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Cleavage of Acetyl Groups for Acetic Acid Production in Kraft Pulp Mills

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CLEAVAGE OF ACETYL GROUPS FOR ACETIC ACID PRODUCTION IN KRAFT PULP MILLS

By

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CLEAVAGE OF ACETYL GROUPS FOR ACETIC ACID PRODUCTION IN KRAFT PULP MILLS

By Ravikant Amogisidha Patil

Thesis Advisor: Dr. Joseph M. Genco

An Abstract of the Thesis Presented
in Partial Fulfillment of the Requirements for the
Degree of Master of Science
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December, 2012

The objective of this thesis was to determine appropriate conditions for cleavage of acetyl groups from northeast hardwood. Currently, acetyl groups end up in a waste product stream in most wood based pulp mills and thus are underutilized.

Recently, a techno-economic analysis was published that evaluated the suitability of the 'Near-Neutral Extraction' process for recovery of acetic acid and ethanol in Kraft pulp mills. The results showed that the proposed process suffered from high capital investment and a low rate of return on investment. Additionally, the revenues generated by the sale of acetic acid were two times greater than the revenues obtained from the sale ethanol; primarily due to the high selling price of acetic acid and the extensive processing required in recovering ethanol. The near-neutral extraction process needs to be simplified to reduce the capital and operating cost. One possibility centers on recovery of acetic acid as the only by-product in the mill, thus avoiding the expense of recovery ethanol with its low revenue stream.

In the present study, the rate of cleavage of acetyl groups from industrial Northeast hardwood chips was estimated for different alkali streams which are available in Kraft pulp mills, and do not adversely affect pulp properties. Caustic, green liquor and white liquor were evaluated as deacetylation agents. All experiments were performed in a laboratory scale digester which simulates conventional large scale digesters used in Kraft pulp mills. The

effects of time, soaking temperature, alkali concentration, extraction temperature, and chip thickness were studied.

It was found that the rate of deacetylation is directly proportional to the initial concentration of hydroxide ions in the liquor. Experimentally, 8% white liquor was considered to be a suitable alkali charge for recovery of acetyl groups. The extraction temperature has a negligible effect on cleavage of acetyl groups, provided that the liquor contains excess hydroxide ions. The low temperature extraction is beneficial in a number of ways: 1) it minimizes unwanted side reactions such as delignification and peeling reactions which occur at high temperature, 2) it reduces the solid content of the liquor and simplifies the downstream separation process, and 3) a high concentration of alkali is maintained thus increasing the driving force for diffusion of the reagent into the wood.

The acetic acid production capacity of an individual Kraft mill was found to be 10-50 times lower than that of a commercial acetic acid plant. Thus, the acetic acid production from an individual Kraft mill will not affect the acetic acid market. However, the expected total acetic acid production from worldwide Kraft pulp mills is more than half of the global acetic acid demand. Thus, Kraft mills have the potential to become a sustainable source of acetic acid if a cost effective sodium acetate separation process can be developed.

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CHAPTER 1

INTRODUCTION

Due to the environmental, economical and supply issues associated with the use of fossil fuels, there is a need to manufacture fuels and chemicals from renewable resources. Lignocellulosic biomass such as woody plant represents a sustainable source of carbon and thus it is a potential feedstock for the production of fuels and chemicals. The use of lignocellulosic materials as the primary feedstock overcomes many of the drawbacks associated with other renewable resources and does not affect the food supply as does corn.

Wood and other lignocellulosic biomass consists primarily of cellulose, hemicelluloses and lignin. In addition, wood also contains small amounts of low molecular weight compounds called as “extractives” and the inorganic matter that is termed “ash”. The amount of cellulose, hemicelluloses and lignin in lignocellulosic biomass varies depending on species.

Figure 1 shows various biomass conversion pathways that have been proposed in the literature [van Heiningen, 2011].

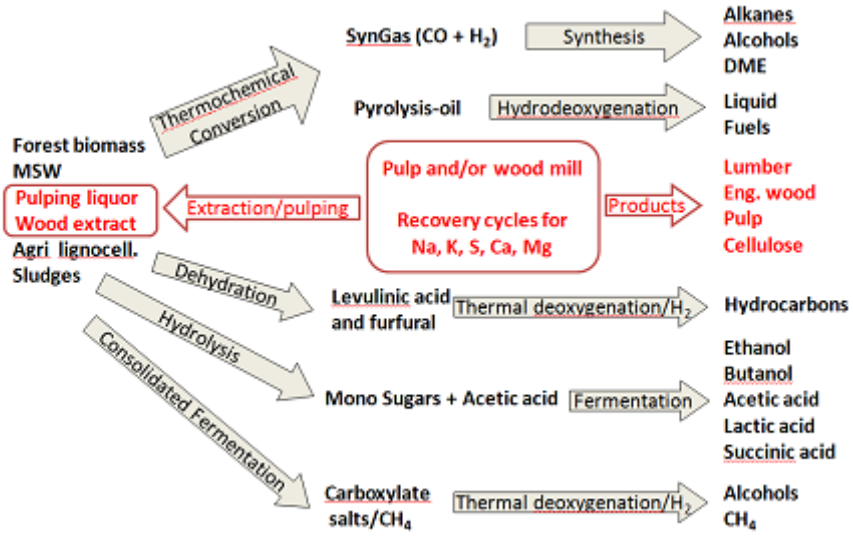


Figure 1.1 Forest Biorefinery Pathways

The production of acetic acid or alternative specialty and commodity chemicals in a biorefinery is thought to be economic only if the new process is integrated into an existing wood products facility such as a pulp mill. This occurs because of the high capital and operating costs associated with the wood handling and preparation systems resulting from inherent complexity in wood processing. Stand-alone biomass conversion facilities have proven to be presently uneconomic [Woolley, 1999 and Mitchell, 2006]. When integrating a new product into an existing wood products facility, it is advantageous to minimize changes to the principal products from the manufacturing operation. For example, integration of a hemicellulose pre-extraction process into a pulp mill requires no change in the final properties of the pulp; and minimal disruption to the normal operation of the facilities. However, the new products can also become economically competitive relative to the existing wood products provided that the price of the new product increases significantly above that of the traditional products [van Heiningen, 2011]

Mao and coworkers (2010) evaluated the 'Near Neutral Extraction' process, which produces both ethanol and acetic acid in a Kraft pulp mill by using green liquor as the extraction solvent. Green liquor in Kraft pulping parlances is an intermediate stream consisting principally of Na_2CO_3 and Na_2S in Kraft pulp mills. The Near Neutral Extraction process involves extraction of hemicelluloses using green liquor prior to Kraft pulping. In Mao's process design study, the pre-extraction reactor was integrated into an existing northeast hardwood Kraft pulp mill. Ancillary unit operations include hydrolysis of the extracted carbohydrates using sulfuric acid, removal of the extracted lignin, liquid-liquid extraction of acetic acid, liming of the residual extract followed by separation of gypsum, fermentation of C-5 and C-6 sugars to ethanol, and upgrading the acetic acid and ethanol products by distillation. The results of Mao's techno-economic study showed that the process suffered from high capital investment which leads to a low rate of return on investment. Furthermore, the revenues generated by the sale of acetic acid were about two

times greater than that of ethanol. The only circumstance where the process was deemed financially viable as originally conceived was for the case of a very large pulp mill that has an existing vessel which could be modified to perform the extraction; and where additional waste treatment and low cost steam are available to accommodate the new processes.

The deacetylation of pendant groups on the xylan or galactoglucomannan polymers in the wood, using a readily-available inexpensive source of alkali, is an alternative route to chemical synthetic acetic acid production. Thus, the goal of the current work is to simplify the near-neutral extraction process in an effort to reduce capital and operating expenditures to improve the rate of return on investment for the process. One method for simplifying the process involves recovery of acetic acid as the only by-product in the mill, thus greatly reducing the equipment and energy requirements for the process. The initial work in the investigation reported here was to determine the appropriate conditions for cleavage of acetyl groups from northeast hardwood. To be a viable process however, a cost effective separation method must be developed for separation of product sodium acetate from the alkaline extraction liquor so that the unused alkali can be returned to the process for further use in pulping.

CHAPTER 2

LITERATURE REVIEW

This chapter contains information about current manufacturing routes for acetic acid, chemical composition of wood, acetyl groups in wood, reaction of acetyl groups in alkaline and acidic condition. Finally, advantages of recovery of acetyl groups and the possible chemicals agents for deacetylation of wood are listed.

2.1 Acetic Acid

Acetic acid is a commodity chemical that is used in a variety of commercial processes. In 2010, the global demand for acetic acid was 9.5 million tons per year [Massingham, 2011]. The demand for acetic acid is increasing by approximately 3 to 4% per year. About 20% of this demand is met by recycling waste streams generated in the synthetic organic chemical industry, while the balance (80%) of the demand for acetic acid is filled by its manufacture from feedstocks that are derived from coal, natural gas, petrochemical and biological sources. Currently, almost all acetic acid produced commercially comes from methanol carbonylation, acetaldehyde oxidation or oxidation of light hydrocarbon in the liquid-phase [Yoneda et al. 2001]. Comparatively smaller amounts are generated by fermentation or by wood distillates.

The methanol carbonylation reaction scheme is illustrated in Equation 2.1. It has been a major route for commercial production of acetic acid for the past 35 years, and will likely remain the preferred route for large scale production [Yoneda et al. 2001]. It accounts for about 75 % of the total worldwide acetic acid production.

$$CH_3OH + CO \xrightarrow{\text{Iridium, 30-60 bar, 150-200 } ^0C} CH_3COOH \quad \text{.....Equation (2.1)}$$

Prior to the commercialization of the methanol carbonylation route, most acetic acid was produced by acetaldehyde oxidation (Equation 2.2). Although it is not competitive with

the methanol carbonylation route, this method still remains the second most important manufacturing method.

$$CH_3CHO + \frac{1}{2}O_2 \xrightarrow{Mn + Cu \text{ or } Co,\ 3\text{-}10 \text{ bar},\ 60\text{-}80\ ^0C} CH_3COOH \quad \text{.....Equation (2.2)}$$

Due to the economic reasons, natural gas and petrochemical feedstocks have been steadily increasing in popularity as a starting material for the production of acetic acid. However, use of natural gas or petrochemical feed stocks suffer from a number of disadvantages including (1) high prices, (2) a limited domestic supplies of crude oil, (3) competitive demand of petroleum feedstocks for the production of alternative organic chemicals, and (4) emission of greenhouse gases. It has been clear for several years that there is a need for an alternative manufacturing method based on renewable feed stocks.

2.2 Lignocellulosic Biomass

The term 'Lignocellulose' is used to describe three-dimensional polymeric composites formed by plants as a structural material. Lignocellulosic feedstock is composed primarily of carbohydrate polymers (cellulose and hemicelluloses) and phenolic polymers (lignin). There are also small amounts of various other compounds such as proteins, acids, salts and minerals that are present. However, the relative distribution of these components varies depending upon the type of species. Hardwoods contain about 45% cellulose, 28-35% hemicellulose and 18-22% lignin; whereas softwoods contain 41-42% cellulose, 25-30% hemicellulose and 25-30% lignin.

Cellulose, lignin and hemicelluloses are the most abundant organic polymers made by photosynthesis. On an energy basis, carbon synthesis by plants is almost ten times higher than its actual consumption. In the present situation, the lignocellulosic biomass is the only sustainable source for production of liquid fuels and chemicals [Huber, 2006]. The cost of lignocellulosic biomass in the United States varies from $12 to $24 per barrel of oil equivalent [Lange, 2007], which is significantly below the cost of crude oil, which is about

$95/bbl currently. However, cost effective technology to economically convert plant biomass to fuels and chemicals is not yet available.

