (Kanungo et al., 2009; Kanungo et al., 2011). The prior data also suggested that uncondensed β-O-4' structures in sugar maple (*Acer saccharum*) were cleaved at a high rate during SAQ cooking at 165^{o}C. Also, EG appeared to trap coniferyl alcohol (CA) and its transformation products, vinylguaicol (VG) and isoeugenol (IE), to form dimers **1 - 3 (Figure 4.2.6)** at high yields. The reactions schemes for the transformation of CA to VG and IE are shown in **Figure 3.5. 4** (Mortimer, 1982) and condensation between a QM and EG to form an α-5 dimer is shown in **Figure 3.5. 5**.

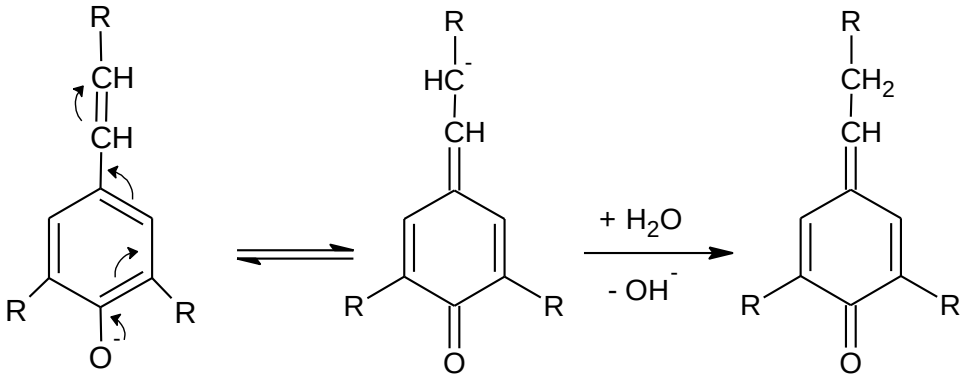


Figure 4.2. 5 Conversion of a phenolate containing an α-β double bond to a QM.

The objectives of this research were 1) to see if the EG trapping mechanism that was observed with CA would be observed with *p*-coumaryl alcohol (*p*-CMA) when sugarcane bagasse is treated, 2) Confirm that similar to sugar maple (Kanungo et al., 2011), sinapyl alcohol (SA) expected from bagasse lignin is not trapped by EG, and 3) examine the feasibility of using EG trapping to estimate the concentration of β-O-4' in native lignin where the A-ring (one forming QM in **Figure 3.5. 3**) is an uncondensed guaiacyl (G) or *p*-hydroxyphenylpropane (H) unit.

4.2.3.4 SAQ + EG Treatment of Sugar Maple and Bagasse

The maple woodmeal was SAQ delignified in the presence of EG and it appeared as if a high fraction of the estimated CA that would be generated was trapped as dimers **1 – 6** in **Figure**

4.2. 6. The MS for the six dimers are shown in **Figures 4.2.7 – 4.2.12**. The yields of un-reacted EG and the six dimers are documented in **Table 4.2. 2**. A segment of the chromatogram from the GC-MS analysis of Kanungo et al. (2011) is shown in **Figure 4.2. 13**. The three peaks are representative of **1** to **3**, respectively. There were smaller peaks observed at retention times (RT) greater than that for **3**. However, based on the limited data collected at that time it was decided that the reproducibility on the yield of those products was less than satisfactory and they were not included in the initial tabulation (Kanungo et al., 2011). Instead, the selected chromatogram (**Figure 4.2. 13**) was one with large peaks for **1** to **3** and very small peaks for the minor products. This chromatogram was selected to demonstrate that the three dimers from sinapyl alcohol that would correspond to **1** to **3** were not detected at significant yields. Those dimers would have eluted ~5 min later than **1** to **3.** However, in subsequent research these minor products **4 - 7** in **Figure 4.2. 14** (sugar maple), **Figure 4.2. 15** (*E. grandis* x *E. urophylla*) and **Figure 4.2. 16** (*Eucalyptus camaldulensis*) were detected more reproducibly and it was decided that they should be included in the tabulation of condensation products. Dimers **1** – **7** are assigned to the peaks in **Figure 4.2. 16**. One reason for their inclusion is that some of these dimers were ultimate products of two CA monomers. Therefore, although only 0.02 mmole of **4** was detected (**Table 4.2. 2**), the dimer was produced from 0.04 mmole of CA and as such the yield of this product is equal in significance to that of **2**.

Based on preliminary data, it appears that dimers **1** to 1**3 (Figure 4.2. 6)** react very slowly in further condensation reaction due to hydrophobicity imparted by their ethyl and vinyl-containing sidechains. When EG was replaced by homovanillyl alcohol in alkaline condensation and the ethyl sidechain of **1** was replaced by a hydroxyethyl sidechain (CH_2- CH_2OH) that dimer appeared to participate in further condensation at a significant rate (Kanungo et al., 2011).

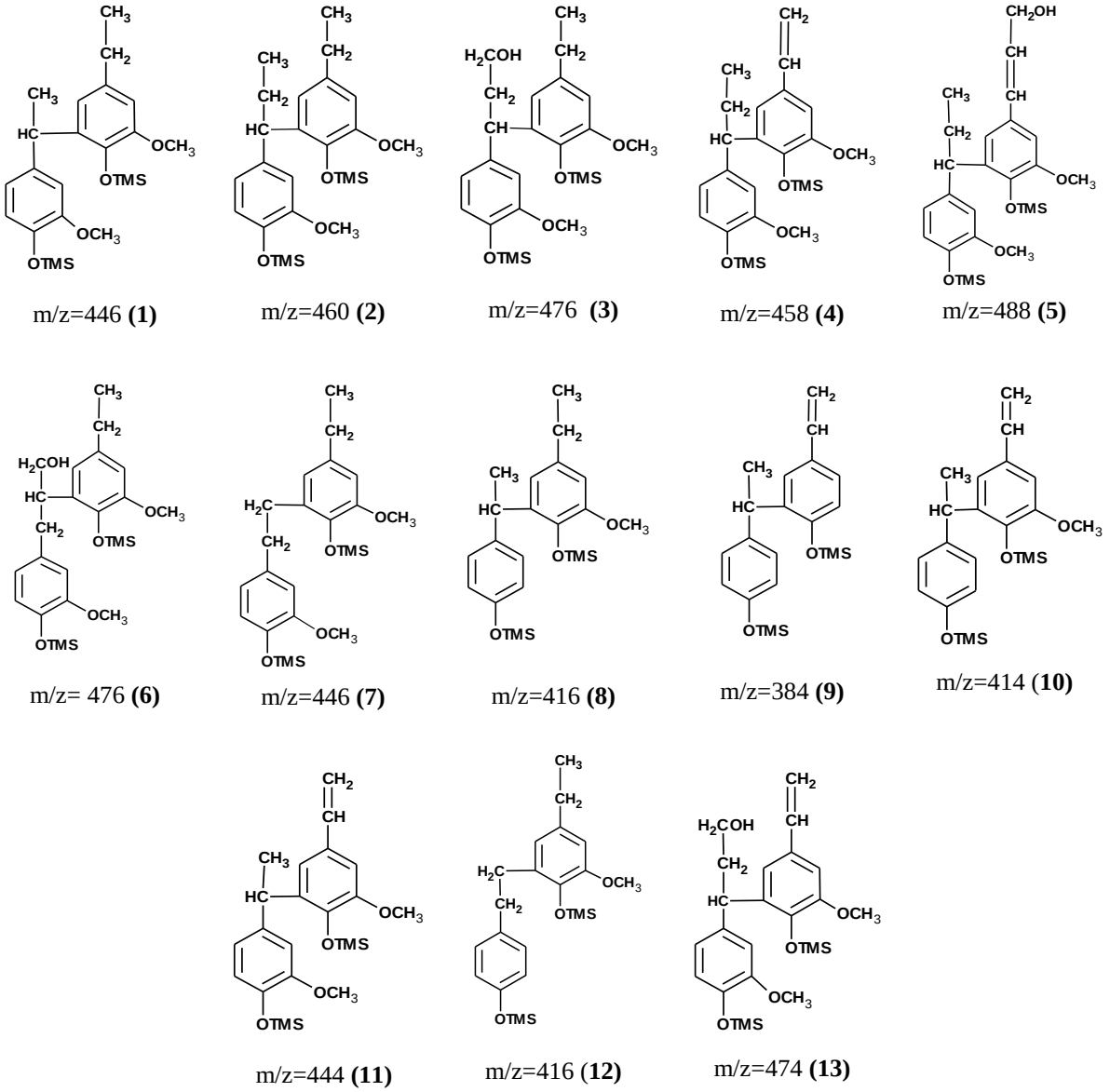


Figure 4.2. 6 Dimeric products from SAQ + EG treatment of sugar maple and bagasse.

The data analyses will start with a discussion of the MS data that are shown in **Figures 4.2.7 – 4.2.12**, respectively for dimers **1 - 6**. The mass spectrum of un-silylated **1** was previously presented and it comprised of fragments with m/z: 302 (M^+, 35), 287 (45), 178 (100) and 163 (76) (Pavlickova et al., 1976; Kanungo et al., 2009). That spectrum converted to the spectrum in **Figure 4.2. 7,** upon silylation of the dimer. The molecular ion with m/z = 446 (**Figure 4.2. 7**) corresponds to **1** with two trimethylsilyl (TMS) groups added. The molecular ion with m/z= 460 (**Figure 4.2. 8**) and m/z =476 (**Figure 4.2. 9**) correspond to **2** and **3**, respectively. The spectrum

for the corresponding GC/MS peak of **3** without silylation was presented by Kanungo et al. (2011). The molecular ion with m/z = 332 is consistent with that of **3** without the two TMS groups. All three spectra for the silylated dimers are characterized by peaks representing M^+ minus 15, 30 and 45, respectively and it appears that this is due to the loss of methyl groups (CH_3). The spectrum in **Figure 4.2. 8** was assigned to **2** because it afforded a molecular ion with m/z = 460. Also, fragments with M^+- 15, M^+- 29, M^+-30, and M^+- 31 that were observed are all easily explained by **2**. The spectrum for the compound (**3**) in **Figure 4.2. 9** does not show much fragmentation of the molecule beyond M^+ minus 15, 30 and 45.

The MS for **4** (**Figure 4.2. 10**) was conclusive with the molecular ions (m/z=458) being the most intense peak and with the M^+-15, M^+-29, and M^+-30 being the three largest fragments (ion counts >15% of that for M^+) at m/z> 233. The MS for **5** (**Figure 4.2. 11**) was also conclusive with the molecular ion (m/z=488) being the most intense peak and M^+-15, M^+-29, M^+-30, M^+-31, all being present at abundance > 15% of that for M^+. The MS for **6** (**Figure 4.2. 12**) was fairly conclusive. The molecular ion was once again the largest peak and fragments with both m/z=267 and m/z=209 were observed. Those two fragments would be generated by cleavage of the Cα-Cβ bond on the left ring. It is assumed that m/z=207 (higher abundance) was derived from m/z=209. Dimerization between vinylsyringol and EG would give m/z=476 for M^+. However, M^+-15 should be a major peak for that dimer (see **Figure 4.2. 7** for spectrum of VG-EG). However, the observed M^+-15 fragment was < 5% of the abundance of the M^+ peak in **Figure 4.2. 12**. No evidence could be found for syringyl (S) containing dimers at the 0.01 mmole level.

A discussion on the expected yield of CA that should be generated from the wood meal will now be attempted. The wood meal contained 24.8% lignin and the S:G ratio of that lignin was 1.25. A reasonable estimation for the molecular weight of a C_9 unit in the lignin of a hardwood like sugar maple is 210 Daltons (Masingale et al., 2009). The number of mmoles of C_9 unit used was approximately 5.90 (0.248 x 5000 mg ÷ 210). A credible estimate of the percentage of the C_9 units containing either an α-OH or an α-ether and involved in β-O-4 linkages is ~30% (30 dimers/100 C_9) (Adler, 1977) and one mole of CA would be generated from one mole of β-O-4' dimer (**Figure 3.5. 3**). The CA would come from the A-ring, the one forming the QM (**Figure 3.5. 3**). If it is assumed that ~44% of the C_9 units were guaiacyl and

55% were syringyl (S:G = 1.25) then A rings would constitute ~30% of the C_9 units in the lignin and 44% of them would be guaiacyl. In all probability, CA would only be produced from uncondensed guaiacyl A- rings and their total would be ~0.78 mmole (5.90 x 0.30 x 0.44). *An uncondensed C_9 unit is defined as one not containing a C-C bond at any ring position except for C-1 (sidechain) nor connected to another C_9 unit by a diaryl ether linkage.* The total yield of CA derived dimers was 0.47 mmole (**Table 4.2. 2**). If it is assumed that all the β-O-4' dimers with uncondensed A-rings were converted to CA then the uncondensed fraction of the total guaiacyl A-rings would be 60% (0.47/0.78). Evtuguin et al. (2001) analyzed *Eucalyptus globulus* by permanganate oxidation and found that 61% of the G units were uncondensed. Using the same permanganate oxidation technique, Bose et al. (2009c) later obtained values of 65.4%, 65.4%, and 69.0%, respectively for the fraction of uncondensed G units from two poplar wood meals along with that from a 1:1:1 mixture of sugar maple (*Acer saccharum*), paper birch (*Betula papyrifera*), and cottonwood (*Populus deltoides Bartr.*).

Finally, it should be noted that the consumption of EG in **Table 4.2. 2** was 0.49 mmoles (1.64-1.15). Therefore, EG appears to react almost exclusively with CA and its transformed products (VG and IE). Of the total EG consumption of 0.49 mmoles, VG, IE and CA consumed 0.41 mmoles.

Table 4.2. 2 Yields of Residual EG and Dimers Generated in SAQ+EG Cooking of Maple Wood

Compound	***m/z***	***Yield, mmoles[1]***	***Derived from CA[4]***
EG		1.14 (1.16)[2, 3]	
VG-EG (**1**)	446	0.11 (0.11)	0.11
IE-EG (**2**)	460	0.03 (0.03)	0.03
CA-EG (**3**)	476	0.27 (0.25)	0.26
IE-VG (**4**)	458	0.02	0.04
IE-CA (**5**)	488	0.01	0.02
CA-EG β-linked (**6**)	476	0.01	0.01
VG-EG β-linked (**7**)	446	0	0

[1] From 5.90 mmoles of C_9 units, see text
[2] Data for repeat experiment in parenthesis
[3] Initial dose of EG = 1.64 mmoles (250 mg)
[4] mmoles of monomers (0.47 in total)

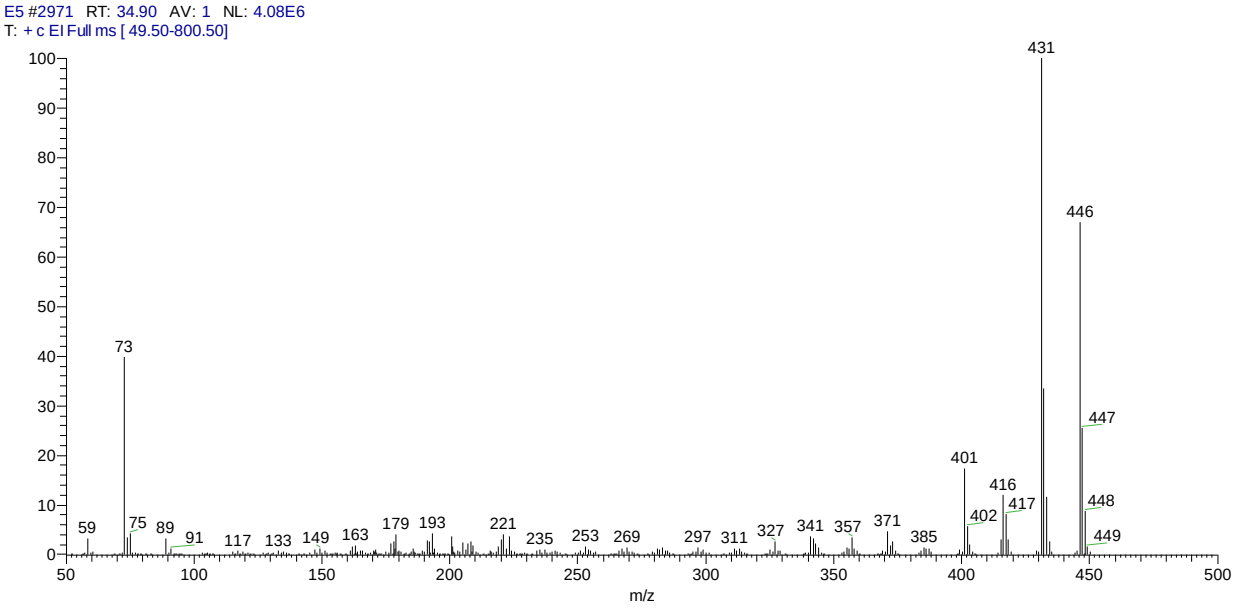


Figure 4.2. 7 Mass spectrum for the compound **1** (VG-EG).

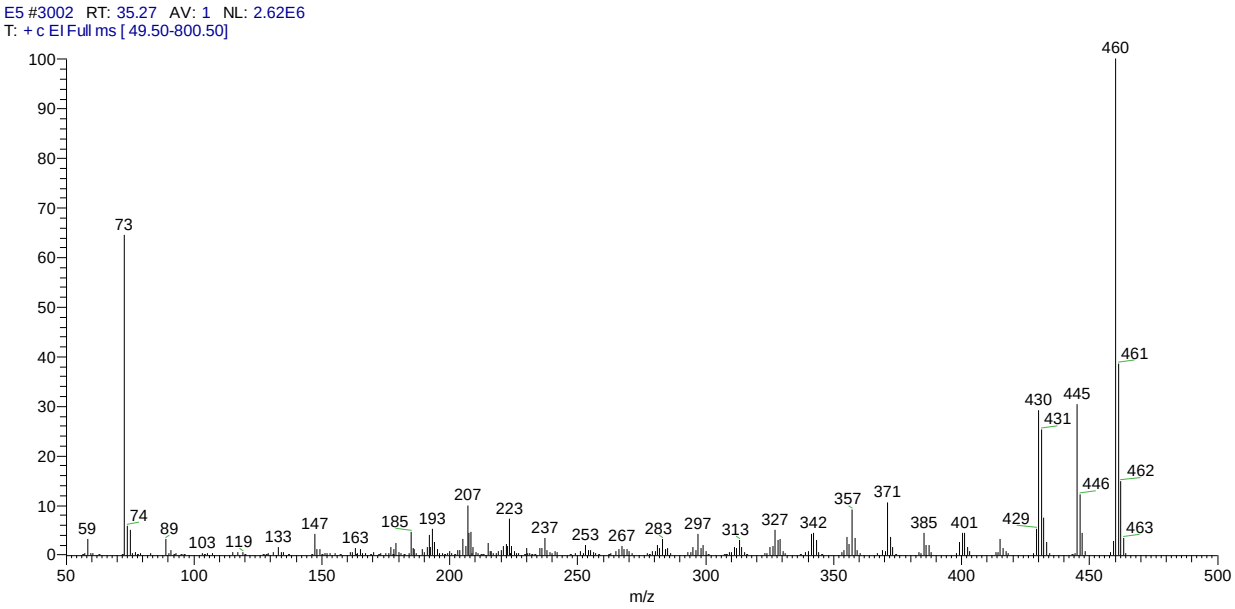


Figure 4.2. 8 Mass spectrum for the compound **2** (IE-EG).

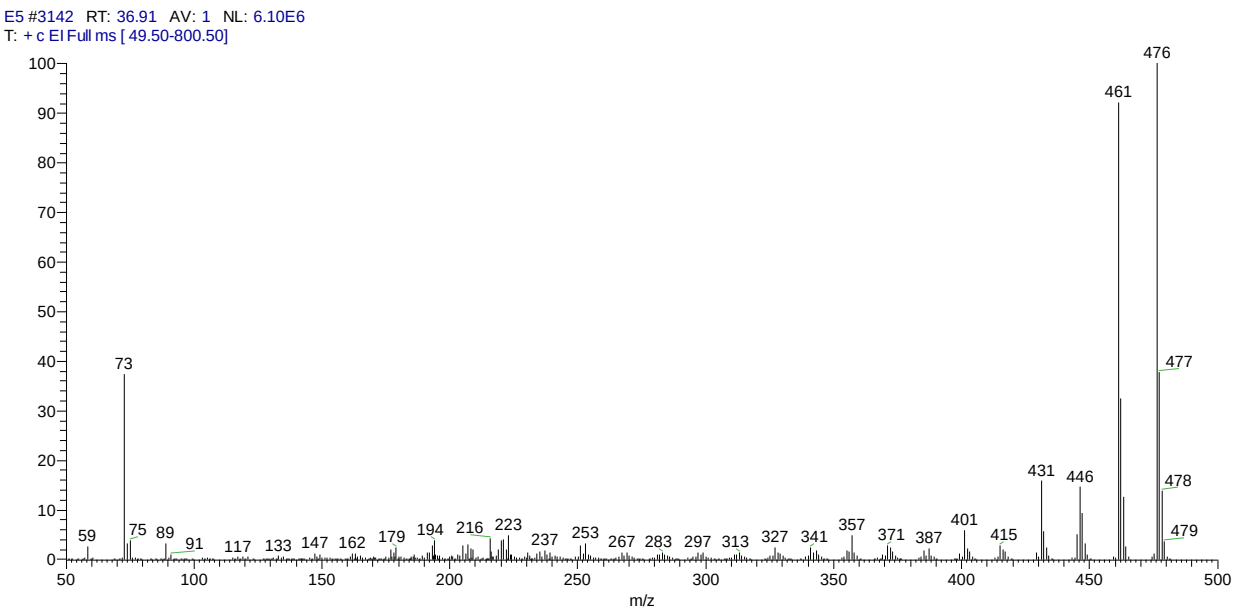


Figure 4.2. 9 Mass spectrum for the compound **3** (CA-EG).

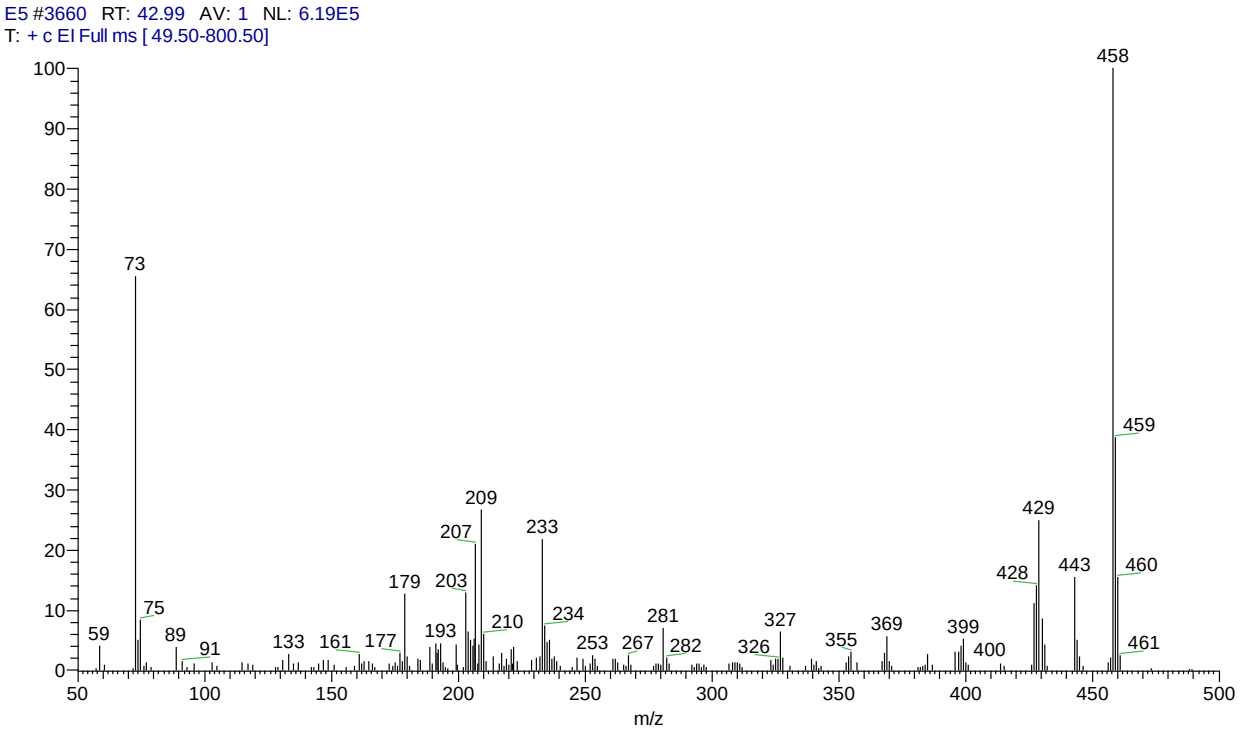


Figure 4.2. 10 Mass spectrum for the compound **4** (IE-VG).

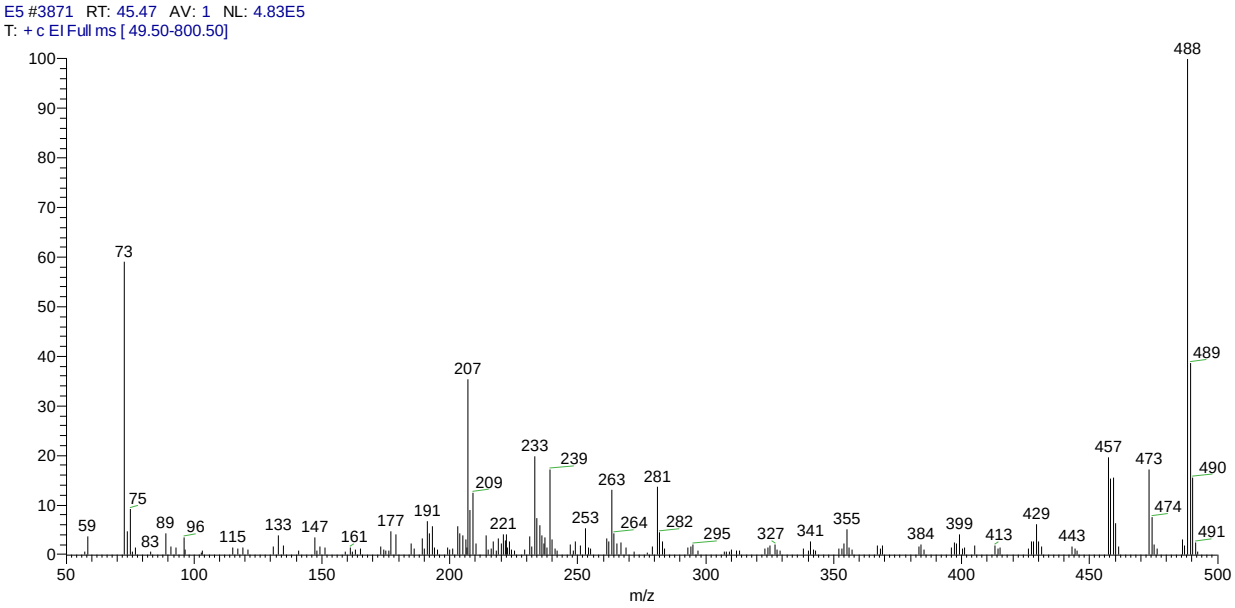


Figure 4.2. 11 Mass spectrum for the compound **5** (IE-CA).

