Hot Water Extraction and Subsequent Kraft Pulping of Pine Wood Chips

by

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Abstract

This research investigated the effects of pre-extraction time, temperature, and pH on the rate and quantity of sugars recovered from Loblolly pine wood chips and the impact this treatment has on pulp kappa number and yield. Composition analysis of raw chips, extracted chips, pulp, and hydrolyzate were performed to assess the hemicellulose extraction efficiency and subsequent loss during kraft pulping of Loblolly pine. A pseudo kinetic model of prehydrolysis extraction was developed from the hydrolyzate sugar concentration data.

Preliminary experiments demonstrated the potential for influencing pulp properties and sugar recovery in hydrolyzate through on-line control of prehydrolysis pH, reaction temperature, and time. A second set of experiments examined these factors and added a presoak period to the design matrix. A third set of experiments used a best case of pre-extraction conditions to test five potential pulping additives.

It was concluded that the extraction rate for all sugars was increased with either increasing temperature from 140 to 170°C or decreasing pH from 4.5 to 3.0. The hydrolysis was selective for hemicellulose as opposed to cellulose by using temperature at 140°C. Both pH and temperature also impacted the degradation rate of sugars in solution. The 24 hour presoak at 25°C with various pH levels had no measurable effect on hydrolysis rate or pulp yield.

The additives tested in this research: anthraquinone, acetaldehyde, ethanolamine, lithium aluminium hydride, and hydroxylamine, were not successful in recovering pulp yield from extracted chips to that of a standard kraft cook with the conditions tested. More work could be justified with hydroxylamine or to test the use of anthraquinone in conjunction with hydroxylamine or another successful additive.

A pseudokinetic model of the extraction was calculated using an activation energy of 27 kcal/mole for hemicellulose hydrolysis and a term for the acid concentration. This modified H-factor model described the sugar extraction data except when significant degradation of sugars was observed. The data for chip weight loss and pulp yield also fit a smooth curve when plotted against the modified H-factor.

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Dr. Gopal has been not just my academic advisor but also a friend from the time of my undergraduate experience at Auburn University from 1985-89 through my professional experience in the pulp and paper industry. I have not always heeded his advice, but I typically have seen its wisdom in hindsight.

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Janine and Elizabeth were children when I started this project and are now beautiful young women. They have reversed roles and been an example to me of getting their homework done and performing well in school.

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Penny has stood beside me, in front of me, behind me… all the time showing me that she loves me just for who I am even though she doesn't always agree with what I do. I hope that my love in return is as apparent.

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List of Abbreviations

AA	Active Alkali, NaOH + Na_2S
AQ	Anthraquinone
AHQ	Anthrahydroquinone
ARA	Arabinose
ASABE	American Society of Agricultural and Biological Engineers
AU	Auburn University
bd	Bone dry
CTO	Chief Technology Officers
DF	Degrees of Freedom
DIW	Distilled Deionized Water
Dp	Degree of Polymerization
EA	Effective Alkali, NaOH + $Na_2S/2$
EISA	Energy Independence and Security Act of 2007
FPL	Forest Products Laboratory
FUR	Furfural
GAL	Galactose
GHG	Greenhouse Gas
GLU	Glucose
HMF	Hydroxymethyl furfural

MAN	Mannose
REA	Residual Effective Alkali
SS	Sum of Squares
SUNY – ESF	State University of New York College of Environmental Science and Forestry
tpd	Tons per day
TTA	Total Titratable Alkali, NaOH + Na_2S + Na_2CO_3
VPP	Value Prior to Pulping
XYL	Xylose

Mathematical Abbreviations:

C_C	Carbohydrate or hemicellulose concentration
C_{C0}	Initial carbohydrate or hemicellulose concentration
C_A	Acid concentration
Ea	Activation energy
R	Ideal gas constant
k_C	Rate constant
k'_C	Combined rate constant at constant pH
k_0	Rate constant at reference conditions of temperature and pH
k'_0	Rate constant at reference pH and constant temperature
T	Process temperature
T_0	Reference temperature

Chapter 1 Introduction

1.1 Research Synopsis

The purpose of this research was to investigate the effects of varying hot water extraction time, temperature, and pH on the rate and quantity of hemicellulose sugars recovered from Loblolly pine wood chips and the effects this prehydrolysis treatment has on kraft pulp yield and the severity of kraft cooking required to reach a pulp kappa number target. The target sugars are currently chemically degraded and/or burned at a low heating value as a component of black liquor in the industrial kraft pulping and chemical recovery process. Recovery of the sugars prior to pulping would allow them to be redirected to a better end use. Composition analysis of raw chips, extracted chips, pulp, and hydrolyzate were performed to assess the hemicellulose extraction efficiency and subsequent hemicellulose yield loss during kraft pulping of Loblolly pine. On line control of the extraction pH and temperature were used to influence the quantity of hemicellulose recovered in the hydrolyzate and the yield and properties of the final pulp. Selected conditions of extraction and cooking were then chosen for evaluation of pulp yield improvement additives.

Reports of previous efforts by other researchers and preliminary work accomplished in this study identified significant reductions in pulp yield and strength following kraft cooking of extracted chips. The reduction in strength is particularly problematic with southern pine pulp since it is included in paper and board products

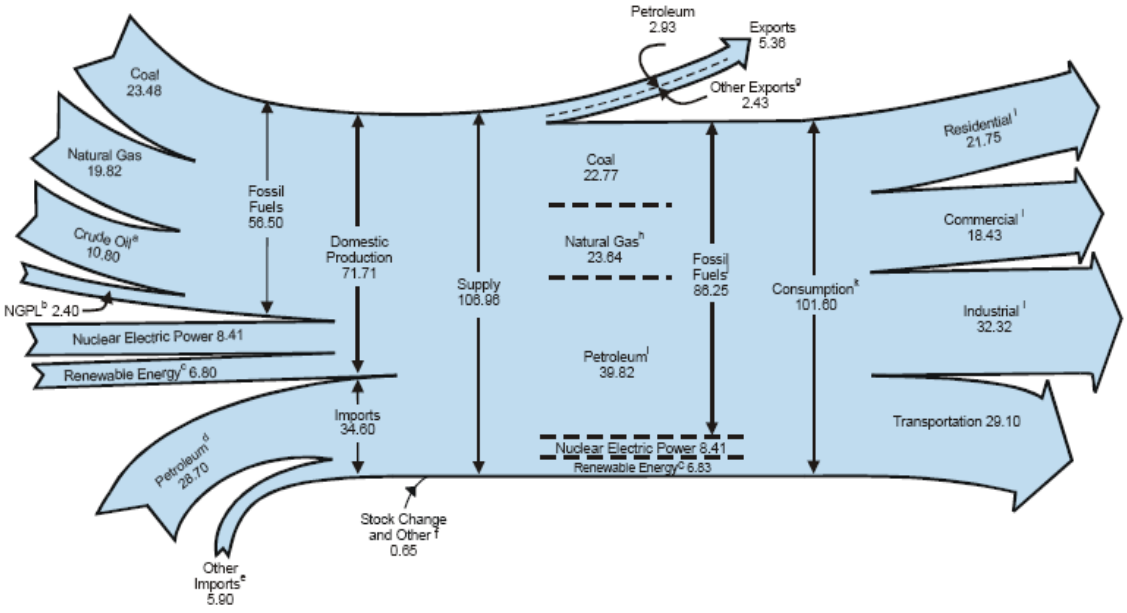
primarily for its strength contribution. Additionally, pine lignin is more sensitive to deactivation (condensation reactions) in acid conditions than hardwood lignin. Therefore, severe extraction conditions will force stronger cooking conditions further reducing yield. Economics of the process are also expected to be more difficult with pine than hardwoods since there is a lower proportion of hemicellulose in the native pine wood. Successful conversion to ethanol of 50% of hemicellulose (12% of the wood weight) from pine wood that is currently processed to kraft pulp represents approximately 280 million equivalent gallons of gasoline per year. This could replace 0.2% of the 2010 U.S. consumption of 138,500 million gallons of gasoline per year (EIA U.S. Petroleum Product Supplied 2010).

Preliminary experiments illustrated the potential for influencing pulp yield and sugar recovery in hydrolyzate liquids by manipulation and control of pH, reaction temperature, and time of prehydrolysis. A second set of experiments contained these influences and added a presoak period to the design matrix. A third set of experiments used a chosen best case of pre-extraction conditions to test the potential advantage of pulping additives in increasing pulp yield.

1.2 Perspective

The United States' dependence on fossil fuel for energy and, in particular, on petroleum for transportation fuels has led to instability in economics, potentially devastating environmental effects, and difficult foreign policy situations. These difficult circumstances could all be improved by substituting domestic renewable energy sources in the place of imported fossil fuels. In 2007, the USA consumed 102 quadrillion Btu (Quads) of energy with 85% of this being derived from fossil sources. Transportation

consumed 29 Quads of energy with most of this in the form of liquid fuels derived from crude oil or petroleum (Department of Energy 2008). Figure 1 shows an energy flow diagram for the United States including energy supply by source and consumption by category (Department of Energy 2008). Renewable sources including solar, wind, biomass, hydropower, and geothermal made up less than 7% of the energy consumed (Energy Information Administration 2008).



[a] Includes lease condensate.
[b] Natural gas plant liquids.
[c] Conventional hydroelectric power, biomass, geothermal, solar/photovoltaic, and wind.
[d] Crude oil and petroleum products. Includes imports into the Strategic Petroleum Reserve.
[e] Natural gas, coal, coal coke, fuel ethanol, and electricity.
[f] Adjustments, losses, and unaccounted for.
[g] Coal, natural gas, coal coke, and electricity.
[h] Natural gas only; excludes supplemental gaseous fuels.
[i] Petroleum products, including natural gas plant liquids, and crude oil burned as fuel.
[j] Includes 0.03 quadrillion Btu of coal coke net imports.
[k] Includes 0.11 quadrillion Btu of electricity net imports.
[l] Primary consumption, electricity retail sales, and electrical system energy losses, which are allocated to the end-use sectors in proportion to each sector's share of total electricity retail sales. See Note, "Electrical Systems Energy Losses," at end of Section 2.

Notes: • Data are preliminary. • Values are derived from source data prior to rounding for publication. • Totals may not equal sum of components due to independent rounding.
Sources: Tables 1.1, 1.2, 1.3, 1.4, and 2.1a.

Figure 1 2007 U.S. energy flow diagram (Department of Energy 2008).

Any of these renewables can fuel electricity production at stationary sources with existing technology, but biomass is uniquely suited to replace petroleum transportation fuel needs at least until battery and fuel cell technologies are fully matured. Biomass can be refined into energy dense alcohols or alkanes for substitution into liquid fuels markets

or even gasified to syngas and burned directly in specially modified engines (Whitley 2008). The U. S. Departments of Energy and Agriculture published a report now known as "The Billion Ton Report" in 2005 with the aim of estimating the capability of sustainably harvested biomass to replace 30% of current U.S. petroleum consumption. The report concludes that this can be achieved with fairly conservative assumptions but not without considerable effort (Perlack, et al. 2005). This research contributes to that effort by investigating a potential method of improving the utilization of an industrial biomass byproduct.

1.3 Dissertation Organization

This report is organized into five sections:

Chapter 1 introduces biorefineries as they exist in 2010 and briefly discusses how they are expected to progress over the next twenty years. The various biomass feedstock materials that are available for conversion to energy are discussed with an emphasis on wood and the chemistry of wood that is pertinent to this research. This is followed by a brief discussion of the history of processing wood into paper and the current state of the art of kraft pulping. Chapter 2 is a review of publications related to the specific area of biorefining that is the topic of this research, Value Prior to Pulping (VPP).

Chapters 3, 4, and 5 present laboratory methods, experiments, and results that were performed to investigate prehydrolysis pulping of loblolly pine with regard to VPP.

Chapter 6 includes a review of literature regarding chemical additives for pulp yield improvement and lab tests that were performed to screen several potential additives when pulping prehydrolyzed chips.

The development of mathematical models to predict sugar recovery from the prehydrolyzate is presented in Chapter 7 along with some review of literature in this area.

Overall conclusions and recommendations for future work are in Chapter 8.

1.4 Biorefineries

A biorefinery is "A facility that uses mechanical, thermal, chemical, and/or biochemical processes to convert biomass into value-added biobased products or key intermediates for the production of chemicals and other materials." (ASABE S593 2006) Common use of the term often implies that fuel or energy must be a primary and potentially salable product analogous to an oil refinery and this convention is followed here. A biorefinery is then viewed as a biomass processing facility that will help the USA reduce its dependence on fossil fuels and in particular imported petroleum. Current production of biofuels consists primarily of ethanol from starch or sugar and biodiesel from vegetable oils or animal fats. Energy efficiency and economics can be improved in all of these processes by proper utilization of byproduct materials and rejected heat.

Ethanol is produced from sugar cane or sugar beets by fermentation with yeast to form "beer" followed by distillation with heat to concentrate the ethanol. Further purification with a molecular sieve can reduce water content if necessary. When the starting material is starch from grain, the additional step of hydrolysis of starch to dextrose with enzymes or weak acid is required. Additional pretreatments are required to prepare other plant materials for fermentation. There are presently 204 ethanol refineries either operating or under construction in the USA with an operating capacity of 13,823 million gallons per year (mgy) and total capacity of 14,295 mgy (Renewable Fuels Association 2011). Most of these plants use corn grain as the feedstock, but milo, barley,

wheat starch, and alternative sources including cheese whey, potato waste, wood waste, waste beer, beverage waste, and sugar cane bagasse are also minimally represented.

Biodiesel is typically produced by lye-catalyzed transesterification of the oil with methanol. In April 2009, there were 137 biodiesel plants with capacity of 2285 mgy that used mostly vegetable oil feedstock but some could use animal fats or multiple feedstocks. (Biodiesel Magazine 2009) Estimated actual production was much lower than capacity due to shortage of feedstock and poor economics. In addition to the capacity listed above, 46 biodiesel plants were idle with a potential capacity of 594 mgy.

The direction of biofuel production in the USA over the next 10 years will likely be influenced heavily by the Energy Independence and Security Act of 2007 (EISA). This act mandates the production of renewable fuels to increase from 9 billion gallons of conventional renewable biofuels in 2008 to a total of 36 billion gallons of renewable fuels in 2022 with a maximum of 15 billion gallons from conventional biofuels and the rest from advanced biofuels. "Conventional biofuel" includes ethanol produced from corn starch, but plants constructed after 2008 must also demonstrate greenhouse gas (GHG) emission reductions of at least 20% when compared to a baseline. "Advanced biofuel" must be made from renewable biomass other than corn starch and must demonstrate a 50% reduction in GHG emissions. "Cellulosic biofuel" is an advanced biofuel made from renewable lignocellulosic feedstock that meets the higher standard of 60% GHG emission reduction (Renewable Fuels Association 2008).

Production processes for cellulosic biofuels can generally be divided into two major categories: the biochemical technologies or "sugar platform" and thermochemical technologies. Processes that fall under the sugar platform separate the sugar monomers

from the rest of the biomass material and ferment the sugars into ethanol. The non-sugar biomass may be burned to fuel the plant or put to some other use, but the maximum yield of biofuel depends on the amount of sugar in the original feedstock and is typically about 90 gallons of ethanol (equivalent to 60 gallons of gasoline) per ton of biomass. Thermochemical processes include gasification and other processes that use heat to break down all of the organic material in the biomass to small, simple molecules and then either burn this mixture directly for fuel or process it further into fuels or chemicals. Biofuel yield in this case depends on the process but could be upward of 100 gallons of gasoline equivalent fuel per ton of biomass.

There has been much written recently about converting "pulp mills" into "biorefineries". A series of articles in Paper 360° discussed the reasons for integrating biorefineries with existing pulp mills (Thorp, Thorp and Murdock-Thorp 2008), the pathway options (Thorp, Thorp and Thorp 2008), the status of current projects (Thorp, Thorp and Murdock-Thorp 2008), and summarizes the economics associated with a hypothetical gasifier and gas-to-liquids plant (B. A. Thorp 2008). The paper and timber industries can be viewed as biorefineries using the ASABE S593 definition above, but they have really been thought of as single product lumber mills or paper mills. The facilities are well suited for transition from mills to biorefineries since they have a long history of experience effectively managing large quantities of biomass including planting, harvesting, transportation, storage, and processing into finished products often with fuel or energy as a byproduct. This reinvention of the pulp mill will hopefully lead to higher material and energy efficiencies, reduced impact on the environment and a sustainable future for the pulp industry in North America even though they already have a history of

efficient and complete use of their raw material. Another pair of articles discussed the technological options (Agenda 2020 CTO Committee Working Group 2008) and business case (Agenda 2020 CTO Committee Working Group 2008) for a stepwise implementation of a thermochemical biorefinery at a pulp mill. The final mill would be fossil fuel energy independent and carbon neutral in addition to producing pulp and paper products and renewable energy. The business case shows the plant to be profitable although the capital intensity is high relative to an analogous fossil fuel plant and the high costs of transporting low energy density biomass to the mill limits the size of the facility.

There are several potential ways to implement a biorefinery concept at a pulp mill that vary from stepwise modification of existing processes to wholesale replacement of sections of the mill. Installation of a hog fuel gasifier to produce syngas to fuel the lime kiln is an example of a small project while modification of the pulp mill or recovery island to produce byproduct ethanol, acetic acid, or Fischer-Tropsch liquids currently have more risk technologically and financially. Wood residue gasifiers have been installed to supply kiln fuel since the 1980s but have struggled with low reliability. Most of the problems are associated with the feed systems and dryers that are required to raise the heating value of the wood residue (Francey, Tran and Jones 2009). Syngas has a lower heating value than the typical kiln fuels natural gas and fuel oil.

The Flambeau River Biofuels project that is expected to be complete in 2013 but has some funding problems (Brochu 2010) is an example of a bigger biorefinery project. The AVAP^{tm} process, a proprietary ethanol solvent pulping and recovery system, was originally proposed for this project (Retsina and Pylkkanen 2007). If constructed as planned in 2009, however, the project will gasify 1000 bone dry tons per day (bd tpd) of

forest residuals and agricultural waste. The syngas will be used to produce renewable biodiesel and paraffin via the Fisher-Tropsch process while excess process heat will be used in the adjacent pulp and paper mill (Patrick 2009). Gasification of black liquor is now ready to move past the demonstration stage and be applied at commercial scale (Barry and Leblanc 2009). Several projects at various stages of development were briefly described in Paper 360° (Thorp, Thorp and Murdock-Thorp 2008).

Twelve different potential pathways for implementation of the biorefinery concept that are in various states of conceptualization to commercialization are illustrated in Figure 2 (Thorp, Thorp and Thorp 2008). These pathways each have advantages or disadvantages based on how close they are to commercialization, expected capital requirement, and potential energy transformation efficiency. As an example, paths that follow the sugar platform to produce ethanol are in general further along technologically and have received a majority of research funding, but have lower potential for energy conversion than paths that can make use of lignin and other organics in addition to fermentable sugars. Pathway #8 of this biorefinery concept is extracting "Value Prior to Pulping" (VPP) which involves pretreating chips to remove valuable chemicals like acetic acid or fermentable sugars before they would be degraded by alkali in cooking the chips to produce pulp. An ideal implementation of VPP would produce no changes in pulp yield or properties from a standard pulp. The only change would be that some of the wood chemicals that are not retained in the pulp would be intentionally directed out of the black liquor to some higher economic end use. Kraft pulping presently removes and degrades a significant percentage of hemicellulose and small amounts of cellulose from

the wood. These sugar degradation products are burned in the chemical recovery unit along with lignin to produce steam for mill operations.

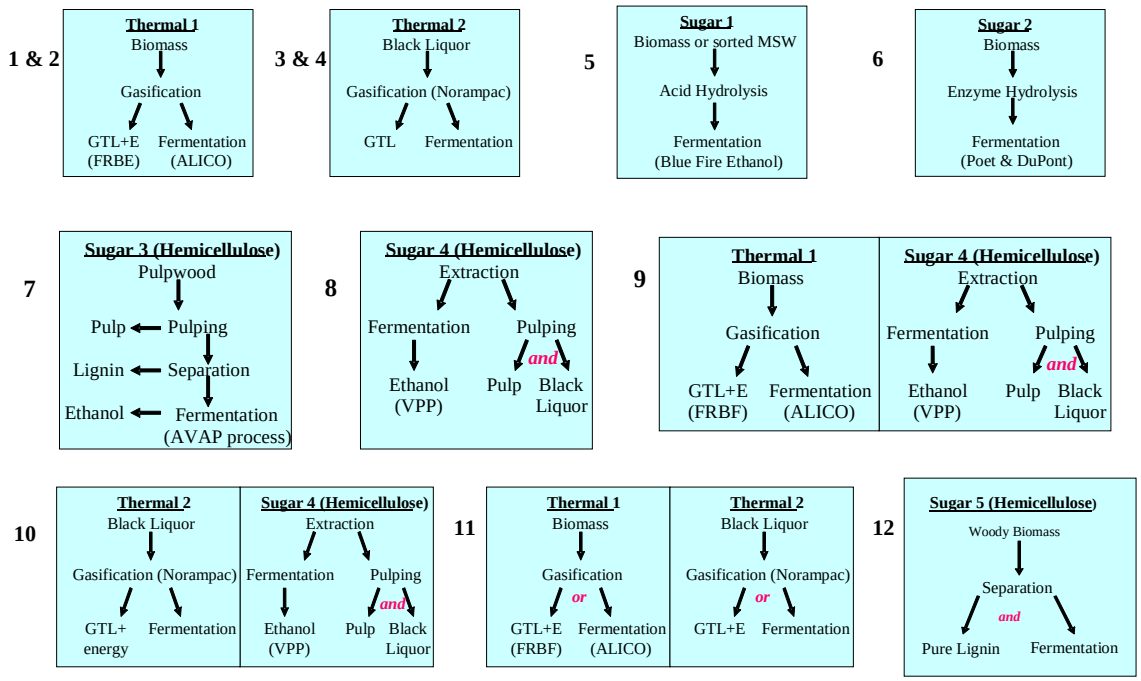


Figure 2 Potential biorefinery pathways (Thorp, Thorp and Thorp 2008).

1.5 Biomass Feedstock

Most of the biorefineries that currently produce liquid fuel as the primary product make ethanol from starch or sugar or biodiesel from vegetable oils. These processes may be close to their production limit politically due to conflicts over using food and farmland to produce fuel. Biofuel production has been blamed for higher food costs worldwide and for deforestation in South America and South East Asia as palm oil plantations replace peat bogs and soybeans replace rain forest (Grunwald 2008). Producing biomass

for fuel on existing crop land can cause a net increase in greenhouse gas emissions due to carbon emissions associated with land use change. This increase in emissions is greatest if using croplands for energy requires clearing new land areas for displaced crops, but there can be a detrimental effect even when no new land is cleared if the new crop sequesters less carbon than the old one did (Searchinger 2008). To minimize the "carbon debt" associated with land use change, an emphasis should be placed on using waste biomass or perennials planted on unused land (Fargione, et al. 2008).

These concerns and others were addressed in the "billion ton report" (Perlack, et al. 2005) in an effort to determine a feasible path for sustainably replacing 30% of 2005 petroleum use with biofuels by 2030. The target for this report of approximately one billion dry tons of feedstock per year came from the assumption that 60 gallons of gasoline equivalent liquid fuel or 90 gallons of ethanol can be produced per ton of biomass. Potential sources of biomass are divided into two groups for this report, agricultural resources and forest resources. Agricultural resources include: corn and soybeans, crop residues, perennial grasses and woody crops, animal manures, food/feed processing residues, and municipal solid waste. Forest resources include logging residues, removal of excess biomass from forest lands, fuelwood, wood processing mill residues, pulping liquors, and urban wood residues. Forest residuals contribute 368million dry tons annually in this estimate or about one third of the total.

Biomass resources can also be categorized by type. The billion ton report lists 87 million tons of grain for ethanol production and 87 million tons of process residues including manure and municipal solid waste. The rest of the material can be called "lignocelluloses": biomass derived from plant cell walls consisting primarily of cellulose,

hemicellulose, and lignin. Lignocelluloses include crop residues like corn stover and wheat straw; energy crops like switchgrass, giant reed, and miscanthus; sugar crops like energy cane and sorghum; and wood. Considerations on which would be the best energy feedstock in a particular geographical area include: dry matter yield per acre per year, soil considerations, water requirement, fertilizer requirement, issues of harvest, storage concerns, ease of drying, invasivity, and potential for competition with food crops. Each plant also has chemical differences that can be concerns including ash composition, hemicellulose type, and extractives composition. Examples of these concerns are high silicate ash content of corn stover and wheat straw and the potential for pine resin and some five carbon sugars to reduce the effectiveness of or stop fermentation.

Lignocelluloses have some common chemical structures and some that are species specific. Cellulose is the most abundant biopolymer in the world and is made up of a long, linear chain of β-D- glucopyranose linked by 1-4 glycosidic bonds (Stenius 2000, 34). A short section of cellulose is illustrated in Figure 3. It forms intra and

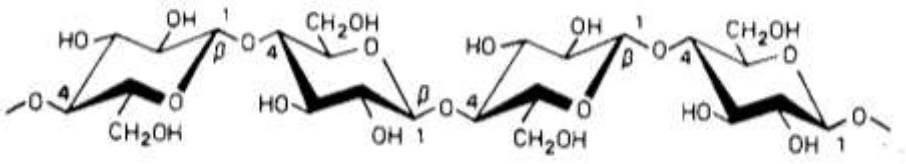


Figure 3 Cellulose structure (Sjostrom 1993, 54).

intermolecular hydrogen bonds that cause it to have crystalline and amorphous regions in the plant cell wall. The crystalline regions cause cellulose to be relatively inert and insoluble in most solvents. The length, or degree of polymerization (Dp), of cellulose

varies with cell type and species. Wood cellulose normally has around 10,000 units while cotton has about 15,000.

Hemicellulose is also a polymer of sugars, but it is shorter, branched, made up of multiple components and in some cases can be water soluble. The branched form inhibits formation of crystalline regions in native hemicellulose, but some types can be crystalline after pulping if the branches are selectively removed (Rydholm 1985, 158). The structure and composition of hemicellulose varies by species and in some cases by cell type and location (Stenius 2000, 36). Examples of hemicelluloses common in softwood are illustrated in Figure 4 and Figure 5.

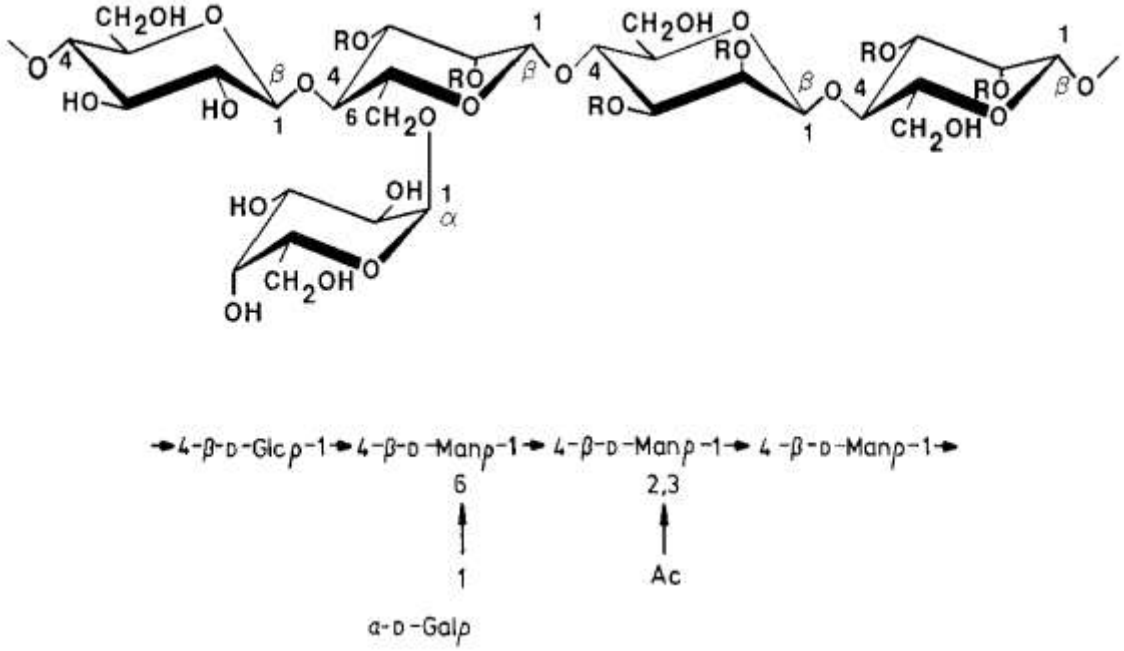


Figure 4 Galactoglucomannan structure (Sjostrom 1993, 65).

Lignin is an amorphous aromatic polymer of phenyl propane units joined mostly with ether linkages or carbon-carbon bonds. Lignin is often thought of as the glue that holds the cell wall fibers together. There is some evidence for bonding between lignin

and carbohydrates, especially hemicelluloses, but the nature of this bonding is not well understood. The structure of lignin has been approximated as shown in Figure 6.

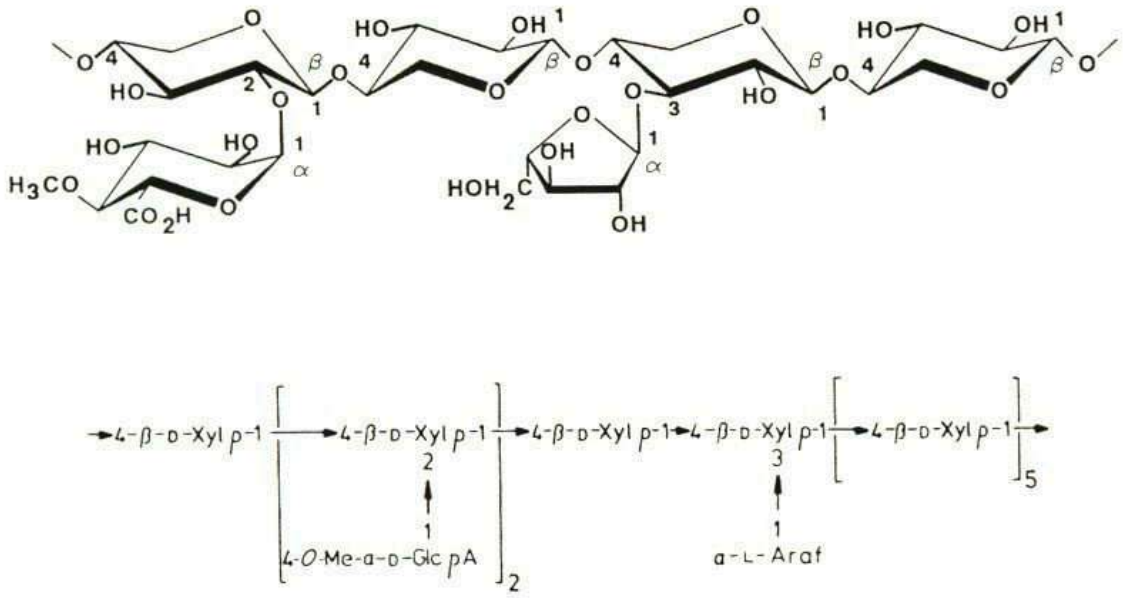


Figure 5 Arabinoglucuronoxylan structure (Sjostrom 1993, 65).

Extractives are generally relatively small, nonstructural and species specific components of lignocelluloses. They are named because they can be extracted from the plant material with organic solvents or water. They typically make up a small fraction of the plant by mass, but may give the plant some of its unique character. For example, the scent and rot resistance of cedar comes from thujaplicin, an aromatic compound with a seven-member ring that is toxic to most wood decay organisms (Sjostrom 1993, 97).

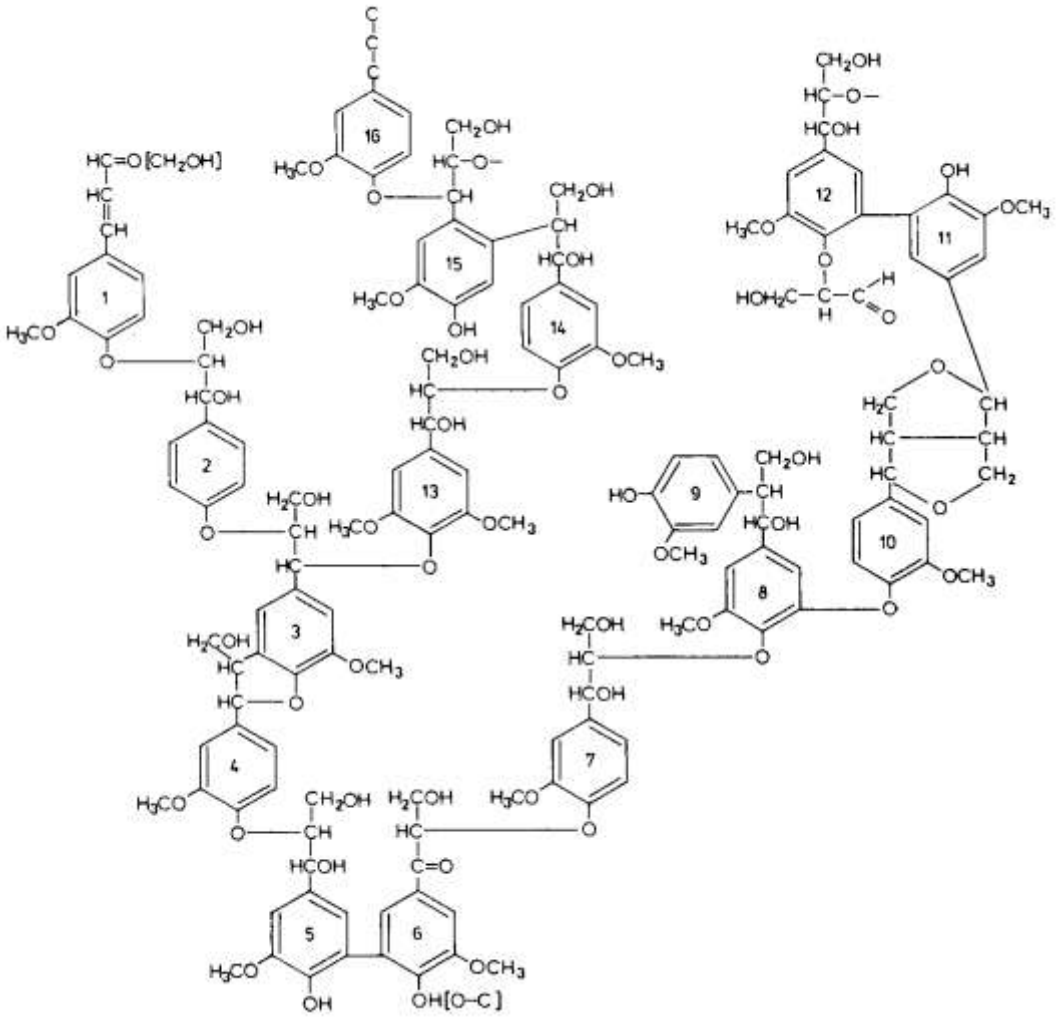


Figure 6 Segment of softwood lignin structure (Sjostrom 1993, 84).

Wood has several advantages over other biomass feedstocks in terms of the handling characteristics during a continuously operating process. It can be sustainably harvested during most of the year and stored for relatively long periods of time as whole logs or chips. The inorganic ash content of wood is typically less than 1% but the inorganic content of bark can be substantially higher at 2-5% (Sjostrom 1993, 107,113) which is one reason bark is typically separated from wood at an early stage of processing. The dry matter yield for wood is similar to other potential energy crops like switchgrass at 4 to 8 dry tons per acre year (Graham, et al. 1995) but harvesting logistics

would be different since it would be performed less often. There is already an infrastructure in place for harvest, transport, and handling of large quantities of wood, but this will need to be modified somewhat to enable the use of harvesting residuals and other materials that are not already sent to the mills.

Wood species are generally classified as hardwood or softwood. These groups vary from each other distinctly not only in physical appearance but also in chemical structure. Most woods have about 40-45% cellulose and less than 5% extractives on a dry basis, but softwoods typically have 25-30% hemicellulose and 25-30% lignin while hardwoods typically have 30-35% hemicellulose and only 20-25% lignin (Stenius, 29). Hemicelluloses in softwood consist mostly of galactoglucomannan and arabinoglucuronoxylan. Hardwood hemicellulose content is made up of mostly glucuronoxylan with some glucomannan. Lignin in softwood is generally classified as "guaicyl" lignin and is made of mostly trans-coniferyl alcohol precursors with some trans-p-coumaryl alcohol. Hardwood lignin is called "guaicyl-syringyl" lignin and is made up of about 50% each of trans-coniferyl and trans-sinapyl alcohols. Wood chemical composition also varies between heartwood, sapwood, and reaction wood within a single tree.

Two sets of carbohydrate reactions were of interest in this research: those that happen in the acid environment of prehydrolysis and those that occur in the alkaline environment of kraft cooking. Hydrolysis of bonds between sugar monomers takes place as long as the carbohydrates are exposed to hot cooking liquor in either case. The rate of hydrolysis increases with temperature above 100°C and as pH is either increased or decreased from near neutral where a minimum rate occurs. Hemicelluloses respond

differently at either end of the pH spectrum. Galactoglucomannan is more active than xylan on the alkaline side while the xylans are more easily hydrolyzed on the acid side (Ingruber, Kocurek and Wong 1985, 34-38). Suggested means of increasing the yield of these two components are also different. A neutral or alkaline treatment prior to acid treatment can increase the yield of glucomannan while xylan loss can be minimized by reducing the residual alkalinity at the end of the alkaline cook. Hydrolysis of various carbohydrate components occurs at different rates with the five-carbon sugars reacting faster than the six-carbon and galactose faster than mannose which is faster than glucose. Cellulose is fairly resistant to acid hydrolysis due to its ordered structure and crystalline regions but is reactive in more severe environments (e.g. mineral acid at temperatures above 120°C) and in areas damaged by mechanical action. The hydrolysis does not cause substantial yield loss in an acidic environment, but it can reduce chain length and increase yield loss in subsequent alkaline treatments. Acid hydrolysis is much faster than the similar alkaline reaction and also has a higher tendency to occur at the end of the polymer chain (Sjostrom 1993, 46).

In addition to random chain scission by hydrolysis, the most important reactions in strong alkali for both cellulose and hemicellulose are the endwise ”peeling” reaction that shortens the chain from the reducing end one sugar monomer at a time and the competing “stopping” reaction that produces an alkali stable end group. Alkaline scission has only a minimal direct effect on yield, but a dramatic effect on degree of polymerization. A large percentage of pulp yield is lost to peeling of reducing sugars in alkaline pulping even though these represent only about 0.2 % by weight of the native wood (Procter and Apelt 1969) because peeling and scission each produces a new

reducing end group that can allow peeling to continue or start again. The stopping reaction kinetically limits peeling to about 60 monosaccharide units (one study found the "zip length" to be 84 for cotton cellulose and 53 for Douglas fir derived holocellulose (Agarwal, McKean and Gustafson 1992)), but peeling will also be terminated by physical inaccessibility in crystalline areas or by dissolution of a shorter chain. Destruction of glucomannan is by peeling and dissolution of smaller fractions. Cellulose yield loss is also primarily by peeling; "primary" during initial heat up and then "secondary peeling" after cleavage at higher temperatures. Xylan removal is by dissolution of soluble fractions rather than peeling (Grace 1989, 48). These mechanisms were determined by using a borohydride to prevent peeling. Sugar monomers are subject to rearrangement to other sugars or conversion to carboxylic acids in strong alkali.

1.6 Pulping Methods

Processes for turning wood into pulp for paper and board manufacture can be divided into methods that preserve wood yield by producing pulp through primarily mechanical forces and methods that chemically purify fibers. Mechanical pulping methods use mechanical force, heat, and or pressure, and sometimes mild chemical treatments to physically disrupt wood structure into pulp. This pulp is suitable for grades of paper that do not require great physical strength or longevity of quality like newsprint. The advantages of these methods are low manufacturing cost with the exception of high energy usage and high yield of pulp that gives good print quality. Chemical pulping methods, on the other hand can produce pulp of controlled chemical purity ranging from removing just enough extractives and lignin to separate fibers to almost pure cellulose depending on product requirements. All pulping methods have continuously evolved to

improve economic performance and to meet new requirements of improved product quality and cleaner environmental performance.

The soda pulping process was first used commercially to manufacture pulp from poplar wood in 1854 (Smook 1982). Modifications to the process included regeneration of alkali for economic purposes through combustion of waste liquor and causticization of sodium carbonate. The kraft process almost completely replaced the soda process after sodium sulfate was substituted as a less expensive replacement for the sodium carbonate make-up chemical and the resulting pulp was found to be stronger. The soda process is similar to the kraft process which will be described later except that sulfur is kept out of the liquor cycle. The process is used only rarely today in cases of local sensitivity to the unpleasant odor of kraft recovery and waste treatment. In these cases, delignification is usually enhanced by the addition of anthraquinone (AQ) to the cook to make the "soda-AQ" process. There is more discussion of AQ in Chapter 6. The only soda AQ mill currently operating in the USA is in Tennessee.

Patents for a pulping process using bisulfites and sulfur dioxide were issued to Tilghman in 1866 and 1867 (Rydholm 1985). Sulfite cooking liquor consists of water, sulfur dioxide, and a base for the resulting bisulfite that depends on the target pH. Commercial processes followed later using magnesium, calcium, sodium and ammonium as the base for the bisulfite. The process grew in popularity because it produced a relatively bright unbleached pulp at good yield on wood that was easy to bleach to higher brightness. The process could also be modified to produce high cellulose dissolving pulps. The sulfite process is very sensitive to bark contamination and extractives, though, which restricts the process to only a few wood species: spruce, fir, hemlock, and a few

hardwoods. Chemical recovery systems were later developed and the sulfite process was the dominant chemical pulping process in the first half of the 20th century. The acid sulfite process has since mostly disappeared due to advancement in bleaching kraft pulp, continuing environmental problems with biological oxygen demand (BOD) in liquid effluent, and atmospheric sulfur dioxide losses (Gullichsen and Fogelholm 1999). Only four acid sulfite mills remained open in the USA in 2006 with a total production of about 450,000 tons per year of bleached pulp. The newest of these mills was constructed in 1969 (Matussek 2006).

Discussion of the sulfite process is included here because the process allowed, in some cases, for efficient manufacture of products from the spent liquor in addition to burning the waste organics for fuel. Ethanol, proteins, vanillin, and lignosulfonates were all produced either directly in the process or from components of the liquor at mills like the one closed by Georgia Pacific in 2001 at Bellingham, WA. The sulfite process is now represented mostly by Neutral Sulfite Semichemical (NSSC) mills that manufacture high-yield high strength fibers from hardwood for corrugating medium although there has been some expression of optimism in the literature for mills that combine alkaline sulfite with AQ catalyst and for mills that mix sulfite with kraft in a combined recovery system (Ingruber, Kocurek and Wong 1985).

Kraft pulping of wood is currently the dominant method of producing chemical pulp for paper and paperboard products. This process uses “white liquor”, a solution of sodium hydroxide and sodium sulfide, to delignify the wood at a very alkaline pH of 12 to 14 and temperature of about 170°C. Industrial white liquor also contains sodium carbonate and other components resulting from the recovery cycle. The kraft process has

mostly replaced the non-sulfur soda process and the sulfite processes because it produces a stronger pulp and it has an efficient process for recovering cooking chemicals. The recovery process also produces energy from burning the organic material in the "black liquor" that is washed from the pulp after cooking. Kraft pulping can be accomplished with most wood species and can handle contaminants like bark and dirt to a certain level. Some contaminants like excess calcium or silica can cause operational difficulties or reduced pulp quality. The primary advantage of kraft pulping over soda is that the time required for delignification is reduced by 50%. This effectively doubles the production rate while giving less time for destructive carbohydrate hydrolysis reactions (Rydholm 1985, 311). Kraft cooking cycles are also shorter than sulfite due to shorter heat-up time and typically higher final cooking temperature. Anthraquinone is sometimes used with kraft pulping but the benefits are lower than that observed with soda cooking (Sjostrom 1993, 156). The justification for using expensive AQ in kraft pulping is usually to relax a bottleneck in pulp production that can be improved by increasing pulp yield.

The kraft cook is performed in a special pressure vessel or digester. The temperature of the cooking reaction controls the rate of reaction and the type of equipment required. The 165 to 170°C typically used in industrial kraft pulping corresponds to about 100 psi since the solution is mainly water. Traditionally, and in many current operations, the cook was a batch operation and the digester was a tall tank that was designed to withstand the pressure, temperature, and corrosive nature of the cooking liquors. For batch digesters, the chips are fed into the vessel followed by steam to remove air followed by a combination of white liquor and spent "black liquor" to make up the required volume. The digester is capped and heated by direct or indirect steaming.

After the appropriate time, a valve at the bottom of the digester is opened and the chips and liquor are "blown" to a separate tank. The release of pressure can help physically break the cooked chips into pulp, but it can also damage the pulp. Since the first Kamyr continuous flow digester was built in 1950, many installations have had continuous digesters where the presteamed chips and liquor slurry feed in the top of the digester and the pulp is released from the bottom in a continuous controlled manner (Smook 1982, 81). There are many different innovations in the ways the liquor and heat are added and recovered from all types of digester systems to improve the yield, strength and chemical makeup of the pulp and the energy economics of the process (Gullichsen and Fogelholm 1999, 52-56).

The aim of chemical pulping is typically to solubilize and remove most of the lignin while leaving the carbohydrate holocellulose, hemicellulose and cellulose, as intact as possible. A standard test of lignin remaining in pulp is the "kappa number". In this test a measured quantity of pulp is reacted with potassium permanganate for ten minutes before quenching with iodide. The solution is then titrated with thiosulfate. A typical brown stock kappa number target for softwood pulp that will be bleached is about 30 which corresponds to about 4.5% lignin remaining in the pulp. Since some of the lignin is bound to carbohydrates and carbohydrates are sensitive to reaction under the same conditions as lignin, the carbohydrate fraction normally receives some damage. It has been reported that under the strong alkaline conditions with pH above 12 in the heating stage of a kraft cook galactoglucomannan is 70% dissolved by 130°C, xylan begins to dissolve after 140°C and is 60% removed by 170°C. Cellulose begins peeling after 120°C followed by alkaline hydrolysis and secondary peeling at higher temperature

(Grace 1989, 46-49). By the end of a conventional cook, all of the pectin, starch, and arabinose, 70% of the galactoglucomannan, about 50% of the xylan, and about 10% of the cellulose would be expected to be removed resulting in a total sugar loss of just over 20% of the original wood (Grace 1989, 26-29) in addition to the roughly 30% of wood that is lignin. These sugars represent the opportunity for VPP.

The pulp or "brown stock" is suspended in black liquor following the cook. Black liquor includes the residual alkali from white liquor and salts of the organic materials removed from the chips. This slurry is typically fed through a screen or "knotter" to remove uncooked chips before washing. Brown stock washing separates the pulp from the black liquor and is typically a multi-stage counter current filtering process. Clean hot water that is typically reused from somewhere else in the mill is used as wash water on the last stage. The filtrate from the last stage is used as wash on the next to last stage. Some of the filtrate from the first stage is reused for digester dilution; the rest is concentrated in the evaporators and then burned in the chemical recovery boiler.

One of the biggest hindrances to expansion of kraft pulping historically was the dark color of the unbleached pulp and difficulty in bleaching without severe strength loss. The development of multistage bleaching followed by the introduction of bleaching with chlorine gas in around 1930 (Rydholm 1985, 280) produced the first fully bleached kraft pulp using a three stage chlorination, caustic extraction, hypochlorite (CEH) bleach plant with washing between stages. Chlorine dioxide (D) was introduced as an industrial bleach chemical in 1946 and by 1957 there were 43 D stages in operation (Dence and Reeve 1996, 81). This allowed southern pine pulp to be bleached to full market brightness while maintaining a strength advantage over sulfite pulps. Bleach plants

mostly stopped using chlorine or hypochlorite in the late 1990s due to environmental regulations and pulp quality concerns. Modern bleach plants typically have oxygen delignification (O) followed by three stage DED, four stage DEDD, or five stage DEDED to reach high brightness with kraft pulp.

Unfortunately, though understandably, most mills are divided up into the "paper" side, the "pulp" side, and the "recovery island" as main production areas for management with the woodyard, waste treatment, converting, and chemical preparation areas included in one of these or considered apart. These areas are often physically set apart from each other by a road or rail line as if to enforce the separation. This is unfortunate because a pulp and paper mill consists of not just a process that transforms wood from logs to chips to pulp to paper, but also several water and chemical process cycles that tie the areas together and often make discovery of the root cause of a disturbance in any area difficult.

The most important of the cycles in the kraft mill is the liquor cycle. The chemistry of the liquor recovery process actually suggests two cycles, the sodium cycle and the calcium cycle. A previously published elegantly simplified diagram of this process is presented as Figure 7 (Sjostrom 1993, 161). In this diagram, the sodium cycle is the top rectangle and the calcium cycle is the triangle below it with the two cycles interacting in causticizing. Starting with "Pulping", white liquor and wood are reacted then separated to pulp and black liquor in washing. The black liquor is burned to make energy and to regenerate the molten sodium carbonate and sodium sulfide "smelt" that is dissolved to form green liquor. The efficiency of this part of the recovery cycle improved dramatically following the invention by Tomlinson in 1927 (Rydholm 1985, 279) and subsequent commercialization in 1934 of the modern recovery boiler (Smook 1982, 130).

The sodium carbonate in green liquor reacts with quicklime to reform sodium hydroxide for white liquor. It is important that the white liquor and lime are effectively separated from each other as calcium in white liquor will cause scaling in the digester equipment and potentially give the pulp a blue shade. Sodium in the lime cycle will make the lime difficult to dry and can cause operational and environmental problems in the lime kiln.

Multistage pulping describes processes where the pulping chemistry is changed deliberately from outside the digester. There are many possible combinations of changes that are possible and there may or may not be washing between stages. Implementation of VPP will require some sort of multistage process. One published example used a mild alkaline extraction before kraft pulping (Al-Dajani and Tschirner 2008). Most work to

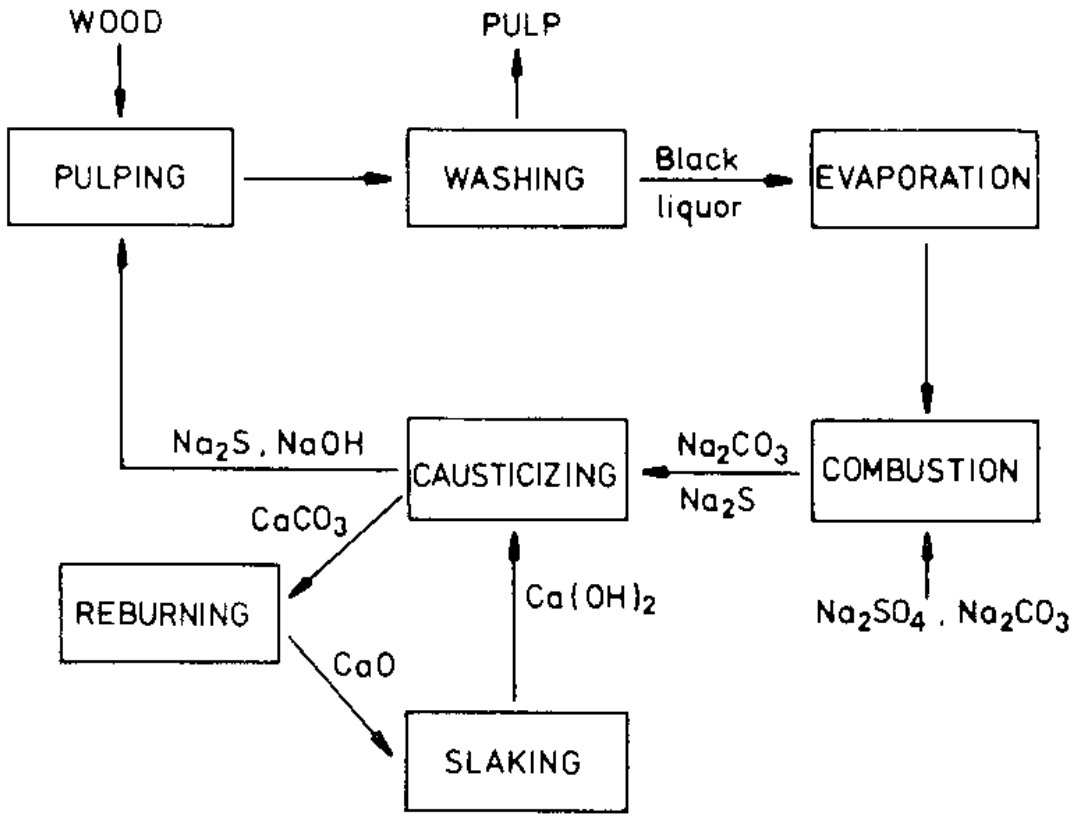


Figure 7 Kraft recovery cycle (Sjostrom 1993, 161).

date has included an acidic prehydrolysis followed by kraft pulping (T. E. Amidon 2006) (T. Amidon 2008) (Yoon, MacEwan and van Heiningen 2006). If done properly, the acid prehydrolysis can selectively remove sugars from hemicellulose while leaving lignin and cellulose mostly intact. Acid-Alkali processes are typically only recommended for producing dissolving pulps since the acid treatment makes the remaining carbohydrates more sensitive to alkaline degradation, but they can also be used to produce specialty paper pulps. These pulps are softer and have higher tear strength and opacity but lower burst and tensile index (Rydholm, 661). There are also many process options that finish cooking with an acidic stage and or contain sulfite in one or more stages.

Choice of pulping process depends on economics, but the economics will often depend on product quality. Hemicellulose content of pulp in particular effects not only the yield of the pulp but also the strength and other paper making properties. A recent study considered strength and yield relationships among ten spruce pulp samples produced from six different laboratory kraft pulping processes (Molin and Teder 2002). The processes included conventional kraft, prehydrolysis kraft, two polysulfide strategies, and two cooks with modified liquor profiles. The resulting pulps all had a klason lignin content of 3.3±1% of wood, but hemicellulose content that varied from a low of 9.8% with the prehydrolysis pulp to a high of 25.4% with the vapor phase polysulfide pulp. Zero span tensile strength was unaffected by the various pulping methods indicating that changes in paper properties attributed to the different pulping methods are not due to changes in individual fiber tensile strength. The specific bond strength between fibers as measured by z-directional tensile and Scott bond also was unaffected by changes in pulp composition but did trend with sheet density. Tensile index decreased while tear index

increased in direct proportion to the cellulose/hemicellulose ratio. Folding endurance and fracture toughness followed a similar trend to the tear index, increasing as the hemicellulose content decreased. These changes were attributed to a decrease in stiffness of fibers as hemicelluloses are removed caused by a change in shear strength and/or bending strength of the fiber wall or a change in shrinkage of the fibers during drying with all of these possibly caused by a change in the aggregation of cellulose microfibrils.

Chapter 2 Review of Previous Work

This section includes previously published work that lends insight to the processing of wood to chemicals and pulp. Previous work that relates to VPP can be roughly divided three ways:

1. Efforts to produce chemically pure "dissolving" pulp grades
2. Efforts to break down wood completely to monomers or "wood hydrolysis"
3. Recent laboratory work with VPP

2.1 Dissolving Pulp

Most pulp is produced to make paper and paperboard. Some is produced for specialty applications like absorbent fillers for diapers or as chemical feedstock for regenerated cellulose like rayon, cellulose acetate, or even food additives. Pulp that is produced as chemical feedstock usually has very specific quality constraints that are based less on physical characteristics (e.g. strength) than they are on chemical characteristics such as pentosan content or degree of polymerization. These products are called "dissolving pulp" and are produced either from bleached sulfite or by a method called prehydrolysis kraft (Rydholm 1985, 281). The prehydrolysis kraft process has the advantage of working with many different wood species. This multistage process begins with acid or water prehydrolysis followed by kraft pulping and then bleaching. The

conditions used in each stage and the stages used in bleaching depend on the intended product.

The hemicelluloses that are dissolved in prehydrolysis are mostly in polymer form. Some are converted to monoses and some of those are decomposed to furfural, hydroxymethyl furfural (HMF), or other acids. Much of the hemicellulose remains in the chips, but is degraded and more easily dissolved in kraft pulping through peeling at the additional reducing end groups. The acidic conditions can also cause lignin condensation making the chips more difficult to delignify in kraft pulping. This tendency can be neutralized by adding metal bisulfite (Rydholm 1985, 657), but this addition may lead to substantial lignin removal in the prehydrolysis. Prehydrolysis of pine reduced xylan degree of polymerization (Dp) from around 200 in the native wood to between 20 and 60 in the pulp. Kraft pulping alone reduced xylan Dp to between 76 and 90 (Grace 1989, 33-35). Xylans are retained in kraft pulp due to relative stability in alkali, reduced solubility as alkalinity drops at the end of the cook, and mass transfer limitations due to branching in the polymer. Prehydrolysis removes arabinose and methyl glucuronic acid side chains from xylans making them more susceptible to degradation and mass transport in subsequent pulping.

Much of the published work in the area of prehydrolysis pulping focused on producing high alpha cellulose chemical pulps from western US wood species hemlock, spruce, and birch, but some of the learning can be extended to the VPP situation with pine. In particular, there is some discussion of the effects of acidity, time and temperature on not only pulp composition and properties, but also on pulping requirements (Richter 1956). One difficulty with this approach relative to VPP is that

yield of sugar or hemicellulose in the hydrolysis extract is less important than reduction of hemicellulose residuals in the final pulp. Therefore the conditions for prehydrolysis and pulping in dissolving pulp manufacture can be selected so that the hemicellulose is removed in any stage of pulping and bleaching while with VPP it is critical that the sugar removal in the first stage be enhanced while removal in subsequent stages is minimized. Water hydrolysis is noted to cause pentosans to be more soluble in subsequent alkaline pulping. The severity of prehydrolysis is determined by acidity, time, and temperature and this severity determines the amount of hemicellulose that is solubilized in prehydrolysis and the amount that is degraded and extracted during subsequent pulping.

There is much discussion of two stage pulping with bisulfite in the first stage since this limits lignin condensation and represents a commercial process competitive with prehydrolysis kraft (Richter 1956). One drawback with the use of bisulfite in the VPP application would be the extraction of considerable amounts of lignin that would then need to be separated from the sugar. Prehydrolysis pulping can be used to optimize pulp properties not just for high alpha cellulose dissolving pulps, but also for improved bleachability or superior tear strength and fold endurance. Tear resistance and fold endurance are initially improved with prehydrolysis, but Mullen burst and tensile index are typically lowered. Extraction of pentosans can be controlled by adjusting prehydrolysis conditions and different wood species will respond differently to hydrolysis. Deactivation (condensation reactions) of lignin must be limited in the prehydrolysis by limiting the combination of extended time, high temperature, and low pH. Softwood lignin is much more sensitive to deactivation than hardwood lignin. Nitric acid and sulfur dioxide increase the amount of deactivation even at application of only

0.5% on wood. Sulfuric acid has no observed effect on the lignin at this same application rate as long as the temperature of prehydrolysis is kept below 120°C.

A study to look at fundamentals of polysaccharide hydrolysis was performed at the Institute of Paper Chemistry (Bernardin 1958). The study used a twin digester system that allowed preheating the liquor and could bring the wood – liquor mixture to 160±1°C in 7 to 9 minutes and be rapidly cooled below 100°C at the proper time. The wood was air-dried shavings of black gumwood and the times studied were 0, 15, 30, 60, and 120 minutes at temperature. The composition of the extracted chips was determined by extraction with alkali and precipitation in alcohol. The total yield of wood was found to be a linear function of the logarithm of hydrolysis time and reduced nearly 30% over two hours. About 55% of the hydrolyzate was recovered as hemicellulose; the remainder was a mixture of extractives, lignin, and degradation products. The study found a rapid reduction in alkali stable hemicellulose in the first 15 minutes of hydrolysis. The average Dp of hemicellulose was reduced by half from 130 to 60 and of cellulose from 1600 to 1200 in the first 30 minutes. Hemicellulose Dp was reduced to 45 and cellulose Dp to 1000 after two hours. Removal rate of polyose from the chips was fairly constant for the first hour and then dropped significantly in the second. The first hour is said to indicate either a zero-order reaction or a diffusion controlled surface reaction which would be consistent with an understanding that hemicellulose was concentrated on the outer layers of the fiber wall. Slow removal in the second hour would then be diffusion controlled removal of dispersed fractions from deeper within the fiber wall. The composition of sugars removed did not change over time, so there is not a selective removal of any hemicellulose fraction in this study.