2.2.1 Cellulose

The Cellulose is a linear homogenous polysaccharide consisting of β-D-glucopyranose units linked to each other through (1→4)-glycosidic bonds [Sjöström, 1993]. Cellulose in woody plants has a degree of polymerization (DP) ranging from 7,000 to 15,000. Cellulose tends to form strong intra- and intermolecular hydrogen bonds, which leads to aggregation of cellulose molecules into macrofibrils. Highly ordered cellulose macrofibrils are crystallized while less ordered ones are amorphous. Due to its fibrous structure and the formation of strong inter and intra molecular hydrogen bond, cellulose has a high tensile strength and is insoluble in many solvents. It should be pointed out that cellulose has completely different physical and chemical properties when compared to starch, which is formed from α-(1→4)-D-glucopyranose units and is present as amylose and amylopectic polymers.

The length of the native cellulose molecule is about 5000 nm (10,000 glucose units). It is proposed that the cellulose chains form elementary fibrils, which consist of 100 cellulose chains. The elementary fibrils arrange into microfibrils containing approximately 20 elementary units. The microfibrils are grouped together in groups of approximately 250, to form macrofibrils. Cellulose provides strength to wood through macrofibrils which are made up of cellulose chains. Macrofibrils are surrounded by both lignin and hemicelluloses. Figure 2.1 shows the fibrillar arrangement of cellulose molecules.

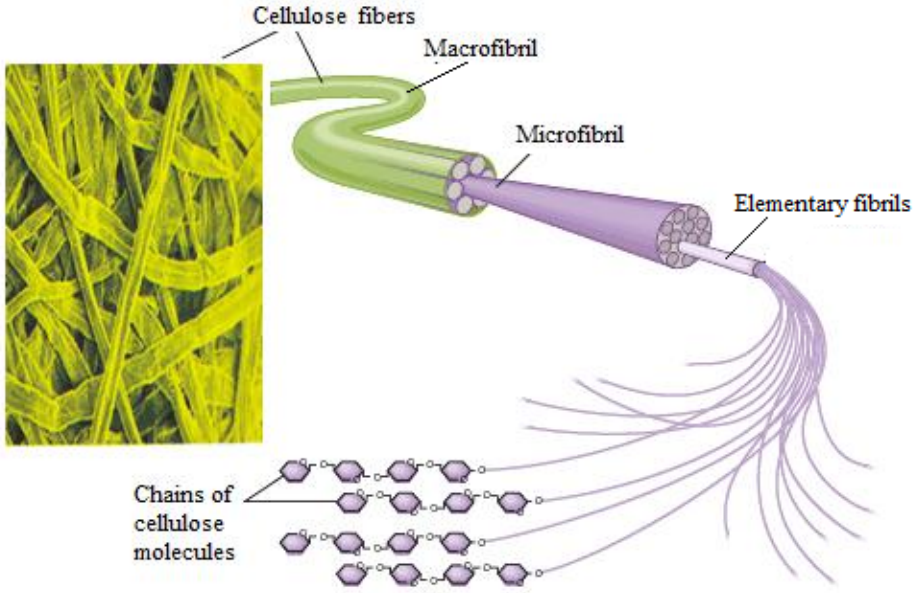


Figure 2.1 Fibrillar Arrangement of Cellulose

2.2.2 Hemicelluloses

Hemicelluloses are heterogeneous polysaccharides. In most cases they are extensively branched and have a low degree of polymerization of around 200 or about 1/10th of the DP of cellulose [Sjöström, 1993]. These side chains inhibit crystallization and result in amorphous hemicellulose polymers. The irregular structure of the hemicellulose molecules minimizes the number of hydrogen bonds that can be formed between hemicellulose molecules and results in a less compact macro structure than that of cellulose. The chemical reactions of hemicelluloses are similar to those of cellulose except that their reactivity is greater.

The fundamental components of hemicelluloses are D-glucose, D-mannose, 4-0-methyl-D-glucuronic acid, D-galactose, D-xylose, L-arabinose and L-rhamnose. Depending on the type of wood, the composition and structure of hemicelluloses in softwoods differ in many ways from those in hardwoods [Sjöström, 1993]. Table 2.1 summarizes the main structural features of the hemicelluloses in both softwoods and hardwoods [Sjöström, 1993].

Wood species	Hemicellulose type	Amount (on % dry wood basis)	Composition			DP
			Units	Molar ratios	C-C Linkage	
Soft wood	Galactoglucomannan	5-8	β-D-Man*p* β-D-Glc*p* α-D-Man*p* Acetyl	3 1 1 1	1 → 4 1 → 4 1 → 6	100
	(Galacto)-glucomannan	10-15	β-D-Man*p* β-D-Glc*p* α-D-Man*p* Acetyl	4 1 0.1 1	1 → 4 1 → 4 1 → 6	100
	Arabinoglucuronoxylan	7-10	β-D-Xyl*p* 4-O-Me-α-D-Gal*p*A α-L-Ara*f*	10 2 1.3	1 → 4 1 → 2 1 → 3	100
Hard wood	Glucuronoxylan	15-30	β-D-Xyl*p* 4-O-Me-α-D-Gal*p*A Acetyl	10 1 7	1 → 4 1 → 2	200
	Glucomannan	2-5	β-D-Man*p* β-D-Glc*p*	1-2 1	1 → 4 1 → 4	200

Table 2.1 The Major Hemicellulose Components in Wood

The major hemicellulose in hardwoods is O-acetyl-4-O-methylglucurono-β-D-xylan, also known as glucuronoxylan. Glucuronoxylan along with arabinoglucuronoxylan in softwoods, are simply termed “xylan”. The content of xylan in hardwood varies from 15 to 30% of the dry wood depending on the hardwood species. Besides xylans, hardwoods also contain 2-5% glucomannan.

Glucuronoxylan has a backbone consisting of β-D-xylopyranose units. The monomeric sugars are linked by (1→4) glycosidic bonds. The O-acetyl groups are mostly located at C-2 and/or C-3 position. There are seven (7) O-acetyl groups per 10 xylose units. In addition, the backbone also carries α-(1→2)-linked, 4-O-methylglucuronic acid residues in the ratio of one group of 4-O-Methyl glucopyranosyl uronic acid per 10 xylopyranose units

(Figure 2.2). Hardwood xylan, unlike the softwood xylan, does not have arabinose side chains [Sjöström, 1993].

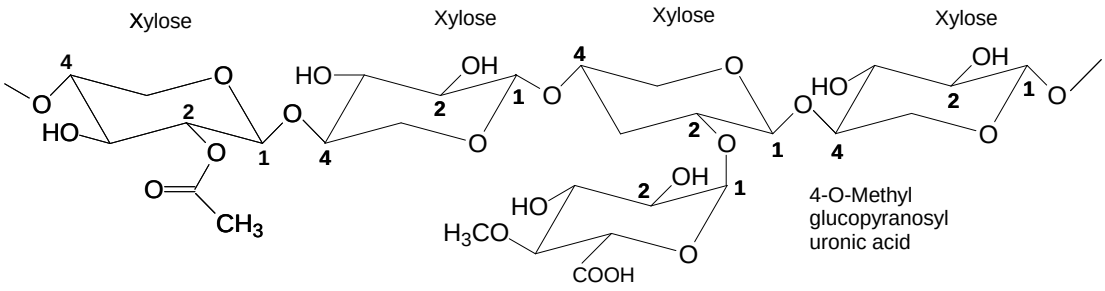


Figure 2.2 Structure of Hardwood Glucuroxylan

2.2.3 Lignin

Lignin is comprised of phenylpropane units that may be oxygenated on any of the side chain positions (Figure 2.3). The ring contains one or two methoxy groups at C-3 or C-4 positions and the C-4 position is linked to either an ether or free hydroxide group.

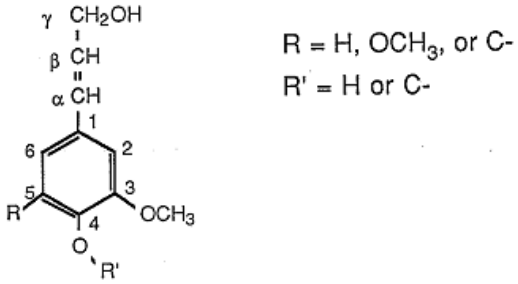


Figure 2.3 Structure of Phenylpropane Unit

The phenylpropane units are randomly cross-linked to each other by a variety of different chemical bonds. These linkages include both C-O-C (ether) and C-C (carbon carbon) linkages. The ether types of linkages represent two thirds or more of the total; while the rest are of the carbon to carbon type. Table 2.2 summarizes various lignin linkages and approximate occurrence of each type of linkage [Fengel and Wegener, 1984].

Linkage type	Dimer Structure	Percent of the total linkages in Hardwood
β-O-4	Aryglycerol- β-aryl ether	60
α-O-4	Noncyclic benzyl aryl ether	7
β -5	Phenylcoumaran	6
5-5	Biphenyl	5
4-O-5	Diaryl ether	7
β -1	1,2-Diaryl propane	7
β - β	Linked through side chains	3

Table 2.2 Proportions of Different Linkages Connecting Phenylpropane Units

2.2.4 Wood Ultrastructure

Of the three cell wall components, cellulose has a partially ordered crystalline structure, whereas the hemicelluloses and lignin are amorphous. Because of regular hydrogen bonds, the cellulose chains are ordered to form macro-fibrils. Figure 2.4 shows the association between cellulose, hemicellulose and lignin in the cell wall of wood [Sixta, 2006].

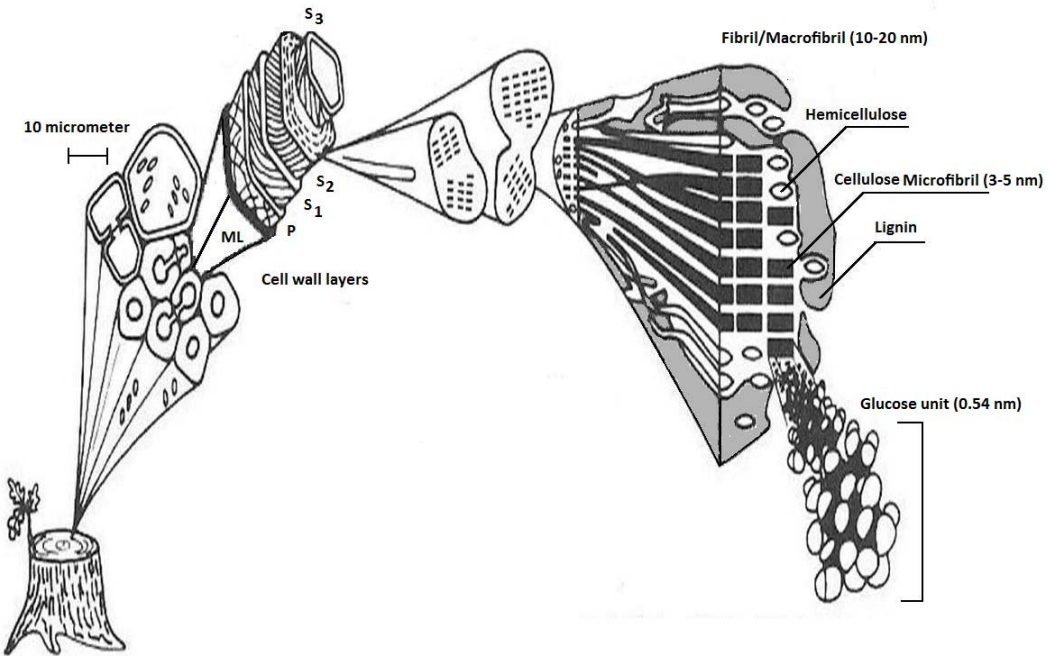


Figure 2.4 Fibrillar Structure of the Cell Wall Layers

2.3 Hydrolysis of Acetyl Groups

The hydrolysis of acetyl (ester) group is a nucleophilic substitution reaction where a nucelophile (OH^- or H_2O) attacks the electron deficient carbon atom of the carbonyl group [Carey, 2003].