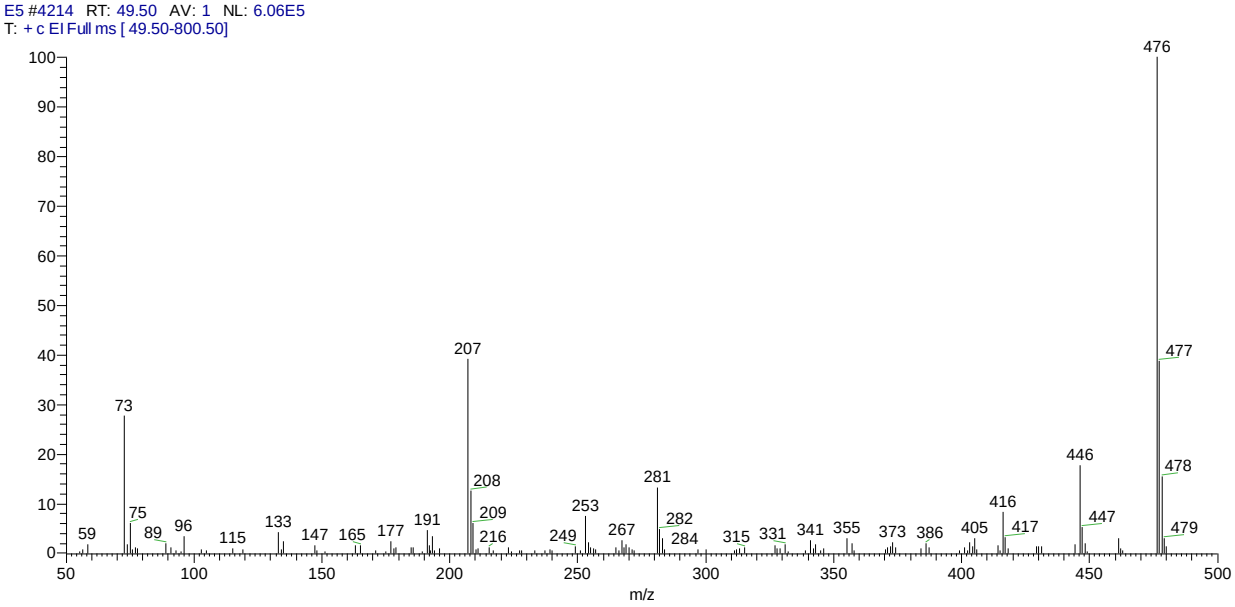


Figure 4.2. 12 Mass spectrum for the compound **6** (CA-EG).

When 5 g of maple wood meal (15 mesh, ethanol-toluene extracted) was treated with the 60 ml of SAQ liquor for H-factor 441 (Materials and Methods) the resulting fibers had a kappa number of 44.5 when EG was excluded and 41.9 when it was included. When WDB was treated similarly the corresponding kappa numbers were 10.1 and 9.0. Could the explanation be a significant difference between the lignin in the two samples in the distribution of A-rings in β-O-4' structures (one forming QM in **Figure 3.5. 3**)? Syringyl A-rings, few of which are condensed,

are very reactive toward soda, SAQ and kraft treatments (Kondo et al., 1987; Tsutsumi et al., 1995). On the other hand, condensed A-rings are known to be unreactive to similar treatments (Gellerstedt et al., 1988; Bose et al., 2009a). Therefore, a lignin with a high concentration of uncondensed A-rings in the G and/or H fraction should be more reactive than one with a lower concentration of uncondensed A-rings.

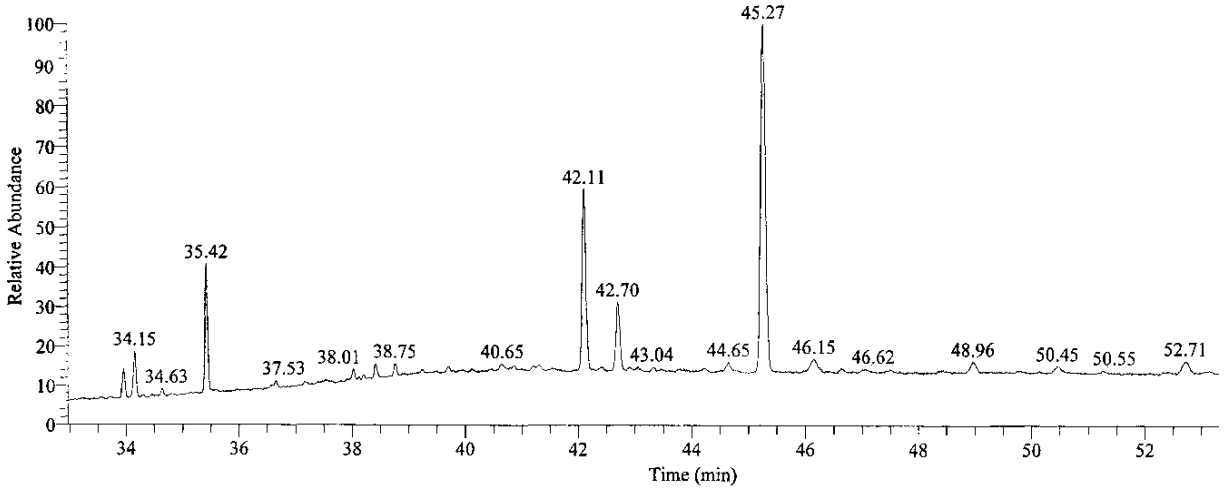


Figure 4.2. 13 A section of GC/MS chromatogram showing dimeric products from SAQ+EG pulping of sugar maple wood meal at a 12:1 liquor to wood ratio (initial results of Kanungo et al. 2011).

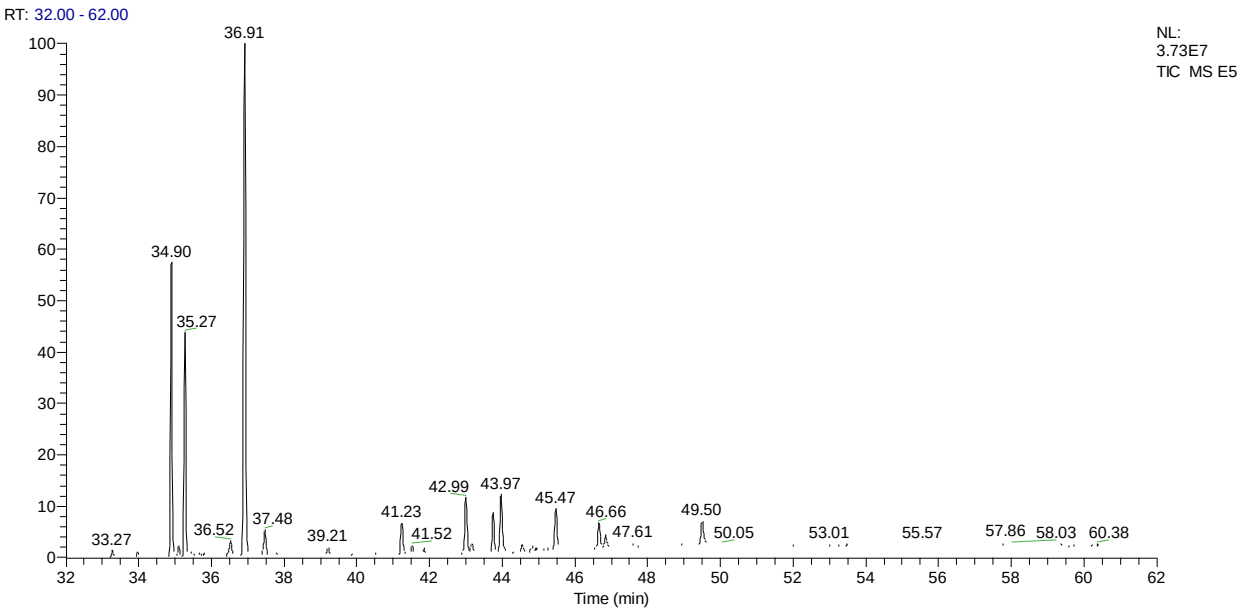


Figure 4.2. 14 A section of GC/MS chromatogram showing dimeric products from SAQ+EG pulping of sugar maple wood meal at a 12:1 liquor to wood ratio (Present research).

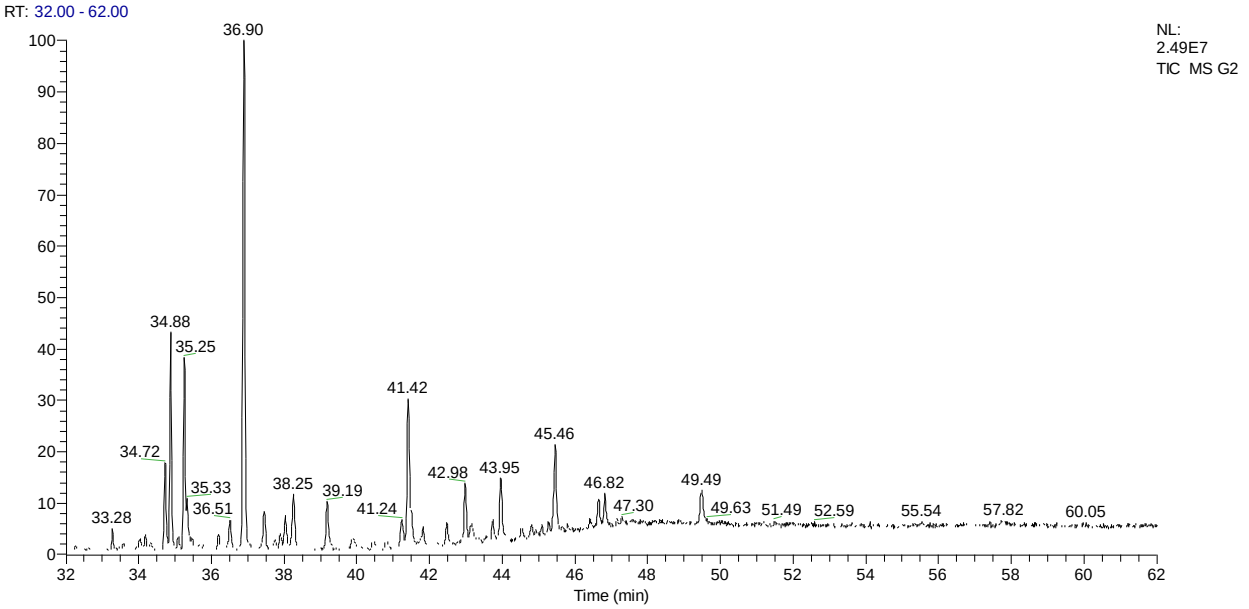


Figure 4.2. 15 A section of GC/MS chromatogram showing dimeric products from SAQ+EG pulping of E. *Grandis* x E. *Urophylla* wood meal at a 12:1 liquor to wood ratio (Present research).

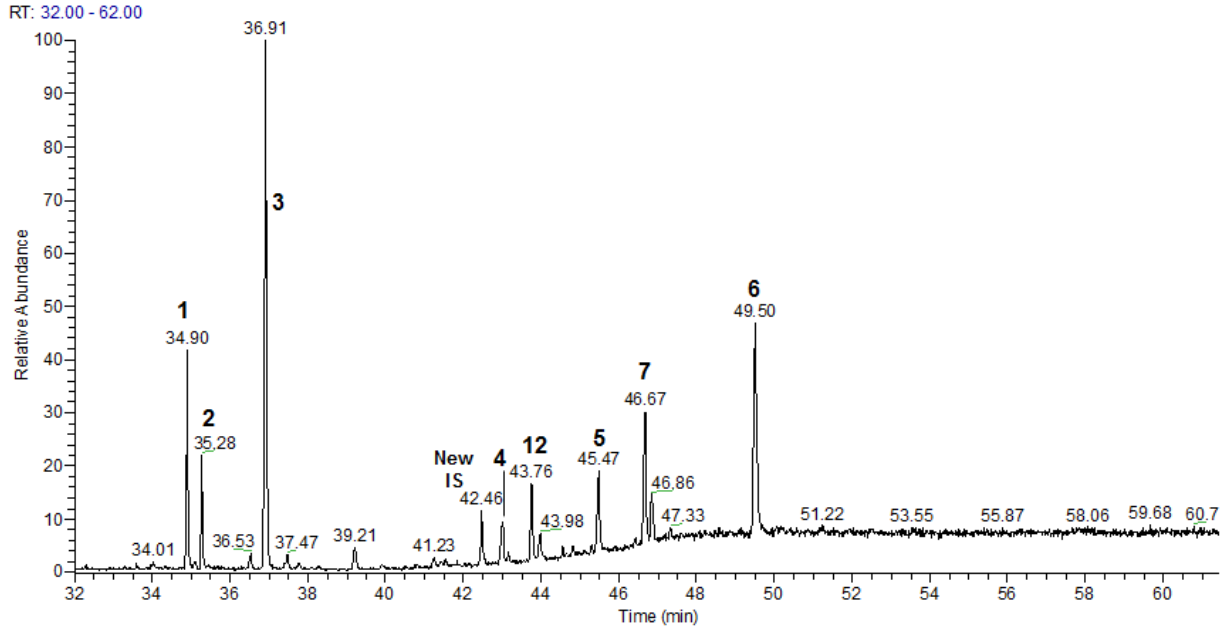


Figure 4.2. 16 A section of GC/MS chromatogram showing dimeric products from SAQ+EG pulping of *Eucalyptus camadulensis* wood meal at a 12:1 liquor to wood ratio (Present research).

Approximately ~ 14% of its C_9 units in bagasse lignin are composed of *p*-coumaric acid (*p*-CMAc) and ferulic acids (FA) that are bonded to the lignin by hydrolysable ether and ester linkages. Xu et al. (2005) exposed bagasse meal to mild alkaline treatment followed by mild acidolysis and estimated that easily hydrolyzed *p*-coumaric acid constituted ~9% of the C_9 units while the value for ferulic acid was ~5%. However, hydrolysis of 14% of the lignin early in SAQ treatment would lower the lignin content of bagasse from 23.7% to ~20.4%. Delignification from ~20.4% lignin content to kappa number 10 after and H-factor of only 441would indicate a lignin that is highly reactive to SAQ treatment.

The bagasse was treated with SAQ and EG and it was obvious that the yields of dimers were much higher than for maple. However, some key assumptions regarding bagasse lignin have to be stated before those data are analyzed. Nada et al. analyzed bagasse lignin recovered from the black liquor of organosolv, soda, SAQ and kraft pulping and found that their methoxyl contents consistently fell in the range of 0.98-1.05 OCH_3/C_9 (Nada et al., 1994a; Nada et al., 1994b). Chen et al. (1998) performed nitrobenzene oxidation (NBO) on bagasse meal and obtained a high total yield of substituted benzaldehyde + benzoic acids (58.1/100 C_9). The yield of these monomers from H, G and S units have to be corrected for *p*-coumaric and ferulic acids that would hydrolyze very early in SAQ and NBO treatments. When these two acids were given the standard NBO treatment, *p*-coumaric acid afforded a 52% molar yield of *p*-hydroxybenzaldehyde while ferulic acid afforded vanillin at 63% yield (Seca et al., 2000). Therefore, the NBO yield of substituted benzaldehydes and benzoic acids from H and G units have to be corrected for contributions from *p*-coumaric and ferulic acids.

The molar yield of *p*-hydroxybenzaldehyde from *p*-coumaric acid would be ~4.7% (9% x 0.52) while the corresponding yield of vanillin from ferulic acid would be ~3.2% (5% x 0.63). The total yields of substituted benzaldehyde + benzoic acid from H, G and S units obtained by Chen et al. were 21.3%, 17.6% and 19.2%, respectively. When the correction above is included the values change to 16.6%, 14.4% and 19.2% and the corrected total yield became 50.2%, which is still very high. The calculated methoxyl content of the lignin based on the uncorrected data of Chen et al. (1998) is 0.96 OCH_3/C_9 while the value increases to 1.05 OCH_3/C_9 when the correction for *p*-coumaric and ferulic acids is included. Based on the corrected data of Chen et al. (1998) it is estimated that bagasse lignin entering the bulk phase of SAQ cooking is composed of

~33% H, 29% G and 38% S. A molecular weight of the average C_9 unit in bagasse lignin was assumed to be 189.5 which is the value reported for softwood lignin with 0.97 OCH_3/C_9 (Dence and Lin, 1992).

A typical GC-MS chromatogram for the products from SAQ-EG cooking of WDB is shown in **Figure 4.2. 17.** Data analyses of dimer yields will start with assignment of structures **8**-**13** in **Figure 4.2. 6**. The MS for **8**, **10**, **11**, and **13** were very consistent with those in **1** – **6**. The spectra for these four dimers are presented in **Figures A1 – A4** in the Appendix. The MS for **9** contained only 5 fragments with m/z > 200 and those were m/z= 384 (M^+), 369 (M^+-15), 219, 218, and 203 (**Figure 4.2. 18**). The molecular ion peak matches the proposed structure and M^+-15 would be expected. Cleavage of the C_1 - Cα bond on the left ring would give fragments with m/z=219 and 165. Fragments with m/z= 219, 218 and 203 (219-1 and 219-1-15) were expected. This is based on a similar fragmentation pattern observed with another α-5 dimer (un-derivatized) where fragments with m/z = 179, 178 and 163 were obtained (Kanungo et al. 2009; Pavlickova et al., 1976). The MS data matches the assigned structure quite well for **12**. Key fragments in the spectrum were m/z=416 (M^+, 100), m/z=237 (22) and m/z=179 (14). Cleavage of the Cα-Cβ bond on the left ring would give two fragments with m/z=237 and m/z=179. The spectra for **7** and **12** are presented in **Figures A5 and A6** (Appendix). The M^+-15 peak was very small for these two β-5' structures. That was also the case for **6**, another β-5' dimer (**Figure 4.2. 12**).

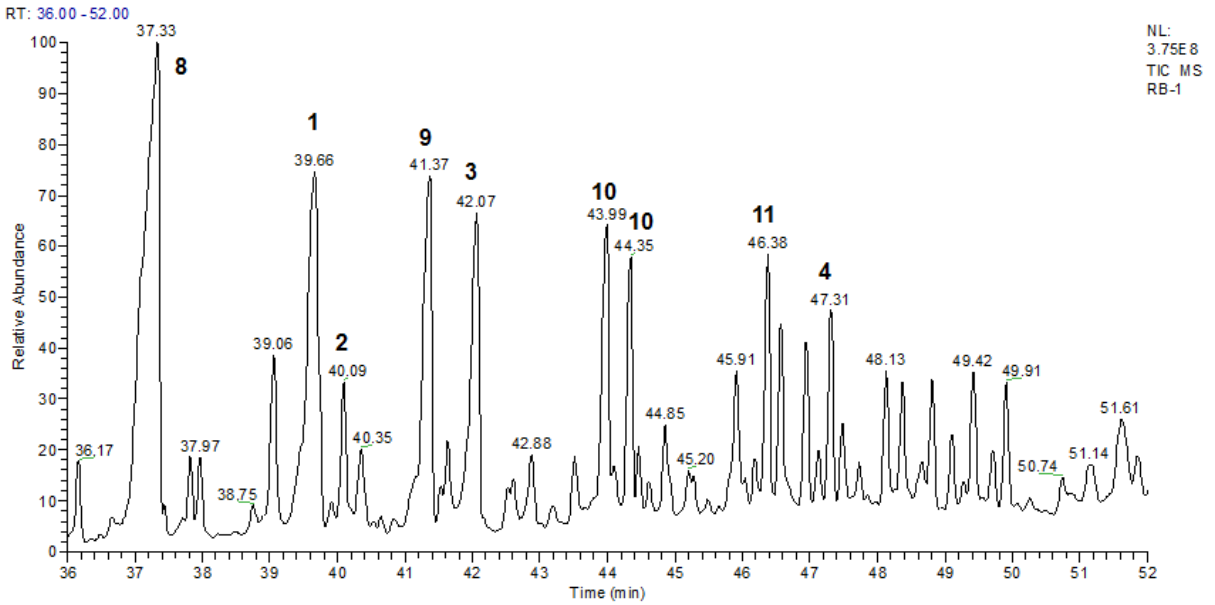


Figure 4.2. 17 Dimeric products from SAQ + EG treatment of bagasse. Dimers identified by retention time of peaks in Table 4.2.3.

The retention times and yields of the key dimers are documented in **Table 4.2. 3**. Once again there was no detection of syringyl containing dimers at the 0.01 mmole level. The first significant observation that the total yield of dimers, from approximately the same amount of lignin, was more than twice as high for bagasse as it was for maple. A second significant observation was that VP (vinylphenol) containing dimers dominated over those containing *p*-CMA and VG containing dimers dominated over those containing CA which was opposite to the situation with maple. Actually, no *p*-CMA containing dimer was detected. The difference in retention time between the **1** and **3** in **Figure 4.2.17** is 2.41 min (42.07 – 39.66). If a similar difference is assumed for the retention times of the VP – EG dimer (**8**) and a possible *p*-CMA – EG dimer then this dimer would elute at ~39.74 min (37.33 + 2.41). The possibility that the 39.66 minute peak was a combination of two peaks was investigated. The two structures would be **1** with m/z = 446 and the other for the *p*-CMA – EG dimer, also with m/z = 446. The mass spectrum taken at 39.42 min and 39.66 minutes are presented in **Figures A7 and A8**. They are identical and very similar to that of **1** shown in **Figure 4.2. 7**. The spectrum in **Figure 4.2. 7** was obtained from SAQ + EG treatment of sugar maple and could not have been derived from the *p*-CMA – EG dimer because the maple contained only traces of H units.

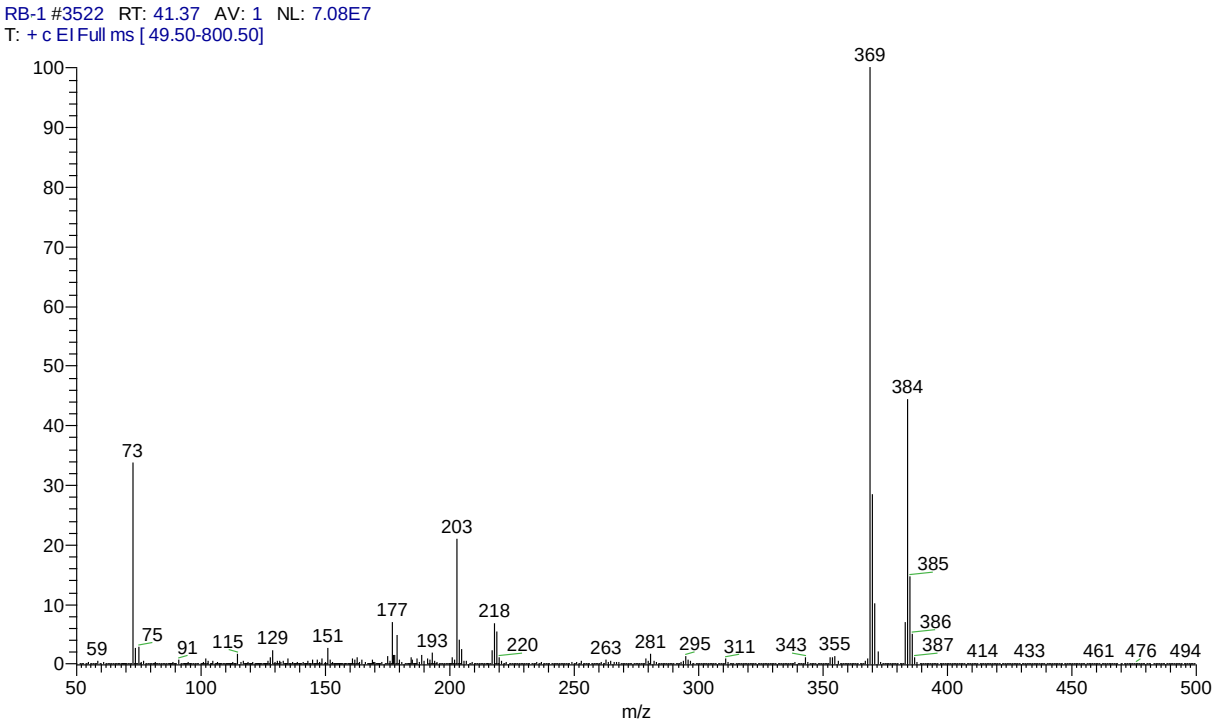


Figure 4.2. 18 Mass spectrum for the compound **9** (VP-VP) dimer.

It is known that the thermal decarboxylation of *p*-coumaric acid to VP and CO_2 (de Groot and Buma, 2005) is catalyzed by acid, base and microwave irradiation (Bernini et al., 2007). Therefore, *p*-coumaric acid and EG (1.64 mmoles of each) were treated identically to the bagasse meal (Materials and Methods) and low yields of **8** and **9** were observed (**Figure 4.2. 19**). The duplicate yield of **8** was 0.17 mmole while that of **9** was 0.06 mmole. Since two moles of *p*-coumaric acid would be required to generate one mole of **9** (a VP-VP dimer), the total conversion of *p*-coumaric acid to **8** and **9** was 0.29 mmole or 18%. The initial amount of C_9 units in the bagasse was 6.25 mmoles (5000 mg x 0.237/189.5) and it will be assumed that 9% of the C_9 units were *p*-coumaric acids and that they were converted to VP-containing products at 18% yield (6.25 x 0.09 x 0.18 = 0.10). Similarly, 5% of the lignin was ferulic acid and it is assumed that it also converted to VG-containing products at 18% yield (6.25 x 0.05 x 0.18 = 0.06). The data in **Table 4.2. 3** are now presented in **Table 4.2. 4** with those corrections and with the total number of *p*-coumaryl alcohol (*p*-CMA) and coniferyl alcohol (CA) derived monomers calculated. The corrected monomer yield was 0.55 mmole for *p*-CMA derived products and 0.49 mmole for CA derived products.

Table 4.2. 3 Uncorrected Yields of Dimers Derived from H and G units in SAQ-EG Treatment of Bagasse

Compound	***m/z***	***Yield, mmoles[1]***	***RT, min[2]***
VP[3]-EG (**8**)	416	0.32 (0.03)[4]	37.33
VG-EG (**1**)	446	0.17 (0.02)	39.66
IE-EG (**2**)	460	0.02	40.09
VP-VP (**9**)	384	0.11 (0.01)	41.37
CA-EG (**3**)	476	0.09 (0.01)	42.07
VP-VG (**10**)	414	0.09 (0.01)	43.99 and 44.35
VG-VG (**11**)	444	0.04	46.38
IE-VG (**4**)	458	0.03	47.31
VP-EG (**12**)	416	0.02	48.13 and 48.37
CA-VG (**13**)	474	0.02	48.82

[1] From 6.25 mmoles of lignin, see text
[2] Retention time in Figure 4.2.17
[3] VP = Vinylphenol
[4] Standard deviation based on three complete analyses

The H, G and S fractions of bagasse lignin excluding ester and ether linked *p*-coumaric and ferulic acids were previously estimated at ~33%, 29%, and 38%, respectively. Excluding the ~9% *p*-coumaric acid and ~5% of ferulic acids that are hydrolysable under mild conditions, the SAQ treatments (β-O-4' cleavage) started with 5.38 mmoles of C_9 units (6.25 x 0.86). The breakdown would be 1.78 mmoles of H units, 1.56 mmoles of G units, and 2.04 mmoles of S units. If it is assumed that 40% of the C_9 units in bagasse lignin contain either an α-OH or an α-ether and involved in β-O-4' linkages (40 dimers/100 C_9) then the total number of A-rings that would be H or G would be approximately: (1.78 + 1.56) x 0.40 = 1.34. Of that total, 1.04 mmoles (0.55 + 0.49) or 78% would be uncondensed. As stated earlier, the S fraction contains few condensed structures and it is therefore concluded that bagasse lignin contain a high concentration of uncondensed C_9 units. This conclusion is in the line with that of da Silva Perez et al. (1998) who recovered bagasse lignin for peroxyformic acid pulping effluent and analyzed it by ^{31}P NMR. Out of a total of 63 phenolic hydroxyl groups (PhOH)/100 C_9 units only 8 of those structures were condensed. A similar trend of low concentrations of condensed PhOH was later reported by Hoareau et al. (2004) who used ^{31}P NMR to analyze bagasse lignin obtained by alkaline extraction and dioxane-HCl acidolysis. This would indicate that not many lignin units in bagasse are joined together by 5-5' biphenyl, β-5', and 4-O-5' diaryl linkages.