No pulping was performed in this study with black gum, but the results can help explain the enhanced removal of hemicellulose and potential for cellulose damage in subsequent alkaline pulping. The decrease in average chain length of hemicellulose would make the carbohydrate both more soluble and easier to move by diffusion out of the fiber and less likely to reprecipitate on the fiber at the end of the alkaline cook. The solubility of lignin and pitch in alkali that would hinder movement in an acidic environment would further allow already hydrolyzed fractions to move out of the fiber. Although very little cellulose was removed in this two hour treatment, there was significant reduction in average Dp of cellulose also. This indicates the potential for greater cellulose damage and yield loss in subsequent alkaline pulping.

An example of efforts to produce dissolving grade pulp using prehydrolysis kraft describes 16 water prehydrolysis cooks with cooking time from 2.5 to 240 minutes, maximum temperature from 140° to 180°C, and heating time to temperature of 30 to 120 minutes (D. J. Brasch 1964). A measured amount of chips were contained in a small basket that was removed following prehydrolysis and replaced with an empty basket prior to the cook. They noted in their procedure that all cooks were started within 30 minutes of completion of the prehydrolysis and that the pulping chemicals were added to give the same active alkali charge and sulfidity for every cook. The composition of the liquors, chips, prehydrolyzed chips and pulp were measured. Final prehydrolysis liquor pH varied from 3.0 for higher time and temperature (150 minutes at 180°C) to 4.2 for milder conditions (60 minutes at 140°C). Final pulp yield and pentosan fraction dropped as the time and temperature of prehydrolysis increased, but the data indicated that it would be possible to optimize the conditions to control the lignin and alpha cellulose content.

Lignin content of pulp was highest following the most severe prehydrolysis and lowest in conditions in the middle range of time and temperature.

In contrast with the results from the study of prehydrolysis of black gum, the various components of the hemicelluloses in pine are expected to be dissolved at different temperatures due to the varied chemistry and solubility of the sugars present. The first stage of a prehydrolysis kraft dissolving pulp process for southern pine was considered in detail through measurement of sugar concentrations in chips, prehydrolyzed chips, and hydrolyzate as a function of time and temperature (Casebier 1969). These studies indicate that acetyl and uronic acid in the wood can be solubilized by room temperature extraction. Arabinose and some galactose were removed in 100°C water. Xylose, mannose, and some glucose were present in the liquid following extractions at 170°C. The ratio of sugars indicates that cellulose was not significantly damaged by this extraction. Significant degradation of the sugars to furfural or hydroxymethylfurfural was observed at higher temperatures and longer reaction times leading to a maximum extracted yield of about 16% from 90 minutes at 175°C or 45 minutes at 180°C. One interesting result was that the analysis of molecular weights in the hydrolyzate showed a maximum of 3100. This indicates that the hemicellulose molecule Dp must be reduced to below about 20 for successful diffusion out of the fiber.

A study of prehydrolysis kraft pulping of Loblolly pine and sweetgum, both southern woods, was performed to investigate how the various carbohydrates behaved during the purification process (Mitchell, et al. 1956). Chips were prehydrolyzed with water at 160°C for three different times up to 75 minutes and then cooked with three different alkali charges. The nine samples of each species were then divided three ways

for three different purification methods and then nitration. Samples were taken at each step for carbohydrate analysis and percentages of the remaining fraction for each component was reported but total yield was not reported. All five carbohydrate components, glucosan, mannan, xylan, galactan, and arabinan, remained in the pine chips following prehydrolysis with the percentage of glucosan increasing while the others decreased slightly. Galactan and arabinan were not detectable in the pulp following cooking while the xylan fraction was reduced by half and mannan reduced by 75% relative to the original wood. Variation in alkali concentration during the cook had no measurable impact on pulp composition. Alpha-cellulose from the pulps had roughly half the mannan and xylan as the pulp at all tested conditions.

2.2 Alcohol Production from Wood Hydrolysis

Manufacturing ethanol and methanol from wood has been considered as an alternative source of liquid fuels for emergency purposes since at least World War I (Zerbe 1985). Two plants to make fuel ethanol were built during this war using a dilute sulfuric acid hydrolysis but they were shut down after the war. Another plant was built during World War II in Oregon that was never operated successfully. Also built during the war was a plant to produce ethanol from the sugar in the spent sulfite pulping liquor from the pulp mill in Bellingham, WA. This plant produced 25 gallons of ethanol per ton of pulp until it was shut down in 2000. Other processes include concentrated acid and enzyme hydrolysis processes, each with their own variations, advantages, and disadvantages. Methanol, or "wood alcohol", was made as a byproduct of charcoal manufacture and is present as a non-condensable gas that must be dealt with in pulp

mills. Methanol can also be produced from syngas that is a result of gasification of wood or coal.

Development of these processes has continued with large efforts in the late 1970s in response to the oil crisis of that time and again in the last ten years as oil prices have continued to rise and there is renewed recognition that substitute fuels must be found. Continuous improvements to the dilute acid process led to the Forest Products Laboratory's "Madison process" that can produce 64 gallons of 95% ethanol from one ton of dry wood waste (Zerbe 1985). A pilot plant was built at TVA in Florence, AL to test a modification to this process. The fungus Trichoderma was identified for further work from over 14,000 tested organisms as a source of cellulose degrading enzymes. This identification has encouraged an entire industry with new applications for enzymes in textiles, food manufacturing, and pulp and paper in addition to continued efforts toward an enzyme based production platform for ethanol from biomass.

Research has also examined methods for the pretreatment of biomass to enhance enzymatic hydrolysis of cellulose. One of the process difficulties in wood hydrolysis is degradation of sugars to furfural or hydroxymethyl furfural (HMF) that can poison the fermentation organisms. Degradation of sugars prompted development of a method of measuring the pH of the reaction liquid during laboratory pretreatment of lignocelluloses for subsequent fermentation to ethanol (Weil 1998). The measurement allowed alkali addition on a pH target during pretreatment to minimize the acid catalyzed degradation of cellulose to glucose and glucose to HMF or other acids. The system sampled the liquid through a cooling coil and a pressure reducing valve before the pH meter. The cooled

liquid was then pumped back in to the reactor. Liquid residence time in the system before the pH probe flow cell was about 1.5 minutes.

2.3 Value Prior to Pulping

Successful application of VPP requires that only the desired components be removed from the wood and that those components and the final pulp are not degraded in the process. For production of ethanol feed sugars this means selected sugars are removed and lignin is left in the wood unchanged during prehydrolysis. Hot water extraction of wood chips is an effective method of separating fermentable sugars from wood prior to pulping. Potential difficulties with this practice include a reduction in yield (Yoon, MacEwan and van Heiningen 2006) and strength (Martinez 2006) of the final pulp. The conditions of extraction also must be optimized for the wood species to maximize recovered sugar and minimize degradation of pulp quality.

Work with pine has special issues that are of lesser concern with hardwoods due to relative importance of pulp strength and differences in lignin and hemicellulose composition. Different species and grades of pulp are included in finished products to impart particular characteristics to those products. Hardwood pulp is included in fine paper to improve optical characteristics like brightness, opacity, smoothness and print quality. These fibers are in tissues to add softness and absorptivity. Softwood fibers are used primarily to give the products strength to meet the physical demands put on the sheet or board but they are also used to make absorbent fluff pulp for hygiene products. Hardwood and softwood also have different amounts and forms of both lignin and hemicellulose. Softwood lignin has a tendency for condensation of ether bonds to stronger carbon –carbon bonds in acidic environments that hardwoods do not have.

Therefore, conditions that work for hardwood may not be appropriate for softwood. Several studies of VPP for hardwood have been performed with some apparent success based in part on the relatively high fraction of hemicellulose in hardwood (Al-Dajani and Tschirner 2008) (T. E. Amidon 2006). Less work has been reported for pine (Yoon, MacEwan and van Heiningen 2006), even though pine pulp is approximately 30% of U.S. production (estimated at 29 million tons/year (Matussek 2006)).

Recent prehydrolysis work with hardwood has produced pre-extracted chips with 8, 12, and 23% mass removal (T. Amidon 2008). Increasing the mass removal to 23% gave a higher quantity and concentration of sugar in the extract but produced pulp with lower handsheet strength relative to a control Kraft pulp at equal freeness. Higher refining energy was required to reach the target freeness with this pulp. Dr. Amidon emphasized a lower pulping requirement, higher "digester yield" to reach the target of 18 kappa number and easier bleaching thus potentially increasing production rates in the digester, but cautioned that this comes at the cost of 12% lower overall yield (40% versus 52% for kraft) and that more experiments could more closely evaluate the costs and benefits. The extraction was performed with water at 160°C for two hours with a 4/1 liquid/solid ratio and was followed by two 15 minute washes with 80°C water. About 70% of the original xylose was removed and this accounted for about 50% of the mass removed. An attempt was made to use wet end starch to reduce the strength loss.

Another paper on the topic of VPP with hardwood had several preliminary observations regarding the effects of hot water preextraction on Sugar maple chips (T. E. Amidon 2006). The most favorable observation was that a pulp could be produced by a Soda-anthraquinone (AQ) cook following pre-extraction that had similar yield and kappa

number to a kraft control pulp. Further, this pulp was easier to bleach and therefore the yield could be improved by reducing the cook time without negatively impacting final pulp properties. The result with similar yield was with a mild extraction that removed the acetyl groups and about 5% of the chip weight as hemicellulose.

This line of research with hardwood was extended in the direction of improving delignification (Bolton 2007). In the case of a very mild prehydrolysis of 15 minutes at 150°C with 1.5% acetic acid, the H-factor for a Soda AQ cook could be reduced 37.5% while the overall yield was slightly improved relative to a kraft control. The explanation proposed for accelerating the cook was that the hydrolysis formed more end groups capable of reducing AQ to AHQ (see Chapter 6) and that diffusion was enhanced through increased void volume in the chips. Very little sugar was extracted under these mild conditions. The use of a mild acid prehydrolysis of 20 minutes at 140°C followed by a carbonate wash for 20 minutes at 160°C was also mentioned to dramatically reduce alkali requirement in SAQ pulping to only 8% on chips. Severity of hydrolysis was measured by kinetics and assumed to be independent of acid concentration while strongly dependent on time and temperature.

A large fraction of the softwood hemicelluloses also appear relatively easy to remove with hot water or acid prehydrolysis. However, a reduction in both strength and yield in the kraft pulp produced from prehydrolyzed southern pine chips have been observed (Yoon, MacEwan and van Heiningen 2006) (Martinez 2006). Speculations about the cause of these losses include:

1. Cellulose damage caused by prehydrolysis reduces individual fiber strength.
2. Bulk hemicellulose removal limits yield and bonding potential.

3. A key hemicellulose fraction is removed that inhibits fiber-fiber bonding.
4. Prehydrolysis makes all or select pulp carbohydrates more susceptible to alkaline degradation.

Yoon, et al reported 3% pulp yield loss after kraft pulping relative to a control pulp when 5% of wood weight was extracted with hot water before pulping and 6% yield loss when 8% was pre-extracted (Yoon and van Heiningen 2008). They also reported difficult refining and reduced tensile strength in the extracted pulp but similar viscosity, zero-span wet tensile, and tear resistance. They conclude that there is little change to the cellulose in pine pulp due to pre-extraction but there is reduced hemicellulose content. One of the goals for the future in Dr. Yoon's work was to return 1/3 of the hemicellulose sugars to the pulp for yield improvement, but a plan was not presented for how this would be accomplished.

Dr. Yoon has continued his work in Dr. Krishnagopolan's group at Auburn University. He has found that pine yield can be preserved following prehydrolysis if sodium borohydride is added to the pulp following the prehydrolysis treatment (Yoon 2009). Sodium borohydride has long been known as a yield preservative in pulping and bleaching but is not used in industry due to high cost.

Potential for VPP is not limited to kraft mills. There has also been work done with thermo-mechanical pulping (TMP) where the pretreatment accomplishes a reduction in refining energy of about 25% in addition to extracting sugar for potential ethanol production. Recent work that compared different acids for this process showed yield loss of up to 30% in a one hour treatment with .01 molar sulfurous acid at 150°C (Rudie, et al.

2007). Very little lignin was removed in this treatment. The primary drawback to this process is a significant reduction in brightness.

In summary, sugar can be removed from hardwood and softwood by heating the wood in water. The rate and quantity of sugar removal can be controlled by controlling the temperature and time of the reaction. Discovery of a financially advantageous method of recovering sugar from softwood is complicated by a lower percentage of hemicellulose in the wood and lignin that is sensitive to the conditions of extraction. It may be possible to further control the type of hemicellulose impacted by the extraction and the impact on pulp properties by addition of chemical additives for pH control or other purposes.

Chapter 3 Experimental Apparatus and Procedures

The experimental portion of this work was conducted in the laboratories of the Chemical Engineering department at Auburn University. The laboratory equipment and chemicals were provided by the Alabama Center for Paper and Bioresource Engineering.

3.1 Materials and Equipment

Loblolly pine chips (Pinus Taeda) produced from two individual 16 year old trees by Rock -Tenn Company in Demopolis, Alabama were screened on a CHIP CLASS ™ laboratory screen using a stack from top to bottom of 45 mm holes, 8 mm bars, and 2 mm bars over the pan. Accepts were taken from the 2 mm bar tray. The screened chips were air dried and stored in plastic zipper bags which were sealed in a 55 gallon drum until needed to maintain uniform moisture content. Bark and knots were manually removed before use. This chip screening method was chosen because it closely simulates the accepted chips that are fed to industrial digesters. Chips that are smaller than 2 mm thickness may pass through internal digester screens and plug downstream equipment. Chips that are larger than 8 mm thickness may not cook completely. Smaller particle size may give more accurate information on the chemical kinetics of the reactions involved but will not give relevant information on mass transfer effects.

Composition analysis of the chips was performed at the USDA Forest Products Lab (FPL) in Madison, WI and at Auburn University (AU). The carbohydrate analyses from the two labs were in very good agreement with each other, but the klason lignin

determination was 2% of wood higher in the AU results. Table 1 shows the wood composition analysis results including the averages of the AU results that were used for further calculation.

Table 1 Loblolly pine wood composition measurements.

Raw Chip Composition, % of Bone Dry Wood							Average	
	AU	AU	AU	AU	FPL	FPL	AU	FPL
Glucan	40.07	40.25	40.83	41.15	41.10	39.60	40.58	40.35
Xylan	7.39	7.43	8.20	8.15	7.11	7.83	7.79	7.47
Galactan	2.38	2.05	2.06	2.23	1.99	2.25	2.18	2.12
Arabinan	1.58	1.50	1.51	1.57	1.36	1.45	1.54	1.41
Mannan	8.90	8.91	9.23	9.35	9.77	8.84	9.10	9.31
Total Carbohydrates							61.19	60.65
K-Lignin %	31.54	31.54	33.24	33.24	30.60	29.60	32.39	30.10
Acid-Soluble Lignin	0.48	0.48	0.33	0.33			0.41	
Ash content	0.31	0.31	0.32	0.32	0.40	0.50	0.32	0.45
Total	92.65	92.47	95.72	96.34	92.33	90.07	94.30	91.20

The approximate hemicellulose composition was determined using the carbohydrate composition analysis and literature values for molar ratios of the sugar monomers and typical values for softwood composition (Sjostrom 1993, 64). Table 2 illustrates the method used to estimate the macromolecular composition of the wood. The estimated wood fraction of each polymer was input in the "Wood" column. These estimates were adjusted until monomer percentages calculated along the bottom of the table were close to those determined in the composition analysis of the wood chips. The glucomannan fraction was estimated to be 1% lower than typical for softwood while the arabinoglucuronoxylan fraction was higher.

White liquor for kraft cooks was prepared from sodium sulfide hydrate and sodium hydroxide pellets and tested by the "ABC" titration with hydrochloric acid. Reagents for pH control were prepared from glacial acetic acid, 10 N sodium hydroxide, and granular sodium carbonate. Other reagents were used as required by analytical

methods. Chemical additives for pulp yield improvement trials are discussed in each section of Chapter 6.

Table 2 Macromolecule composition estimation matrix.

				Ratios							
	Mass Percent			GLU	XYL	GAL	ARA	MAN	Ace	GLUpA	Unit
Macromolecule	Typical*	Wood	Carb	162	132	162	132	162	45	177	MW
Galactoglucomannan	5-8	5.00	7.76	1	0	1	0	3	1	0	855
Glucomannan	10-15	9.00	13.98	1	0	0.1	0	4	1	0	871
Arabinoglucuronoxylar	7-10	10.80	16.77	0	10	0	1.3	0	0	2	1846
Cellulose	37-41	38.00	59.01	1	0	0	0	0	0	0	162
Galactan		1.20	1.86	0	0	6	1	0	0	0	1104
Arabinan		0.40	0.62	0	0	0	1	0	0	0	132
		64.40	100.00	40.62	7.72	2.17	1.55	9.54	0.73	2.07	64.40
										sugars	61.60

* Typical values taken from Sjostrom 1993, p. 64.

The extractions and cooks were performed in a M/K Systems Inc. twin laboratory digester with liquor circulation as illustrated in Figure 8. Some of the cooks were performed in 500 ml stainless steel “bomb” containers that were placed in water in the M/K digester. The digester system was modified over the course of the experiments. Modifications to the equipment included a crossover line to allow for transfer of liquor (wash) from one digester to the other, systems for online pH measurement and adjustment, and a back-up temperature sensor. The modifications added approximately 250 ml to the volume of the circulation piping.

The back-up temperature sensor was installed in the circulation loop as the reference point for all temperature measurements and H-factor calculations beginning with the prehydrolysis designed experiment. The original sensor was found to read two degrees higher than other sensors at room temperature and approximately three degrees higher at cook temperature. The original sensor was retained so an estimate of the back-

up temperature measurement could be used to recalculate the temperature readings when results from earlier tests were compared to those of the designed study and later.

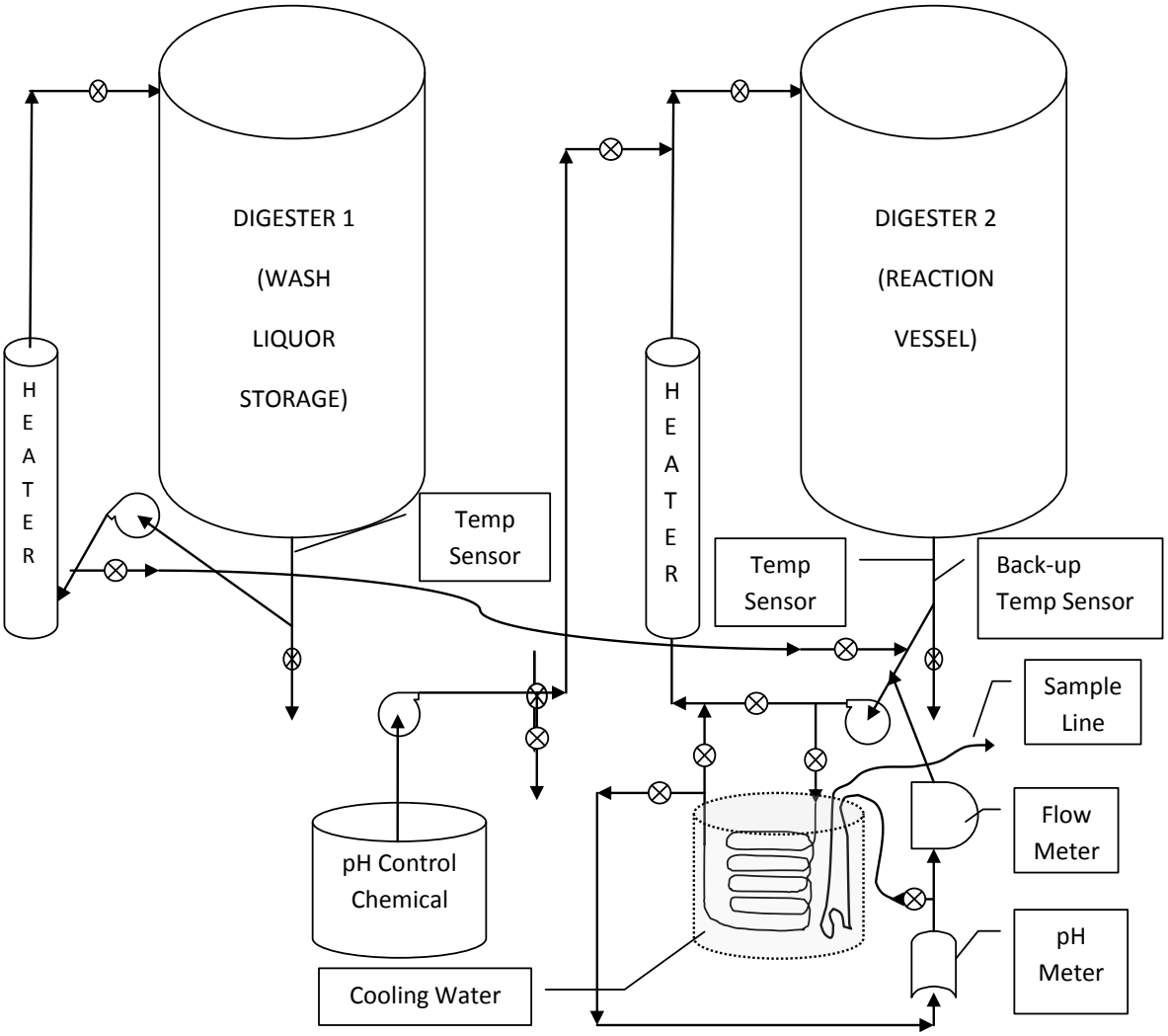


Figure 8 M/K Digester configuration.

Several options were considered for pH control including manual sampling, cooling a side stream to room temperature for external measurement, and two different systems of online measurement. A system of buffers was briefly considered, but was not attempted since the pH target and the potential effects of the buffer chemical on the prehydrolysis were not known. Samples of the prehydrolyzate were taken at various

times and the pH was measured in the early experiments, but the limited frequency of samples, reduction of circulation volume and time lag of cooling the samples was not acceptable for control. The system for cooling a side stream for pH measurement discussed earlier was also considered, but the time lag in the system was fairly long and the system was complicated (Weil 1998). A commercial apparatus for measuring pH at digester temperature and pressure in sulfite cooks was patented in 1968. This system had separate glass, reference and temperature probes with pressure and temperature control on the reference (Ingruber, Kocurek and Wong 1985, 52-53). This system would have been impractical on the laboratory digester due to the liquid volume required.

A Rosemount Model 3300HT pH probe was selected for this research and installed in a cooled side stream bypass line to monitor pH continuously. This probe is simple to maintain and can be used up to 145°C @ 100 psi. The online pH measurement then provided timely information and required a minimum of cooling from the maximum circulation temperature of 170°C used in the studies. A large cooling requirement would slow the response time of the digester temperature control system.

The system for alkali or acid addition to the primary circulation loop consists of a LMI diaphragm pump and a couple of valves. The required reagent is pumped from a graduated cylinder so the volume can be measured. When the control requirement changes from acid to alkali as the extraction proceeds, the change is a simple switch of the cylinder and then to flush the feed line using the digester pressure and the feed pump from either end of the line to the drain valve. Acetic acid was used to lower the pH. Sodium hydroxide was used to raise pH for the earliest experiments, but was replaced with sodium carbonate after sugar degradation was observed.

A room temperature (24°C) soak period at various conditions was performed in plastic zipper bags prior to the prehydrolysis step. A vacuum oven was used to remove air from the dry chips for the pre soak and in the case of bomb cooks with raw chips.

3.2 Experimental Procedures

The moisture content of the air-dried chips was checked by drying samples in an oven at 105°C before they were bagged, a few weeks after they were bagged, and again a year later prior to a cook. The results were all within 8±0.2% moisture. 91.82% solids was used to calculate chip weight for all experiments. In the preliminary experiments, the calculated amount of dried chips for each prehydrolysis was weighed and put in the chip basket. The dry chips were weighed into beakers that were placed in the vacuum oven covered with soak solution for the designed experiment and later tests. The oven vacuum was run up to 26 inches of mercury vacuum until air bubbles stopped appearing on the chips. Two or three runs in the oven were sometimes required to make sure all chips were covered with solution after the vacuum was released. The wet chips were then placed in plastic bags for the pre-soak period in the designed experiment. The soak solution was added to the bags to saturate the chips at a liquor-to-wood ratio of 2. The bags were then closed and left at room temperature (24°C) for 24 hours. After the soak period, the wet chips were placed in the chip basket for the prehydrolysis.

The prehydrolysis extractions and the kraft cooks completed before the designed experiment were performed in the digester with liquor circulation. The kraft cooks for the designed experiment and later tests were performed in the 500 ml “bombs” so only 70 grams of chips would be required and up to three cooks could be performed at once with the same time/temperature profile. The liquor circulation allowed the flexibility of

sampling the hydrolyzate and controlling the pH of the circulation. A generalized method for a digester extraction followed by digester cook is described here followed by a generalized description of a bomb cook. Modifications to these methods and key measurements were recorded for each cook in the lab notebook and a Microsoft Excel spreadsheet that was then used to perform calculations to allow comparison of the cooks. Examples of these spreadsheets are included in Appendix 3.

Water was added to the digester to just cover the chips and the liquor circulation was started. Any chemical for pH adjustment prior to the start of the extraction was added at this point. After the water had circulated for a few minutes, additional water was added to just cover the chips to make up for the volume in the circulation piping and any water absorbed by the chips. Additional water was then added to account for the volume of samples to be taken. The top of the digester was bolted down and the control profile was started. The digester vent was closed when the circulation temperature reached 90°C. The digester was vented to remove the remaining air when the temperature reached 100°C and again at 105°C. All liquid additions or removals from the digester were measured so the sugar concentration measurements in the hydrolyzate samples could be related to the chip mass. The programmed temperature ramp was 45 minutes to temperature target for all runs before the implementation of pH monitoring. The ramp was extended to one hour after the first two runs with pH measurement due to heat loss in the side stream loop. This heat loss was reduced by insulating the circulation piping and carefully adjusting the pH meter temperature control during the ramp. Small samples of the circulating prehydrolyzate were taken at set temperatures and regular time intervals after the digester reached target temperature. These samples were then tested

for carbohydrate composition. The prehydrolysis liquid was drained through a cooling coil and collected at the end of the designated time period.

A wash sequence was followed after the prehydrolysis. Various methods were used on different preliminary runs including using heated water and heating the wash circulation to 105°C. Room temperature water (25°C) was added for wash in the designed experiment runs to aid in cooling the chips and digester. The resulting wash temperature was about 60°C and was recorded for each cook. Cooling the chips reduced evaporation during weighing following extraction. After the wash, the digester was drained under pressure before opening. A sample of wash was taken for pH and composition analysis. The chip basket was removed from the digester and the chips were transferred to a zipper bag for weighing. A sample of 10% of the prehydrolyzed chips was removed for composition analysis before the chips were returned to the digester for immediate cooking or separated into 70 g dry chip equivalent samples in individual zipper bags and put in the refrigerator for later "bomb" cooking.

Several different cooking conditions were used in the preliminary cooks. All later cooks used synthetic white liquor made up of sodium hydroxide and sodium sulfide with 30% sulfidity. The white liquor was added to the chips for 20% active alkali on dry raw chips followed by sufficient water to cover the chips. This caused relatively high liquor to wood ratios of around 7. Following a digester cook, the black liquor was slowly drained through a coil in an ice bath. A sample of black liquor was collected for pH and/or residual alkali testing. The digester was then opened and fresh water circulated to wash and cool the pulp. The pulp was then removed and washed further in a filter sock before it was defiberized in a laboratory blender, squeezed dry, and homogenized. The

homogenized pulp was spread in a tray to air dry to improve uniformity before weighing for yield and kappa number analysis.

The bombs were used for the kraft cooks to determine the standard yield versus kappa number curve, the kraft portion of the designed experiments, and the yield improvement treatments. In each case, the equivalent of 70 grams of dry raw chips was processed in the bomb. The weight of extracted chips was determined by ratio of the total weight of wet chips to the original weight of dry chips charged to the digester. The chips were placed in the bombs and the bombs were shaken down so the chips would fit closely. The white liquor or other reagents were mixed in labeled graduated cylinders so they would be premixed before they were contacted with the chips. All reagents were charged based on a liquor to wood ratio of 7.0 for 70 g dry chip weight regardless of pretreatment. In the case of dry chips, the bombs were placed in a vacuum oven to remove air. About 10% of the liquor was reserved until after this treatment so the bombs would not foam over. The bombs were capped and shaken vigorously for two minutes before they were placed in the M/K digester. The digester was filled with water to just cover the bombs and then sealed for the cook. The digester was not vented during the bomb cook.

The time for the cook was calculated based on an H-factor target and the programmed temperature profile. The H-factor was calculated as the cook progressed to account for differences in the temperature ramp and transition to steady temperature operation of each cook. Examples of these determinations are included in Appendix 3. When the time for reaction of the bomb cooks was complete, the circulation water was directed through the in-line cooling coil to cool the system before the bombs were

removed from the digester and placed in an ice water bath for further cooling. The bombs were then opened and the cooked chips dumped into the filter sock for washing. After washing, the pulp was blended, homogenized and spread on a pan for drying.

When the bombs were used for intermediate yield additive treatments, the chips were typically not dumped from the bombs before kraft cooking. Instead, liquid was poured from the bombs as needed to be replaced by the concentrated white liquor to maintain the original liquor to wood target. A sample of this intermediate liquid was retained for further analysis. Some other specific method changes were required for application of the yield additives. These changes are discussed in Chapter 6.

3.3 Analytical Procedures

Tappi standard methods and methods published by the National Renewable Energy Laboratory in 2004 were followed for testing the composition of chips, pulp, and hydrolyzate. These methods include:

Tappi T236 cm-85 Kappa Number of Pulp

NREL Preparation of Samples for Compositional Analysis

NREL Determination of Total Solids in Biomass

NREL Determination of Structural Carbohydrates and Lignin in Biomass

NREL Determination of Sugars, Byproducts, and Degradation Products in Liquid Fraction Process Samples

Customary methods were used for testing white liquor strength and black liquor residual alkali. These methods are included in Appendix 2.

Chapter 4 Prehydrolysis of Pine Wood Chips

4.1 Preliminary Work

An undergraduate lab group performed the preliminary work discussed in this section in spring 2006 as a class project under the direction of Dr. Krishnagopalan and this researcher. Samples of the prehydrolyzate were taken every 15 minutes up to a 3 hour reaction time for water extraction at 170°C. The measured sugar concentration trends shown in Figure 9 illustrate that reaction time beyond two hours had little net improvement in sugar recovery. Similar experiments were performed with acetic acid

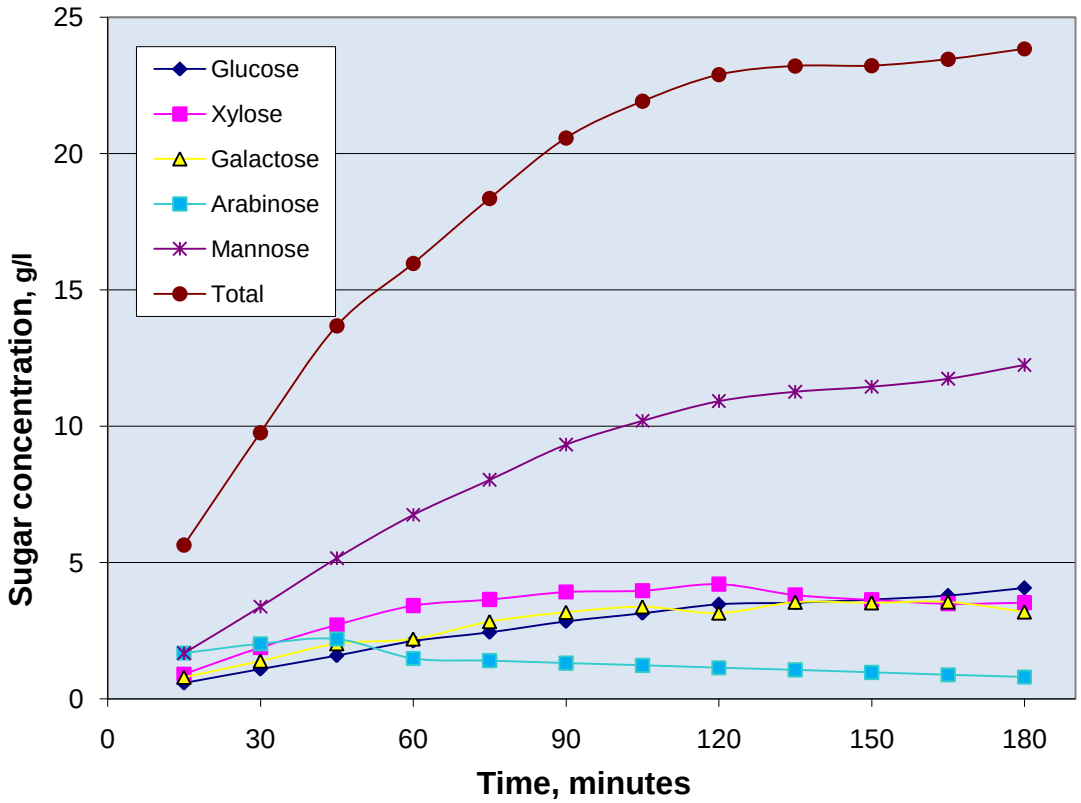


Figure 9 Extracted sugar concentration as a function of time for water hydrolysis.

added at a charge of 3% on wood to drop the initial pH to 3.5. The composition analysis results were similar, but the time required for reaction was reduced with the sugar concentration in the hydrolyzate approaching a maximum in one hour instead of two. The maximum concentration of sugar recovered in the extractions corresponds to approximately 50% of the hemicellulose in Loblolly pine. The ratio of galactose: glucose: mannose is approximately 1: 1: 3 indicating that cellulose was minimally affected even by these extreme treatments. The concentrations of xylose, galactose, and arabinose peaked and then fell over the course of the treatment indicating that these components may be degraded by the severity of the treatment. Many of the arabinose and some of the mannose measurements reported are estimates due to interference between these two components in the HPLC Column. The lab group did not attempt to measure yield of the pulp.

The prehydrolyzed chips were pulped to a target kappa number of 30 ±2. The pulp was processed in a valley beater and handsheets were prepared for property testing. Selected pulp properties for three of these cooks are listed in Table 3. These tests indicated reductions of 25% and 15% in burst and tensile index and a dramatic decrease in air permeability when compared to a control kraft pulp. The cook numbers correspond to different conditions: Cook 1 was a kraft cook without prehydrolysis. Cook 2 had a 2 hour prehydrolysis treatment with water at 170°C before kraft cooking. Cook 3 had a 1 hour prehydrolysis treatment at 170°C with an acetic acid charge of 3% on wood added at the beginning of the prehydrolysis followed by kraft cooking.

Table 3 Preliminary study, selected conditions and results.

Cook	1	2	3
Prehydrolysis time, hours	0	2	1
Prehydrolysis solution	-	Water	Acetic acid, 3% of wood
Kappa number	30.0	29.3	30.2
Burst Index, kpa	6.8	5.0	5.1
Tensile Index, kN/M	190	162	162
Porosity, seconds	37.5	99.6	69.9

The preliminary studies suggest that hemicelluloses are easily removed from pine chips with mild acid or water at typical kraft cooking temperature and that cellulose yield and quality are relatively unaffected by this treatment. However, degradation of the extracted sugars during the time at temperature and reduction in strength of the pulp after kraft cooking the prehydrolyzed chips hint that successful VPP extraction may be significantly different than conventional kraft pulping. A procedure that will extract the sugars without degradation and without reducing the strength of pulp will require at a minimum that the time and temperature of the reaction be controlled.

4.2 Second Preliminary Work

Further preliminary work was done to test modifications to laboratory equipment and investigate potential variables for further testing. Much of this work was presented at the August 2008 TAPPI Engineering Pulping and Environmental (EPE) Conference in Portland, Oregon (Smith, Cullinan and Krishnagopalan 2008).

Several digester cooks produced control kraft pulps and kraft pulps from chips that had been water extracted for 30 minutes, 60 minutes, or 2 hours at 170°C. Kraft cooking was to a kappa number target of 30. The temperature target and cook time were both varied to seek this target, so the H-factor is used to facilitate comparison of these cooks. The H-factor is a severity parameter that combines the effects of temperature and

time into a single variable. It is discussed further in Chapter 7 under kraft pulping models. The plot of kappa vs. H-factor in Figure 10 shows that the chips with a 30 minute prehydrolysis treatment required lower H-factor to cook to a target kappa number while the chips from the two hour pre-treatment required more severe conditions to cook to 30 kappa than raw chips. White liquor was charged at 20% active alkali on bone dry raw chips, so the prehydrolyzed chips saw a slightly higher alkali charge on chip weight. The higher difficulty in cooking the two hour chips is in accordance with previous results wherein higher temperature, alkali, or both were required to reach the same kappa target following extended prehydrolysis of softwood at 170°C (Richter 1956). Further experimentation could determine the optimum pretreatment time and temperature as it relates to cook time and yield at a given kappa.

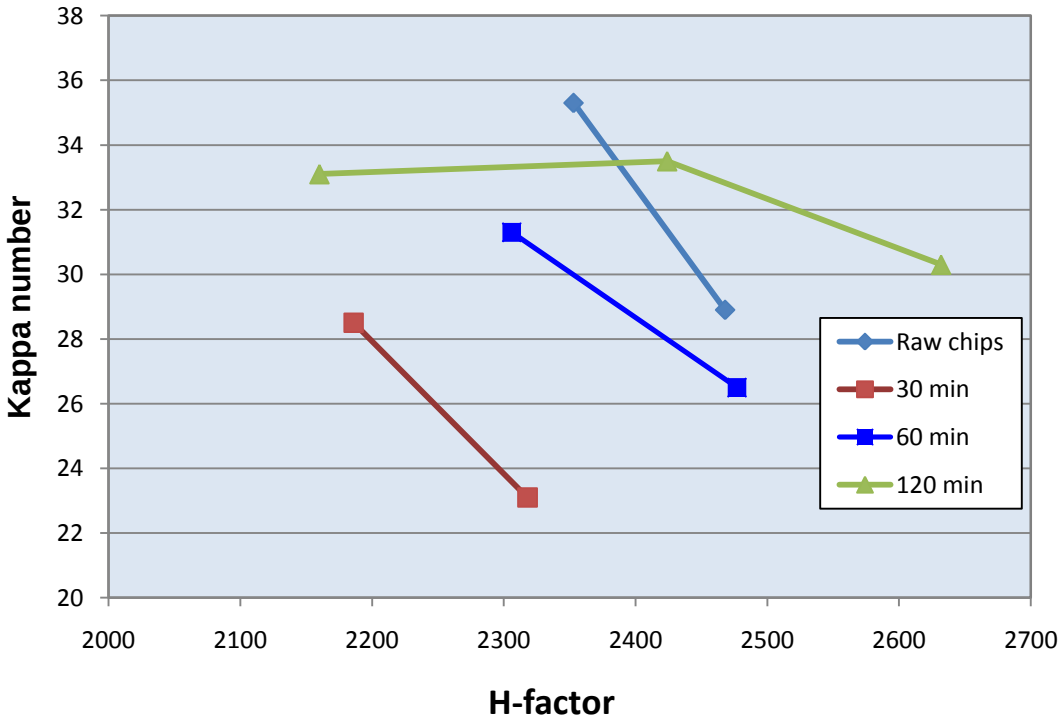


Figure 10 Pulp kappa number as a function of cooking H-factor. Legend indicates pre-treatment time.

4.3 pH Controlled Prehydrolysis of Pine Wood Chips

Six preliminary prehydrolysis runs were also performed with the pH measurement and pH adjustment chemical addition systems in place. Addition of the pH measurement loop increased the circulation volume and changed the energy balance on the digester, so the time-to-temperature ramps for these cooks took up to 67 minutes compared to 45 minutes for previous runs. The composition analysis results are indexed using H-factor as a reference that combines time and temperature following the example of Yoon (Yoon, MacEwan and van Heiningen 2006) to facilitate comparison between the pH adjusted prehydrolyzate samples and those from a run with no pH adjustment. Each of the first three runs was held at 170°C for two hours following the ramp. A second set of three batches was then run with the time at temperature to maximize sugar recovery determined by the prehydrolyzate sugar concentration curve. The pH profiles for the first set are shown in Figure 11 along with a representative pH profile for a run without pH control and a representative temperature profile taken from the acid run. Two runs had an initial charge of NaOH and are designated "0.1% NaOH" and "0.3% NaOH". The third had an initial charge of acetic acid and is designated "3% Acetic". The pH was controlled with 0.5 N NaOH at pH 5 after it dropped to that level in the cases of high initial pH. The chips were allowed to react for 30 minutes before the caustic feed was started to control the pH at 5 in the acid case. A sample of prehydrolyzed chips was taken following the wash in each case for moisture determination and composition analysis; the rest were stored in the refrigerator to be divided later for "bomb" cooking.

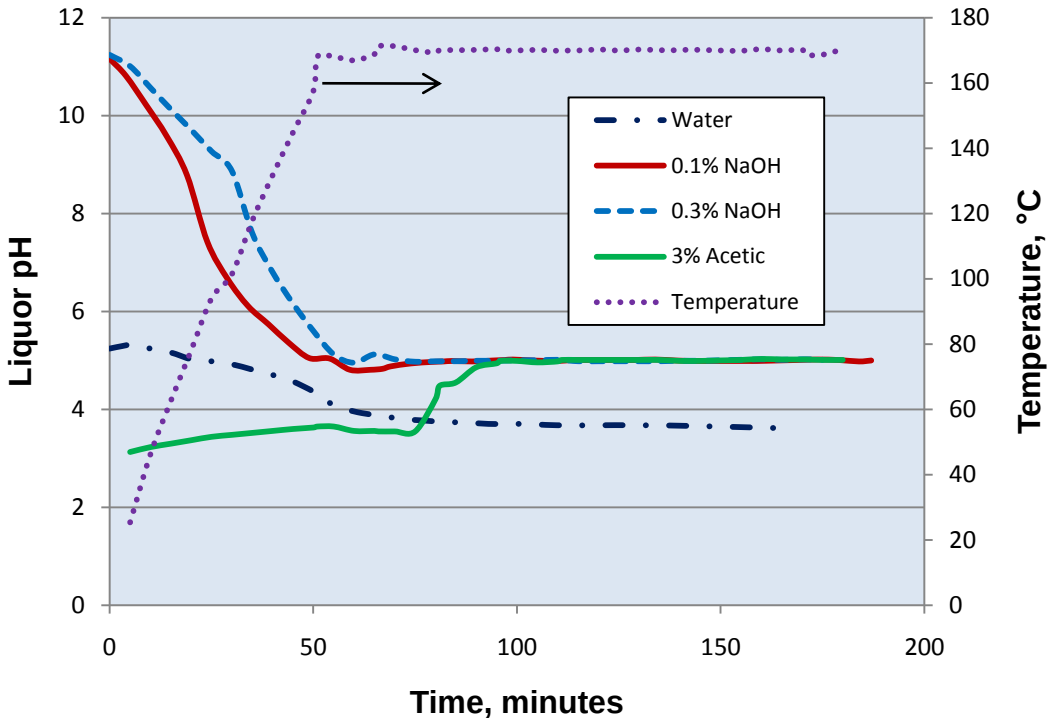


Figure 11 Prehydrolysis pH and temperature profiles. Legend indicates initial chemical addition.

The pulp yield results for the bomb cooks from all of the prehydrolysis cooks are plotted against the kappa number in Figure 12. There is an apparent trend of reduced yield with increased severity of prehydrolysis. The comparison of pulp yield should be made at the same kappa number or over the same range since the kappa number itself is a measurement of lignin yield. Since one cannot make that comparison with all of this data, this limited data set should be interpreted as if each point sat on a line with slope similar to the line through the "Kraft" data. The conventional kraft pulp has the highest yield with the two hour treated pulp without pH control having the lowest yield. The two hour pulps that received pH adjustment fall closer to the 30 minute treated pulp. There remains a significant gap between the conventional pulp and all of the pretreated samples.

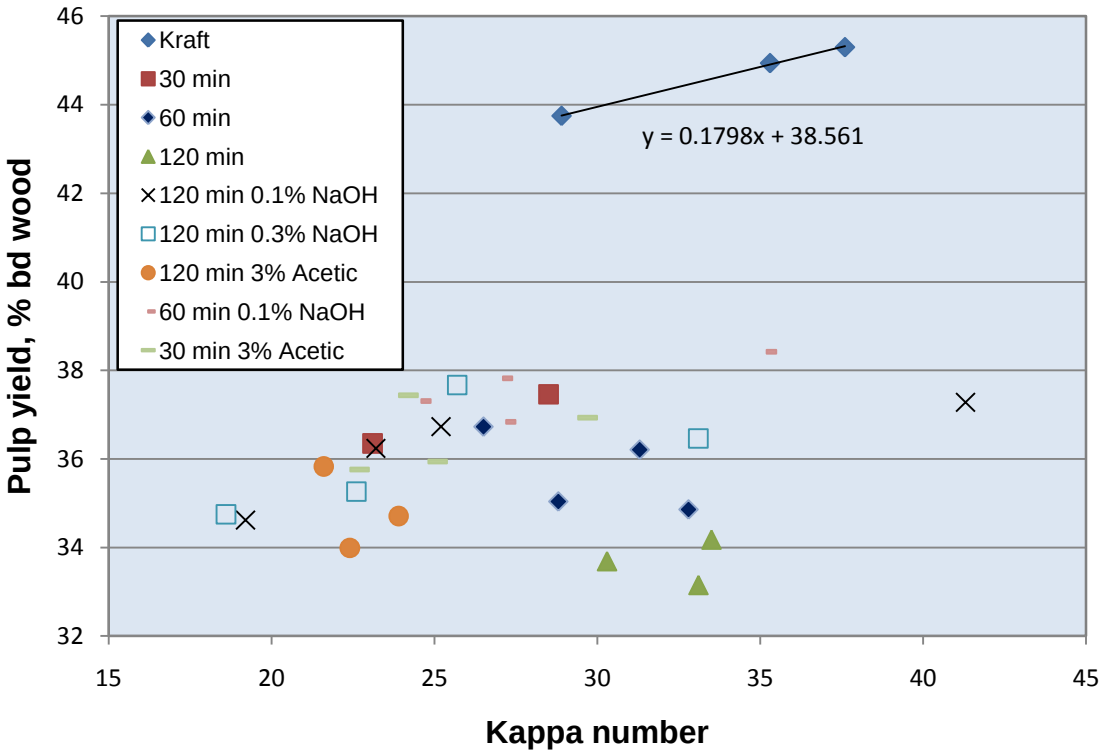


Figure 12 Pulp yield as a function of kappa number for all prehydrolysis runs (Legend identifies prehydrolysis time and initial chemical charge if present).

The samples of the prehydrolyzate liquid were tested for sugar composition following a secondary hydrolysis. The results of this testing are shown in Figure 13 through Figure 16 which plot the extract carbohydrate composition as a percent of original dry wood as a function of time. The quantity of arabinose and xylose and total sugar that is detected reaches a maximum at some point and then begins to decline in all of the runs. This is likely due to degradation of the pentoses. Furfural is detected as a potential degradation product. The first two data points for arabinose in each plot are actual measurements; the rest are estimates since the arabinose peak was at least partially obscured by the mannose peak in the HPLC chromatograms. It was assumed for the estimate that degradation of arabinose would be at a rate similar to that of xylose. The

quantity of glucose and mannose detected increases slowly in all runs except for the run with initial acid addition.

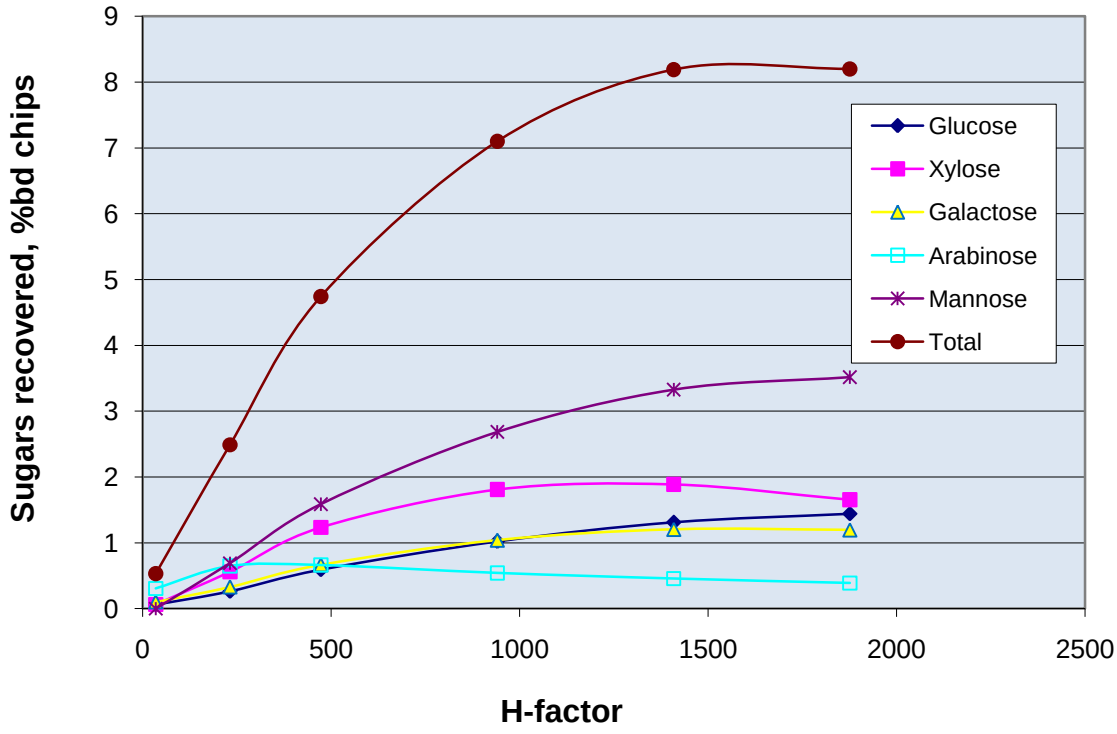


Figure 13 Sugar recovery as a function of H-factor for water hydrolysis.

The quantities of galactose and glucose trend together for at least the first hour after reaching temperature target (approximately 1000 H factor) of the runs with no pH control and caustic added shown in Figure 13, Figure 14, and Figure 15. The quantity of mannose is roughly triple that of galactose and glucose indicating that the source of these three carbohydrates is likely galactoglucomannan with a ratio of 1:1:3 for the galactose, glucose, and mannose monomers. After this time, however, the quantity of galactose in solution begins to decline while the glucose and mannose continue to rise.

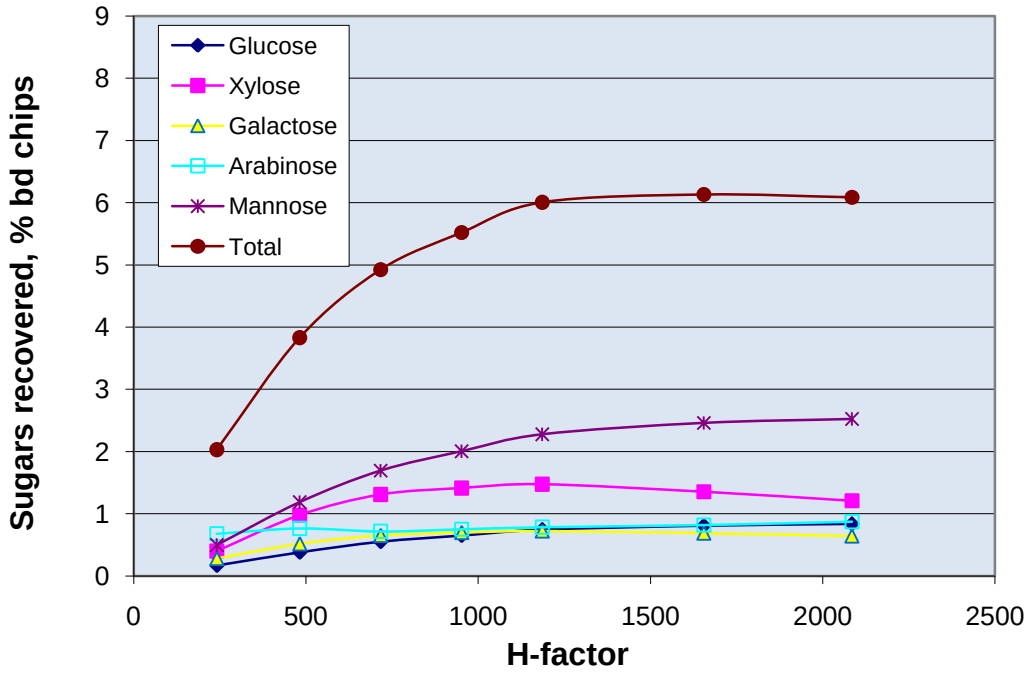


Figure 14 Sugar recovery as a function of H-factor for prehydrolysis with an initial charge of 0.1% NaOH followed by control with 0.5 N NaOH to pH 5.

Addition of caustic prior to the beginning of heating and then later to control pH at 5 has an inhibitory effect on the extraction of all of the sugars except arabinose as shown in Figure 14 and Figure 15 where total sugar recovery is reduced by 25% and 33% respectively. Arabinose extraction is not reduced, but this is expected since it has been shown to be soluble even under the very mild conditions of room temperature and 100°C extractions (Casebier 1969).

The plot of sugar extracts in Figure 16 shows a very different profile than the others. The maximum in glucose, xylose, galactose, mannose and total sugar all occur much earlier than in the other runs. The maximums are also much higher with the initial acid addition than those with caustic addition, but the final quantities are similar with the exception of xylose, which drops very quickly after addition of caustic begins.

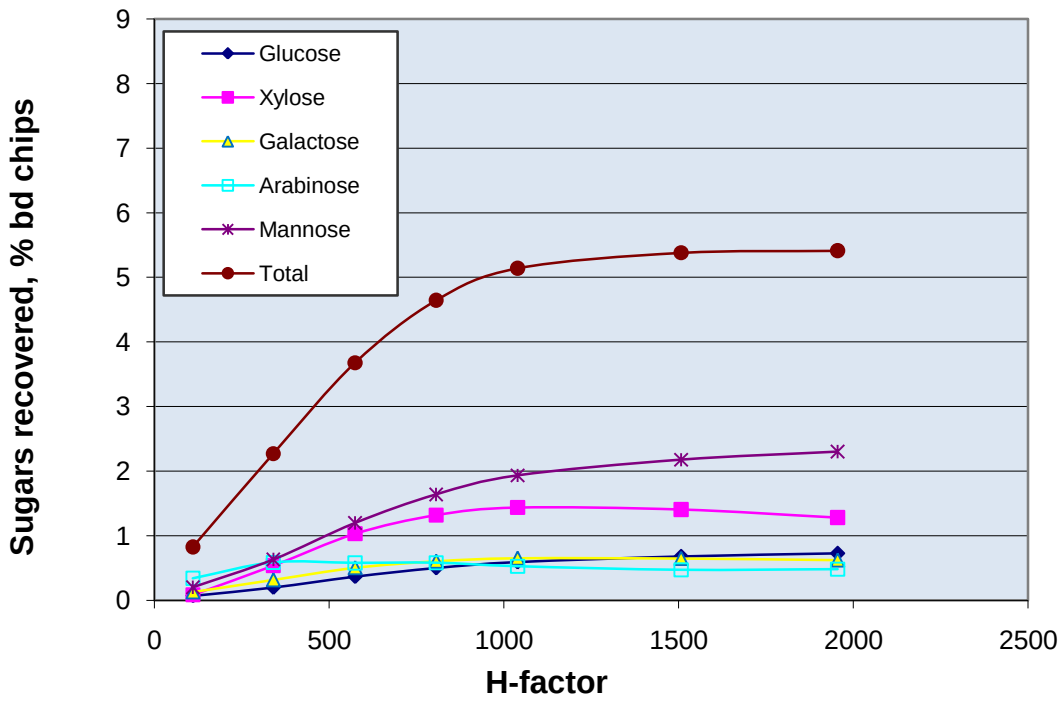


Figure 15 Sugar recovery as a function of H-factor for prehydrolysis with an initial charge of 0.3% NaOH followed by control with 0.5 N NaOH to pH 5.

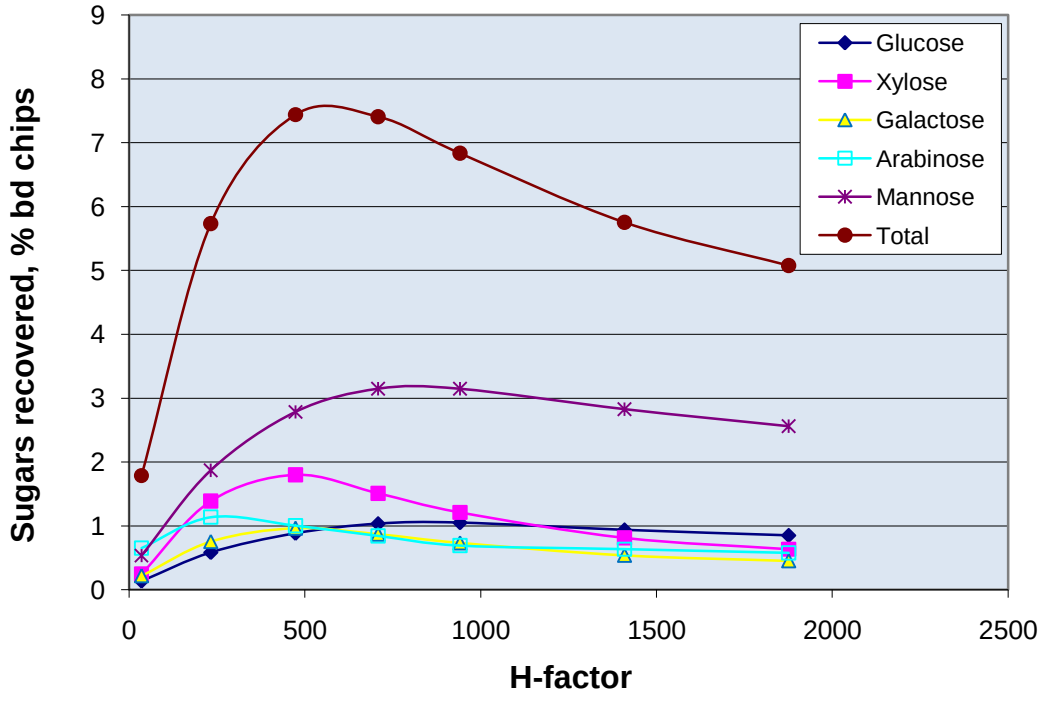


Figure 16 Sugar recovery as a function of H-factor for prehydrolysis with an initial charge of 3% acetic acid followed by control with 0.5 N NaOH to pH 5.

4.4 Material Balances

The aim of VPP is to extract sugars from pine chips that would be removed in kraft pulping while maintaining yield and strength of the pulp after kraft cooking. From an overall material balance perspective, the goal is to move sugar from the black liquor to the VPP extract in order to divert that material to higher value products. Raw chips, prehydrolyzed chips, prehydrolyzate liquid and pulps were tested for yield and sugar composition for comparison of the overall material balance for the water prehydrolysis of kraft pulp. The results of this testing are displayed in Figure 17 through Figure 23. "Black Liquor" is a calculated value that includes everything not accounted for in the pulp or prehydrolysis extract. The value represented by "Black Liquor" includes all degradation products from the prehydrolysis and any other components of the extract that are not specifically measured.