2.3.1 Hydrolysis of Acetyl Groups in Alkaline and Acidic Medium

Figure 2.5 shows the mechanism of base catalyzed hydrolysis of O-acetyl groups. Due to the strong nucleophilicity, hydroxide ions can spontaneously attack weakly electrophilic carbonyl carbon atom of acetyl group and form a tetrahedral intermediate. This intermediate then collapses with loss of the leaving group. Finally, the leaving group (OX^-) functions as a base and deprotonates the acetic acid.

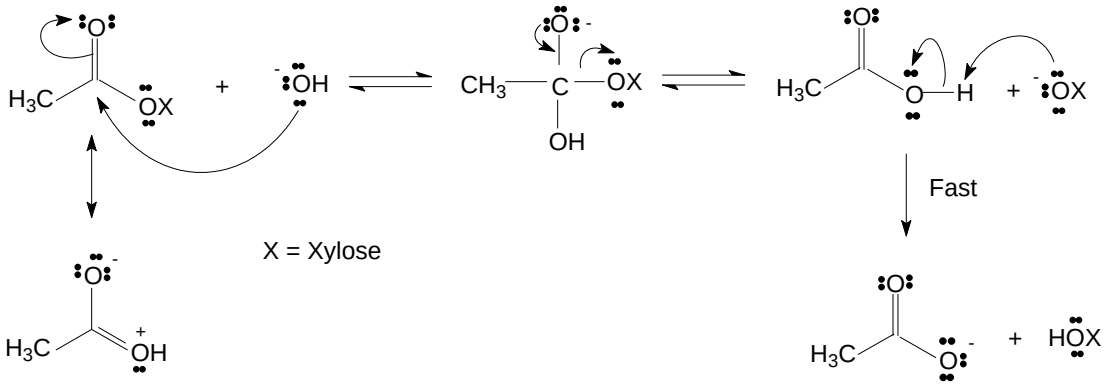


Figure 2.5 Mechanism of Hydrolysis of Acetyl Groups in Alkaline Medium

Figure 2.6 shows the acid catalyzed cleavage of acetyl groups. Strong acids such as HCl or H_2SO_4 can reversibly protonate carbonyl group, and the protonation further polarizes the pi-bond on the carbonyl group. The protonated carboxylic group then becomes extremely susceptible to attack by even a weak nucelophile such as alcohol or water. Thus, water molecule can then attack the carbonyl carbon atom to form a tetrahedral intermediate which upon further protonation results in the loss of leaving group and forms acetic acid.

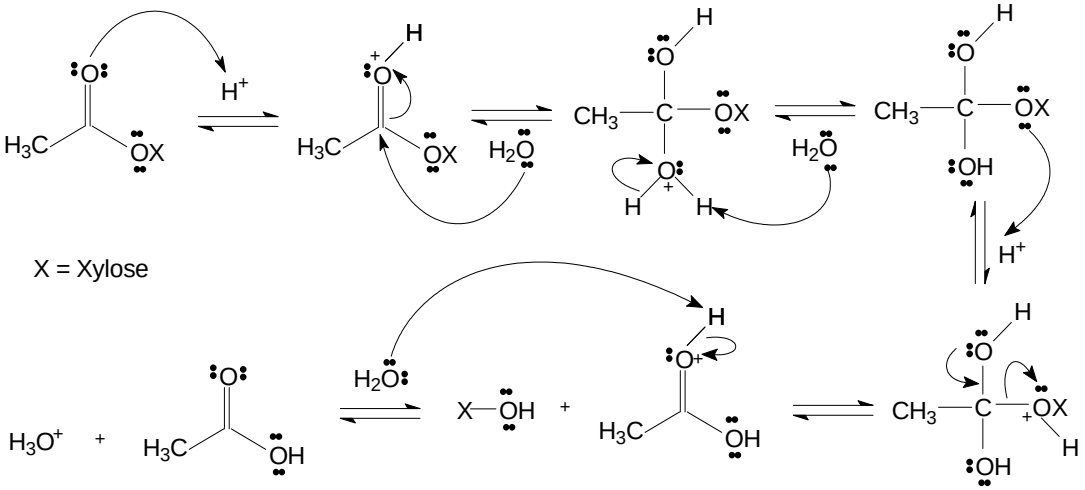


Figure 2.6 Mechanism of Hydrolysis of Acetyl Groups in Acidic Medium

It should be noted that the acid catalyzed hydrolysis of acetyl groups is a reversible reaction because hydrogen ion gets regenerated at the end of the deacetylation reaction. By contrast, the alkali catalyzed hydrolysis of acetyl groups is reversible because hydroxide ion gets attached to the xylan.

2.3.2 pH vs pKa Relationship for Acetic Acid

Acetic acid is a weak acid and its pKa is 4.8 [Walton, 2010]. Figure 2.7 shows the effect of pH on ionization of acetic acid.

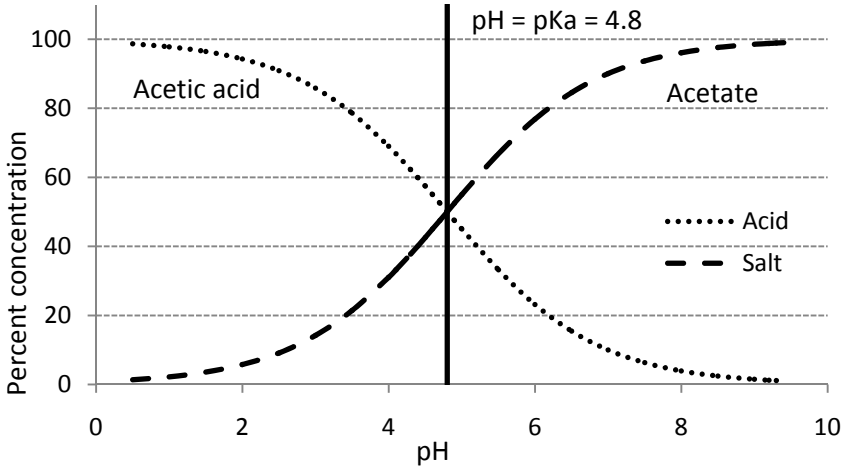


Figure 2.7 Effect of pH on Ionization of Acetic Acid

The equilibrium concentration of acetic acid is governed by equation 2.3:

$$pH = pK_a + \log \frac{\left[CH_3COO^-\right]}{\left[CH_3COOH\right]} \quad \text{.....Equation (2.3)}$$

2.3.3 Behaviour of Acetyl Groups during Kraft Pulping

Softwood Pulp: In softwoods, the removal of acetyl groups from dissolved O-acetyl glucomannan results in a crystalline ordered structure of glucomannan through increased hydrogen bonding between these polymers. The solubility of glucomannan in water is reduced due to its crystallization and it becomes absorbed onto cellulose surfaces, thus improving its papermaking properties [Laffend and Swenson 1968a].

However, in Kraft pulping, the deacetylated glucomannan is further dissolved by hydrogen bonding with hydroxide groups that are present in the high pH liquor. However, towards the end of the cook, as the pH of the pulping liquor is reduced, glucomannan remaining in the cooking liquor becomes less soluble and becomes sorbed onto the cellulose in the pulp [Laffend and Swenson 1968a]. This is referred to in Kraft parlances as "hemicellulose redeposition".

The effect of glucomannan acetyl content on papermaking properties was investigated by adding the same amounts of acetylated and deacetylated glucomannan into two pulp samples. The performance of individual pulp samples after addition of glucomannan was compared with that of a control cook. It was found that pulps containing glucomannan had improved strength properties relative to that of the control. The pulp containing deacetylated glucomannan showed slightly higher tear strength, breaking length and tensile energy absorption (TEA) values. The higher strength properties of pulp containing the deacetylated glucomannan was thought to result from increased fiber to fiber bonding and improved bond distribution [Laffend and Swenson 1968b].

Hardwood Pulp: For poplar hardwood, Zanuttini and co-workers (2005) demonstrated that the tensile strength of chemimechanical pulp increases with deacetylation resulting from

alkaline treatment on wood. The increased strength was considered to be due to the increased bonding between hemicelluloses and celluloses.

2.4 Diffusion of Alkali into Wood Chips

In softwoods, liquor penetrates through thin walled early wood tracheids, ray cells and the pits connecting them; whereas in hardwoods, liquor penetrates through vessels, fiber tracheids, longitudinal parenchyma and pits connecting them [Sjöström, 1993]. The hardwood vessels are wider (30-130 μm) than softwood tracheids (2-50 μm).

In order to ensure homogenous reaction rate inside wood chips, it is necessary to achieve a uniform concentration of chemicals and distribution of heat inside the wood chip. When the wood is added to the digester, the wood chips contain a significant amount of air in the interior. The air in the wood chips expands and diffuses outward during the cooking process. The outward diffusion of air creates an additional resistance for the inward penetration of alkali. Therefore, it is essential to remove the air from the chips before contacting them with the cooking chemicals.

To remove air from the wood chips, steam is applied at a point at which the chips are charged to the digester. This is done through steam packing in a batch digester, or in a steaming vessel in a continuous digester [Smook, 2002]. Following steaming, the wood chips are then impregnated with cooking liquor. The penetration of cooking liquor into wood chips occurs in two stages. The primary penetration occurs by flow of liquor into the wood chips and is controlled by the pressure difference between the liquor and the interior of the chips. The primary penetration also increases with cooking temperature due to a reduction in the viscosity of the liquor. The secondary penetration occurs through diffusion in completely soaked wood chips. Diffusion is controlled by the concentration gradient of ions and the effective capillary cross sectional area available for liquor penetration. Secondary penetration is often controlled by the outward diffusion of air entrapped in the chips; provided no pre-steaming was done previously.

The effective capillary cross-sectional area (ECCSA) is the area of paths available for diffusion (Stone, 1957). The ECCSA is a fraction between 0 and 1; and in essence is a correction factor to the nominal area of the chip. The ECCSA factor when multiplied by the nominal chip area gives the true area available for diffusion. The ECCSA for wood samples can be estimated by measuring the ratio of the ion transport capacity of the wood and the conductivity of the liquid medium. This technique is illustrated in Figure 2.8. This method was originally proposed by Stone (1957). The ECCSA of wood is around 50 % of the geometric area in the longitudinal direction and much less in the radial (10%) and tangential (6.5%) direction. Thus, if one measures the nominal area of the chip, this area is much larger than the actual area available for diffusion (and liquid penetration) into the chip.

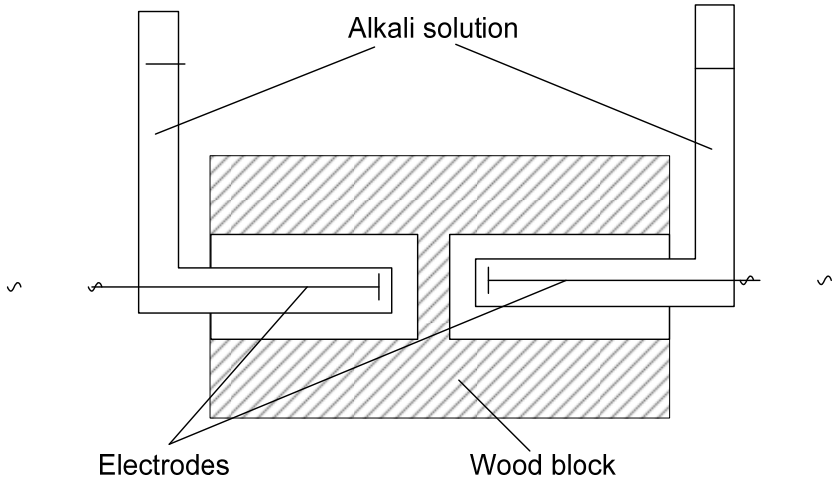


Figure 2.8 Measurement of ECCSA

Stone (1957) has shown that for a 3.1 mm thick eucalyptus wood chip, the ECCSA of wood becomes equal in all three directions after 24 hours of soaking under strongly alkaline conditions; that is with pH values between 12.5-13.5 at 25 ^{0}C. This effect is due to swelling and opening of the cell wall capillaries under strongly alkaline condition.