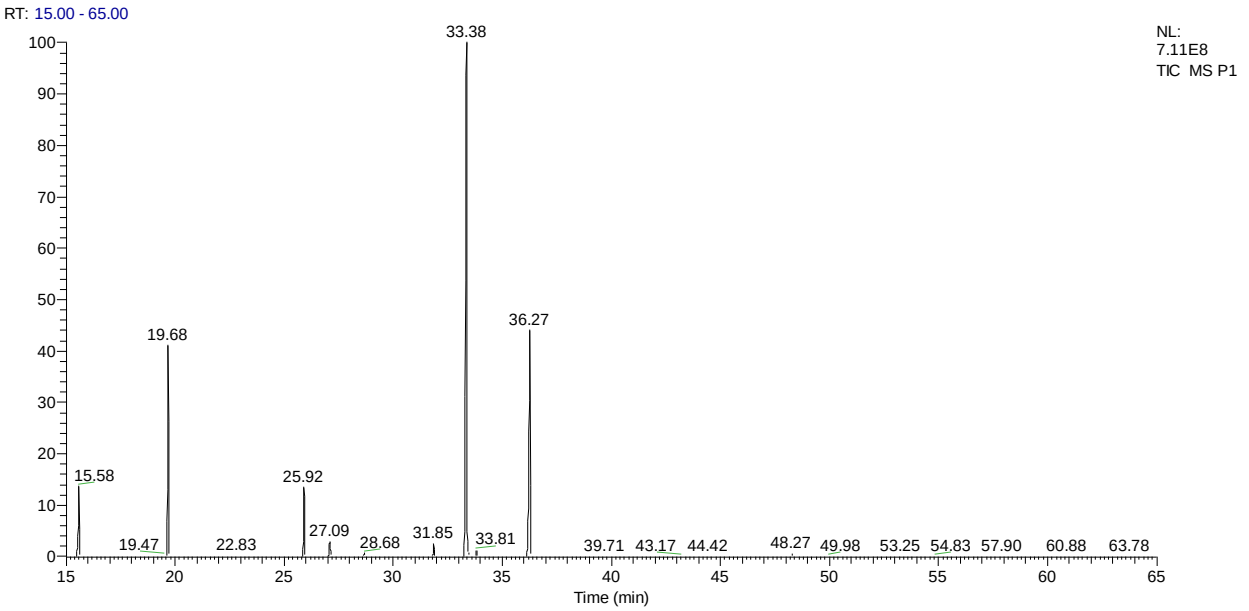


Figure 4.2. 19 GC/MS chromatogram for alkaline condensation of *p*-CMAc – EG. Peak at 33.38 min is for **8**, while 36.27 min is for **9**, 25.92 min is for *p*-CMAc, 19.68 min for internal standard and 15.58 min is for *p*-hydroxybenzoic acid (*p*-HBA).

Table 4.2. 4 Yields of Monomers Derived from H and G units and Application of Correction for Conversion of *p*-Coumaric Acid and Ferulic Acids to Dimers

Compound	***m/z***	***Dimeric Yield, mmoles***	***Derived from p-CMA***	***Derived from CA***
VP-EG (**8**)	416	0.32	0.32	
VG-EG (**1**)	446	0.17		0.17
IE-EG (**2**)	460	0.02		0.02
VP-VP (**9**)	384	0.11	0.22	
CA-EG (**3**)	476	0.09		0.09
VP-VG (**10**)	414	0.09	0.09	0.09
VG-VG (**11**)	444	0.04		0.08
IE-VG (**4**)	458	0.03		0.06
VP-EG (**12**)	416	0.02	0.02	
CA-VG (**13**)	474	0.02		0.04
Total p-CMA derived, mmoles			***0.65 (0.55)***[1]	
Total CA derived, mmoles				***0.55 (0.49)***[2]

[1]Corrected for VP-containing products derived from *p*- coumaric acid, see text
[2]Corrected for VG-containing products derived from ferulic acid, see text

In summary, it appears that when 15 mesh meal from hardwood and bagasse were SAQ delignify to H-factor 441 almost all of the β-O-4’ linkages with A-rings that were uncondensed

G and H units were cleaved. The primary products from β-O-4' cleavage were CA and *p*-CMA and these monomers were ultimately trapped in high yield by EG. The α-carbon atom in CA, *p*-CMA and their transformation products appear to react rapidly with the C-5 position of EG. The estimates of β-O-4' concentrations with uncondensed A-rings from the G and H fraction of sugar maple and bagasse lignin by this approach (quantification of dimers from CA and *p*-CMA) were in close agreement with results previously reported by traditional but more tedious methods such as permanganate oxidation and ^{31}P NMR. The entire SAQ + EG procedure would take less time than that required for lignin isolation for spectroscopic analyses. The lignin isolation recovery yield is generally <70% if significant modifications are to be avoided. The time requirement for SAQ + EG would also be less than that for the pre-methylation step in permanganate oxidation analysis (Gellerstedt, 1992; Bose et al., 1998). Of all the G units that are A-rings in β-O-4' linkages in sugar maple lignin, ~60% of them are uncondensed. Thirty β-O-4' linkages /100 C_9 units (30 dimeric or 60 C_9 units) were assumed (Adler, 1977). The G and H fractions of bagasse lignin contain high concentrations of β-O-4 dimeric units with at least one of the C_9 unit being uncondensed. Out of a total of 3.34 mmoles of H and G units (1.56 + 1.78 in the text), the amount that were uncondensed A-rings in β-O-4' linkages was 1.04 mmoles (0.55 + 0.49, **Table 4.2. 4**), a ratio of 0.31. The corresponding values for the G fraction in sugar maple lignin were 0.47 mmole of uncondensed A-rings in β-O-4' linkages from 2.60 mmoles (5.90 x 0.44) of total G units, a ratio of only 0.18. A likely reason as to why the lignin in WDB is delignified faster by SAQ liquor is its much higher concentration of uncondensed β-O-4' units as compared to sugar maple lignin.

4.2.3.5 Additional Pulping and Bleaching Trials

The results from *p*-CMAc - EG condensation would suggest the *p*-CMAc and ferulic acid (FA) are likely to participate in condensation reactions during SAQ, KAQ or K/NAQ cooking. Since these two monomers total ~14% of the C_9 units (Xu et al., 2005) and are connected to the lignin polymer by hydrolysable ester and ether bonds, attention has to be paid to their reactivity or else a bagasse pulp with a low unbleached kappa but poor bleachability may be the result. The WDB was KAQ delignified in the M&K digester and NH_4OH pretreatment was investigated. This pretreatment should solubilize and remove some of the *p*-CMAc and FA before the KAQ

treatment. Also, even if some *p*-CMAc and FA condense unto the residual lignin during pretreatment they may not affect the subsequent KAQ stage too adversely since both *p*-CMAc and FA contain dissociable PhOH and COOH groups. That is assuming that their decarboxylation to VP and VG respectively, would be minor at the low alkalinity of the N stage. The pH of the N stage is ~10.3 when 160^{o}C is attained and the end pH is typically 10.1 – 10.2. The cooking results for K/NAQ and N→KAQ cooking of WDB are presented in **Table 4.2. 5** and their bleaching results for the OD_0EpD_1 and QPD_0EpD_1 sequences are presented in **Table 4.2. 6**. It can be seen that the N→KAQ pulp achieved 15.7 kappa number at 61.4% yield while K/NAQ with both KOH and NH_4OH in the cooking stage afforded and average kappa number of 19.0 at 61.2% yield. However, the total H-factor was 887 for N→SAQ as compared to 644 for K/NAQ.

Table 4.2. 5 Effect of 1.0 M NH_4OH Pretreatment on KAQ Cooking of WDB[1]

	K/NAQ	***N→KAQ***
Pretreatment		
NH_4OH in liquor, M[2]	-	1.0
Treatment Temp., ^{o}C	-	160
H-Factor	-	243
Cooking Stage		
KOH, % on DB	15.0	15.0
NH_4OH in liquor, M[2]	1.0	0
Cooking temp., ^{o}C	160	160
H Factor	644	644
Total H factor	644	887
Final Yield, % on DB	61.1 (61.3)[3]	61.4
Kappa number	19.8 (18.1)[3]	15.7

[1] Initial and end pH of 10.3 and 10.2 in NH_4OH Pretreatment
[2] 10:1 L to B ratio
[3] Value for cook performed at a later date

Delignification by O or QP stages was impressive in terms of kappa number reduction but brightness development was poor. Oxygen lower the kappa number of the SAQ pulp from 19.0 to 6.9 but increased its brightness from 35.0% Elrepho to only 41.6% Elrepho. The corresponding values for QP were kappa number 6.1 and 55.3% Elrepho. The N→KAQ pulp

demonstrated improved bleachability but brightness development was much poorer than for hardwood kraft or SAQ pulps. Application of 0.5% ClO_2 on pulp in the D_1 stage improved the brightness of the N→KAQ pulp from 78.8% Elrepho (kappa number 1.4) to only 86.9% Elrepho

Table 4.2. 6 OD_0EpD_1 and QPD_0EpD_1 Bleaching Characteristics of K/NAQ and N→KAQ pulps from WDB

	OD_0EpD_1 on K/NAQ pulp	***QPD_0EpD_1 on K/NAQ pulp***	***QPD_0EpD_1 on N→KAQ pulp***
Unbleached			
Kappa number	19.0	19.0	15.7
Brightness, % Elrepho	35.0	35.0	40.1
After O or QP Stages			
Kappa number[1]	6.9	6.1	5.9
Brightness, % Elrepho	41.6	55.3	58.7
D_0 Stage			
Kappa Factor in D_0[2]	0.30	0.30	0.30
End pH in D_0	2.2	2.3	2.2
Ep Stage			
Kappa number	1.8	1.6	1.4
Brightness, % Elrepho	74.1	75.1	78.8
D_1 Stage			
ClO_2, % on pulp	0.5	0.5	0.5
End pH	3.4	4.0	4.4
Brightness, % Elrepho	84.8	84.7	86.9

[1] 2.0% H_2O_2 on pulp in P stage
[2] % ClO_2 = 0.114 x kappa number

Another area in this comprehensive investigation of bagasse pulping and bleaching chemistry was the role of lignin-carbohydrate complexes (LCC). A high kappa number bagasse pulp was needed for investigation of LCC cleavage by bleaching chemicals. It was desired to treat bagasse K/NAQ pulp with sizable amounts of bleaching chemicals but maintain a kappa number >15 after treatment. A CDB-Carb sample was prepared from CC in the M&K digester and further cooked by K/NAQ. The temperature profile in the K/NAQ stage was 60 min to 160°C and 60 min at temperature with 10% KOH on CDB in 1.0 M NH_4OH. A pulp with kappa number of 61.9 was obtained and it appeared to be quite responsive to QP treatment. The used of 5.0% NaOH and 4.0% H_2O_2 on pulp lowered the kappa number from 61.9 to 18.4 (**Table 4.2. 7**). The pulp was bleached further by D_0EpD_1 using the chemical doses that are used in the

laboratory for unbleached hardwood pulps with kappa numbers in the range of 15-20. The D_0EpD_1 bleaching results are summarized in **Table 4.2. 7** along with the corresponding results for a 20.3 kappa number SAQ pulp made from sugar maple. The D_0EpD_1 bleaching response of the 18.4 kappa number K/NAQ pulp was clearly inferior to that of the maple pulp.

Table 4.2. 7 QPD_0EpD_1 Bleaching of K/NAQ and KAQ pulps from CDB-Carb and D_0EpD_1 bleaching of maple SAQ pulp

	QPD_0EpD_1 on K/NAQ pulp	***D_0EpD_1 on maple pulp*[1]**	***QPD_0EpD_1 on KAQ pulp***
Unbleached			
Kappa number	61.9	20.3	12.6[2]
Brightness, % Elrepho	<25	38.7	35.5
After QP Stages			
Kappa number	18.4[3]	--	3.7[4]
Brightness, % Elrepho	38.0	--	67.7
D_0 Stage			
Kappa Factor in D_0	0.20	0.20	0.30
End pH in D_0	2.6	2.8	2.3
Ep Stage			
Kappa number	2.4	3.4	--
Brightness, % Elrepho	64.1	71.5	88.1
D_1 Stage			
ClO_2, % on pulp	0.8	0.8	0.5
End pH	3.8	4.0	4.3
Brightness, % Elrepho	82.9	89.4	93.5

[1] Results from Francis et al. (2006)
[2] 23% KOH on CDB
[3] 4.0% H_2O_2 on pulp in P stage
[4] 2.0% H_2O_2 on pulp in P stage

The extent of delignification during the O and QP stages was always high for KAQ and K/NAQ pulps from both WDB and CDB-Carb and there were indications from the *p*-CMAc-EG condensation experiment that condensed structures containing carboxylate groups might have been generated during SAQ treatment (to be discussed shortly). The possibility was investigated that highly charged and alkali soluble condensed structures were being generated in the solution phase during KAQ or K/NAQ cooking and condensing on to the residual lignin. In such a case, the use of high alkalinity in the KAQ stage may not cleave the C-C bonds connecting adjacent C_9

units in the residual lignin but simply solubilize the entire polymer due to the increased concentration of carboxylates. The CDB was KAQ delignified with 23% KOH (no NH_4OH) and H-factor 644 (90 min at 160°C). A pulp with kappa number of 12.6 was obtained and somewhat surprisingly it achieved a brightness of 93.5% Elrepho after QPD_0EpD_1 bleaching (**Table 4.2. 7**).

When the *p*-CMAc-EG condensation was performed there was 18% conversion of *p*-CMAc to **8** and **9** (previously discussed, **Figure 4.2. 19**). Interestingly, residual *p*-CMAc was only 3% of the initial dose and there was no evidence of significant conversion of *p*-CMAc to other monomers. It is possible that a condensation scheme like the one in **Figure 4.2. 20** might have produced oligomeric or polymeric products that would not be detectable by GC/MS. To investigate further, *p*-CMAc was self-condensed under SAQ conditions. The *p*-CMAc residual was 4%, while there was a 10% conversion to **9,** and a 2% conversion to *p*-hydroxybenzoic acid (*p*-HBA). The GC/MS chromatogram is shown in **Figure 4.2. 21** and it can be seen that no other monomer or dimer was generated at high yield. The 15.56 min peak was for *p*-HBA (MS in **Figure A 9**); 19.69 min for the internal standard, benzhydrol (MS in **Figure A 10**); 25.96 min for *p*-CMAc (MS in **Figure A 11**) and 36.30 min for **9**. It is possible that a reaction such as that in **Figure 4.2. 20** might have occurred. If the vinylic group in a trimeric structure such as that in **Figure 4.2. 20** were to be condensing on to the residual lignin during KAQ or K/NAQ then 1) it would probably increase the solubilization of low and medium molecular weight (MW) polymers and 2) increase the degree of solvation (not salvation) of high MW polymers thus making them more reactive to the pulping chemicals.

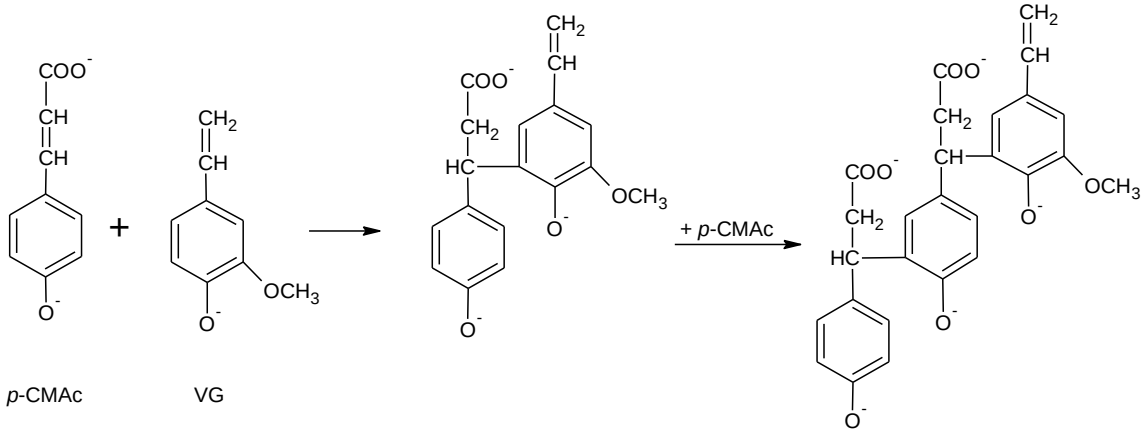


Figure 4.2. 20 Possible trimeric condensation product from *p*-CMAc that would be highly charged.

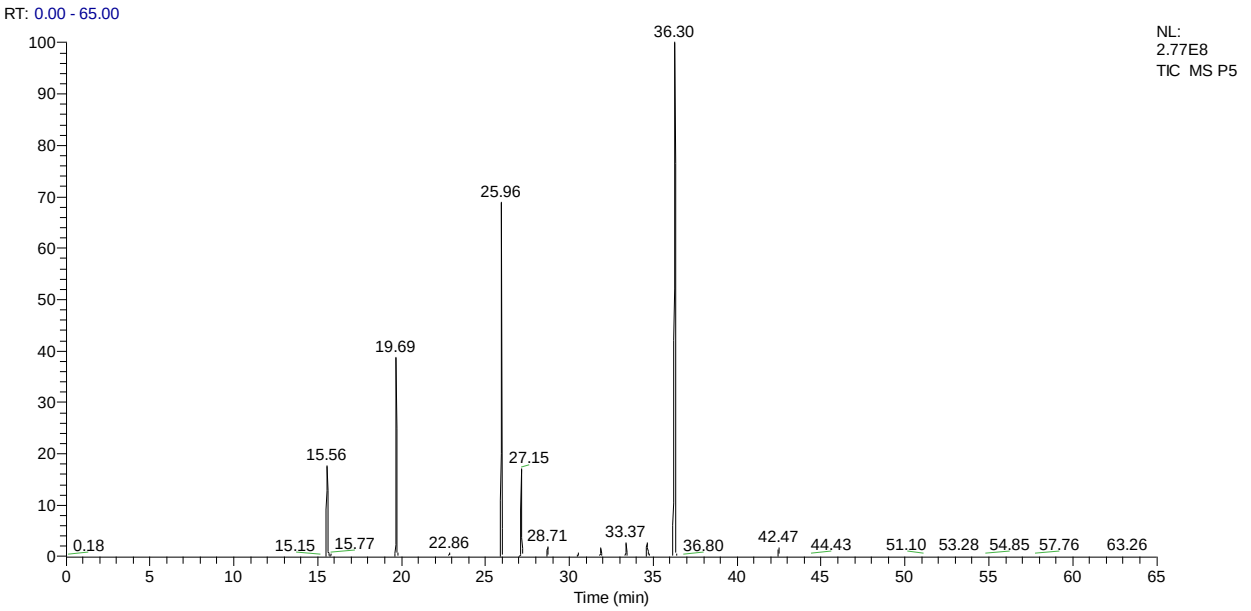


Figure 4.2. 21 GC/MS chromatogram for products from self-condensation of *p*-CMAc under SAQ conditions.

4.2.4 Summary of the Section

Bagasse is much more responsive to SAQ, K/NAQ and KAQ cooking than are most hardwoods. Under identical cooking conditions, bagasse meal achieved a kappa number of 10.1 while the value for sugar maple was 44.5. The non-syringyl fraction of bagasse lignin contained a much higher concentration of uncondensed β-O-4' structures as compared to sugar maple and this is the probable explanation for its higher reactivity towards SAQ. However, bagasse K/NAQ and KAQ pulps produced under low alkalinity conditions were less responsive to OD_0EpD_1 bleaching than were hardwood SAQ pulps. Results are presented tentatively showing that *p*-coumaric acid (*p*-CMAc) and ferulic acid (FA), that are abundant in bagasse lignin, may be involved in condensation reactions during K/NAQ and KAQ that lowers lignin reactivity due to the increase in the number of C-C interunitary linkages. However, it also appears that the condensed products from *p*-CMAc and FA may be rich in COOH groups and this could increase the solubility of the oligomers and polymers aid in lignin extraction if high alkalinity is used in pulping or if highly alkaline bleaching stages were to be used. The bleachability of bagasse KAQ pulp improved dramatically when the KOH dose in cooking was increased from 15% on bagasse to 23%. These KOH doses correspond to 10.7% NaOH and 16.4% NaOH on bagasse, respectively (equal $[OH^-]$).

4.3 Other Technical Consideration- Silica, Pulp Strength, Xylan Recovery, etc.

4.3.1 Introduction to the Section

Some of the drawbacks of pulp manufacture from bagasse as compared to typical hardwoods are: higher silica content, lower drainage on a paper machine, and lower strength pulp. However, a major advantage of bagasse is its higher xylan content as compared to most hardwoods. In this section, a preliminary investigation was performed to see if a mildly acidic pretreatment of bagasse ahead of KAQ cooking could dissolve significant amounts of the Ca, Mg, and xylan from the fibers before the cooking stage. If the Ca and Mg are removed then it would be expected that the oligomeric silicates would be highly soluble in the alkaline cooking liquor and be separated from the pulp during the washing stage (Froass et al., 1997). Since there are no plans to concentrate the black liquor by evaporation then scaling should not be a significant problem. If the xylans were to be extracted then hopefully they can be converted to useful products in the future. Emphasis was placed on mild acidic extraction that should afford xylan with M_W in the range of 10,000. From the pulp production standpoint it was also important to know if xylan removal would significantly improve drainage of the resulting fibers during papermaking.

4.3.2 Materials and Methods

Pulping and bleaching procedures were similar to those used in Section 4.2. CDB pretreatments were similar to carbonate pretreatments but different chemicals were used. Pretreatment of WDB was similar to N pretreatment but with chemicals other than NH_4OH. Again, once the WDB was placed in the digester vessel it was not removed until after the cooking stage. Pretreatment effluents were diluted 1: 9 with 3M nitric acid and analyzed for metals by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Strength and drainage analyses were by Tappi standard methods. Finally, lignin and carbohydrate analyses were similar to Sections 4.1 and 4.2.

4.3.3 Data and Data analyses

4.3.3.1 Some Preliminary Data on Silica Control

Two of the CDB-Carb effluents from Section 4.2 were analyzed for metals content with particular emphasis on Ca and Mg. Under alkaline conditions (pH 9-11) these alkaline earth metals form colloidal Ca-silicates and Mg-silicates that are visible to the naked eye. The Ca-silicate is sticky on a wide range of surfaces while Mg-silicate tends not to be sticky (Froass et al., 1997). When stainless steel wire mesh were placed in the SiO_2 solutions containing Mg^{++} and Ca^{++}, the photomicrographs in **Figure 4.3. 1** were obtained. There was minimal deposition of Mg-silicates (A) but significant adsorption of Ca-silicates on to the mesh (Froass et al., 1997).

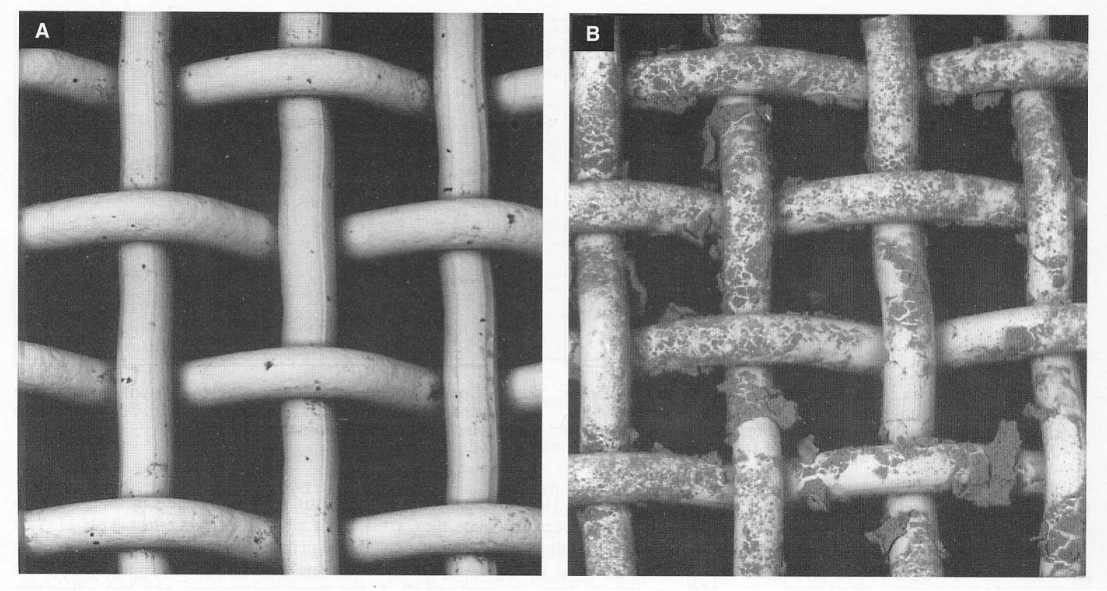


Figure 4.3. 1 Photomicrograph (20x) of silicate scale deposition on stainless steel mesh placed in 38.0 mM SiO_2 solution, pH 9.2, 60°C for 48 h; 3.5 mM Mg^{++} (A) and 1.5 mM Ca^{++} (B). Source: Froass et al. (1997).

A logical way of preventing or minimizing silica problems is to use chemical pretreatments to remove Ca from the fiber before alkaline treatment. Garcia-Perez et al. (2002) analyzed the charcoal, bio-oil and aqueous phase fractions of a pyrolysis oil made from bagasse. The metals were concentrated in the charcoal. The Ca concentrations (mg/kg or ppm) in the three phases were 5384 ppm, 34 ppm, 17 ppm, respectively while the corresponding values for Mg

were 2257, 2 and < 0.1 (Garcia-Perez et al., 2002). From the data of those authors it was estimated that the bagasse contained ~1400 ppm Ca, ~600 ppm Mg and ~80 ppm Al. Unfortunately, Si or silica content was not determined (Garcia-Perez, 2002).

When the two CDB-Carb effluents from the treatment of CC were analyzed they were found to contain average concentrations of 790 ppm Ca, 520 ppm Mg and 1,660 ppm Si. The first experiment in this section was to investigate chemical depithing of CC using hot water extraction (CDB-HW). This pretreatment would be at a pH lower than that used for CDB-Carb and more Ca dissolution from the fibers would be expected.

Samples of CC were pretreated at 14:1 L:B (liquor to bagasse) ratio and with a temperature profile of 60 min. to 160^{o}C and 60 min. at that temperature. In one case only water was used for the treatment (CDB-HW) while in the other 4.0% Na_2O on bagasse from Na_2CO_3 was added to the water (CDB-Carb). The pH profile once 160^{o}C was attained is shown in **Figure 4.3. 2.** The end pH was 4.8 in the case of Carb pretreatment and 3.2 in the case of HW pretreatment. The chemically depithed fibers were recovered and in each case 300g were K/NAQ delignified with KOH+NH_4OH+AQ. The chemical doses were 15% KOH and 0.1% AQ on bagasse in a liquor containing 1.0 M NH_4OH and used at a 12:1 L:B ratio. The temperature profile was 60 min. to 160^{o}C and 60 min. at that temperature. These mild conditions were used to see if the HW pretreated bagasse would be much more responsive to K/NAQ and afford a pulp with significantly lower kappa number. The yields and kappa number of the resulting pulps are documented in **Table 4.3. 1**. It can be seen that HW pretreatment afforded a much lower final yield, 31.1% on CC as compared to 35.0% for Carb pretreatment. It also produced a pulp with a much higher kappa number (48.4 *vs.* 36.5) which was contrary to expectation.