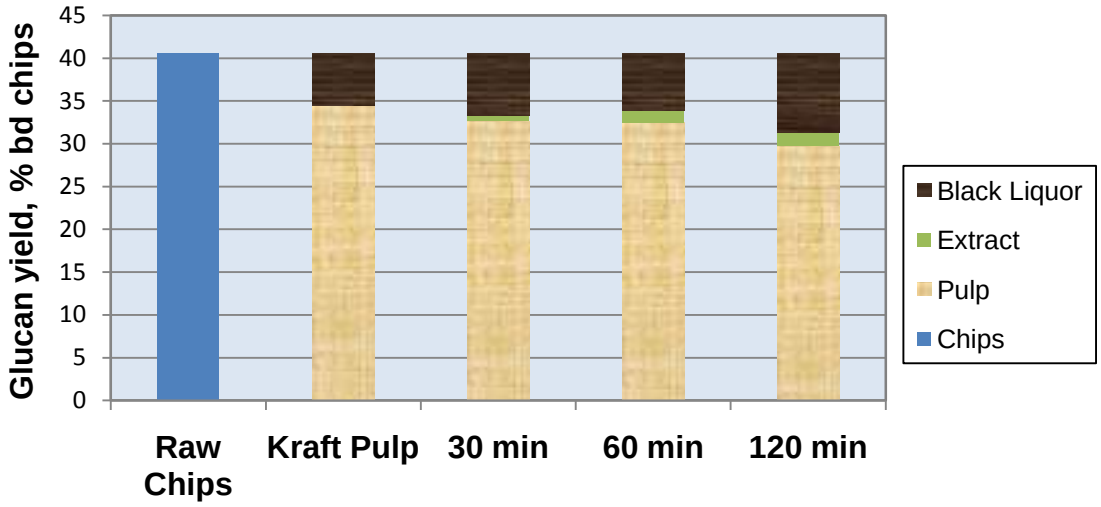


Figure 17 Glucan disposition for water hydrolysis.

The glucan dispositions shown in Figure 17 and Figure 18 demonstrate that only a small fraction of glucan is measured in the extract. As the more severe 2 hour extraction

treatment is done, the glucan in the extract increases to 1.6% of wood, but the glucan in black liquor increases by over 3%. The pretreatment effectively moved glucan from finished pulp to extract and black liquor which was counter to the goal of moving glucan from black liquor to extract. The most favorable tested conditions relative to the goals of VPP were either one hour water hydrolysis or 30 minutes with acid added. The more severe treatments affected the glucan especially in two ways. First, more time was available for prehydrolysis. Second, the deactivation of lignin forced a more severe cook that gave more time for alkaline hydrolysis and secondary peeling.

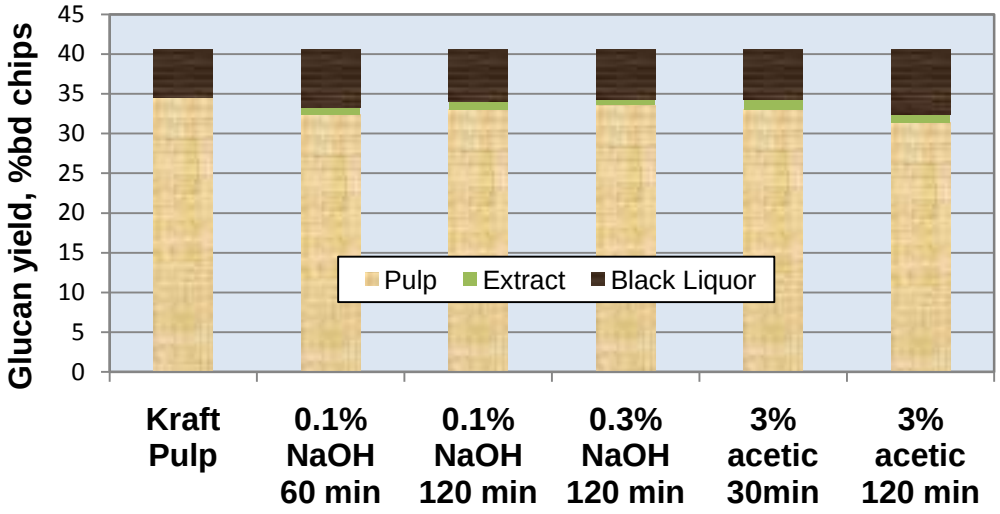


Figure 18 Glucan disposition for pH controlled hydrolysis.

The xylan disposition change shows a trend similar to glucan. Figure 19 and Figure 20 illustrate that the extraction reduces xylan yield in the pulp rather than reducing the quantity in black liquor. Xylan remaining with the pulp is cut roughly in half by a 30 minute water hydrolysis and roughly in half again by continuing the treatment to two hours. More than half of the xylan remains in the kraft pulp while only about one eighth remains in the pulp pretreated for two hours. The most promising extraction condition

from the standpoint of pulp yield was the 30 minute 3% acetic acid treatment, but even this treatment sent more xylan into the black liquor than conventional kraft pulping.

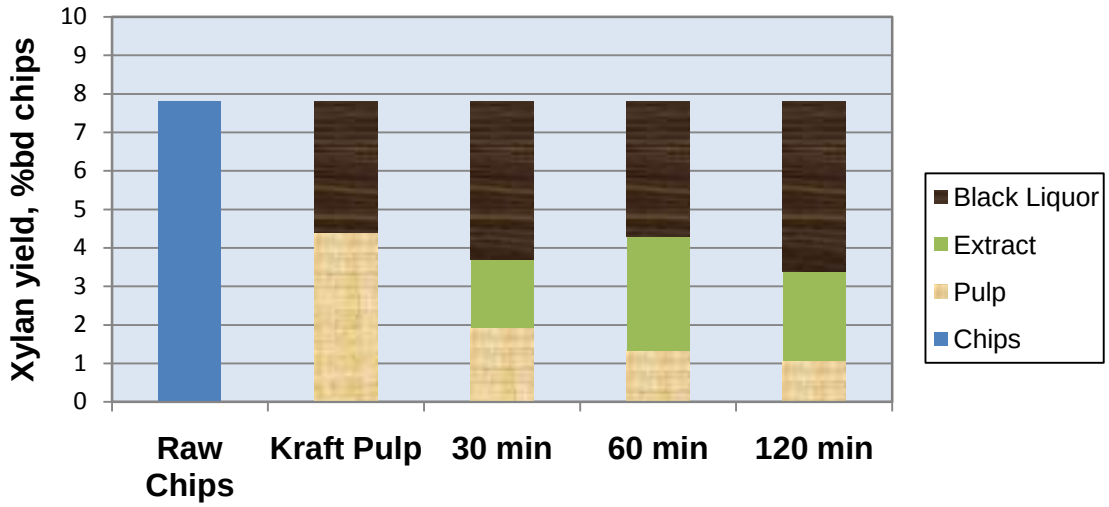


Figure 19 Xylan disposition for water hydrolysis.

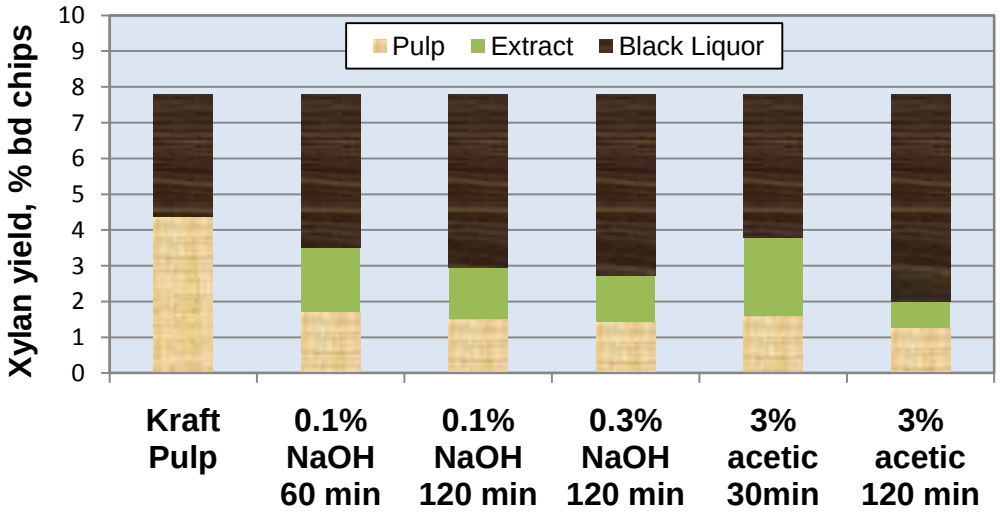


Figure 20 Xylan disposition for pH controlled hydrolysis.

Mannan disposition shown in Figure 21 and Figure 22 illustrates some progress toward the goals of VPP. Mannan remaining in the pulp is reduced from about 25% of

original wood mannan in kraft pulp to less than 10% remaining in the pretreated pulps, but mannan in the black liquor is reduced by half in the two hour treatment.

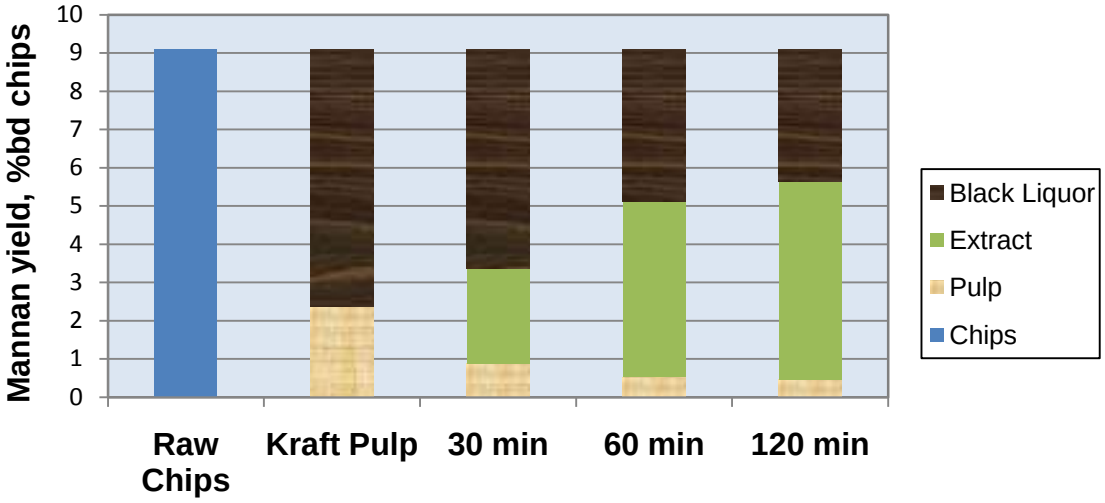


Figure 21 Mannan disposition for water hydrolysis.

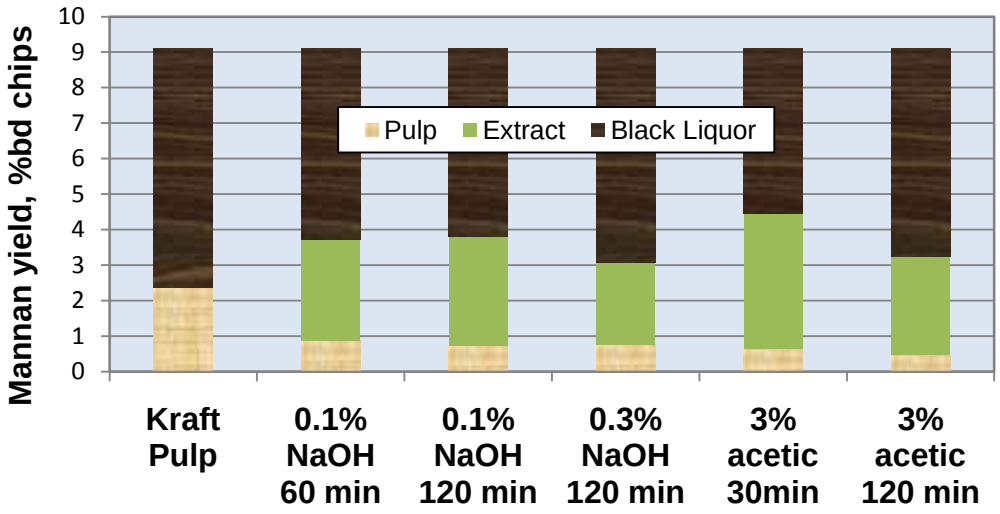


Figure 22 Mannan disposition for pH controlled hydrolysis.

The plots of total chip weight disposition in Figure 23 and Figure 24 illustrate that hydrolysis of pine chips by water alone followed by kraft pulping does not accomplish the goals of VPP. The net movement of sugar is only from the high value pulp to the

extract. The calculated mass of material in the black liquor has not been changed by the treatment, but this calculation does not include acetic acid, lignin or carbohydrate degradation products in the extract.

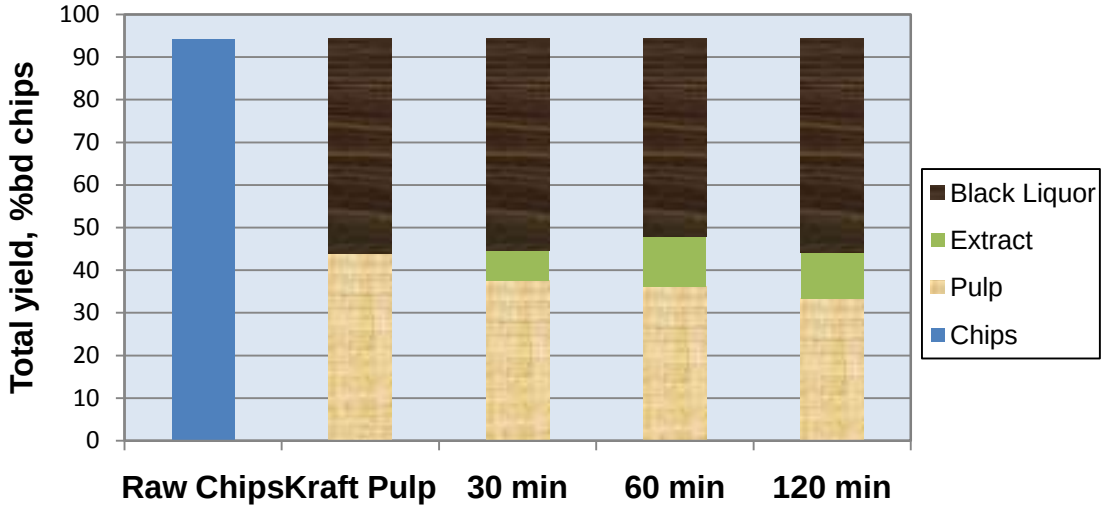


Figure 23 Total disposition for water hydrolysis.

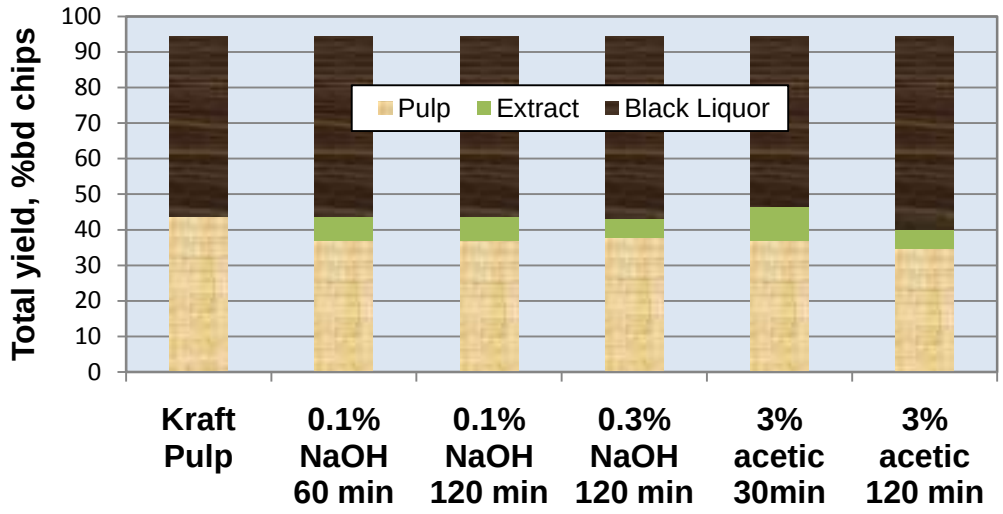


Figure 24 Total disposition for pH controlled hydrolysis.

4.5 Prehydrolysis Conclusions

Kraft pulps were produced following prehydrolysis performed under various conditions to explore the disposition of hemicelluloses. It is possible to manipulate the yield of final pulp and extract by changing the conditions of prehydrolysis. Online monitoring and manipulating pH of the extracting solution is a useful tool in this study as it provides detailed information about the reaction conditions and allows them to be more closely controlled.

It can be concluded from these experiments that careful control of the pretreatment/ extraction conditions and the cooking conditions is required for value prior to pulping from southern pine to be an economically viable process. The most favorable condition tested at 170°C from the standpoint of moving sugar from black liquor to hydrolyzate is a 30 minute pretreatment with an initial charge of 3% acetic acid. Further work should concentrate on maintaining pulp yield relative to extracted sugar yield.

Chapter 5 Prehydrolysis Designed Study

The purpose of the designed experiments was to look further at the effects of changing prehydrolysis time, temperature, pH, and room-temperature-presoak pH with the intent of maximizing sugar removal while limiting any negative impact on pulp properties. An ideal result would be to remove as much of the sugar as is typically removed in kraft pulping. The previous results narrow the list of causes of yield and strength losses in pine to primarily hemicellulose effects. Understanding of prehydrolysis effects on kraft pulping has been extended in this study through a detailed look at the material balance in the process. The use of pH monitoring and control in the prehydrolysis step allows further investigation into some of these effects. The Latin square experimental design illustrated in Table 4 allows the combined effects of the four factors to be looked at together with the relative impact of each factor in fewer experiments. This design assumes that interactions among the factors pH, temperature, and presoak condition are negligible or that the impact of one or two of the factors is expected to be much greater than the other(s) (Ostle 1963).

Table 4 Latin square experimental plan.

A1B1C1	A1B2C3	A1B3C2
A2B1C2	A2B2C1	A2B3C3
A3B1C3	A3B2C2	A3B3C1

5.1 Designed Experiment Factors

5.1.1 Variation of Prehydrolysis Time

The experimental digester was configured to allow sampling of the hydrolyzate while the reaction proceeds. Extractions run under various conditions with sampling on a 15 minute interval for up to 3 hours were discussed in Chapter 4. This data determined the optimal time for extraction at 170°C to be between 30 minutes and two hours from the standpoint of maximum sugar recovery. In the designed experiments, the extraction was run for two hours at temperature. Following the designed experiment, three conditions were repeated but the extractions were terminated at an earlier time based on hydrolyzate sugar concentration measured in the two hour run. The sugar concentrations measured in composition analysis are related to the original chip weight by careful measurement of the volume of liquids added and removed from the digester.

5.1.2 Variation of Temperature

A proper understanding of the effects of temperature of prehydrolysis on sugar recovery rates and pulp yield after extraction will improve technical knowledge of VPP and aid a design engineer in evaluation of process options. If the prehydrolysis is to be performed in the digester, then a high temperature will not impact the capital cost of the equipment, but it will slow production due to residence time used for prehydrolysis and could increase operating costs if additional heating is required. If the prehydrolysis is to be performed in a separate vessel, then the construction cost will depend on temperature according to the pressure rating required.

The preliminary studies were performed in the laboratory digester at 170°C. Since prehydrolysis at a lower temperature is slower and therefore would require a larger

reactor, there should be an optimum temperature taking into account sugar release, hydrolyzate end-use compatibility, pulp strength effects, if any, and a capital cost factor. Previous work suggests 150°C to 160°C as optimal for water hydrolysis in production of dissolving grades (Bernardin 1958) (Mitchell, et al. 1956) (Richter 1956) so the designed experiment included a range centered on 155°C.

5.1.3 Variation of pH

In previous work, the maximum sugar yield for water hydrolysis was observed when the extract had a pH of about 3.5 (Yoon, MacEwan and van Heiningen 2006). The pH was dependent on the integrated time and temperature of extraction in these experiments, however and was not controlled independently. In the preliminary studies in this research, application of NaOH for pH control appeared to have an inhibitive or even destructive effect on extracted sugars. Initial application of acetic acid greatly accelerated the rate of hydrolysis and extraction. In other work, the use of a mineral acid, 0.5% sulfuric, in the hydrolysis produced similar hydrolysis effects at 120°C to those observed with water in the same time at 170°C (Richter 1956). The additional constraint to not introduce chemicals with sulfur outside of the conventional kraft cook was initially placed on this research. This constraint limited the choices of pH control agents and potential additives. Acetic acid was chosen for pH reduction since this could, theoretically, be a product of the VPP extraction and possibly available from on-site production. The use of a buffer at a pH range of 3.5 to 4.5 has also been suggested (Francis 2006). A buffer could be an option after an appropriate pH target is identified. Economics will be an important factor in determining an industrial pH control method if one is recommended.

Lower pH and higher temperature are each expected to accelerate the hydrolysis of hemicellulose, the degradation of dissolved sugar monomers, and condensation of lignin. Observation of each of these effects at various pH levels should aid in the choice of an optimal pH depending on which effect is most important to success of the process. Highly alkaline environments also quickly degrade dissolved sugar monomers. Sodium carbonate was used in place of sodium hydroxide to raise the pH in the designed experiment to reduce the possibility of a locally high pH.

5.1.4 Variation of Presoak Conditions

The intention of the presoak was to rehydrate the dried chips and test any effect of changing the pH of the rehydrating liquor on prehydrolysis and on subsequent kraft pulping. The chips were air- dried when received to limit degradation of the chips due to biological growth and to reduce variability over time in measuring the quantity of wood for each test. Liquor penetration in air-dried chips is much slower than that in wet chips, however, and can lead to increased pulp quality variability attributable to chip size (Jimenez, McKean and Gustafson 1990). This delay is attributed to the required dissolution and diffusion of air trapped in the chips. To optimize movement of reactants in and out of the chips, air should be removed from the chips. This is accomplished industrially by replacing the air with water vapor in presteaming.

Soaking the chips in liquid to remove the air does take longer than presteaming them, but the capillaries between tracheids in the chips facilitate this happening quickly. The chip voids should be completely full of the presoak when the chip weight is 67% water (Rydholm, 295-297) or at a liquor-to-wood ratio of 2. The presoak was accelerated

by placing the chips, covered in the presoak solution, in a vacuum oven until bubbling stopped at 26 inches of Mercury.

Prehydrolysis kraft is a multistage process, but adding a presoak stage provided an opportunity to test more effects. Other forms of multistaging could follow the lead of some sulfite mills by beginning with buffered liquor at near neutral and then adding acid to meet the pH target for hydrolysis (Ingruber, Kocurek and Wong 1985, 303). In this manner, presoak at high pH may preserve some hemicellulose through both the prehydrolysis and kraft cook. Presoak at low pH may improve hydrolysis rate and yield. Previous studies indicate that acetyl and uronic acid along with small amounts of arabinogalactan in the wood can be solubilized by room temperature extraction with water (Casebier 1969). Samples of the different soak solutions were retained for composition analysis.

5.2 Hydrolysis Target

Approximately 20% of the wood weight as sugars is lost to the black liquor in the laboratory kraft process at Auburn University. Ideally, then the goal in VPP is to recover 20 percent of the wood as hemicellulose in the hydrolyzate. The difficulty is that the kraft cook after pretreatment also removes carbohydrates and this removal appears to be enhanced by the prehydrolysis. The question is then expanded to be not only how much can be removed by extraction, but also what characteristics of the process should be observed to demonstrate sufficient extraction for value while minimizing damage to the primary product, the wood pulp.

Wood weight loss in hydrolysis and sugar recovered from the hydrolyzate do not have a simple relationship, therefore both chip weight loss before pulping and

composition of the hydrolyzate liquid as a function of time were measured. The need to measure both was demonstrated in the preliminary work as illustrated in Figure 25. One might expect that some non-sugar material is removed and that some of the removed sugars are degraded by the extraction process. An example of the latter is the "Acetic" data. The point labeled "Max" is the total sugar analyzed after 30 minutes of hydrolysis. The point below it in the chart is the result after two hours in the same prehydrolysis run. The chip weight loss after two hours is used for both points. Sodium hydroxide was added to raise the pH to 5.0 beginning at 30 minutes in this run.

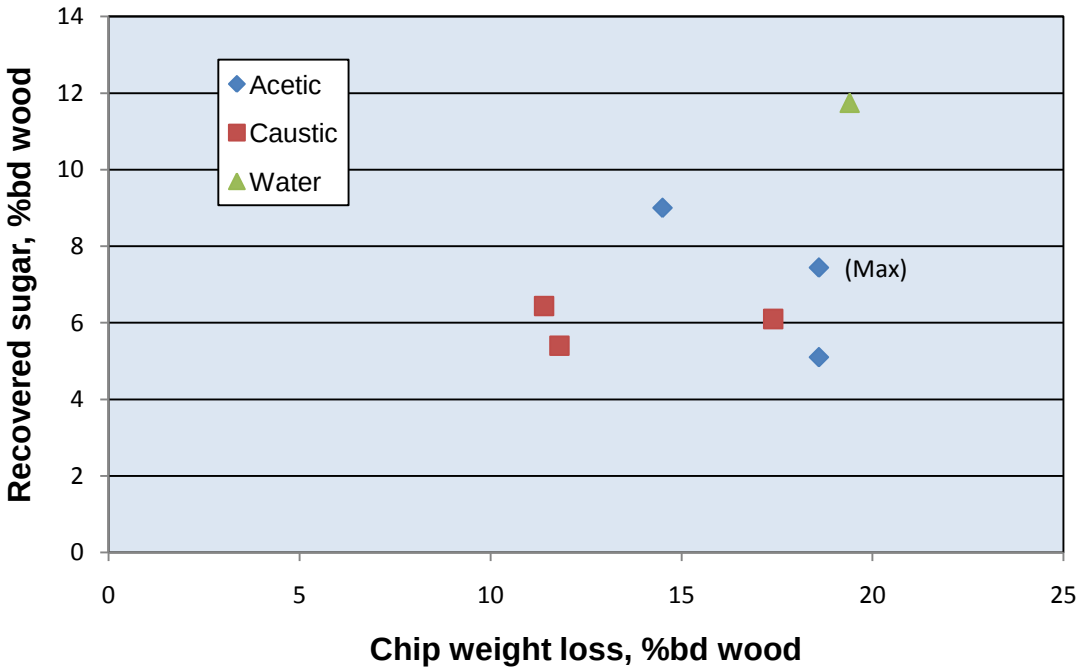


Figure 25 Hydrolyzate sugar vs. chip weight loss.

5.3 Experimental Design

The prehydrolysis screening experiments consist of a Latin square of three factors at three conditions (Hendrix 2002). A fourth factor, prehydrolysis time-at-temperature,

was measured by way of sugar recovery in the hydrolyzate for all conditions. The factors and conditions are listed in Table 5 along with the letter and number corresponding to each factor. As an example, "A1" refers to prehydrolysis pH 3.0.

The experimental plan is represented by a square with nine experiments illustrated in Table 4. The design tests each level of each factor at all three levels of the other factors. The experiments were performed in random order.

Table 5 Latin square conditions for prehydrolysis screening.

Factor:	Prehydrolysis pH	Prehydrolysis Temperature, °C	Pre-Soak pH
Condition	A	B	C
1	3.0	140	3.5
2	3.5	155	7(DI Water)
3	4.5	170	10

The randomized prehydrolysis runs were assigned a letter label for reference in the order the cooks were performed. Subsequent prehydrolysis cooks that followed the initial nine were coded with letters in the order the cooks were performed for ease of reference. The initial nine cooks and the conditions they represent are listed in Table 6.

Each of the first nine runs was programmed to circulate for two hours after the ramp from 30°C to target temperature. The ramp to target temperature was programmed to take 45 minute for cooks "A" and "B". The digester came to temperature late relative to the program, however and control was difficult at the transition from ramp to steady operation. The ramp was changed to one hour for run "C" and all subsequent prehydrolysis runs. Samples of the prehydrolyzate liquid were taken via a cooling coil

and stored in a refrigerator for secondary hydrolysis and sugar composition analysis. Each prehydrolyzate sample was given a time assignment relative to first reaching the temperature target and relative to the start of the ramp.

Table 6 Latin square experiment order and labeling.

Label	pH	Temperature, °C	Pre Soak pH
A	3.0	170	7
B	4.5	155	7
C	4.5	170	3.5
D	3.5	140	7
E	3.5	155	3.5
F	3.5	170	10
G	3.0	155	10
H	4.5	140	10
I	3.0	140	3.5

Two sets of two and six sets of three bomb kraft cooks were performed using dry chips to develop standard information for comparison of the prehydrolyzed chips. The results of the first set of two were not used as some of the chips remained undercooked after the bombs were opened. The liquor to wood ratio was increased slightly after this by using the vacuum oven to remove air from the chips. The remaining seven sets of cooks used the same chip mass: 70 g bone dry, liquor charge: 20% active alkali at 30% sulfidity, liquor to wood ratio: 6.0, temperature target: 165°C, and ramp to temperature of one hour. The time at temperature was changed to vary the H-factor. Pulp kappa number and total yield were measured after the pulp had been washed and dried. These

data were then used to plot kappa number as a function of H-factor and yield as a function of kappa number. These plots are illustrated in Figure 26 and Figure 27.

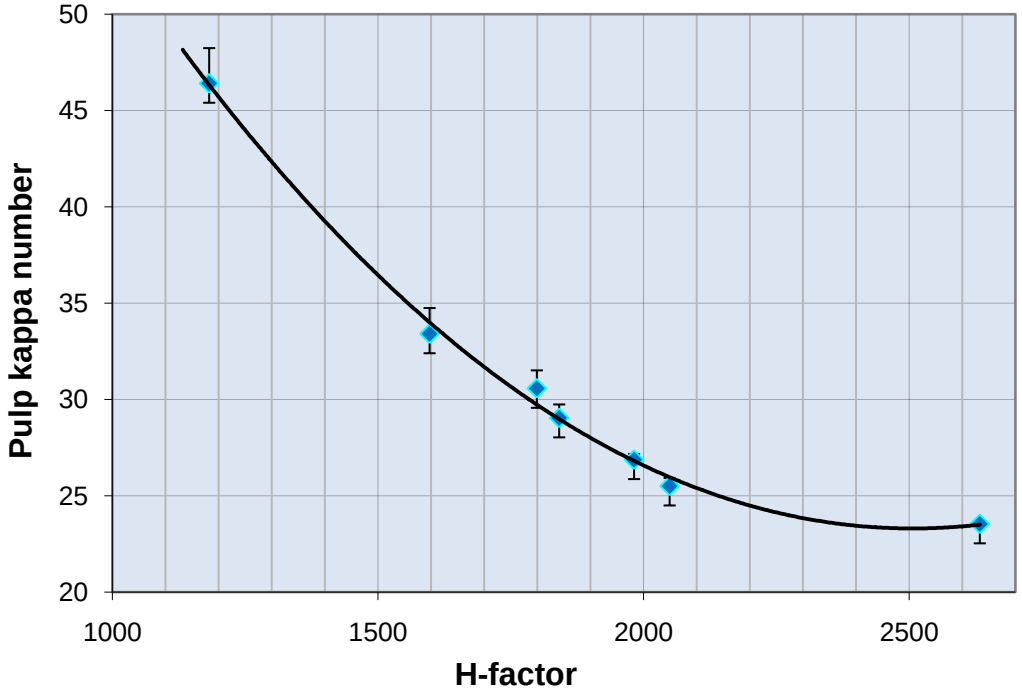


Figure 26 Kappa number as a function of H-factor for raw chips.

The standard condition of 1850 H-factor for producing a lignin content of 30 kappa number was interpolated from the results of cooks 2-5 and was also tested with resulting averages for the three bombs of kappa number 29.0 and 45.0% yield. Those data are also included in Figure 26 and Figure 27. The curve displayed in Figure 26 is a third order polynomial fit by Microsoft Excel ® that approximates the curve that was drawn manually to chose the standard H-factor. The yield calculated at kappa 30 for raw chips, 44.63%, was used as the standard for comparison to the prehydrolyzed chip cooks.

Each sample of prehydrolyzed chips was divided into six subsamples. Five of the subsamples represented 70 g dry chips. Part of the remaining subsample was used to measure the moisture content of the chips for calculation of weight loss during

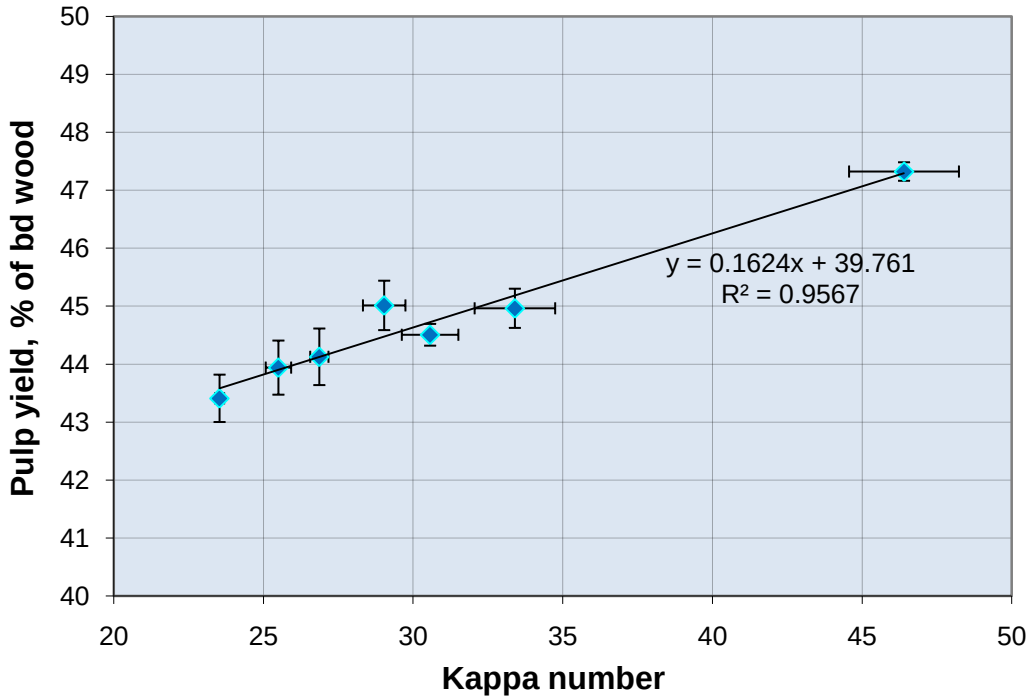


Figure 27 Pulp yield as a function of kappa number for raw chips.

prehydrolysis and the rest was reserved for composition analysis. The first subsample of chips from each prehydrolysis run was cooked to 1850 H-factor; the conditions that were calculated to produce a kappa number of 30 from the dry chips. The second subsample was cooked with the same conditions except that 0.1% AQ was added. The chips for the third cook were grouped together based on the kappa number of the pulp from the first cook. The H factor was then changed for each group in an attempt to produce a pulp on the opposite side of kappa number 30 from that achieved in the first cook. Chips for the fourth and fifth cooks were again grouped together based on target H factor. The fourth cook was used to add a bracketing condition or a central condition around kappa 30. The aim of the fifth cook was similar to the third except that it also used AQ. The results of the cooks with AQ are discussed in Chapter 6.

5.4 Results

5.4.1 Prehydrolyzate Composition

Five different sugars were measured in the composition analysis: arabinose, galactose, glucose, mannose, and xylose. A secondary hydrolysis was part of the test method since the samples contained oligomers and monomers. The absolute value of arabinose and mannose for samples taken at higher times from tests at 155°C and 170°C were estimates due to the peaks for these two sugars blending on the chromatogram. The mannose peak covered the arabinose peak in most cases since it was larger. The arabinose concentration was estimated and the measured concentration of mannose was reduced by 10% for these samples per Auburn University Chemical Engineering Department laboratory standard practice. The sugar concentration measured in the samples was related to the original wood weight using the wood weight charged to the digester and the calculated volume of solution circulating in the digester and contained in the wet chips. The mass transfer time between the chip voids and the free liquor was assumed to be short relative to the time between samples. The dissolved sugar concentration and temperature were then considered to be uniform since the prehydrolyzate liquor was completely turned over by the digester circulation approximately once per minute.

Other components of the hydrolyzate potentially include acid-soluble lignin, acetic acid, uronic acid, and degradation products, but these were not quantified in this study. The acid-soluble lignin concentration was measured for some of the preliminary hydrolyzate samples discussed in Chapter 4, but these measurements and material balances both consistently indicated that this component was less than 1% of wood and

consequently it was not measured for this portion of the research. The acetyl component of the galactoglucomannan and the methyl-glucopyranosyluronic acid component of the arabinoglucuronoxylan were also not measured even though collectively they were estimated to make up about 3% of the dry wood (0.7% and 2.1% respectively based on typical softwood hemicellulose compositions (Sjostrom 1993, 63-66)). Acetic acid measurements would have been confounded by the use of acetic acid for pH control. Uronic acid measurements are not a standard test in this lab at Auburn University and would be complicated by the lack of available uronic acid standards. Peaks for the primary degradation products for pentoses and hexoses, furfural (FUR) and hydroxymethylfurfural (HMF) respectively, were observed on some of the chromatograms and notes of a qualitative nature were made regarding their presence or absence, but no attempt was made to quantify these or any other degradation products.

The results of the prehydrolyzate composition analysis reveal a strong dependence of sugar in solution on reaction temperature and pH. The effect of the presoak condition was less obvious and is discussed later in this chapter. Higher temperature and lower pH both increased the rate of sugar dissolution. The highest temperature and lowest pH condition did not yield the highest recovered sugar quantity, however, due to degradation of the monomers after their release into solution. The hydrolyzate sugar composition data as a function of time are presented in Figure 28 through Figure 36 and discussed in rough order of increasing maximum total recovered sugar quantity.

The slowest sugar removal was at pH 4.5 and 140°C. Figure 28 shows an almost linear increase in total sugar concentration over the time at temperature. This is the combination of relatively fast removal of arabinose in the first 45 minutes that then

slowed and initially slow dissolution of the other four sugars that then accelerated over the last hour. The total sugar removed after two hours represents less than 3% of the dry wood and only about 12% of the hemicellulose. Arabinose is a disproportionate 37% of the total recovered since 69% of the original arabinose was found in the hydrolyzate. No FUR or HMF peaks were observed in the hydrolyzate sample chromatograms for this run.

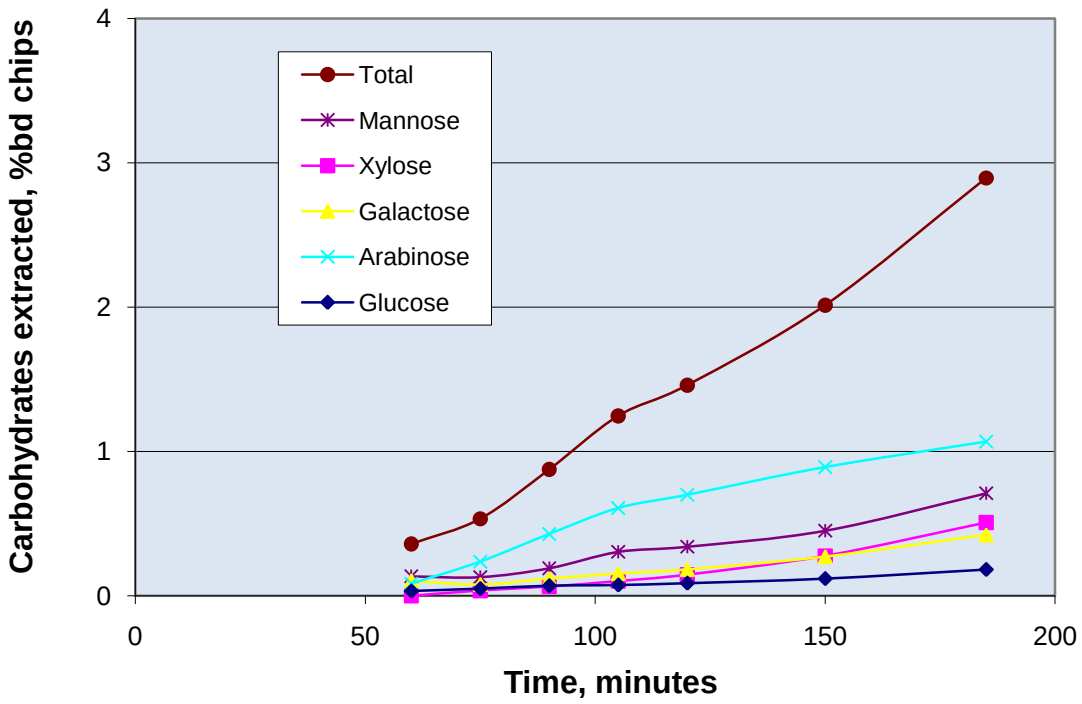


Figure 28 Sugar recovered as a function of time for prehydrolysis cook "H" pH 4.5, 140°C, 10.5 pH Soak.

Reducing the pH from 4.5 to 3.5 at the same temperature nearly doubled the total sugar removed but was still only 5.5% of wood or 23% of hemicellulose. Figure 29 shows again an almost linear increase over the two hours at 140°C. The sugar recovered was doubled with the exception of arabinose. The individual sugar trends were similar to the higher pH condition. A very small FUR peak was observed in the final sample indicating that degradation of pentoses was beginning even under these mild conditions.

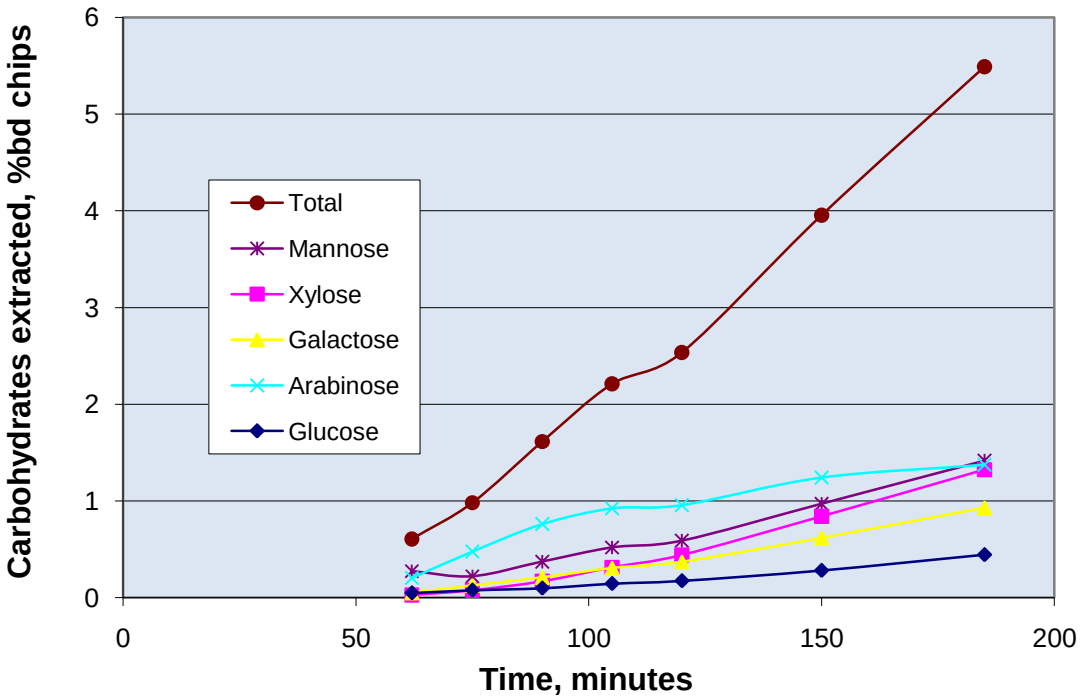


Figure 29 Sugar recovered as a function of time for prehydrolysis cook "D" pH 3.5, 140°C, DIW Soak.

Conditions B and I yielded results very similar to each other, showing that changes in temperature and pH can be used to control the extent of hydrolysis. In this case, lowering the pH from 4.5 to 3.0 countered the effect of lowering the temperature from 155°C to 140°C. As shown in Figure 30 and Figure 31, the total yield of sugars was moderate in these cases at between 7 and 8% of wood and the rate of appearance of sugars in the hydrolyzate only slightly decreased in the second hour. In these two tests and all remaining tests in the designed study, essentially all of the arabinose is removed from the chips. The responses of glucose, xylose, galactose, arabinose, and mannose were very similar to their counterparts in the two tests. Very small FUR peaks were observed in the chromatograms beginning after one hour for 155°C and pH 4.5 and after 90 minutes for 140° and pH 3.0

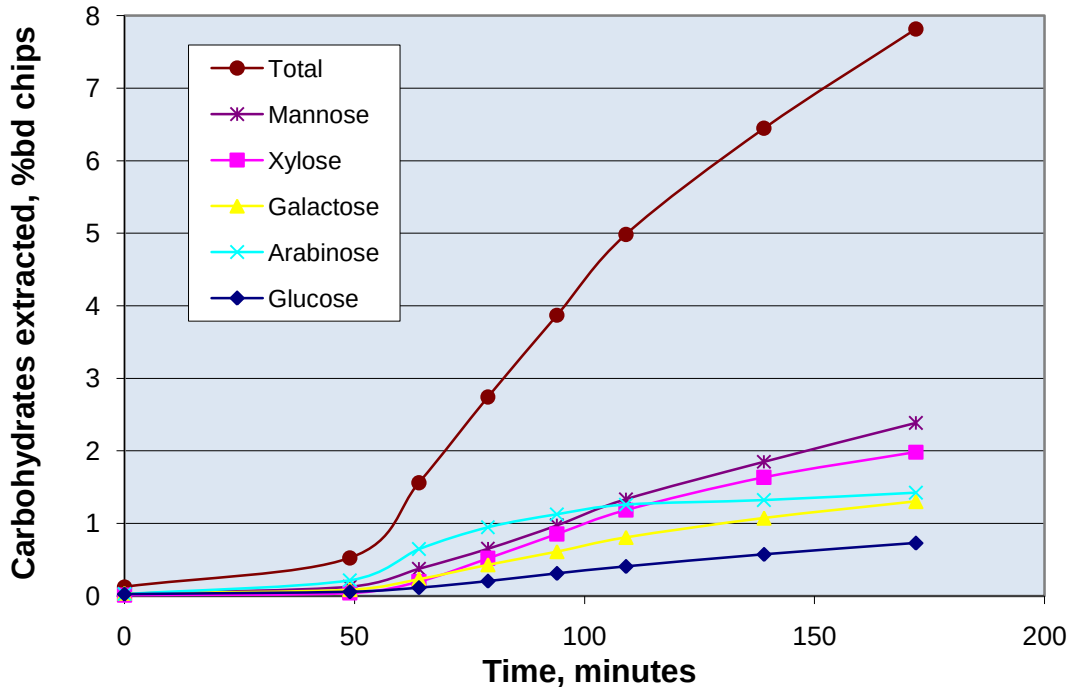


Figure 30 Sugar recovered as a function of time for prehydrolysis cook "B" pH 4.5, 155°C, DIW Soak.

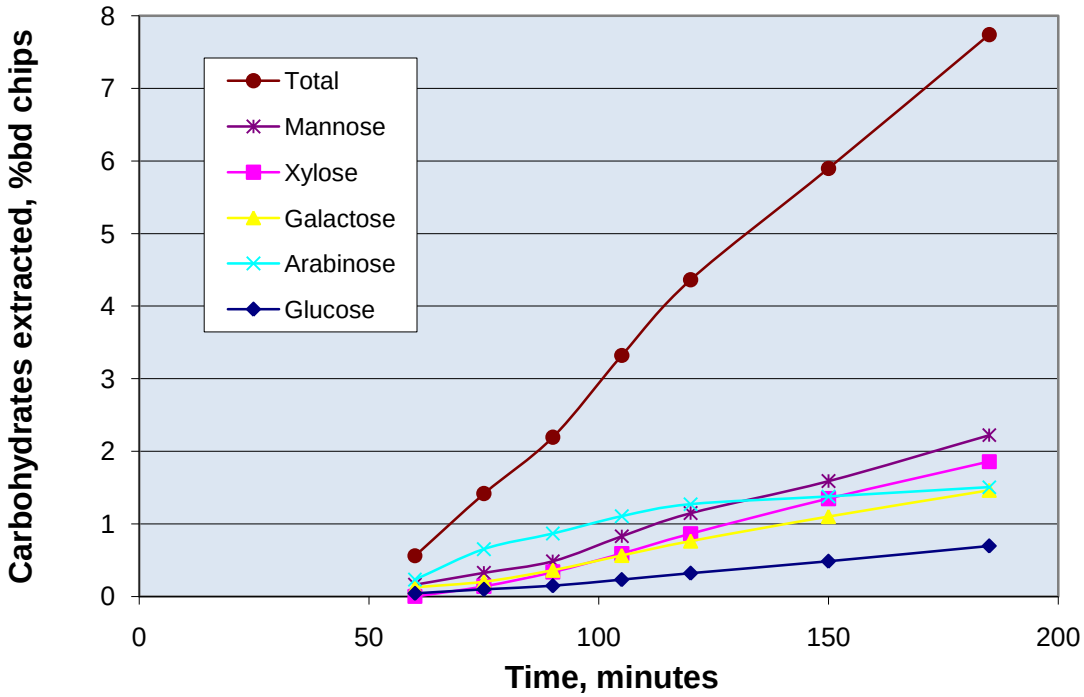


Figure 31 Sugar recovered as a function of time for prehydrolysis cook "I" pH 3.0, 140°C, pH 3.1 Soak.

Conditions C, A, and F, the tests at 170°C shown in Figure 32, Figure 33, and Figure 34, were similar in the very fast initial appearance of sugars followed by a reduction in total sugar quantity due to degradation of primarily the pentoses: xylose and arabinose. Both the initial rate of recovery and the rate of degradation were increased at lower pH. This phenomenon produces optimums relative to sugar recovery in time and in pH for operation at 170°C. The optimum time was 90 minutes for pH 4.5 and 3.5 but only 60 minutes for pH 3.0. The best pH of the three tested at 170°C is 3.5 where 56% of the wood hemicellulose sugars are found in the hydrolyzate. FUR was observed after only ten minutes at 170°C in all three tests and the peak was large after 45 minutes at pH 3.0. HMF was observed after 90, 45, and 20 minutes respectively as pH decreased from 4.5 to 3.5 and finally to 3.0. These observations confirm significant degradation of both pentose and hexose at 170°C and especially as the pH dropped below 4.5.

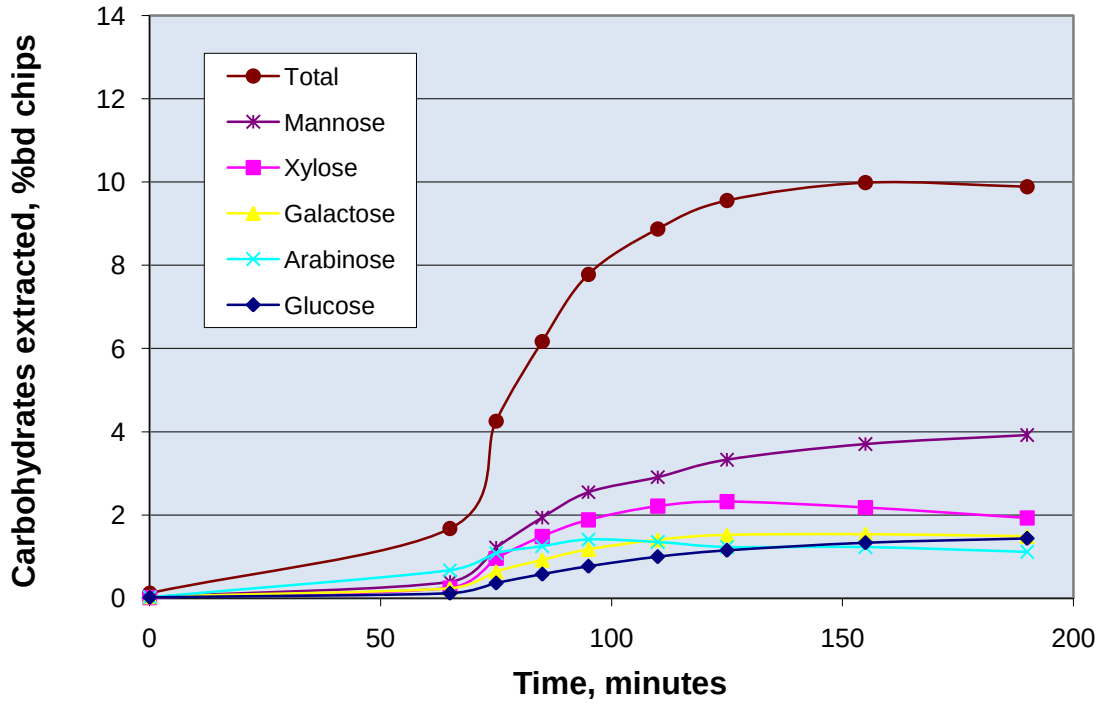


Figure 32 Sugar recovered as a function of time for prehydrolysis cook "C" pH 4.5, 170°C, pH 3.1 Soak.

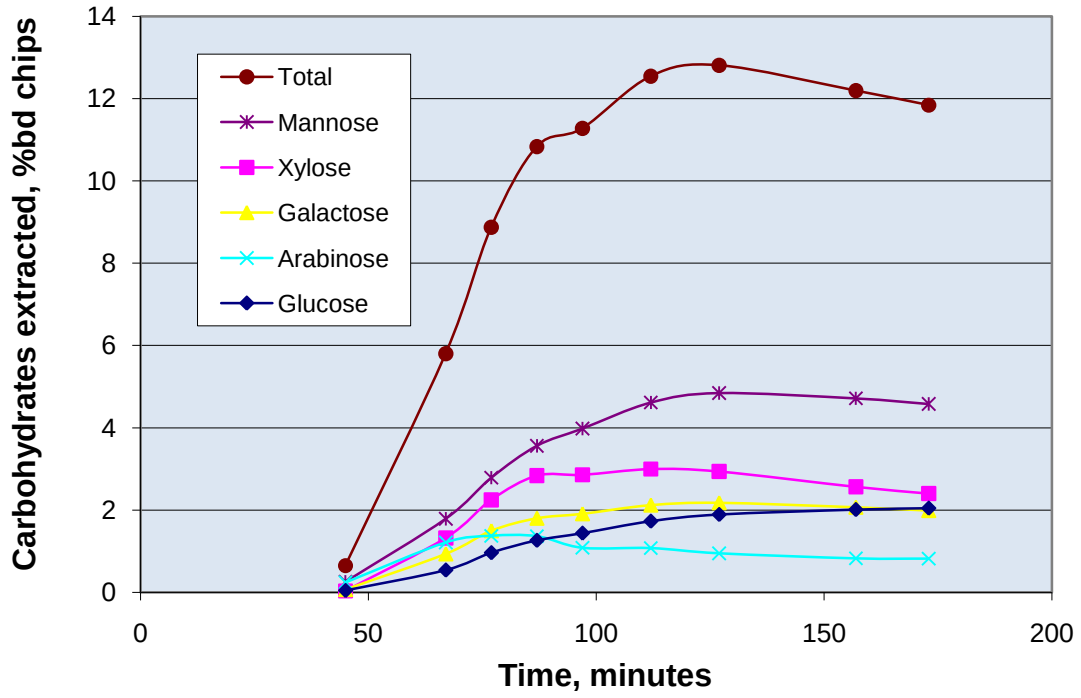


Figure 33 Sugar recovered as a function of time for prehydrolysis cook "A" pH 3.0, 170°C, DIW Soak.

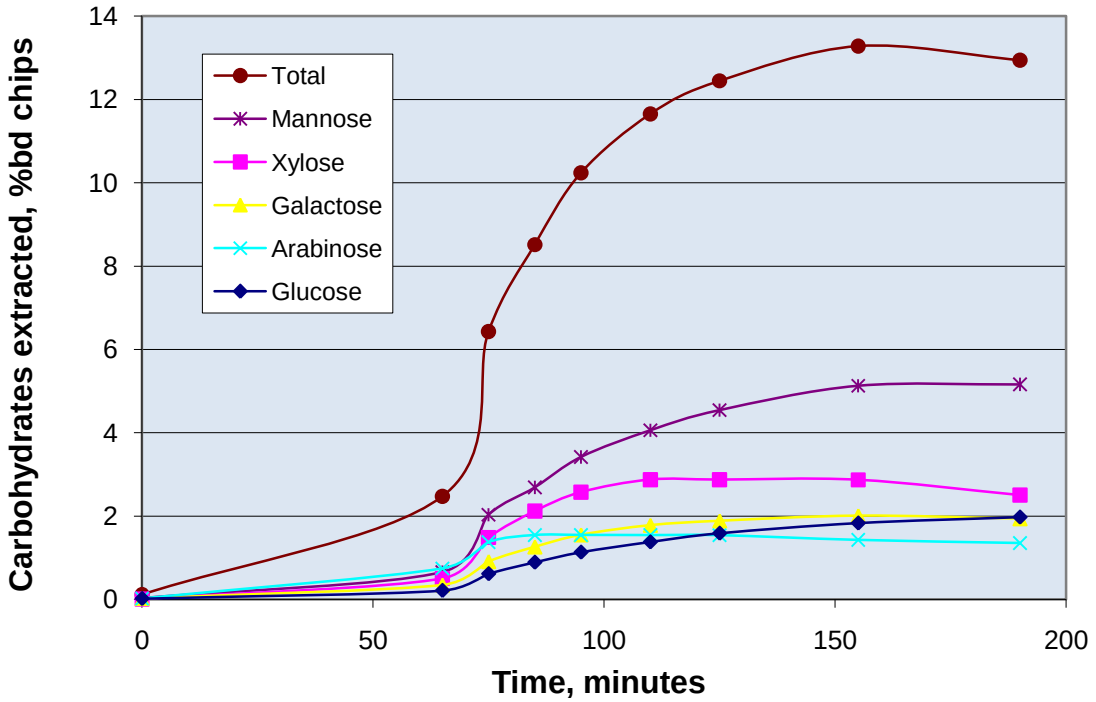


Figure 34 Sugar recovered as a function of time for prehydrolysis cook "F" pH 3.5, 170°C, pH 10.5 Soak.

The lower two pH levels tested at 155°C potentially gave the best results overall. The results of these tests, illustrated in Figure 35 and Figure 36, show a continual increase in concentration of all sugars over the test period with the exception of arabinose which was completely removed from the chips within the first hour. Galactose was also completely removed by the end of the test at pH 3.0. The arabinose data at higher times

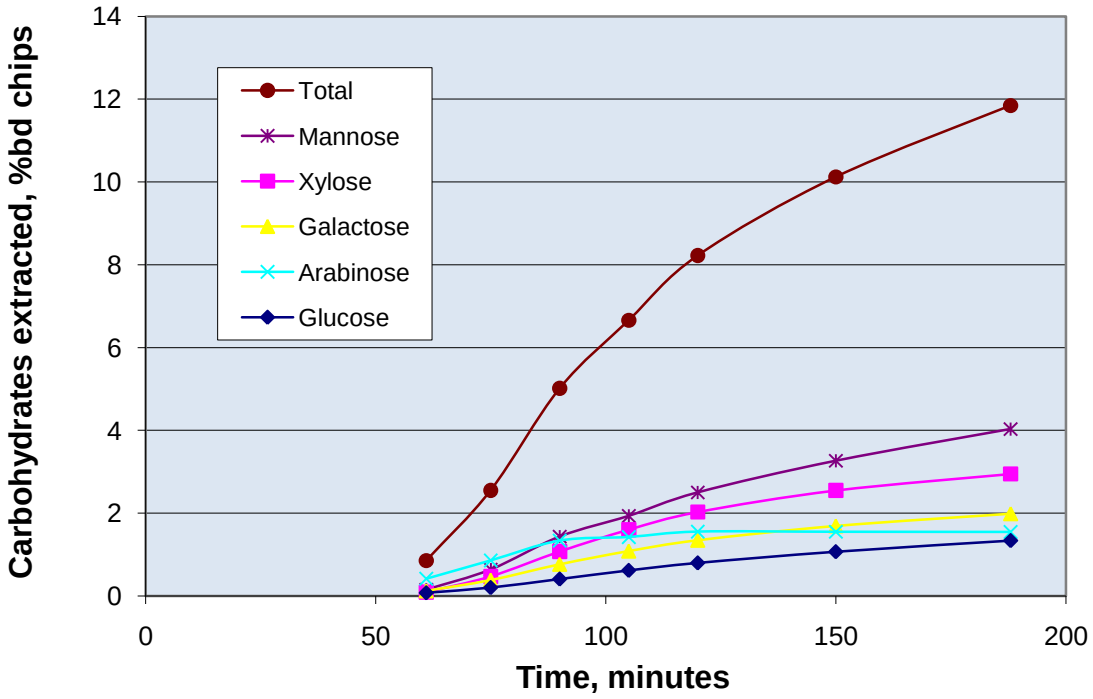


Figure 35 Sugar recovered as a function of time for prehydrolysis cook "E", pH 3.5, 155°C, pH 3.1 Soak.

was obscured by the mannose data, so it was not possible to tell if there was significant degradation of arabinose under these conditions. The maximum percent hemicellulose removed in these two conditions, 50% and 57% are very similar to the maximum removed at the same pH at 170°C, but the trends indicate that more sugars could be recovered at 155°C if the prehydrolysis were allowed to continue for a longer time period. A small FUR peak was observed after 30 minutes at pH 3.5 and after only 15

minutes at pH 3.0. Pentose degradation appeared significant at pH 3.0 after 45 minutes and a small HMF peak appeared in the 90 minute sample of this run.