Inalbon and co-workers (2008a) reported the effect of temperature on ECCSA in the tangential direction as a function of pH under alkaline conditions using 0.4 mm thick aspen chips. Figure 2.9 shows Inalbon's data for the ECCSA of aspen chips at 20 ^{0}C, 45 ^{0}C and 90 ^{0}C

after 60 minutes of treatment as a function of the pH of the liquid. In Figure 2.9, Inalbon (2008a) included the results reported by Stone (1957) for reference. The results obtained at the lower temperatures (20-45 ^{0}C) are in agreement with Stone's results. A steep decline in the ECCSA curves occur as the pH of the liquor is lowered from 12.5-13 to 10.5-11 when the temperature is raised from 25 ^{0}C to 90 ^{0}C. The reason for this shift in the ECCSA curve is thought to result from the high reactivity of the wood components at high temperature. The specimens used by Stone (1957) were thicker than those used by Inalbon (2008a); hence they required longer stabilization time.

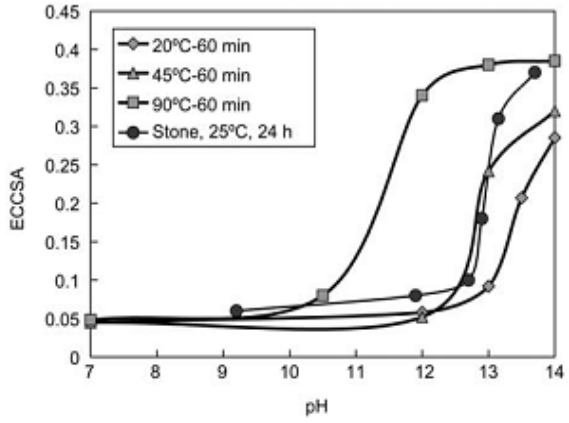


Figure 2.9 ECCSA in Tangential Wood Direction vs pH

Inalbon (2008a) also reported the effect of temperature and alkali concentration on the ECCSA values for the tangential direction of the wood samples as a function of the acetyl group content in wood. Figure 2.10 illustrates that for high temperature and high levels of deacetylation, the ECCSA values for the wood increase significantly; whereas the data in Figure 2.11 shows that the deacetylation is a determining factor in the ECCSA value of wood. The alkali action is indirectly exerted through the deacetylation reaction. The alkali concentration does not have a direct effect on the ECCSA above a certain threshold value [Inalbon, 2008a].

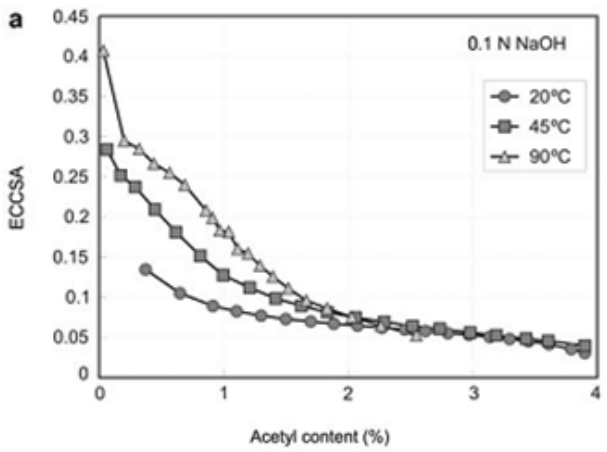


Figure 2.10 Effect of Temperature on ECCSA in Tangential Wood Direction

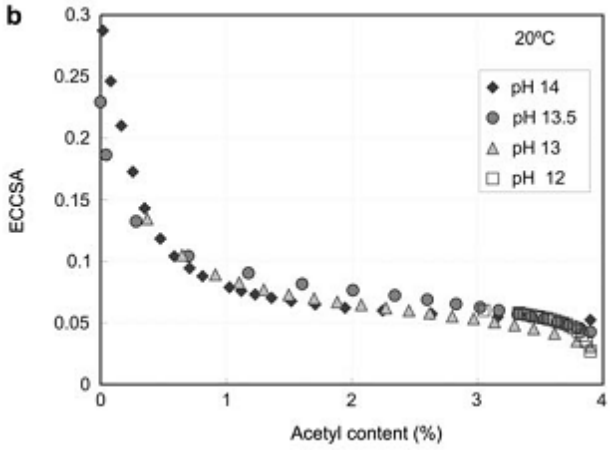


Figure 2.11 Effect of Alkali Concentration on ECCSA in Tangential Wood Direction

Consequently, ECCSA was experimentally correlated to acetyl content and temperature through an empirical equation shown as equation 2.4 (Inalbon, 2009).

$$ECCSA = a + b\left(C_{Acetyl}\right) - c\left(C_{Acetyl}\right)^{3} - d\left(C_{Acetyl}\right)T + e\left(C_{Acetyl}\right)^{2}T + fT \quad \text{.....Equation (2.4)}$$

Where,(C_{Acetyl}) is the acetyl group content in the wood, (T) is the temperature, and the constants(a, b, c, d, e ,f) are empirically evaluated from the experimental data.

2.5 Advantages of Recovery of Acetyl Groups

There are three advantages to the deacetylation of the hemicellulose which will be reiterated here for clarity.

Facilitation of the Fermentation Process: The acetic acid alone or in mixture with other inhibitors can hamper the ethanol fermentation process, which necessitates the removal of acetic acid from the fermentation feedstock. As acetic acid is lipophilic, it can diffuse through the cytoplasmatic membrane and can detrimentally affect cell metabolism [Lohmeier-Vogel and co-workers, 1998]. Although the effect of acetic acid can be reduced by conducting the fermentation at high pH (above or around 7.0), fermentation at this pH range gives low yields.

Economic Benefits: In the Kraft pulping process, the acetyl groups usually end up in the recovery boiler where they are burned for generating steam and electricity. Since, the chemical value of acetyl groups is much higher than the value of its energy content, the separation of acetyl groups can potentially provide economic benefits and can increase the economic competitiveness of the struggling pulp mills

Improved Penetration: When the acetyl groups are removed from wood, the penetration of pulping liquors will improve, and this potentially could reduce the amount of shives and increase the screened yield of the brownstock pulp.

2.6 Selection of Chemical Agent for Hydrolysis of Acetyl Groups

As discussed previously, the recovery of acetic acid from wood biomass needs to be integrated into existing Kraft pulp mill. Consequently, it is expected that the any chemical agent used for recovery of acetyl groups must not adversely affect the pulp yield and properties. It has already been shown that the use of dilute alkali streams, that are available in kraft pulp mills, such as green liquor and caustic for pre-extraction of wood, does not affect pulp yield and properties severely [Walton, 2010 and Yoon, 2011]. However, it should be noted that due to the cost of NaOH, the dilute NaOH pre-extraction may not be

economically feasible for a Kraft pulp mill. One would have to balance the capital and operating cost for the process against the revenues received from the acetic acid.

2.7 Previous Work

The intrinsic kinetics of the alkaline deacetylation reaction using milled cottonwood has been reported by Zanuttini and coworkers (1997). According to the kinetics, the intrinsic rate of cleavage of acetyl groups from wood hemicelluloses is 2^{nd} order with respect to acetyl content and 1.35^{th} order with respect to NaOH concentration. The kinetic rate expression for cleavage of acetyl groups from wood hemicellulose is

$$r = - k C_{Acetyl}^{2} C_{NaOH}^{1.35} \quad \text{.....Equation (2.5)}$$

where (C_{Acetyl}) is the concentration of acetyl groups in the wood, (C_{NaOH}) is the caustic concentration of the solvent, and (k) is the rate constant.

Inalbon and coworkers (2009) have reported a model for the diffusion of sodium hydroxide into wood and its reaction with acetyl groups. The mathematical results obtained from the model were in agreement with the experimental data obtained for 4 mm thick eucalyptus wood chips contacted with caustic liquor at very high liquor to wood ratio. In Kraft pulping, full strength white liquor cleaves off most acetyl groups during the heat-up period [Rydholm, 1965]. Walton (2010) and Luo (2012) have reported data on the concentration of component sugars, lignin, formic acid, lactic acid and acetyl group following extraction of industrial wood chips using green liquor as the solvent.

It is well known that the alkali streams available in Kraft pulp mill can be used to hydrolyze acetyl groups in wood hemicelluloses. However, the rate of cleavage of acetyl groups from industrial wood chips for various charges of white liquor, green liquor and caustic has not yet been determined. Data of this type would be helpful to optimize the

process for recovery of acetic acid or alkali acetate following extraction in Kraft pulp mills being considered as a biorefinery.

CHAPTER 3

EXTRACTION EXPERIMENTS USING INDUSTRIAL WOOD CHIPS

This chapter contains information about wood chips and chemicals used in the experiments, reactor setup, types of experiments performed and analytical methods.

3.1 Materials

All experiments were performed using mixed northeastern hardwood chips obtained from a local pulp mill. Wood chips were mostly a mixture of maple (66%), birch (26%) and beech (12%). The moisture content in the chips was about 37.5 to 40%. The acetyl group content was estimated to be about 3.5-4% on an oven dry basis. The chip length and thickness distribution of the samples was representative of chips used in Kraft pulp mills (Figure 3.1). Since the wood chips were already screened for maximum and minimum allowable thickness in the mill, no additional screening was performed in the laboratory.

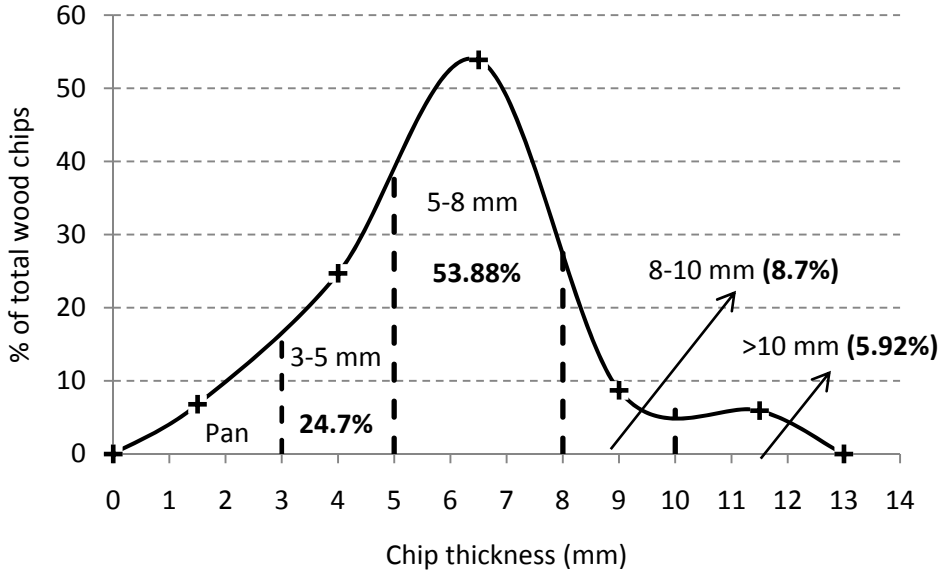


Figure 3.1 Chip Thickness Distribution

For each sample of chips received from the mill, the solid content, % acetyl groups, lignin content and the thickness distribution were analyzed to ensure uniformity of chips in all experiments. Chemicals used in the extraction experiments such as NaOH (100% pure),

Na_2S (61.5% pure), Na_2CO_3 (100% pure) were of the industrial grade. Standards used for calibration in the analytical work were of the analytical grade. The composition of white liquor is expressed as a percentage of effective alkali charge based on dry wood mass expressed in terms of grams of sodium oxide [Sjöström, 1993]. The causticizing efficiency of white liquor was assumed to be 76.4 percent. Table 3.1 shows the composition of the green liquor used in this investigation [Mao, 2010]

Chemicals	**Composition**
Sodium Hydroxide (NaOH)	9.0 gm/L as Na_2O
Sodium Sulfide (Na_2S)	29.1 gm/L as Na_2O
Sodium Carbonate (Na_2CO_3)	70.0 gm/L as Na_2O
Total Titratable Alkali (TTA)	108.1 gm/L as Na_2O

Table 3.1 Chemical Composition of Green Liquor Used in the Experiments

All experiments were carried out at the constant liquor to wood ratio (L/W) of 4 L/Kg, which is representative of commercial Kraft pulping. Mathematically, liquor to wood ratio is represented as:

$$r = \left(\frac{m_{liquor} + m_{water\ in\ wood}}{m_{dry\ wood}} \right) = \left(\frac{grams\ of\ liquor}{grams\ of\ dry\ wood} \right) \quad \text{.....Equation (3.1)}$$

Where m_{liquor} is the mass of cooking liquor, $w_{water\ in\ wood}$ is the mass of water in the wood chips, and $m_{dry\ wood}$ is the mass of dry wood added to the extraction vessel.