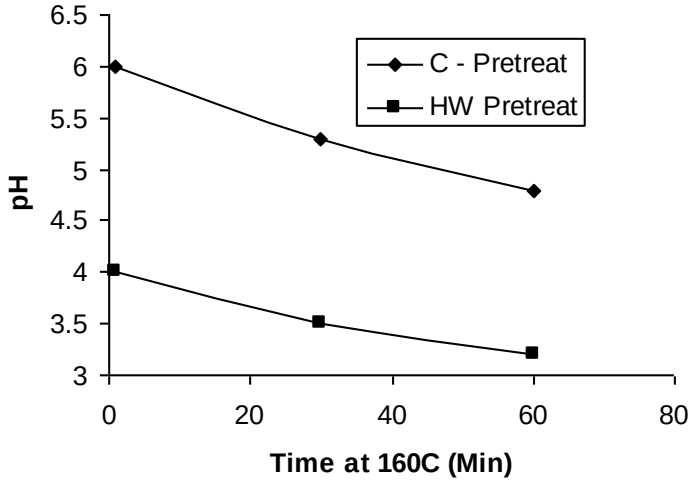


Figure 4.3. 2 pH versus time of Carbonate and Hot Water pretreatment of crushed cane (CC).

Table 4.3. 1 Effect of acidity in pretreatment on K/NAQ cooking of CC

	CDB-Carb	***CDB-HW (60 min)***
Pretreatment		
End pH	4.8	3.2
Yield, % on CC	62.0 (62.6)[1]	55.3 (54.3)[1]
Klason + ASL[2]	19.4 + 4.5	23.1 + 2.3
Cooking Stage		
Cooking Yield, % [3]	56.2	56.7
Fiber Yield, % on CC[4]	35.0	31.1
Kappa number	36.5	48.4
Rejects, %	<0.2	<0.2

[1]Duplicate results
[2]ASL = acid soluble lignin
[3]Based on 300g of pretreated CC
[4]0.623x 56.2=35.0

Both pretreatments when coupled with K/NAQ cooking afforded pulps with minimal amounts of rejects. The unscreened pulps were refined 2,000 PFI revolutions (light load) and the resulting sheets analyzed for drainage and strength properties. It can be seen that Carb pretreatment afforded a pulp with strength properties equal or superior to typical bagasse kraft or SAQ pulps (**Table 4.3. 2**). Khristova et al. (2006) produced a 12.2 kappa number bagasse pulp by the SAQ process. When the fibers were refined and sheets made, they obtained a tear index of

only 6.1 $mNgm^2/gm$ for 74.4 Nm/gm^2 tensile index. In the present case the tear index was 7.6 $mNgm^2/gm$ for 75.5 Nm/gm^2 tensile index. However, HW pretreatment at end pH 3.2 caused a significant loss in tensile strength and some loss in tear. A similar effect was observed in this laboratory when sugar maple chips were HW pretreated for 60 minutes at 160^oC ahead of kraft cooking (**Figure 4.3. 3**).

Table 4.3. 2 Sheet density, strength properties and Canadian Standard Freeness (CSF) of Carbonate and Hot Water pretreated K/NAQ pulps from crushed cane (CC)

	CDB-Carb	***CDB-HW***
Basis weight, g/m^2	65.0	66.3
Apparent density, g/cm^3	0.857	0.812
Tensile Index, Nm/gm^2	75.5	51.9
% Stretch	3.41	2.79
Tear Index, $mNgm^2/gm$	7.6	6.5
CSF, mL	240	261
PFI revolutions	2000	2000

No pulp bleaching trials were performed on these samples because of their high kappa numbers. Also, the HW effluent was not characterized for metals because of the poor delignification and strength results for the CDB-HW pulp. An acetic acid/acetate buffered pretreatment (CDB-Acet) with end pH 4.0 was attempted and those results will be discussed shortly.

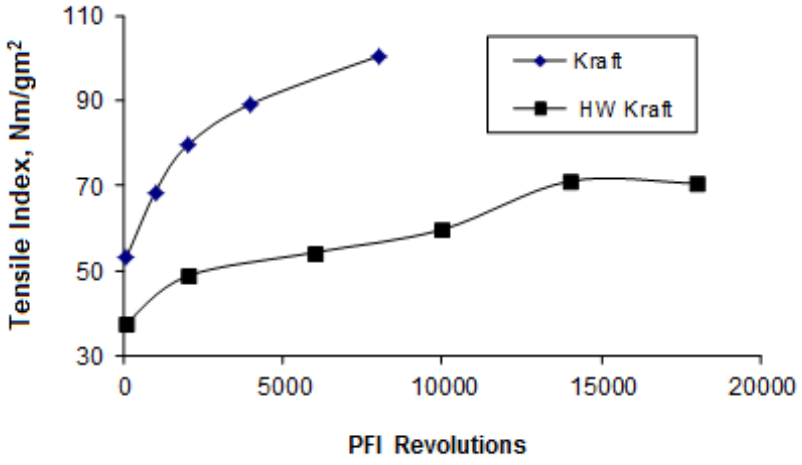


Figure 4.3. 3 Effect of HW pretreatment (60 min at 160°C) on tensile strength of kraft pulp from sugar maple (*Acer saccharum*).

4.3.3.2 Preliminary Results for Acidic Pretreatments Applied to WDB

The WDB was pretreated and/or cooked in the M&K digester vessels lined with course cotton cloth. Two changes were made to the experimental protocol based on the results obtained when CC was the starting material. The first is that acidity was varied in the pretreatment to give end pH higher than 3.2, and second, the acidic pretreatment was followed by the N→KAQ cooking sequence described in Section 4.2.

The effect of acid pretreatment was investigated in the A →N→KAQ sequence where A=acidic pretreatment (end pH<5.0) and N=neutralization with NH_4OH. Three different levels of acidity were used followed by the standard NH_4OH neutralization in **Table 4.2. 5,** i.e. 10:1 L to B ratio, 1.0M NH_4OH, 30 min at 160^oC. The KAQ conditions were also similar to those in **Table 4.2. 5**. The three A-stages were as follow: 1) 0.25% acetic acid on WDB, 60 minutes to 160^oC and 30 minutes at temperature (CDB-AA); 2) same as above but without acetic acid, i.e. HW only, and 3) 0.02M sodium acetate in liquor, 60 minutes to 160^oC and 60 minutes at temperature (CDB-Acet). The acetate would combine with acetic acid liberated from the xylan in WDB to form a buffer. All treatments were performed at a 10:1 L to B ratio. The results are presented in **Table 4.3. 3** and it can be seen that all the A →N→KAQ pulps gave a higher kappa number and a lower final yield than the N→KAQ control. Once the WDB was placed in the digester vessel it was not removed until after the SAQ treatment. The initial belief was that some of the acid soluble lignin (ASL) that was generated in the pretreatment, including *p*-CMAc and FA, participated in acid catalyzed condensation reactions with the residual lignin remaining in the WDB fibers. The extent of condensation would be expected to increase with acidity (Bose and Francis, 1999; Bose et al., 1999) and most of the H units in WDB lignin would have four sites available for condensation. As discussed in Section 4.2, the literature suggests that H units constitute >35% of the C_9 units in WDB lignin when *p*-CMAc is included (Chen et al., 1998). Therefore, as acidity in the A-stage increases the lignin entering KAQ was believed to be more condensed and less reactive. This hypothesis will be investigated further in Section 4.4.

Table 4.3. 3 Effect of pH in Acid Pretreatment of WDB Ahead of KAQ Cooking[1]

	None	*Sodium Acetate*[2]	*Hot Water*[3]	*Acetic Acid*[4]
Pretreatment				
pH 0 min @ 160°C	-	5.0	4.6	4.4
pH 30 min @ 160°C	-	4.7	4.1	3.9
pH 60 min @ 160°C	-	4.5		
After N→KAQ				
Kappa number	15.7	20.0	21.7	26.9
Brightness, % Elrepho	40.1	36.2	34.8	32.0
Unscreened Yield, %	61.4	58.3	56.0	56.2
Rejects, %	<0.2	<0.2	<0.2	<0.2

[1] All treatments at 10:1 L to B
[2] 0.02M sodium acetate in liquor, 60 min at 160°C
[3] 30 min at 160°C
[4] 0.25% acidic acid on DB, 30 min at 160°C

Three of the pulps in **Table 4.3. 3** were bleached by QPD_0EpD_1 and the bleaching characteristics of the three pulps are documented in **Table 4.3. 4**. It can be seen that final brightness of the acetate pretreated pulp was slightly lower than that of the control pulp while the HW pretreated pulp had significantly lower brightness. Once again, the kappa number decrease of all three pulps as a result of QP treatment was quite impressive. The treatments with 3.0% NaOH and 2.0% H_2O_2 on pulp lower the kappa number of the control pulp by 62%, for the CDB-Acet it was 69%, and for the CDB-HW it was 71%.

The acetate pretreatment (end pH 4.5) looked promising. Although the bleached brightness of the CDB-Acet pulp was 85.5% as compared to 86.9 for the control; that is not a sizeable difference when you consider that the CDB-Acet pulp had an unbleached kappa number of 20.0 as compared to 15.7 for the control (**Table 4.3. 3**). As will be discussed shortly, the CDB-Acet pulp had strength properties that were comparable to the control. CDB-Acet pretreatments were then attempted on CC and an end pH~4.0 was targeted. This was achieved with 0.025 M sodium acetate, 60 minutes to 160°C and 60 minutes at temperature. This effluent was analyzed in duplicate and somewhat surprisingly their concentrations of metals and silica were similar to those obtained for the carbonate pretreatment with end pH 4.8. It is possible that almost all of the easily extracted Ca and Mg were removed at both pH 4.0 and 4.8. This easily extracted Ca and Mg would likely be the fraction that is most reactive towards silica under

alkaline conditions. However, it was decided not to perform any additional research in this area because of the difficulties associated with accurate Si determinations (as well as those of metals strongly bound to silica) in fibers and complex solutions as well. An accurate but tedious lithium metaborate fusion method was used by Froass et al. (1997) for the determination of Si-Ca-Mg solid complexes.

Table 4.3. 4 QPD_0EpD_1 Bleaching Characteristics of the Acid Pretreated and Control N→KAQ Pulps from WDB

	Control	***Acetate Pretreated***	***HW Pretreated***
Unbleached			
Kappa number	15.7	20.0	21.7
Brightness, % Elrepho	40.1	36.2	34.8
QP Stages			
Kappa number[1]	5.9	6.2	6.4
Brightness, % Elrepho	58.7	56.8	54.9
D_0 Stage			
Kappa Factor	0.30	0.30	0.30
End pH in D_0	2.2	2.0	2.0
Ep Stage			
Kappa number	1.4	1.5	1.5
Brightness, % Elrepho	78.8	75.8	74.1
D_1 Stage			
ClO_2, % on pulp	0.5	0.5	0.5
End pH	4.4	4.2	4.1
Brightness, % Elrepho	86.9	85.5	82.2

[1] 3.0% NaOH and 2.0% H_2O_2 on pulp in the P stage

4.3.3.3 Physical Properties of WDB Pulps and WDB/ Eucalyptus Mixtures

The control, acetate pretreated, and HW pretreated pulps in **Table 4.3. 3** where analyzed for strength properties, sheet density and light scattering coefficient (LSC). The three unbleached pulps samples were refined 1,000 PFI revolutions at light load. The results are documented in **Table 4.3. 5** and in this case neither the acetate nor HW pretreatment caused a significant decrease in strength. The respective end pH was 4.5 for acetate and 4.1 for HW (**Table 4.3. 3**).

The 74.0 tensile index at 6.8 tear index for the N→KAQ pulp is once again superior to those of Khristova et al. (2006). The tensile, tear and LSC results of Khristova et al. (2006) are also included in **Table 4.3. 5.** Somewhat surprisingly, the acidic pretreatments did not cause an increase but a decrease in CSF. An increase in CSF was observed for CDB-HW in Table 4.3.2 and an increase is also frequently observed when hardwoods are HW pretreated before pulping.

Table 4.3. 5 Physical and Drainage (CSF) Properties of Acid Pretreated and Control N→KAQ Pulps from WDB[1]

	Control (N→KAQ)	***Acetate Pretreated***	***HW Pretreated***
Sheet density, g/cm^2	0.808	0.811	0.805
CSF, mL	410	385	375
Tensile Index, Nm/gm^2	74.0 (74.4)[2]	68.8	69.4
Tear Index, mNgm^2/gm	6.8 (6.1)	6.8	7.2
% Strain	3.2	3.3	3.2
Light Scattering, m^2/kg	22.2 (18.0)	21.2	22.0

[1] Refined 1,000 PFI revolution at light load
[2] Results reported by Khristova et al. (2006)

An sample supply of the K/NAQ pulp in **Table 4.2. 6** was available. That pulp was made from WDB and had an unbleached kappa number of 19.0. It was mixed into a commercially obtained oxygen delignified eucalyptus kraft pulp at 10 wt% and 20wt%. In order to see the effect of the HW pretreatment of WDB on WDB/eucalyptus mixtures a milder HW pretreatment was performed on the WDB and that was followed by K/NAQ cooking under conditions similar to the control sample. The HW was performed at 10:1 L to B, 40 min to 150^{o}C and 60 minutes at temperature with an end pH= 4.0. The control eucalyptus pulp (O_2 delignified) was refined 4,000 PFI revolutions at light load to achieve 90 tensile index and CSF of 373ml. When the WDB pulp was refined 2,000 PFI revolutions and mixed into the eucalyptus pulp, 10% substitution caused only minor decreases in pulp strength, CSF and LSC while 20% substitution caused significant decreases (**Table 4.3. 6**). At the 10% substitution level, CSF decreased from 373 ml to only 363 ml. However, CSF decreased to 340ml when 20% WDB substitution was used. When the HW→WDB pulp was substituted a significant decrease in tensile index was observed even at 10% WDB (**Table 4.3. 6**). It should be noted that unscreened WDB and HW→WDB pulps were

used for evaluation of all handsheet properties. If rejects were causing bonding disruptions then there should have been a significant amount of scatter in the data. This was not observed. In general, all the bagasse pulps with kappa number <20 appeared to be very clean and contained a minimal amount of rejects. No specks were visible to the naked eye for any of the bleached bagasse pulps.

Table 4.3. 6 Physical Properties of Kraft Eucalyptus and Kraft Eucalyptus/WDB Pulp Mixtures

	Eucalyptus Control	***10% K/NAQ***	***20% K/NAQ***	***10% HW→K/NAQ***	***20% DB HW→K/NAQ***
Sheet density, g/cm^2	0.772	0.775	0.796	0.789	0.800
CSF, mL	373	363	340	364	327
Tensile Index (Nm/gm^2)	92.0	90.9	88.6	86.6	80.9
Tear Index (mNgm^2/gm)	8.0	7.8	7.8	7.8	7.9
% Strain	4.2	4.3	4.0	4.1	3.6
Light Scattering, m^2/kg	28.1	27.4	25.6	27.4	25.4

From the overall strength results it would appear that if acid treatments were to be used for Ca removal, improved bleachability and/or xylan extraction then an acetate pretreatment should be used. There is a risk of strength loss once the acidolysis end pH is lowered below ~4.5. The loss in strength, CSF and LSC were relatively minor at 10% DB substitution and should be tolerable to most mills. The loss in strength, CSF and LSC at 20% DB substitution were significant and would probably be tolerated only for tissue grades due to the much higher water retention value of bagasse pulps as compared to hardwood pulps (Banavath et al., 2011). In the present investigation sugar maple kraft or SAQ pulps could be pressed to ~24% consistency in vacuum aided dewatering in a Buchner funnel. Under nearly identical conditions (g fibers/unit area) the K/NAQ or KAQ pulps from WDB or CC could only be pressed to ~17% consistency.

4.3.3.4 Xylan Extraction in Pretreatments

The acetate pretreated fibers in the previous two sub-sections had nearly equal bleachability and strength to the N→KAQ control. That A-stage was repeated on WDB in one of the M&K digesters and a fraction of the acidolyzed fibers were given the standard NH_4OH

pretreatment (30 min at 160°C in 1.0 M NH_4OH). The A-treated and A →N treated fibers were analyzed for the major constituents (glucan, xylan and lignin) plus arabinan. The results are compared to untreated WDB in **Table 4.3. 7**. The fiber yield after A-treatment was 89.7% and it decreased to 75.5% after A →N. When the yield loss of individual components were calculated based on chemical composition of the treated fibers and the fiber recovery yield it showed that 4.7 wt% xylan was extracted from WDB after the acetate stage and 11.1% after A→N. An example calculation is as follows: the A-treated fibers contained 23.0% xylan and was recovered at 89.7% yield. A 100 g sample of WDB would contain 25.3 g of xylan while the A-treated sample would contain 20.6 g (23.0 x 0.897) with a xylan loss corresponding to 4.7 g. When the yield losses of the individual components were totaled it gave values of 9.4 wt% after acetate and 22.9% after A →N. The corresponding values for total yield loss based on mass of recovered fibers were 10.3% and 24.5%, respectively. If the A-stage and N-stage effluents were to be mixed, the combined effluent would have a pH~10.0. Evaporation of the ammonia would lower the alkalinity to pH <9 and lignin precipitation may be possible with the aid of coagulating agents (Section 3.5.5). Such a process could result in a fairly pure xylan stream. The pH in the A-stage was in the range of 4.5 to 5.0 while the pH in the N-stage was in the range of 10.1 – 10.3. Xylan extraction under these pH conditions should afford particles with average MW (M_W) in the range of 10,000 (Kleen et al., 2011). If xylan degradation is significant under the N-stage conditions then a longer time and/or higher temperature could be used to recover more of it in the A-stage. Once the xylan is removed by ultrafiltration, then some of the A-stage effluent could be recycled to maintain a buffered system. An alkali would be used to raise the pH of the effluent from the range of 4.0 – 4.5 back to ~5.0. When that liquor is used on a fresh WDB sample, the pH of the treatment would slow fall back to 4.0 – 4.5 due to acetic acid formation from hydrolysis of acetyl groups in the xylan.

Table 4.3. 7 Chemical Composition of Untreated, A-Treated, and A→ N Treated WDB

	Untreated	***A-Treated***[1]	***A→N Treated***[2]
Glucan, % on Sample	41.5	45.7 (0.5)[3]	53.3 (1.3)
Xylan, % on Sample	25.3	23.0 (4.7)	18.8 (11.1)
Arabinan, % on Sample	1.2	0.7 (0.6)	0.7 (0.7)
Lignin, % on Sample	23.7	22.4 (3.6)	18.4 (9.8)

[1] Fibers recovered at 89.7% yield on WDB
[2] Fibers recovered at 75.5% yield on WDB
[3] Yield loss, wt% on WDB

4.3.4 Summary of the Section

If an acidic pretreatment with end pH 4.0 - 4.8 were to be applied to bagasse (WDB or CC) it appears that a significant amount of Ca and Mg would be removed from the fibers and this should help to minimize silica scaling problems under alkaline conditions. These acidic pretreatments results in a higher unbleached kappa number after K/NAQ of KAQ cooking but the bleachability of the pulp produced with acetate pretreatment (pH 4.5 to 5.0) appears to be approximately equal to the control pulp.

A 10% substitution of bagasse K/NAQ pulp into oxygen bleached eucalyptus kraft caused only minor decreases in strength properties, LSC and CSF. However, strength properties and CSF decreased significantly when 20% substitution was attempted. It was demonstrated that it may be possible to recover medium to high MW xylan from the A- and N-stages of an A→N→KAQ cooking process. In the present case, the amount of xylan solubilized in those two effluents was estimated at 11.7% based on starting WDB and yet a final pulp yield of 58.3% was still obtained (based on starting WDB).

4.4 Further Research on Acidic Pretreatments

4.4.1 Introduction to the Section

The results for acidic pretreatments in Section 4.3 indicated that their effect on the combined pulping and bleaching process was negative. Lower bleached brightness and fiber yield were obtained when 160°C pretreatments with end pH < 4.8 were used. However, the maximum KOH dose that was used in the KAQ stage was 15% on starting WDB or CDB. In this section, further research was performed on acidic pretreatments. Acetate and HW pretreatments were performed on CC and the resulting CDBs were converted to 15 mesh meal then KAQ or K/NAQ delignified in the PARR reactor at a higher alkalinity.

The effect of the amount of sugar bound to the residual lignin, i.e. LCC concentration was also investigated. It was anticipated that hot water pretreatment (HW) of hardwood chips at 160^{o}C would afford partial cleavage of LCC (Jonaik et al., 1987; Taneda et al., 1987; Lawoko et al., 2006) and this was indeed observed by Nicholson et al (2011). When HW times of 0, 30, 60, 90 and 120 min at 160^{o}C were applied to sugar maple (*Acer saccharum*) chips and kraft pulping subsequently used to produce pulp fibers with kappa number ~17, the concentrations of strongly bound xylan on the residual lignin (enzymatic isolation) were 0.69% for HWP = 0 min (control pulp); 0.36% for HWP = 60min; 0.25% for HWP = 90 min and 0.20% for HWP = 120 min.

The approach of Nicholson et al. (2011) was to prepare kraft and soda-anthraquinone (SAQ) pulps from control and HW chips. The residual lignin (RL) in the pulps was recovered by enzymatic dissolution of the free carbohydrates with the strongly bound carbohydrates remaining on isolated residual lignin. Those bound carbohydrates were then hydrolyzed from the isolated residual lignin or enzymatic lignin (EL) and converted to sugar monomers by a 4% H_2SO_4 treatment at 121^{o}C for 60 minutes. The key to the approach was repeatable and reproducible determinations of sugar monomers at low concentrations. An NMR method was recently reported where 500 mg of biomass was hydrolyzed in 47 ml of 40% H_2SO_4. That method proved to be quite repeatable and reproducible for sugars monomers at 2% of the 500 mg (anhydro basis) which corresponds to 10 mg in 47 ml or 0.212 mg/ml (Bose et al., 2009b; Alves et al., 2010). It was thought that if 250 mg of the EL were to be hydrolyzed in 10 ml of 4% H_2SO_4 and the hydrolyzate concentrated by evaporation *in vacuo* to ~1.5 ml then a hydrolyzed monomer at 0.2 wt % on EL would give a solution phase concentration of 0.5 mg in 1.5 ml or 0.33 mg/ml.

This would afford the luxury of using an exhaustive enzymatic hydrolysis protocol for carbohydrate depolymerization and dissolution with the hope that reproducibility and repeatability would be improved if only the very strongly bound sugar monomers or fragments were to remain on the EL.

When HW times of 0 min, 30 min, 60 min, 90 min and 120 min (at 160^{o}) were applied to the sugar maple chips ahead of kraft pulping, the rate of the delignification increased significantly with increasing HW retention time. When time in the kraft stage was varied, the regression lines correlating kappa number with H-factor in **Figure 4.4. 1** were obtained. At an H-factor of 600, kappa numbers of approximately 35, 22, 17, 15 and 13 were obtained for HW times of 0, 30, 60, 90 and 120 min, respectively. When the various pretreatments were used to produce kraft pulps with kappa number ~17, the EL xylan contents were 0.69% for HW = 0 min (control pulp); 0.36% for HW = 60min; 0.25% for HW = 90 min and 0.20% for HW = 120 min (previously discussed). The HW for 120 min had an end pH of 3.2 yet the EL from the resulting kraft pulp still contained ~29% as much bound xylan (0.20/0.69) as the EL from the control pulp. A HW of 60 min was also applied ahead of SAQ cooking of sugar maple and a 12.8 kappa number pulp was obtained after an H-factor of only 663. The control SAQ pulp attained a kappa number of 20.8 after an H-factor of 1297. The EL xylan contents were 0.84% for the control pulp and 0.35% for the HW pulp.

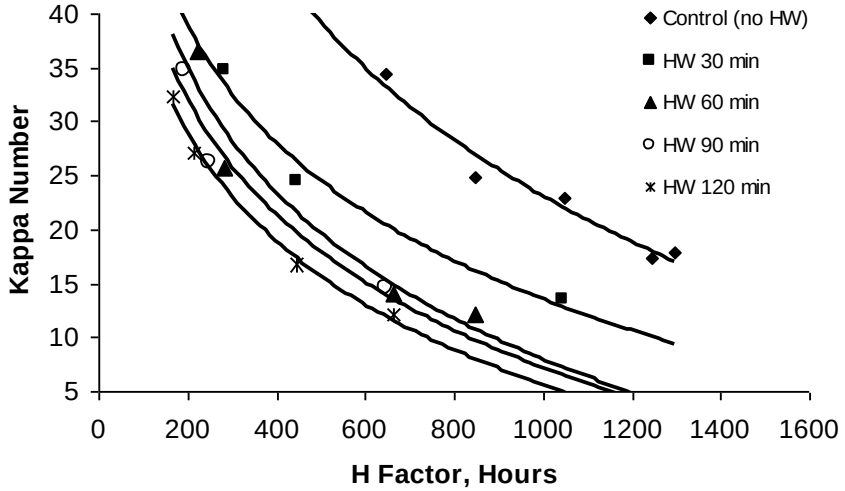


Figure 4.4. 1 Effect of HW retention time on the rate of kraft pulping of sugar maple (Nicholson et al. ,2011).

Selected kraft and SAQ maple pulps were then bleached by the D_0EpD_1 sequence (no oxygen) and decreases in kappa number and increases in brightness are documented in **Table 4.4. 1**. The bound xylan content on the EL of each unbleached pulp is also given. It can be seen that for both kraft and SAQ pulps there is an increase in bleached brightness with decreasing EL xylan content.

Table 4.4. 1 D_0EpD_1 Bleaching results for control and HWP kraft and SAQ sugar maple pulps[1]

Pulp	***Unbleach. Kappa No.***	***Xylan on EL, %***	***Total[2] ClO_2***	***Brightness, % Elrepho***	
				After D_0Ep	***After D_0EpD_1***
Kraft	17.9	0.69	1.66	74.2 (3.2)[3]	84.2
Kraft	17.9	0.69	2.20[4]	75.1 (2.9)	90.9
HW(60)-kraft[5]	14.1	0.36	1.37	80.6 (1.5)	91.8
HW(90)-kraft	14.5	0.25	1.40	82.9 (1.4)	93.1
HW(120)-kraft	27.2	0.17	2.37	83.7 (1.4)	> 94.0
HW(120)-kraft	16.8	0.20	1.58	85.1 (1.2)	> 94.0
SAQ	20.8	0.84	1.88	71.4 (3.3)	82.8
HW(60)-SAQ	12.8	0.35	1.27	80.5 (1.4)	91.4

[1] ClO_2 dose factor of 0.076 x kappa in D_0 stage; Only 0.3% ClO_2 on pulp in D_1 stage
[2] % on pulp
[3] Kappa number in parenthesis
[4] ClO_2 dose factor of 0.095 x kappa in D_0 stage; 0.5% ClO_2 on pulp in D_1 stage
[5] HW(60) = 60 min of HWP

The HW pretreatment was more efficient at lowering the xylan content of the bagasse EL than it was for sugar maple yet it had a negative effect on subsequent delignification of the bagasse. When it appeared as if acidic pretreatments were unable to significantly improve the combined pulping and bleaching process for bagasse fibers, acidic self-condensation of *p*-CMAc was investigated to get some preliminary ideas as to possible rate of lignin-lignin condensation under acidic pretreatment conditions.