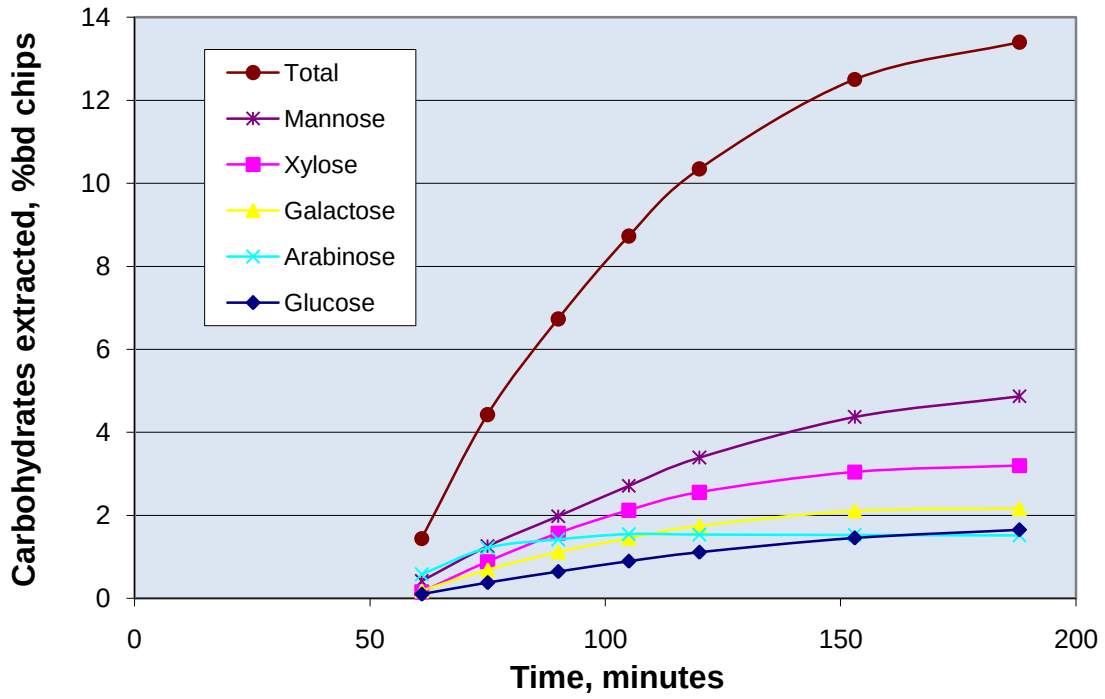


Figure 36 Sugar recovered as a function of time for prehydrolysis cook "G", pH 3.0, 155°C, pH 10.5 Soak.

Several conclusions can be made from this group of data by examination of Figure 28 to Figure 36. For convenience, Figure 37 shows the total sugar curves from all nine conditions. The colored lines for each curve are based on temperature: Yellow is 140°C. Brown is 155°C. Blue is 170°C. It is clear that higher temperature increases the rate and total amount of sugar recovered for all conditions except for sugar recovered after more than one hour for pH 3. Similarly, reducing pH in the range 4.5 to 3.0 increases the rate and total amount of sugar for all temperatures except for 170°C after 30 minutes of reaction time where the response at pH 3.5 began to exceed the response at pH 3.0 due to degradation of sugars. The solution pH is represented in the chart by the shape

of the data points: Square is 3.0. Triangle is 3.5. Circle is 4.5. The presoak pH is represented by the color of the data points: White is 10. Black is 7. Green is 3.5. There is no clear trend for presoak pH among these results. For example, presoak at pH 10 has the two highest results, but also the lowest.

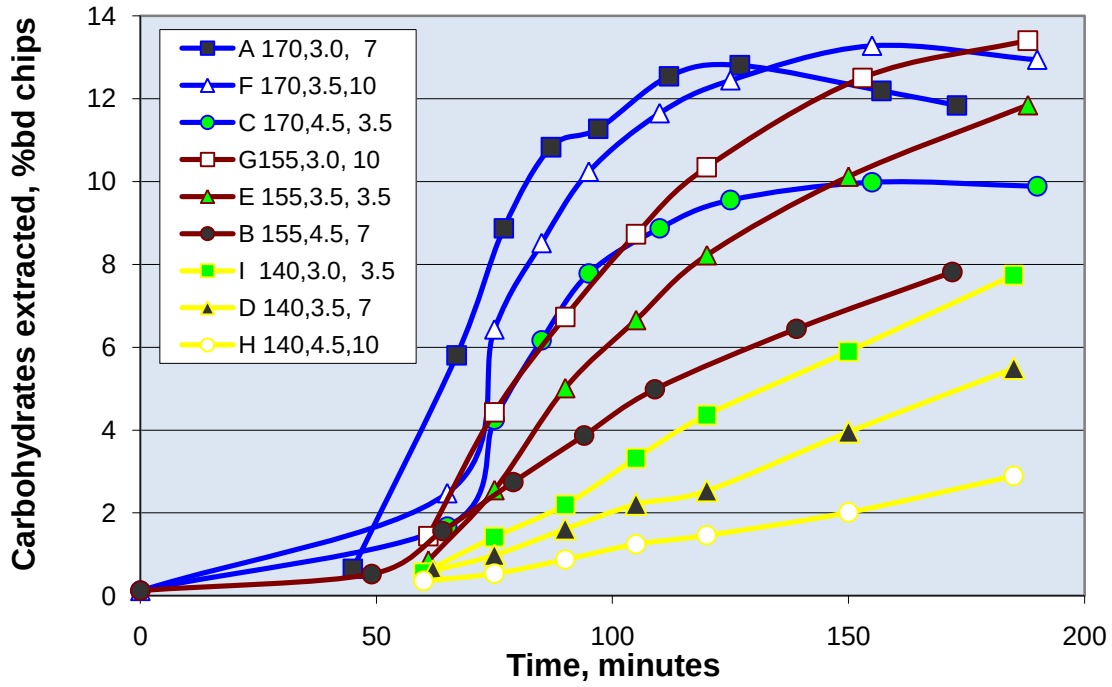


Figure 37 Total sugar recovered as a function of time for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

Comparing the behavior of each sugar for all nine conditions is also valuable.

Arabinose was removed from the chips quickly under all test conditions. Even at 140°C and pH 4.5 (Condition H) 69% of the arabinose in the raw chips was removed after two hours and the trend indicates that the remainder would be in solution in less than three hours. Arabinose is expected to significantly degrade after it enters solution at 170°C, but the arabinose data at higher times was obscured by the growing mannose peak on the chromatogram. As can be seen in Figure 38, the arabinose concentration reaches a

maximum in the 170°C tests after about 10 to 30 minutes at temperature. After this time, the quantity in solution drops as either the degradation rate exceeds the dissolution rate or all of the arabinose has entered solution and begins to degrade. The degradation rate is much slower at the lower temperatures and, therefore most of the arabinose remains in solution at the conclusion of the test. Arabinose is a small fraction of the wood and hemicellulose, 1.5% and 7% respectively, but is a disproportionately large part of the final hydrolyzate, 12-37% depending on extraction conditions, since it enters solution so readily. Arabinose would be an even higher proportion of the dissolved sugar under any of these conditions if the prehydrolysis treatment was stopped early.

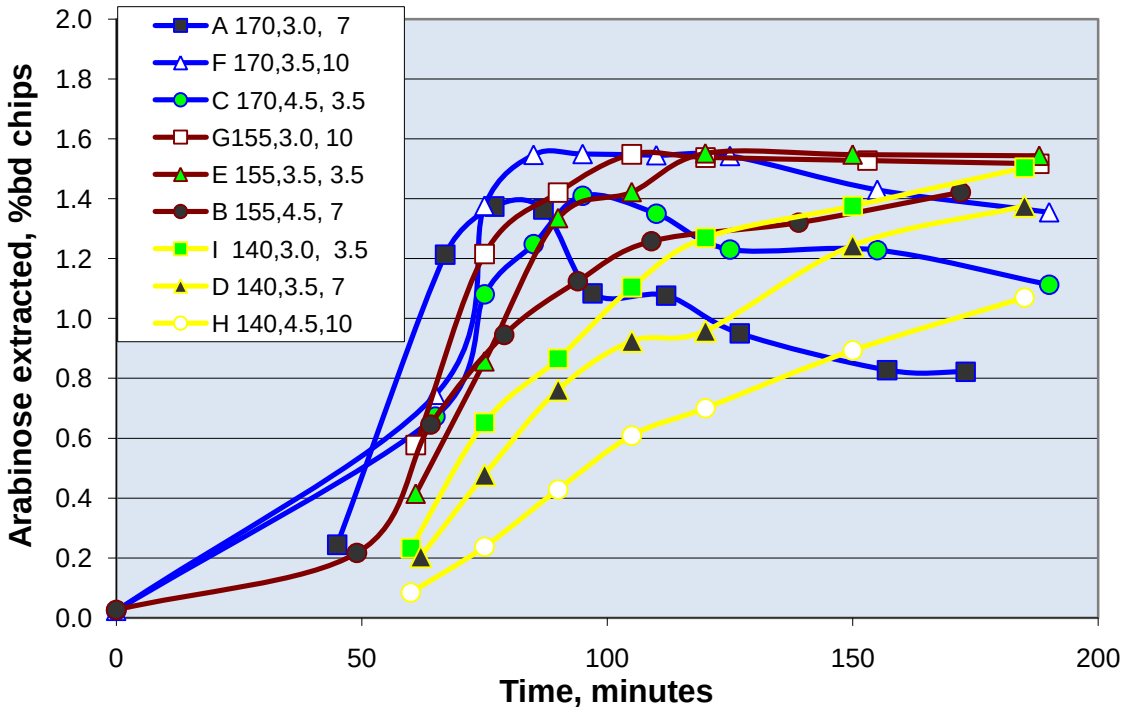


Figure 38 Arabinose recovered as a function of time for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

Galactose removal from the chips was much more widely varied than arabinose with only 20% of the original galactose removed at 140°C and pH 4.5 and 100%

recovered at 155° and pH 3.0. As shown in Figure 39, the rate of removal and quantity recovered increased with time, increasing temperature and dropping pH for all tests at 140 and 155°C. The observed behavior of galactose at 170°C was more complicated with the rate of removal and the rate of degradation both appearing to be pH dependent. The reduced rate of removal at pH 4.5 followed by significant degradation at the high temperature forced the recovered galactose to reach a maximum at 1.5% of wood or about 70% of the galactose available. The high rate of removal and degradation at pH 3.0 allowed a maximum of 100% recovery after 60 minutes at temperature but only 91% after 105 minutes. Both rates were slowed slightly at pH 3.5 as 92% of the galactose was recovered after 90 minutes at temperature.

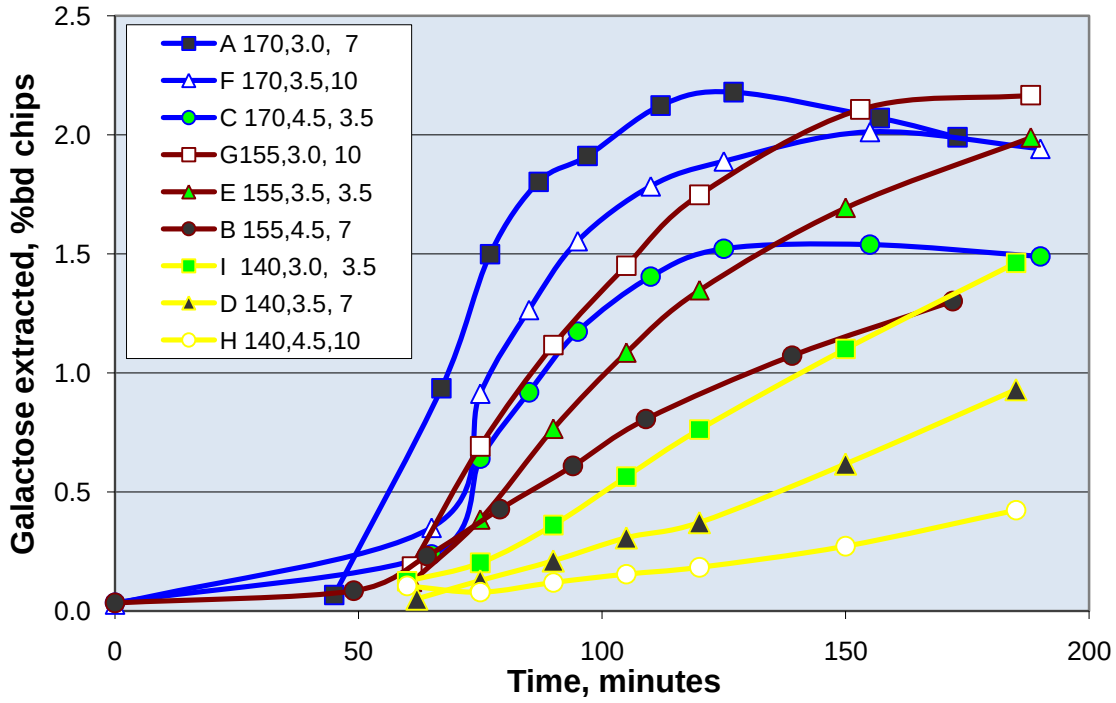


Figure 39 Galactose recovered as a function of time for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The glucose recovery trends illustrated in Figure 40 were the simplest of the five sugars with recovery increasing with time under all conditions. Additionally, recovery increased with temperature at all pH levels and increased with acidity at all temperatures. The rate of recovery did begin to decrease at longer times for the tests at 170°C and for the test at pH 3 and 155°C. The final recovered quantity varied dramatically from less than 0.2% of wood up to slightly higher than 2%. The lower quantity represented only 7% of the glucose attributed to hemicellulose, while the highest was 78%.

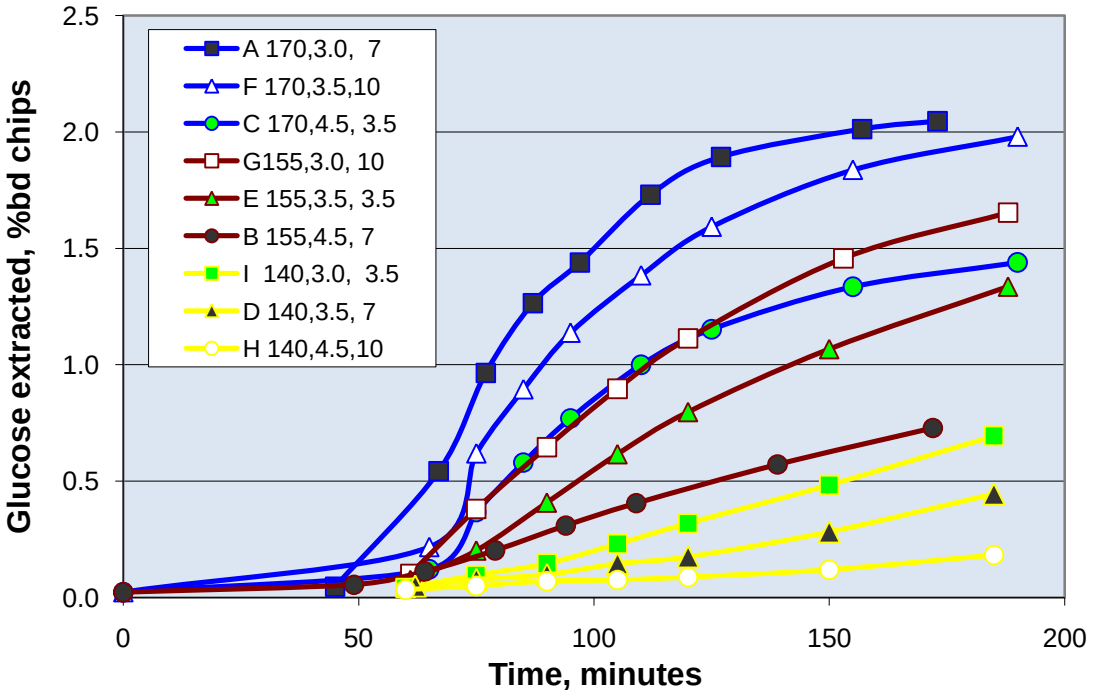


Figure 40 Glucose recovered as a function of time for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

Mannose is the most plentiful sugar recovered at the end of the prehydrolysis for all conditions except for 140° and pH 4.5. It is also the most plentiful during the course of the prehydrolysis with the exception of arabinose during the early part of the extractions. This is due not to efficiency of extraction, however, but to the fact that

mannose is 40% of the initial wood hemicellulose. The efficiency of extraction varies from 7% up to a maximum of 57%. The shapes of the mannose trends illustrated in Figure 41 are very similar to the glucose trends with the exception of the two conditions at 170° and lower pH. This should be expected since the two sugars are found on the same hemicellulose molecule. In the milder extractions, the initial rate is slow before accelerating toward the end of the reaction. In the stronger conditions, the initial rate is fast before slowing as the extraction nears 50% of the mannose in the wood. Evidence of degradation is observed at 170°C where the rate slows dramatically after about one hour and the concentration even decreases at pH 3.0. One potential indicator of an improvement due to the high pH presoak would have been a lower recovery of mannose from the chips pretreated at alkaline pH. This does not appear to be significant.

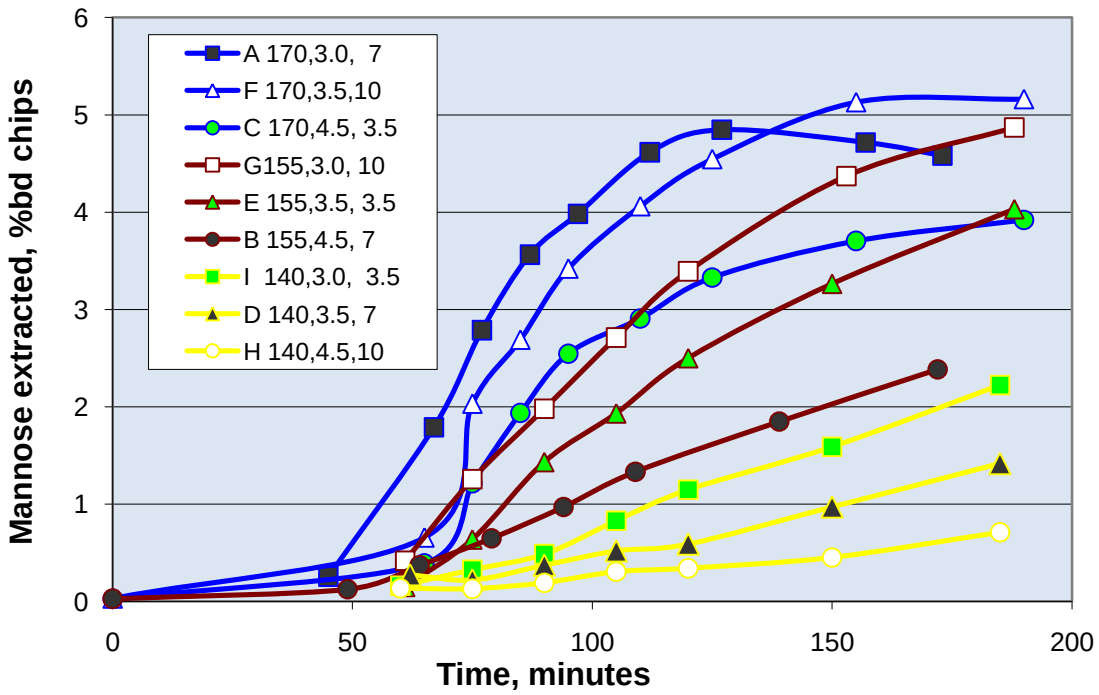


Figure 41 Mannose recovered as a function of time for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

Xylose is the second most plentiful sugar in the hemicellulose and, in most cases, it is the second most plentiful sugar recovered in the hydrolyzate. The trends shown in Figure 42 and relationship to pH and temperature are similar to the other sugars with the exception of the pronounced degradation observed at 170°C. The rate of degradation is equal to or greater than the rate of removal from the chips after 30 minutes of reaction for all conditions at this high temperature. The recovery rate of xylose was the lowest of all the sugars and varied from 7% to a maximum of 41% of the sugar in the original wood while it consistently represented about 25% of the sugar found in the hydrolyzate.

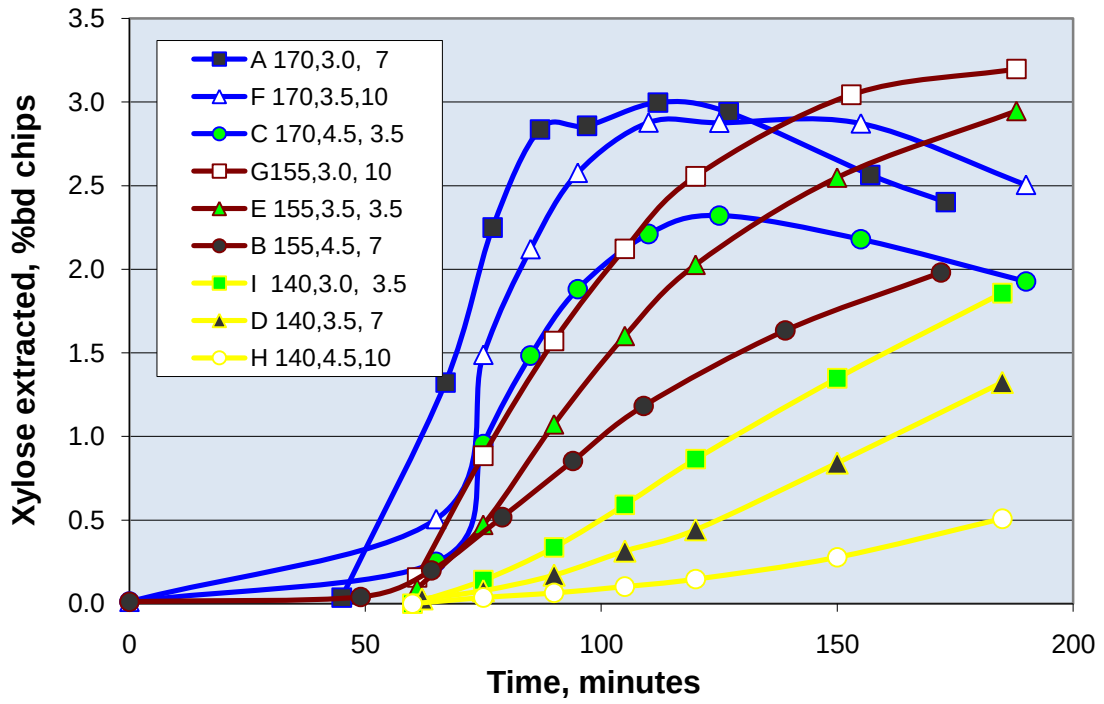


Figure 42 Xylose recovered as a function of time for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

Glucose is unique among the sugars because it is also available for removal from the cellulose component. One method of considering the impact of the prehydrolysis on cellulose is to consider the ratio of glucose to mannose recovered relative to the amount

present in the hemicellulose since these sugars are together in the backbone chain of the glucomannans and therefore would be expected to be removed at about the same rate and degraded at a similar rate since they both have six carbons. A ratio close to 0.275 would indicate very little impact on cellulose while a higher ratio would indicate that some of the glucose likely came from cellulose. This ratio can be compared visually by putting the two sets of sugar data on the same plot with separate axes and adjusting the scales of the dependent axes so their magnitude is close to the ratio of the two sugars calculated to be in the original wood hemicellulose, 0.275. As can be seen in Figure 43 where the glucose data from four tests is connected by solid lines and the mannose data from the

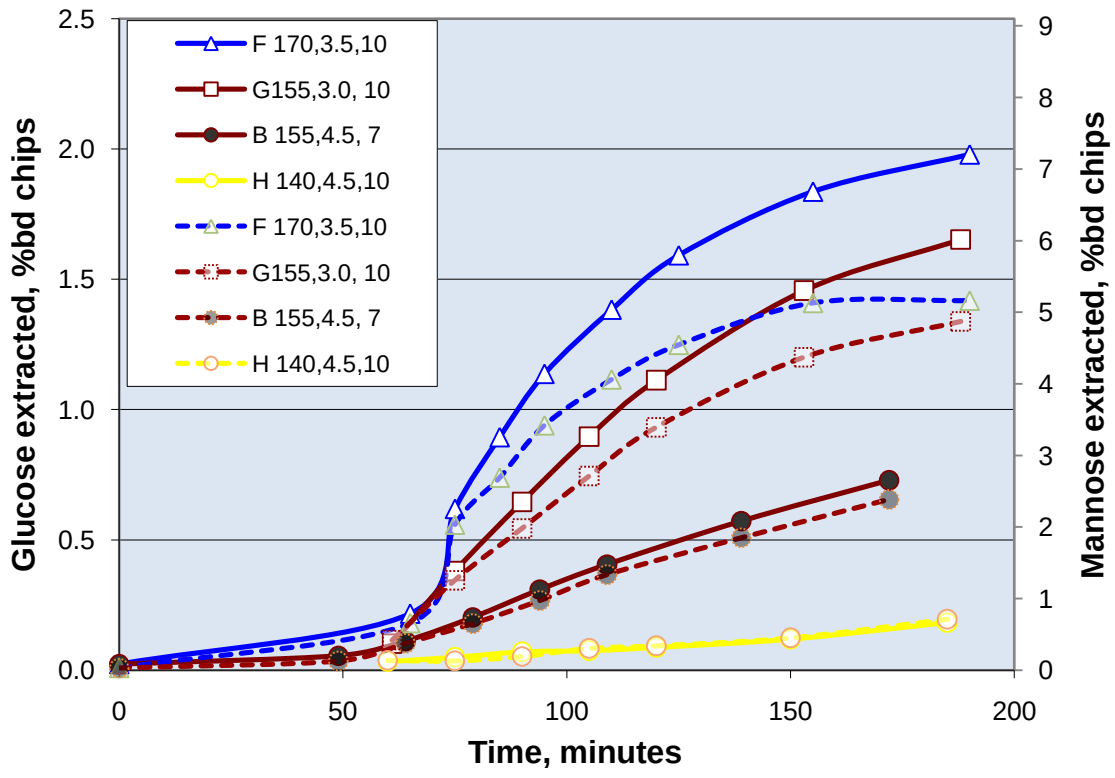


Figure 43 Glucose and mannose recovered as a function of time compared for four conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH. Glucose has solid connections. Mannose connections are dashed.).

same tests is illustrated with dashed lines, the plots of the mildest condition, test H, almost exactly overlay each other while the stronger conditions, tests G and F, yield much more glucose in relation to mannose.

The impact on cellulose appears to increase with time, as pH drops, and especially as temperature increases in the range studied. The impact illustrated in this chart likely understates the real damage done to the cellulose since only relatively small oligomers are removed from the chips. For glucose from cellulose to be recovered in solution the hydrolysis must occur very close to an end of the molecule or there must be two hydrolytic cleavages very close together.

Since the experiments were designed in a Latin square, the three tested factors can be compared to each other by averaging the results of the three tests at each level (Hendrix 2002). The average results are comparable because each contains the variability associated with each other factor at all three levels.

An analysis of variance can also be performed to test for the significance of each factor in changing the results. Minitab 15, a statistical software package published by Minitab, Inc., was used to test a general linear regression model of the three factors for several results. The sugar recovery quantities were considered at the maximum level as well as the amounts measured in the final (2 hours) and 45 minute samples. Temperature was identified as the strongest factor at all three positions with percentage contribution ranging from 68% for the "Final" samples to 87% for the samples at 45 minutes. The second largest contributor was pH which ranged from a 12% contribution at 45 minutes to 28% at maximum sugar. The presoak condition was attributed from 3 to 4% contribution for "final" and "max" samples but was not significant at the 5% level of

confidence. Presoak was only attributed to 1% of the variation in the data for the 45 minute sample, but this contribution was determined to be significant statistically. The adjusted R-squared for the models was very good at 99.1, 99.6, and 99.9 respectively for Final, Max, and 45 minutes samples. The residual error was 1% or less for all three. The results of the Minitab 15 analysis for these and other variables are shown in Appendix 1.

5.4.2 Chip Weight Loss

Chip weight loss is plotted as a function of temperature for the nine study conditions in Figure 44. The same color and shape scheme is used as in the sugar plots so all three factors can be observed in one figure. The data marker for condition "D" is partially obscured by the marker for condition "H". Weight loss is higher at lower pH at all temperatures, if only slightly at 140°C. Loss is also higher at higher temperature at all

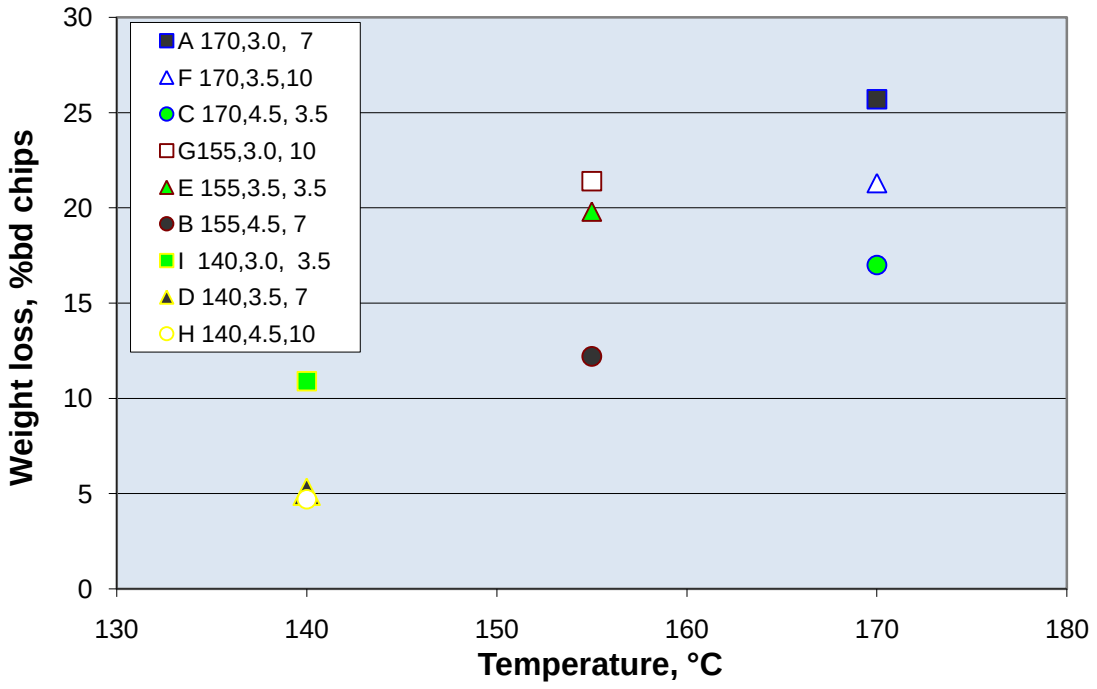


Figure 44 Chip weight loss in prehydrolysis as a function of reaction temperature for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

pH levels. Examination of Figure 44 suggests the presoak at pH 3.5, indicated by green shape fill, may have increased weight loss slightly, but the ANOVA indicated that presoak was not significant for chip weight loss. The only statistically significant variable was temperature which was attributed 76% of the variation.

Maximum recovered sugar is plotted as a function of weight loss in Figure 45. The reference line is a least squares linear fit that was forced to intercept at 0. The marker for condition "F" is partially obscured by the marker for Condition "G". The final recovered sugar values for the high temperature conditions were slightly lower than the maximum values used here. All the plotted values are close to the plotted line except for two. The most severe prehydrolysis condition, test A, had high degradation of sugars resulting in high weight loss relative to sugar recovery. Condition D shows higher sugar recovery than weight loss, an impossibility. The weight loss measurement in this case is

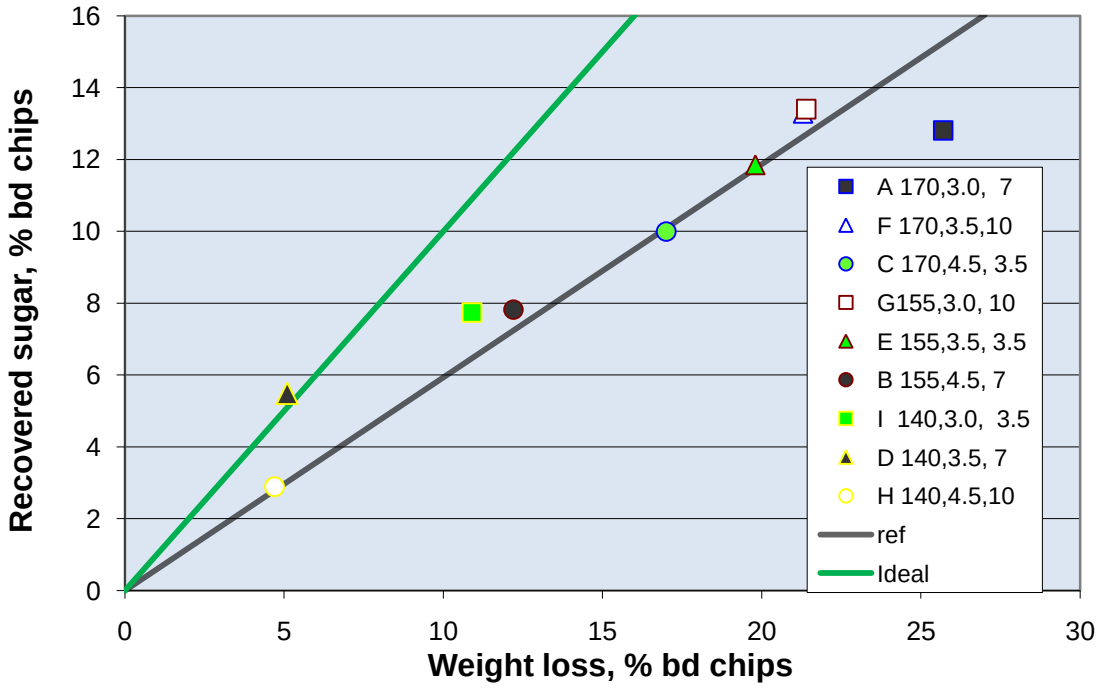


Figure 45 Recovered sugar as a function of chip weight loss for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

probably in error. The prehydrolyzed chip weight measurement is very sensitive to the solids content measurement in the wet chips. Condition D had the highest measured dry solids content. The method was changed later to duplicate this measurement.

5.4.3 Pulp Yield

The H-factor for the bomb cooks with raw chips was varied from a low of 1200 to a high of 2600 to allow estimation of the required H-factor to reach a lignin content of kappa number 30 that was the chosen standard pulp. The broad range also demonstrates for this set of chips the manner in which kappa number varies with cook time and the way that pulp yield varies with kappa number. These data are plotted in Figure 26 and Figure 27. Each point in the plots represents the average measurement from two or three bombs that were cooked at the same time. The error bars indicate one standard deviation in either direction from the average. The kappa number standard deviation decreased from 1.84 to 0.15 kappa units as H-factor increased in the study range. The average standard deviation was 0.82, but the pooled standard deviation that takes into account the limited number of degrees of freedom in each test was 1.02. The standard deviation of yield did not trend with H-factor and varied from 0.16% to 0.49% of wood with average and pooled values of 0.35% and 0.37% respectively. Variability accounted for in these numbers includes that attributed to the raw chips and to each individual bomb cook from measurement and handling, i.e. measurement of the dry chips, liquor, water, dry pulp, moisture content, and kappa number. Handling included the choice of bomb, positioning in the digester, mixing of chips and liquor, washing and drying of pulp.

Figure 26 and Figure 27 illustrate for raw chips the “ease” of cooking to a given kappa number and the expected yield at a given kappa number. Important numbers that

come from these plots are that a cook of approximately 1800 H-factor is required to reach kappa 30 and the expected yield from a conventional kraft cook of the Loblolly pine chips utilized for this research in the laboratory digester at Auburn University at kappa 30 is about 44.5%. The required H-factor was estimated to be 1850 before the final two cooks were performed and 1850 was used to target the "standard" cook for the prehydrolyzed chips. The plots also are important for the shapes of the curves. The pulp kappa number vs. H-factor curve is approximated by a third order polynomial for this plot, but the observation that reducing the kappa number below about 25 requires a much more extreme cook is important. The linear nature of the yield vs. kappa curve and the slope, 0.16, are important guides taken from Figure 27 for interpreting other data.

The two hour prehydrolysis treatment had a dramatic impact on the required cooking severity in some cases but had very little effect in others. As shown in Figure 46, the chips prehydrolyzed at 170°C with pH below 4.5 required 25 to 75% longer cooks than the standard for raw chips to reach a target of 30 kappa number, while the chips from the test at 155° and pH 4.5 reached the target in 25% less time than the standard. The chips from all but the two tests at high temperature and low pH had lower than 30 kappa number after the standard cook, but in three cases had higher lignin content than the raw chips after shorter cooks. The chips from the mildest treatment had slightly lower lignin content than the raw chips over the whole tested range of conditions. These results are similar to those shown in Figure 10 where the shorter length of pretreatment at 170°C cooked to a lower kappa number at a given H-factor while a longer cook was required to process the chips pretreated for longer than one hour. The H-factor required to reach the target of 30 kappa with each set of prehydrolyzed chips was estimated from

this chart using manually drawn curves. The curves shown are "power" trendlines from Microsoft Excel ® and approximate the manually drawn curves that were used.

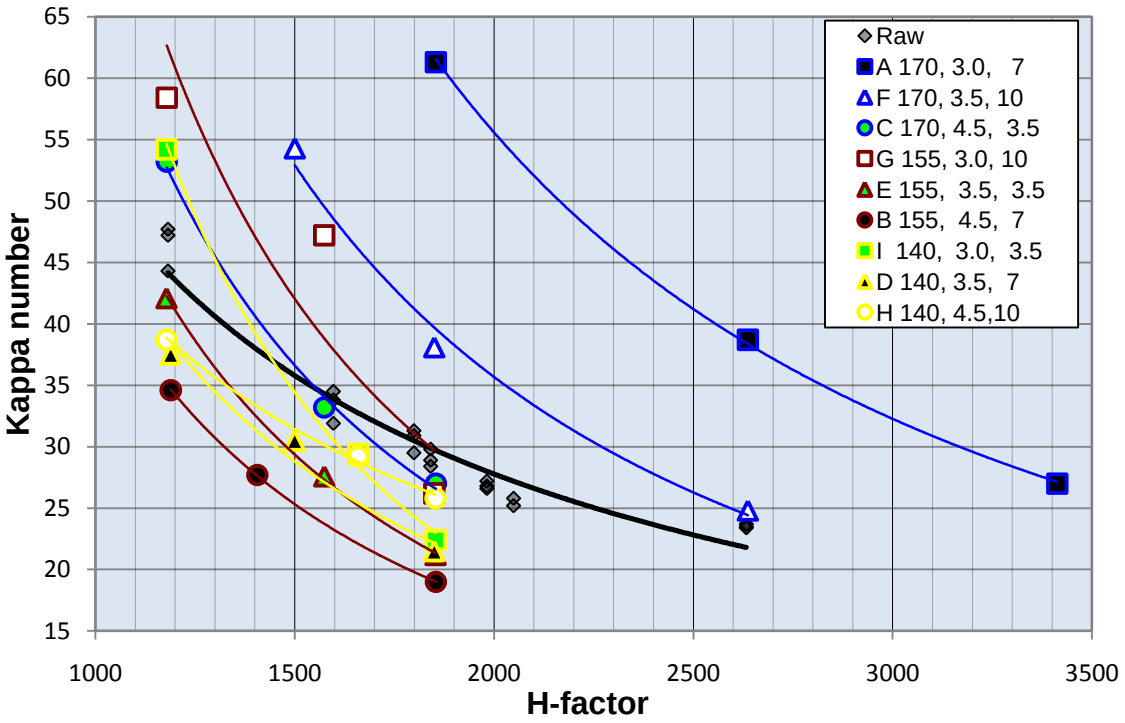


Figure 46 Pulp lignin content as a function of H-factor for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

There appear to be at least two effects that are working counter to each other regarding the prehydrolyzed chips response to kraft cooking. The pretreatment opens up the chip structure by breaking bonds and removing some carbohydrates thus reducing mass transfer limitations to lignin removal in cooking. Extended time at high temperature and low pH causes condensation reactions in the lignin structure that make this lignin resistant to alkaline attack in cooking. At low temperature and high pH in the test conditions H, D, and B, kraft cooking becomes easier as the conditions become stronger. For moderate conditions E, I, C, and G, kraft cooking becomes harder as prehydrolysis conditions become stronger and lignin condensation becomes more

important, but reaching kappa 30 or below remains easier than for a standard process. Finally, at the high temperature and low pH conditions F and A, lignin condensation effects dominate and reaching the target lignin content requires a much longer cook.

A precise interpretation of the impact of the prehydrolysis on cooking severity required to reach a kappa number target and on pulp yield cannot be made because the alkali charge was not optimized for each condition. The liquor charge was calculated based on the original dry chip weight, not the prehydrolyzed chip weight. The white liquor chemical and water charged to each bomb were held constant while the weight of wood remaining after prehydrolysis varied. The liquor to wood ratio varied from a high of 8.3 for condition "A" to a low of 6.4 for condition "H" compared to the 6.0 used for the raw chips. Black liquor residual alkali was not titrated for these tests, but the pH of the black liquor was measured instead as verification that there was not significant leakage in or out of the bombs and that the alkali was not completely depleted before the end of the cook.

Yield loss relative to the standard process is significant in even the mildest of the tested prehydrolysis conditions as seen in Figure 47. The effects of the two main factors, pH and temperature, were also consistent within the range of this research: pulp yield loss increased with temperature at every pH level and with acidity at every temperature. Kraft pulp yield at 30 kappa was calculated using the best fit linear regression of the three cooks. The slopes of these lines averaged 0.10% per kappa unit, but varied from 0.025 to 0.25. The slope is slightly lower on average for the prehydrolyzed chips than the raw chips since there is less carbohydrate relative to lignin at the beginning of the cook. There is higher variability in the yield data for the prehydrolyzed chips than with the raw

chips since they were weighed when they were wet from the prehydrolysis. The presoak was added to test the possibility of reducing yield loss, but the soak condition was not statistically significant according to ANOVA of this data. Temperature was attributed 70% of the variance and pH 29% with an adjusted R-squared of 98.4.

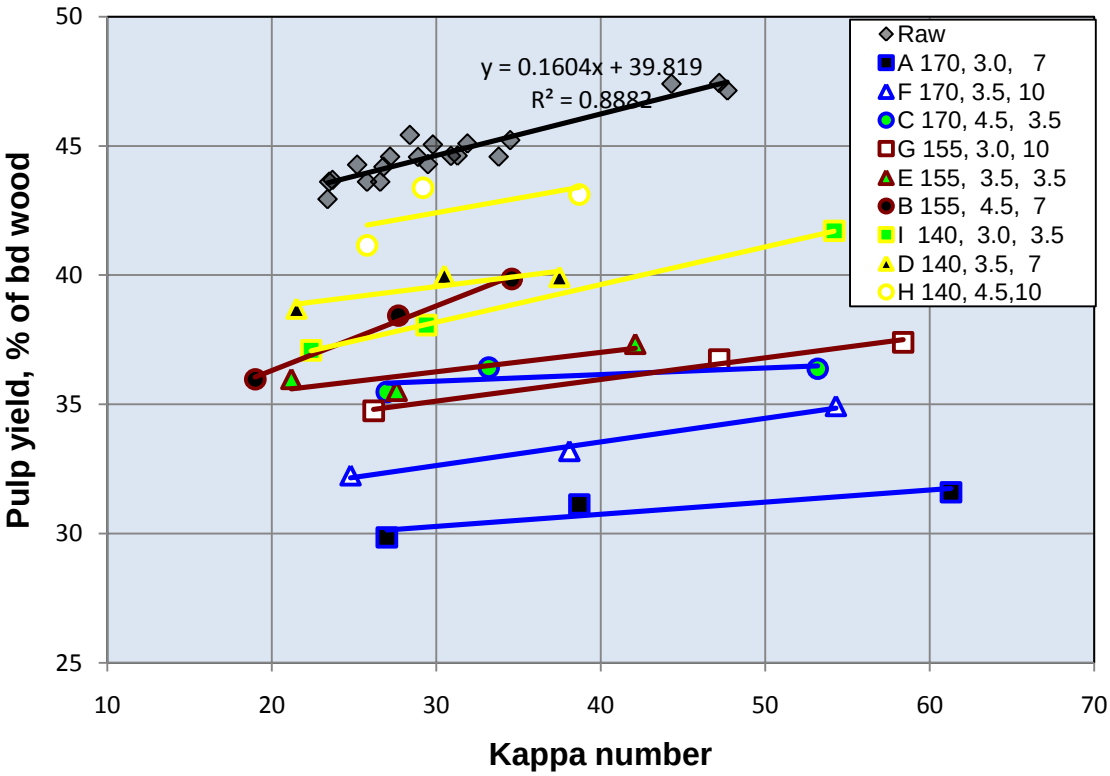


Figure 47 Yield as a function of kappa number for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

Yield loss relative to sugar recovered is a key comparison in evaluating the financial impact of prehydrolysis. Figure 48 shows the calculated pulp yield at 30 kappa number as a function of the measured maximum recovered sugar expressed as a percentage of the original bone dry chip weight. The trend line is a linear regression of the nine data points forced to pass through the calculated pulp yield for untreated chips. The data markers for the high temperature tests at 170°C all fall below the trend line even using the maximum values. The actual final values would be slightly lower. The data

markers for 155°C all fall above the trend line while the low temperature values are very close to the line. The pH and presoak pH conditions appear randomly relative to the line. Statistically, all three factors were significant in ANOVA of this ratio, even though pH was only attributed 2% of the variance. Temperature accounted for 68% and presoak 30%. This was the only tested situation where the presoak was deemed significant by ANOVA. The R-squared was 99.9. The average values for the three sets of three conditions for this ratio are 1.253, 1.106, and 1.272 for presoak pH levels of 3.5, 7, and 10 respectively. The data shown in Figure 48 indicate that 155°C and presoak conditions away from neutral can improve pulp yield relative to recovered sugar.

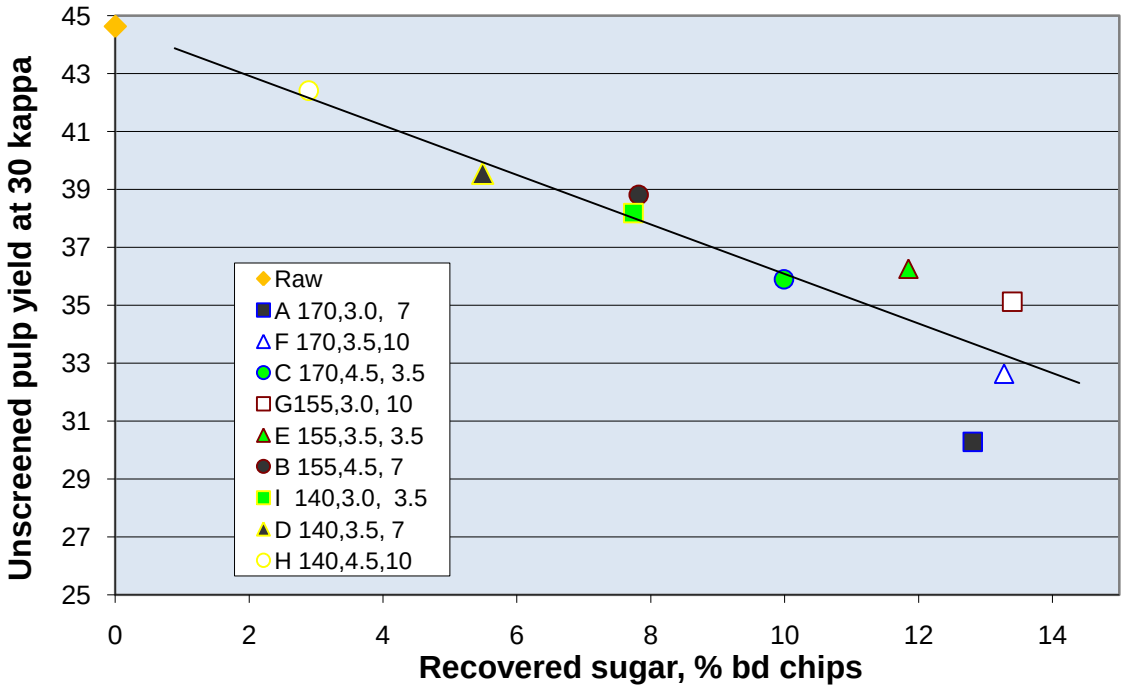


Figure 48 Pulp yield as a function of recovered sugar for all conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

5.4.4 Additional Cooks

Ten additional prehydrolysis tests were performed at conditions that appeared interesting after the first nine tests. Tests J and K were intended to test stronger presoak

conditions. Tests L, M, N, and O did not use a presoak, but the vacuum oven was used to remove air from the chips. Preparing the chips in this manner required about one hour from the time the chips were first wet with solution to the start of the temperature ramp. The intention of test L was to limit degradation by reducing the temperature after a set time period. Tests M, N, and O were designed to extract a target amount of the wood as sugar by repeating conditions E, G, and F at shorter time periods. Table 7 compares operating conditions and results for condition E with these first six additional tests.

Table 7 Conditions and results for additional prehydrolysis cooks.

Cook	E	J	K	L	M	N	O
Presoak pH	3.16	2.97	11	none	none	none	none
pH target	3.5	3.5	3.5	3.5	3.5	3	3.5
Temperature	155	155	155	170, 155	155	155	170
Minutes at Temperature	120	120	120	30, 90	60	45	20
H factor	450	452	458	717	252	201	392
%Weight loss	19.8	15.7	18.5	16.4	8.4	18.6	19.9
Max Sugar	11.51	10.34	7.77	11.44	7.69	9.61	9.63
%Rec / % Wt Loss	0.58	0.66	0.42	0.70	0.92	0.52	0.48
Kraft yield at 30kappa	36.3	37.3	38.7	35.2	37.8	37.03	36.41
Yield Loss	8.4	7.3	6.0	9.4	6.8	7.6	8.2
%Rec / %Y Loss	1.37	1.41	1.30	1.21	1.13	1.26	1.17
H factor to 30	1480	1380	1700	1450	1360	1520	1320

The remaining four prehydrolysis tests were all the same and were used to produce chips for tests of potential yield improving additives. These tests each processed enough chips to test 12 different conditions in bombs. The results of the additive tests are discussed in Chapter 6.

Acetic acid was used at a charge of 2% on wood for the presoak in test J which was otherwise intended to have the same conditions as test E. This only dropped the pH of the presoak to 2.97 compared to the 3.16 in runs C, E, and I. The results were similar to but not exactly the same as those for test E. Both chip weight loss and sugar recovery were higher in E while pulp yield and cooking severity required were better in J. The

operating pH and temperature targets for both runs were the same, but the actual achieved pH and temperature were slightly different. The actual measurements are plotted in Figure 49. The pH for test E is slightly lower than that for test J over most of the time frame of the experiment. Acetic acid was added slowly to reduce the pH until about 15 minutes past the end of the ramp in both cases. During test E, the operator decided the pH remained close enough to the target of 3.5 that it did not need to be adjusted upward. Sodium Carbonate was used in test J beginning one hour after the ramp to adjust the pH back to target of 3.5. The variation in pH during cooling of the reactor is typical of all the tests as is the temperature variation at the transition from ramp to steady operation at the target. The temperature data displayed is the data that was used for calculation of H factor with steady operation at about 152°C. The reactor temperature was controlled automatically with the digester temperature sensor at 155°C.

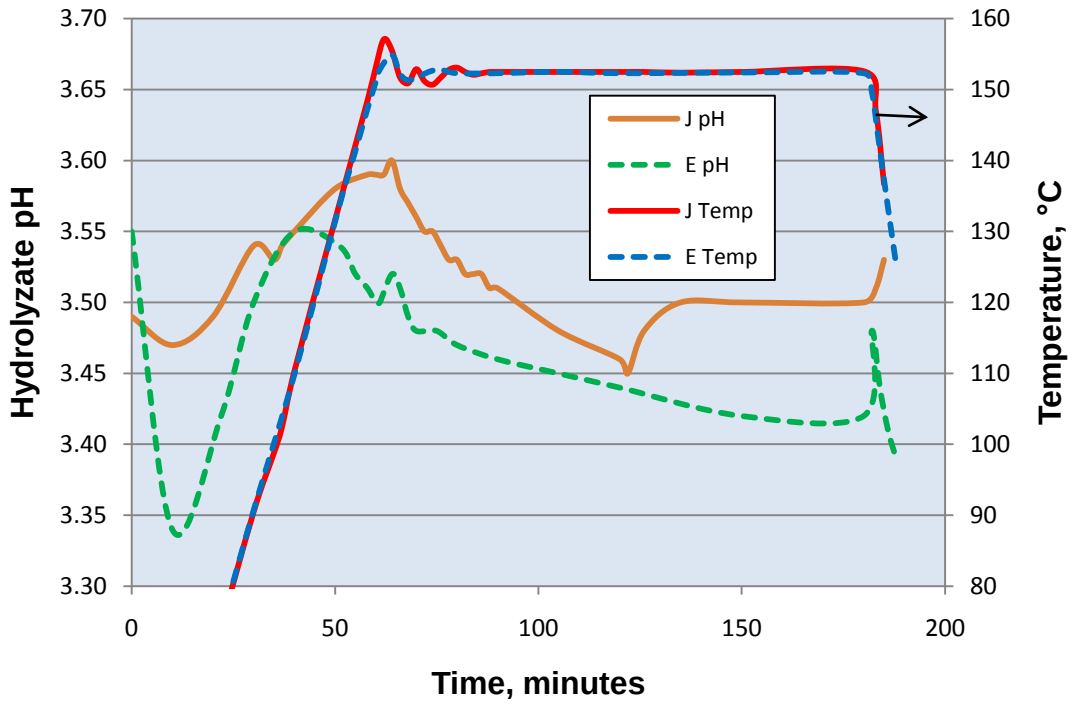


Figure 49 pH and temperature for prehydrolysis cooks "E" and "J".

The maximum sugar recovery data for E and J presented in Table 7 are slightly different than what is reported elsewhere in this document. Sugar recovery standards are analyzed along with the samples in composition analysis and are used to adjust the results for degradation during the analysis. When the total sugar recovery for runs E and J were compared and found to be substantially different, 11.85% and 9.8% respectively, the test records were compared and it was noticed that the recovery ratios for glucose and mannose were unusually low at 91% for E and unusually high at 103% for J. When a typical standard recovery ratio of 98% was used in both cases, the sugar recovery measurements for the two runs were much closer as listed in the table. The remaining difference in sugar recovery measured in the samples can be attributed to the slight difference in pH over the course of the reaction. Lowering the presoak pH was intended to increase the rate of sugar removal from the chips, but did not appear to make a difference in this test.

Sodium carbonate was added to the presoak solution at a charge of 2% on wood for test K. The solution pH was 11.0 at the beginning of the presoak and dropped to 9.22 after 24 hours. The intention of this test was to attempt to maintain higher pulp yield. Dilute acetic acid was used to control pH during the prehydrolysis. The pulp yield was slightly higher, but the quantity of sugar recovered in the hydrolyzate was lower, so the ratio of sugar recovered to yield lost was not improved. The chips produced in this treatment also required a slightly stronger cook to reach 30 kappa. The conclusion following test K was that the 24 hour presoak at 25°C in the range of pH 3 and 11 had a very small, if any impact on either sugar recovered in hydrolyzate or pulp yield, so this treatment was discontinued for the remaining tests.

A two level temperature control was attempted for condition L to test the possibility of increasing sugar recovery by limiting the degradation of sugars seen at the highest temperature in this study. The temperature was held for 30 minutes at 170°C and then dropped to 155°C for 90 minutes. Dilute acetic acid was used to control pH initially and 0.2 N sodium carbonate was used after 30 minutes at temperature. Sugar recovery increased in this test relative to condition J, but so did yield loss. The glucose: mannose ratio for the mixed temperature run was between those for the trials that used just 155°C or just 170°C for the entire time, but much closer to that of the 170°C run. This suggests that cellulose may have been more strongly affected by the use of high temperature for part of the test. Lignin does not seem to have been significantly deactivated by this treatment, however as the H-factor required to reach 30 kappa was only 1450.

Conditions M, N, and O were replicates of conditions E, G, and F but held at shorter time periods with the intention of extracting 8 - 10% of the wood as sugar. The ratio of recovered sugar to yield loss was improved by the shorter treatment at 170°C, but was not as good for the two conditions at 155°C. Thus the optimal reaction time and extraction target with reference to this ratio is different for each given set of reaction conditions. Both are higher for 155°C than for 170°C.

Limited results from the last four prehydrolysis tests are included in this chapter because they can be used to help understand the level of variability associated with the experimental process and the analysis methods. Prehydrolysis runs P, Q, R, and S were intended to be identical with prehydrolysis liquor added to the chips in the vacuum oven at pH 3.5 followed by a prehydrolysis treatment with the pH controlled at 3.5 with dilute acetic acid. The temperature profile included a one hour ramp to 155°C that was held for

68 minutes before cooling. The chips were divided into 12 different samples equivalent to 70 g bone dry untreated chips based on a ratio of wet treated chip weight to dry untreated chips. Duplicate samples were also taken to measure chip dry fraction. A careful procedure was followed to mix the treated chips before they were divided and to portion the chips equally into each sample from the main bag.

Variability in the chip weight loss measurement was identified as a potential problem in the designed experiment when the sugar recovered was higher than the weight loss measured for condition D. Duplicate samples of chips were taken for the chip dry fraction measurement in an attempt to reduce this problem. The pooled standard deviation of the dry fraction measurement for the eight chip samples is 0.0127. This suggests that the weight loss for prehydrolysis Q is 13.6% ±3.4% or somewhere between 10.2% and 17% given one standard deviation.

Composition analysis was performed on the liquid samples from runs P, Q, and R to determine sugar recovery. The data from these runs are illustrated in Figure 50. This figure has been modified in an attempt to show how close the data from the three runs are. The "Total Sugar" data has been plotted against a secondary Y axis to expand the primary axis. Run P is illustrated with "Plus" symbols. Run Q is illustrated with triangles. Run R is illustrated with square markers and lines. The data from the three runs are basically identical with the exception of the 120 minute data set from run P that is slightly higher than the other two. This lack of variability among these three runs implies that the method of producing and analyzing these samples is very consistent. The liquid samples from these three runs were prepared for analysis on the HPLC and run in

sequence with standards checked before and after each set of seven samples. The wash samples are not shown on the plot.