3.2 Experimental Setup

All extraction experiments were carried out in a seven-liter, externally heated, laboratory scale circulating digester located in the Process Development Center at the University of Maine. This digester had been designed previously to simulate conventional

large scale digesters used in kraft pulp mills. Hence, it was chosen for the current study. Figure 3.2 shows a schematic diagram of the digester.

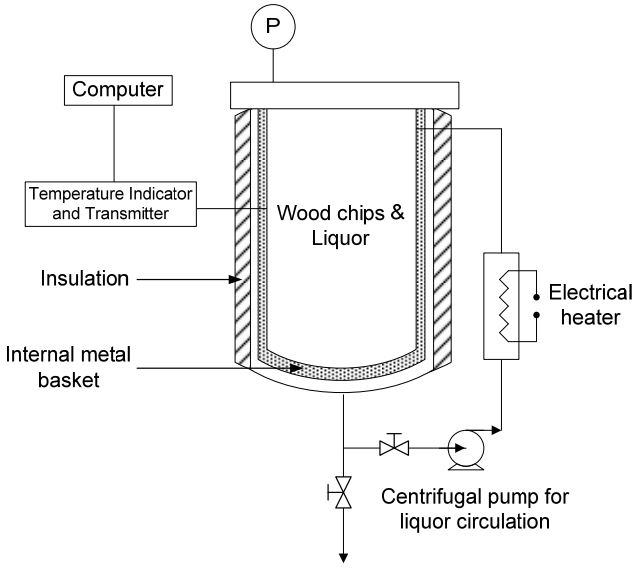


Figure 3.2 Laboratory Scale Circulating Digester

The digester has an internal metal basket which holds the wood chips. A centrifugal pump circulates liquor through an external heater. The basket has a metal screen at the bottom to prevent wood chips from going into the pump. The digester has both temperature and pressure indicators. To begin the extraction, the desired amount of wood chips and liquor solution were placed in the digester. The liquor circulation pump was then turned on. The set point for digester temperature was adjusted as per the temperature-time requirements of each experiment. Ten (10 mL) samples of the extraction liquor were taken all along the heat-up and top-temperature extraction periods. A sufficient number of samples were taken to define the time versus concentration de-acetylation curve. At the end of the extraction period, the digester was cooled to below 100 ^{0}C. When the digester pressure was below 5 psi, the digester lid was opened and the extract was drained. The mass of drained extract was recorded. A sample of drained liquor was preserved for further analysis. Macerated wood chips were removed from the digester after draining the extract.

These chips were then weighed and stored in a plastic bag for subsequent analysis of the acetyl content in the wood. The experimental parameters evaluated in this study were the time, soaking temperature, alkali concentration, extraction temperature and chip thickness. To facilitate study of these variables, different sets of experiments were carried by varying the parameter under study and keeping other parameters constant (Table 3.2).

Experiment No.	**Wood charge(oven dry basis) , Liquor type**	**L/W Ratio**	**Time-Temperature Ramp**
Effect of soaking(pre-treatment) condition			
1	800 gms, 0.5N NaOH	4	**30 minutes soaking at 27 ^{0}C** followed by extraction at 160 ^{0}C
2	800 gms, 0.5N NaOH	4	**30 minutes soaking at 120 ^{0}C** followed by extraction at 160 ^{0}C
3	800 gms, 0.5N NaOH	4	**No soaking,** extraction at 160 ^{0}C
Effect of alkali concentrations			
4	800 gms, **2 % Green Liquor** (on TTA basis)	4	15 Minutes soaking at 113 ^{0}C followed by 90 minutes extraction at 165 ^{0}C
5	800 gms, **8 % Green Liquor** (on TTA basis)	4	15 Minutes soaking at 113 ^{0}C followed by 90 minutes extraction at 165 ^{0}C
6	900 gms, Full Strength White liquor (**15.9 % EA**)	4	15 Minutes soaking at 113 ^{0}C followed by 90 minutes extraction at 165 ^{0}C
7	900 gms, Half Strength White liquor (**8 % EA**)	4	15 Minutes soaking at 113 ^{0}C followed by 90 minutes extraction at 165 ^{0}C
Effect of extraction temperature			
8	900 gms, Half Strength White liquor (8 % EA)	4	15 Minutes soaking at 113 ^{0}C followed by 90 minutes extraction at **120 ^{0}C**
9	900 gms, Half Strength White liquor (8 % EA)	4	105 minutes extraction at **100 ^{0}C**
10	900 gms, Half Strength White liquor (8 % EA)	4	105 minutes extraction at **80 ^{0}C**
11	900 gms, Half Strength White liquor (8 % EA)	4	105 minutes extraction at **50 ^{0}C**

Table 3.2 List of Experiments

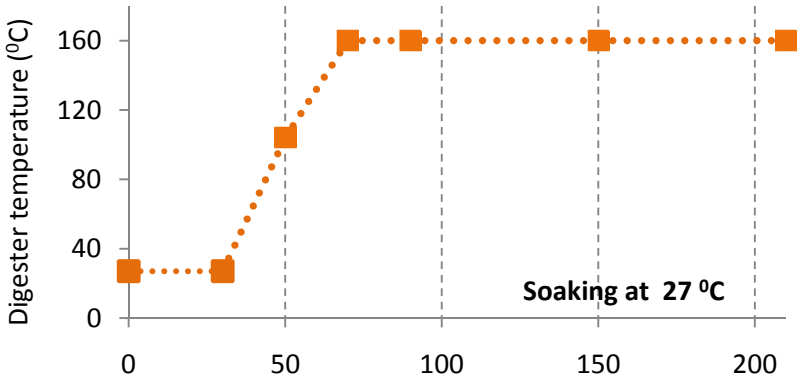
The weight of the wood chips was about 800-900 grams for all experiments. This mass of wood chips ensures that the digester was filled with wood, liquor and a small vapor space. Also, the chips were completely immersed in cooking liquor.

3.2.1 Experiments to Study the Effect of Soaking Conditions

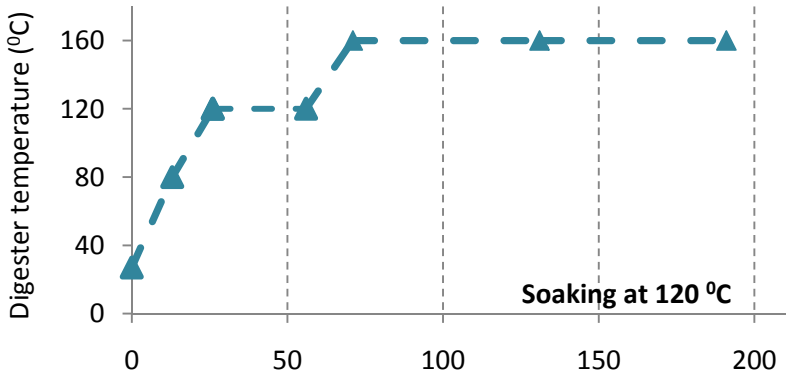
The wood chips used in the extraction experiments were soaked in dilute alkali for 30 minutes at the different temperatures shown in Table 3.2. The purpose of the soaking experiments was to study the effect of liquor penetration into the wood chips on the cleavage of acetyl groups from the hemicellulose polymers. Experiment No. 1, 2 and 3 were conducted by varying the soaking conditions: (1) 30 minutes soaking at 27 ^{0}C, (2) 30 minutes soaking at 120 ^{0}C and (3) no soaking.

The ambient temperature while performing all experiments was about 25-30 ^{0}C. The 27 ^{0}C soaking temperature was selected to study the effect of soaking under ambient conditions on the rate of cleavage of acetyl groups from wood chips. Soaking at 120 ^{0}C was intended to simulate the low pressure steaming process in pulp mills. Finally, the no soaking condition was chosen to simulate the liquor penetration into the wood chip during the heat-up period in a digester. The extraction temperature of 160 ^{0}C was based on experimental data for hemicellulose pre-extraction reported by Luo (2012) and Walton (2010). The alkali concentration of 0.5 N NaOH was selected to operate the pre-extraction process within the pH range of Kraft pulping liquor. The 0.5N NaOH concentration was also based on Inalbon's experimental parameters for studying deacetylation of 4.4 mm thick wood chips (Inalbon, 2009).

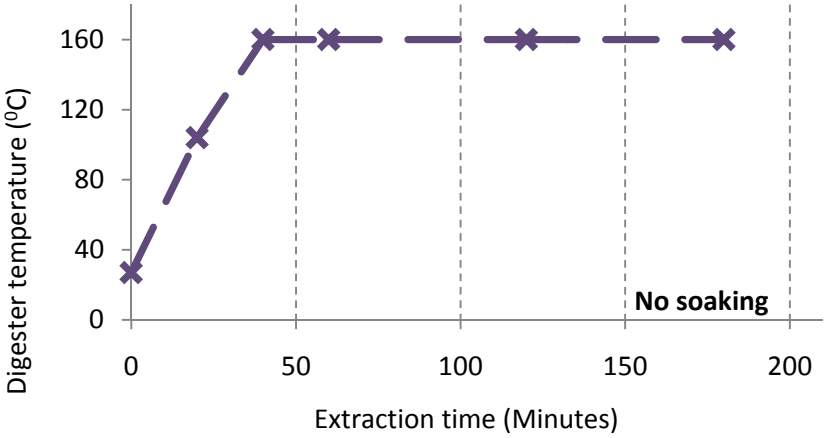
Figure 3.3 shows the time-temperature ramp for each of these experiments. The symbols marked on these plots show the points at which the extract samples were removed from the digester.



A Soaking At 27 ^{0}C



B Soaking at 120 ^{0}C



C. No Soaking Condition or Liquor Penetration during Heat Up Period

Figure 3.3 Temperature Ramp for Different Soaking Conditions

3.2.2 Experiments to Study the Effect of Alkali Type and Charge

A second set of experiments was performed by varying the alkali concentrations and type of alkali used for extraction. These experiments were designated No. 4, 5, 6 and 7. Alkali evaluated were (1) 2% Green Liquor, (2) 8% Green Liquor, (3) 8% White Liquor and (4) 15.9 % White Liquor. The different charges of green liquor and white liquor used in the experiment represent upper and lower limit on respective alkali type, which can be used in the extraction of the wood chips. Figure 3.4 shows the time-temperature ramp for these experiments. The 30 minute soaking time was reduced to 15 minutes to more accurately represent chip steaming time that takes place in a continuous digester producing Kraft brown stock. This change in the experimental protocol was made at the suggestion of a process engineer who works in a local Kraft pulp mill. The final point on the time versus temperature ramp, 113 ^{0}C, represents the blow tank temperature; where the mixture of superheated vapour and wood chips were discharged at a reduced pressure (Figure 3.4).