4.4.2 Materials and Methods

4.4.2.1 Enzymatic Lignin Preparation

The flow sheet in **Figure 4.4. 2** was followed and the procedure was identical to that of Nicholson et al. (2011). There were three stages of enzymatic hydrolysis (EH) with commercial cellulases and hemicellulases. After each EH the broth was adjusted to pH 2 with HCl and centrifugation used to precipitate the lignin rich fraction. That fraction was re-dispersed in aqueous pH 2 solutions (HCl) and re-precipitated three times before it was treated to the subsequent EH or LCC purification step.

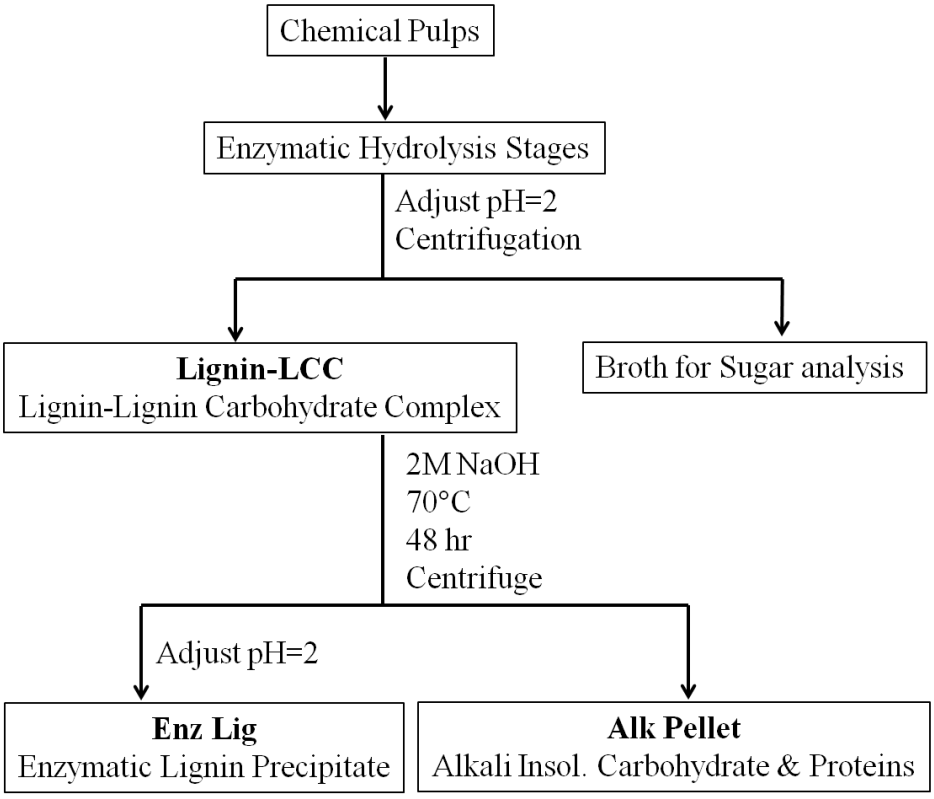


Figure 4.4. 2 Process Flow Diagram for Isolation of Enzymatic Lignin from Chemical Pulps.

Cellulase and hemicellulase enzymes prepared from *Trichoderma reesei* were provided by Iogen Corporation, Ottawa, Ontario, Canada. One unit of cellulase activity is defined as the release of 1.0 μmol of reducing end groups from carboxymethylcellulose (CMC) in one minute under specified conditions while one unit of hemicellulase activity corresponds to the release of

1.0 μmol of reducing end groups from wheat arabinoxylan (WAX). An appropriate volume of the supplied enzyme (s) was added to the pulp slurries to obtain the desired enzyme dose per unit mass of pulp. The enzymatic hydrolyses were carried out at pH 4.6 in acetate buffer containing 6.942 g/l sodium acetate (trihydrate) and 2.917 ml/l glacial acetic acid. A consistency of 5% was obtained by the dilution of pulp in the buffer. An orbital shaker was utilized to maintain agitation at 150 rpm, while the temperature was maintained at 40ºC for a period of 48 hours.

The first stage digestion used the cellulase enzyme at a dosage level of 360 unit/g of pulp. The second stage used the cellulase enzyme at a dosage level of 120 unit/g of pulp (based on initial mass). This adjustment was made to accommodate the reduction in mass of the pulp by about 2/3 due to dissolution of carbohydrates in the first EH. Concurrently, the volume of buffer used was decreased to 1/3 of the stage 1 volume. The third stage utilized both enzymes, cellulase at a dosage level of 120 unit/g of pulp, and a high hemicellulase dose of 720 units/g pulp (based on initial mass). According to the supplier, the cellulase rich enzyme had a significant amount of hemicellulase activity and the enzymes were quite effective in depolymerizing the carbohydrate fraction of pulps to sugar monomers. When the broths (**Figure 4.4. 2**) from the first two EH stages were analyzed the amounts of glucose and xylose detected normally correspond to ~ 70 wt% of the non-lignin fraction of the pulp. The glucose and xylose yields were converted to an anhydro sugar basis before their weights were compared to that of the starting pulp. In polymeric form the MW of a glucose unit is 162 instead of 180 and that of a xylose unit is 132 instead of 150.

The wet isolated Lignin-LCC product (**Figure 4.4. 2**) resulting from the enzymatic hydrolysis of a pulp was purified by dissolution in 2M NaOH at a wet solid/2M NaOH ratio of 1:10. Nitrogen was bubbled through the liquid for several minutes to drive out dissolved O_2 and fill the headspace, and the blanketed solution was sealed in a plastic airtight Nalgene bottle. The bottle was placed in a 70°C water bath for 48 h, with occasional shaking to facilitate lignin dissolution. The hot liquid was then cooled to room temperature and centrifuged at 3,000 rpm for 15 min. to separate un-dissolved carbohydrate and enzyme proteins to give a solid phase called alkaline pellet. The solution phase was then acidified to pH 2 and centrifuged, re-dispersed in aqueous pH 2 solutions (HCl) and re-precipitated three times to remove residual salts, and freeze dried to give the final product, enzymatic lignin (EL).

4.4.2.2 Chemical and Spectroscopic Analyses

The EL was hydrolyzed in 4% H_2SO_4 in accordance with previously reported procedures (Kiemle et al., 2004; Mittal et al., 2009). The hydrolyzate was concentrated to >25% H_2SO_4 by evaporation and analyzed by ^{1}H NMR (Bose et al., 2009b; Alves et al., 2010). A typical ^{1}H NMR spectrum of the hydrolyzate from an EL is shown in **Figure 4.4. 3** and monomer concentrations were calculated by the equation (5). Lignin contents were determined by Klason and acid soluble lignin analyses (Bose et al., 2009c) and estimated for chemical pulps (< 65% yield) by measurements of the kappa number (TAPPI Method T 236-cm 85, 1985).

$$Wt\ \%\ Sugar\ (in\ EL) = \frac{Sugar\ Peak\ Area^{1}}{GlcN\ Peak\ Area} \times \frac{mol\ GlcN}{RF = 1} \times \frac{MW\ Sugar^{2}}{EL\ (g)} \times 100 \qquad (5)$$

[1] Combined area for α and β anomers; glucosamine (GlcN) is the internal standard
[2] For an anhydro or bound sugar monomer (132 for pentoses; 162 for hexoses)

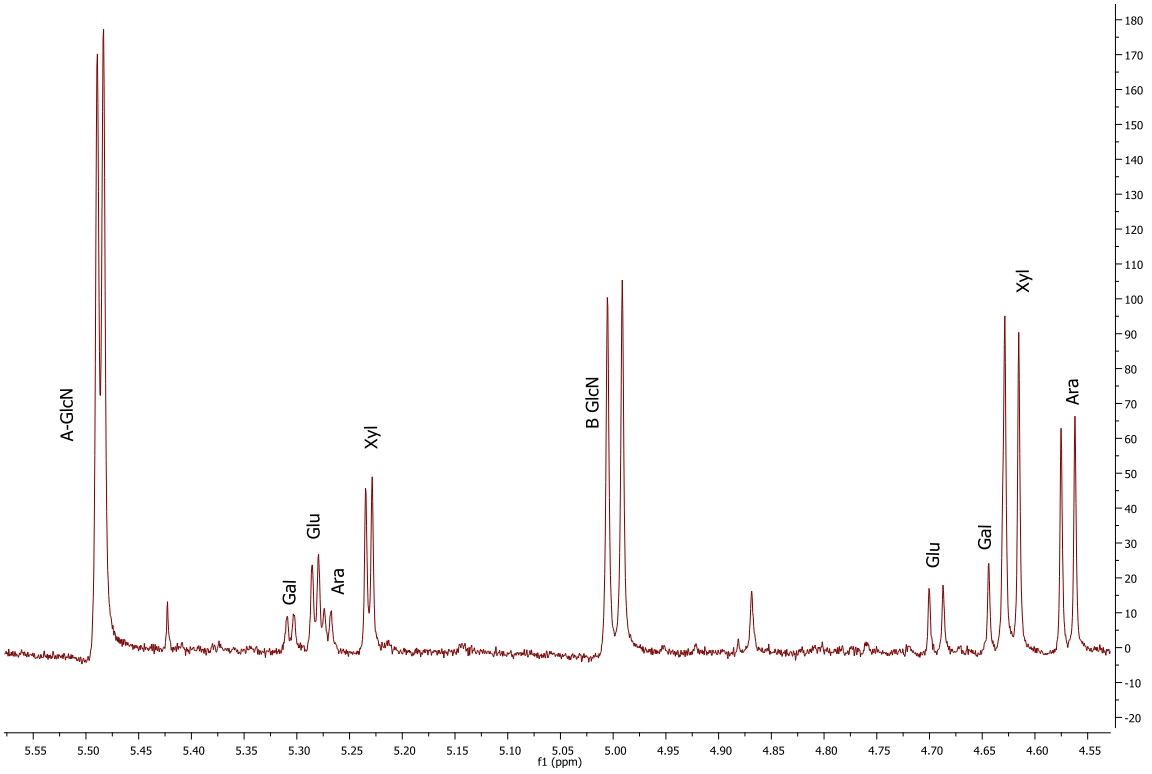


Figure 4.4. 3 Peak Assignments in 1H NMR Analysis of Hydrolyzed Sugars from EL in 25 - 40 wt% H_2SO_4. Peaks between 4.55 – 4.70 ppm are for C1-β protons; 5.20 – 5.35 are for C1-α protons. GlcN - acronym for glucosamine the internal standard.

4.4.3 Data and Data Analyses

4.4.3.1 KAQ and K/NAQ Delignification of Control and Acid Pretreated Meal in PARR Reactor

It was shown in **Table 4.2. 7** that when 23% of KOH on CDB-Carb was used in KAQ delignification a pulp with a kappa number 12.6 was obtained and it was brightened to 93.5% Elrepho by the QPD_0EpD_1 bleaching sequence. In Section 4.3 it was shown that bleached brightness was lowered by acidic pretreatments but the maximum amount of KOH that was used in the N→KAQ sequence was 15% KOH on starting WDB. The initial and final KOH concentrations for the 90 min (160°C) KAQ treatments that produce the control and acid pretreated N→KAQ pulps in **Table 4.3. 3** were 0.27M and ~ 0.13M, respectively. The initial concentration was derived from theoretical calculations, i.e. mass of KOH and volume of cooking liquor used while the final concentration was based on acid-base titration to end pH 8.3. It was of interest to see if beneficial effects would be observed for the acid pretreatments if the KOH concentration in the KAQ or K/NAQ stage was maintained close to 0.20M throughout the entire treatment.

The carbonate, acetate and HW pretreatments in Section 4.3 that afforded end pH of 4.8, 4.0 and 3.2, respectively, were re-applied to CC. All the pretreatments were for 60 min at 160°C (Section 4.3.3). The CDB samples were converted to 15 mesh particles and KAQ delignified in 0.2M KOH at 160°C. The KAQ conditions for the PARR reactor (Section 4.2) were used. It was assumed that the KOH concentration did not fall much below 0.2M because of the 50:1 L to B ratio. The dose in this trial was 56% KOH on starting bagasse. Kappa number versus cooking time is shown in **Figure 4.4. 4** for the three CDB sample as well as the solvent extracted WDB. The CDB-Carb and WDB achieved nearly identical kappa number after 45 min, 60 min and 90 min. The kappa numbers were lower for the acetate pretreated fibers as compared to CDB-Carb and WDB (**Figure 4.4. 4**). Fiber yields for the KAQ stage were 60.0% for WDB; 52.6% for CDB-Carb; 51.2 for CDB-Acet; and 42.7% for CDB-HW. The trial was repeated but 0.5M NH_4OH was included in the cooking liquor. On this occasion the WDB fibers achieved a lower final kappa number as compared to the CDB-Carb fibers (7.9 *vs.* 9.9). Also, the ranking of CDB-Carb, CDB-Acet and CDB-HW in regards to final kappa number was 9.9, 8.9 and 13.8, respectively (**Figure 4.4.5**). It was concluded that a HW pretreatment at 160°C with the end pH

3.2 had an adverse effect on the delignification of bagasse. This conclusion appears to contradict those of Sabatier et al. (1993) and Jahan et al. (2009). Both of those groups observed an increase in alkaline delignification rate when hot water pretreatment was applied to bagasse. This topic will be re-visited later.

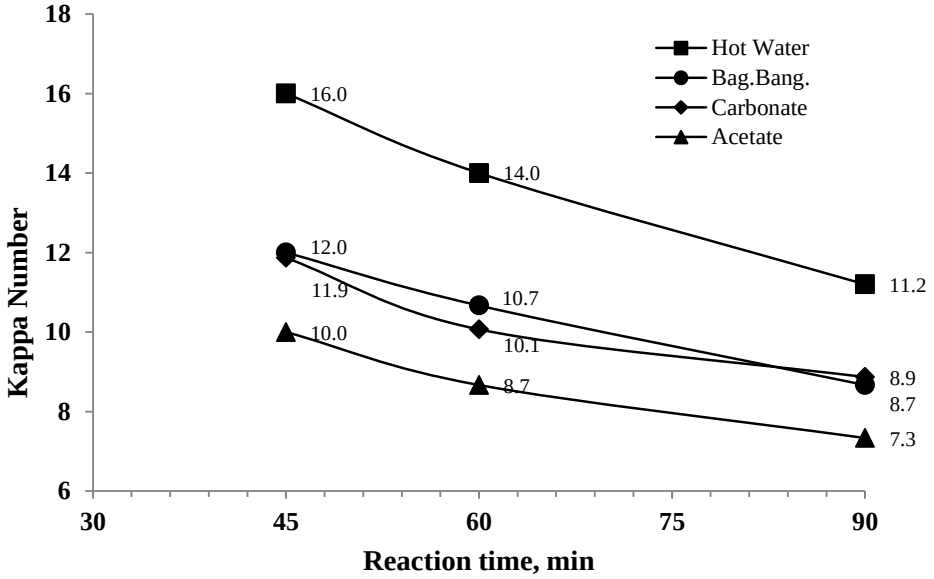


Figure 4.4. 4 KAQ Delignification of WDB and CDB in PARR Reactor (0.2 M KOH, 140°C).

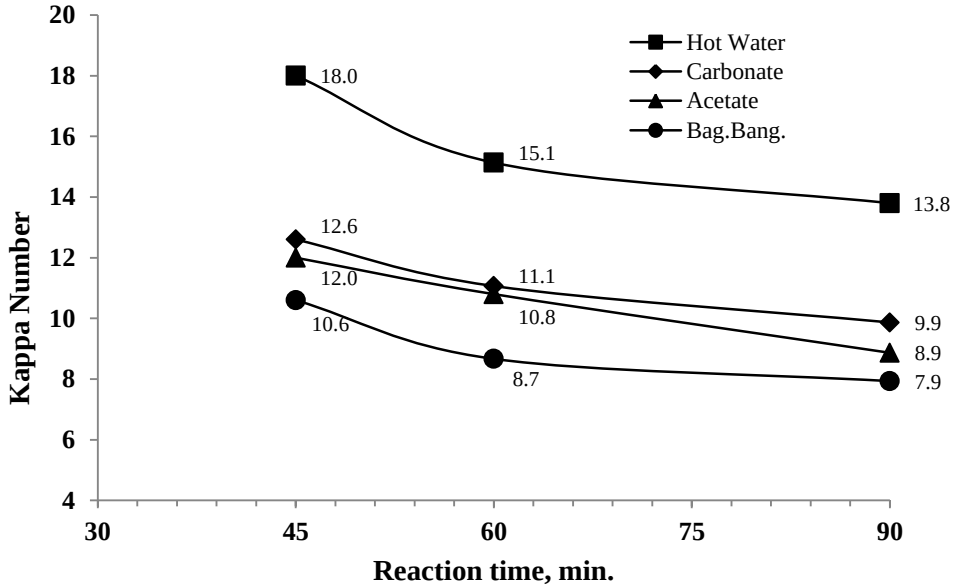


Figure 4.4. 5 K/NAQ Delignification of WDB and CDB in PARR Reactor (0.2 M KOH + 0.5 M NH_4OH, 140°C).

4.4.3.2 Effect of Acidity in Pretreatment on LCC Concentration

From the results above, it appeared as if acidolysis of lignin-carbohydrate linkages did not dramatically increase the rate of alkaline cooking as was previously observed with hardwoods (Nicholson et al., 2011). The three pretreatments above (Carb, Acet and HW) were repeated on CC along with a carbonate-bicarbonate pretreatment which comprised of 2.0% Na_2O on CC from both Na_2CO_3 and $NaHCO_3$ (CDB-Bicarb). The pretreatment was also for 60 min at 160°C and the pH profile in this case was 5.4, 5.0 and 4.7 after 0 min, 30 min, and 60 min at 160°C, respectively. The corresponding values for the CDB-Carb were 6.0, 5.3 and 4.8 (**Figure 4.3. 2**). The four CDB samples were delignified under mild K/NAQ conditions to produce high kappa number pulps as described in Section 4.2.3.5. The temperature profile in the K/NAQ stage was 60 min at 160°C and 60 min at temperature with 10% KOH on CDB in 1.0 M NH_4OH (12:1 L to B). The pretreatment and cooking results for the four samples are documented in **Table 4.4. 2** while QPD_0EpD_1 bleaching results are presented in **Table 4.4. 3**. It can be seen that the CDB-Acet sample afforded a slightly lower kappa number after cooking as compared to CDB-Carb and CDB-Bicarb. It also afforded a slightly higher bleached brightness (~ 1 point) but this increase was trivial compared to the 7-10 points brightness increase obtained to HW pretreatment of maple chips ahead of both kraft and SAQ cooking (**Table 4.4. 1**). In the present case, HW pretreatment increased the kappa number after cooking and afforded a significantly lower bleached brightness. It can be concluded that neither mild acidolysis (CDB-Acet) nor moderate acidolysis (CDB-HW) significant improved subsequent pulping and bleaching responses of bagasse. It should be noted however, that once again QP delignification was impressive. The kappa number decrease from 69.3 to 19.1 for the CDB-HW pulp corresponds to 72% delignification.

The QP stages were repeated on the four pulp samples (kappa number down to 18-19) and enzymatic lignin isolated from them. Lignin recovery on a carbohydrate-free basis was in the range of 65% to 75% on the total lignin for all samples. The four ELs were then acidolyzed and the released sugars quantified in duplicate. The EL contained lower amounts of sugars as the pH of the pretreatment decreased. However, there was basically no correlation between bleached brightness and bound xylan or arabinan content (**Table 4.4. 4**). These results are dramatically different from those for sugar maple in **Table 4.4. 1**. Either the LCC in bagasse are significantly

different from those in sugar maple or the negative effect of lignin-lignin condensation outweighed the beneficial effect of the LCC cleavage.

Table 4.4. 2 Effect of acidity in pretreatment on mild K/NAQ cooking of CC

***Pretreatment*[1]**	***CDB-Carb***	***CDB-Bicarb***	***CDB-Acet***	***CDB-HW***
Chemical (s)	Na_2CO_3 [2]	Na_2CO_3/$NaHCO_3$ [2]	0.025 M NaAc	None
End pH	4.8	4.7	4.0	3.2
Yield, % on CC	62.0 (62.6)[3]	62.0 (61.3)	61.0 (59.7)	55.3 (54.3)
Klason + ASL	19.4 + 4.5	--	--	23.1 + 2.3
Cooking Stage				
Cooking Yield, %	61.0	60.6	61.5	64.6
Fiber Yield, % on CC	38.0	37.3	37.1	35.4
Kappa number	61.9	61.5	58.8	69.3

[1] All pretreatments were for 60 min at 160°C
[2] 4.0% Na_2O on CC
[3] Yield from duplicate pretreatments

Table 4.4. 3 QPD_0EpD_1 Bleaching of K/NAQ Pulps from four different CDB from CC

	CDB-Carb	***CDB-Bicarb***	***CDB-Acet***	***CDB-HW***
Unbleached				
Kappa number	61.9 (10.4%)[1]	61.5	58.8	69.3 (12.2%)[1]
Brightness, % Elrepho	<25	<25	<25	<25
After QP Stages				
Kappa number	18.4[2]	18.6	18.2	19.1
Brightness, % Elrepho	38.0	37.6	38.5	39.2
D_0Ep Stages				
Kappa Factor in D_0	0.20	0.20	0.20	0.20
End pH in D_0	2.6	2.7	2.5	2.4
End pH in Ep	12.0	12.0	12.0	12.0
Ep Stage				
Kappa number	2.4	2.4	2.2	2.7
Brightness, % Elrepho	64.1	64.5	65.6	62.8
D_1 Stage				
ClO_2, % on pulp	0.8	0.8	0.8	0.8
End pH	3.8	4.0	4.0	3.7
Brightness, % Elrepho	82.9	83.1	84.0	81.2

[1] Total lignin content (Klason + ASL) in parentheses
[2] 4.0% H_2O_2 on pulp in P stage

Table 4.4. 4 Effect of sugar content bound to residual lignin in K/NAQ pulps on bleaching

Sample	*Kappa number*[1]	*Xylan on EL*	*Arabinan on EL*	*Bleached Brightness, %*
CDB-Carb	18.4	14.2 (12.3)[2]	0.7 (0.6)	82.9
CDB-Bicarb	18.6	12.1 (11.6)	0.6 (0.7)	83.1
CDB-Acet	18.2	5.7 (5.9)	0.1 (0.2)	84.0
CDB-HW	19.1	0.7 (0.6)	0 (0)	81.2

[1] After QP
[2] wt% on EL as anhydro sugar; duplicate result in parentheses

4.4.3.3 Preliminary Investigation of Lignin-Lignin Condensation under Acidic Conditions

It appears that condensation of vinylphenol (VP) or vinylguaiacol (VG) with another monomer led to hydrophobic dimers as discussed in Section 4.2.3.4. If that as indeed the case, the condensation of VP or VG on to the surface of lignin polymers would be expected to significantly decrease the reactivity of such polymers. It was decided to compare the rate of VP-VP condensation (resulting from *p*-CMAc) to the similar reaction under alkaline conditions. In Section 4.2.3.5 it was shown that when *p*-CMAc was self-condensed in 0.4M NaOH at 165°C for 60 min there was a 4% residual of *p*-CMAc, a 10% conversion to **9** and a 2% conversion to *p*-HBA. In this section, *p*-CMAc was self-condensed for 60 min at 165°C but in a pH 3.5 aqueous solution (acetic acid) instead of NaOH. The pH increased from 3.5 to ~ 4.0 during the treatment. The GC-MS chromatogram of the products is shown in **Figure 4.4. 6**. Only peaks for the internal standard, residual *p*-CMAc and a VP-VP dimer were observed. In this case the residual *p*-CMAc was 19% while the yield of the VP-VP dimer was 15%. Therefore, less *p*-CMAc end up in condensed products as compared to the alkaline case but there was more VP-VP condensation. Although further research is recommended, the high rate of ultimate VP condensation (starting with *p*-CMAc) under acidic conditions is a negative attribute that has to be controlled in subsequent design of acidic pretreatment of bagasse.

The MS of the VP-VP dimer in the chromatogram in **Figure 4.4. 6** (RT=36.38 min) is compared to that obtained from alkaline condensation of *p*-CMAc in **Figure 4.4. 7**. It can be seen that in the alkaline case the m/z=369 peak is ~ 2 times as large as m/z=384. Also, the MS was nearly identical to the VP-VP dimer obtained from SAQ +EG treatment of bagasse (**Figure 4.2. 18**). However, under the acidic case the m/z=384 peak was ~ 2 times as large as m/z=369.

We assume that the reason is due to α-6’ or β-6’ condensation under acidic condition and the reaction scheme in **Figure 4.4. 8** is presented as a possible explanation. The m/z= 177 and 179 peaks are more intense in the MS for acidic condensation **Figure 4.4. 7**). If the VP-VP dimer is β-5’ or β-6’ linked (**Figure 4.4. 8**) then α-β bond cleavage on the left aromatic ring would produce a fragment with m/z = 179.

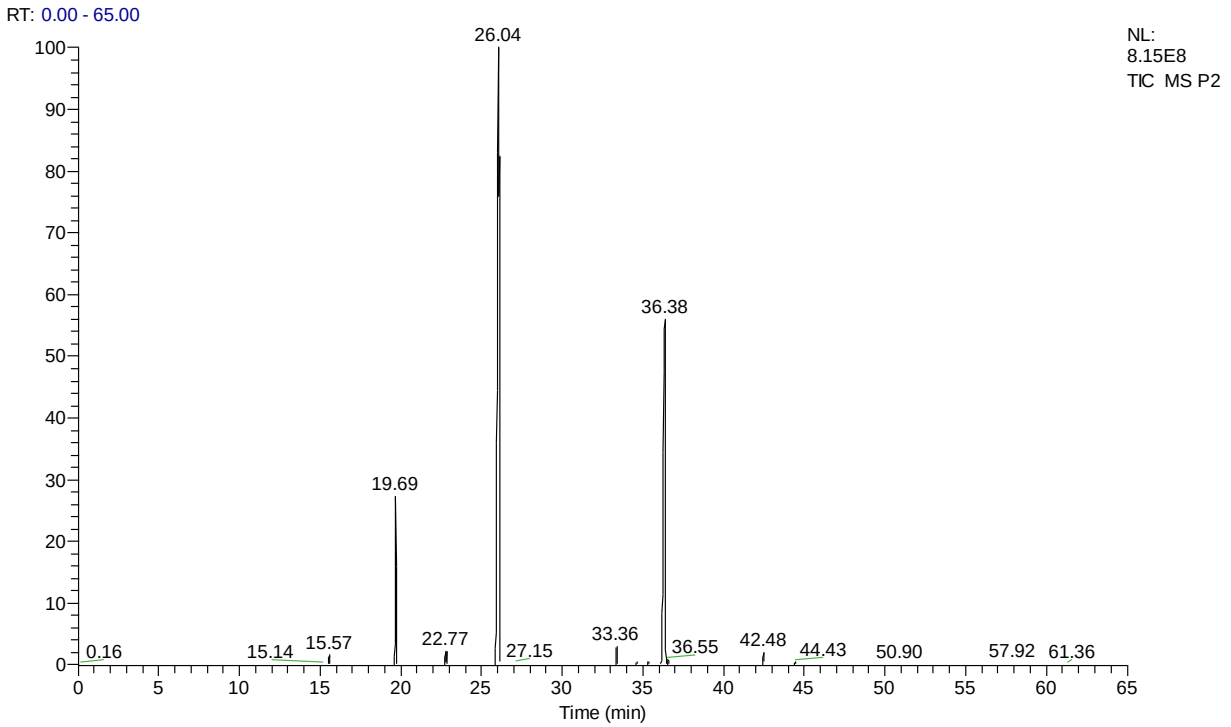


Figure 4.4. 6 Self-Condensation of *p*-CMAc under acid conditions (160°C, initial pH 3.5, 60 min). RT of 19.69 min for internal standard, 26.04 min for *p*-CMAc and 36.38 min for a VP-VP dimer.