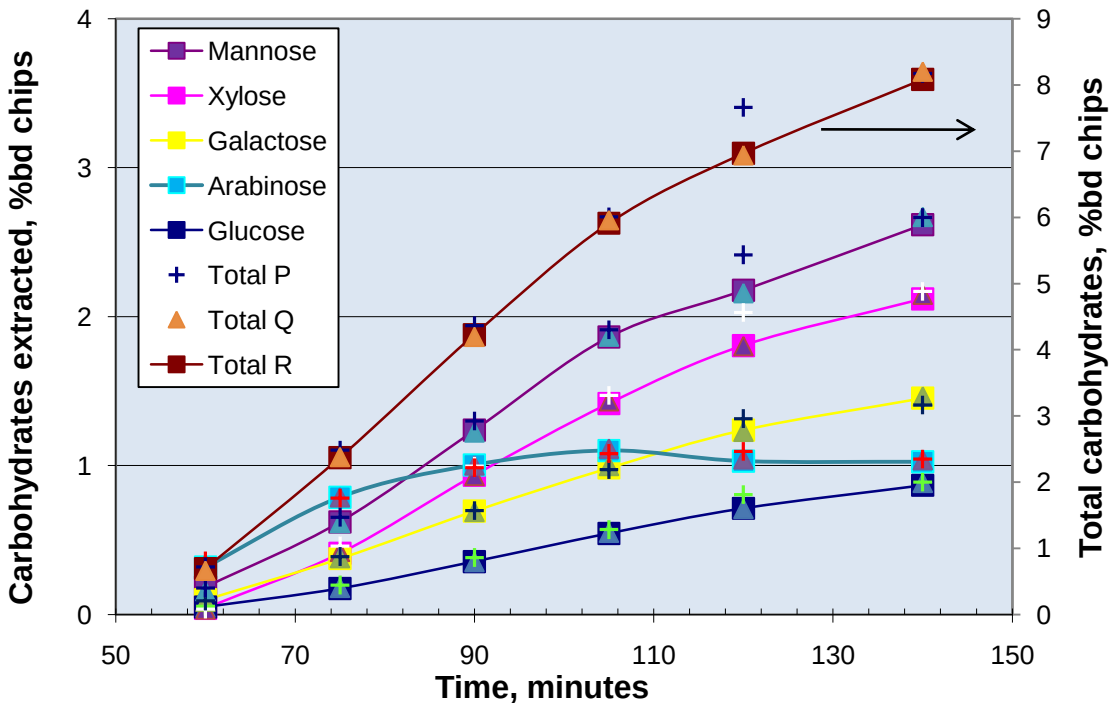


Figure 50 Recovered sugar measurements as a function of time for prehydrolysis cooks "P", "Q", and "R". Individual sugars from top to bottom based on final data points are mannose, xylose, galactose, arabinose, and glucose.

Six of the chip samples from run S were bomb cooked without any additive using the standard cook profile to estimate the variability in pulp kappa number and yield measurements of the bomb cooks with wet chips. The resulting pulps had an average kappa number of 26.6 with a standard deviation of 0.92 and average yield of 37.36% with a standard deviation of 0.79. The kappa number standard deviation is similar to that of the cooks with raw chips, but the yield standard deviation is more than doubled. This increase can probably be attributed to dividing the wet prehydrolyzed chips into smaller samples for bomb cooking.

Chapter 6 Pulp Yield Recovery

Pulp yield on wood is a huge financial driver in the industry. A 1% change in yield can mean millions of dollars per year to a pulp mill. Typical brown stock kraft pulp yield of Pine is only 47% compared to an ideal yield of 68% if pulping was purely selective to lignin and extractives. The extra yield loss can be attributed to cellulose (4%), glucomannan (13%), and xylan (3%) (McDonough 1998). Glucomannan losses in alkaline pulping are about equally from dissolution and peeling and not strongly dependent on alkali concentration or temperature. Xylan losses are due to dissolution and are highly dependent on both temperature and alkali concentration. Cellulose loss is due to peeling and secondary peeling at higher temperature.

Prehydrolysis that is expected to be part of a VPP strategy increases yield loss beyond what is observed in conventional kraft pulping. Acid prehydrolysis removes sugar from wood through random cleavage of polysaccharides. This treatment produces oligomers and monomers that are dissolved and recovered in the prehydrolyzate, but it also damages the polymers that remain in the chips. These damaged polymers are then more susceptible to peeling and dissolution typical of kraft pulping.

Several methods have been proposed and attempted for increasing pulp yield from the conventional kraft process. These include modifications to the raw material, modifications to the cooking process, and the use of chemical additives. Investigations of how modifications to raw materials or the cooking process may relate to VPP are outside

the scope of this research and therefore are only introduced briefly for context. This research is concentrated on the effect of extraction of hemicellulose prior to pulping on pulp yield. A few potential methods of improving pulp yield in the context of chemical addition to the digester or additional pretreatment steps prior to cooking were tested. Discussion of these additives and the laboratory work performed to test them are the focus of this chapter.

Pulp yield can be improved by changing the raw material: the wood chip. It has been shown by modeling and mill studies that chip thickness screening and optimization can improve yield by reducing rejects and reducing delignification variability from chip to chip (Jimenez, McKean and Gustafson 1990). Optimization of chipping technique can also improve pulp yield and strength while minimizing the need for screening (Wang and Gullichsen 1998). The quality of the wood itself can also be changed through selective hybridization and eventually through genetic modification to control wood composition (MacRae and Cotterill 1998).

Modified cooking or extended delignification methods were developed in the 1970s and 80s with the intention of reducing the kappa number before bleaching without reducing strength or yield. Several different commercial methods for both continuous and batch cooking were developed based on the principles of maintaining alkali concentration low and even, having a high sulfide concentration in the initial part of the cook, and maintaining a low dissolved lignin concentration. Innovation in these methods has continued by adding white liquor addition points and changing flows in continuous cooking and changing composition and order of addition of liquors in batch cooking. The result is a potential yield increase of about 2% at the same kappa number. Addition

of polysulfide and/or AQ to a modified cook can result in an additional 1 to 2% yield improvement (Courchene 1998).

Chemical additives can be used in pulping to reduce reactions of carbohydrates or increase reactivity of lignin. One method of increasing pulp yield is to stabilize the carbohydrates with regard to peeling by treating the carbonyl end group with an oxidizing or reducing agent. Often, however, the concentration of additive required is not economical or the effect is difficult to measure at mill scale. Additives that have been tried previously include sodium dithionite, sodium borohydride, polysulfide, hydrogen sulfide, Anthraquinone (AQ), and surfactants (Courchene 1998). Sodium borohydride and polysulfide are both effective at improving glucomannan yield but can actually lead to increased xylan losses if the alkali in the cook is not adjusted. They also are most effective at lower cook temperatures. AQ functions catalytically on both primary wood components by oxidizing carbonyl groups for increased yield and reducing lignin for improved delignification. AQ and polysulfide can also be used in combination for a synergistic effect resulting in up to 4% yield improvement. Surfactants can also help by improving chemical penetration therefore reducing rejects at the same total yield.

Five additives were screened as to their potential to improve pulp yield. Sodium borohydride and sodium polysulfide were not included because they were being tested by another member of Auburn University's research group (Yoon 2009). Hydrazine looked promising based on a literature search (Gillespie 1964) but was not tested following a recommendation from Dr. Susanne Striegler of the Auburn University Chemistry Department that personal exposure to toxic quantities of the carcinogen would be too

difficult to avoid in the lab or industrial environment. Acetaldehyde was substituted for the recommended formaldehyde based on similar logic.

Since this was a screening study, it was not feasible to attempt to hit a target kappa number or optimize the alkali charge so the yield at each condition could be compared on an equivalent basis. It was assumed instead that pulp yield is a linear function of kappa number in the kappa number range observed in this group of studies (van Donkelaar 1998) and that the slope of that function is approximately 0.1% per kappa unit as observed in the designed experiment discussed in Chapter 5 of this research. No correction was made for variation in residual alkali. The temperature target for all the kraft cooks was 165°C. Reducing the temperature may increase pulp yield by reducing alkaline cleavage and secondary peeling. This was not attempted due to the increase in time of cook that would be required.

Discussion of each additive begins with a description of the chemical and any potential handling concerns since these products may not be typical to the industry. This is followed by literature examples of the use of the product in similar situations if it is available and discussion of expected reactions. Laboratory tests with the product are then described followed by results and conclusions. General conclusions regarding this research are given at the end of the chapter.

6.1 Anthraquinone

Anthraquinone (AQ) is typically delivered to a pulp mill in slurry form of 50-70% solids with a surfactant to aid in dispersal. The mixture must be agitated to avoid settling in storage tanks. 9, 10- Anthraquinone powder, 97% grade was purchased from Alfa Aesar for this research. AQ is considered harmful with limited evidence of carcinogenic

effect. It can enter the body through skin absorption, breathing of dust, or consumption of dust (Alfa Aesar MSDS 2007). It is included in the California Proposition 65 list of chemicals known to cause cancer or reproductive toxicity (California Office of Environmental Health Hazard Assessment 2010). AQ is only barely soluble in water or white liquor, but can be dissolved by hot organic solvents.

Anthraquinone has been such an important factor in industrial pulp yield improvement efforts since the 1970s that it was discussed in nine of the 25 presentations at TAPPI's "Breaking the Pulp Yield Barrier Symposium" in 1998. A collection of papers discussing AQ pulping has also been published (Goyal 1997). AQ accelerates delignification and protects polysaccharides from degradation, so the benefits can be utilized by a mill in several ways. Application of AQ is typically justified based on increased pulp production. Production increases are a result of increased yield, increased digester throughput, and decreased black liquor solids firing in the chemical recovery boiler. An industry survey reported yield increase of 0.5 to 5% of wood with most results from 1 to 1.5% with a typical dosage of 0.05% on wood (Laubach 1998). Other potential justifications for AQ could include reducing sulfidity or reducing bleaching requirement.

This investigator has personal experience with the use of AQ in a mill environment. The additive was used to reduce alkali required in the digester and improve yield. Together these effects allowed the mill to increase pulp production under a chemical recovery limitation. A yield increase of 1% was estimated based on a reduction of black liquor solids fired per ton of pulp produced and composition analysis of the pulp.

The principle reactions of interest for AQ in pulping are oxidation of the reducing end groups of polysaccharides and reduction of lignin through several potential paths

(Lindenfors 1980). The oxidized polysaccharides are stabilized relative to the peeling reaction by conversion to carboxylic acids. One of the potential reactions with lignin inhibits condensation reactions. AQ itself functions catalytically in both sets of reactions. It is reduced by the polysaccharides to anthrahydroquinone which is oxidized back to anthraquinone by reaction with lignin (Sjostrom 1993, 157).

Two of the five chip subsamples from each of the nine tests in the designed experiment were cooked with the addition of 0.1% AQ on raw wood weight. The first cook with AQ used the standard digester control profile to reach 1850 H-factor. The H-factor for the second cook with AQ for each sample was chosen so 30 kappa number would be bounded by the kappa number of the two cooks. Only sample A had a kappa number higher than 30 from the first run, so the H-factor for the second cook of chips from sample A was much higher than standard at 3400. The other second cook H factor targets were lower than standard. The pattern in cook severity required to reach 30 kappa number for the nine sets of subsamples with AQ was similar to the pattern for cooks without AQ. The required cook time decreased as the prehydrolysis conditions became more severe and reached a minimum with condition E at 155°C and pH 3.5. The required cook time then increased with prehydrolysis severity finally becoming longer than standard with sample A.

The H-factor required to reach 30 kappa number was estimated by reading from the plot of this data shown as Figure 51. The curves shown are "power" trendlines from Microsoft Excel ® and approximate the manually drawn curves that were used to estimate the H-factor. The average H-factor required to reach 30 kappa number with AQ for the nine sets of chip samples was 1531; 283 points less than the 1814 required without

AQ. This is a 27 minute shorter cook at 165°C. Cook time can also be a significant consideration when determining an optimal prehydrolysis. Two of the better conditions from the standpoint of pulp yield and sugar recovery were conditions E and G, 155°C at pH 3.5 and 3.0 respectively. The H-factor required to reach 30 kappa number was 290 points lower for E than G without AQ and 400 points lower with AQ.

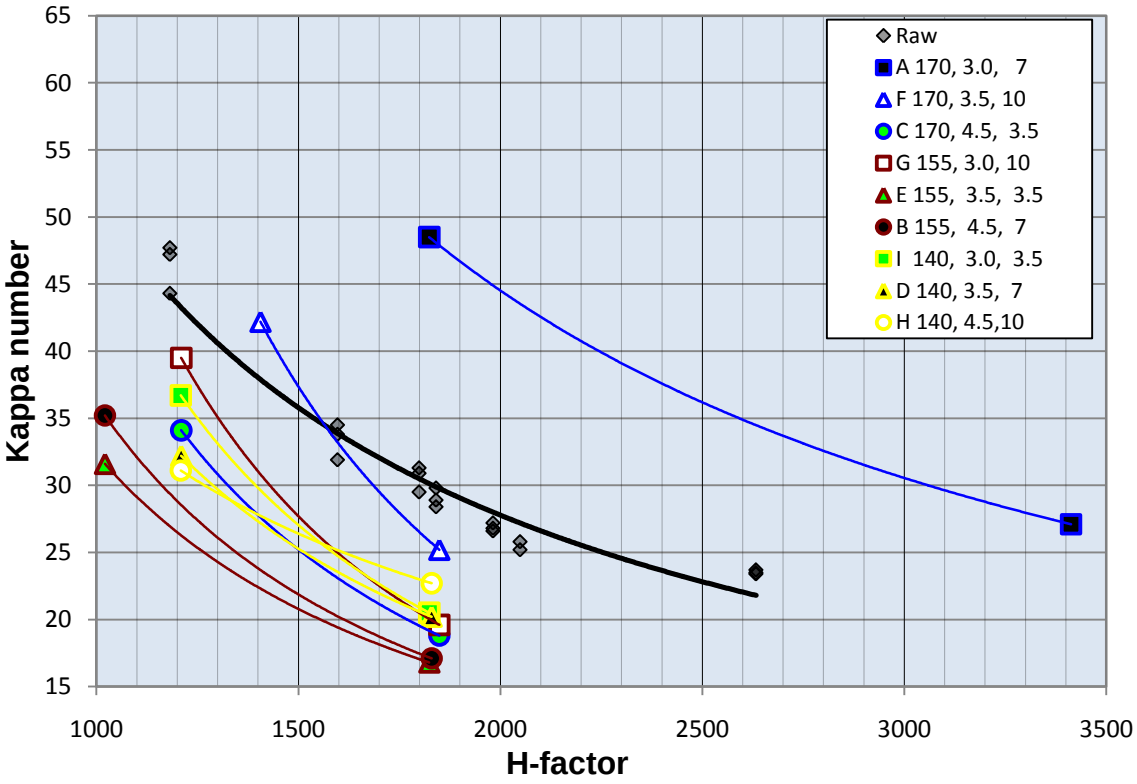


Figure 51 Kappa number as a function of H-factor for AQ cooks (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The pulp yield measurements from each subsample were plotted as a function of kappa number in Figure 52 along with data from the cooks with raw chips for reference. The yield at 30 kappa number was calculated using the equation of the line between the two data points. The improvement in yield varied from 0 to 1.8% of wood with an average of 0.74%. The three highest yield improvements with AQ occurred with the

three prehydrolysis runs that were performed at pH 3.5. The two runs with no improvement were prehydrolyzed at pH 4.5.

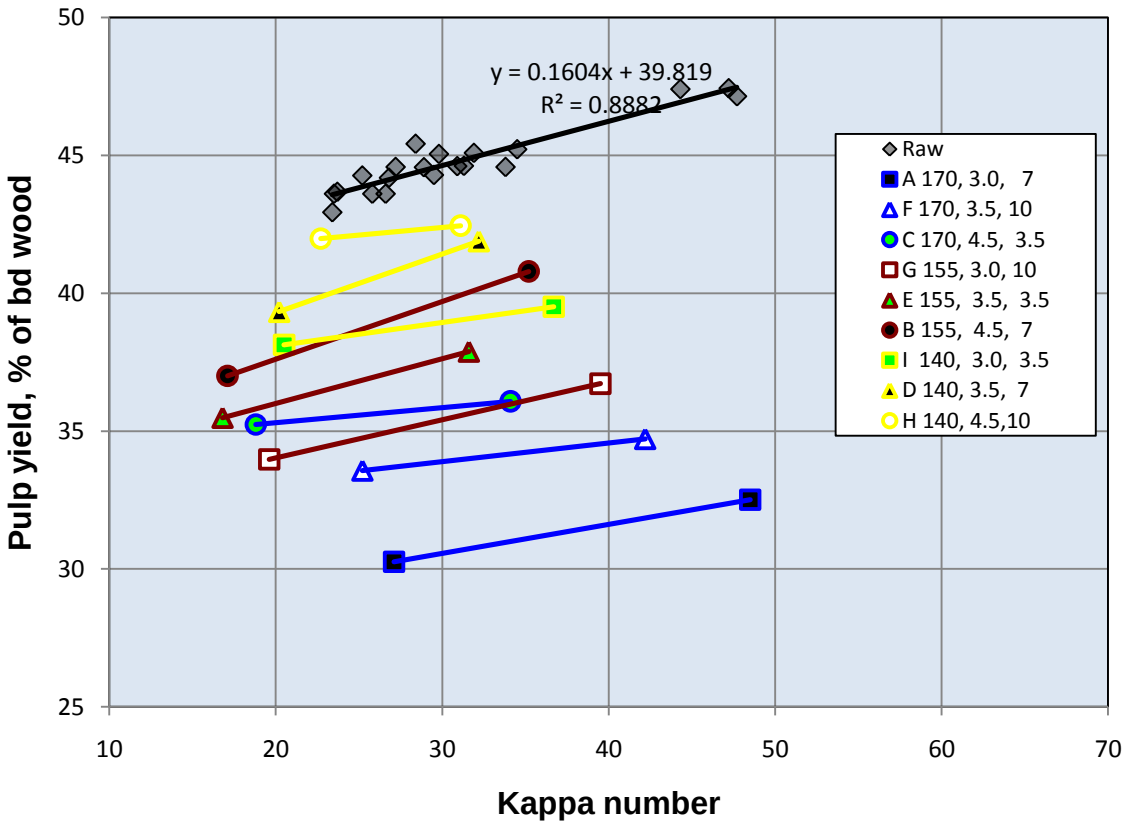


Figure 52 Pulp yield as a function of kappa number for AQ cooks (Legend indicates trial label, temperature, reaction pH, and presoak pH).

Chips from prehydrolysis runs J, K, and L were also cooked with and without AQ. Subsamples 1 and 3 were cooked without AQ. Subsamples 2, 4, and 5 were cooked with AQ. The temperature control profile for subsample 4 was changed so the temperature was ramped up to 150°C and held for 75 minutes and then ramped to 165°C and held for 80 minutes. This profile had the same cumulative H-factor as cook #5 but the time was extended to be the same as cook #1. The H-factor required to reach 30 kappa number was reduced for the AQ cooks, but the yield was only improved by the AQ

addition for condition L. The pulp yield measurements from all subsamples are plotted vs. kappa number for conditions J, K, and L in Figure 53. The yield to kappa relationship was not changed by the modified temperature profile for conditions J and L. This subsample had a lower yield for condition K.

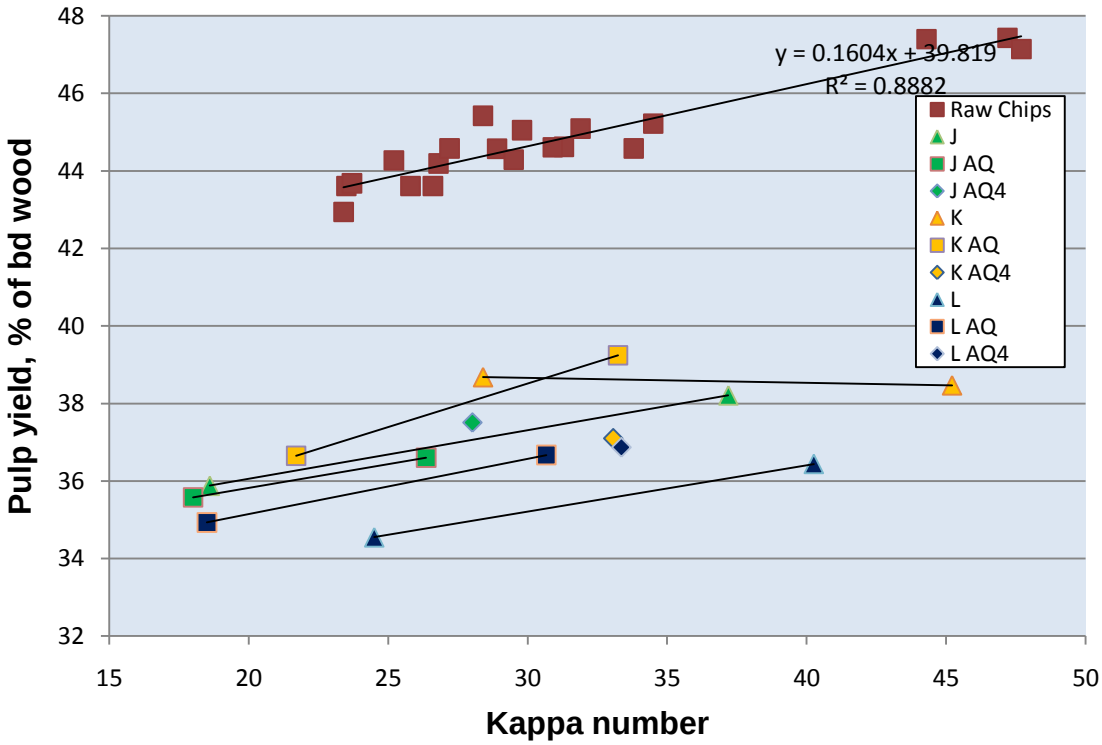


Figure 53 Pulp yield as a function of kappa number for additional cooks with and without AQ. Legend indicates trial label with the modifiers "AQ" for inclusion of AQ in the kraft cook and "AQ4" for modification of the temperature control profile.

The average increase in yield of about 1% from application of 0.1% AQ was expected from literature and the investigator's personal experience. The indication from the design study samples that pH of prehydrolysis could influence effectiveness of AQ was interesting, but not confirmed with the follow up samples J, K, and L. No further work with AQ alone as an additive is recommended as the results observed in this research closely match what has already been documented. The beneficial effects of AQ

on pulp yield and delignification rate have been shown to be additive when it is applied along with polysulfide (Courchene 1998). It might prove beneficial to try AQ along with other chemicals or process changes that improve yield to determine if these effects are also additive. Attempts in this research to improve the effect of AQ by dissolving it in acetaldehyde or ethanolamine before addition to the white liquor are discussed in those sections.

6.2 Acetaldehyde

Acetaldehyde, 99.5% was purchased from Acros Organics for this research. It is a volatile, flammable clear liquid that can be irritating to the eyes and respiratory system. There is also limited evidence of acetaldehyde acting as a carcinogen. As such, it is included on the California Proposition 65 list (California Office of Environmental Health Hazard Assessment 2010). The boiling point for acetaldehyde is 21°C, but the flash point is -27°C. Acetaldehyde should be stored in a refrigerator approved for flammables. It is very soluble in water (Acros Organics MSDS 2010).

No literature references were found for using acetaldehyde for pulp yield improvement. A patent was issued in 2001 for the addition of an aldehyde to a chlorine dioxide delignification bleaching stage to improve delignification (Jiang, van Lierop and Berry 2001). The kappa number was about one point lower and the final brightness about one point higher with the addition of 2% formaldehyde. In another test, the kappa number was 0.6 lower after the addition of 1% glucose to the D0 stage. The aldehyde was mixed with the pulp just prior to the addition of chlorine dioxide and the D0 stage was pH adjusted to 3.0 with sulfuric acid. Treatment was at 50°C for 30 minutes.

A possible reaction of acetaldehyde with the carbonyl end group of the carbohydrates is an aldol condensation that could then limit peeling of this end group. Aldol condensation can occur between any two aldehydes and is base catalyzed. To avoid condensation of acetaldehyde with itself, the additive was added with water to the chips and given time to diffuse into the wood chips at room temperature for 60 minutes before 1% sodium hydroxide on chips was added dropwise to raise the pH. The bombs were then closed and shaken before being left to rest for 90 minutes. After 90 minutes, a measured amount of soak solution was removed and replaced with white liquor for the standard cook. Three bombs were prepared in this manner. One was a blank that underwent the same treatment without acetaldehyde. The other two had 1% or 5% acetaldehyde by weight on chips.

Acetaldehyde was tested in four bomb cooks from prehydrolysis "S". Pulp yield as a function of kappa number for these four samples, the blank, and the six samples used to determine the "Standard" kappa and yield results are shown in Figure 54. The blank sample had the lowest kappa number, the 5% sample the highest. The 5% sample also had a higher yield of pulp than the other two, but all five were very close to the "Standard" line.

The red "Standard" line and point and green "Upper" and "Lower" lines in Figure 54 are generated from the measurements from cooks S7 to S12 that were all performed without additives or additional treatment. The red line was generated by plotting a line of slope 0.1 through the average yield and kappa for these six cooks. The green lines indicate one standard deviation or 0.8% in yield from the standard line. The standard deviation in kappa number was 0.9 units. All of the yield data from the cooks with

acetaldehyde was within one standard deviation in yield from standard at the measured kappa number. None of the tests were within one standard deviation of the standard kappa measurement. The closest point to standard kappa number was the "blank" test that did not have any acetaldehyde added.

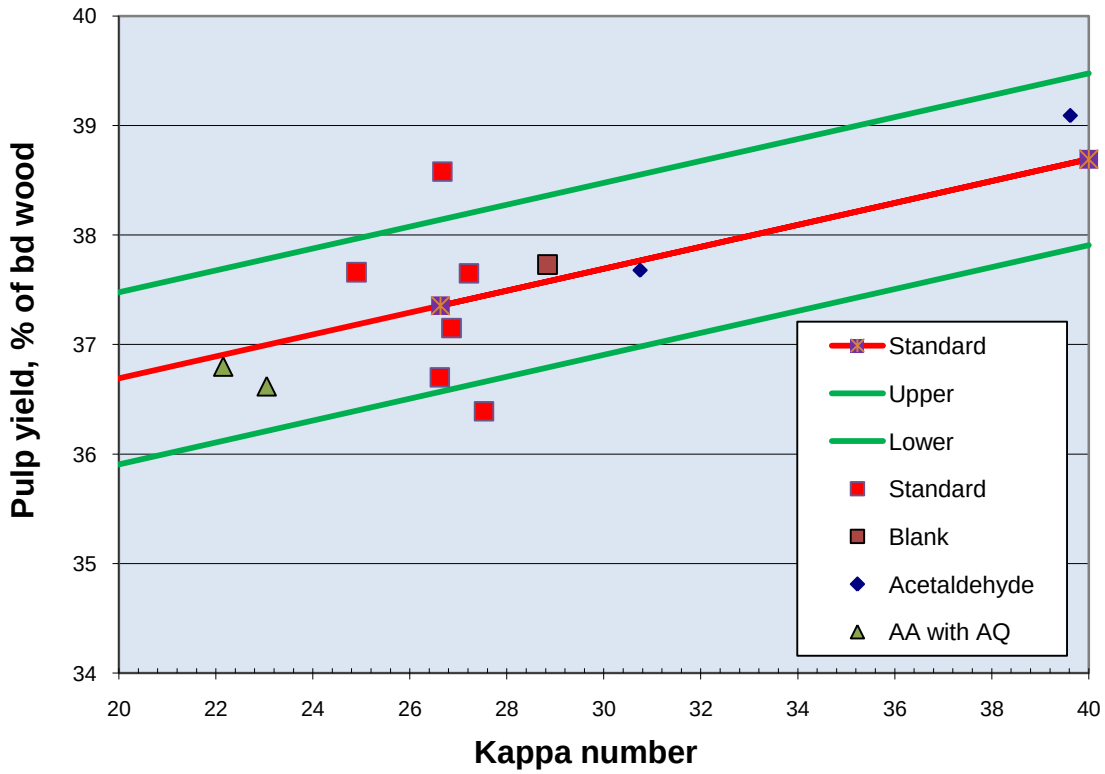


Figure 54 Yield as a function of kappa number for acetaldehyde treated and untreated prehydrolyzed chips.

One difficulty in working with acetaldehyde is the low boiling point of 21°C. The additive was kept in the refrigerator until just before it was measured and a pipette was used to quantitatively transfer the measured amount into the water immediately before it was added to the chips. The bombs were immediately closed and shaken before the rest time. An odor was present even with these precautions.

The two attempts to use acetaldehyde to dissolve AQ were more eventful. Initially acetaldehyde was added directly to the dry AQ powder. A paste formed, but quickly dried back to powder. Some water was then added to the AQ with no effect on the dried paste now stuck on the beaker side. Acetaldehyde was added to the water and the AQ paste released from the beaker. The entire mixture was then added to the chips before the white liquor was added. The beaker with AQ inside was placed in an ice water bath for the second attempt. The paste remained after the acetaldehyde was added. When white liquor was added directly to the paste, there was a crackling sound as the solution turned orange. A dispersed particulate formed when water was added to this solution before the entire mix was added to the chips for cooking. The kappa number was reduced below the standard in these two cases, but the yield remained proportional to the standard line.

The conclusion from these four experiments is that acetaldehyde addition increased the yield and kappa number without changing the standard relationship between the two. The use of acetaldehyde to aid in dissolution of AQ had no significant effect on pulp yield. No further work is recommended with acetaldehyde as an agent to increase yield of pulp from prehydrolyzed chips either with or without AQ.

6.3 Ethanolamine

Ethanolamine is both a primary amine and a primary alcohol that is also known as monoethanolamine. It reacts as a weak base and is produced by reacting ethylene oxide with aqueous ammonia (Morrison and Boyd 1983, 547). Ethanolamine is a colorless, viscous liquid with an ammonia-like odor. It is classified as moderately flammable. Exposure should be kept below the odor threshold (2 to 4 ppm) to avoid irritation to eyes

and lungs. Ethanolamine should be stored in a cool, dry, well ventilated area in properly labeled tightly sealed containers. Small spills should be soaked up with noncombustible absorbent material (Occupational Safety and Health Administration n.d.). Ethanolamine, 99% was purchased from Acros Organics for this research.

The closest literature example for the use of ethanolamine for yield improvement is a patent for a pretreatment of wood prior to soda cooking that would increase yield and improve strength properties of the resulting pulp (Procter and Chow 1978). The primary purpose of the process was to produce a pulp with properties comparable to kraft pulp without the use of sulfur, but the pretreatment was also claimed to increase the yield of kraft pulp by about 2%. The method called for pretreatment with 5 to10% amine and 0.5 to 3% sodium hydroxide based on the weight of wood at a liquor to wood ratio of 5 to 1in a pressure vessel with nitrogen over pressure of about 25 psi. The treatment would be held at 120° to160°C for 30 to 60 minutes. The solution would be drained from the chips after treatment for recovery and reuse of the remaining amine. Cooking liquor would then be added for the soda or kraft cook.

Ethanolamine has also been referenced for use in preserving strength and yield of cellulose as an additive in bleaching, as a co-solvent with water and soda for solvent pulping, and for improving decay resistance of wood. None of these additional applications specifically relate to the use of ethanolamine for yield improvement after prehydrolysis, but they do give a range of conditions that were used as a starting point for screening the chemical for this purpose.

A patent was issued in 1981 for the use of amines to inhibit cellulose degradation in a hypochlorite bleaching stage (Breslin and Cosper 1981). The invention called for the

use of 0.05 to 0.2% of monoethanolamine on pulp added with the bleaching chemicals, 0.5% sodium hydroxide, and water to bring the pulp to 10% consistency. The bleaching reaction was then allowed to proceed for 60 minutes at 110°F. The additive increased pulp viscosity after bleaching from 14.7 to 16.6 cps. Pulp strength properties were also improved.

Ethanolamine has also been suggested for use in solvent pulping. In one example, the ethanolamine concentration varied from 5 to 15% and was used along with soda at 2.5 to 7.5% concentration. The wood was cooked at 165 to 195°C for 30 to 90 minutes. The maximum yield was attained with the lowest temperature, longest time, lowest soda concentration and highest ethanolamine concentration (Jimenez, et al. 2004).

Upgrading of wood is a chemical modification that is performed to improve biological resistance or dimensional stability of wood without increasing flammability. A study of upgrading wood with ethanolamine used solutions ranging from 1.6 to 20% ethanolamine in water (Humar, et al. 2003). The treatment was performed by soaking wood in the solution at room temperature for times from 7 hours to 2 weeks. Vacuum was used to improve uptake of the solution in the wood blocks. Measurements indicated that the treatment improved resistance to fungal rot due to chemical reaction of the ethanolamine with both hemicellulose and lignin. The improvement in rot resistance was attributed to an increase in the pH of the wood from 5.1 to 9 following the treatment.

Ethanolamine reacts with the carbonyl end of carbohydrates and benzene ring groups in lignin (Humar, et al. 2003). The reaction with carbohydrates could limit degradation during pulping due to peeling of this end group. Reactions with lignin could restrict condensation reactions (Procter and Chow 1978).

Ethanolamine was tested with the chips from prehydrolysis run "P". Ten different bomb cooks were performed with various chemical addition rates, temperatures, and time of intermediate treatment. General conditions for each treatment and results are shown in Table 8. For treatments P1, P2, and P3, a 30 minute ramp was used and then held for one hour at temperature. After this time the bombs were removed from the digester and opened. 129 ml of intermediate solution was poured from the bombs and replaced with white liquor. The bombs were then closed, shaken well and put back in the digester for the cook to 1400 H-factor. The pH of the intermediate solution was measured and recorded. The procedure for P4, P5, and P6 was the same except the ramp time was increased to 40 minutes since the temperature was higher. The ramp time was increased to one hour for P7 and P8. P9 was left at room temperature for the two hours required to process P7 and P8 and then cooked with P7 and P8 after the solutions had been changed. P10 had AQ mixed with ethanolamine as discussed earlier. The AQ appeared to dissolve in the ethanolamine initially, but then some precipitate formed when white liquor and water were added to the beaker.

Table 8 Treatment conditions and results for ethanolamine treatment.

Bomb	EA%	Temp	NaOH%	pH	kappa	Yield%
P1	0	80°C	1%	8.91	25.1	37.25
P2	0.5	80°C	1%	10.04	28.0	37.43
P3	5	80°C	1%	10.85	25.2	37.16
P4	0	110°C	1%	6.59	25.9	37.36
P5	0.5	110°C	1%	8.16	27.5	38.11
P6	5	110°C	1%	10.30	29.7	38.21
P7	0.5	140°C	1%	5.64	30.6	38.59
P8	2	140°C	1%	7.52	36.4	37.45
P9	5	25°C	1%	11.45	23.4	37.09
P10 aq	2	110°C	2% WL	9.80	25.1	37.14

The yield is plotted as a function of kappa number for all the tests in Figure 55. The red "Standard" line and point and green "Upper" and "Lower" lines are generated from the measurements from cooks S7 to S12 that were all performed without additives or additional treatment. All of the yield data was very close to being within one standard deviation in yield from standard at the measured kappa number. Only two of the tests with ethanolamine treatment were within one standard deviation of the standard kappa measurement. Two of the closest points were the "blank" tests, P1 and P4, which did not have any ethanolamine added. The test with AQ had results almost identical to the blank.

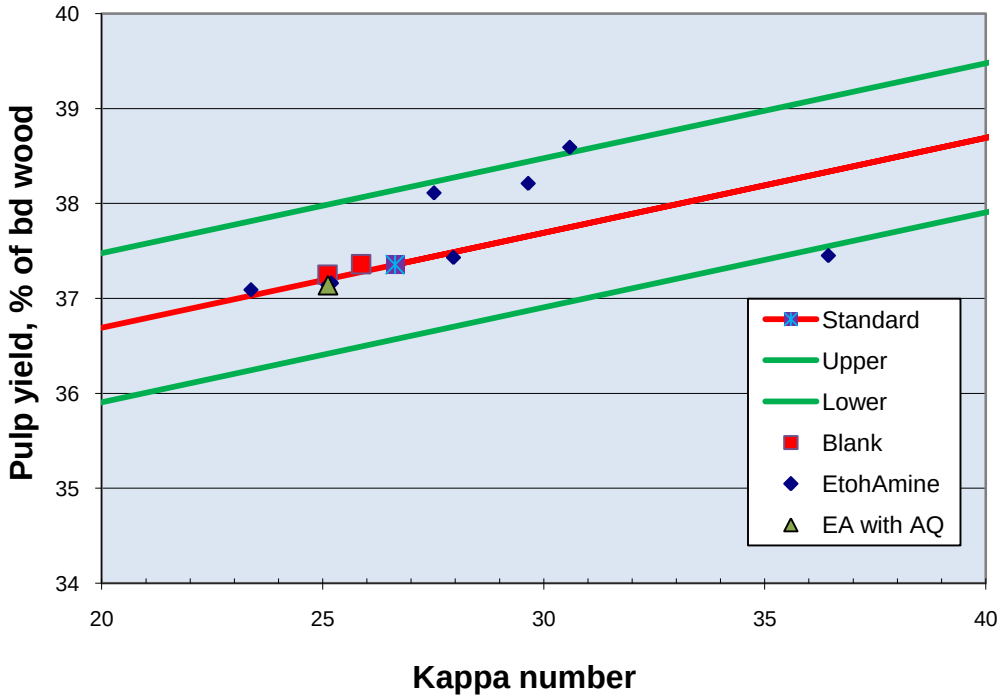


Figure 55 Yield as a function of kappa number for ethanolamine treatment.

The ethanolamine treatment had very little, if any, effect on the yield of pulp from prehydrolyzed chips. The treatments did increase or decrease the kappa number of the pulp in certain cases. The highest yield was generally observed at higher temperature and higher percentage of ethanolamine, but the differences from standard were small and

possibly not significant. The lowest kappa number resulted from the run with the highest pH following intermediate treatment, P9. The high pH prior to addition of white liquor may have increased swelling in the chips and therefore increased the rate the white liquor was transported into the chips, resulting in the three point reduction in kappa number. The two highest kappa numbers were measured following runs with low pH and high temperature in the intermediate treatment. In these cases, the depletion of alkali at higher temperature may have caused condensation of lignin resulting in higher kappa number.

Even though the ethanolamine appeared to dissolve the AQ, this did not improve pulp yield.

If additional studies are attempted with ethanolamine as an agent to increase yield of pulp from prehydrolyzed chips, higher dosage of ethanolamine and sodium hydroxide should be tested in the higher temperature range of 120° to 160°C. It also might be instructive to apply an overpressure of nitrogen as suggested in the patent for pretreatment prior to soda cooking (Procter and Chow 1978).

6.4 Lithium Aluminium Hydride

Lithium aluminium hydride ($LiAlH_{4)}$ was purchased from Acros Organics for this research. The primary difficulty working with this product is that it reacts violently with water to release hydrogen gas that may ignite spontaneously. This can cause severe burns if the powder comes in contact with skin or eyes. The melting point of $LiAlH_4$ is 125°C which is also the decomposition temperature (Acros Organics MSDS 2010).

Lithium aluminium hydride is a versatile reducing agent for organic synthesis, but example reactions were performed in organic solvents (Morrison and Boyd 1983, 473). $LiAlH_4$ can be used to reduce aldehydes to alcohols (Morrison and Boyd 1983, 754).

This reaction is similar to the sodium borohydride reduction of the end groups of carbohydrates to prevent peeling. The reaction of $LiAlH_4$ with water is very fast.

Five chip samples from prehydrolysis "R" were used to test the effect of $LiAlH_4$ on pulp yield. The hydride was added to the pulp and liquor in different ways for each sample in an attempt to find a method to contain the fast reaction. For R1, 0.2% on wood of the hydride was placed in the bottom of a graduated cylinder. The white liquor and water were poured over it and this solution was then poured into the bomb reactor over the chips. The chips and liquor were placed in the bomb first for R2 before 0.5% of the hydride was added to the top of the reactor. A gas was immediately released followed by a flame and popping sound. The hydride was measured into the bomb reactor at a dosage of 1.0% on wood for R3. The chips were added on top of the hydride followed by the white liquor and water. All three bombs were capped quickly and shaken before they were placed in the digester for cooking. There was a concern, especially for R1 and R2, that the hydrogen off gassed prior to capping the bombs. Small plastic weighing dishes were modified for R4 and R5 so the dish would fit in the top of the bomb. The hydride was measured for a 1% dose in the weighing dish. The chips were placed in the bombs followed by water and white liquor. Only enough white liquor was added to R4 to raise the pH to about 10. The full dose of white liquor was added to R5. The full weighing dishes were carefully floated on top of the chips and liquor and the bombs were capped. R4 was then shaken and placed in the digester where it was heated to 120°C and held for 60 minutes. R5 was shaken and set aside. The bomb reactor for R4 was cooled in an ice water bath after it was removed from the digester. It was opened and sufficient solution was poured from the reactor so the remainder of the white liquor could be added. The

bomb was then closed, shaken again, and R4 and R5 were placed in the digester for the cook. Both were cooled in ice water before they were opened. Some pressure was released when R4 and R5 were opened for the first time following the addition of the hydride. R6 was a standard cook with no additive and no pretreatment.

The yield is plotted as a function of kappa number for the tests with $LiAlH_4$ in Figure 56. The standard, upper, and lower lines are generated from the S7 to S12 cooks without additive. The "blank" point is R6. All the yield results are within one standard deviation of the standard line. Samples R3 and R4 had higher kappa numbers than standard. Samples R4 and R5 had higher yield than the other samples and the standard.

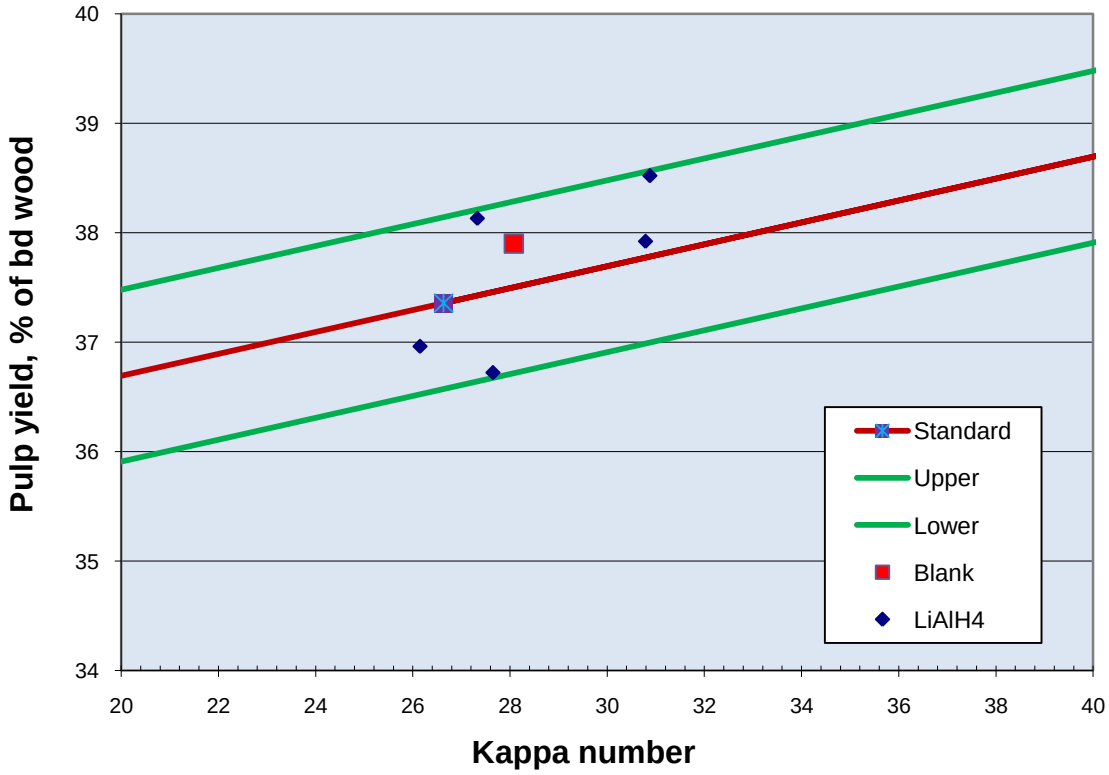


Figure 56 Yield as a function of kappa number for lithium aluminium hydride treatment.

The yield of pulp was not increased by the addition of $LiAlH_4$ like it would have been expected to have been increased by the addition of sodium borohydride. The improved hydride addition method utilizing the weighing dishes may have allowed the reaction to be contained in the bomb and contributed to the higher yield in those two cases, but the yield improvement remained small. No further work is recommended with $LiAlH_4$ as an agent to increase yield of pulp from prehydrolyzed chips.

6.5 Hydroxylamine

Hydroxylamine is typically stored and transported as either a chloride or sulfate salt. Hydroxylamine hydrochloride was purchased from Acros Organics for this research. It is an irritant to eyes and skin and is suspected of causing cancer, but is not on California's Proposition 65 list of potential carcinogens. Immediate medical attention is required following exposure to eyes or skin. Hydroxylamine hydrochloride decomposes at 152°C and can produce hydrogen chloride gas. It is very soluble in water (Acros Organics MSDS 2010).

Hydroxylamine can be used to eliminate reducing sugars in various applications. Patents have been issued for modifying or removing reducing sugars to increase pulp yield (Paterson 1968), purify citric acid preparations (Borchert 1981), and as a bleaching aid for mechanical pulp (Beurich and Scholl 1988). Each of these patented applications claims that it doesn't matter which form of hydroxylamine is used unless there are other considerations that might recommend one form over the others. Compatibility with the kraft liquor cycle would favor the sulfate form if one of these were used.

Different reaction conditions are recommended for each of these three applications. Hydroxylamine sulfate or bisulfate was added directly to the white liquor

for pulp yield improvement. Some additional alkali was required to neutralize the hydroxylamine. A cook with 6.35 parts hydroxylamine bisulfate improved unscreened and screened yield from 48.4% and 44.7% to 52.8% and 48.1% respectively and improved viscosity 30%. The control cook was performed with the same conditions except for the modification of chemicals. The inventor suggests the method to be particularly useful for pine (Paterson 1968). Substantially milder conditions were successful in eliminating reducing sugars from trisodium citrate, possibly since it is a homogeneous reaction. Recommended conditions for this treatment are pH 9 to 10, 60°C, and 12 hours reaction time. The charge of hydroxylamine is approximately stoichiometric at 0.1% for every 0.25% of reducing sugar (Borchert 1981). Hydroxylamine is used in the mechanical pulp bleaching application as a reductive bleaching agent along with various chelant solutions that are the primary subject of the patent. The reaction conditions for examples that included hydroxylamine were pH 6 to 8, 60°C for 1 to 2 hours with 0.5 to 1% hydroxylamine. The bleaching agent could be added to the wood chips before pulping or to the disintegrated pulp (Beurich and Scholl 1988).

Other studies identified hydroxylamine as an interesting additive for pulp yield improvement. A study of the effects of twenty two additives on the yield stability of hydrocellulose after boiling in 1 N NaOH found six that increased the yield by at least 10%. The most effective was sodium borohydride followed closely by hydroxylamine hydrochloride (Clayton and Marraccini 1966). The screening tests were performed on specially prepared partially hydrolyzed cellulose samples to increase the sensitivity to the peeling reaction. Hydroxylamine increased the yield of the hydrocellulose to 90%

compared to 52% for the control sample. In Kraft pulping of spruce and birch with hydroxylamine hydrochloride or sulfate additive the results were less dramatic, but still significant with a 3% increase in carbohydrate yield on wood while at the same time generating a 3% decrease in lignin yield on pulp with a 5% charge on wood. Tests with 1% sodium borohydride in this same study generated a 7% increase in carbohydrate yield but also a 1% increase in lignin yield. Tests with soda pulping had higher carbohydrate yield improvements, but the lignin content remained very high in all pulp samples. The authors suggested that the hydroxylamine reacted preferentially with lignin degradation products, therefore reducing the effect in kraft pulping where these products would be more prevalent earlier in the cook. When compared to sodium borohydride, the hydroxylamine was more effective on hardwood than softwood. The authors cite a previous study with sodium borohydride wherein yield increases were primarily due to increased glucomannan content since xylans are removed by dissolution of oligomers instead of peeling (Aurell and Hartler 1963).

When the required reaction time for pretreatment with hydroxylamine was tested, the resistance to peeling of the hydrocellulose continued to gradually rise even after two hours of pretreatment with hydroxylamine in 1 N NaOH at 100°C. The time dependence of peeling resistance is due to the slow conversion of oxime to nitrile. Test cooks were performed by adding the hydroxylamine directly to the white liquor (Clayton and Jones 1970). These tests indicated that hydroxylamine addition at less than 1% would accelerate delignification but not improve carbohydrate yield. Application of 6.6% hydroxylamine increased carbohydrate yield by 4% of wood.

A study that compared the end group stabilizing efficiency of hydrogen sulfide treatment under various conditions of time, temperature and pH to that of eighteen other reagents also found hydroxylamine to be one of the best (Procter and Apelt 1969). This study used a hydrocellulose with number average degree of polymerization of 46 to test the stabilizing effect toward alkaline peeling. Molecules with stabilized end groups would not change in alkali while unmodified molecules would likely be completely hydrolyzed. The hydroxylamine performed well when added with the hydrocellulose directly to the refluxing 1 N sodium hydroxide test solution with 55 and 85% of the end groups stabilized with 0.05 M and 0.2 M hydroxylamine. When 0.05 M hydroxylamine was used as a pretreatment in water or a carbonate buffer at pH 10, it only achieved stabilization in 40 and 45% of the molecules respectively. The author attributes the lower stabilization to lower accessibility of the end groups at reduced pH, but sodium borohydride was actually more efficient when used as a pretreatment with 89 and 86% stabilization in water and pH 8 buffer compared to 79 percent when added directly to the alkali. The concentrations of reagents used in this study were similar to what could be seen in pulping when compared on a reducing end group weight basis.

Hydroxylamine has also been studied as an additive to increase the delignification rate of soda cooking. In a study with bagasse pith, 10% hydroxylamine hydrochloride was added with 16% sodium hydroxide on pith. The solution was boiled for one hour at atmospheric pressure before washing. The black liquor was acidified and washed with water to produce a high lignin sample that was then prepared for UV and IR analysis. The analysis confirmed that hydroxylamine does form an oxime with the coniferyl aldehyde that contributes to acceleration of delignification. Potentiometric titrations of

the additive solutions and the black liquor also confirmed this mechanism (Ahmed, Saad and Mohamed 1987).

The protective effect of hydroxylamine on carbohydrates is due to the reversible formation of an oxime at the reducing end of the polysaccharide. This oxime is subject to three competing reactions in the presence of alkali. The oxime can revert to the aldehyde, convert to a nitrile that stabilizes the polysaccharide or it can be "peeled" by alkali which produces a new reducing end group and allows continued peeling of the polysaccharide. The reactions of hydroxylamine in this system are summarized in Figure 57 (Clayton and Jones 1970). Another reaction shown is the degradation of hydroxylamine by alkali to ammonia, nitrogen, and water.

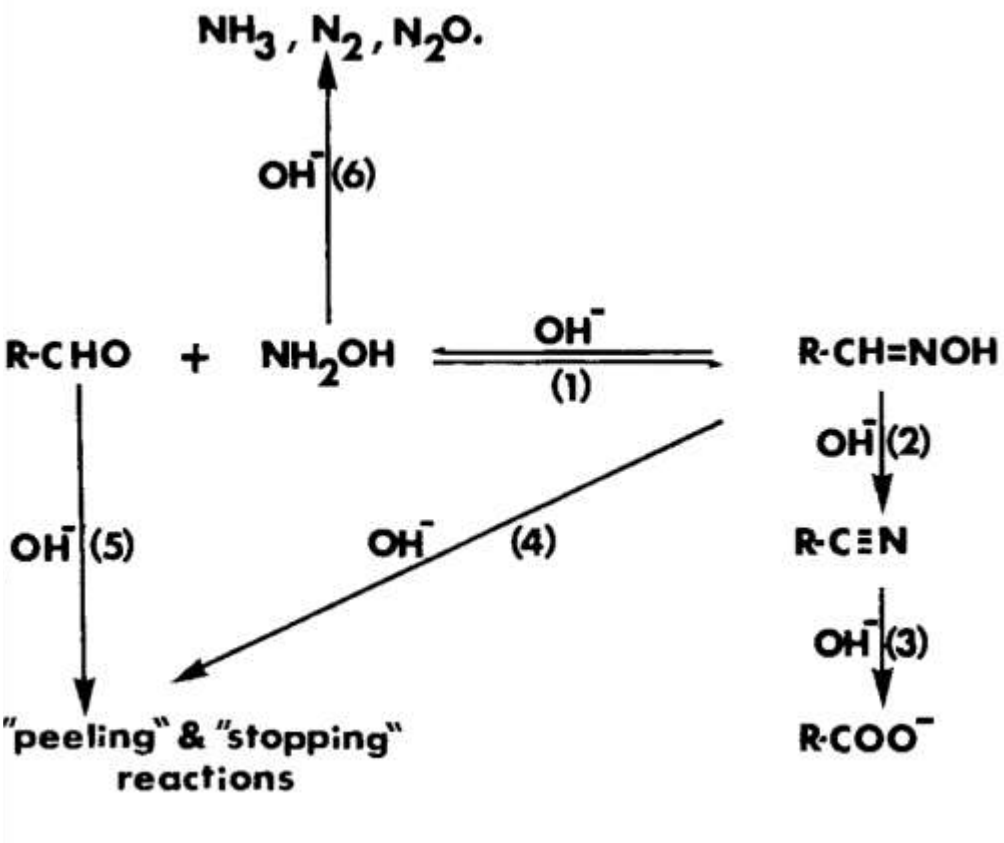


Figure 57 Reaction pathways with hydroxylamine (Clayton and Jones 1970).

Hydroxylamine appears to increase pulp yield by first reducing the rate of peeling through formation of the oxime and second preventing subsequent peeling if the oxime degrades to a nitrile. Both depend on the reaction with the carbohydrate carbonyl reducing end group to form an oxime. This oxime remains subject to peeling, but at a slower rate than the original reducing sugar. The oxime must convert to a nitrile which then subsequently degrades in alkali to a carboxylate ion in order to permanently protect the rest of the polymer. The primary reaction of the oxime in alkali is to form the nitrile if there is a large excess of hydroxylamine. The peeling and stopping reactions of the hydrocellulose and the oxime are both suppressed in this case. The primary reaction of the oxime in alkali is peeling if there is a very low concentration of hydroxylamine with the peeling reaction about twice as fast as the desired degradation to a nitrile (Clayton and Jones 1970).

Two mechanisms for production of the oxime are proposed, one to occur optimally at pH 4 to 5 and the other to occur above pH 9. The reaction of hydroxylamine with a carbonyl is expected to be very slow either below about pH 2 or near neutral at 25°C (Jencks 1959). This maximum in rate below neutral pH is a function of two competing rate-limiting factors: acid concentration for catalysis of the dehydration step from the addition complex and free hydroxylamine base concentration for formation of the addition complex with the carbonyl (pKa of hydroxylamine is 6.0). The rate of oximation of benzaldehyde and acetone with hydroxylamine increased with hydroxide concentration in the range of pH 10 and 12.5. These reactions had a minimum in rate between about pH 8 and 10. The explanation given for this behavior is that the reaction can be catalyzed by the specific base, hydroxide, or a general acid, either oxonium or

water depending on the pH (Williams and Bender 1962). In discussion of the hundred to thousand fold difference in rate of dehydration of the intermediate carbinolamines formed in the reactions with acetone and benzaldehyde, the authors argue the rate must be controlled by the "relief of steric strain" that should be greater in the case of the ketone. This reasoning would imply that the reaction with a carbohydrate would be even slower since the steric relief in the aldehyde would be low and the dehydration would not have the advantage of resonance interaction that is present in the aromatic ring.

There are several different opinions in literature about what the best conditions are for first forming the oxime. The exact conditions of solvent, reagent, temperature, and pH all should be carefully controlled according to several sources, but none of these sources specify what all these conditions should be (Morrison and Boyd 1983, 756-757) (Rojas-Escudero, et al. 2004). A study of preparation of sugar samples for gas chromatography found that a 5% hydroxylamine hydrochloride concentration worked best in several organic solvents and sodium acetate in water. The best reaction conditions in the sodium acetate solution were 60°C for 30 minutes (Rojas-Escudero, et al. 2004). Neither the concentration nor pH of sodium acetate solution was specified. In this and other studies solvents other than water were recommended for the best reaction yield. Those recommended were ethanol with pyridine (Portnoy, Reine and Arthur 1972) and aniline (Rojas-Escudero, et al. 2004) among others tested. A diagnostic procedure for producing the oxime from cinnamaldehyde is: " …0.12 g of the oil…was dissolved in ethanol (3 ml) and treated with a solution of hydroxylamine hydrochloride (0.15 g) and anhydrous sodium acetate (0.3 g) in water (5 ml)" for several hours. The precipitate was

then recrystallized for melting point determination (Birkinshaw, Chaplen and Findlay 1957).

Catalysts have been reported that increase either the rate or yield of the production of oximes. Silica gel is reported to catalyze production of oximes quantitatively and with a stoichiometric amount of hydroxylamine, but this reaction is carried out under "dry" conditions (Hajipour, et al. 1999). Ultrasonic radiation is also reported to improve the rate and yield of oximes from condensation of aldehydes or ketones with hydroxylamine hydrochloride (Li, Li and Li 2006), but this has only been demonstrated on a laboratory scale. Methylamine can function as a nucleophilic catalyst in oximation with hydroxylamine by reversibly forming the intermediate ketimine (Williams and Bender 1962).

Like the literature references for producing an oxime, references for producing a nitrile from the oxime refer to homogeneous reactions in organic solvents such as dry dichloromethane (Chaudhari and Akamanchi 1999) (Telvekar and Akamanchi 2004). In particular, it is emphasized that for the highest efficiency, the solvent should be dry in order to encourage the dehydration reaction. The use of aqueous alkali is listed as one option for this reaction but no process conditions are listed (Meudt, Scherer and Boehm 2008).

The chip samples from prehydrolysis run "Q" were used to test hydroxylamine under a variety of conditions. The chemical charges, reaction temperature, pH data where available, and pulp kappa and yield for each run are listed in Table 9. All were held at the pretreatment temperature for 60 minutes except for Q7, Q8, and Q9 which had no pretreatment time. The ramp time depended on the target: 30 minutes for 60°C, 40

minutes for 110°C, or 45 minutes for 120°C. Sodium hydroxide or white liquor was added to all the bombs that had a pretreatment with the aim of reaching an outlet pH target of either 9 to 10 or 4 to 5. Q1 was a blank sample. The bombs were cooled following the pretreatment and sufficient solution was poured off to be replaced with white liquor for the kraft cook. Hydroxylamine was added directly to the chips with the white liquor for Q7, Q8, and Q9 before cooking with the standard H-factor target of 1400 used for all P, Q, R, and S cooks discussed in this chapter.

Table 9 Hydroxylamine treatment conditions and results.

			NaOH% or				pH	
Label	Bomb	Hydrox%	WL, ml	Temp	kappa	Yield%	in	out
Blank	Q1	0.0	1.0%	60°C	23.7	35.97		10.39
60°C NaOH	Q2	0.16	1.0%	60°C	27.5	37.73		9.79
	Q3	2.0	1.0%	60°C	22.1	36.40		4.85
110°C NaOH	Q4	1.0	1.0%	110°C	22.0	38.18	11.11	5.37
	Q5	1.0	1.5%	110°C	22.6	37.48	12.49	6.49
	Q6	2.0	1.5%	110°C	18.9	37.86	10.24	5.27
to WL	Q7	0.16	129	165°C	27.2	37.35		
	Q8	1.0	129	165°C	26.7	36.55		
	Q9	2.0	129	165°C	32.0	38.63		
120°C WL	Q10	5.0	1.5	120°C	31.2	38.68		1.87
	Q11	5.0	6	120°C	25.1	38.58	5.0+	4.40
	Q12	5.0	18	120°C	29.8	37.59	12.20	9.37

The results listed in Table 9 are plotted in Figure 58 along with the standard red and green lines. All but four of the results were either on or within the green lines indicating one standard deviation from the standard yield-kappa relationship while only three were within one standard deviation from the standard kappa number. It is notable that the blank result had lower yield and kappa than the standard average and the lowest yield of any of the conditions tested in this yield improvement study. The yield improvements observed in Q4, Q6, and Q11 are 1% of wood higher if they are measured against the blank for run Q instead of the standard from run S.