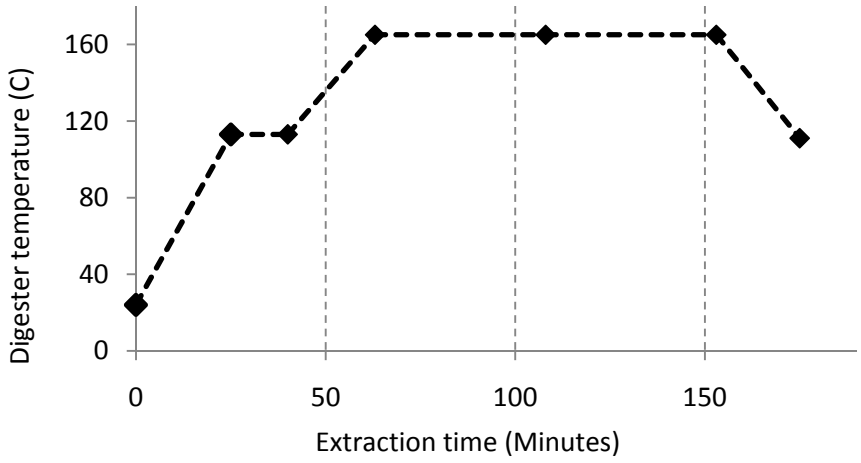


Figure 3.4 Time Temperature Ramp for Alkali Concentration Effect Studies

3.2.3 Experiments to Study the Effect of Extraction Temperature

Based on the results of the variation in alkali charge, 8% white liquor was found to be suitable for recovery of acetyl groups and was chosen for studying the effect of the extraction temperature. Optimization of extraction temperature allows minimizing the energy requirements for process and reduces unwanted side reactions.

The effect of the extraction temperature was studied by performing a third set of experiments (Experiment No: 8, 9, 10 & 11). The extraction temperatures for each of these experiments were 120 ^{0}C, 100 ^{0}C, 80 ^{0}C and 50 ^{0}C, respectively. Figure 3.5 shows the time-temperature ramp for these experiments. Soaking at 113 ^{0}C increases the efficiency of high temperature extractions such as 150 -170 ^{0}C. However, for extraction temperatures below 120 ^{0}C, 113 ^{0}C soaking was excluded from the ramp and the total extraction time was increased by 15 minutes.

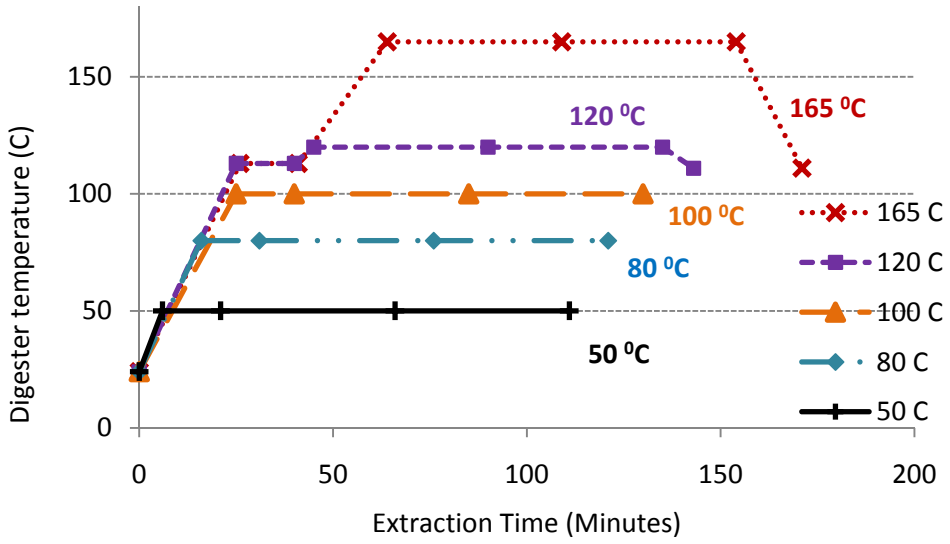


Figure 3.5 Time Temperature Ramp For Extraction Temperature Effect Studies

3.3 Analytical Methods

Following the extraction, the macerated wood chips were analysed for solid content, organic content and acetyl content. The extract samples were analysed for solid content, organic content, organic acids, sugars and lignin. Figure 3.6 shows the scheme followed for

analysis of wood extract and wet macerated wood chips in the current study. Mass balance calculations were performed to estimate the content of acetyl groups and the overall wood mass (solids). Details of the mass balance calculations are provided in Appendix E.

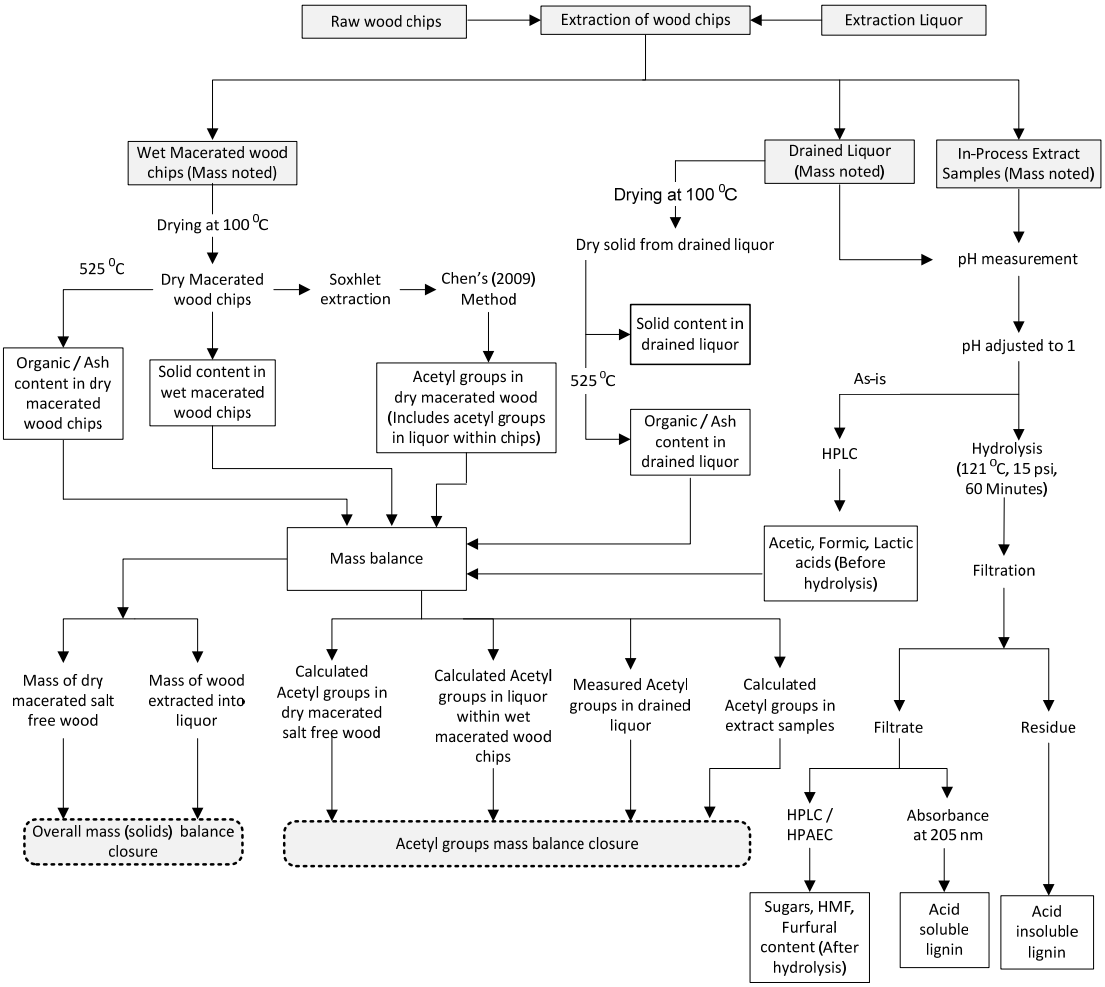


Figure 3.6 Scheme for the Analysis of Wood Extracts and Wet Macerated Wood

3.3.1 Analysis of Raw Wood Chips

All mixed northeast hardwood samples were received from a local mill. These chip samples were stored in polythene bags in a refrigerator to preserve the original moisture content in the wood chips. A sample of raw wood chips was analyzed for solid content by drying it in a 100 ^{0}C oven until constant weight of solid residue was obtained. In a similar manner, the ash content was measured by combustion at 525 ^{0}C followed by gravimetric analysis of the residue [TAPPI standard method T211 om-85]. Dry wood chips obtained

following the drying at 100 ^{0}C were ground in a Wiley mill to obtain wood meal that passed a 20 mesh screen. The wood meal was then extracted in a soxhlet extraction apparatus using acetone to obtain extractive-free wood meal. The extractive-free wood meal was then used to determine the acetyl and the lignin content in the raw wood. The acid insoluble lignin content was determined gravimetrically according to the method of Effland (1977). The acid soluble lignin content was determined by following Tappi Useful Method 250. The acetyl content in the raw and macerated wood was determined by extraction with caustic following the method described by Song et al. (2008).

3.3.2 Analysis of In-Process Wood Extracts and Drained Liquor

The mass of drained liquor was measured after it was collected. All extract samples were stored in the refrigerator prior to analysis. The extract pH was measured using a pH meter after calibrating it using buffer at pH values equal to 4 and 10. Solid and ash content was measured as described previously. The solid and ash content were used to calculate the amount of wood extracted into the liquor.

Organic Acids: It was found that the organic acids are lost during the acid hydrolysis of highly alkaline (pH>12) wood extracts. Consequently, organic acids were measured using samples of unhydrolyzed extract. Additionally, the High Performance Liquid Chromatography (HPLC) column used in this study could only separate and analyze organic acids in their protonated form. Thus, it was necessary to adjust the pH of all samples to a pH of one (pH=1) to protonate the acids. The sodium acetate neutralization reaction is:

$$CH_3COO^-Na^+ + HCl/H_2SO_4 \rightarrow CH_3COOH + NaCl/Na_2SO_4 \quad \text{---Equation (3.2)}$$

All samples were diluted 5 times to ensure that the final concentrations fell in the calibration range of the HPLC instrument. In order to prevent the HPLC column from becoming clogged with solids, all samples were either filtered using 0.45 um syringe filter or centrifuged at 14,000 RPM for 10 minutes to remove solid particles prior to being injected into the HPLC

instrument. The HPLC system (Shimadzu) consisted of a Bio-Rad Aminex HPX-87H column (CTO-10A), a Shimadzu RID detector, an autosampler (SIL-20AC) and a pump (LC-10AT). The HPLC was operated using 5 mM H_2SO_4 solution as a mobile phase at the flow rate of 0.6 ml/minute. The column was maintained at a temperature of 60 ^{0}C.

Hydrolysis of Wood Extracts: Wood extract contains most sugars in oligomeric form [Luo, 2012]. Therefore, it was necessary to hydrolyze the extract to convert carbohydrate oligomers into sugar monomers for analysis using the HPLC. In the present study, extracts were hydrolyzed after adjusting their pH to 1 using 72% H_2SO_4 [Tunc, 2008]. The hydrolysis was then carried out for 1 hour at 121 ^{0}C and 15 psi in an autoclave located in the Process Development Center at the University of Maine. After hydrolysis, the extract was allowed to cool to room temperature and returned to the original mass by adding few drops of water.

Acid Insoluble and Acid Soluble Lignin: The acid insoluble lignin in the sample was determined by gravimetric analysis by filtering the hydrolyzed extract and drying the solid at 105 ^{o}C. The acid soluble lignin was determined by UV absorbance of the filtrate at 205 nm using an extinction coefficient of 110 (L/g cm) for hardwoods [Alen and Hartus, 1988].

Monosugars, Furfural and HMF: The liquid obtained following the filtration of hydrolyzate was analyzed using the HPLC system to estimate component monosugars (glucose, arabinose, xylose, mannose and galactose) as well as furfural and the hydroxymethyl furfural (HMF) content. It should be noted that the xylose, mannose and galactose (XMG) peaks overlap and exit the HPLC system as a single peak. The methods used in this analysis have been described by Luo (2012).