It was mentioned earlier that Sabatier et al. (1993) and Jahan et al. (2009) observed that HW pretreatment accelerated alkaline delignification of bagasse. Kraft delignification was accelerated in the case of Sabatier et al. (1993) while SAQ delignification was accelerated in the case of Jahan et al. (2009). In the case of Sabatier et al. (1993), the extent of depithing, including wet treatment, was more extensive than in the present case. It is possible that more *p*-CMAc was hydrolyzed and washed out of the fiber during the depithing protocol of Sabatier et al. (1993). In the case of Jahan et al. (2009) the HW treatment temperature was 150°C and the end pH was

3.57. It was possible that the milder HW pretreatment was closer to the CDB-Acet case that was practiced in the present research and found to be slightly beneficial.

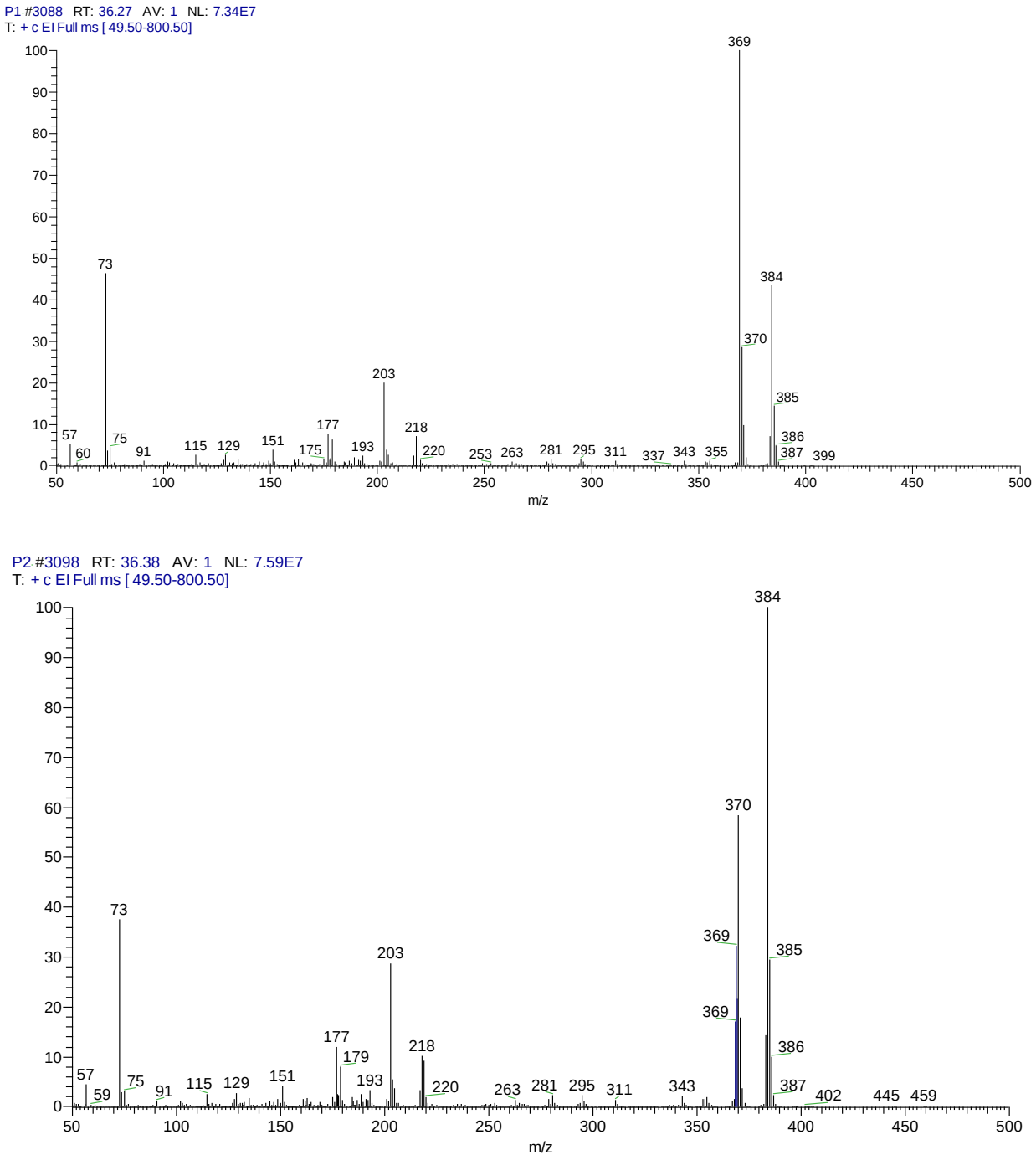


Figure 4.4. 7: MS for VP-VP dimers from self-condensation of *p*-CMAC; alkaline case (top) and acidic case (bottom).

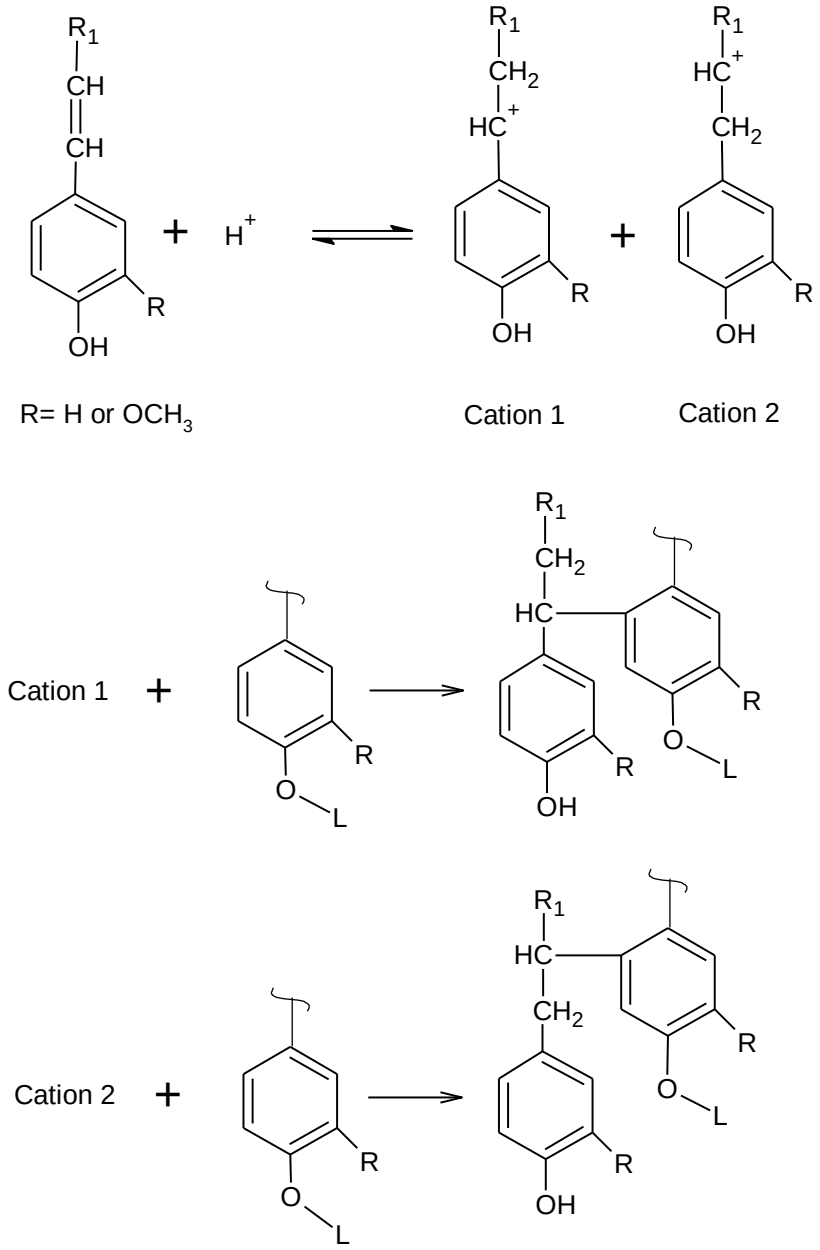


Figure 4.4. 8 Possible condensation reactions under acidic conditions for compounds containing α-β double bonds.

4.4.4 Summary of the Section

The results clearly showed that a HW pretreatment for 60 min at 160°C and end pH 3.2 retarded subsequent delignification by KAQ and K/NAQ. Also, the HW pretreated pulps were more difficult to bleach. On the other hand, a pretreatment buffered with sodium acetate/acetic acid and with end pH ~4.0 improved both pulping and bleaching slightly. Both of these acidic

pretreatment cleaved LCC and resulted in a residual lignin with less bound sugars. However, it appeared as if acid-catalyzed condensation was significant during these pretreatments. When *p*-CMAc was self-condensed in an aqueous pH 3.5 solution for 60 min at 165°C there was significant decarboxylation of *p*-CMAc to vinylphenol (VP) and a VP-VP dimer accounted for 15% of the starting *p*-CMAc. Based on results obtained in Section 4.2.3.4, it would appear that significant condensation of VP on to the surfaces of lignin polymers during on acidic pretreatment would lower the reactivity of those polymers in subsequent reactions.

4.5 Oxygen Addition to KAQ Cooking after Most of the β-O-4' Linkages are Cleaved

4.5.1 Introduction to the Section

The prior literature on oxygen addition to alkaline AQ cooking was reviewed in Section 3.5.4. Oxygen addition at the start of a cook afforded inferior results while addition late in the cook offered superior delignification, at least with softwoods. However, based on a theoretical evaluation of the results so far obtained in this project it was concluded that a small oxygen addition to KAQ pulping of bagasse after H-factor 50-100 would likely improve subsequent bleachability. A kappa number of 13.3 was attained after KAQ cooking of CDB-Carb to an H-factor of 70 (Section 4.2.3.2). If can be assumed that a majority of the β-O-4' were cleaved by that stage. As discussed in Section 4.2.3.3 the CA, *p*-CMA and their transformation products react most rapidly with the monomer EG. Furthermore, of the 0.49 mmole of EG consumed in SAQ+EG treatment of sugar maple, 0.41 mmole was with the CA and CA derived monomers (Section 4.2.3.3). Therefore, in KAQ delignification of bagasse the monomers from β-O-4' cleavage after H-factor ~ 70 would be expected to first condensed with molecules of low molecular weight in the dissolved phase. It is anticipated that the products from such condensation would slowly condense with the residual lignin (in the fibers) throughout the remainder of cook.

What is proposed is that O_2 should react preferentially with the low molecular weight condensed products formed after H-factor ~ 70 and increase the amount of COOH groups they contain. As discussed in Sections 4.2.3.4 and 4.2.3.5 condensation of more hydrophilic fragments on to the residual lignin should be more helpful than condensation of more hydrophobic fragments. Gellerstedt (1996) extracted and characterize the residual lignin from unbleached and O_2 bleached softwood kraft pulp. It was observed that oxygen bleaching in $[OH^-]$ < 0.1M and < 100°C increase the COOH content of the residual lignin by 67% (Gellerstedt, 1996). It is anticipated that oxygen addition at ≥140°C and $[OH^-]$ > 0.2M would be quite efficient at producing COOH groups. In this section the addition of O_2 to KAQ was investigated. Oxygen injection has to be kept low because it results in a rapid consumption of OH^- for about 4 min after its addition. The goal of modifying the intermediates that apparently condense on to the residual lignin has to be balanced against lower alkalinity for the duration of the cook.

4.5.2 Materials and Methods

4.5.2.1 Oxygen and EG Additions to KAQ Cooking

Both the PARR reactor (**Figure 4.2. 1**) and M&K digesters have ports in the reactor covers for the injection of liquid and gases with an applied pressure greater that that inside the reactors. When oxygen was used, an increase O_2 pressure of 20 psi to the PARR reactor corresponded to a chemical dose of ~ 1.2 wt% O_2 on starting bagasse (~ 1.8 wt% for 30 psi). The O_2 dose was ~ 1.1 wt% on starting bagasse when 20 psi was added to the M&K digesters. KAQ + EG delignification was investigated in the PARR reactor and the chemical injection vessel (**Figure 4.2. 1**) was used. Bagasse (5 g O.D. of WDB), KOH and AQ were added to give a solution volume of 230 ml. The EG (250 mg or 500 mg) was placed in the chemical injector along with 20 ml of KOH and the solution was injected with nitrogen pressure.

4.5.3 Data and Data Analyses

4.5.3.1 Estimation of the β-O-4' Cleavage by EG Addition to KAQ Cooking

Extracted WDB (ethanol/toluene), 0.15 M KOH and AQ were added to the PARR reactor and the heater and stirrer turned on. After ~ 2 min, EG in 0.15M KOH was injected. Delignification was allowed to continue for a total of 90 min without any sample withdrawal. With EG dose of 250 mg, the procedure above was repeated with EG injections at 10 min, 20 min, 30 min and 40min. It can be seen that the formation of dimers **1-13** as a result of β-O-4' (Section 4.2.3.4) was highest when the EG was added at the start of the cook (2 min) and decreased gradually to near zero for a 40 min EG addition **(Figure 4.5. 1**). This result indicated that only a small amount of β-O-4' cleavage occurred after 40 min of reactions. However, the total yield of **1-13** from 5 g of WDB was only ~ 16% has high as when 5 g of WDB was treated with 250 mg of EG in 60 ml of 0.4M NaOH. The experiment was repeated with 2 min and 40 min injections and the use of 500 mg of EG. In this case, 0.46 mmole of dimers were detected for the 2 min injection and 0.11 mmole for the 40 min injection **(Figure 4.5. 1**). Also, the relative distribution amongst the seven most abundant dimers was similar to that when 60 ml of 0.4M NaOH. These dimer yields were high enough for the conclusion to be drawn that a majority of the β-O-4' cleavage occurred within the first 40 min of reactions. The significantly lower total

dimer yield in the PARR reactor cases is probably a function of the lower EG concentrations. When 500 mg of EG was in the 250 ml treatment, its concentration was 2 mg/mL. When SAQ+ EG treatments were performed in 60 ml of 0.4M NaOH the EG concentration was 4.17 mg/mL. More research is recommended.

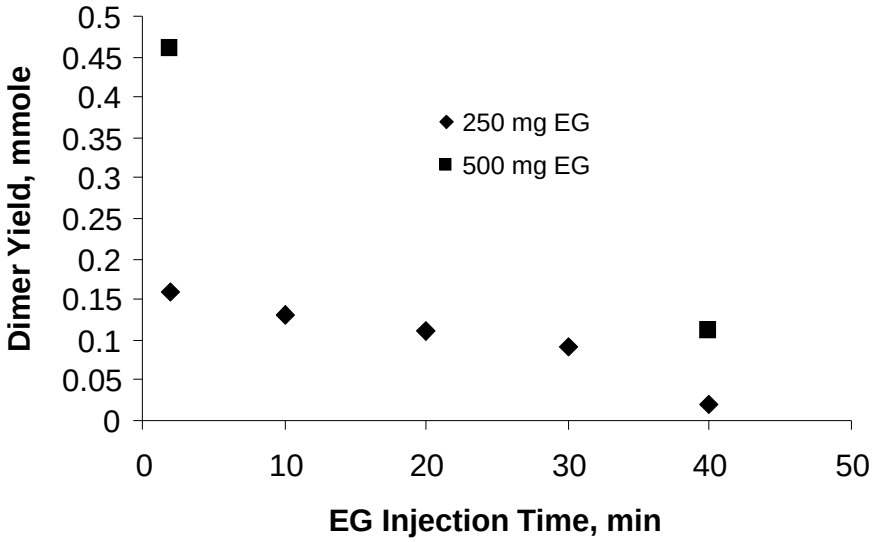


Figure 4.5. 1 Total yield of Dimers 1 – 13 from SAQ + EG treatment of WDB in the PARR Reactor.

4.5.3.2 Oxygen Addition after Majority of β-O-4' Cleavage

The standard PARR cooking of CDB-Carb (Section 4.2.3.1) was repeated along with runs where O_2 was added early in the cook (injection times varying from 26 min to 40 min). Three different conditions were tested: 0.15 M KOH at 140°C, 0.20 M KOH at 140°C and 0.2M KOH at 160°C. In all cases, a lower kappa number was obtained after 90 min when O_2 was added (**Figure 4.5.2- 4.5.4**). Oxygen addition to KAQ cooking of extracted (ethanol/toluene) WDB was also investigated and it caused a decrease in kappa number after 90 min as well (**Figure 4.5. 5**).

The next step was to produce large enough pulp samples from PARR reactor runs for their bleachability to be investigated. Three control cooks (no oxygen) were performed on the same day using unextracted WDB. The starting sample size was increased from 5.0 g to 7.5 g in 250 ml of 0.15M KOH at 140°C. The next day the experiment was repeated but 30 psi O_2 was

added to the three runs after 40 min of cooking. The three cooks were combined into one sample for the KAQ case while those from KAQ + O_2 where combined into another sample. The control pulp had a kappa number of 20.1 at fiber yield of 65.5% while the KAQ + O_2 combination had corresponding values of kappa number 19.1 at 65.4% fiber yield. It should be noted that when 5g of extracted WDB was used in the control cook a kappa number of 13.5 was obtained **Figure 4.5. 5**). The 20.1 kappa number in the present case is reasonable in light of the presence of extractives in the WDB and poorer mixing in the reactor when consistency is increased from 2% (5g in 250 ml) to 3% (7.5 g in 250 ml).

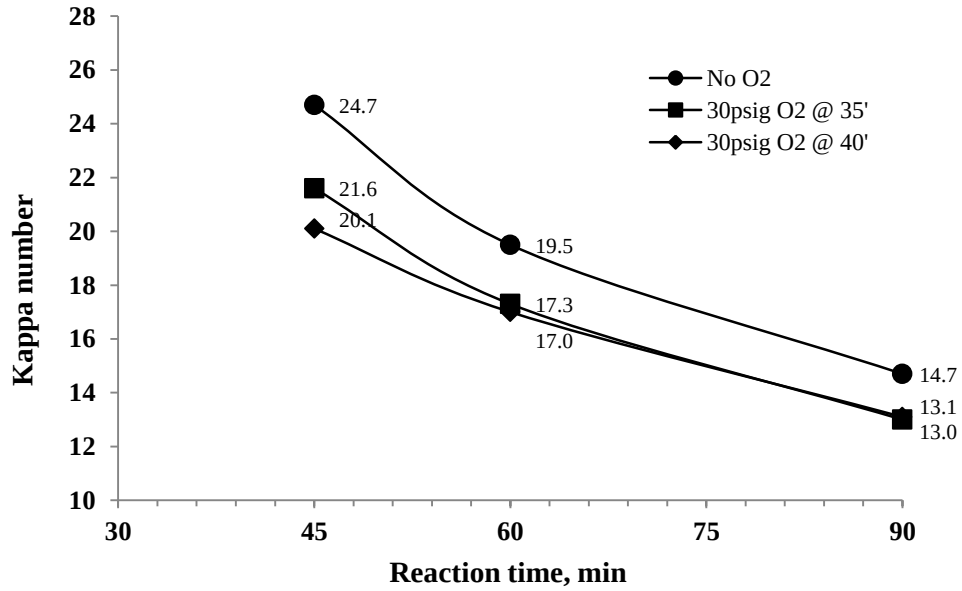


Figure 4.5. 2 Effect of O_2 addition to KAQ cooking of CDB-Carb (0.15 M KOH, 140°C).

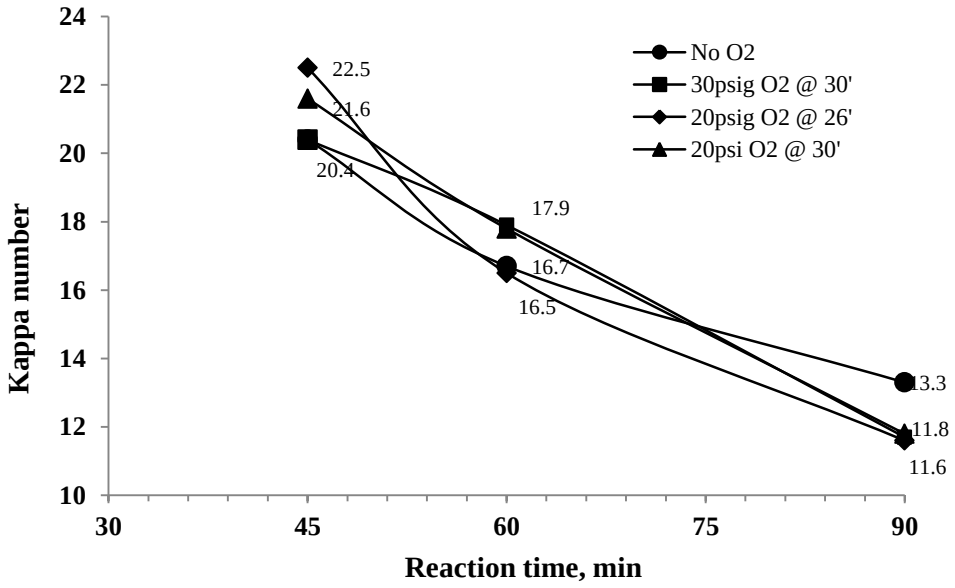


Figure 4.5. 3 Effect of O_2 addition to KAQ cooking of CDB-Carb (0.20 M KOH, 140°C).

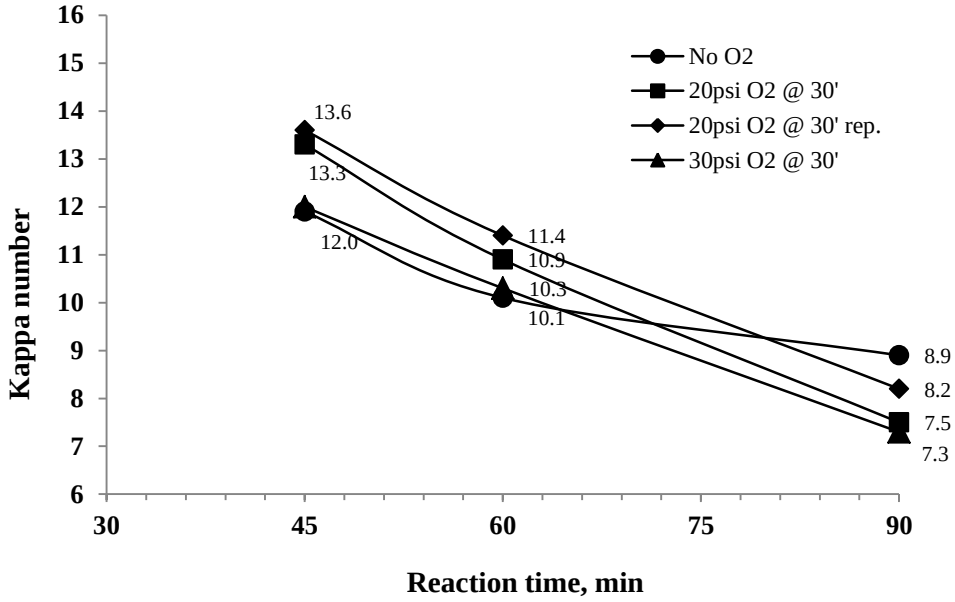


Figure 4.5. 4 Effect of O_2 addition to KAQ cooking of CDB-Carb (0.20 M KOH, 160°C).

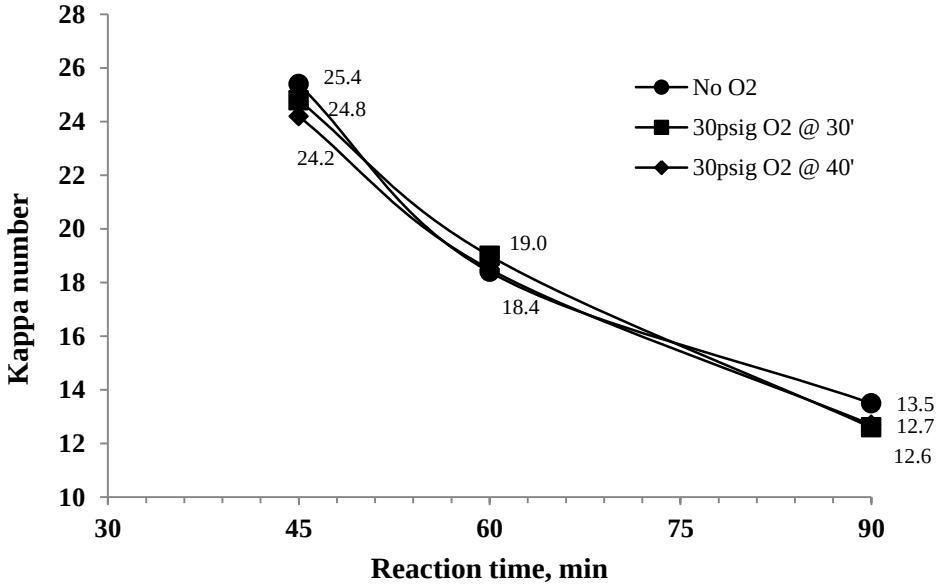


Figure 4.5. 5 Effect of O_2 addition to KAQ cooking of solvent extracted WDB (0.15 M KOH, 140°C).

The shortened QPD_1 sequence was used for bleaching and the results are summarized in **Table 4.5. 1**. The P stage was performed with the 3% H_2O_2 and 4% NaOH on pulp in order to achieve a low enough kappa number for further delignification and brightening under D_1 stage conditions. It can be seen that the KAQ + O_2 obtained a lower kappa number and higher brightness after both QP and QPD_1. The 2.2 point higher brightness after QPD_1 for a hard to bleach pulp is quite significant.

Table 4.5. 1 QPD_1 Bleaching of KAQ and KAQ + O_2 pulps from WDB (0.15 M KOH, 140°C, PARR Reactor)

	KAQ	***KAQ + O_2***
Unbleached		
Kappa number	20.1	19.1
Pulp Yield, %	65.5	65.4
Brightness, % Elrepho	<30	<30
After QP Stages		
Kappa number	5.7[1]	4.8
Brightness, % Elrepho	65.1	66.8
D_1 Stage		
ClO_2, % on pulp	1.0	1.0
End pH	3.5	3.5
Kappa Number	2.6	2.3
Brightness, % Elrepho	76.1	78.3

[1] 3.0% H_2O_2 on pulp in P stage

Once again, a 1.0% ClO_2 on pulp dose under D_1 stage conditions only increased the brightness of the control pulp from 65.1% to 76.1%. This poor performance is most likely due to the low alkalinity in the KAQ stage, i.e. a maximum of 0.15M OH^-.

The next step was to investigate O_2 addition at higher alkalinity. The bleaching characteristics of KAQ pulp made from CDB-Carb and using 23% KOH on bagasse are described in **Table 4.2. 7**. Although not previous reported the initial and final [OH^-] in that case were 0.34M and 0.20M. The initial concentration was derived from theoretical calculations, i.e. mass of KOH and volume of cooking liquor used while the final concentration was based on acid-base titration to end pH 8.3. The 23.0% KOH on CDB-Carb cooking was repeated but with 20 psi O_2 added after the temperature ramp and 10 min at 160°C (H-factor 109). The cooking liquor had a residual [OH^-] of 0.17M and a pulp with kappa number 14.0 was obtained. Even though this pulp had a higher unbleached kappa number than the control (14.0 *vs.* 12.6) and a lower brightness (32.4% *vs.* 35.5%) it bleached to an identical final brightness as the control (93.5%). Some of the cooking results and the relevant bleaching resulted are documented in **Table 4.5. 2**.