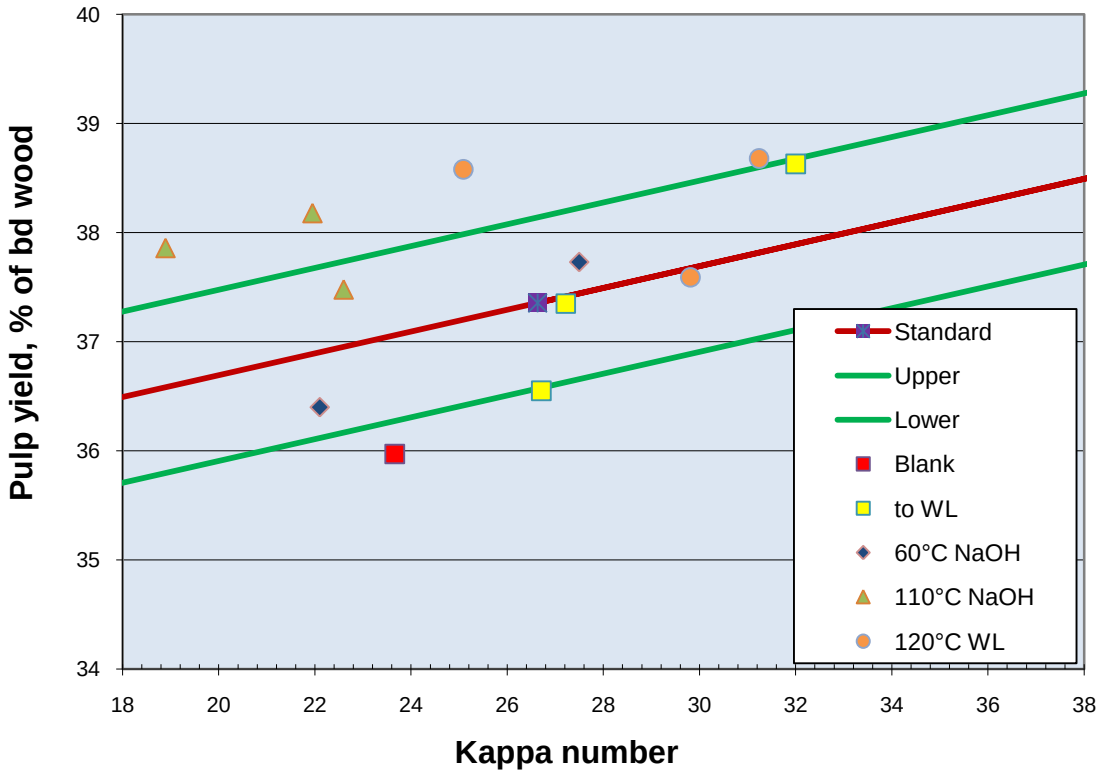


Figure 58 Pulp yield as a function of kappa number with hydroxylamine treatment.

The variety of conditions was chosen to screen the impact of hydroxylamine dosage, alkali source and strength, temperature of pretreatment, and pretreatment pH on the pulp kappa number and yield at a given kappa number. It is difficult to draw general conclusions from this data about the impact of any of these factors on yield improvement due to the small differences, but specific subsets of the samples can be compared to direct future work.

For dosage rate, the two treatments that had only stoichiometric additions of hydroxylamine, Q2 and Q7, were the closest in both yield and kappa number to the standard average indicating little effect. Increasing the dosage from 1% to 2% reduced the kappa number by 3.7 for Q5 and Q6 at 110°C but raised the kappa number by 5.3 for

Q8 and Q9 when the hydroxylamine was added to the kraft cooking liquor. The yield was improved in both cases by 0.38% and 2.08% of wood, respectively.

High and low yield results were found with both sodium hydroxide and white liquor as the alkali source. Addition of hydroxylamine directly to the white liquor for a standard kraft cook resulted in higher yield and kappa number at the highest dosage tested, 2% on wood, but the lower dosages of hydroxylamine gave kappa and yield very near the standard average. Higher kappa number measured for sample Q9 was unexpected since the hydroxylamine is expected to react with both lignin and carbohydrate to accelerate delignification while increasing yield. This change may have been due to consumption of alkali by the hydroxylamine HCl. The yield change remained within one standard deviation of the standard for all three samples. The alkali charge is only an independent variable if the hydroxylamine charge is held the same for the samples under comparison since these two together strongly influence the solution pH. Comparison of Q4 with Q5 shows increasing the alkali charge increased the solution pH out of the preferred range of 4 to 5. The pulp showed a slight increase of 0.6 in kappa number and a decrease of 0.7% in yield. Similarly, comparison of Q10, Q11, and Q12 shows that the charge of alkali that results in the proper final pH produces the best results of yield and kappa number.

In addition to the general observation that the four best examples of pulp yield improvement relative to standard were pretreated at 110 or 120°C, samples Q3 and Q6 can be compared to look at temperature related differences. The alkali charges are different, but the final pH measurements for these two samples are fairly close. The kappa number for the pulp pretreated at the higher temperature is 3.2 points lower while

the yield is 1.46% higher. These differences indicate that while the kappa number of Q3 is low at 22.1, increasing the temperature improved reaction with both lignin and carbohydrate.

Hitting a target final pretreatment solution pH by manipulation of alkali charge in response to hydroxylamine charge proved difficult. Samples Q2 and Q12 finished in the higher target range of 9 to 10 pH while samples Q3 and Q11 were in the lower range of 4 to 5 pH with Q4 and Q6 just above this range. The results indicate the lower range is to be preferred where Q4, Q6, and Q11 all had a kappa number below average and yield significantly higher than the standard at the measured kappa number.

Pretreatment with hydroxylamine produced the best improvement in both pulp yield increase and kappa number decrease of any of the additives tested in this study. Control of solution pH in the range of 4.0 to 5.5 was the most critical factor in success as long as there was at least a 1% charge of hydroxylamine. The improvement in yield in three samples was significant, but not sufficient to return the yield of pulp from prehydrolyzed chips back to the yield from untreated chips of above 44% of wood. Hydroxylamine addition directly to the digester for the kraft cook did not bring an improvement in this study, but a much lower dosage was used than that recommended in the literature examples in an attempt to improve potential economics.

Larger yield improvements were expected with hydroxylamine based on the literature. Further work with hydroxylamine should be attempted to verify the proper pH target, temperature of pretreatment, and dosage rate. Other options for pH control agents are sodium sulfide and ammonium hydrosulfide. Discovery of the optimal temperature and pH sequence for nitrile formation from the oxime should also increase yield. Since

hydroxylamine is reactive with both lignin and carbohydrates, it would be helpful to document the relative reactivity of those wood components as functions of pH and temperature. Improved understanding of these relationships may allow more selective production of oxime and nitrile from carbohydrates without degradation of the hydroxylamine or side reactions with lignin. An example of an additional experiment would be to attempt to produce the oxime at pH 4 where lignin would be insoluble and then add alkali to drive degradation of the oxime to a nitrile.

6.6 General Yield Improvement Conclusions

Pulp yield was difficult to measure even in a laboratory setting due to variability in moisture content of the extracted chips and pulp and the variability of chip composition and size if the chip sample is small. This screening study indicated only modest yield improvements from the additives and conditions tested. Analysis of the results of the study indicated that division of a sample of wet chips into smaller samples for comparative study doubles the variability in pulp yield. A larger set of data is then required to statistically demonstrate a change. Replicates of the study conditions were not performed as the study was only intended to identify additives worthy of further future study.

Based on a combination of literature results and results in this study hydroxylamine is recommended for further study as a yield additive. AQ could also be included in some cooks after proper conditions for yield improvement with hydroxylamine are determined.

Further attempts to improve pulp yield should include optimization of alkali charge to a residual target in addition to kappa number targeting.

Chapter 7 Value Prior to Pulping Model

A mathematical model of a process can be used in process design to predict optimal conditions, test modifications to a built process or new material specifications (Jimenez, McKean and Gustafson 1990), and, after the process is built, to aid in process control. There have been many different predictive models developed for kraft pulping. They include simple kinetic models, models that include mass and heat transfer considerations and empirical models that are accurate but limited to the boundary conditions under which the data were gathered for model development. The form of the model will depend on the assumptions that are made to simplify the actual physical situation into something that can be described mathematically. The appropriate type of model and development method depends on the intended end use for the model. Fundamental models provide understanding of a process and facilitate testing of variable changes on specific property values. Empirical or input/output models may have no fundamental significance or applicability outside of the specific process they were developed for, but they are typically easier to develop and provide a suitable basis for process control (Saucedo and Krishnagopalan 1999). Models published prior to 1983 have been discussed and summarized previously including descriptions of the models and their individual advantages and disadvantages (Grace 1989, 45-73). This chapter includes discussion of a variety of models used to describe wood hydrolysis and pulping to provide a context for the development of a complete VPP model.

An ideal VPP model would predict sugar recovered from prehydrolyzate and pulp characteristics following prehydrolysis and pulping of wood. The inputs available to this model would include the wood composition and process conditions of the prehydrolysis and pulping operations. The VPP model would be general enough that the wood composition data is sufficient characterization of the raw material. In addition, ideally, it should have a flexible structure so that changes in pulping or prehydrolysis conditions could be easily incorporated into the model and still give good estimates of prehydrolyzate composition and quantity and pulp kappa number, yield, and composition. The model would require at least two different stages of calculation, one each for prehydrolysis and pulping. The primary input for each stage would be the composition and quantity of wood chips entering the stage. Additional pulp or chip treatments could then be considered by adding additional stages. Composition information would be formatted to include quantity of sugar monomers and approximations as to how these monomers are distributed into polysaccharide molecules.

This research does not attempt to complete the ideal VPP model. Development of the ideal model will require experiments that isolate kinetic and mass transfer effects and composition analysis of not only sugar monomers, but also oligomers and degradation products. The experiments performed in this research were intended to screen water extraction variables and potential yield improvement additives for process conditions that would facilitate industrial implementation of VPP with Loblolly pine. This development looks only at the first stage of the ideal VPP model: the prehydrolysis. The development attempts to produce a model that incorporates pH, temperature, and time to improve understanding of how these interact in the extraction of sugars from wood chips. A

variety of model forms were considered in this development in hope that in addition to representing the data available from this research, understanding of what would be required to develop the ideal model would be improved.

7.1 Historical Development

7.1.1 Wood hydrolysis or prehydrolysis models

The prehydrolysis factor or "P-factor" is used to combine time and temperature in the first stage of a prehydrolysis-kraft cook into a single variable (Brasch and Free 1965). The development is compared to Vroom's H-factor (discussed in kraft pulping models), but the approximation that the reaction rate trebles for each 10°C rise in temperature is used instead of the Arrhenius law. They do not include liquor pH in the correlation because it is controlled by the release of acid from the wood in water prehydrolysis and is therefore already a function of time and temperature. They state that initial pH might be important in the case of mineral acid prehydrolysis but specifically exclude that case from this work. Another limitation to use of the P-factor is that the second stage or kraft conditions have to be the same for all cooks in order to make direct comparisons of the pulps prepared with different P-factor. Included in the paper are plots of various characteristics of the prehydrolyzed chips, hydrolyzate, and final pulp as a function of prehydrolysis factor. For reference, prehydrolysis with a 40 minute heat up time to 170°C and then one hour at 170°C yielded a prehydrolysis factor of 2400. A single stage kraft pulp was prepared for the "0" P-factor sample. Yield of chips and pulp dropped very quickly with rising P-factor before leveling off after about 5000 P-factor. Hydrolyzate pH leveled off at 3.0 at about 10000 P-factor. Pentosans in the chips dropped quickly to about 5% at 2000 P-factor and then continued a slower decline while

pentosans in the final pulp dropped very quickly and then leveled at just under 2% after 2000 P-factor. Kappa number reached a minimum and alpha cellulose a maximum at about 1000 P-factor. The authors' explanation of these results is that the initial hydrolysis is of easily accessible carbohydrates while later hydrolysis is mass transfer limited in the first stage. The maximum in alpha cellulose signals a transition to hydrolysis of cellulose while the minimum in kappa number shows the extent of lignin condensation after the pH drops below 3.5.

The P-factor is an example of a severity parameter, a single value that incorporates the contributions of more than one variable to allow simple comparisons of different conditions. In the cases of the P-factor and H-factor, those variables are time and temperature. Chum added an acidity function to previous severity measurements by adding a fitted parameter that is species specific and then adjusting the severity factor by the pH value (Chum 1990). This "combined severity parameter" is then used to compare water and solvent based acid-catalyzed fractionation of Aspen. In the case of a first order reaction, the fitted parameter can be derived from the activation energy or the activation energy can be calculated from the fit data. Fractionation experiments on Aspen were performed with various concentrations of methanol in water with sulfur dioxide, sulfuric acid or phosphoric acid catalyst. This data was compared to published data on water-based dilute acid hydrolysis of Aspen. The combined severity parameter produced a good correlation for xylan removal in both cases and for lignin removal in the solvent situation. There was no effect of varying methanol concentration in the 40 to 70% range studied.

Species specific kinetic models have also been developed for prehydrolysis of hardwoods. An effort to model autohydrolysis xylan removal from five different hardwoods at 170°C proposed dividing the hemicellulose into fast and slow reacting components that were removed by parallel first order reactions (A. H. Conner 1984). The rate constants for the two reactions correlated well with the fast reaction approximately 20 times faster than the slow reaction for all five species. The constants varied widely among species with red oak approximately four times faster than American elm. The authors discussed a decreased initial fast xylan removal as the proportion of uronic acid groups in xylan increased from one species to another, but then opined that the difference between fast and slow hydrolysis did not depend on the chemical nature of the polymer, but instead on the accessibility of the hemicellulose from within the lignin matrix.

Further work by this same group considered hydrolysis with 0.1 M HCl at 120°C (Conner, Libkie and Springer 1985) and 5% acetic acid at temperatures from 170 to 240°C (Conner and Lorenz 1986). In the case with HCl, the faster reaction was from 10 to 15 times faster than the slower reaction for all species, but the slow rate was almost the same for all. Once again, the fast rate correlated with the uronic acid/ xylan ratio, but in this case the fastest species was only 1.5 times faster than the slowest. The authors of the 1985 paper speculate that the higher acid concentration of HCl may simply dwarf interspecies differences in acetyl content and that mass transfer effects are probably more important at the lower temperature. The group considered the production of furfural and other degradation products in addition to xylan in the study at higher temperatures. They again used the two component model but found the fraction of slow reacting xylan to decrease with increasing temperature so that at 240°C the slow reacting fraction was

replaced by a small non-reactive fraction. This again suggests the fast and slow phenomena are due to mass transfer rather than chemical structure differences. They assumed the complex reactions involved in the degradation of xylan could be modeled with apparent rate constants for a single reaction.

When the best fit values for each rate constant were used to predict concentrations of oligomers and monomers of xylan, the model over predicted monomers in the early time, and under predicted them in the later times of reaction. This was corrected by adding a time variance to the rate constant for the monomer production reaction:

$$k_2 = k_2^{max}(1 - \exp(-Bt)) \quad (1)$$

The constants k_2^{max} and B were determined in the fitting process. The logic in this form was that hydrolysis of the oligosaccharides is a random process and thus more likely to produce free xylose monosaccharides as the length of the oligomers is reduced over time. The model then fit the data well and was used to predict time and temperature for maximum yield of anhydroxylose in the prehydrolyzate. The best yield was found at higher temperatures, but this was a pretreatment process for wood hydrolysis, not pulping. Addition of acetic acid reduced the time to maximum xylan yield, but did not change the maximum quantity of xylan removed. An advantage of using water or acetic acid over dilute mineral acid is that the prehydrolyzate should not require neutralization prior to use. A potential disadvantage is the production of more oligomers with the weaker acid.

Values of the activation energy for xylan hydrolysis that are reported in the literature are presented in Table 10. These values are determined from modeling of experimental data with feedstock including corn cobs (Nabarlatz, Farriol and Montane

2004) and various hardwood species including red oak (Conner and Lorenz 1986), aspen (Springer 1966), and paper birch (Maloney, Chapman and Baker 1985).

Table 10 Hydrolysis activation energy values from literature.

Activation Energy			
kJ/mole	kcal/mole	Conditions	Source
Xylan Hydrolysis			
88	21.0	5% Acetic Acid	Conner, 1986
108	25.8	Water Autohydrolysis	Conner, 1986
116	27.7	5% Acetic Acid, "fast" reaction	Conner, 1986
118	28.2	Dilute HCl	Springer, 1966
119	28.4	Xylose monomer from oligomer	Nabarlatz, 2004
127	30.4	"fast" reaction in dilute H2SO4	Maloney, 1984
127.3	30.4	"Reactive" xylan polymer to oligomer	Nabarlatz, 2004
136	32.5	Water "fast" reaction	Conner, 1986
251.7	60.2	"Less reactive xylan poly to olig	Nabarlatz, 2004
Arabinose Hydrolysis			
106.2	25.4	Arabinose from xylan oligomer	Nabarlatz, 2004

7.1.2Kraft pulping models

There have been many mathematical models of pulping developed to predict the impact of changing reaction conditions on particular variables. One of the simplest and most useful for kraft pulping is Vroom's "H-factor" that indexes lignin removal as a function of time and temperature (Grace 1989, 49-54). The H-factor is used successfully in industry to help digester operators adjust temperature to maintain pulp uniformity during production rate changes. The model gives a reaction rate relative to an assigned value of 1.0 at 100°C using the Arrhenius law with assumed activation energy of 134 kJ/mol. The relative reaction rate is then integrated as a function of time using the cooking schedule. The result of the integral is the H-factor, a single number that describes the exposure of the chips to temperature changes along the entire cook

schedule. The H-factor has been correlated to yield as well as lignin content of pulp when also given the applied effective alkali (Hatton 1973).

H-factor has been used more recently to combine time and temperature in predicting weight loss during water hydrolysis of pine chips. Weight loss was plotted vs. H-factor for various temperature and time of reaction combinations. The authors concluded that the activation energy for water hydrolysis must be similar to that for kraft delignification, 32 kcal/mol (Yoon, MacEwan and van Heiningen 2006).

A model for pulping based on a single chip evolved over several years (Gustafson, et al. 1983). The original model considered wood to be an infinite slab with set thickness made up of lignin, carbohydrate, and acetyl groups. The acetyl was considered separately because of its effect on alkali concentration. The equations used to describe pulping included kinetics divided into initial, bulk, and residual periods and mass transfer of alkali with a diffusivity that depended on temperature, lignin remaining in wood, and alkali concentration. Mass transfer of other species were not considered because all reactions were considered to be irreversible, sulfide concentration was assumed constant, and the model output concentrations were for well washed pulp. Another input to the model was the lignin content remaining when delignification changed from bulk to residual. This model was used to make predictions about potential problems with chip size variation and to interpret experimental data in this area.

Gustafson's model was later modified so it could be used to simulate extended pulping methods (Pu, McKean and Gustafson 1991). This required a more detailed consideration of the initial period of pulping particularly with regard to the carbohydrate reactions and a revised accounting of consumption of alkali. Cellulose and hemicellulose

are considered separately to improve yield predictions. The carbohydrate reactions are also no longer a function of lignin concentration, but of the carbohydrate reduced by an "unreactive %" of the species, 5% for hemicellulose and 32% for cellulose.

The model was used to simulate Rapid Displacement Heating (RDH) batch pulping where the chips are heated quickly with warm and then hot black liquor before white liquor is added. Each of these liquors is displaced by the following one with the aim of saving energy and reducing residual lignin sent to bleaching. The results of experiments and modeling had two surprising results: The yield/kappa relationship was similar to conventional pulping and the delignification kinetics were similar as well. These results were found even though RDH pulping reaches a much lower kappa number at the same H-factor. The explanations for these results were that the initial pulping period was accomplished in the black liquor portion of the cook and the transition from bulk to residual delignification is reduced from 50 kappa to 20. Yield is proposed to be the same because reduced carbohydrate losses in initial pulping due to the relatively low alkali black liquor at the beginning are balanced by reduced xylan precipitation from the relatively high alkali black liquor at the end of the cook.

The geometric basis for Gustafson's model was later changed from an infinite slab to a sphere with equivalent specific surface area of an average chip (Agarwal and Gustafson 1997). This allows diffusion in three dimensions to be approximated while maintaining the mathematical simplicity of the one dimensional model. The model results suggest that decreasing temperature while increasing alkali charge may reduce the fiber–to-fiber kappa variability. This could allow low kappa pulping at similar productivity and yield.

7.2 Model Development

In the current research, model development began with the simplest approach using the H-factor as the basis of development and the total sugar recovered as the primary variable of interest. Adjustment of the activation energy in the H-factor and the addition of a pH dependence to the relative rate constant produce a method of comparing extraction severities of various prehydrolysis conditions on an equivalent basis.

7.2.1 The Modified H-factor

The H-factor was used previously as a guide for comparing chip weight loss data from hot water extraction for up to 90 minutes at temperatures from 160 to 190°C (Yoon, MacEwan and van Heiningen 2006). The pH of the hydrolysis solution was measured at the end of each extraction in that study and was found to decrease slowly with increasing H-factor. The first attempt at modeling in this study was to compare chip weight loss and total sugar recovered from the nine tests in the Latin square designed experiment discussed in Chapter 5 on the basis of H-factor alone.

The chip weight loss displayed as a function of H-factor in Figure 59 shows that the pH of the solution must be included in the analysis. The weight loss is substantially higher at lower pH for all tested pH and H-factor levels with the exception of the low H-factor test at pH 3.5 that may exhibit lower than expected weight loss due to an error in measurement of chip moisture (refer to Chapter 5). The plot of total sugar recovered in the hydrolyzate as a function of H-factor shown as Figure 60 also illustrates the need to include pH. The legend includes the letter indicating the test, the temperature target, solution pH target, and presoak pH. The solution pH in Figure 60 is represented by the shape of the data marker, the temperature by line color, and the presoak pH by marker

color. The data for the three different pH levels are generally grouped together on the plot with the lower pH showing higher recovery at a given H-factor.

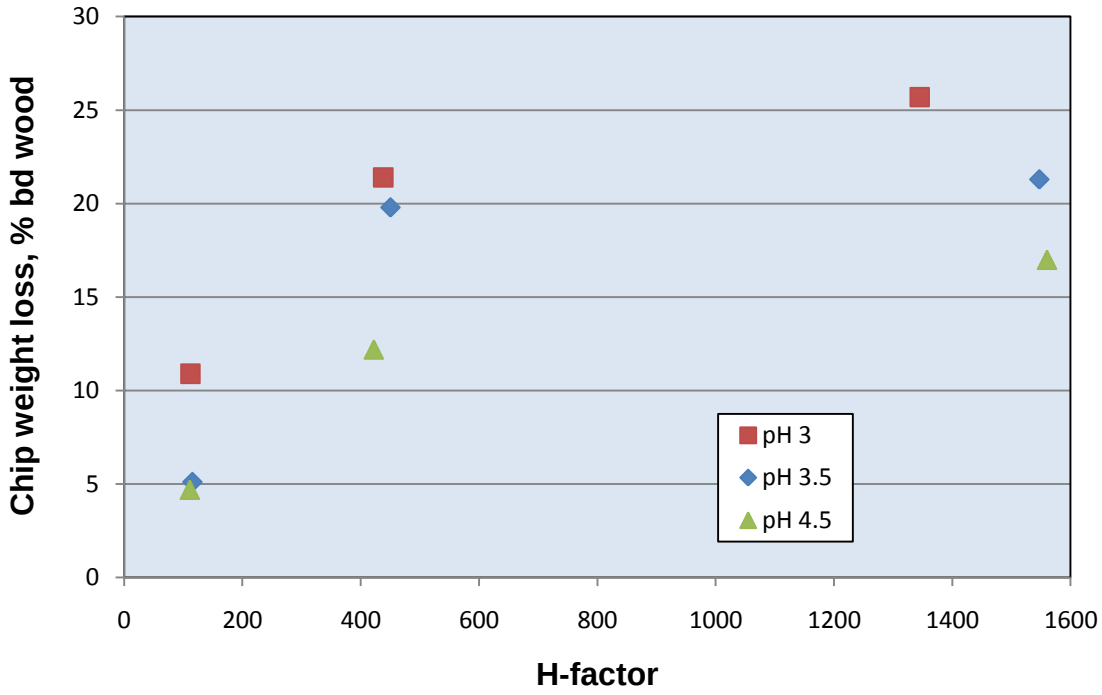


Figure 59 Chip weight loss from prehydrolysis as a function of H-factor.

There is also a general trend in each pH group in Figure 60 for the higher temperature to show a lower sugar recovery at the same H-factor. A possible reason for the trend with temperature is that the activation energy used to calculate the H-factor, 32 kcal/mol, is higher than many of the reported values for the hydrolysis reactions that produce the sugars listed in Table 10. A second possible explanation is that the measured quantity, recovered sugars, is an intermediate product in a series of reactions and that the activation energies for the reactions that degrade the sugars in solution are higher than those for the reactions that produce the sugars. Reported values for dehydration of xylose to furfural vary from 29 to 32 kcal/mol (Nabarlatz, Farriol and Montane 2004).

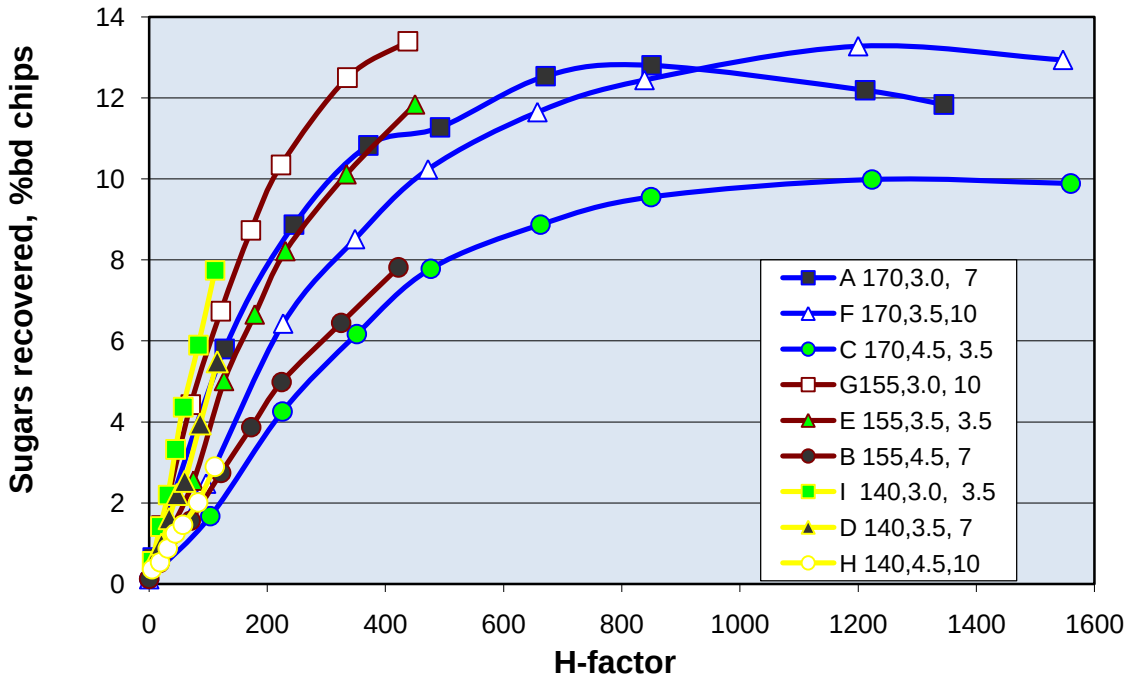


Figure 60 Total sugar recovered as a function of H-factor (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The potential explanations for the data taken at different temperatures not matching at the same H-factor were tested by recalculating the H-factor using different activation energies and comparing the data from each pH group graphically. Figure 61 illustrates the recovered sugar data collected at pH 3 for all three temperatures plotted against a modified H-factor calculated using 27 kcal/mol as the activation energy. This value agrees with reported values shown in Table 10and allowed a good fit for most of the data. The 140° and 155°C data overlay each other very well, while the data taken at 170°C still shows reduced recovery at the same modified H-factor. The data markers for the 140°C runs have been removed for clarity in the rest of the plots of this type in this chapter. The data from the tests at pH 3.5 are similarly plotted in Figure 62. As at pH 3, the two lower temperature tests plot on the same line while the test at 170°C shows lower recovery. The recovery at higher temperature is not reduced as much at pH 3.5 as at pH

3.0. Finally, the data at pH 4.5 are shown in Figure 63 and shows that the modified H-factor is able to account for the variation due to temperature among these three tests up to a two hour time at temperature. These plots suggest that both reasons for the inability of the conventional H-factor to account for the variation of measured sugar recovery exist. Adjustment of the activation energy to 27 kcal/mol properly accounted for differences due to temperature except in the cases where significant degradation of extracted sugars is suspected.

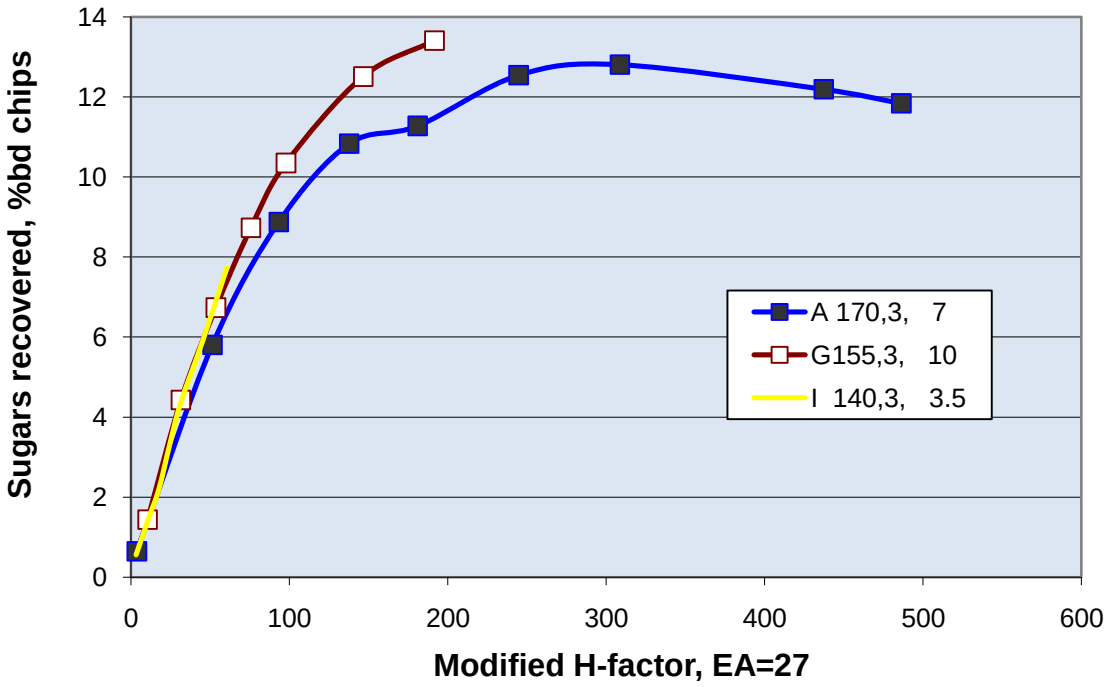


Figure 61 Total sugar recovered at pH 3.0 as a function of H-factor with EA = 27 kcal/mole (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The mathematical form of the pH influence can be determined by looking at an assumed kinetic rate law for a reaction depending on native wood carbohydrate concentration, C_C, and acid concentration, C_A:

$$\frac{dC_C}{dt} = k_C C_A^n C_C^\alpha \qquad (2)$$

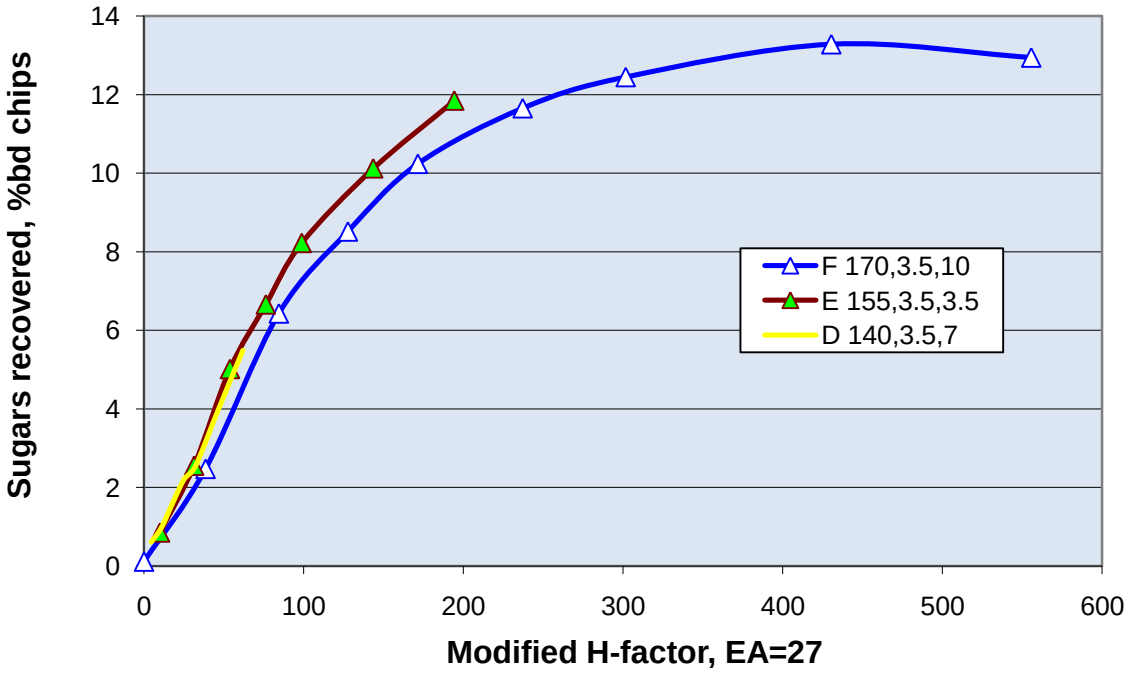


Figure 62 Sugar recovered at pH 3.5 as a function of H-factor with EA = 27 kcal/mole (Legend indicates trial label, temperature, reaction pH, and presoak pH).

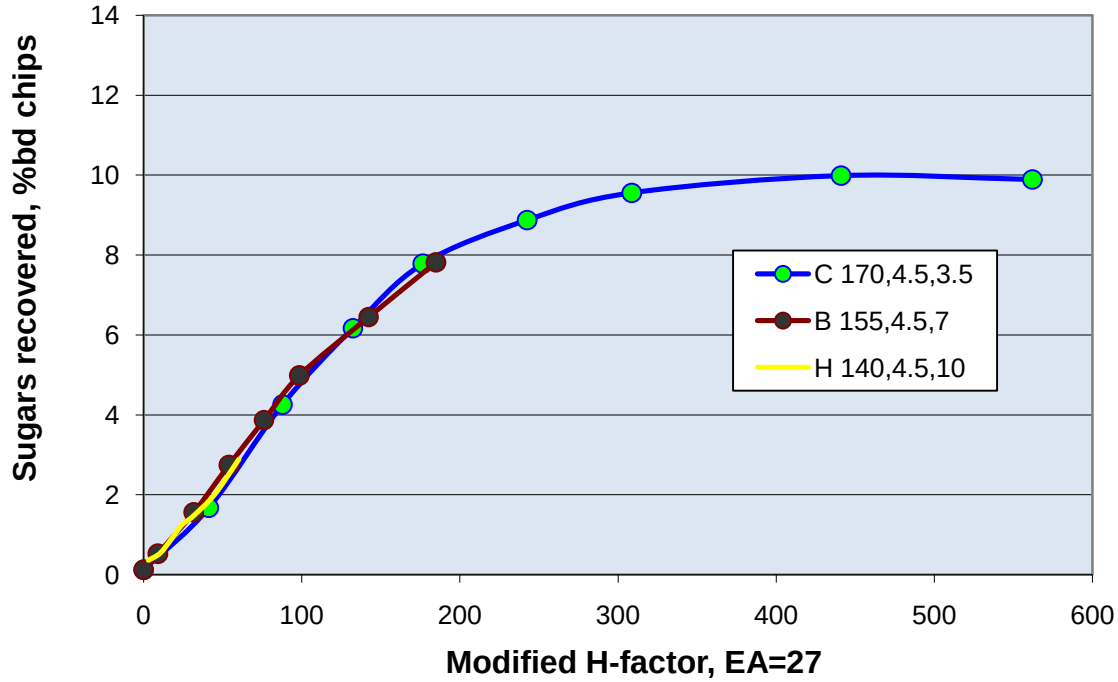


Figure 63 Total sugar recovered at pH 4.5 as a function of H-factor with EA = 27 kcal/mole (Legend indicates trial label, temperature, reaction pH, and presoak pH).

Since the pH was maintained at a target level for these experiments and the acid is not consumed in the reaction, the acid concentration term can be considered to be part of the rate constant along with the temperature effects that have already been shown to follow the Arrhenius relationship:

$$k'_C = k_0 C_A^n e^{\frac{Ea}{R}(\frac{1}{T_0} - \frac{1}{T})} \quad (3)$$

If only the three tests performed at 140°C are used for this part of the development, then degradation effects should be minimal and the temperature term can be included in the constant:

$$k'_C = k'_0 C_A^n \quad (4)$$

Taking the natural log of both sides:

$$\ln k'_C = \ln k'_0 + n \ln C_A \quad (5)$$

A plot of $\ln(k_C)$ against $\ln(C_A)$ will have a slope of the exponent, n, for the acid term. The individual k_C's were calculated from the slope of a plot of $\ln(C_{C0}/C_C)$ vs time where C_{C0} is the total initial carbohydrates, 62% of wood, and C_C is calculated as C_{C0} minus the sugars measured in the hydrolyzate. The exponent for acid was calculated to be 0.317.

The modified H-factor references for each test in the designed experiment were recalculated using the new k_C. The number 25 is a proportionality constant added to return the new modified H-factor to approximately the same scale as the original for this data:

$$k'_C = 25 C_A^{0.317} e^{\frac{27000}{1.987}(\frac{1}{373} - \frac{1}{T})} \quad (6)$$

All nine sets of recovered sugar data are plotted as a function of the modified H-factor including pH in Figure 64. All of the variability in this data is covered by the modified H-factor except for that caused by degradation of sugar monomers in solution at 170°C and either pH below 4.5 or time at temperature longer than 45 minutes.

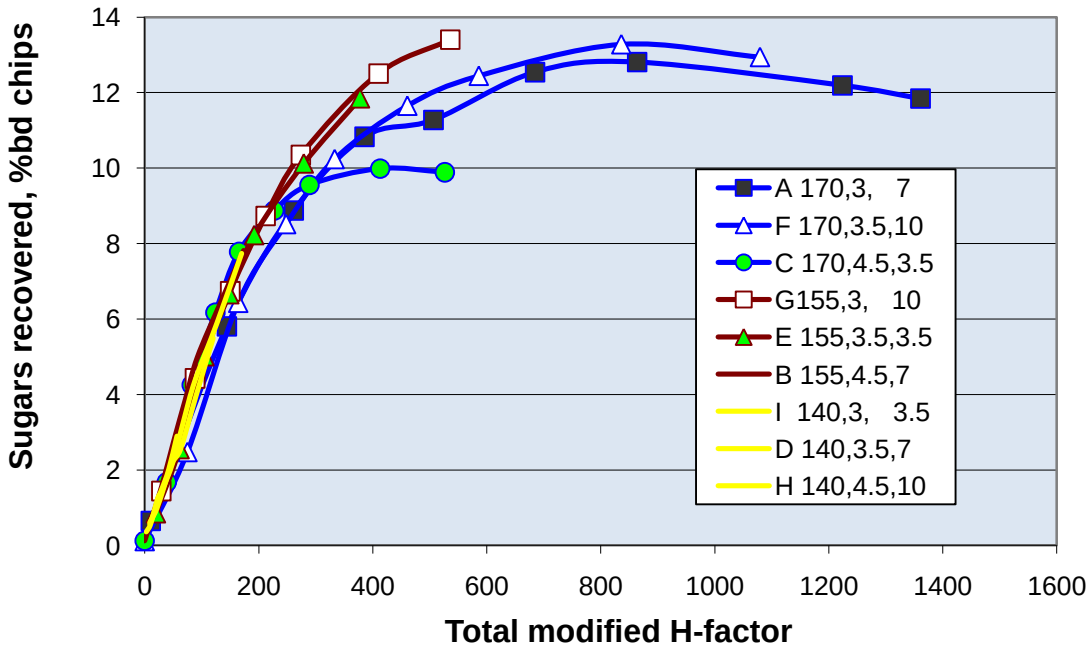


Figure 64 Total sugar recovered as a function of the modified H-factor (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The spreadsheet that was used to calculate the modified H-factor was constructed so the activation energy, Ea, and the order exponent for the pH effect, n, could be varied to gauge the impact of changing these parameters on the appearance of the final composite curve of all nine prehydrolysis tests. The constant was then calculated to force the modified H-factor to equal the conventional H-factor for condition "A", the most severe case. Activation energies from 25 to 29 kcal/mole yielded acceptable appearance with 27 kcal/mole the best fit for the tests with little to no degradation of sugars.

Changing the exponent, n, on the acid term yielded acceptable fit from 0.26 to 0.33 with 0.31 the best. The proportionality constant, k_0, was 23.5 with the "best" parameters.

Each sugar was also considered separately for variation of activation energy and pH effects on extraction from wood. The activation energy was chosen by comparing plots of three sets of three tests at the same pH but different temperatures. The best number for each sugar varied from a low of 23 kcal/mole for arabinose to a high of 29 kcal/mole for glucose, but the value of 27 kcal/mole determined for total sugar would have worked well in all cases. The exponent for the acid term was first calculated using the rate of appearance of each sugar at 140°C in a similar manner to that used for the total sugars discussed previously yielding exponents from 0.23 for glucose to 0.41 for xylose, but the calculated values did not work well when tested graphically. The number used for the plots was chosen by comparing three sets of three tests at the same temperature but different pH levels. These exponents varied in a much smaller range from 0.26 for arabinose to 0.31 for glucose and galactose. When different values of the parameters appeared to be optimal in the three plots, the plot of the less severe condition was given priority since degradation of sugars would be a smaller consideration. The determination of the two parameters separately in comparisons of three tests at a time can lead to a suboptimal set relative to when the data from all nine tests are observed together, but the differences were not large. The modified H-factor was calculated with the parameters determined from the two sets of three separate plots for charts of the five sugars shown here.

The plots of each sugar as a function of the modified H-factor make it obvious what conditions cause degradation of each sugar. Glucose, shown in Figure 65, appears

to have very little degradation, but as was discussed in Chapter 5, this is at least partially due to recovery of sugar hydrolyzed from cellulose in addition to hemicellulose under the conditions that cause degradation of monomers in solution. The activation energy for glucose hydrolysis was estimated to be 29 kcal/mole through visual inspection of the three plots at different pH levels, but 27 kcal/mole appeared better when all nine tests were viewed together.

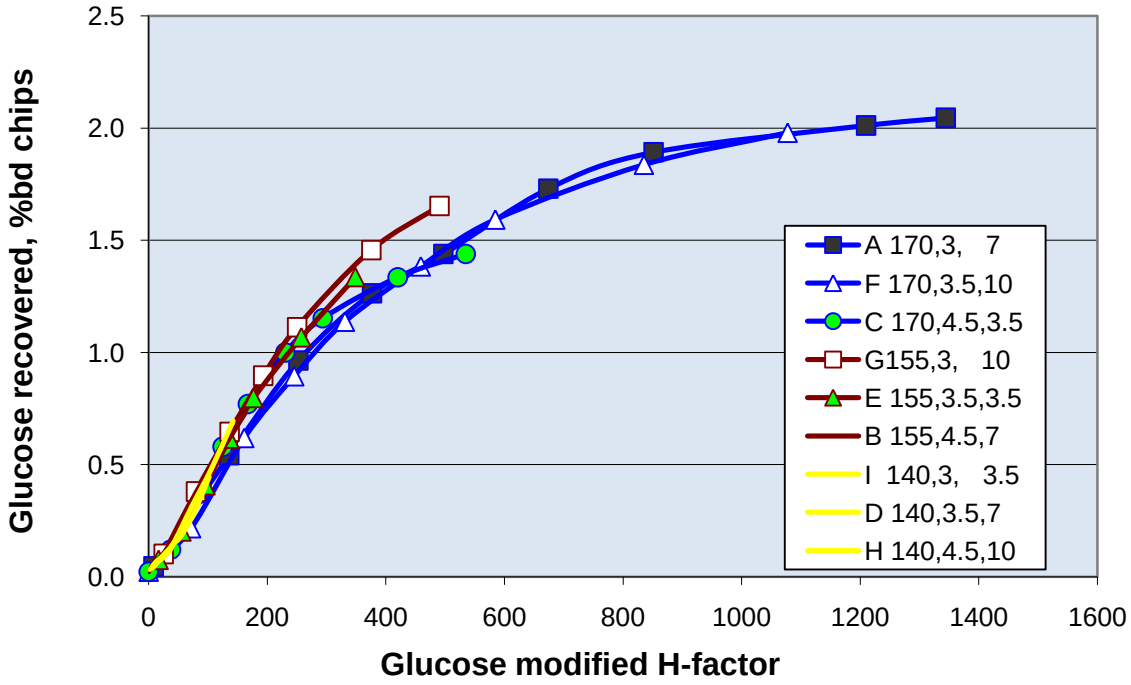


Figure 65 Glucose recovered as a function of the modified H-factor (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The pentoses, xylose and arabinose, showed the most deviation from an imagined smooth extension of the composite curve beyond 500 modified H-factor. The recovered xylose is plotted against a modified H-factor calculated using 26 kcal/mole for activation energy, 0.30 for the acid exponent, and a proportionality factor of 26.9 in Figure 66. This figure shows the data from the tests at 170°C begin to deviate from the composite curve at about 300 modified H-factor. There must have been sufficient xylose monomers in

solution that the rate of degradation to furfural began to exceed the rate of xylose monomers or oligomers entering solution.

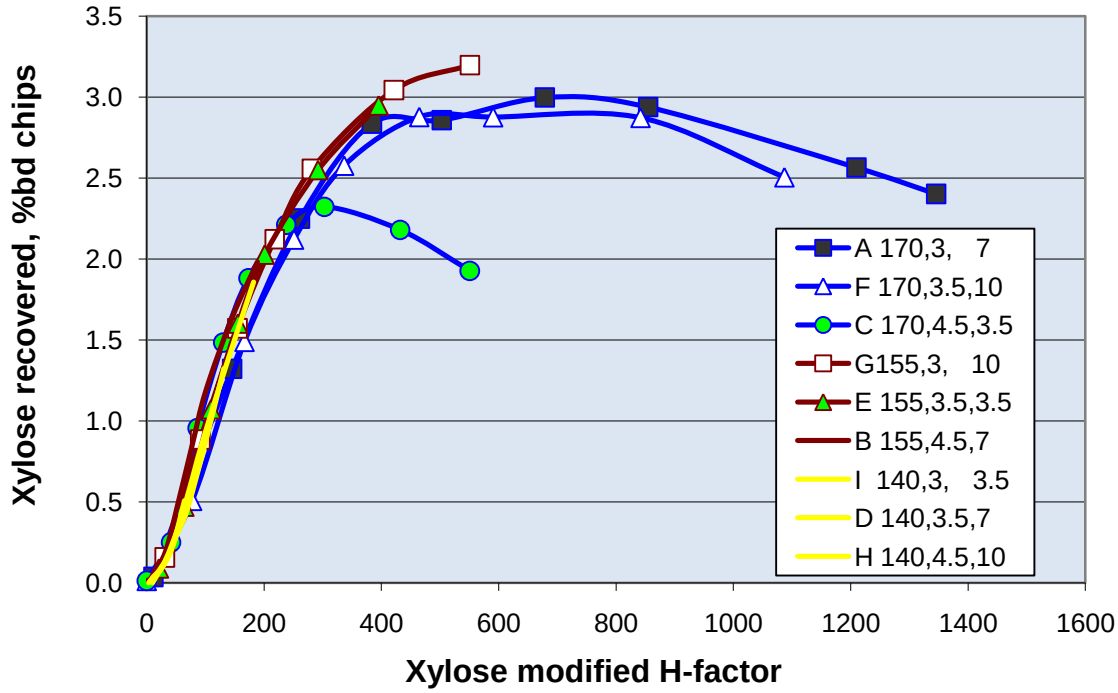


Figure 66 Xylose recovered as a function of the modified H-factor (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The modified H-factor for galactose was calculated with an activation energy of 25 kcal/mole and an acid exponent of 0.31 for Figure 67. The deviation from the composite curve, and therefore the expected degradation rate, was greater for galactose than for the other hexoses, glucose and mannose. This could be because galactose was more likely to enter solution as a monomer since it is derived from sidechains of the galactoglucomannan that are susceptible to acid hydrolysis and arabinogalactans that are soluble in water (Sjostrom 1993, 65).

Arabinose is completely hydrolyzed by 200 modified H-factor, so the composite curve of all the data should then form a flat line at 1.55%. The data plotted in Figure 68

indicates that arabinose begins to degrade from that point, but the arabinose data in that range are only estimates in most cases due to interference from the larger mannose peak. The fit parameters used for this plot were 23 kcal/mole for Ea, 0.26 for n, and 37.3 for k_0, but the appearance of the plot was not very sensitive to these values.

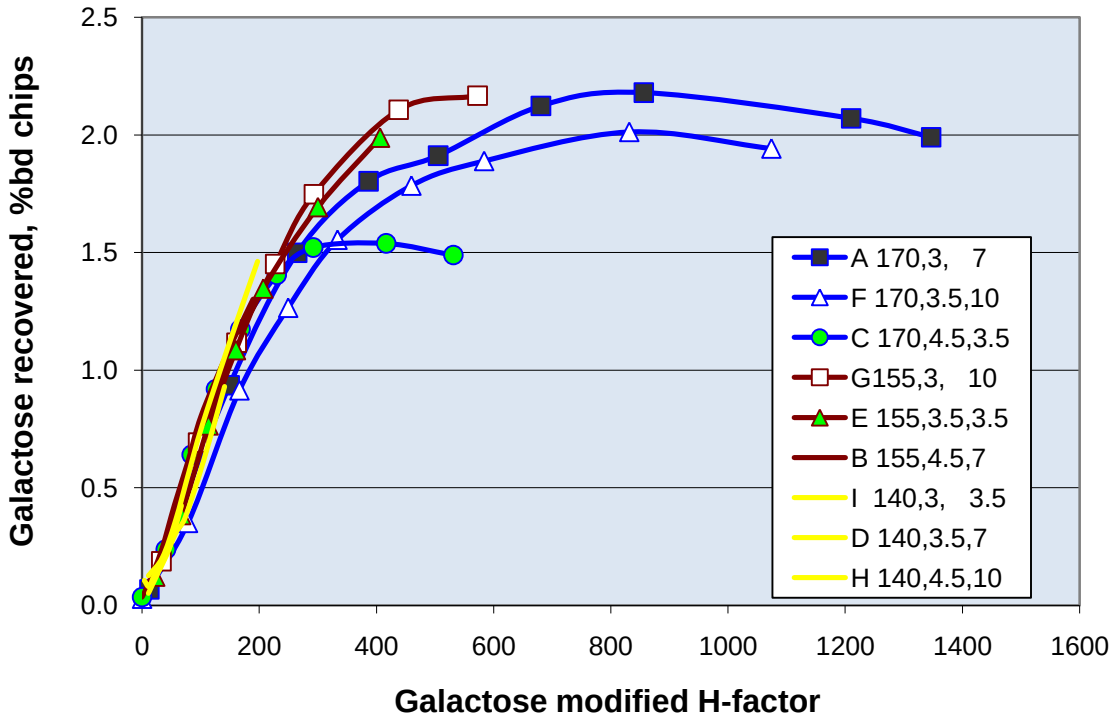


Figure 67 Galactose recovered as a function of the modified H-factor (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The mannose recovered sugar data in Figure 69 shows deviation from the composite curve beginning at about 300 modified H-factor. The modified H-factor was calculated using 27.5 kcal/mole for Ea, 0.29 for n, and 18.5 for k_0. The degradation of mannose and arabinose may be more sensitive to pH than the other sugars since the curve for run "A" at 170°C and pH 3.0 was lower than that for run "F" at 170°C and pH 3.5 at higher modified H-factor.

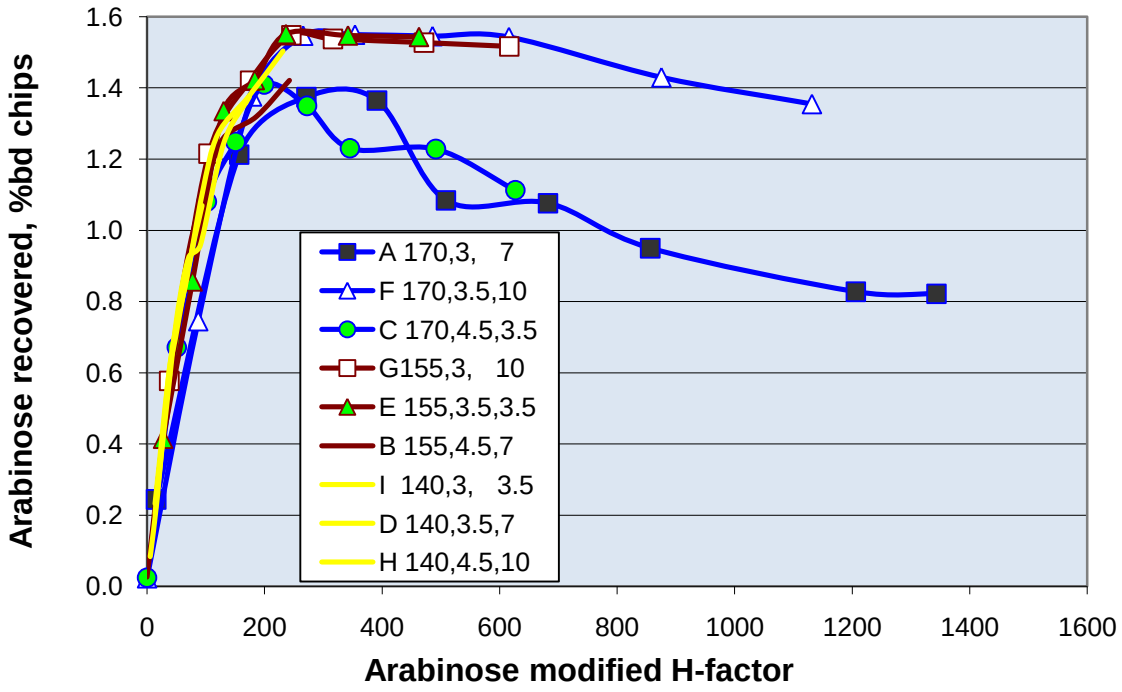


Figure 68 Arabinose recovered as a function of the modified H-factor (Legend indicates trial label, temperature, reaction pH, and presoak pH).

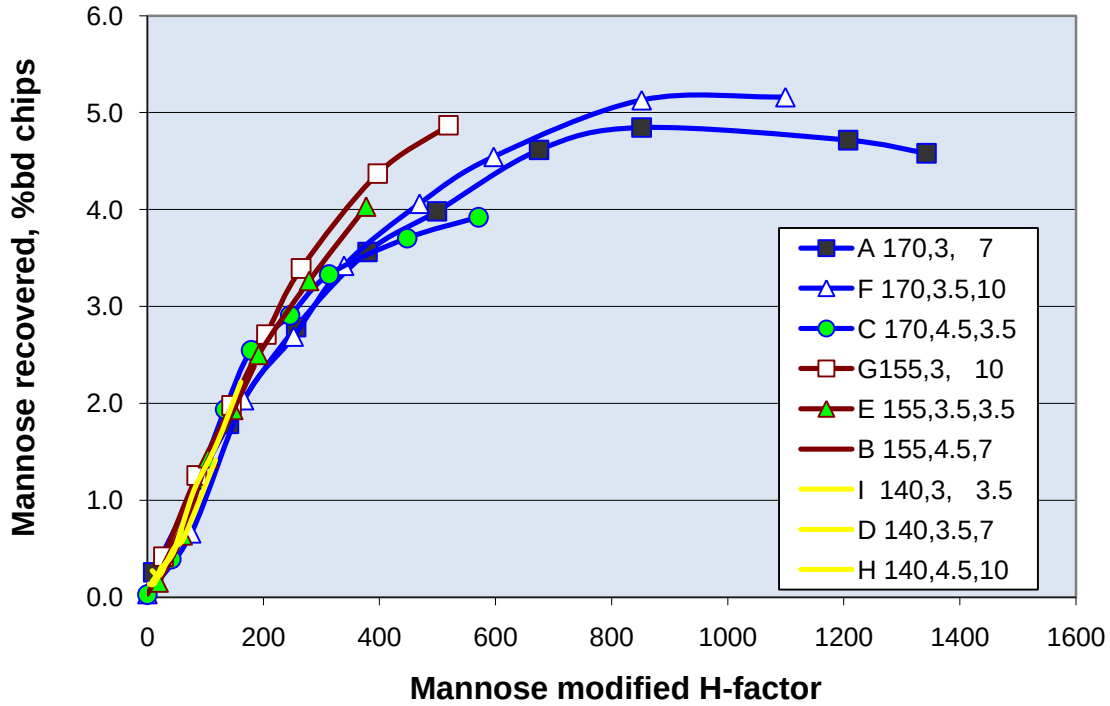


Figure 69 Mannose recovered as a function of the modified H-factor (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The modified H-factor with pH adjustment can be useful for predicting the behavior of more than just the sugar recovery from which it was derived. The wood weight loss and pulp yield at 30 kappa number were also plotted as functions of the modified H-factor. Figure 70 shows an improvement over Figure 59 as to the data being closer to a single relationship, but there is still a lot of scatter. The scatter in the data is likely due to errors in this measurement as discussed before. The pulp yield data all align on one relatively smooth curve in Figure 71 with the untreated reference pulp shown as "Raw". The comparison of pulp yield can be made because all of the data is referenced to a standard of 30 kappa number since the modified H-factor refers only to the conditions of the prehydrolysis. This plot indicates a significant pulp yield loss of 6% relative to the standard pulp after only 200 modified H-factor.

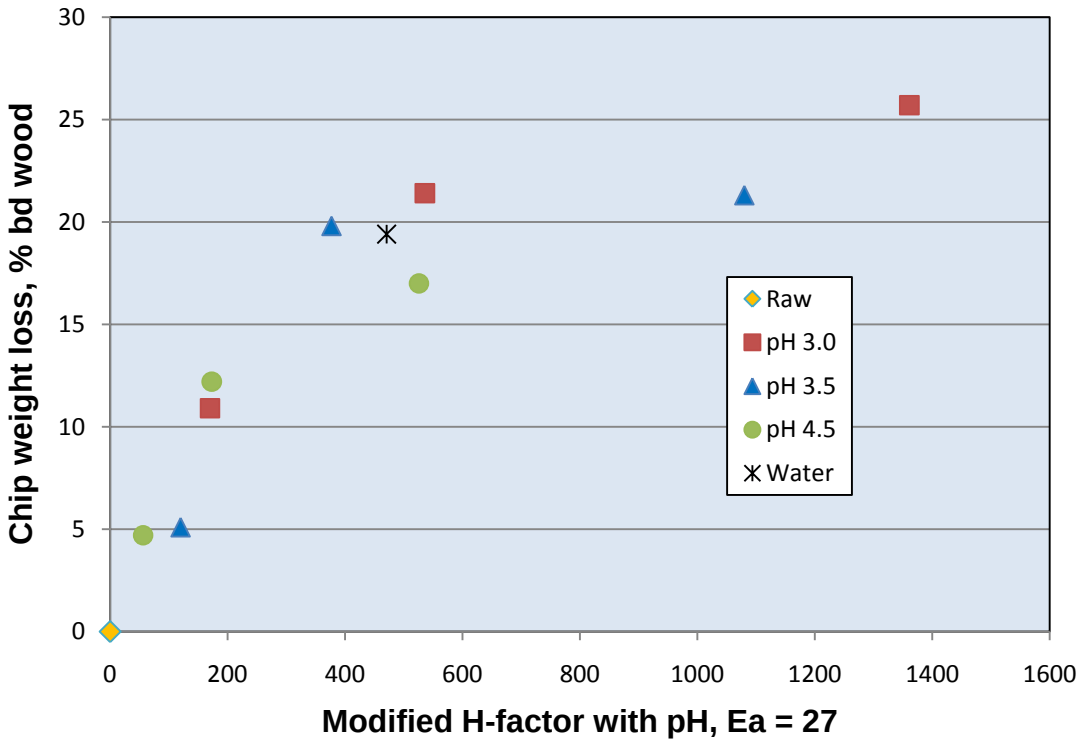


Figure 70 Chip weight loss from prehydrolysis as a function of modified H-factor.