3.3.3 Analysis of Wet Macerated Wood chips

Macerated wood chips were weighed and stored in a polythene bag after removal from the digester to avoid any loss in the liquor within the wood chips. The solid and ash content were determined as described previously. The solid and ash content were then used

to calculate amount of liquor held within the wet macerated wood chips. The acetyl group content was determined by following the method described by Song et al (2008).

CHAPTER 4

RESULTS AND DISUSSION

The Kraft process uses a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S) as the pulping liquor (white liquor), whereas the soda process uses concentrated sodium hydroxide (NaOH) solution in a similar capacity. Carbohydrate reactions with alkali are similar in both Kraft and Soda pulping since carbohydrate reactions are not influenced by the presence of sulphur compounds.

In highly concentrated NaOH solutions such as Kraft cooking liquor or soda cooking liquor, the initial consumption of alkali is mostly attributed to the neutralization of acid groups. The alkali is also consumed for swelling, dissolution of loosely bound sugar units without degradation, primary peeling reactions and stopping reactions which occur during heat-up period.

Once the temperature reaches 140-170 ^{0}C, alkali is consumed by secondary peeling reactions of newly generated shorter fragments [Rydholm, 1967]. In alkaline solutions, the hydrolysis of sugar chain occurs at the ends rather than at the random locations on the chain as observed in the dilute acidic hydrolysis. The alkaline hydrolysis of glycosidic bond occurs at a very slow rate compared to acid hydrolysis.

Apart from carbohydrate degradation reactions, lignin degradation reactions also consume significant amount of alkali. In soda pulping, OH^- acts as a nucelophile for delignification, whereas in Kraft pulping both hydroxide (OH^-) and bisulfide (HS^-) act as nucelophiles. The bisulfide ion accelerates delignification reactions due to its stronger nucleophilicity as compared to hydroxide ion [Sjöström, 1993].

In green liquor extraction, the hydroxide and the bisulfide ions undergo similar reactions as that in white liquor. The bicarbonate ions (HCO_3^-) cause deacetylation of hemicelluloses at intermediate pH and generate CO_2 which increases the internal pressure in the reactor.

In the figures shown in the results section, the error bar represents 95% confidence limit on a particular analytical measurement and means that there is a 95% probability that the given variable will fall between the specified limits.

4.1 Effect of Soaking Conditions

The experiments to determine the effect of soaking (pre-treatment) condition were carried out using 0.5 N NaOH (Table 3.1).

4.1.1 Effect of Soaking Conditions on Extract pH

Figure 4.1 illustrates the effect of soaking condition on the pH of the extract. The extract pH decreases as extraction proceeds further, indicating an increase in the consumption of alkali. In alkaline cooking process, all acid group neutralization reactions excluding deacetylation are considered to consume one fifth of the caustic that the deacetylation reactions consume [Inalbon, 2009]. In the present experimental conditions, the amount of sodium hydroxide charged (4% as Na_2O) is about twice the stoichiometric requirement for the neutralization of all acid groups in the wood such as acetyl and uronic acids. Hence, the extract pH remains almost constant during the heat-up period because of the high alkali concentration.

As discussed previously, at high temperature, carbohydrates undergo primary and secondary peeling reactions, which consume most of alkali. Thus, it is expected that a significant drop in pH would occur at high temperature. This effect can be observed in Figure 4.1, where the pH drop towards the end of the extraction process is substantial for all experiments.

It can also be observed in Figure 4.1 that, near the end of the extraction process, the extract pH varies depending upon the soaking condition employed. Soaking at 27 ^{0}C results in penetration of the less reactive cold liquor, and consequently the alkali consumption is lowest. By contrast, soaking at 120 ^{0}C or the no soaking condition leads to the penetration of

hot liquor, which is more reactive than cold liquor. The high alkali consumption was observed when soaking at 120 ^{0}C and the no soaking are thought be due to both increased reactivity and the increased amount of liquor penetrated at high temperature. Increased liquor penetration at high temperatures can be attributed to the reduction in viscosity at high temperature. Soaking at 120 ^{0}C is statistically different than the no soaking condition because calculated error bars do not overlap. Thus, it is apparent that soaking at 120 ^{0}C results in increased alkali consumption compared to the no soaking condition. Thus, overall alkali consumption decreases in the following order: Soaking at 120 ^{0}C, no soaking and soaking at 27 ^{0}C.

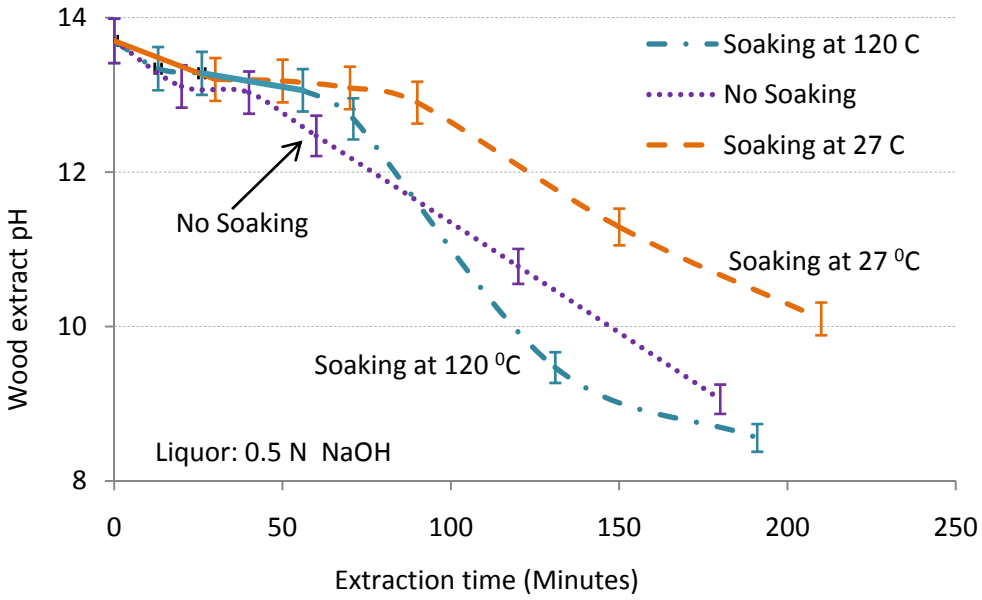


Figure 4.1 Effect of Soaking Conditions on Extract pH

4.1.2 Effect of Soaking Conditions on Acetic Acid Concentration in Extract

Figure 4.2 shows the effect of soaking condition on concentration of acetic acid in acidified wood extract as a function of time. The continuous lines in the plot illustrate the soaking period. As explained previously, the effectiveness of soaking condition decreases in following order: soaking at 120 ^{0}C, no soaking followed by soaking at 27 ^{0}C. It can be expected that the extent of alkali penetration also decreases in the same order. Accordingly,

soaking at 120 ^{0}C gives the highest acetic acid concentration; while soaking at 27 ^{0}C gives lowest acetic acid concentration. No soaking results in the intermediate acetic acid concentration. The maximum obtainable concentration was calculated by using amount of acetyl groups in raw wood and the liquor to wood ratio. This value represents an upper limit for acetic acid concentration in the acidified extract (Figure 4.2).

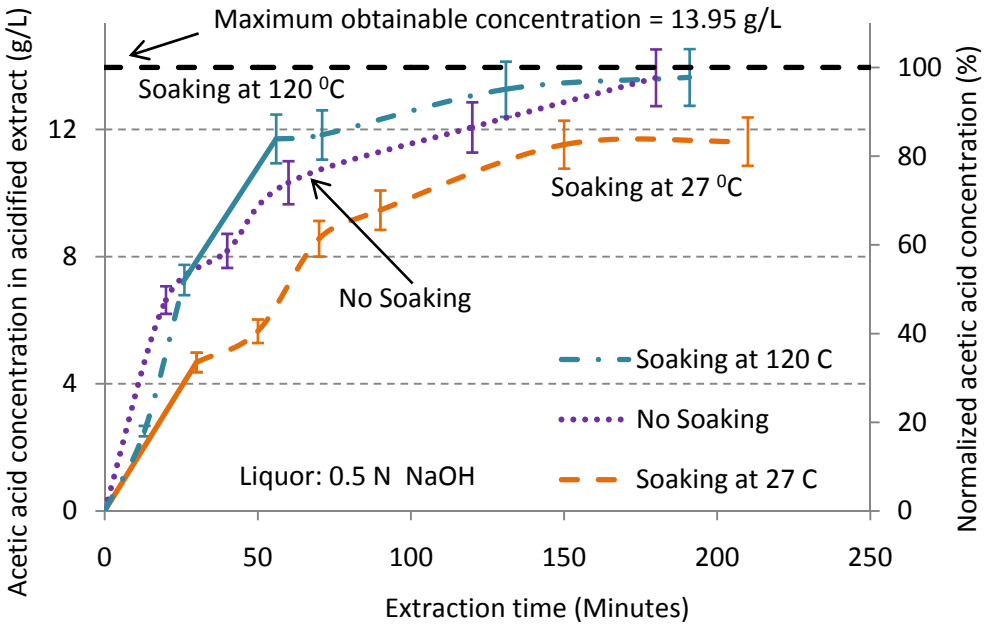


Figure 4.2 Effect of Soaking Conditions on Acetic Acid Concentration in Extract

4.2 Effect of Alkali Charge

As explained previously, effect of alkali charge was evaluated by using 2% green liquor, 8% green liquor, 8% white liquor and 15.9 % white liquor. The extraction temperature for these experiments was 165 ^{0}C.

4.2.1 Effect of Alkali Charge on Extract pH

The effect of alkali type and alkali charge on wood extract pH is shown in Figure 4.3. It can be observed from Figure 4.3 that the pH of the 15.9% white liquor extracts remains unchanged during the extraction period. The main reason for constant pH is the high initial concentration of caustic in the white liquor. The initial amount of the hydroxide ions in the

liquor is about 4.5 times the stoichiometric requirement for the neutralization of all acid groups in the wood. The second reason for the high pH is the limited consumption of cooking chemicals due to the short extraction time as compared to the normal Kraft cooking (5-6 Hrs) required for complete alkali consumption and dissolution of lignin at the same temperature conditions [Sjöström, 1993].

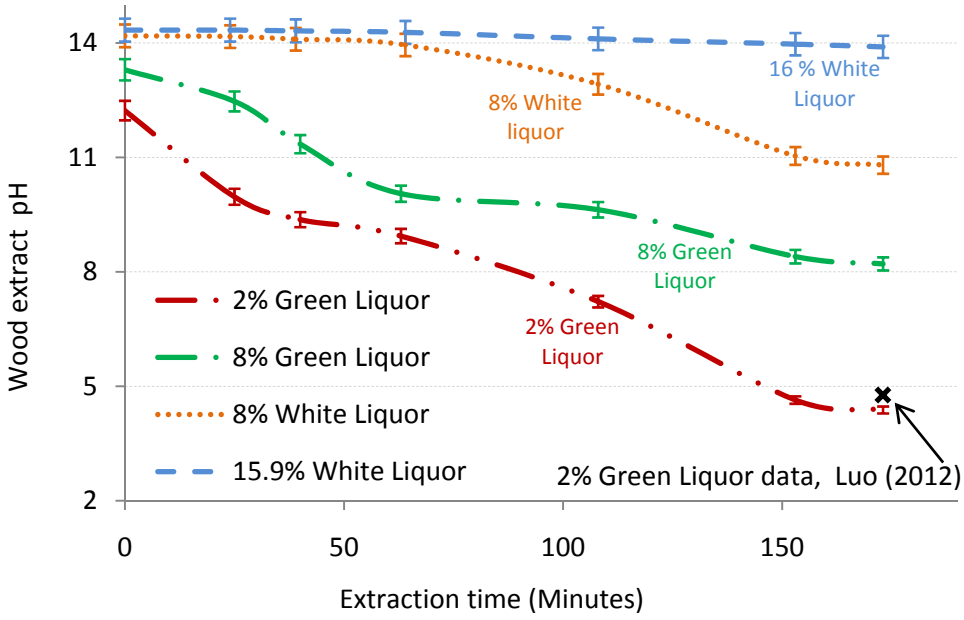


Figure 4.3 Effect of Alkali Charge on Extract pH

In 8% white liquor extraction, the initial amount of hydroxide ions in the liquor is about 2.25 times the stoichiometric requirement for the neutralization of all acid groups in the wood. Thus, the extract pH remains constant during the heat-up period. Further drop in the pH is due to the sugar and lignin degradation reactions.