Table 4.5. 2 QPD_0EpD_1 Bleaching of KAQ and KAQ + O_2 pulps from CDB-Carb (23% KOH on bagasse, 160°C, M&K Digester)

	KAQ pulp	***KAQ + O_2***
Unbleached		
Kappa number	12.6[1]	14.0[2]
Pulp Yield, %	51.4	51.0
Brightness, % Elrepho	35.5	32.4
After QP Stages		
Kappa number	3.7[4]	3.9
Brightness, % Elrepho	67.7	63.8
D_0 Stage		
Kappa Factor in D_0	0.30	0.30
End pH in D_0	2.3	2.3
Ep Stage		
End pH in Ep	12.0	12.0
Kappa number	--	--
Brightness, % Elrepho	88.1	87.4
D_1 Stage		
ClO_2, % on pulp	0.5	0.5
End pH	4.3	4.1
Brightness, % Elrepho	93.5	93.5

[1] Initial and final [OH^-] of 0.34 M and 0.20 M., [2] Initial and final [OH^-] of 0.34 M and 0.17 M.

4.5.4 Summary of the Section

KAQ pulping starts with cleavage of β-O-4’ linkages to produce CA and *p*-CMA. These two monomers transform into other monomers still containing the α-β double bond. Based on a theoretical evaluation of the likely condensation reactions that these monomers would participate in, it was anticipated that O_2 addition after a majority of the β-O-4’ have been cleaved should have a favorable effect on such reactions and ultimate result in improved bleachability. Preliminary results on oxygen additions (< 2.0 wt% on bagasse) at H-factor < 110 indicated that such additions improved bleachability.

5.0 CONCLUSIONS

The idea to be investigated was a more efficient utilization of sugarcane bagasse as compared to burning for energy. An approach that appeared feasible for regions in Brazil such as São Paulo State, where sugar plantations, sugar and pulp mills are in close proximity, was to use the bagasse for the production of unbleached chemical pulp. The pulping process should produce an effluent (black liquor) with significant market value and as such it could be disposed of thus avoiding chemical recovery. The processing of black liquor for chemical recovery is normally expensive in terms of capital cost. Small bagasse pulp mills would produce unbleached pulp that would be mixed with unbleached eucalyptus kraft pulp and bleached at an existing kraft mill. Bagasse pulp would constitute only 10-20% of furnish entering the bleaching process.

The only major drawback that could be envisioned was that the bagasse pulp would not respond well to the bleaching reagents normally used for hardwood kraft or SAQ pulps. If this pulp substitution process were to be commercialized the plan would be to avoid chemical recovery from bagasse pulping. Ammonia (NH_4OH) would be used in a possible pretreatment and KOH, with or without ammonia, used in the SAQ stage. The effluent containing potassium and nitrogen would be used to fertilize growing sugar cane in nearby fields. The following topics were investigated:

This research started with the refinement of analytical methods for biomass compositional analyses. Summative analyses of 100% ±1.5% were obtained for eucalyptus, bagasse and bamboo. Also, after acid and acid followed by NH_4OH neutralization pretreatments, mass loss based on changes in fiber yield and xylan, lignin and glucan contents correlated very well with overall mass loss based on fiber recovery. The total calculated xylan + lignin + glucan losses were 90% of the total yield loss after both the A and A→N pretreatments.

Bagasse fibers were delignified at a much higher rate than hardwood chips by AQ-catalyzed alkaline pulping, i.e. SAQ, KAQ or K/NAQ. The higher rate of mass transfer into bagasse fibers was not a major contributor to the improvement because the huge differences in reaction rates were observed when both biomasses were converted to 15 mesh meals and solvent extracted with ethanol/toluene. The major contributor to the higher rate delignification appears to be 67% more uncondensed β-O-4’ linkages in the non-syringyl fraction of bagasse lignin. The

concentration of uncondensed β-O-4'dimeric units was estimated by SAQ + ethylguaiacol delignification method that was recently developed in this laboratory (Kanungo et al., 2011) and applied to an non-wood for the first time in the present investigation.

When low alkalinity is used in KAQ or K/NAQ cooking of bagasse the resulting pulp was difficult to bleach to high brightness by O, P and D stages. It appears that lignin condensation was the cause of the problem. Preliminary investigations suggested that *p*-coumaric acid (*p*-CMAc) and ferulic acid (FA) that constitute ~14% of bagasse lignin hydrolyzed early in the cooking process and participated in the condensation reactions. It also appeared that the condensed lignin may contain some of the COOH originally would be extracted under high alkalinity situation. When bagasse was delignified with 15% KOH on biomass a pulp with poor bleachability was obtained. However, when 23% KOH on biomass was used the bleachability of the resulting pulp was equal or superior to most hardwood kraft pulp.

Hot water or acidic pretreatments of bagasse retarded delignification in subsequent cooking (KAQ and K/NAQ) and bleaching (QPD_0EpD_1) and resulted in a lower bleached brightness as compared to the control. Preliminary research on self-condensation of *p*-CMAc suggested that vinylphenol (VP) occurred to a greater extend under acidic conditions (165°C, pH 3.5-4.0). The VP was generated from decarboxylation of *p*-CMAc and its vinyl group imparted hydrophobicity when it condensed with other monomers. It condensation on to lignin oligomers would be expected to impart hydrophobicity and decrease reaction rates of the oligomers in subsequent treatments.

Finally, strength and drainage data indicated that 10% inclusion of unbleached bagasse KAQ or K/NAQ pulp into unbleached eucalyptus kraft pulp had only a minor negative effect. The overall results from this research indicated that 10% inclusion of bagasse pulp into eucalyptus kraft is technically feasible. However, a 20% inclusion significantly retarded both strength and drainage.

6.0 RECOMMENDATIONS FOR FUTURE WORK

1) Condensation reactions and rates of those reactions have to be thoroughly examined for *p*-CMAc and FA under both acidic and alkaline conditions.

2) Methods of removing *p*-CMAc and FA from bagasse lignin prior to activating pretreatments and cooking of the fibers have to be investigated.

3) Since KOH would not be recovered, it is recommended that the treatment scheme below be investigated as means of minimizing KOH use. Impressafiners (screw presses) would be used to squeeze out KOH and re-use it. The flow sheet described in **Figure 6. 1** would require 151 g KOH/ Kg of biomass or 15.1% (56 x 1.8x 1.5). The two digesters would be designed for a maximum H-factor of 600 in total and the two impressafiners attached to digesters would only press to < 33% consistency. The first stage of the cooking at low alkalinity would take advantage of the ease of depolymerization of bagasse lignin and would afford significant delignification. The second stage of cooking at ~0.9M would extract condensed lignin structures and achieve a kappa number in the 12-14 range.

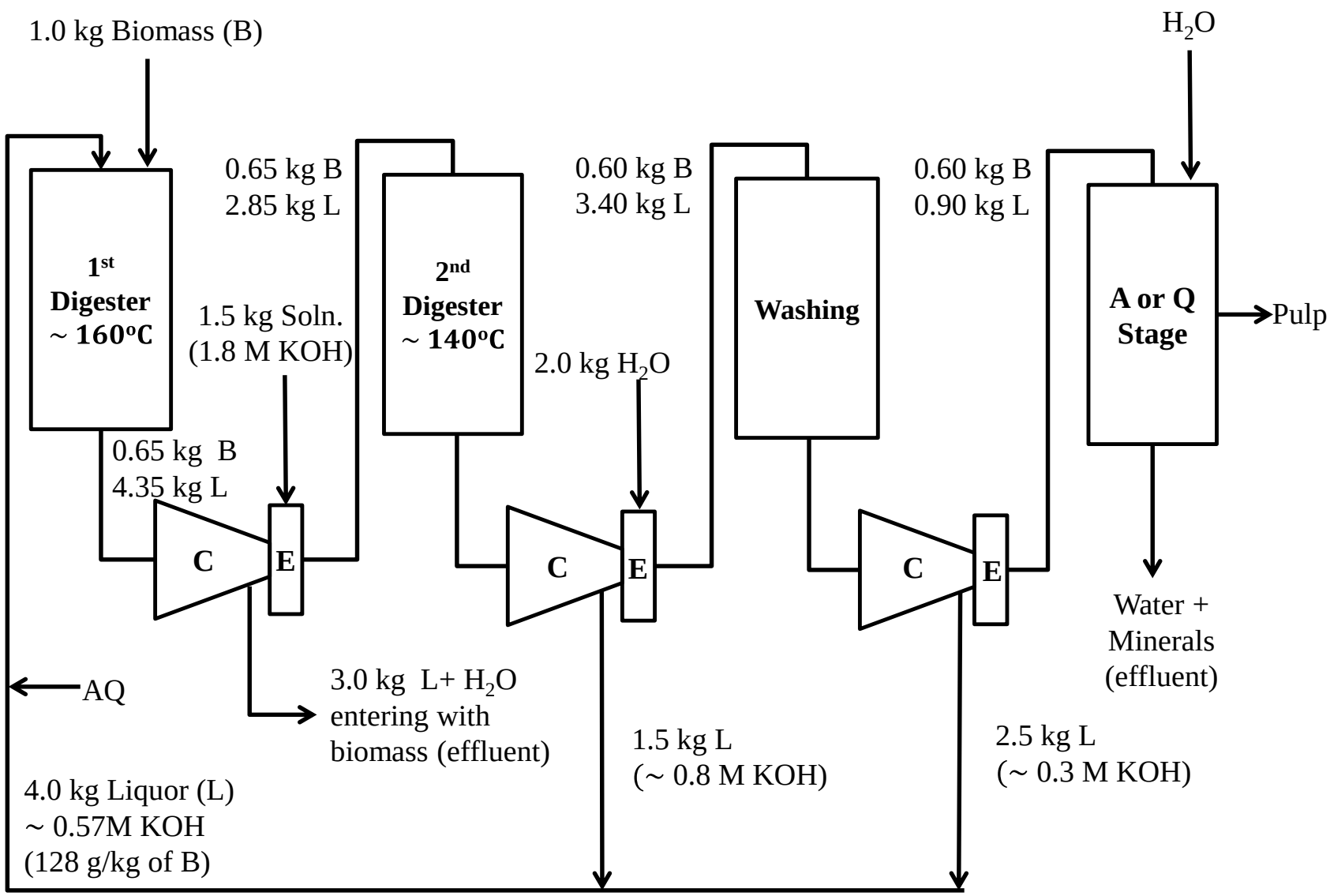


Figure 6. 1 Two-stage KOH cooking.

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Xu, F., Sun, R.-C., Sun, J., Liu, C.-F., He, B.-H., & Fan, J.-S. (2005). Determination of Cell Wall Ferulic and p-Coumaric Acids in Sugarcane Bagasse. *Analytica Chimica Acta, 552*, pp. 207-217.

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8.0 APPENDICES

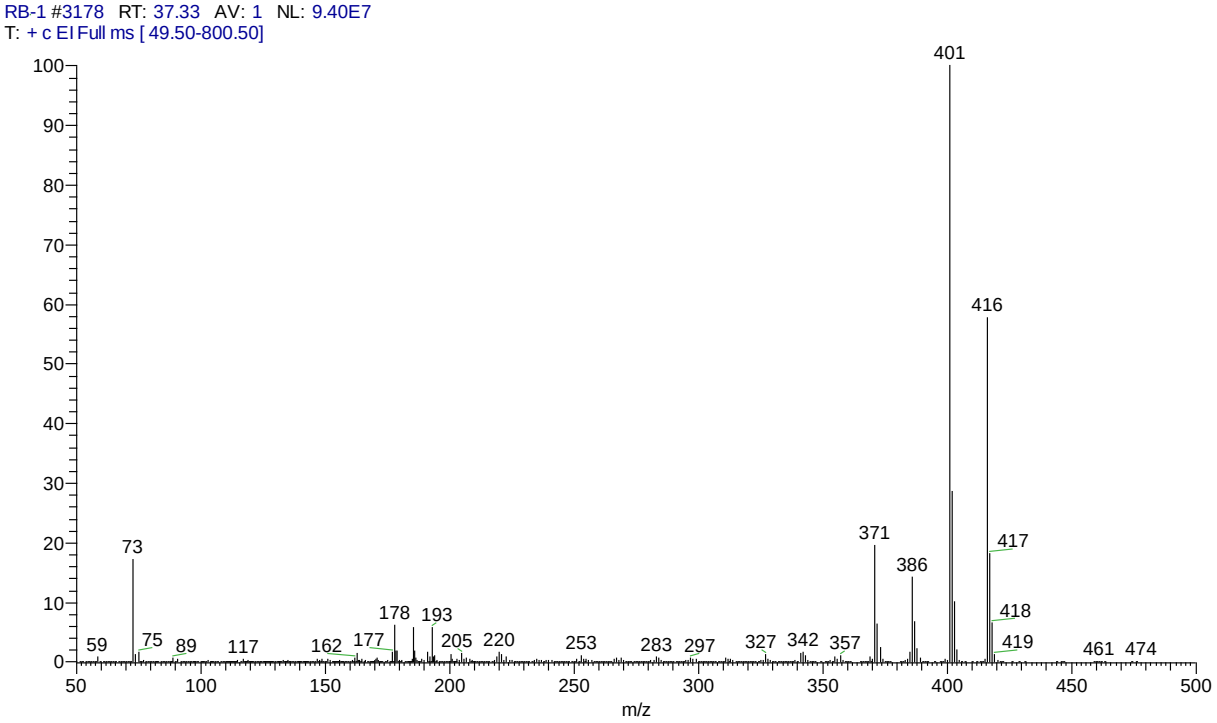

Figure A 1 Mass spectrum for the compound **8**, an α-5’ linked VP-EG dimer with MW of 416.

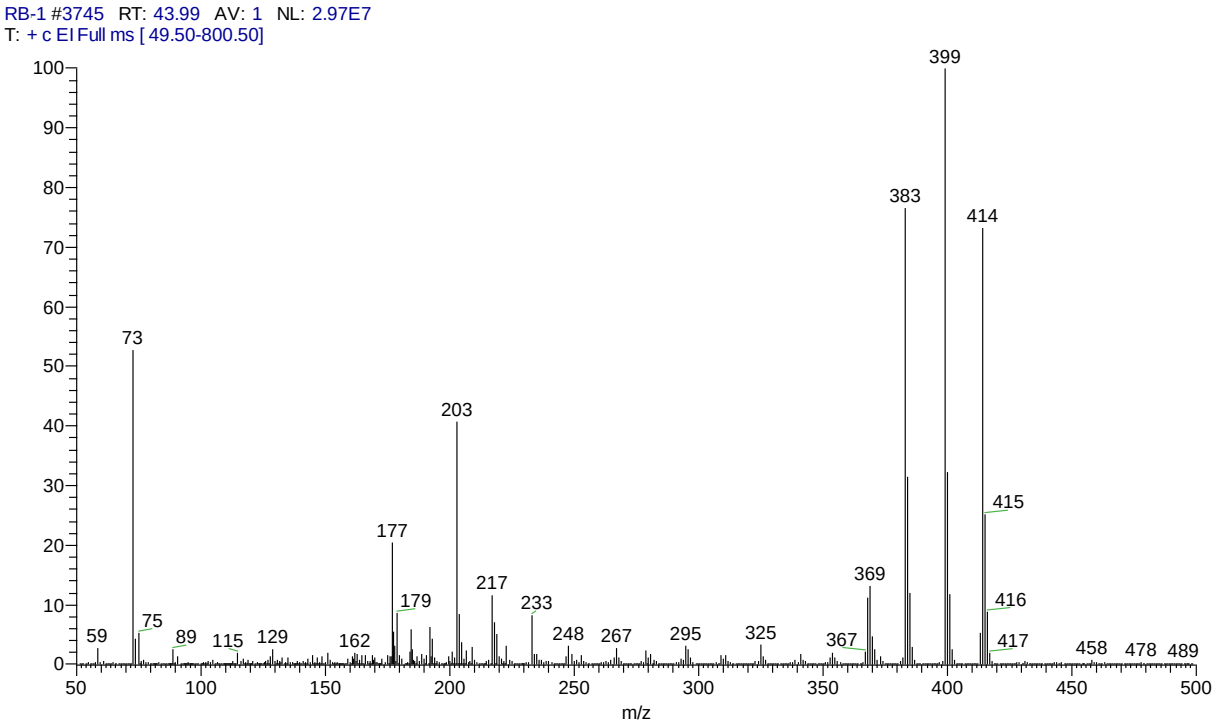

Figure A 2 Mass spectrum for the compound **10**, an α-5’ linked VP-VG dimer with MW of 414.

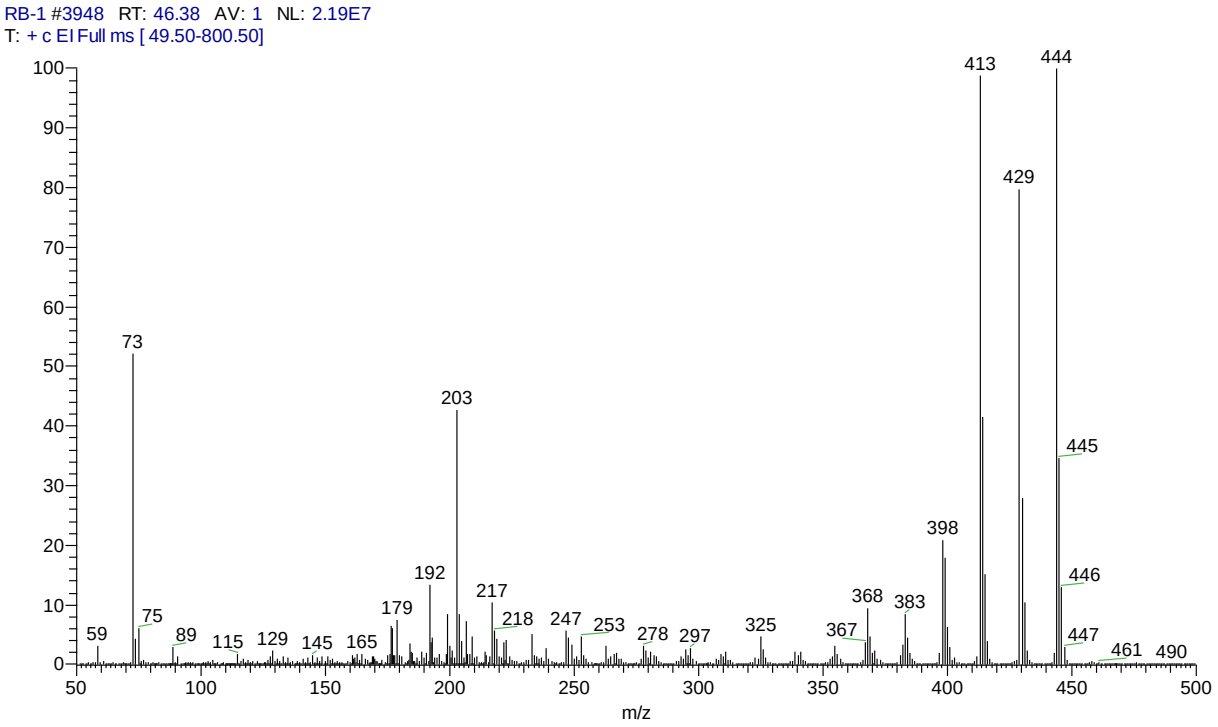

Figure A 3 Mass spectrum for the compound **11**, an α-5’ linked VG-VG dimer with MW of 444.

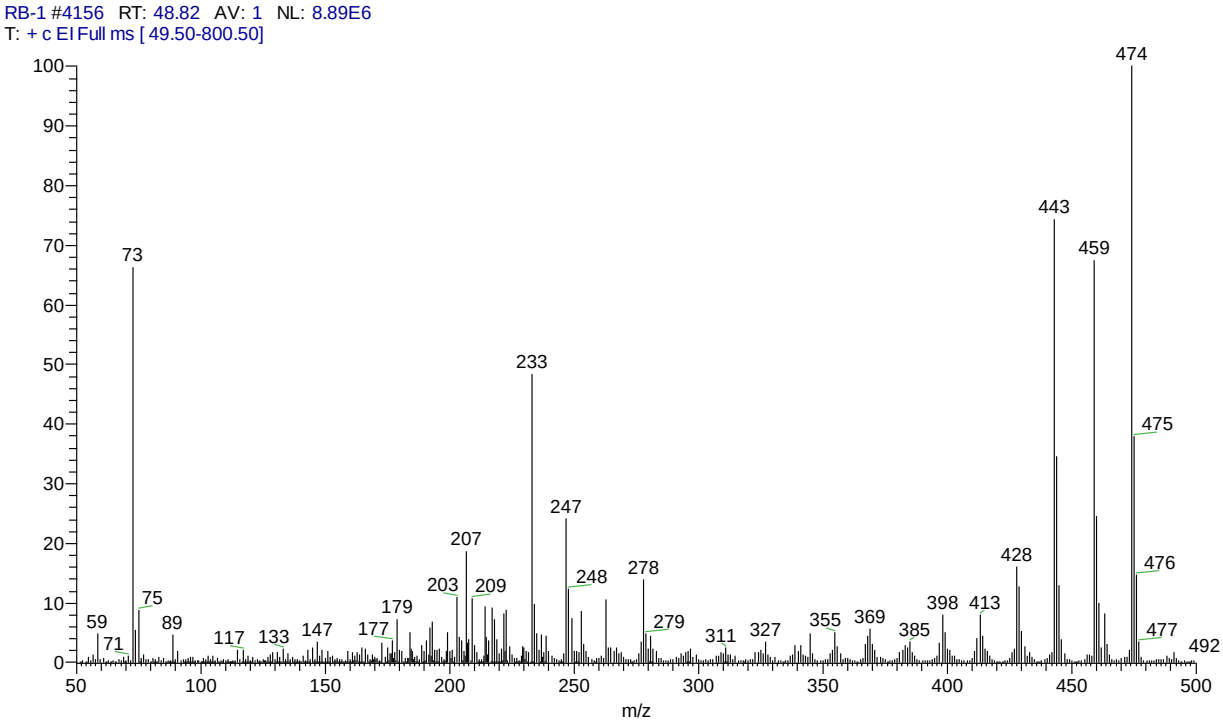

Figure A 4 Mass spectrum for the compound **13**, an α-5’ linked CA-VG dimer with MW of 474.

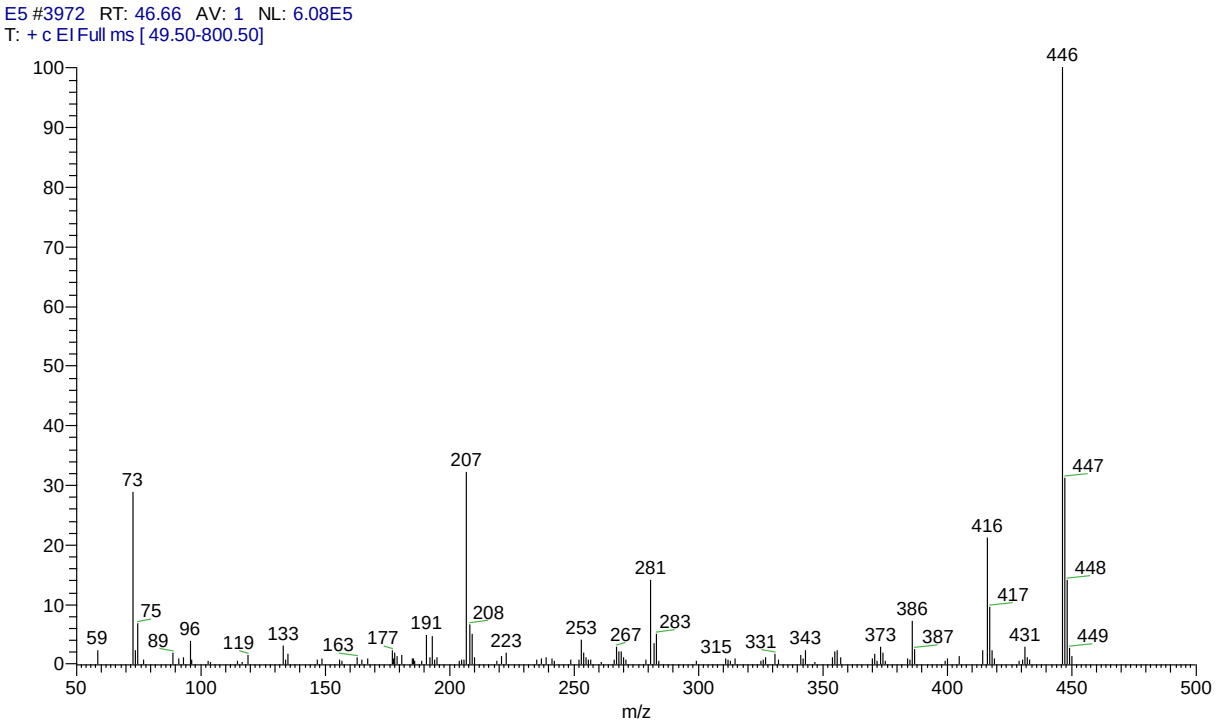

Figure A 5 Mass spectrum for the compound **7**, a β-5’ linked VG-EG dimer with MW of 446.

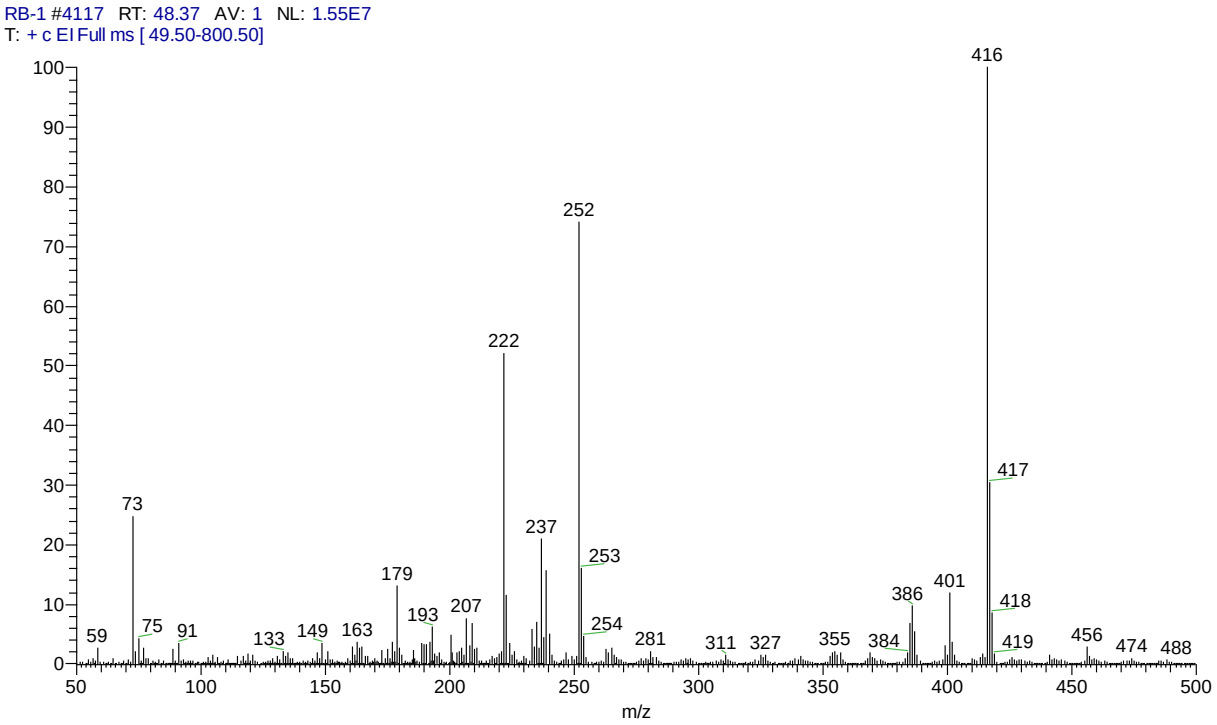

Figure A 6 Mass spectrum for the compound **12**, a β-5’ linked VP-EG dimer with MW of 416.