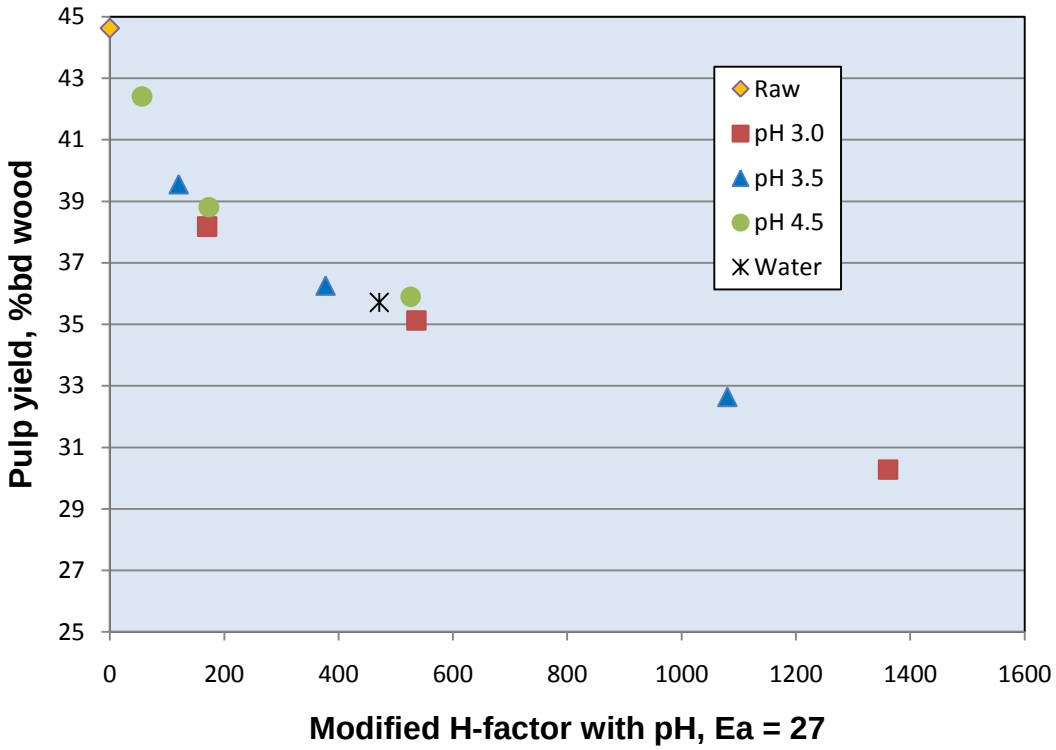


Figure 71 Prehydrolyzed kraft pulp yield at 30 kappa as a function of modified H-factor.

Comparisons of pulp characteristics can also be made using the modified H-factor if the pulping conditions for the kraft cook are all the same. The cook that was performed on the first subset of chips from each of the nine prehydrolysis test conditions was with the same liquor charge and to the same H-factor, 1850. The yield from each of these cooks is plotted as a function of modified H-factor with pH in Figure 72. Again, a fairly smooth curve could be drawn through this collection of data that previously would have had three separate lines; one for each pH level. A final example is the plot of the kappa number from these cooks shown in Figure 73. A plot of this type would make it very easy to pick the optimum prehydrolysis conditions to minimize lignin content of pulp. An additional prehydrolysis test designed to end at a modified H-factor of 300 would help to define the lower range of this dataset.

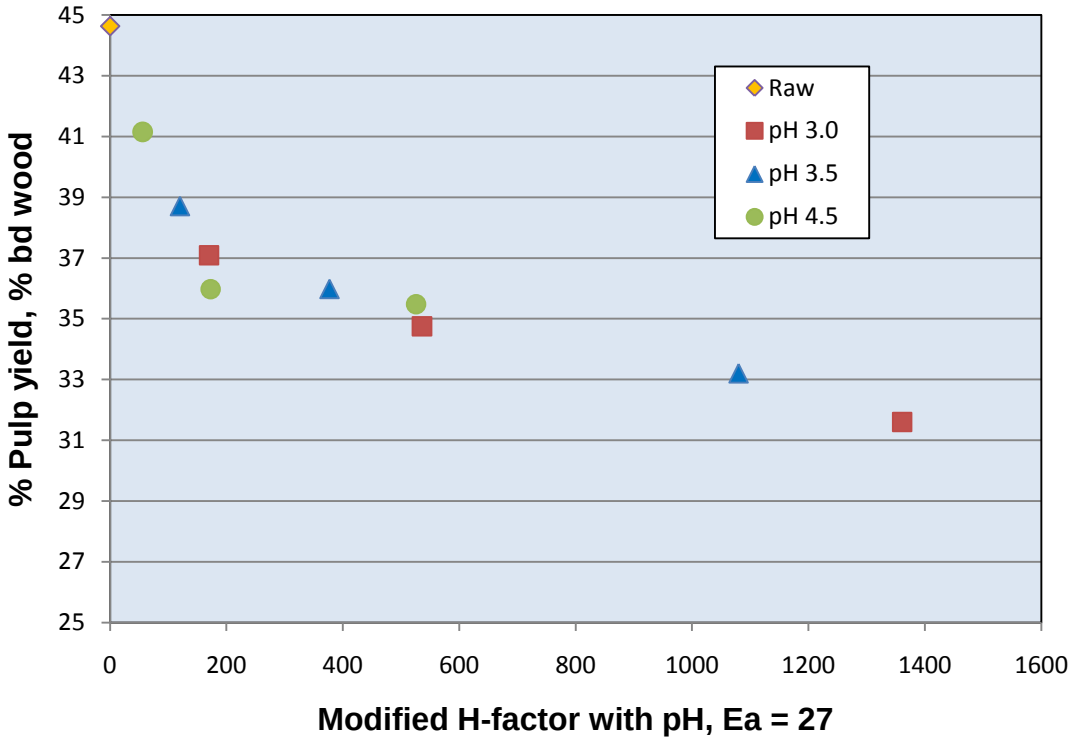


Figure 72 Pulp yield after "standard" cook as a function of modified H-factor.

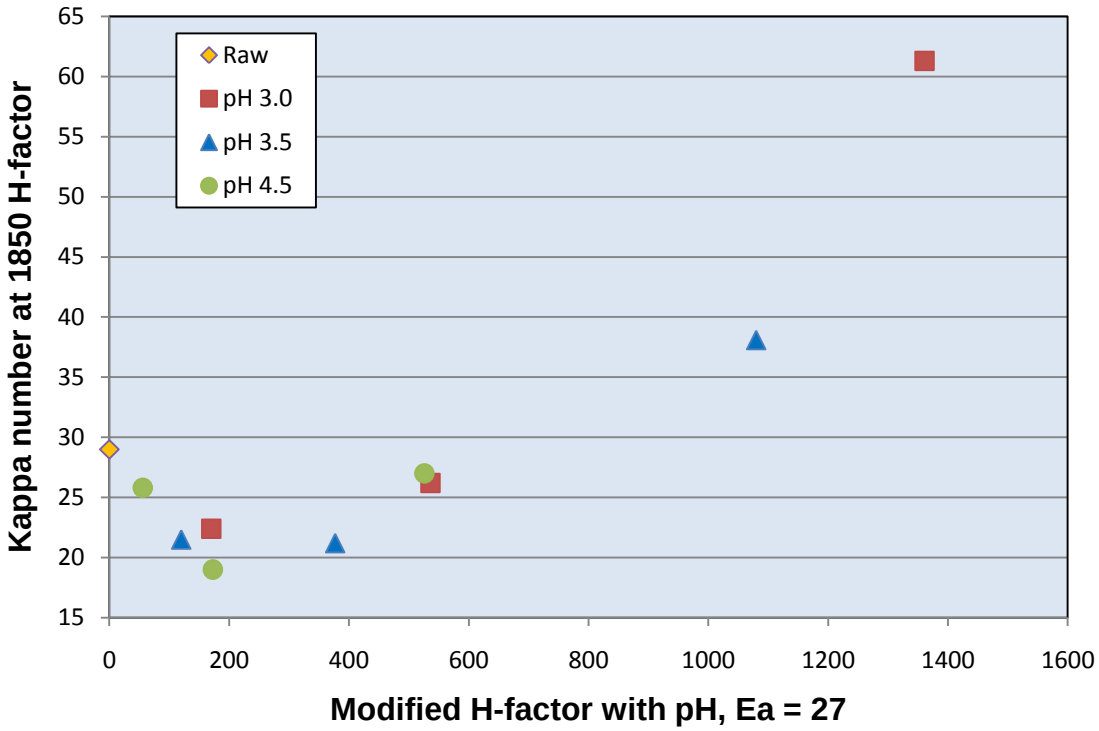


Figure 73 Kappa number after "standard" cook as a function of modified H-factor.

The total recovered sugar data displayed in Figure 37 was modeled by putting the differential rate equation in Polymath 6.10 with the necessary explicit equations:

$$\frac{dC_C}{dt} = k_C C_A^{0.31} C_C \tag{7}$$

The rate constant is defined here:

$$k_C = k_0 \, e^{\frac{27000}{1.987}\left(\frac{1}{373} - \frac{1}{T}\right)} \tag{8}$$

The initial rate constant, k_0, was determined to be 0.00078 minute^{-1} by matching the curve generated in Polymath 6.10 with the data taken at 140°C and pH 3.0. The Polymath program for the total sugars represented by these equations is fairly simple and is illustrated in Figure 74. Cc0 is defined here as the initial hemicellulose mass fraction of the dry wood.

Differential equations

```
1 d(Cc)/d(t) = -kc*Ca^n*Cc
```

Explicit equations

```
1  Ttarg = 140
2  pH = 3.0
3  k0 = 0.00078
4  n = 0.31
5  Ea = 27000
6  Cc0 = 0.2361
7  Tini = 30
8  T1 = if(t<60) then (t*(Ttarg-Tini)/60+Tini+273) else (Ttarg + 273)
9  T0 = 373
10 R = 1.987
11 Ca = 10^(-pH)
12 kc = k0*exp(Ea/R*(1/T0-1/T1))
13 S = 100*(Cc0-Cc)
```

Figure 74 Modified H-factor model equations for Polymath 6.10.

This program was run for the nine conditions by changing the temperature target and the pH. The time, temperature, and sugar (S) outputs were exported to Microsoft

Excel ® for calculations and plotting. Selected examples of the predicted values of carbohydrates extracted are plotted with the corresponding experimental values as a function of time in Figure 75. The predicted values are shown with lines in the same colors as before for different temperatures. The lines for the experimental data are reduced in size to improve visual clarity of the plot.

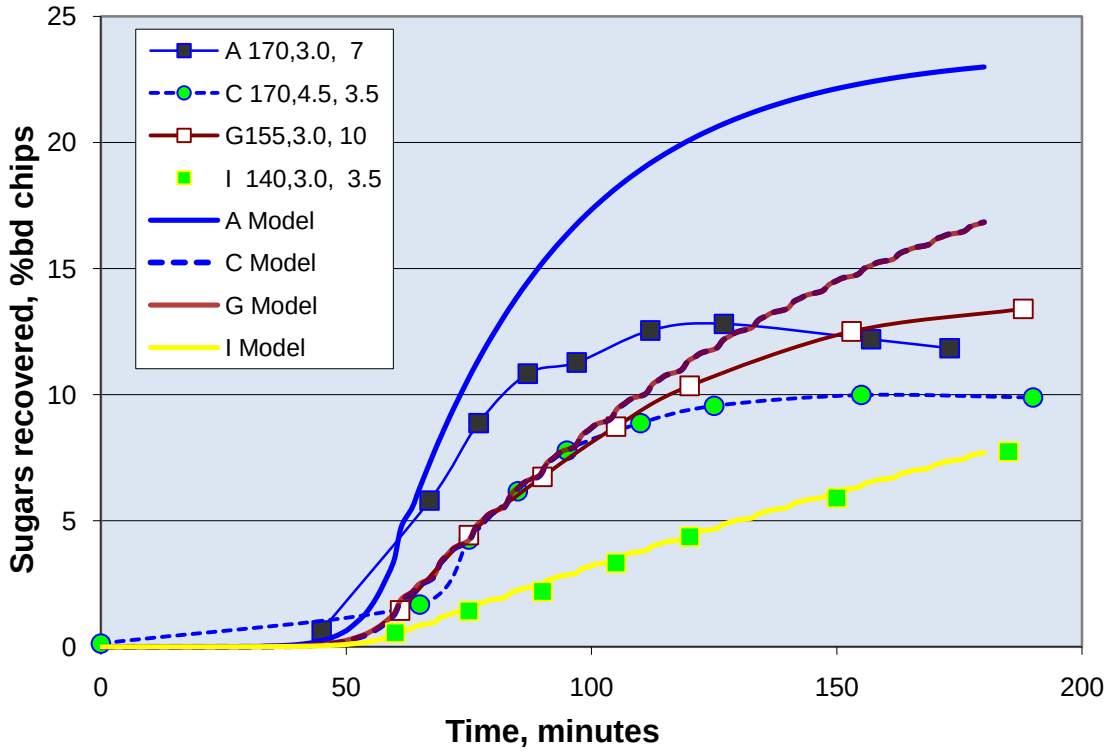


Figure 75 Total recovered sugars compared to predicted values as a function of time for selected conditions (Legend indicates trial label, temperature, reaction pH, and presoak pH).

The four experimental conditions that had very little degradation of sugars, represented in Figure 75 by condition I, are modeled well with this system of equations. The data from more severe conditions, illustrated by condition A, digress significantly from the predictions. The predicted values for condition C, 170°C and pH 4.5, are so close to the predicted values for G, 155°C and pH 3.0, that the line for condition C is

almost completely covered, but the data from the higher temperature run shows higher deviation from the model prediction due to more degradation of monomers in solution.

The modified H-factor for the predicted values was calculated with the time and temperature data output from Polymath. The predicted and experimental values are then plotted together as a function of modified H-factor in Figure 76. The experimental values align with the predicted values up to approximately 250 modified H-factor before the more severe conditions digress. These two examples of comparisons of predicted extraction of sugars and actual recovery of sugars show that the model can be a useful guide in choosing proper extraction conditions.

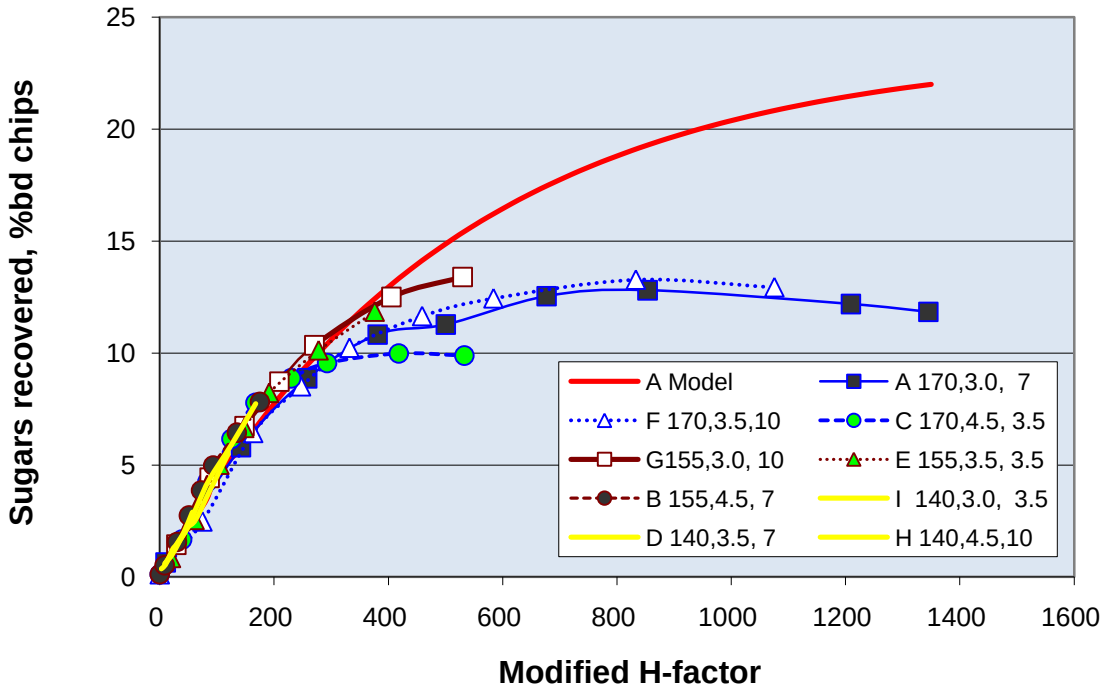


Figure 76 Model predictions and experimental values as a function of modified H-factor (Legend indicates trial label, temperature, reaction pH, and presoak pH).

7.2.2 Validation

The model was tested with data from a prehydrolysis run that was performed with the pH meter installed but without pH adjustment. The H-factor for this run was recalculated using the modified H-factor parameters of 27 kcal/mole activation energy, pH exponent of 0.31, and a correction factor of 23.5. The pH and temperature were recorded on approximately five minute intervals for this test. The temperature for the calculation was estimated from the digester temperature since the second temperature probe had not been installed at the time of the test. The pH started at 5.3 and gradually dropped to 3.67 at the end of the test after one hour at the temperature target of 170°C. The pH was 4.24 at the end of the temperature ramp. Samples of the prehydrolyzate liquor were taken on fifteen minute intervals beginning with the end of the temperature ramp. The degradation products furfural and hydroxymethylfurfural were observed in the chromatograms beginning with the 15 minute and 45 minute samples respectively.

The validation data set, labeled "wtr 51208", is plotted as a function of the modified H-factor along with the nine data sets used to set the parameters in Figure 77. The validation data are slightly offset below the other nine sets, but are only about 10% lower than the other data from tests at 170°C. The chip weight loss was measured after the prehydrolysis extraction. The pulp yield at 30 kappa number was also calculated from four bomb cooks with chips from this run. These two measurements are shown in Figure 70 and Figure 71 with the label "Water". These two points fit right in line with the other data in these plots illustrating good agreement of this run with those used to calibrate the modified H-factor.

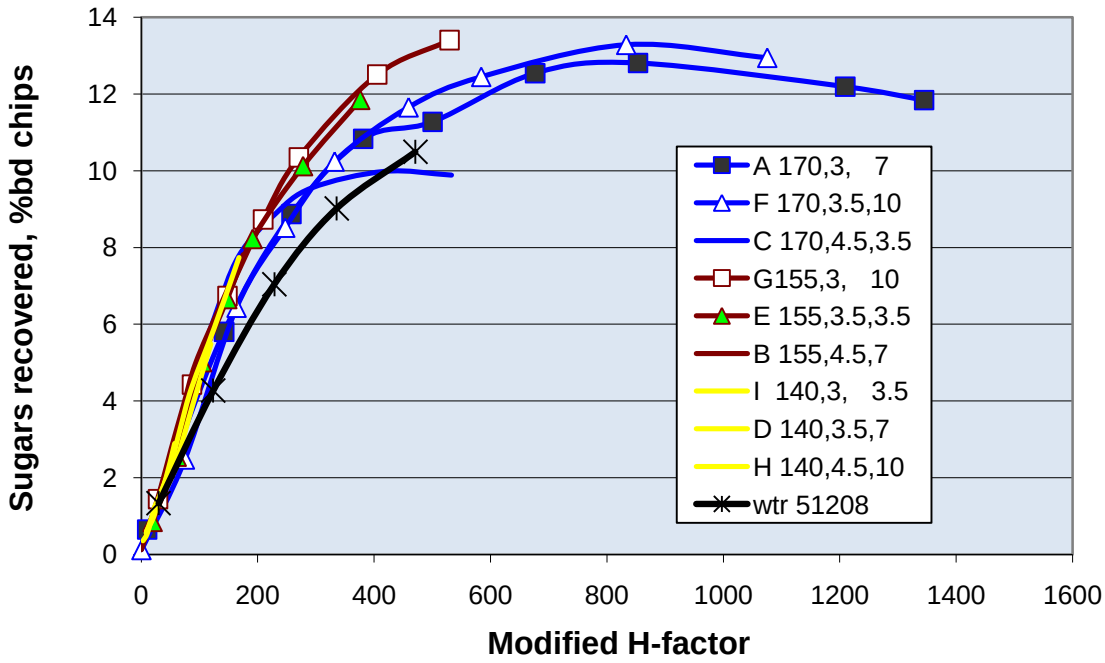


Figure 77 Total recovered sugar as a function of modified H-factor (Legend indicates trial label, temperature, reaction pH, and presoak pH. Data labeled "wtr 51208" is validation data).

7.2.3 Additional Improvements Required

The modified H-factor with pH is a functional tool to compare prehydrolysis runs with different pH and temperature, but it was derived from a small range of pH and temperature. It would be interesting to see how well data from outside these ranges are represented.

Chapter 8 Conclusions and Suggestions for Future Research

This research started with a basic question: What conditions of prehydrolysis extraction of Loblolly pine chips can produce a sufficient quantity of sugars in the prehydrolyzate solution to support production of marketable products including ethanol while continuing to produce high quality bleachable grade kraft pulp? Answering this question, in whole or in part, significantly contributes to the body of chemical engineering knowledge and to the economic welfare of the pulp and paper industry. Extracting the sugar turns out to be relatively simple but a method for performing this extraction without damaging the pulp yield and strength remains to be found. The process of searching for this method produced significant conclusions and elucidated ideas for the direction of future efforts that are discussed in this chapter.

8.1 Conclusions from this Research

Based on the limitations of the experimental data obtained in this research, the following conclusions can be drawn:

The knowledge of prehydrolysis for value-prior-to-pulping of pine chips is extended to include the contribution of solution pH independent of time and temperature.

The pH and temperature of the extraction solution can be used independently or in concert to control the extent of sugar removal and the rate of degradation of monomers in solution.

Five potential yield improvement additives were tested with two that show potential for future development.

A kinetic model of the prehydrolysis was developed that accounts for pH and temperature variation in the form:

$$\frac{dC_C}{dt} = k_C C_A^n C_C^\alpha \tag{9}$$

When originally planned, the experiments for this research were intended to be performed in four phases: screening of prehydrolysis conditions, targeting, validation, and comparison. The screening phase included the designed experiment discussed in Chapter 5. Three experimental conditions identified in screening were rerun utilizing a reduced reaction time in an attempt to optimize time, temperature, and pH profiles for prehydrolysis and pulping yields. The validation phase was intended to consist of repeating key conditions from prehydrolysis through pulp washing in an unbroken process to avoid any uncertainty introduced by multiple handling steps and storage of the chips between cooking stages. The final comparison phase then would produce sufficient pulp with a standard kraft cook and the identified optimal multistage cook to produce refining curves and handsheets for strength testing of the pulp.

The process validation and comparison steps were not completed because no condition was identified in the screening or targeting phases that produced pulp at an acceptable yield. Experiments with chemical additives that might help recover this lost yield were substituted for these last two phases. No immediately promising conditions were identified in these experiments, but additional work with anthraquinone and hydroxylamine is justified. A simple kinetic model for sugar extraction was developed based on the results of the screening experiments.

8.1.1 Prehydrolysis Experiments

The designed experiment was intended to show if the selective removal of hemicelluloses can be controlled by manipulation of three prehydrolysis variables: time, temperature, and pH. The sugar extraction rate for all sugars was increased with either increasing temperature from 140 to 170°C or decreasing pH from 4.5 to 3.0. The hydrolysis was selective for hemicellulose as opposed to cellulose by using temperature at 140°C or pH at 4.5 for reaction at 155°C. The maximum in extraction yield at pH 3.5 that was observed in previous work (Yoon, MacEwan and van Heiningen 2006) was a function of total severity integrating time, temperature, and pH rather than a function of pH alone.

Both pH and temperature were found to have a significant impact on degradation of sugars in solution. Degradation products were not observed in the chromatograms of samples taken at 140°C, but they were observed in all tests at 170°C. For the tests at 155°C, only very small amounts of furfural were observed after one hour at pH 4.5 but significant quantities of both furfural and hydroxymethylfurfural appeared at pH 3.0. Sodium hydroxide was used for pH control in the preliminary work at 170°C and significantly degraded sugars in solution. Sodium carbonate was thus chosen as the agent for increasing pH in the designed experiment and did not appear to increase degradation between 140 and 170°C.

A presoak period at room temperature with various pH levels was also tested with very little effect. It is likely that the conditions of the presoak were too mild. The low pH presoak was expected to accelerate extraction. Either the experimental pH was not low enough or the temperature not high enough to enhance extraction. The high pH

presoak was intended to stabilize the galactoglucomannan toward subsequent acid hydrolysis. The curves for mannose shown in Figure 69 that represent presoak at high pH do not differ from the others in any greater way than in the figures representing other sugars as a function of the modified H-factor. A literature reference found after the experiments were completed suggests that the degree of stabilization can be measured by the amount of acetyl removed (Ingruber, Kocurek and Wong 1985, 36). A reference has not yet been found describing the recommended process conditions for this pretreatment.

8.1.2 Yield Improvement

Chemical pulping additives have been demonstrated to be successful in substantial yield recovery in other work performed in this lab at Auburn University (Yoon 2009), but none of the five additives tested in this research were successful in recovering yield close to a standard kraft cook with the conditions tested thus far. More work could be justified with hydroxylamine or possibly to test the use of anthraquinone in conjunction with hydroxylamine or another successful additive. No further work is recommended with acetaldehyde, ethanolamine, or lithium aluminium hydride.

8.1.3 Modeling Results

The H-factor was used as the basis for the development of a pseudokinetic model of prehydrolysis. The model was developed from sugar concentration data taken from nine prehydrolysis tests at three levels each of pH and temperature. The modified H-factor was calculated using a lower activation energy than that used for kraft pulping, 27 kcal/mole, and was multiplied by the calculated acid concentration raised to the 0.31 power. This modified H-factor was able to represent all of the data from the nine runs on a single curve except when significant degradation of sugars in solution was observed.

The data for wood chip weight loss and pulp yield from all nine runs and a validation set fit a smooth curve in proportion to the error in the measurement when plotted against the modified H-factor. This model is helpful in choosing prehydrolysis process conditions to minimize degradation of sugars and to minimize kappa number after kraft cooking.

8.2 Suggestions for Further Investigation

This section includes ideas that have not yet been researched and ideas that have been more thoroughly looked into. Included are ideas that were thought of early in this research and others that were added as the report was written. The ideas are divided into the three general areas of work presented in this report.

8.2.1 Prehydrolysis Variables

Additional experiments would further define pH and temperature relationships in multiple stage treatment of chips. Potential experiments include an extension of the presoak used in the designed experiment to true multistage tests with higher temperature and higher and lower pH conditions in presoak and wash stages. These tests would attempt to change the relationship between sugar extraction and pulp yield.

Analysis of carbohydrates in the spent liquor from a batch cook with continuous liquor flow at low alkali concentrations revealed that carbohydrate dissolution begins almost immediately and that 20% is lost before any significant lignin is removed (Courchene 1998). A mild alkaline treatment has also been applied for extraction of hemicellulose from aspen wood chips prior to pulping. The yield of sugar in the extract was low, but the pulp yield was unaffected by the treatment (Al-Dajani and Tschirner 2008). This may indicate that a mildly alkaline wash at moderate temperature after a

mild prehydrolysis could increase the yield of recovered sugars in the hydrolyzate while limiting the negative effect of prehydrolysis on pulp yield.

An example of this approach would be an acetic acid prehydrolysis to a modified H-factor of 100 followed by an alkaline soak with green liquor at 90°C before conventional kraft pulping. This should increase sugar yield while improving pulp yield and other properties.

Three of the tests following the designed experiment were intended to target a selected range of sugar extraction (8-10%) to compare pulp yield at similar sugar recovery or similar weight loss. The modified H-factor should make it easier to reach the target sugar level with different prehydrolysis conditions.

One of the potential problems with VPP extraction is degradation of the released sugars at the more severe conditions of high temperature and either low or high pH. One possible method of reducing this effect would be to perform a counter-current extraction wherein cold (<100°C) chips are fed to one end of a continuous reactor while liquor at a higher temperature and low pH is fed to the other end. In this manner, the chips would gradually rise to process temperature across the reactor as the hydrolyzate is cooled while flowing the opposite direction. Evaluation of this process could be performed using a series of small batch reactors with one continuous flow of liquid between them.

It would be interesting to find out what chemical difference contributes to strength loss of prehydrolyzed pulp relative to standard kraft pulp and what effect modification of prehydrolysis conditions has on strength. A study of the effects of different types of alkaline carbohydrate degradation in holocellulose showed that pulp variables like yield and viscosity do not always predict pulp strength (Agarwal and Gustafson 1995). The

authors wrote that dissolution, peeling, and chain scission should be tracked separately to accurately predict effects on pulp properties. Direct dissolution of hemicellulose reduces pulp yield significantly and depends on alkali concentration. This has the general effect of increasing viscosity because shorter chains are removed but decreasing strength. Primary peeling has a minimal effect on viscosity because longer chains are reduced slightly in length but shorter chains can be completely dissolved. Chain cleavage followed by secondary peeling has a smaller effect on yield, but decreases both viscosity and fiber strength. The prehydrolysis stage adds another group of reactions that change the nature of the chips before pulping. In addition to pulp yield and the strength properties of tensile, tear, zero-span tensile, and burst, the prehydrolysis could change bulk, porosity, refining energy requirement, bleachability, and pulp softness. These other properties should also be tested when a method of maintaining yield with VPP of pine chips is found.

References disagree about the effect of direct steam for heating the chips for prehydrolysis (Rydholm 1985, 665) (Richter 1956, 199). Potential advantages would be fast heat up, easy control of reaction temperature, and a high liquor-to wood ratio leading to more concentrated sugars in the extract. Disadvantages of using steam alone include potential nonuniformity of treatment including local pH differences that can lead to lignin condensation and difficulty bleaching.

8.2.2 Additional Yield Improvement Research

The alkali charge used for the kraft cooks should be optimized to a residual target to minimize yield loss due to excess alkali. The alkali requirement should be lower than

that for a conventional cook since much of the alkali in a conventional cook is consumed by degradation products of hemicelluloses.

The acid prehydrolysis likely increased the number of reducing end groups available to alkaline peeling. Reagents that function to stop peeling should also be more reactive. It may be a question of finding the right conditions for reagents that we are already familiar with. For example, AQ functions catalytically to preserve carbohydrates by oxidizing the reducing end groups, but the yield improvement observed from application of AQ in this research was modest while acceleration of delignification was pronounced. A possible method to apply the AQ under conditions that are more conducive to reaction with carbohydrates would be to supply a secondary oxidizing agent like oxygen to regenerate the AQ. After the AQ gets a head start with the damaged carbohydrates, the conditions could be shifted to those of a more conventional kraft cook. The AQ could then function to protect any new reducing end groups formed by the conditions of kraft cooking.

More work with hydroxylamine could identify the proper pH and temperature to optimize prevention of peeling by selective reaction with the reducing end groups of the polysaccharides. This process would probably require the successive steps of producing an oxime that degrades to a nitrile to stabilize the end group. One possible test would be to add hydroxylamine to the prehydrolysis extraction for the first step.

Other additives that showed promise in literature were cyanide (A. R. Procter 1975) and ammonium hydrosulfide (Cho, Chiang and Sarkanen 1986). Each of these additives would have handling concerns and would require modification to the chemical recovery systems.

Hydrogen gas was suggested as a possible supplement to polysulfide addition or as a reducing agent on its own under the proper conditions.

8.2.3 Model Enhancement

As discussed earlier, the model presented in this research is a simple and practical way of combining pH, temperature, and time effects into one parameter for comparing the effects of different levels of these variables on sugar release during extraction, chip weight loss, and pulp yield after kraft cooking of the prehydrolyzed chips. However, the model has limitations:

The model has only been tested within the range of variables used for its development: pH from 3.0 to 4.5, temperature from 140° to 170°C, and up to two hours at the temperature target.

The model does not account for degradation of sugars in the hydrolyzate.

The model does not infer what changes have occurred within the chip due to the prehydrolysis.

The model does not explicitly account for heat or mass transfer.

The proven range of the current model can be expanded by additional tests similar to the nine in the design study. Some of the tests that only reached low modified H-factor levels at their conclusion could be repeated for longer times. Additional testing could be performed at lower temperature and pH targets to expand these ranges. Neither higher temperature nor higher pH (while remaining in the acid range) appear to be fruitful areas of additional research at this time in a single stage extraction due to increased degradation at higher temperature and longer reaction time required at higher pH.

Removing the other limitations listed above will require a more complicated model and additional measurements. Degradation of sugars can be accounted for by adding a second reaction rate equation to the model. The second equation could be similar to the one used to develop the modified H-factor, but instead of depending on the concentration of hemicellulose it would depend on the concentration of sugar monomers in solution. This would require a new dataset that included measurement of monomers in the hydrolyzate samples before the secondary hydrolysis that is performed as part of the analysis. Measurement of degradation products like furfural, hydroxymethylfurfural, levulinic acid, and formic acid may also help with the development.

Inference of chemical changes within the chip could be made with information about the extent of removal of monomers and oligomers from the native wood polysaccharides. The difficult part comes in determining the damage that is done to the polymers that remain in the chips. The prehydrolysis treatment releases sugars to the liquor that were measured as monomers after secondary hydrolysis. The oligomers in solution can also be characterized by composition and molecular weight measurements. It may be possible to measure the composition of different size fractions. The appearance of different oligomers and monomers would then be used to estimate rate parameters for the various hydrolysis reactions involved and estimate the effect on polymers that are not removed. The information about the modified wood chip would then be fed to another module that would model the kraft pulping portion of the process. The output of the pulping model would be a chemical description of the pulp including composition and degree of polymerization of the polysaccharides that remain.

An approach similar to this has been used to model the autohydrolysis of xylan hemicelluloses found in corncobs (Nabarlatz, Farriol and Montane 2004). The corncob xylan model considered xylan hydrolysis to oligomers that entered solution and were then hydrolyzed to monomers that were subject to potential degradation reactions. The kinetic rate parameters for all of the reactions were fit with an optimization package using solution composition data. This effort was simpler than the one that would be required for pine chips since only arabinoxylan was involved. The model for pine would include two types of galactoglucomannan, arabinoglucuronoxylan, arabinogalactan, and cellulose.

Transport processes were an important consideration in several older models of pulping (Grace 1989, 62-68) and have been readdressed more recently (Simao, et al. 2008), (Dang and Nguyen 2008). Heat transport on a chip scale is likely not an important consideration in this process for the temperature and time ranges considered thus far. Without any calculations, consider an ice cube dropped into hot water. A typical ice cube is roughly twice as thick as the largest screened chip and requires the latent heat of the phase change in addition to sensible heat to melt and yet does so quickly relative to the one hour given for heating the system to temperature in the experiments for this research.

In contrast, mass transfer considerations must be included in the development of an accurate model of a heterogeneous reaction system like pulping. An example of why this is necessary is a recent study that showed that proper accounting for mass transfer of alkali into wet chips must include not only diffusion inside the chips but also consideration of the film between the free liquor and the chip (Simao, et al. 2008). This study used measurements of alkali concentration in free liquor and the liquor entrapped in

the chip to develop a lumped parameter model. Another experimental approach to separate mass transfer and kinetic effects was to cook very thin chips and standard chips under the same conditions with the assumption that mass transfer effects in the cooks of thin chips would be minimal (Agarwal and Gustafson 1997). Mass transfer of reaction products out of the chips is not a concern in modeling pulping since the chips are subject to further physical treatment and washing after digestion, but it is a consideration in VPP since the product consists of only the sugars that are removed from the intact chips before pulping. An example of this concern is the maximum molecular weight observed in prehydrolysis extract oligomers of 3100 (Casebier 1969). Experimental methods of determining mass transfer effects might be to use small chips to have more "pure" kinetic information or to isolate mass transfer effects by performing composition analysis on segments of chips that have undergone prehydrolysis.

8.2.4 Improvements to Testing or Experimental Procedures

Several areas were identified over the course of the experiments that should be investigated to improved precision or accuracy of the data that is produced:

Several different methods of cooking have been utilized in the lab at Auburn University to treat chips and produce pulp for this research and another similar project. Compare variability associated with multiple digester cooks to the use of bomb cooks for multiple cooks from the same set of chips or for a small set of chips through multiple stages of processing.

Measure and reduce run-to-run variability on the HPLC. Improve measurement of arabinose and mannose on the HPLC. Dilution of the samples may help separate the peaks.

Lignin concentration was not measured in most of the liquid samples. Methods for measuring both acid soluble lignin and acid insoluble lignin in these samples should be tested to help complete the material balance on the weight loss that is not accounted for in the sugar composition measurements.

Improve chip weight loss measurement. The problems here appear to be associated with moisture measurement. A larger sample may be required to be representative of the cook. Variability in pulp yield from bomb cooks may be in part caused by measurement of the wet chips.

Concentrations of acetyl and uronic acids were not measured in this research. The extraction rates of acetyl and glucuronic acids relative to other components of the hemicellulose could be instructive in understanding the behavior of the hemicelluloses. Removal of acetyl groups from glucomannan is said to stabilize this polymer to acid attack. Glucuronic acid is considered to be resistant to acid hydrolysis (Sjostrom 1993, 45) and the rate of xylan hydrolysis has been correlated to the ratio of uronic acid to xylan (A. H. Conner 1984). This resistance may contribute to slow xylose removal in acid but fast further degradation in alkali. The lab at Auburn University does test for acetic acid in liquid solutions, but this was not tested in this research since acetic acid was added to the solutions for pH control in most experiments. This lab does not currently have a test for glucuronic acid. Two methods were referred to in literature (A. H. Conner 1984).

8.3 Final Comments

This quest has not found exactly what it was looking for: A simple set of industrially relevant process conditions for extracting VPP from Loblolly pine chips in a

modern kraft pulp mill without significantly reducing the yield or quality of the pulp. The quest has improved the scientific understanding of the impact of pH and temperature over time on the extraction of sugars from pine chips, the degradation of those sugars in solution, and the reduction in yield after kraft pulping. This knowledge will aid future efforts toward developing an economically practical method for implementation of VPP.

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Appendix 1 Minitab 15 Statistical Results

General Linear Model: Max Sugar, Final, ... versus pH, Temp, ...

Factor	Type	Levels	Values
pH	fixed	3	0, 1, 2
Temp	fixed	3	0, 1, 2
Soak	fixed	3	0, 1, 2

Analysis of Variance for Max Sugar, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	2	31.673	31.673	15.837	83.00	0.012
Temp	2	77.196	77.196	38.598	202.28	0.005
Soak	2	2.653	2.653	1.326	6.95	0.126
Error	2	0.382	0.382	0.191		
Total	8	111.903				

S = 0.436819 R-Sq = 99.66% R-Sq(adj) = 98.64%

Analysis of Variance for Final, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	2	28.251	28.251	14.125	29.55	0.033
Temp	2	70.441	70.441	35.220	73.68	0.013
Soak	2	3.940	3.940	1.970	4.12	0.195
Error	2	0.956	0.956	0.478		
Total	8	103.587				

S = 0.691408 R-Sq = 99.08% R-Sq(adj) = 96.31%

Analysis of Variance for 45min, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	2	15.111	15.111	7.556	200.24	0.005
Temp	2	115.151	115.151	57.576	1525.86	0.001
Soak	2	1.346	1.346	0.673	17.83	0.053
Error	2	0.075	0.075	0.038		
Total	8	131.684				

S = 0.194251 R-Sq = 99.94% R-Sq(adj) = 99.77%

Analysis of Variance for Wt loss%, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	2	96.816	96.816	48.408	10.98	0.083
Temp	2	339.616	339.616	169.808	38.52	0.025
Soak	2	4.616	4.616	2.308	0.52	0.656
Error	2	8.816	8.816	4.408		
Total	8	449.862				

S = 2.09947 R-Sq = 98.04% R-Sq(adj) = 92.16%

Analysis of Variance for 30k Yield, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	2	31.307	31.307	15.653	70.32	0.014
Temp	2	75.977	75.977	37.989	170.66	0.006
Soak	2	0.577	0.577	0.288	1.29	0.436
Error	2	0.445	0.445	0.223		
Total	8	108.305				

S = 0.471809 R-Sq = 99.59% R-Sq(adj) = 98.36%

Analysis of Variance for Yield Loss, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	2	31.307	31.307	15.653	70.32	0.014
Temp	2	75.977	75.977	37.989	170.66	0.006
Soak	2	0.577	0.577	0.288	1.29	0.436
Error	2	0.445	0.445	0.223		
Total	8	108.305				

S = 0.471809 R-Sq = 99.59% R-Sq(adj) = 98.36%

Analysis of Variance for %Rec/%Yloss, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	2	0.013902	0.013902	0.006951	48.84	0.020
Temp	2	0.175915	0.175915	0.087957	617.97	0.002
Soak	2	0.049565	0.049565	0.024782	174.11	0.006
Error	2	0.000285	0.000285	0.000142		
Total	8	0.239666				

S = 0.0119304 R-Sq = 99.88% R-Sq(adj) = 99.52%

Analysis of Variance for H factor to 30, using Adjusted SS for Tests

Source	DF	Seq SS	Adj SS	Adj MS	F	P
pH	2	598822	598822	299411	2.47	0.288
Temp	2	1633089	1633089	816544	6.74	0.129
Soak	2	299089	299089	149544	1.23	0.448
Error	2	242422	242422	121211		
Total	8	2773422				

S = 348.154 R-Sq = 91.26% R-Sq(adj) = 65.04%

Appendix 2 Non-Standard Test Methods

A2.1 ABC Liquor test

A Test:

1. pipette 5 ml clear liquor to 250 ml erlenmeyer
2. Add 50 ml water
3. Add 25 ml 10% $BaCl_2$
4. Add phenolphthalein (thymol phthalein)
5. Titrate with 0.5 N HCl until pink(blue) disappears
6. Record A, do not refill buret

B Test:

1. Add 5 ml 40% formaldehyde
2. wait 30 seconds
3. Titrate with 0.5 N HCl until pink(blue) disappears
4. Record B, do not refill buret

C Test:

1. Add methyl orange
2. Titrate with 0.5 N HCl until red first appears
3. Record C

Calculations:

$Na_2S = 6.4*0.5/0.5167*(B-A)$

$NaOH = 3.2*0.5/0.5167*(2*A-B)$

$Na_2CO_3 = 3.2*0.5/0.5167*(C-B)$

$Sulfidity\% = Na_2S/(Na_2S + NaOH)$

$TTA = Na_2S + NaOH + Na_2CO_3$

$AA = Na_2S + NaOH$

$EA = NaOH + Na_2S/2$

A2.2 Black Liquor Residual Alkali Test

1. Pipette 10ml Black Liquor into 90ml DI water
2. Titrate with 0.5 N HCl to pH 11.3
3. Record Volume, V

EA Residual, g/l = N*V*31/10

EA Residual, g = (N*V*31/10)*Volume of liquor charged,l

EA Residual, %on wood = EA Residual, g/ Chip Mass, g

REA 2, g/l =31*((0.95*V/10)-0.012)*N

REA 2 %on wood = REA 2, g/l * Volume of liquor charged ,l / Chip Mass, g

Appendix 3 Cook Worksheets and Calculations

The cook worksheets were used to record data during the cook and also to make calculations with this data. A summary listing of all the worksheets and four examples of cook worksheets are included in this document. The worksheets are each different depending on what was actually done in the cook. The simplest worksheets like "A4" contain only limited information about the time/temperature profiles after the cook plan. Later worksheets like "A9" have more detailed temperature and pH listings with calculations of H-factor. The red numbers on the cook plan pages are calculated values.

The worksheets were modified somewhat to improve the view for printing. Each worksheet starts with the prehydrolysis followed by the kraft cook data. The listings of pH and temperature then follow with recalculations of this data to improve the H-factor and modified H-factor integrations as illustrated in "A19". Kraft cooks like "A27" do not have prehydrolysis data. When the kraft cook was performed in bombs, each was detailed separately. When chips from separate prehydrolysis runs were cooked together in bombs, the bomb cook data was only listed in one worksheet and the other worksheets refer to this location.

Copies of all the cook worksheets are in the pulp and paper lab (presently Wilmore 156) and are retained by the author.

Ref	Date	Cook	Objective	Notes
	10/03/07	1003	Prehydrolysis test	Temp control high overshoot
A1	10/10/07	1010	2 hr Prehydrolysis test	good T control
A2	10/17/07	1017	30 minutes preH at 170	
A3	10/23/07	1023	kraft cook	control profile manual errors
A4	10/24/07	1024	30 minutes preH at 170	replicate
A5	11/05/07	1105	kraft cook	
A6	11/07/07	1107	2 hr Prehydrolysis cook	
A7	12/15/07	1215	2 hr Prehydrolysis cook	target 30 kappa
A8	02/28/08	22808	preH cook to test pH mods	
A9	03/06/08	0.1%NaOH	preH pH 5	0.2N NaOH pH control
A10	03/25/08	0.3%NaOH	test initial NaOH charge	0.5N NaOH pH control
A11	03/27/08	3% Acetic	initial Acetic charge	0.5N NaOH pH control
	04/04/08	BombCook1	target 30 kappa	
	04/08/08	BC2	Chips from 3/06,25,27/08	
	04/11/08	BC3		
	05/08/08	BC4		
A12	05/12/08	51208	Water preH to 1400H factor	leaking at pH probe
A13	05/16/08	51608	0.1% NaOH for 1 hour at pH5	
A14	05/17/08	51708	3% acetic for 30minutes	started NaOH after 15 minutes
	05/19/08	BC1a	target 30 kappa	
	05/22/08	BC2a	Chips from 5/12,16,17/08	
	06/28/08	BC3a		
	07/12/08	BC4a		
A15	05/23/09	BK1	Bomb Kraft Cook 1	uncooked in each, Bomb 4 leak
A16	05/25/09	PreH A	pH 3.0, 170, pH 7 presoak	ramp long, flow problems
A17	05/26/09	PreH A2		ramp long, cook time short
A18	05/27/09	PreH B	4.5, 155, 7	ramp long, cook time short
A19	05/28/09	PreH C	4.5, 170, 3.5	ramp extended to one hour
A20	05/29/09	BK2		
A21	06/01/09	PreH D	3.5, 140, 7	
A22	06/02/09	PreH E	3.5, 155, 3.5	
A23	06/03/09	PreH F	3.5, 170, 10.5	
A24	06/08/09	PreH G	3.0, 155, 10.6	
A25	06/09/09	PreH H	4.5, 140, 10.6	
A26	06/10/09	PreH I	3.0, 140, 3.5	
A27	06/11/09	BK3		
A28	06/19/09	BK4		
A29	06/20/09	BK5		
	06/24/09	BC D1F1G1	Stand conds for Kappa30	Random Order
	06/25/09	BC A1B1C1		
		BC E1H1I1		
	06/26/09	BC CFG2	Stand cond w/ AQ	Random Order
	06/29/09	BC BDH2		
		BC AEI2		
A30	07/01/09	BK6		
	07/02/09	BC BD3		
	07/03/09	BC EI3		
	07/04/09	BC CGH3		
	07/05/09	BC AF3		
A31	07/06/09	BK7	Low kappa cook	
A32	07/07/09	BK8	"standard" cook test	
	07/18/09	BC CEG4		
	07/19/09	BC A4A5		

	07/20/09	BC DF4	
		BC BE5	
	07/21/09	BC HI4	
		BC CDG5	
	07/23/09	BC HI5	
		BC B4F5	
A33	08/05/09	PreH J	lower pH presoak
A34	08/06/09	PreH K	
A35	08/07/09	PreH L	Step down T from 170 to 155
	08/11/09	BC JKL1	
	08/12/09	BC JKL2	
	08/20/09	BC JKL3	
	08/21/09	BC JKL5	
	09/10/09	BC JKL4	
A36	09/22/09	PreH M	3.5, 155 no soak, 1hr at T
A37	09/23/09	PreH N	3.0, 155, no S, 45min at T
A38	09/24/09	PreH O	3.5, 170, 20min at T
	09/25/09	BC MNO1	Stand conds for Kappa30
		BC MNO2	Higher Kappa
	09/28/09	BC MNO3	
	10/06/09	BC MNO4	
A39	10/12/09	PreH P	
	10/15/09	BC P123	Ethanolamine
	10/16/09	BC P456	
	10/23/09	BC P789	
A40	10/26/09	PreH Q	
A41	10/30/09	PreH R	
	11/04/09	BC Q123	Hydroxylamine
	11/06/09	BC Q456	
	11/11/09	BC Q789	
	11/12/09	BC R123	LiAlH4
A42	11/13/09	PreH S	
	11/14/09	BC S123	Acetaldehyde
	11/18/09	BC Q10 R45	
	11/20/09	BC R6 Q1112	
	11/23/09	BC P10 S45	
	11/24/09	BC MNO5	
	11/25/09	BC S101112	Standard Cook
	11/29/09	BC S789	

Prehydrolysis Cook Plan

10/24/07

Time	Activity	Data	Calc				
PreH	Clean Digester, drain, close valve		302.52	g AD Chips	250	g BD Chips to Cook	
	Measure mass of chips, put in basket, g	302.67	24.76		91.82	%Chip Moisture	
	measure volume of water added to just cover chips, ml	1670	277.912	BD Chips	10	%preH Chip Sample	
	Add volume for samples	150	1844.76	total water			
831	Start Pump, start Profile 22		6.64	preH wtr/wood			
	Close lid, leave vent cracked open				Profile 22	Prehydrolysis	
	Close vent at 100°C target				Asurd Soak	Off	
856	Open vent briefly at 100°C measurement				Controls	Active	
	Open vent briefly at 105°C measurement				Time Seg	0:00:00	300
	Sample liquid at appropriate times	150			Time Seg	0:44:20	1680
	Manually help controller at end of ramp				Controls	Off	
Turnaround					Delay	0:00:10	
946	Vent digester at end of prehydrolysis				Controls	Active	
	open drain, blow through ice water, Collect hydrolyzate				Time Seg	0:00:30	1700
	turn pump off				Time Seg	0:30:00	1700
	Purge coils with short pulse of air pressure				Controls	Off	
	Measure volume of hydrolyzate	1310			End of	Profile	
	Verify all pressure released		384.76	water in chips			
	Open lid				Profile 1	Wash	
	Close drain valve				Controls	Active	
	Add measured volume of wash water to digester	1560			Time Seg	0:00:00	770
	turn pump on				Time Seg	0:05:00	1050
	close lid, close vent				Time Seg	0:05:00	1050
1001	run wash Profile 1				Controls	Off	
	open drain valve to blow through ice water				End of	Profile	
	Measure volume of wash	1320	624.76	water in chips			
	Verify all pressure released						
	Remove chip basket					White Liquor	
	Dump chips into plastic beaker					10/02/07	test date
	Weigh total chips	685.5	902.67	est	WL		Sample
	Remove chip sample by weight	68.55				2	Volume,l
	Return remaining chips to basket	616.95			ml 0.5N HCl		
	Return basket to digester		20	%AA		26.30	A
	Close drain valve		50	AA g		29.7	B
	Add measured volume of white liquor to digester	544	544	liq Vol ml		30.5	C
	measure volume of water added to just cover chips	1025	366.95	water in chips			
	Start pump		1935.95	total water	gpl Na2O		
			7.74	Cook liq/wood		21.1	Na2S
Cook	Start Cook profile 23					70.9	NaOH
1026	Close lid					2.5	Na2CO3
	Vent digester at 100°					22.90%	Sulf%
	Vent digester at 105°					94.4	TTA
1115	Manually adjust controller at end of ramp	171				92.0	AA
1348	Vent digester at end of cook					81.4	EA
	open drain, blow through ice water, Collect black liquor						
	turn pump off						
	Purge coils with short pulse of air pressure						
	Measure volume of black liquor	1510			Profile 23	Kraft Cook	
	Verify all pressure released				Controls	Active	
	Open lid				Time Seg	0:00:00	600
	add two liters of water				Time Seg	0:46:20	1680
	circulate				Controls	Off	
	drain				Delay	0:00:10	
	Remove chip basket		100.05	AD Pulp	Controls	Active	
30	Dump chips into wash bag, wash well		93.64	%Pulp Dry	Time Seg	0:00:30	1700
	Defibrate pulp in blender		93.69	BD Pulp	Time Seg	2:30:00	1700
45	Squeeze dry		37.46	%Yield	Controls	Off	
	homogenize in mixer, spread to dry		28.5	Kappa	End of	Profile	

	Time	Minutes	Dig Temp2	kr	avg	H Factor
	1026	0	60	0.01	-	-
	1042	16	100	1.02	0.51	0.1
Max T reduced 2° for temp offset	1113	47	168	792.35	396.69	205.1
	1348	197	168	792.35	792.35	2,186.0
	1353	202	168	792.35	792.35	2,252.0
	1358	207	59.9	0.01	396.18	2,285.0
	1363	212	59.9	0.01	0.01	2,285.0

Prehydrolysis with bomb Cook Plan — 3/6/08 "0.1% NaOH"

Time	Activity	Data	Calc				
PreH	Clean Digester, drain, close valve		363.03	g AD targ	300	g BD Chips to Cook	
	Measure mass of chips, put in basket, g	363.05	29.70		91.82	%Chip dry matter	
	measure volume of water added to just cover chips, r	2300	333.353	BD Chips	10	%preH Chip Sample	
	Add volume for samples(50ml 0.2N NaOH)	150	3362.70	total water		0.1% NaOH	
1001	Start Pump, start Profile 22		10.09	preH wtr/wood			
	Close lid, leave vent cracked open				Profile 22	Prehydrolysis	
1023	Close vent at 100°C target				Asurd Soa	Off	
1025	Open vent briefly at 100°C measurement				Controls	Active	
1029	Open vent briefly at 105°C measurement				Time Seg	0:00:00	300
	Sample liquid at appropriate times	186			Time Seg	0:44:20	1680
824	Manually help controller at end of ramp				Controls	Off	
Turnaround					Delay	0:00:10	
1308	Vent digester at end of prehydrolysis	no			Controls	Active	
3	open drain, blow through ice water, Collect hydrolyzate				Time Seg	0:00:30	1700
	turn pump off				Time Seg	2:00:00	1700
	Purge coils with short pulse of air pressure	883			Controls	Off	
	Measure volume of hydrolyzate, NaOH used	2640			End of	Profile	
	Verify all pressure released		536.70	water in chips			
10	Open lid				Profile 1	Wash	
	Close drain valve				Controls	Active	
	Add measured volume of wash water to digester	3000			Time Seg	0:00:00	250
	turn pump on				Time Seg	0:05:00	250
	close lid, close vent				Time Seg	0:05:00	250
1350	run wash Profile 1				Controls	Off	
1400	open drain valve to blow through ice water				End of	Profile	
	Measure volume of wash	2900	636.70	water in chips			
30	Verify all pressure released						
	Remove chip basket						
	Dump chips into plastic beaker				preH chips		
	Weigh total chips	899.67	970.05	est w	30.23		
	BD preH chips	275.29	17.4%	loss d	9.25		
	wet chips remaining	869.44		dry frac	0.305987		
	BD preH chips remaining	266.0					
Bomb	Cook 1	4	70	BD Chips	White Lqr	4/2/08	test date
	measure wet chips needed	228.84	228.77	target l	0.5N HCl	29.20	A
42	Add measured volume of white liquor to bomb	132	20	%AA g	14	34.2	B
	Add volume of water to reach 5.8 l/w	115	132	liq Vol ml		34.4	C
	Seal bombs and shake well		158.818	water in chip	gpl Na2O	31.0	Na2S
Cook	place bombs and water in Digester		405.818	total water		74.9	NaOH
	Start pump	2:38	5.80	Cook liq/wood		0.6	Na2CO3
1004	Start Cook profile 23					29.24%	Sulf%
	Close lid	171				106.5	TTA
1042	Manually adjust controller at end of ramp					105.9	AA
1342	Vent digester at end of cook and run cooling coil	640.39	640.6	wet chips remain		90.4	EA
	Verify all pressure released				Profile 23	Kraft Cook	
1402	Open lid				Controls	Active	
30	drain				Time Seg	0:00:00	300
1422	Cool bombs in water before opening				Time Seg	0:59:20	1690
	Take sample of black liquor		34.13	AD Pulp	Controls	Off	
45	Dump chips into wash bag, wash well		92.619	%Pulp Dry	Delay	0:00:10	
1625	Defibrate pulp in blender		31.61	BD Pulp	Controls	Active	
	Squeeze dry		37.28	%Yield	Time Seg	0:00:30	1710
	homogenize in mixer, spread to dry		41.3	Kappa	Time Seg	2:38:00	1710
					Controls	Off	
					End of	Profile	
Bomb	Cook 2	6	70	BD Chips	White Lqr	4/2/08	test date
	measure wet chips needed	228.76	228.77	target l	0.5N HCl	29.20	A
42	Add measured volume of white liquor to bomb	139	21	%AA g	14.7	34.2	B
	Add volume of water to reach 5.8 l/w	171	139	liq Vol ml		34.4	C
	Seal bombs and shake well		158.762	wtr in chips	gpl Na2O	31.0	Na2S
Cook	place bombs and water in Digester		468.762	total water		74.9	NaOH
	Start pump	2:38	6.70	Cook liq/wood		0.6	Na2CO3
940	Start Cook profile 23					29.24%	Sulf%
	Close lid	172				106.5	TTA
1104	Manually adjust controller at end of ramp					105.9	AA
1318	Vent digester at end of cook and run cooling coil	411.52	411.84	wet chips remain		90.4	EA
	Verify all pressure released		125.92	BD Chips	Profile 23	Kraft Cook	
1402	Open lid				Controls	Active	

30	drain				Time Seg	0:00:00	600	
1422	Cool bombs in water before opening				Time Seg	0:59:20	1700	
	Take sample of black liquor		31.71	AD Pulp	Controls	Off		
45	Dump chips into wash bag, wash well		92.547	%Pulp Dry	Delay	0:00:10		
1625	Defibrate pulp in blender		29.35	BD Pulp	Controls	Active		
	Squeeze dry		34.62	%Yield	Time Seg	0:00:30	1720	
	homogenize in mixer, spread to dry		19.2	Kappa	Time Seg	2:38:00	1720	
					Controls	Off		
					End of	Profile		
Bomb	Cook 3	5	60	BD Chips	White Lqr	4/2/08	test date	
	measure wet chips needed	196.06	196.09	target	l 0.5N HCl	29.20	A	
	Add measured volume of white liquor to bomb	119	21	%AA g	12.6	34.2	B	
	Add volume of water to reach 5.8 l/w	153	119	liq Vol ml		34.4	C	
	Seal bombs and shake well		136.068	wtr in chips	gpl Na2O	31.0	Na2S	
Cook	place bombs and water in Digester		408.068	total water		74.9	NaOH	
	Start pump	2:38	6.80	Cook liq/wood		0.6	Na2CO3	
845	Start Cook profile 23					29.24%	Sulf%	
	Close lid	171				106.5	TTA	
945	Manually adjust controller at end of ramp					105.9	AA	
1223	Vent digester at end of cook and run cooling coil	215.2	215.78	wet chips remain		90.4	EA	
	Verify all pressure released		65.8485	BD Chips	Profile 23	Kraft Cook		
1243	Open lid				Controls	Active		
	drain				Time Seg	0:00:00	300	
1250	Cool bombs in water before opening				Time Seg	0:59:20	1700	
	Take sample of black liquor		28.04	AD Pulp	Controls	Off		
45	Dump chips into wash bag, wash well		95.15	%Pulp Dry	Delay	0:00:10		
1625	Defibrate pulp in blender		26.68	BD Pulp	Controls	Active		
	Squeeze dry		36.73	%Yield	Time Seg	0:00:30	1715	
	homogenize in mixer, spread to dry		25.2	Kappa	Time Seg	2:38:00	1715	
					Controls	Off		
					End of	Profile		

Time	Minutes	Dig Temp2	kr	avg	H Factor
845	0	25	0.0	-	-
945	60	171	1,014.1	507.0	507.0
1153	47	171	1,014.1	1,014.1	287.3
1431	215	171	1,014.1	1,014.1	3,126.7
1436	220	171	1,014.1	1,014.1	3,211.2
1441	225	59.9	0.0	507.0	3,253.4
1446	230	59.9	0.0	0.0	3,253.4

			72.9976	BD Raw Chips				
Bomb	Cook 4	6	60	BD Chips	White Lqr	4/2/08	test date	
	measure wet chips needed	197.01	196.09	target	l 0.5N HCl	29.20	A	
	Add measured volume of white liquor to bomb	138	20	%AA g	14.59953	34.2	B	
	Add volume of water to cover chips	210	138	liq Vol ml		34.4	C	
	Seal bombs and shake well		136.727	wtr in chips	gpl Na2O	31.0	Na2S	
Cook	place bombs and water in Digester		484.727	total water		74.9	NaOH	
	Start pump		8.04	Cook liq/wood		0.6	Na2CO3	
802	Start Cook profile 23	802				29.24%	Sulf%	
	Close lid					106.5	TTA	
906	end of ramp 4 minutes late					105.9	AA	
1130	Vent digester at end of cook and run cooling coil	17.51	18.77	wet chips remain		90.4	EA	
	Verify all pressure released		5.35784	BD Chips	Profile 23	Kraft Cook		
	Open lid				Controls	Active		
	drain				Time Seg	0:00:00	300	
	Cool bombs in water before opening				Time Seg	0:59:20	1700	
	Take sample of black liquor		28.09	AD Pulp	Controls	Off		
	Dump chips into wash bag, wash well		94.19	%Pulp Dry	Delay	0:00:10		
	Defibrate pulp in blender		26.46	BD Pulp	Controls	Active		
	Squeeze dry		36.24	%Yield	Time Seg	0:00:30	1715	
1328	homogenize in mixer, spread to dry		23.2	Kappa	Time Seg	2:28:00	1715	
					Controls	Off		
					End of	Profile		

Time	Minutes	Dig Temp2	kr	avg	H Factor
802	0	25	0.0	-	-
902	60	171.5	1,056.3	528.1	528.1
1130	208	171.5	1,056.3	1,056.3	3,133.6
1135	215	171.5	1,056.3	1,056.3	3,256.9
1140	220	171.5	1,056.3	1,056.3	3,344.9
1145	225	59.9	0.0	528.1	3,388.9
1150	230	59.9	0.0	0.0	3,388.9

	Time	minutes	pH 1	Dig Temp	kr	Avg	H Factor	NaOH Vol	Total Water	Sample
	1001	0	11.16	25.6	0.000	0	0			
	1005	4	10.81	41.3	0.000	0.00	0.00			
	1010	9	10.21	57.6	0.004	0.00	0.00			
	1015	14	9.58	73.1	0.036	0.02	0.00			
	1020	19	8.78	88.5	0.258	0.15	0.01			
	1025	24	7.42	98.4	0.846	0.55	0.06			
	1030	29	6.66	110.4	3.287	2.07	0.23			
	1035	34	6.11	125.4	15.974	9.63	1.03			
	1040	39	5.74	138.6	58.383	37.18	4.13			
	1045	44	5.36	151	183.29	120.84	14.20			
	1050	49	5.05	158.1	342.59	262.94	36.11			
	1055	54	5.04	164.1	572.05	457.32	74.22			
	1100	59	4.81	167.8	779.34	675.69	130.53			
	1105	64	4.81	168.5	825.81	802.57	197.41			
0	1108	67		170	934.35	880.08	241.42			2500
	1110	69	4.88	170.2	949.80	942.08	272.82			
	1115	74	4.94	170.6	981.43	965.62	353.29			
	1120	79	4.97	170.3	957.62	969.53	434.08			
15	1123	82		170.3	957.62	957.62	481.96			2625
	1125	84	4.99	170.3	957.62	957.62	513.88			
	1130	89	4.98	169.9	926.71	942.17	592.40			
	1135	94	5	170.1	942.05	934.38	670.26			
30	1138	97		170	934.35	938.20	717.17			2750
	1140	99	5.02	169.9	926.71	930.53	748.19			
	1145	104	5	170.2	949.80	938.26	826.38			
	1150	109	4.99	170.1	942.05	945.92	905.20			
45	1153	112		170	934.35	938.20	952.11			2875
	1155	114	5.01	170	934.35	934.35	983.26			
	1200	119	5.01	170.2	949.80	942.08	1,061.77			
	1205	124	5.01	169.8	919.14	934.47	1,139.64			
60	1208	127		170	934.35	926.74	1,185.98			3000
	1210	129	5.01	170.2	949.80	942.08	1,217.38			
	1215	134	5.02	170	934.35	942.08	1,295.88			
	1220	139	5	170.1	942.05	938.20	1,374.07			
	1225	144	4.99	170	934.35	938.20	1,452.25			
	1230	149	4.99	170	934.35	934.35	1,530.11			
	1235	154	4.99	170	934.35	934.35	1,607.98			
90	1238	157		170.1	942.05	938.20	1,654.89			3200
	1240	159	4.99	170.2	949.80	945.92	1,686.42			
	1245	164	5	170	934.35	942.08	1,764.92			
	1250	169	5.01	163.7	553.07	743.71	1,826.90			
	1255	174	5.02	167.5	760.19	656.63	1,881.62			
	1300	179	5.01	170.5	973.43	866.81	1,953.85			
	1305	184	4.98	171	1,014.06	993.75	2,036.66			
120	1308	187	5	170	934.35	974.20	2,085.37			3360

Prehydrolysis Cook Plan			A3B3C1	5/28/09	pH4.5	170°C	pH 3.5
Time	Activity	Data	Calc		380	g BD Chips to Cook	
Soak	Measure mass of chips, put in Ziploc, g	460.03	459.84	g AD targ	91.82	%Chip Moisture	
1145	Add Soak Solution	807.169	37.63	wtr in chips	10	%preH Chip Sample	
1300	After Soak pH	4.18	422.40	BD Chips			
PreH	Clean Digester, drain, close valve	30	844.80	Soak Water			
1250	Put wet chips in basket in dig, add weight		2.00	Soak l/w			
1300	measure volume of water added to just cover chips, ı	2600	3601.80	PreH water	0.25%	Acetic Acid	
1302	add acid (ml CH3COOH)	1	8.53	preH wtr/wood			
1304	Add volume for samples	100			Profile 22	Prehydrolysis	
1310	Start Pump, start Profile 22				Asurd Soa	Off	
	Close lid, leave vent cracked open				Controls	Active	
1340	Close vent at 100°C target				Time Seg	0:00:00	300
1342	Open vent briefly at 100°C measurement				Time Seg	1:00:00	1700
804	Open vent briefly at 105°C measurement				Time Seg	2:00:00	1700
	Sample liquid at appropriate times				Controls	Off	
824	Manually help controller at end of ramp				End of	Profile	
Turnaround							
	Vent digester at end of prehydrolysis	no					
	open drain, blow through ice water, Collect hydrolyza	86	pH control vol				
	turn pump off						
	Purge coils with short pulse of air pressure		684.80	water in chips			
	Measure volume of hydrolyzate	2917			Profile 1	Wash	
	Verify all pressure released				Controls	Active	
	Open lid				Time Seg	0:00:00	250
	Close drain valve				Time Seg	0:05:00	250
	Add measured volume of wash water to digester	2770			Time Seg	0:05:00	250
	turn pump on		3455	total wash	Controls	Off	
	close lid, close vent				End of	Profile	
	run wash Profile 1		870.80	wtr in chips			
	open drain valve to blow through ice water						
	Measure volume of wash	2584					
	Verify all pressure released				preH chips		
	Remove chip basket		1293.20	est w	29.99		
	Dump chips into plastic beaker		17.0%	loss d	9.45		
	Weigh total chips	1112.2		dry frac	0.3151		
	BD preH chips	350.444					
	wet chips remaining	1082.16					
	BD preH chips remaining	340.994					

Bomb	Cook 1	6	70	BD Chips	White Lqr	6/25/09	test date
	measure wet chips needed	184.305	222.15	184.30536	ıl 0.5N HCl	26.5	A
	Add measured volume of white liquor to bomb	145	20	%AA g	14	31.2	B
	Add volume of water to reach 5.8 l/w	159	145	liq Vol ml		32	C
900	Seal bombs and shake well		126.23	water in chip	gpl Na2O	29.1	Na2S
Cook	place bombs and water in Digester		430.23	total water		67.5	NaOH
	Start pump		7.41	Cook liq/wood		2.5	Na2CO3
910	Start Cook profile 4					30.13%	Sulf%
	Close lid					99.1	TTA
1104	Manually adjust controller at end of ramp					96.6	AA
1342	Vent digester at end of cook and run cooling coil					82.1	EA
	Verify all pressure released				Profile 4	Kraft Cook	
1402	Open lid				Controls	Active	
30	drain				Time Seg	0:00:00	300
1422	Cool bombs in water before opening				Time Seg	0:59:20	1660
	Take sample of black liquor	13.4	26.55	AD Pulp	Controls	Off	
45	Dump chips into wash bag, wash well		93.54	%Pulp Dry	Delay	0:00:10	
1625	Defibrate pulp in blender		24.83	BD Pulp	Controls	Active	
	Squeeze dry		35.48	%Yield	Time Seg	0:00:30	1680
	homogenize in mixer, spread to dry		27	Kappa	Time Seg	2:50:00	1680
					Controls	Off	
					End of	Profile	

Bomb	Cook 2	4	70	BD Chips	White Lqr	6/25/09	test date	
	measure wet chips needed	184.305	222.15	target	ıl 0.5N HCl	26.5	A	
	Add measured volume of white liquor to bomb	145	20	%AA g	14	31.2	B	
	Add volume of water to reach 5.8 l/w	159	145	liq Vol ml		32	C	
	Seal bombs and shake well		126.23	wtr in chips	gpl Na2O	29.1	Na2S	
Cook	place bombs and water in Digester		430.23	total water		67.5	NaOH	
	Start pump		7.41	Cook liq/wood		2.5	Na2CO3	
940	Start Cook profile 4					30.13%	Sulf%	
	Close lid					99.1	TTA	
1042	Manually adjust controller at end of ramp					96.6	AA	
1318	Vent digester at end of cook and run cooling coil					82.1	EA	
	Verify all pressure released				Profile 4	Kraft Cook		
1402	Open lid				Controls	Active		
30	drain				Time Seg	0:00:00	300	
1422	Cool bombs in water before opening				Time Seg	0:59:20	1660	
	Take sample of black liquor	13.45	26.35	AD Pulp	Controls	Off		
45	Dump chips into wash bag, wash well		93.62	%Pulp Dry	Delay	0:00:10		
1625	Defibrate pulp in blender		24.67	BD Pulp	Controls	Active		
	Squeeze dry		35.24	%Yield	Time Seg	0:00:30	1680	
	homogenize in mixer, spread to dry		18.8	Kappa	Time Seg	2:50:00	1680	
					Controls	Off		
					End of	Profile		

Bomb	Cook 3	4	70	BD Chips	White Lqr	7/3/09	test date	
	measure wet chips needed	184.305	222.15	target	ıl 0.5N HCl	27.6	A	
	Add measured volume of white liquor to bomb	139	20	%AA g	14	32.5	B	
	Add volume of water to reach 5.8 l/w	165	139	liq Vol ml		32.8	C	
	Seal bombs and shake well		126.23	wtr in chips	gpl Na2O	30.3	Na2S	
Cook	place bombs and water in Digester		430.23	total water		70.3	NaOH	
	Start pump		7.41	Cook liq/wood		0.9	Na2CO3	
845	Start Cook profile 4					30.15%	Sulf%	
	Close lid					101.6	TTA	
945	Manually adjust controller at end of ramp					100.6	AA	
1223	Vent digester at end of cook and run cooling coil					85.5	EA	
	Verify all pressure released				Profile 4	Kraft Cook		
	Open lid				Controls	Active		
	drain				Time Seg	0:00:00	300	
	Cool bombs in water before opening				Time Seg	0:59:20	1660	
	Take sample of black liquor	13.53	27.39	AD Pulp	Controls	Off		
1333	Dump chips into wash bag, wash well		92.98	%Pulp Dry	Delay	0:00:10		
1625	Defibrate pulp in blender		25.47	BD Pulp	Controls	Active		
	Squeeze dry		36.38	%Yield	Time Seg	0:00:30	1680	
	homogenize in mixer, spread to dry		53.2	Kappa	Time Seg	1:46:00	1680	
					Controls	Off		
					End of	Profile		

			70	BD Raw Chips				
Bomb	Cook 4	4	70	BD Chips	White Lqr	7/3/09	test date	
	measure wet chips needed	184.305	222.15	target	ıl 0.5N HCl	27.6	A	
	Add measured volume of white liquor to bomb	139	20	%AA g	14	32.5	B	
	Add volume of water to cover chips	165	139	liq Vol ml		32.8	C	
	Seal bombs and shake well		126.23	wtr in chips	gpl Na2O	30.3	Na2S	
Cook	place bombs and water in Digester		430.23	total water		70.3	NaOH	
	Start pump		7.41	Cook liq/wood		0.9	Na2CO3	
802	Start Cook profile 4					30.15%	Sulf%	
	Close lid					101.6	TTA	
906	end of ramp 4 minutes late					100.6	AA	
1130	Vent digester at end of cook and run cooling coil					85.5	EA	
	Verify all pressure released				Profile 4	Kraft Cook		
	Open lid				Controls	Active		
	drain				Time Seg	0:00:00	300	
	Cool bombs in water before opening				Time Seg	0:59:20	1660	
	Take sample of black liquor	13.57	27.35	AD Pulp	Controls	Off		
	Dump chips into wash bag, wash well		93.22	%Pulp Dry	Delay	0:00:10		
	Defibrate pulp in blender		25.50	BD Pulp	Controls	Active		
	Squeeze dry		36.42	%Yield	Time Seg	0:00:30	1680	
1328	homogenize in mixer, spread to dry		33.2	Kappa	Time Seg	2:20:00	1680	
					Controls	Off		
					End of	Profile		

			70	BD Raw Chips			
Bomb	Cook 5	4	70	BD Chips	White Lqr	7/3/09	test date
	measure wet chips needed	184.305	222.15	target	ıl 0.5N HCl	27.6	A
	Add measured volume of white liquor to bomb	139	20	%AA g	14	32.5	B
	Add volume of water to cover chips	158	139	liq Vol ml		32.8	C
	Seal bombs and shake well		126.23	wtr in chips	gpl Na2O	30.3	Na2S
Cook	place bombs and water in Digester		423.23	total water		70.3	NaOH
	Start pump		7.29	Cook liq/wood		0.9	Na2CO3
802	Start Cook profile 4					30.15%	Sulf%
	Close lid					101.6	TTA
906	end of ramp 4 minutes late					100.6	AA
1130	Vent digester at end of cook and run cooling coil					85.5	EA
	Verify all pressure released						
	Open lid						
	drain						
	Cool bombs in water before opening						
	Take sample of black liquor	12.75	27.06	AD Pulp			
	Dump chips into wash bag, wash well		93.33	%Pulp Dry			
	Defibrate pulp in blender		25.26	BD Pulp			
	Squeeze dry		36.08	%Yield			
1328	homogenize in mixer, spread to dry		34.1	Kappa			

Profile 4	Kraft Cook	
Controls	Active	
Time Seg	0:00:00	300
Time Seg	0:59:20	1660
Controls	Off	
Delay	0:00:10	
Controls	Active	
Time Seg	0:00:30	1680
Time Seg	1:47:00	1680
Controls	Off	
End of	Profile	

PreH C

Time	minutes	pH	Dig Temp	kr	Avg	H Factor	OmegaT	kr	avg	H Factor
1310	0	4.47	25.7	0.00	-	-	23.5	0.00	-	-
1320	10	4.52	53.3	0.00	0.0	0.00	51.6	0.00	0.0	0.0
1330	20	4.75	76.4	0.06	0.0	0.00	74	0.04	0.0	0.0
1340	30	4.69	94.8	0.55	0.3	0.06	92.9	0.44	0.2	0.0
1350	40	4.68	120.2	9.36	5.0	0.88	118.9	8.17	4.3	0.8
1400	50	4.67	145.1	107.25	58.3	10.60	143.6	93.37	50.8	9.2
1405	55	4.62	156.4	295.49	201.4	27.38	155	261.38	177.4	24.0
1408	58	4.57	161.2	447.28	371.4	45.95	159.5	386.61	324.0	40.2
1410	60	4.53	164.1	572.05	509.7	62.94	162.2	487.07	436.8	54.8
1412	62	4.48	166.6	705.37	638.7	84.23	164.7	601.68	544.4	72.9
1414	64	4.43	169.2	874.89	790.1	110.57	167.1	735.35	668.5	95.2
1415	65	4.38	170	934.35	904.6	125.64	167.8	779.34	757.3	107.8
1417	67	4.4	172.2	1,118.19	1,026.3	159.85	170	934.35	856.8	136.4
1419	69	4.48	171.7	1,073.63	1,095.9	196.38	168.8	846.51	890.4	166.1
1421	71	4.44	169.7	911.62	992.6	229.47	167.1	735.35	790.9	192.4
1425	75	4.49	169.7	911.62	911.6	290.25	167	729.26	732.3	241.2
1430	80	4.49	170.3	957.62	934.6	368.13	167.6	766.52	747.9	303.6
1435	85	4.46	170.1	942.05	949.8	447.28	167.4	753.90	760.2	366.9
1445	95	4.49	170.1	942.05	942.0	604.29	167.3	747.67	750.8	492.1
1500	110	4.47	169.9	926.71	934.4	837.89	167.2	741.48	744.6	678.2
1515	125	4.5	170.3	957.62	942.2	1,073.43	167.4	753.90	747.7	865.1
1545	155	4.49	170.1	942.05	949.8	1,548.34	167.2	741.48	747.7	1,239.0
1610	180	4.49	170	934.35	938.2	1,939.26	167	729.26	735.4	1,545.4
1612	182	4.46	163.5	543.81	739.1	1,963.89	159	370.31	549.8	1,563.7
1614	184	4.45	153	219.07	381.4	1,976.61	147.9	138.57	254.4	1,572.2
1616	186	4.45	140	66.66	142.9	1,981.37	134.8	40.55	89.6	1,575.2
1618	188	4.45	131.1	28.25	47.5	1,982.95	125.9	16.80	28.7	1,576.1
1620	190	4.45	124.6	14.73	21.5	1,983.67	119.1	8.34	12.6	1,576.5

Time	NaOH Vo	Total Wate	Sample	
1310		3515.8		
1320		3515.8		
1330		3515.8		
1340		3515.8		
1350		3515.8		
1400		3515.8		3516
1405		3515.8		3516
1408		3515.8		3516
1410		3515.8		3516
1412		3515.8		3516
1414		3515.8		3516
1415		3489.8	-26	3516
1417		3489.8		3490
1419		3489.8		3490
1421	0	3489.8		3490
1425	22	3485.8	-26	3512
1430		3485.8		3486
1435	10	3469.8	-26	3496
1445	3	3446.8	-26	3473
1500	10	3430.8	-26	3457
1515	7	3411.8	-26	3438
1545	20	3405.8	-26	3432
1610		3405.8		3406
1612		3405.8		3406
1614		3405.8		3406
1616		3405.8		3406
1618		3405.8		3406
1620	14	3379.8	-40	3420
	86		-222	

see A17 (A) for cook1 details

6/26/09 BC CFG2

Time	Minutes	Dig Temp2	kr	avg	H Factor	OmegaT	kr	avg	H Factor
930	0	26.8	0.00	-	-	24.8	0.00	-	-
1000	30	98.7	0.88	0.44	0.2	97.2	0.74	0.4	0.2
1028	58	162.6	503.90	252.39	118.0	160.5	421.28	211.0	98.7
1030	60	167.1	735.35	619.62	138.7	165	617.03	519.2	116.0
1032	62	167.5	760.19	747.77	163.6	165	617.03	617.0	136.5
1034	64	167.7	772.90	766.54	189.1	165.1	622.23	619.6	157.2
1036	66	168	792.35	782.63	215.2	165.4	638.08	630.2	178.2
1038	68	168	792.35	792.35	241.6	165.4	638.08	638.1	199.5
1040	70	168	792.35	792.35	268.0	165.2	627.47	632.8	220.5
1320	230	168	792.35	792.35	2,381.0	165	617.03	622.3	1,879.9
1322	232	163.5	543.81	668.08	2,403.3	157.2	316.84	466.9	1,895.5
1324	234	158.2	345.57	444.69	2,418.1	150.5	175.26	246.0	1,903.7
1326	236	150.1	169.07	257.32	2,426.7	145.2	108.25	141.8	1,908.4
1328	238	140.9	72.56	120.81	2,430.7	136.5	47.77	78.0	1,911.0
1330	240	131.7	29.97	51.26	2,432.4	127.5	19.74	33.8	1,912.1
1332	242	123.6	13.30	21.63	2,433.1	119.6	8.79	14.3	1,912.6
1334	244	116.5	6.34	9.82	2,433.4	112.4	4.09	6.4	1,912.8

	DigT old	DigT New	OmT	OmT n
ramp	138.7	61.8	116.0	51.7
cook	2,242.3	2,242.3	1,763.9	1,764.8
cool	52.5	51.6	32.9	32.2
total	2,433.4	2,355.7	1,912.8	1,848.6

see A24 (G) for cook3 details

7/18/09 BC CEG4

Time	Minutes	Dig Temp2	kr	avg	H Factor	OmegaT	kr	avg	H Factor
1155	0	26.9	0.00	-	-	24.7	0.00	-	-
1225	30	98.5	0.86	0.43	0.21	97.2	0.74	0.4	0.2
1253	58	162.7	508.19	254.52	118.99	161.1	443.48	222.1	103.8
1255	60	167.2	741.48	624.84	139.82	165.6	648.86	546.2	122.0
1257	62	167.8	779.34	760.41	165.17	165.7	654.31	651.6	143.8
1259	64	168	792.35	785.84	191.36	165.7	654.31	654.3	165.6
1301	66	168	792.35	792.35	217.77	165.6	648.86	651.6	187.3
1303	68	168	792.35	792.35	244.19	165.6	648.86	648.9	208.9
1305	70	168	792.35	792.35	270.60	165.6	648.86	648.9	230.5
1307	72	168	792.35	792.35	297.01	165.5	643.45	646.2	252.1
1309	74	168	792.35	792.35	323.42	165.5	643.45	643.4	273.5
1343	108	168	792.35	792.35	772.42	165.4	638.08	640.8	636.6
1452	177	168	792.35	792.35	1,683.63	165.3	632.76	635.4	1,367.4
1502	187	168	792.35	792.35	1,815.69	165.4	638.08	635.4	1,473.3
1505	190	168	792.35	792.35	1,855.31	165.3	632.76	635.4	1,505.0
1515	200	168	792.35	792.35	1,987.36	165.4	638.08	635.4	1,610.9
1517	202	165.9	665.35	728.85	2,011.66	160.9	435.96	537.0	1,628.8
1519	204	153.7	233.08	449.21	2,026.63	148.2	142.40	289.2	1,638.5
1521	206	142.3	82.73	157.90	2,031.90	136.8	49.17	95.8	1,641.7
1523	208	130.8	27.42	55.08	2,033.73	125.5	16.14	32.7	1,642.8
1525	210	119.8	8.98	18.20	2,034.34	114.5	5.13	10.6	1,643.1
1527	212	111.6	3.75	6.36	2,034.55	107.6	2.41	3.8	1,643.2

	DigT old	DigT New	OmT	OmT n
ramp	139.8	62.2	122.0	54.2
cook	1,847.5	1,847.5	1,488.9	1,489.0
cool	47.2	45.8	32.3	31.2
total	2,034.6	1,955.5	1,643.2	1,574.4

see A24 (G) for cook 5 details

							b	23.54	pH	4.5
PreH C recal							n	0.31		0.948
time	digT	kr	avg	H Factor	OmegaT	kr	avg	H Factor	Mod kr	Mod H Fact
0	25.7	0.0	-	0.0	23.5	0.00	0	0.0	0.00	0.0
10	53.3	0.0	0.0	0.0	51.6	0.00	0.00	0.0	0.00	0.0
20	76.4	0.1	0.0	0.0	74	0.04	0.02	0.0	0.06	0.0
30	94.8	0.6	0.3	0.1	92.9	0.44	0.24	0.0	0.47	0.1
31	97.34	0.7	0.7	0.1	95.5	0.60	0.52	0.1	0.62	0.1
32	99.88	1.0	0.9	0.1	98.1	0.82	0.71	0.1	0.80	0.1
33	102.4	1.3	1.2	0.1	100.7	1.10	0.96	0.1	1.03	0.1
34	105.0	1.8	1.6	0.1	103.3	1.49	1.30	0.1	1.32	0.1
35	107.5	2.4	2.1	0.2	105.9	2.00	1.74	0.1	1.70	0.1
36	110.0	3.2	2.8	0.2	108.5	2.67	2.33	0.2	2.16	0.2
37	112.6	4.2	3.7	0.3	111.1	3.55	3.11	0.2	2.75	0.2
38	115.1	5.5	4.8	0.3	113.7	4.70	4.13	0.3	3.49	0.3
39	117.7	7.2	6.3	0.5	116.3	6.21	5.46	0.4	4.42	0.3
40	120.2	9.4	8.3	0.6	118.9	8.17	7.19	0.5	5.57	0.4
41	122.7	12.1	10.7	0.8	121.37	10.57	9.37	0.7	6.92	0.5
42	125.2	15.6	13.9	1.0	123.84	13.63	12.10	0.9	8.57	0.6
43	127.7	20.1	17.9	1.3	126.31	17.51	15.57	1.1	10.59	0.8
44	130.2	25.7	22.9	1.7	128.78	22.44	19.98	1.5	13.05	1.0
45	132.7	32.9	29.3	2.2	131.25	28.67	25.56	1.9	16.04	1.2
46	135.1	41.9	37.4	2.8	133.72	36.51	32.59	2.4	19.67	1.5
47	137.6	53.2	47.6	3.6	136.19	46.37	41.44	3.1	24.06	1.9
48	140.1	67.4	60.3	4.6	138.66	58.72	52.54	4.0	29.37	2.3
49	142.6	85.2	76.3	5.9	141.13	74.14	66.43	5.1	35.75	2.9
50	145.1	107.3	96.2	7.5	143.6	93.37	83.76	6.5	43.42	3.5
51	147.4	131.9	119.6	9.5	145.88	115.23	104.30	8.2	51.85	4.3
52	149.6	161.9	146.9	11.9	148.16	141.88	128.56	10.4	61.80	5.3
53	151.9	198.3	180.1	14.9	150.44	174.31	158.10	13.0	73.51	6.4
54	154.1	242.3	220.3	18.6	152.72	213.69	194.00	16.2	87.29	7.8
55	156.4	295.5	268.9	23.1	155	261.38	237.54	20.2	103.45	9.3
56	158.0	339.6	317.6	28.4	156.5	298.09	279.74	24.9	115.58	11.2
57	159.6	390.0	364.8	34.4	158	339.63	318.86	30.2	129.02	13.2
58	161.2	447.3	418.6	41.4	159.5	386.61	363.12	36.2	143.91	15.5
59	162.7	506.0	476.7	49.4	160.85	434.10	410.36	43.1	158.68	18.0
60	164.1	572.1	539.0	58.3	162.2	487.07	460.58	50.7	174.86	20.8
61	165.4	635.4	603.7	68.4	163.45	541.51	514.29	59.3	191.21	23.8
62	166.6	705.4	670.4	79.6	164.7	601.68	571.60	68.8	208.98	27.2
63	167.9	785.8	745.6	92.0	165.9	665.35	633.51	79.4	227.48	30.8
64	169.2	874.9	830.4	105.8	167.1	735.35	700.35	91.1	247.50	34.8
65	170.0	934.3	904.6	120.9	167.8	779.34	757.34	103.7	259.93	39.0
66	171.1	1,022.4	978.4	137.2	168.9	853.52	816.43	117.3	280.64	43.5
67	172.2	1,118.2	1,070.3	155.1	170	934.35	893.94	132.2	302.89	48.4
68	172.0	1,095.7	1,106.9	173.5	169.4	889.41	911.88	147.4	290.56	53.3
69	171.7	1,073.6	1,084.7	191.6	168.8	846.51	867.96	161.9	278.70	58.1
70	170.7	989.5	1,031.6	208.8	167.95	789.08	817.80	175.5	262.66	62.6
71	169.7	911.6	950.6	224.6	167.1	735.35	735.35	176.9	247.50	66.8
75	169.7	911.6	911.6	285.4	167	729.26	732.30	225.7	245.77	83.3
80	170.3	957.6	934.6	363.3	167.6	766.52	747.89	288.0	256.32	104.2
85	170.1	942.0	949.8	442.4	167.4	753.90	760.21	351.4	252.75	125.4
95	170.1	942.0	942.0	599.4	167.3	747.67	750.79	476.5	250.99	167.4
110	169.9	926.7	934.4	833.0	167.2	741.48	744.58	662.6	249.24	229.9
125	170.3	957.6	942.2	1068.6	167.4	753.90	747.69	849.6	252.75	292.6
155	170.1	942.0	949.8	1543.5	167.2	741.48	747.69	1223.4	249.24	418.1
180	170.0	934.3	938.2	1934.4	167	729.26	735.37	1529.8	245.77	521.3
181	166.8	714.2	824.3	1948.2	163	521.28	625.27	1540.2	185.17	524.9
182	163.5	543.8	629.0	1958.6	159	370.31	445.79	1547.7	138.78	527.6
183	158.3	347.1	445.4	1966.1	153.45	227.98	299.14	1552.6	92.19	529.5
184	153.0	219.1	283.1	1970.8	147.9	138.57	183.28	1555.7	60.58	530.8
185	146.5	122.0	170.5	1973.6	141.35	75.69	107.13	1557.5	36.38	531.6
186	140.0	66.7	94.3	1975.2	134.8	40.55	58.12	1558.5	21.49	532.0
187	135.6	43.6	55.1	1976.1	130.35	26.23	33.39	1559.0	14.88	532.4
188	131.1	28.2	35.9	1976.7	125.9	16.80	21.52	1559.4	10.22	532.6
189	127.9	20.4	24.3	1977.1	122.5	11.88	14.34	1559.6	7.63	532.7
190	124.6	14.7	17.6	1977.4	119.1	8.34	10.11	1559.8	5.67	532.8

BC CEG4

time	digT	kr	avg	H Factor	OmegaT	kr	avg	H Factor
0	26.9	0.00	0	0.0	24.7	0.00	0	0.0
1	29.29	0.00	0.00	0.0	27.1	0.00	0.00	0.0
2	31.67	0.00	0.00	0.0	29.5	0.00	0.00	0.0
3	34.06	0.00	0.00	0.0	32.0	0.00	0.00	0.0
4	36.45	0.00	0.00	0.0	34.4	0.00	0.00	0.0
5	38.83	0.00	0.00	0.0	36.8	0.00	0.00	0.0
6	41.22	0.00	0.00	0.0	39.2	0.00	0.00	0.0
7	43.61	0.00	0.00	0.0	41.6	0.00	0.00	0.0
8	45.99	0.00	0.00	0.0	44.0	0.00	0.00	0.0
9	48.38	0.00	0.00	0.0	46.5	0.00	0.00	0.0
10	50.77	0.00	0.00	0.0	48.9	0.00	0.00	0.0
11	53.15	0.00	0.00	0.0	51.3	0.00	0.00	0.0
12	55.54	0.00	0.00	0.0	53.7	0.00	0.00	0.0
13	57.93	0.00	0.00	0.0	56.1	0.00	0.00	0.0
14	60.31	0.01	0.01	0.0	58.5	0.00	0.00	0.0
15	62.7	0.01	0.01	0.0	60.95	0.0	0.01	0.0
16	65.09	0.01	0.01	0.0	63.3667	0.0	0.01	0.0
17	67.47	0.02	0.01	0.0	65.7833	0.0	0.01	0.0
18	69.86	0.02	0.02	0.0	68.2	0.0	0.02	0.0
19	72.25	0.03	0.03	0.0	70.6167	0.0	0.02	0.0
20	74.63	0.04	0.04	0.0	73.0333	0.0	0.03	0.0
21	77.02	0.06	0.05	0.0	75.45	0.0	0.04	0.0
22	79.41	0.08	0.07	0.0	77.8667	0.1	0.06	0.0
23	81.79	0.11	0.10	0.0	80.2833	0.1	0.08	0.0
24	84.18	0.15	0.13	0.0	82.7	0.1	0.11	0.0
25	86.57	0.20	0.18	0.0	85.1167	0.2	0.15	0.0
26	88.95	0.27	0.24	0.0	87.5333	0.2	0.20	0.0
27	91.34	0.37	0.32	0.0	89.95	0.3	0.27	0.0
28	93.73	0.49	0.43	0.0	92.3667	0.4	0.36	0.0
29	96.11	0.65	0.57	0.0	94.7833	0.6	0.48	0.0
30	98.5	0.86	0.75	0.0	97.2	0.7	0.64	0.0
31	100.8	1.12	0.99	0.1	99.4821	1.0	0.85	0.1
32	103.1	1.45	1.28	0.1	101.764	1.2	1.10	0.1
33	105.4	1.88	1.67	0.1	104.046	1.6	1.43	0.1
34	107.7	2.43	2.16	0.2	106.329	2.1	1.86	0.1
35	110	3.13	2.78	0.2	108.611	2.7	2.40	0.2
36	112.3	4.02	3.58	0.3	110.893	3.5	3.08	0.2
37	114.6	5.15	4.59	0.3	113.175	4.4	3.96	0.3
38	116.8	6.58	5.87	0.4	115.457	5.7	5.06	0.4
39	119.1	8.38	7.48	0.6	117.739	7.2	6.46	0.5
40	121.4	10.63	9.50	0.7	120.021	9.2	8.21	0.6
41	123.7	13.46	12.05	0.9	122.3	11.64	10.41	0.8
42	126	17.00	15.23	1.2	124.6	14.70	13.17	1.0
43	128.3	21.41	19.20	1.5	126.9	18.53	16.62	1.3
44	130.6	26.89	24.15	1.9	129.2	23.28	20.91	1.6
45	132.9	33.68	30.29	2.4	131.4	29.19	26.24	2.1
46	135.2	42.09	37.89	3.0	133.7	36.49	32.84	2.6
47	137.5	52.47	47.28	3.8	136.0	45.51	41.00	3.3
48	139.8	65.24	58.85	4.8	138.3	56.63	51.07	4.2
49	142.1	80.93	73.08	6.0	140.6	70.28	63.45	5.2
50	144.4	100.15	90.54	7.5	142.8	87.02	78.65	6.5
51	146.7	123.65	111.90	9.4	145.1	107.50	97.26	8.1
52	148.9	152.31	137.98	11.7	147.4	132.49	120.00	10.1
53	151.2	187.20	169.76	14.5	149.7	162.93	147.71	12.6
54	153.5	229.57	208.39	18.0	152.0	199.91	181.42	15.6
55	155.8	280.92	255.24	22.2	154.3	244.76	222.34	19.3
56	158.1	343.01	311.96	27.4	156.5	299.02	271.89	23.9
57	160.4	417.94	380.48	33.8	158.8	364.53	331.77	29.4
58	162.7	508.19	463.07	41.5	161.1	443.48	404.00	36.1
59	165	614.45	561.32	50.9	163.4	536.95	490.22	44.3
60	167.2	741.48	677.97	62.2	165.6	648.86	592.91	54.2
61	167.5	760.19	750.83	74.7	165.7	651.58	650.22	65.0
62	167.8	779.34	769.76	87.5	165.7	654.31	652.94	75.9
63	167.9	785.82	782.58	100.5	165.7	654.31	654.31	86.8
64	168	792.35	789.09	113.7	165.7	654.3	654.31	97.7
65	168	792.35	792.35	126.9	165.65	651.6	652.94	108.6
66	168	792.35	792.35	140.1	165.6	648.9	650.22	119.4

67	168	792.35	792.35	153.3	165.6	648.9	648.86	130.2
68	168	792.35	792.35	166.5	165.6	648.9	648.86	141.1
69	168	792.35	792.35	179.7	165.6	648.9	648.86	151.9
70	168	792.35	792.35	192.9	165.6	648.9	648.86	162.7
71	168	792.35	792.35	206.1	165.55	646.1	647.50	173.5
72	168	792.35	792.35	219.3	165.5	643.4	644.80	184.2
73	168	792.35	792.35	232.5	165.5	643.4	643.45	194.9
74	168	792.35	792.35	245.8	165.5	643.4	643.45	205.7
108	168	792.35	792.35	694.8	165.4	638.1	640.76	568.8
177	168	792.35	792.35	1606.0	165.3	632.8	635.42	1299.5
187	168	792.35	792.35	1738.0	165.4	638.1	635.42	1405.4
188	168	792.35	792.35	1751.2	165.4	638.1	638.08	1416.0
189	168	792.35	792.35	1764.4	165.4	638.1	638.08	1426.7
190	168	792.35	792.35	1777.6	165.3	632.8	635.42	1437.3
200	168	792.35	792.35	1909.7	165.4	638.1	635.42	1543.2
201	167	726.23	759.29	1922.4	163.15	527.9	583.01	1552.9
202	165.9	665.35	695.79	1933.9	160.9	436.0	481.95	1560.9
203	159.8	396.72	531.03	1942.8	154.55	251.2	343.60	1566.6
204	153.7	233.08	314.90	1948.0	148.2	142.4	196.82	1569.9
205	148	139.84	186.46	1951.2	142.5	84.3	113.34	1571.8
206	142.3	82.73	111.28	1953.0	136.8	49.2	66.73	1572.9
207	136.6	48.00	65.36	1954.1	131.15	28.4	38.78	1573.6
208	130.8	27.42	37.71	1954.7	125.5	16.1	22.26	1573.9
209	125.3	15.81	21.62	1955.1	120	9.2	12.65	1574.2
210	119.8	8.98	12.40	1955.3	114.5	5.1	7.15	1574.3
211	115.7	5.83	7.40	1955.4	111.05	3.5	4.33	1574.3
212	111.6	3.75	4.79	1955.5	107.6	2.4	2.97	1574.4

BC CFG2

time	digT	kr	avg	H Factor	OmegaT	kr	avg	H Factor
0	26.8	0.00	0	0.0	24.8	0.00	0	0.0
1	29.2	0.00	0.00	0.0	27.2	0.00	0.00	0.0
2	31.6	0.00	0.00	0.0	29.6	0.00	0.00	0.0
3	34.0	0.00	0.00	0.0	32.0	0.00	0.00	0.0
4	36.4	0.00	0.00	0.0	34.5	0.00	0.00	0.0
5	38.8	0.00	0.00	0.0	36.9	0.00	0.00	0.0
6	41.2	0.00	0.00	0.0	39.3	0.00	0.00	0.0
7	43.6	0.00	0.00	0.0	41.7	0.00	0.00	0.0
8	46.0	0.00	0.00	0.0	44.1	0.00	0.00	0.0
9	48.4	0.00	0.00	0.0	46.5	0.00	0.00	0.0
10	50.8	0.00	0.00	0.0	48.9	0.00	0.00	0.0
11	53.2	0.00	0.00	0.0	51.3	0.00	0.00	0.0
12	55.6	0.00	0.00	0.0	53.8	0.00	0.00	0.0
13	58.0	0.00	0.00	0.0	56.2	0.00	0.00	0.0
14	60.4	0.01	0.01	0.0	58.6	0.00	0.00	0.0
15	62.8	0.01	0.01	0.0	61.0	0.01	0.01	0.0
16	65.1	0.01	0.01	0.0	63.4	0.01	0.01	0.0
17	67.5	0.02	0.01	0.0	65.8	0.01	0.01	0.0
18	69.9	0.02	0.02	0.0	68.2	0.02	0.02	0.0
19	72.3	0.03	0.03	0.0	70.7	0.03	0.02	0.0
20	74.7	0.04	0.04	0.0	73.1	0.04	0.03	0.0
21	77.1	0.06	0.05	0.0	75.5	0.05	0.04	0.0
22	79.5	0.08	0.07	0.0	77.9	0.07	0.06	0.0
23	81.9	0.11	0.10	0.0	80.3	0.09	0.08	0.0
24	84.3	0.15	0.13	0.0	82.7	0.13	0.11	0.0
25	86.7	0.21	0.18	0.0	85.1	0.17	0.15	0.0
26	89.1	0.28	0.24	0.0	87.5	0.23	0.20	0.0
27	91.5	0.37	0.33	0.0	90.0	0.31	0.27	0.0
28	93.9	0.50	0.44	0.0	92.4	0.41	0.36	0.0
29	96.3	0.66	0.58	0.0	94.8	0.55	0.48	0.0
30	98.7	0.88	0.77	0.1	97.2	0.74	0.64	0.0
31	101.0	1.14	1.01	0.1	99.5	0.96	0.85	0.1
32	103.3	1.48	1.31	0.1	101.7	1.24	1.10	0.1
33	105.5	1.92	1.70	0.1	104.0	1.61	1.43	0.1
34	107.8	2.48	2.20	0.2	106.2	2.07	1.84	0.1
35	110.1	3.18	2.83	0.2	108.5	2.67	2.37	0.2
36	112.4	4.08	3.63	0.3	110.8	3.42	3.04	0.2
37	114.7	5.22	4.65	0.3	113.0	4.37	3.90	0.3
38	117.0	6.66	5.94	0.4	115.3	5.57	4.97	0.4
39	119.2	8.47	7.56	0.6	117.5	7.09	6.33	0.5
40	121.5	10.74	9.60	0.7	119.8	8.98	8.04	0.6
41	123.8	13.58	12.16	0.9	122.1	11.36	10.17	0.8
42	126.1	17.12	15.35	1.2	124.3	14.32	12.84	1.0
43	128.4	21.54	19.33	1.5	126.6	18.02	16.17	1.3
44	130.7	27.02	24.28	1.9	128.9	22.60	20.31	1.6
45	132.9	33.81	30.42	2.4	131.1	28.28	25.44	2.0
46	135.2	42.21	38.01	3.1	133.4	35.29	31.79	2.6
47	137.5	52.56	47.38	3.8	135.6	43.94	39.62	3.2
48	139.8	65.28	58.92	4.8	137.9	54.58	49.26	4.0
49	142.1	80.90	73.09	6.0	140.2	67.64	61.11	5.1
50	144.3	100.02	90.46	7.5	142.4	83.61	75.62	6.3
51	146.6	123.37	111.69	9.4	144.7	103.13	93.37	7.9
52	148.9	151.82	137.59	11.7	146.9	126.92	115.02	9.8
53	151.2	186.42	169.12	14.5	149.2	155.84	141.38	12.1
54	153.5	228.41	207.42	18.0	151.5	190.94	173.39	15.0
55	155.8	279.25	253.83	22.2	153.7	233.45	212.20	18.6
56	158.0	340.68	309.97	27.4	156.0	284.81	259.13	22.9
57	160.3	414.76	377.72	33.7	158.2	346.74	315.78	28.1
58	162.6	503.90	459.33	41.3	160.5	421.28	384.01	34.5
59	164.9	609.31	556.60	50.6	162.8	510.35	465.82	42.3
60	167.1	735.35	672.33	61.8	165.0	617.03	563.69	51.7
61	167.3	747.67	741.51	74.2	165.0	617.03	617.03	62.0
62	167.5	760.19	753.93	86.7	165.0	617.03	617.03	72.3
63	167.6	766.52	763.35	99.5	165.1	619.63	618.33	82.6
64	167.7	772.90	769.71	112.3	165.1	622.23	620.93	92.9
65	167.9	782.57	777.74	125.2	165.3	630.11	626.17	103.4
66	168.0	792.35	787.46	138.4	165.4	638.08	634.10	113.9

67	167.9	785.82	789.09	151.5	165.4	638.08	638.08	124.6
68	167.8	779.34	782.58	164.6	165.4	638.08	638.08	135.2
69	167.9	785.82	782.58	177.6	165.3	632.76	635.42	145.8
70	168.0	792.35	789.09	190.8	165.2	627.47	630.12	156.3
71	168.1	795.64	794.00	204.0	165.2	627.47	627.47	166.8
72	168.1	798.94	797.29	217.3	165.2	627.47	627.47	177.2
73	168.1	798.94	798.94	230.6	165.2	627.47	627.47	187.7
74	168.1	798.94	798.94	243.9	165.2	627.47	627.47	198.1
75	168.1	795.64	797.29	257.2	165.2	627.47	627.47	208.6
76	168.0	792.35	794.00	270.4	165.2	627.47	627.47	219.0
77	168.0	792.35	792.35	283.6	165.2	627.47	627.47	229.5
78	168.0	792.35	792.35	296.8	165.2	627.47	627.47	240.0
79	168.0	792.35	792.35	310.1	165.2	624.85	626.16	250.4
80	168.0	792.35	792.35	323.3	165.2	627.47	626.16	260.8
230	168.0	792.35	792.35	2304.1	165.0	617.03	622.25	1816.5
231	165.8	657.05	724.70	2316.2	161.1	443.48	530.26	1825.3
232	163.5	543.81	600.43	2326.2	157.2	316.84	380.16	1831.6
233	160.9	434.10	488.95	2334.4	153.9	236.19	276.51	1836.2
234	158.2	345.57	389.83	2340.9	150.5	175.26	205.72	1839.7
235	154.2	242.53	294.05	2345.8	147.9	137.94	156.60	1842.3
236	150.1	169.07	205.80	2349.2	145.2	108.25	123.09	1844.3
237	145.5	111.27	140.17	2351.5	140.9	72.22	90.23	1845.8
238	140.9	72.56	91.92	2353.1	136.5	47.77	60.00	1846.8
239	136.3	46.86	59.71	2354.1	132.0	30.86	39.32	1847.5
240	131.7	29.97	38.41	2354.7	127.5	19.74	25.30	1847.9
241	127.7	20.04	25.00	2355.1	123.6	13.23	16.49	1848.2
242	123.6	13.30	16.67	2355.4	119.6	8.79	11.01	1848.4
243	120.1	9.22	11.26	2355.6	118.1	7.47	8.13	1848.5
244	116.5	6.34	7.78	2355.7	116.5	6.34	6.91	1848.6

Kraft Bomb Cook Plan

Time	Activity		Data	Calc				
						6/11/09	70	g BD Chips to Cook
prep	Clean Digester, drain, close valve			76.24	g AD Chips		91.82	%Chip solids
1330	Measure mass of chips, put in bomb, g		76.24	6.24	wtr in chips		0	%preH Chip Sample
				70.0036	BD Chips			White Liquor
								5/23/09 test date
1420	Add measured vol of white liquor to bomb		144	20	%AA			ml 0.5N HCl
1420	measure vol of wtr added to just cover chips		270	14	AA g			27.05 A
	Use vacuum oven to remove air from chips			144	liq Vol ml			31.5 B
1430	Seal bombs and shake well			420.24	total water			32.6 C
Cook	place bombs and water in Digester			6.00	Cook liq/woo	gpl Na2O		27.6 Na2S
13:30	Start pump		4		Bomb			70.0 NaOH
	Start Cook profile 4							3.4 Na2CO3
	Close lid							28.25% Sulf%
14:30	Manually adjust controller at end of ramp		168					100.9 TTA
1715	Vent digester at end of cook and run cooling coil							97.5 AA
	Verify all pressure released							83.8 EA
	Open lid			33.31	AD Pulp	Profile 4	Kraft Cook	
	drain			92.86	%Pulp Dry	Controls	Active	
30	Cool bombs in water before opening			30.93	BD Pulp	Time Seg	0:00:00	300
	Take sample of black liquor			44.19	%Yield	Time Seg	0:59:20	1660
45	Dump chips into wash bag, wash well			26.8	Kappa	Controls	Off	
	Defibrate pulp in blender, Squeeze dry					Delay	0:00:10	
	homogenize in mixer, spread to dry	BL pH	13.21			Controls	Active	
						Time Seg	0:00:30	1680
BOMB #2						Time Seg	3:04:00	1680
prep	Clean Digester, drain, close valve			76.24	g AD Chips	Controls	Off	
	Measure mass of chips, put in bomb, g		76.24	6.24	wtr in chips	End of	Profile	
				70.0036	BD Chips			
	Add measured volume of white liquor to bomb		144	20	%AA			
	measure volume of water added to just cover chips		270	14	AA g		70	g BD Chips to Cook
	Seal bombs and shake well			144	liq Vol ml		91.82	%Chip solids
				420.24	total water		0	%preH Chip Sample
Cook	place bombs and water in Digester			6.00	Cook liq/wood			White Liquor
13:30	Start pump		5		Bomb			5/23/09 test date
	Start Cook profile 4							ml 0.5N HCl
	Close lid							27.05 A
1430	Manually adjust controller at end of ramp		168					31.5 B
1715	Vent digester at end of cook and run cooling coil							32.6 C
	Verify all pressure released					gpl Na2O		27.6 Na2S
	Open lid			33.54	AD Pulp			70.0 NaOH
	drain			93.05	%Pulp Dry			3.4 Na2CO3
30	Cool bombs in water before opening			31.21	BD Pulp			28.25% Sulf%
	Take sample of black liquor			44.58	%Yield			100.9 TTA
45	Dump chips into wash bag, wash well			27.2	Kappa			97.5 AA
	Defibrate pulp in blender, Squeeze dry							83.8 EA
	homogenize in mixer, spread to dry	BL pH	13.14					
BOMB #3								
prep	Clean Digester, drain, close valve			76.24	g AD Chips			
	Measure mass of chips, put in bomb, g		76.24	6.24	wtr in chips			
				70.0036	BD Chips			
	Add measured volume of white liquor to bomb		144	20	%AA		70	g BD Chips to Cook
	measure volume of water added to just cover chips		270	14	AA g		91.82	%Chip solids
	Seal bombs and shake well			144	liq Vol ml		0	%preH Chip Sample
				420.24	total water			White Liquor
Cook	place bombs and water in Digester			6.00	Cook liq/wood			5/23/09 test date
13:30	Start pump		6		Bomb			ml 0.5N HCl
	Start Cook profile 4							27.05 A
	Close lid							31.5 B
1430	Manually adjust controller at end of ramp		168					32.6 C
1715	Vent digester at end of cook and run cooling coil					gpl Na2O		27.6 Na2S
	Verify all pressure released							70.0 NaOH
	Open lid			32.77	AD Pulp			3.4 Na2CO3
	drain			93.17	%Pulp Dry			28.25% Sulf%
30	Cool bombs in water before opening			30.53	BD Pulp			100.9 TTA
	Take sample of black liquor			43.61	%Yield			97.5 AA
45	Dump chips into wash bag, wash well			26.6	Kappa			83.8 EA
	Defibrate pulp in blender, Squeeze dry							
	homogenize in mixer, spread to dry	BL pH	13.06					

Time	Minutes	Dig Temp	kr	avg	H Factor	OmegaT	kr	avg	H Factor
1547	0	26.1	0.00	-	-	24.10	0.00	-	-
1617	30	100	1.02	0.51	0.3	98.8	0.89	0.44	0.2
1632	45	134.1	37.89	19.45	5.1	132.6	32.73	16.81	4.4
1642	55	157.2	316.84	177.36	34.7	155.3	268.36	150.55	29.5
1645	58	164.1	572.05	444.44	56.9	162.1	482.94	375.65	48.3
1647	60	167.8	779.34	675.69	79.4	165.5	643.45	563.20	67.1
1649	62	168.6	832.65	805.99	106.3	166	670.93	657.19	89.0
1651	64	168.8	846.51	839.58	134.3	165.9	665.35	668.14	111.2
1653	66	168.5	825.81	836.16	162.1	165.7	654.31	659.83	133.2
1655	68	168.3	812.27	819.04	189.4	165.5	643.45	648.88	154.9
1659	72	168.1	798.94	805.60	243.2	165.3	632.76	638.10	197.4
1700	73	168	792.35	795.65	256.4	165.2	627.47	630.12	207.9
1800	133	168	792.35	792.35	1,048.8	165	617.03	622.25	830.2
1950	243	168	792.35	792.35	2,501.4	164.9	611.87	614.45	1,956.7
1952	245	166.9	723.21	757.78	2,526.7	160	403.60	507.74	1,973.6
1954	247	155.9	282.86	503.04	2,543.4	148.9	151.72	277.66	1,982.8
1957	250	141.5	76.76	179.81	2,552.4	137	50.12	100.92	1,987.9
2000	253	128.9	22.71	49.74	2,554.9	124.5	14.58	32.35	1,989.5
2002	255	120.9	10.07	16.39	2,555.5	116.3	6.21	10.39	1,989.9
2008	261	100	1.02	5.54	2,556.0	98.8	0.89	3.55	1,990.2

	DigT old	DigT New	OmT	OmT n
ramp	79.4	69.2	67.1	58.5
cook	2,422.0	2,435.3	1,889.6	1,899.9
cool	54.6	39.9	33.5	24.0
total	2,556.0	2,544.4	1,990.2	1,982.3

time	digT	kr	avg	H Factor	OmegaT	kr	avg	H Factor
0	26.1	0.00	0	0.0	24.1	0.00	0	0.0
1	28.6	0.00	0.00	0.0	26.6	0.00	0.00	0.0
2	31.0	0.00	0.00	0.0	29.1	0.00	0.00	0.0
3	33.5	0.00	0.00	0.0	31.6	0.00	0.00	0.0
4	36.0	0.00	0.00	0.0	34.1	0.00	0.00	0.0
5	38.4	0.00	0.00	0.0	36.6	0.00	0.00	0.0
6	40.9	0.00	0.00	0.0	39.0	0.00	0.00	0.0
7	43.3	0.00	0.00	0.0	41.5	0.00	0.00	0.0
8	45.8	0.00	0.00	0.0	44.0	0.00	0.00	0.0
9	48.3	0.00	0.00	0.0	46.5	0.00	0.00	0.0
10	50.7	0.00	0.00	0.0	49.0	0.00	0.00	0.0
11	53.2	0.00	0.00	0.0	51.5	0.00	0.00	0.0
12	55.7	0.00	0.00	0.0	54.0	0.00	0.00	0.0
13	58.1	0.00	0.00	0.0	56.5	0.00	0.00	0.0
14	60.6	0.01	0.01	0.0	59.0	0.00	0.00	0.0
15	63.1	0.01	0.01	0.0	61.5	0.01	0.01	0.0
16	65.5	0.01	0.01	0.0	63.9	0.01	0.01	0.0
17	68.0	0.02	0.02	0.0	66.4	0.01	0.01	0.0
18	70.4	0.02	0.02	0.0	68.9	0.02	0.02	0.0
19	72.9	0.03	0.03	0.0	71.4	0.03	0.02	0.0
20	75.4	0.05	0.04	0.0	73.9	0.04	0.03	0.0
21	77.8	0.07	0.06	0.0	76.4	0.06	0.05	0.0
22	80.3	0.09	0.08	0.0	78.9	0.08	0.07	0.0
23	82.8	0.13	0.11	0.0	81.4	0.11	0.09	0.0
24	85.2	0.17	0.15	0.0	83.9	0.14	0.13	0.0
25	87.7	0.23	0.20	0.0	86.4	0.20	0.17	0.0
26	90.1	0.32	0.27	0.0	88.8	0.27	0.23	0.0
27	92.6	0.43	0.37	0.0	91.3	0.36	0.32	0.0
28	95.1	0.57	0.50	0.0	93.8	0.49	0.43	0.0
29	97.5	0.76	0.67	0.0	96.3	0.66	0.58	0.0
30	100.0	1.02	0.89	0.1	98.8	0.89	0.77	0.0
31	102.3	1.32	1.17	0.1	101.1	1.15	1.02	0.1
32	104.5	1.71	1.52	0.1	103.3	1.49	1.32	0.1
33	106.8	2.21	1.96	0.1	105.6	1.92	1.71	0.1
34	109.1	2.85	2.53	0.2	107.8	2.47	2.20	0.2
35	111.4	3.65	3.25	0.2	110.1	3.17	2.82	0.2
36	113.6	4.67	4.16	0.3	112.3	4.05	3.61	0.3
37	115.9	5.96	5.32	0.4	114.6	5.17	4.61	0.3
38	118.2	7.58	6.77	0.5	116.8	6.57	5.87	0.4
39	120.5	9.62	8.60	0.6	119.1	8.33	7.45	0.6
40	122.7	12.17	10.89	0.8	121.3	10.53	9.43	0.7

41	125.0	15.35	13.76	1.1	123.6	13.28	11.90	0.9
42	127.3	19.31	17.33	1.3	125.8	16.70	14.99	1.2
43	129.6	24.24	21.78	1.7	128.1	20.95	18.83	1.5
44	131.8	30.34	27.29	2.2	130.3	26.22	23.59	1.9
45	134.1	37.89	34.11	2.7	132.6	32.73	29.48	2.4
46	136.4	47.36	42.62	3.4	134.9	40.82	36.78	3.0
47	138.7	59.05	53.21	4.3	137.1	50.79	45.81	3.7
48	141.0	73.45	66.25	5.4	139.4	63.05	56.92	4.7
49	143.3	91.14	82.30	6.8	141.7	78.07	70.56	5.9
50	145.7	112.82	101.98	8.5	144.0	96.45	87.26	7.3
51	148.0	139.33	126.07	10.6	146.2	118.88	107.66	9.1
52	150.3	171.67	155.50	13.2	148.5	146.19	132.54	11.3
53	152.6	211.04	191.36	16.4	150.8	179.39	162.79	14.0
54	154.9	258.87	234.96	20.3	153.0	219.65	199.52	17.4
55	157.2	316.84	287.85	25.1	155.3	268.36	244.01	21.4
56	159.5	386.61	351.72	31.0	157.6	327.10	297.73	26.4
57	161.8	470.77	428.69	38.1	159.8	397.86	362.48	32.4
58	164.1	572.05	521.41	46.8	162.1	482.94	440.40	39.8
59	166.0	668.13	620.09	57.1	163.8	557.76	520.35	48.4
60	167.8	779.34	723.73	69.2	165.5	643.45	600.60	58.5
61	168.2	805.58	792.46	82.4	165.8	657.05	650.25	69.3
62	168.6	832.65	819.12	96.1	166.0	670.93	663.99	80.4
63	168.7	839.56	836.10	110.0	166.0	668.13	669.53	91.5
64	168.8	846.51	843.03	124.0	165.9	665.35	666.74	102.6
65	168.7	836.10	841.31	138.1	165.8	659.81	662.58	113.7
66	168.5	825.81	830.95	151.9	165.7	654.31	657.06	124.6
67	168.4	819.01	822.41	165.6	165.6	648.86	651.58	135.5
68	168.3	812.27	815.64	179.2	165.5	643.45	646.15	146.3
69	168.3	812.27	812.27	192.7	165.5	643.45	643.45	157.0
70	168.2	805.58	808.92	206.2	165.4	638.08	640.76	167.7
71	168.2	805.58	805.58	219.7	165.4	638.08	638.08	178.3
72	168.1	798.94	802.26	233.0	165.3	632.76	635.42	188.9
73	168.0	792.35	795.65	246.3	165.2	627.47	630.12	199.4
133	168.0	792.35	792.35	1038.6	165.0	617.03	622.25	821.6
243	168.0	792.35	792.35	2491.3	164.9	611.87	614.45	1948.1
244	168.0	792.35	792.35	2504.5	164.9	611.87	611.87	1958.3
245	166.9	723.21	757.78	2517.1	160.0	403.60	507.74	1966.8
246	161.4	454.98	589.10	2526.9	154.5	249.03	326.31	1972.2
247	155.9	282.86	368.92	2533.1	148.9	151.72	200.38	1975.6
248	151.1	184.94	233.90	2537.0	144.9	105.62	128.67	1977.7
249	146.3	119.75	152.35	2539.5	141.0	73.02	89.32	1979.2
250	141.5	76.76	98.26	2541.2	137.0	50.12	61.57	1980.2
251	137.3	51.58	64.17	2542.2	132.8	33.49	41.80	1980.9
252	133.1	34.37	42.97	2543.0	128.7	22.19	27.84	1981.4
253	128.9	22.71	28.54	2543.4	124.5	14.58	18.38	1981.7
254	124.9	15.18	18.95	2543.7	120.4	9.56	12.07	1981.9
255	120.9	10.07	12.62	2544.0	116.3	6.21	7.88	1982.0
256	117.4	6.99	8.53	2544.1	113.2	4.46	5.34	1982.1
257	113.9	4.82	5.91	2544.2	110.1	3.19	3.83	1982.2
258	110.5	3.30	4.06	2544.3	107.1	2.27	2.73	1982.2
259	107.0	2.25	2.78	2544.3	104.0	1.61	1.94	1982.3
260	103.5	1.52	1.88	2544.3	100.9	1.13	1.37	1982.3
261	100.0	1.02	1.27	2544.4	98.8	0.89	1.01	1982.3