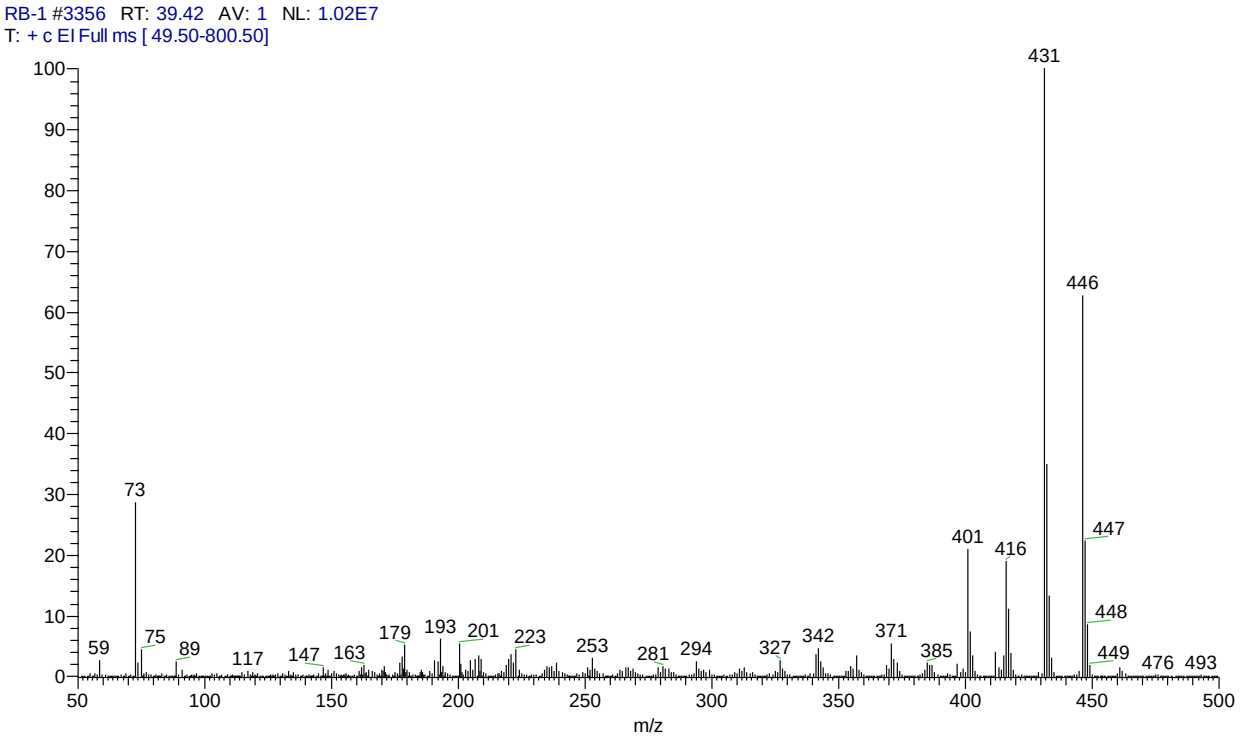

Figure A 7 Mass spectrum for compound (s) responsible for the 39.66 min peak in Figure 4.2.17. MS taken at 39.42 min is identical to that taken at 39.66 min in Figure A 8.

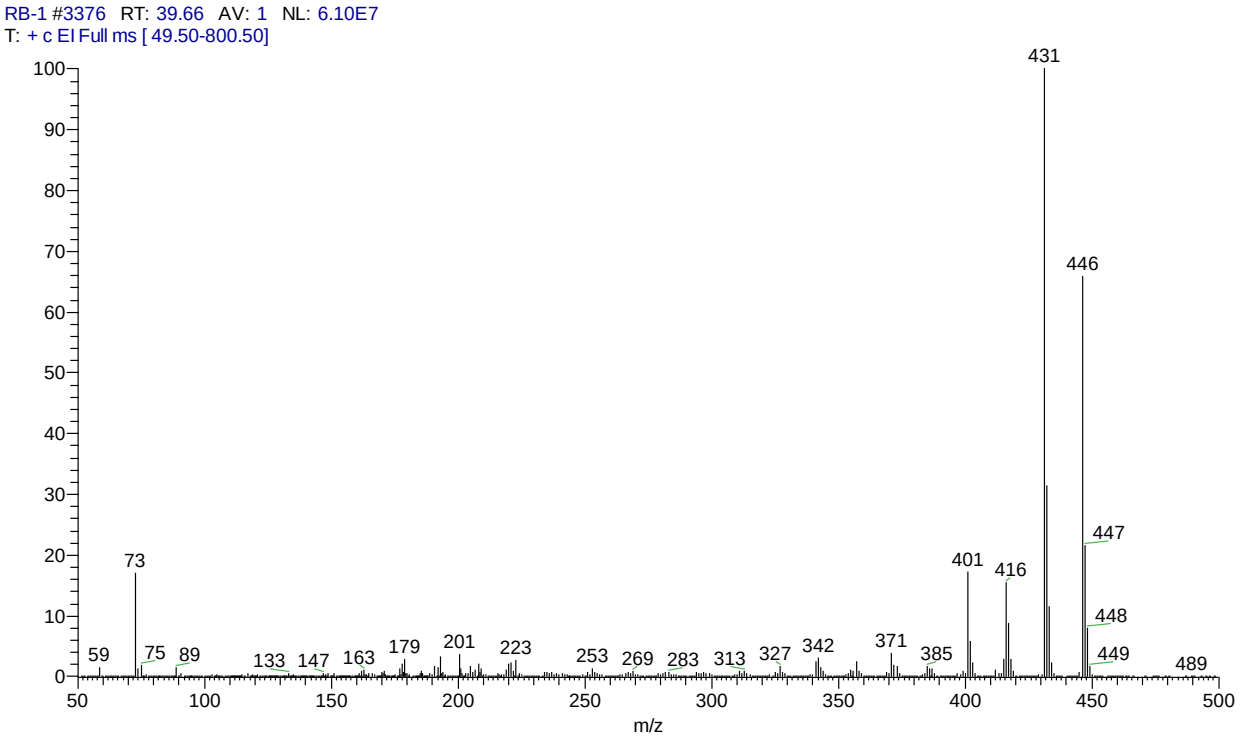

Figure A 8 Mass spectrum for compound (s) responsible for the 39.66 min peak in Figure 4.2.17. MS taken at 39.66 min is identical to that taken at 39.42 min in Figure A 7.

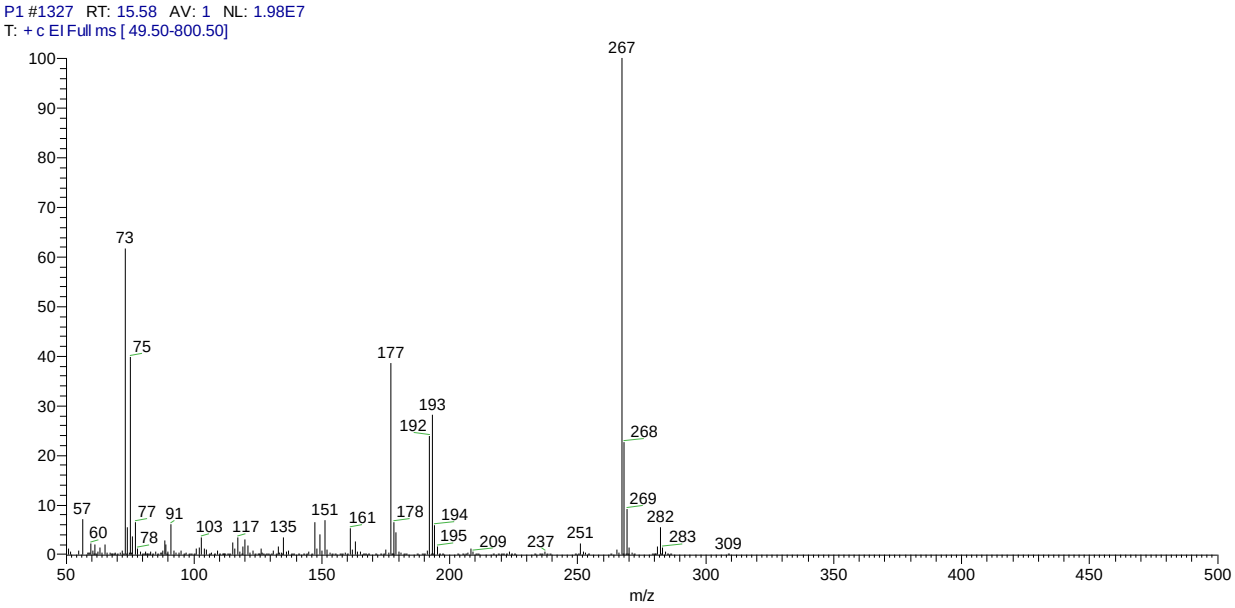

Figure A 9 Mass spectrum for the silylated *p*-HBA.

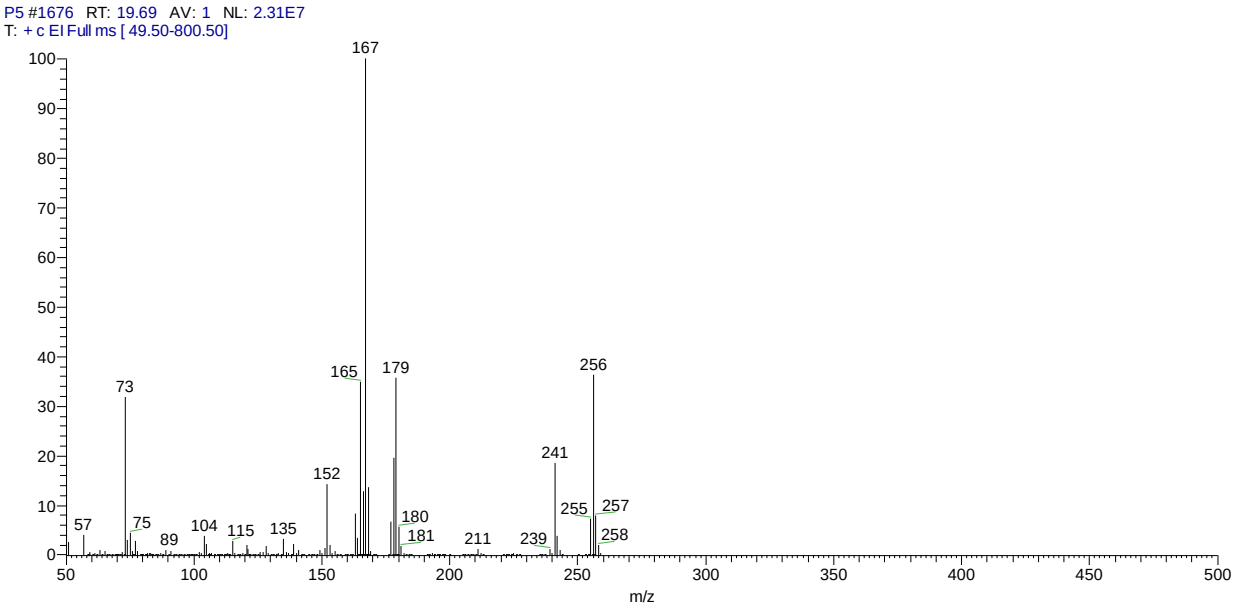

Figure A 10 Mass spectrum for the internal standard, silylated benzhydrol.

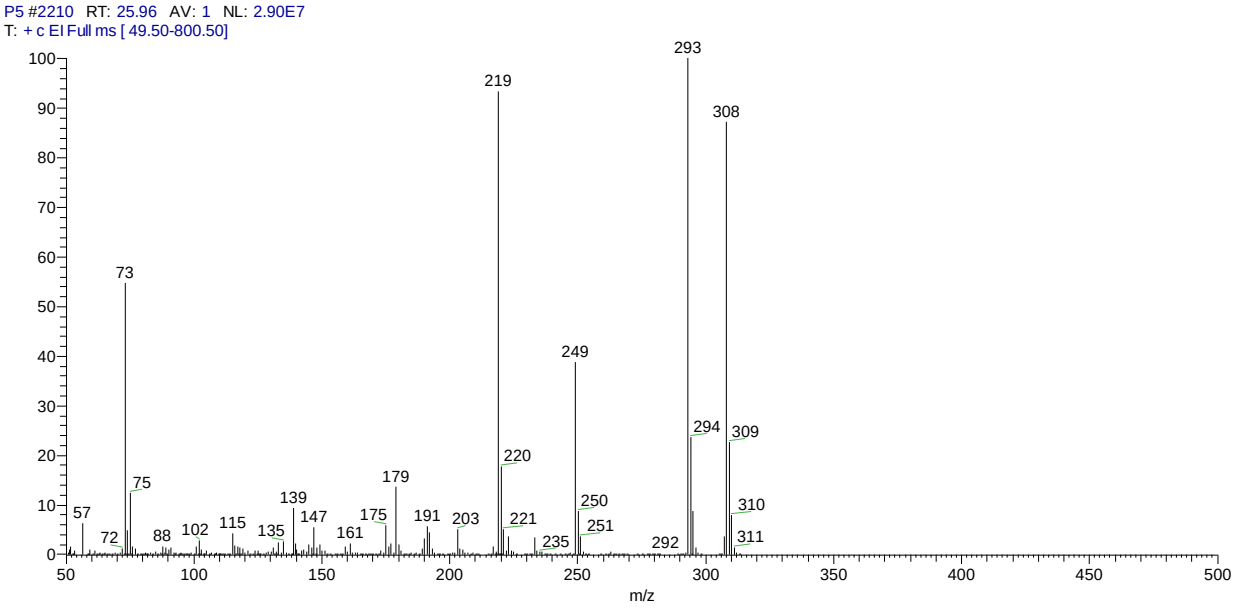

Figure A 11 Mass spectrum for silylated *p*-CMAc.

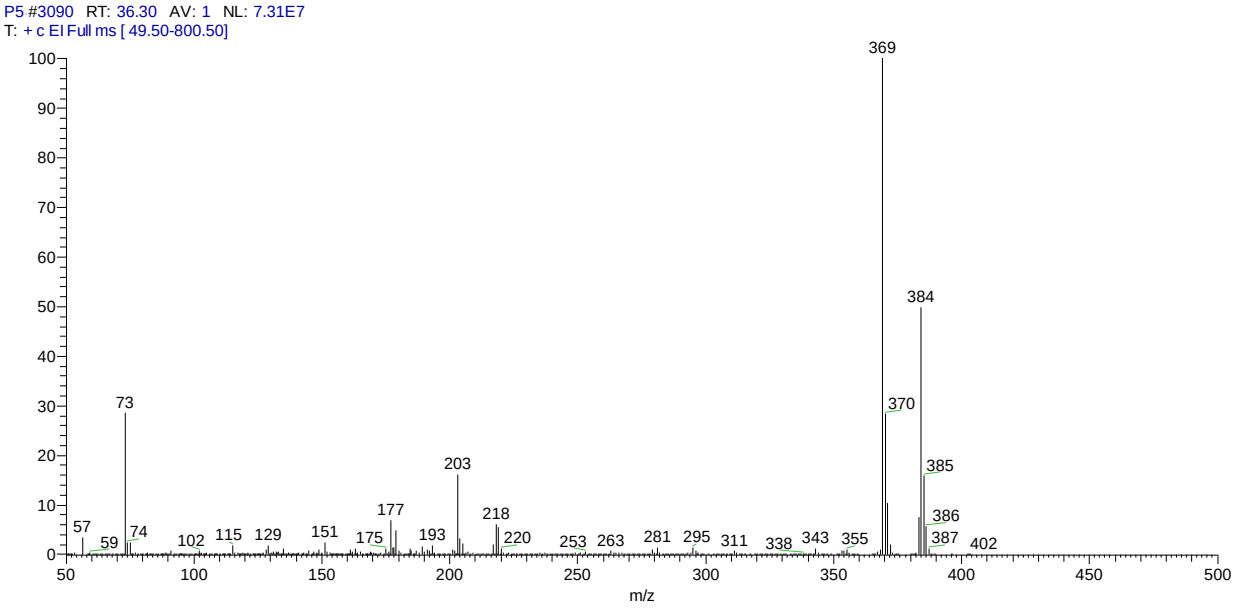

Figure A 12 Mass spectrum for the compound **9**.

CURRICULUM VITAE

PERSONAL INFORMATION:

Ericka Figueiredo Alves
Rua José da Cruz Reis, 158 apt 600
Viçosa, MG, Brazil
36570-000
Phone: (55) 3138915593
Email: erickafalves@yahoo.com.br

EDUCATION

The State University of New York College of Environmental Science and Forestry, Syracuse NY
Ph.D. in Paper Engineering (in progress) **(2007-present)**

Research: "Simultaneous Production of Paper and Chemical Bio-products from Sugarcane Bagasse"

Major Techniques Developed: Lignin and carbohydrate quantification by Gas Chromatography-Mass Spectrometry (GC-MS), Nuclear magnetic resonance (NMR), and Biomass pulping in a Parr High Pressure -Reactor.

Cumulative GPA: 3.7

Scholarship: Awarded by CAPES-Fulbright

Universidade Federal de Viçosa, UFV, Brazil
M.S. in Forestry Science **(2003-2006)**

Thesis: "Interactions between Fibers and Vessel Elements on the Eucalyptus Kraft Pulp with Offset Printing Inks".

Major Techniques Developed: Pulp component separation by Bauer-McNett. Thermal gravimetric analysis (TGA), Differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR) analysis.

Cumulative GPA: 3.0

Scholarship: Awarded by the National Counsel of Research (Brazil) – CNPq

Universidade Federal de Viçosa, UFV, Brazil
B.S. in Forest Engineering **(2000-2003)**

Scholarship: Awarded by the National Counsel of Research (Brazil) – CNPq from August, 2001 thought July, 2002 for Scientific Initiation.

Cumulative GPA: 3.5

AWARDS

The Renata Marton Award for Graduate Students in Paper and Bioprocess Engineering **(2009)**

The Best Presentation Award for Master's research at the 39th Pulp and Paper International Congress and Exhibition (ABTCP - TAPPI) Sao Paulo, Brazil **(2006)**

The Praise's Vote Award based on academic performance as the top student of the 2003 Forest Engineering class. **(2003)**

WORK EXPERIENCE

International Colloquium on Eucalyptus Pulp
Secretariat of the 3rd ICEP **(January- May 2007)**
Elaborated the conference program, location team coordinator during the conferences, and writing final reports for sponsors.

Universidade Federal de Viçosa
Pulp Bleaching Laboratory Coordinator **(August – December 2006)**
Coordinator of several projects for the major pulp and paper producers of South America. These included Aracruz Cellulose, BahiaSul, Suzano, Votoratim Cellulose e Papel, Arauco among other companies. Also, participated in lab trials, analyzed results and wrote technical reports.

Aracruz Cellulose S.A., Barra do Riacho, Brazil
Internship **(May – November 2002)**
Undergraduate internship at the world leader in the production of bleached pulp from eucalyptus receiving an overview of the pulp production process. Also elaborating, developing and

executing projects focused on improvements in delignification and bleaching process.

Pulp and Paper Laboratory Bleaching field, Viçosa, Brazil
Internshi **(May – July 2001)**
Conducted research at the University Pulp and Paper Laboratory under the advisement of Dr. Jorge Colodette, examining different bleaching processes and all related analyses in the verification of pulp quality.

LANGUAGES

Portuguese – native language
English- Speak fluently and read / writes with high proficiency
Spanish - Can participate in slow-speaking oral conversations

PUBLICATIONS AND PAPERS

ALVES; E.F.; BOSE, S.K.; FRANCIS, R.C.; COLODETTE, J.L.; LAKOVLEV, M.; VAN HEININGEN, A. Carbohydrate Composition of Eucalyptus, Bagasse and Bamboo by a Combination of Methods. Carbohydrate Polymers. Vol. 82, Issue 4, Pages 1097-1101, Nov. 2010.

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MASINGALE, M.P.; ALVES, E.F.; KORBIEH, T.N.; BOSE, S.K.; FRANCIS, R.C. An Oxidant to Replace Nitrobenzene in Lignin Analysis. Bio-Resources. Vol.4, Issue 3, Pages 1139-1146, 2009.

ALVES, E. F.; OLIVEIRA, R. C. de.; SILVA, L. H. M. Da; COLODETTE, J.L.Thermal and spectroscopic Analyses on the Molecular Interaction between Eucalyptus Kraft Pulp Components and Offset Printing Inks. Braz. Arch. Biol. Technol. Vol.52, Issue 3, Pages 689-699, 2009.

SHACKFORD, L. D.; SANTOS, C. A.; COLODETTE, J.L.; ALVES, E.F. Optimizing the Alkaline Extraction for Eucalyptus Kraft Pulp Bleaching. Tappi Journal. Vol. 8, Issue 1, Pages 12-19, 2009.

ALVES, E. F.; OLIVEIRA, R. C. de.; SILVA, L. H. M. Da; COLODETTE, J.L Interação de Fibras e Elementos de Vasos de Polpa Kraft de Eucalipto com Tintas de Impressão Offset. O Papel, Vol. Março, Pages 54-70, 2007.

SANT'ANNA-SANTOS, B F.; SILVA, L. C. da ; AZEVEDO, A. A.; ARAÚJO, J. M. de ; ALVES, E. F.; SILVA, E. A. M. da; AGUIAR, R. M. E. Effects of Simulated Acid Rain on the Foliar Micromorphology and Anatomy of Tree Tropical Species. Environmental and Experimental Botany, Vol.58 (1-3), 2006.

TECHNICAL PAPERS

COLODETTE, J. L. ; TAVARES, C.A. N. ; ALVES, E.F. Utilização dos Produtos Hidrocol Obs e Ch Visando Aumentar a Eficiência de Linhas de Fibras de Eucalipto Amostra CE. 2006.

COLODETTE, J. L. ; TAVARES, C.A.N.; ALVES, E. F . Utilização dos Produtos Hidrocol OBS e CH Visando Aumentar a Eficiência de Linhas de Fibras de Eucalipto - Amostra VE. 2006.

COLODETTE, J. L. ; TAVARES, C.A. N. ; ALVES, E.F. Efeito do Produtohidrocol OBS no Branqueamento de Fibras de Eucalipto. 2006.

COLODETTE, J. L.; ALVES, E.F. ; BANDEIRA, M. A. ; PAULA, O. C. Avaliação das Seqüências de Branqueamento D(EO)DP e A/D(EO)DP e seus Impactos Ambientais para o Projeto Losango. 2006.*

PRESENTATIONS IN CONFERENCES

ALVES, E. F.; OLIVEIRA, R. C. de; SILVA, L. H. Mendes da; COLODETTE, Jorge Luiz . Interação de fibras e elementos de vasos de polpa kraft de eucalipto com tintas de impressão offset. 39th Pulp and Paper International Congress. São Paulo, Brazil, October, 2006.

PUBLICATIONS IN CONFERENCE PROCEEDINGS

ALVES, E. F., FRANCIS, R. C., COLODETTE, J. L. Pulping and Bleaching Characteristics – Bagasse versus Hardwood. Manuscript accepted (Aug 2011) to the 44th ABTCP Conference, São Paulo, Brazil, October, 2011.

ALVES, E. F.;BOSE, S.K.; FRANCIS, R.C. Trapping of p-coumaryl and Coniferyl Alcohol during Soda/AQ Treatment- A Means of Estimating Uncondensed β-O-4 in Native Lignin. In: 16t^{h} ISWFPC, Proceedings…Tianjin, China, 2011.

NICHOLSON, D.J.; DUARTE, G.V.; ALVES, E.F.; FRANCIS, R.C. Understanding and Quantifying LCC- One Key Step in Transforming a Pulp Mill into a Biorefinery. In: 5rd ICEP - International Colloquium on Eucalyptus Pulp, Proceedings.... Arraial d`Ajuda, Brazil, 2011.

ALVES, E. F.; OLIVEIRA, R. C. de.; SILVA, L. H. M. Da; COLODETTE, J.L Thermal Analyses Studies on the Interactions between Eucalyptus Kraft Pulp Components and Offset Printing Inks. In: 3rd ICEP - International Colloquium on Eucalyptus Pulp, Proceedings.... Belo Horizonte, Brazil, 2007.

ALVES, E. F.; OLIVEIRA, R. C. de.; SILVA, L. H. M. da. Estudos Térmicos e Espectroscópicos da Mistura dos Componentes da Polpa Branqueada de Eucalipto com a Tinta de Impressão Offset. In: SYMPOSIUM OF SCIENTIFIC INICIATION, Vicosa, Brazil, 2007.

ALVES, E. F.; COSTA M. M.; da; COLODETTE, J. L. Influência da Composição de Grupos Cromóforos e Leucocromóforos (hexa's) da Polpa Kraft na sua Branqueabilidade. In: SYMPOSIUM OF SCIENTIFIC INICIATION, 11, 2002, Viçosa, MG, 2002. Proceedings... Viçosa, Brazil, 2002.

SANT'ANNA-SANTOS, B F.; AZEVEDO, A. A; SILVA, L. C. da; ALVES, E. F. Efeitos da Chuva Acida sobre a Estrutura e Micromorfologia Foliar de Espécies Arbóreas do Parque Estadual do Rio Doce- MG. In: SYMPOSIUM OF SCIENTIFIC INICIATION, 11, 2002, Viçosa, MG, 2002. Proceedings... Viçosa, Brazil, 2002.

SANT'ANNA-SANTOS, B F.; AZEVEDO, A. A; SILVA, L. C. da; ALVES, E. F.; TINÔCO, S. B. de. Efeitos da Chuva com Flúor sobre a Estrutura Foliar de Espécies Arbóreas do Parque Estadual do Rio Doce- MG. In: SYMPOSIUM OF SCIENTIFIC INICIATION, 11, 2002, Viçosa, MG, 2002. Proceedings... Viçosa, Brazil, 2002.

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SANT'ANNA-SANTOS, B F.; ALVES, E. F ; SILVA, L. C. da ; AZEVEDO, A. A Efeitos da Chuva Acida Sobre a Estrutura da Lâmina Foliar de Gallesia gorazema moq. (phytolaccaceae). In: NATIONAL BOTANICAL CONGRESS, 52, 2001, João Pessoa, Paraíba, Proceedings... João Pessoa, Brazil, 2001.

PARTICIPATION IN CONFERENCES

Sustainability & Forest Bio Refinery II: Bringing Bio-based Products to Market Syracuse, NY, October, 2008

Forest Bio-Refinery: Establishing a Path Forward to Cellulosic Ethanol and other Bio-products. Liverpool, USA, October, 2007

3rd ICEP - International Colloquium on Eucalyptus Pulp. Belo Horizonte, Brazil, March, 2007

39th Pulp and Paper International Congress. São Paulo, Brazil, October, 2006

38th Pulp and Paper International Congress. São Paulo, Brazil, October, 2005

37th Pulp and Paper International Congress. São Paulo, Brazil, October, 2004

Seminar of Eucalyptus Fibers Quality for Paper Production. Viçosa, Brazil, September, 2004

36th Pulp and Paper International Congress. São Paulo, Brazil, October, 2003

1st International Colloquium on Eucalyptus Kraft Pulp. Viçosa, Brazil, September, 2003