The fresh green liquor contains mostly Na_2S and Na_2CO_3 and a very little amount of NaOH. Thus, the pH of the green liquor extracts was always lower than the white liquor extracts. The initial amount of hydroxide ions in the 8% and 2% green liquor are 0.57 and 0.14 times the stoichiometric requirement for acid group neutralization reactions, respectively. Therefore, the initial hydroxide ions are rapidly consumed. When all hydroxide

ions are depleted and the pH falls below 5, unreacted acetyl groups still attached to the hemicelluloses, are hydrolyzed by hydronium ion through the acid catalysed pathway of hydrolysis of esters.

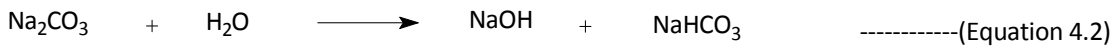
Below is the overall reaction scheme for hydrolysis of acetyl groups thought to be occurring.

Case 1.Deacetylation reaction in white liquor and 0.5 N NaOH [Carey, 2003]

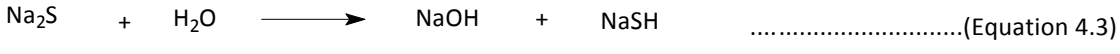
-----(Equation 4.1)

Case 2. Deacetylation reaction in green liquor

The deacetylation reaction in green liquor depends on the green liquor charge and the final pH. Luo (2012) has reported that the green liquor extract contains sodium acetate or acetic acid and CO_2 depending upon the extract pH. Consequently, the mechanism postulated here will depend upon the final pH. Both sodium carbonate and sodium sulfide react with water to generate additional hydroxide ions.

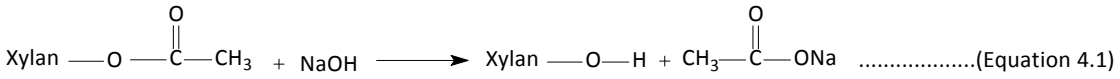


----------(Equation 4.2)



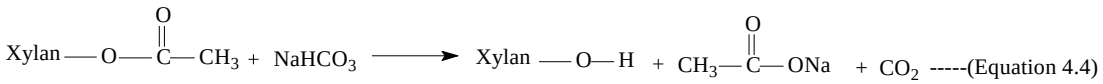
.....(Equation 4.3)

At high pH, where NaOH predominates; sodium acetate is formed.



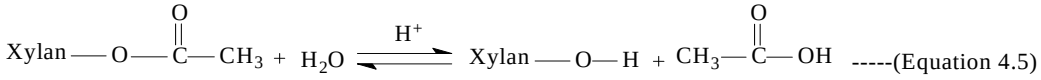
.....(Equation 4.1)

At intermediate pH, where $NaHCO_3$ is present; sodium acetate is formed. The formation of CO_2 increases the internal pressure in the reactor [Leschinski et al. 2009]



-----(Equation 4.4)

When the pH falls below 5, acetic acid is formed.



-----(Equation 4.5)

The pH at the end of the 2% green liquor extraction agrees with the pH value reported in the literature by Luo (2012) under the experimental conditions of 2% green liquor charge, L/W ratio of 4 and H-Factor of about 771 Hrs. The H-factor is a parameter used by pulp industry to combine both time and temperature into a single variable [Sjöström, 1993].

4.2.2 Effect of Alkali Charge on Acetic Acid Concentrations in Extract

Figure 4.4 illustrates the effect of the alkali charge on acetic acid concentration in the acidified extract. The rate of cleavage of acetyl groups from the hemicelluloses backbone is a direct function of the initial hydroxide ion concentration in the cooking liquor. In highly alkaline liquor such as white liquor and 0.5 N NaOH, acetyl groups are rapidly hydrolyzed from hemicelluloses; whereas in less alkaline liquor such as green liquor, acetyl groups are slowly cleaved off the xylan backbone. There are two possible reasons for such difference in the rate of hydrolysis. First, the rate of penetration of hydroxide ions into wood chips decreases as hydroxide ion concentration in the liquor is reduced. Thus, the rate of penetration of hydroxide ions is lower in green liquor as compared to white liquor. Secondly, the molecular mechanisms by which the acetyl groups are removed from hemicelluloses are dependent on hydroxide ion concentration, which will be subsequently discussed.

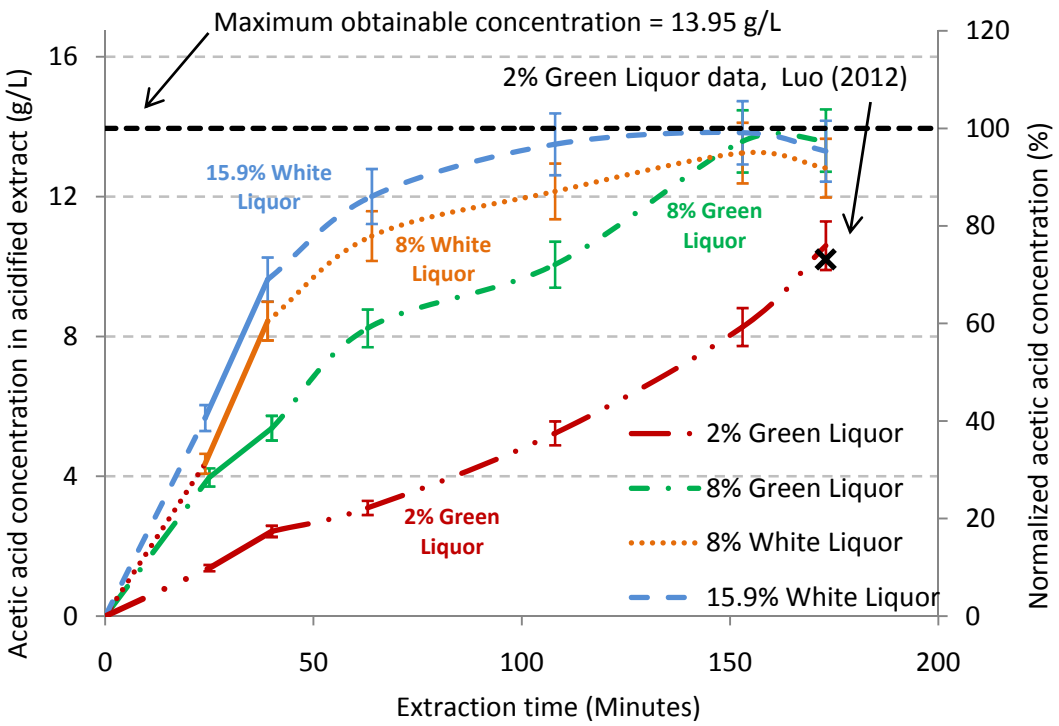


Figure 4.4 Effect of Alkali Charge on Acetic Acid Concentration in Extract

4.3 Effect of Extraction Temperature

The effect of extraction temperature was studied using 8% white liquor. The temperatures that were evaluated include: 165 ^{0}C, 120 ^{0}C, 100 ^{0}C, 80 ^{0}C, 50 ^{0}C.

4.3.1 Effect of Extraction Temperature on Extract pH

The effect of extraction temperature on the extract pH is illustrated in Figure 4.5. The temperatures investigated span the temperature range from 50 ^{0}C to 165 ^{o}C. The plot has been simplified for clarity by removing the error bars on most data points. However, all points have the same percent (%) error. A significant increase in the extract pH was observed when the extraction temperature was reduced from 165 ^{0}C to 120 ^{0}C. The corresponding reduction in alkali consumption is mostly due to the decrease in secondary peeling reactions and bulk delignification, all of which occur predominately at elevated temperatures. The decrease in carbohydrate extraction due to peeling and hydrolysis and delignification rates can be observed in Figure 4.6 and Figure 4.10, respectively.

However, for the extraction temperatures below 120 ^{0}C, the alkali consumption does not appreciably change with temperature. As explained previously, for a low temperature pretreatment, acid group neutralization account for most alkali consumption. Also, neutralization reactions extremely fast and controlled by diffusion, and thus are not affected by temperature. Thus, pH remains constant. However, applicable reactions slightly decrease with the extraction temperature, which can be observed from a small increase in the pH with a decrease in the extraction temperature (Figure 4.5). The liquors obtained from white liquor extraction experiments were analyzed for residual alkali content (Appendix B).

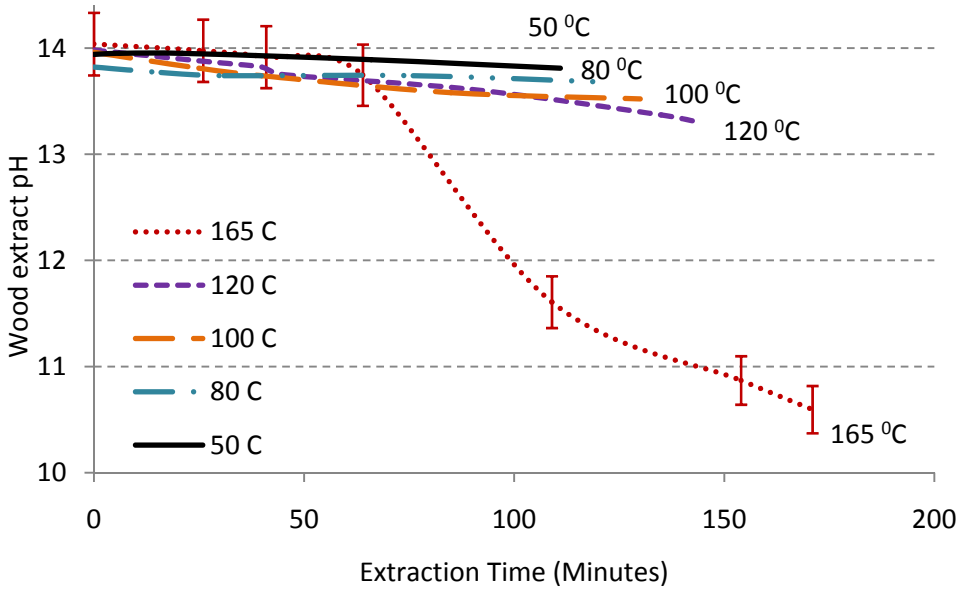


Figure 4.5 Effect of Extraction Temperature on Extract pH

4.3.2 Effect of Extraction Temperature on Monosugar Concentration in Extract

Figure 4.6 illustrates the effect of extraction temperature on the total sugar concentrations in the hydrolyzed extract. The amount of total sugar extracted into the liquor decreases significantly from 165 ^{0}C to 120 ^{0}C. This is attributed to the reduction in alkaline hydrolysis of sugar chains which normally occurs at a temperature above 140 ^{0}C [Rydholm, 1967]. Below 120 ^{0}C, the decrease in sugar concentration is considerably less pronounced compared to the decrease seen when the temperature is reduced from 165 ^{o}C to 120 ^{0}C.

Carbohydrate dissolution below 120 ^{o}C is thought to represent dissolution of loosely bound sugar units [12]. Prior to acid hydrolysis of the extract, the concentration of monosugars in the extract samples was almost negligible.

The HPLC column that was originally used in this study was unable to separate xylose, mannose and galactose. Consequently, a High Performance Anion Exchange Chromatography (HPAEC) was used to separate component sugars and to estimate the relative distribution of monosugars in the hydrolyzed extracts. It was found that the relative composition of the component sugars in the extract samples was essentially constant and did not vary appreciably with the extraction time or extraction temperature. The distribution of component sugars in the extract samples was roughly 10 % arabinose, 11 % galactose, 7 % glucose, 70 % xylose and 2% mannose.

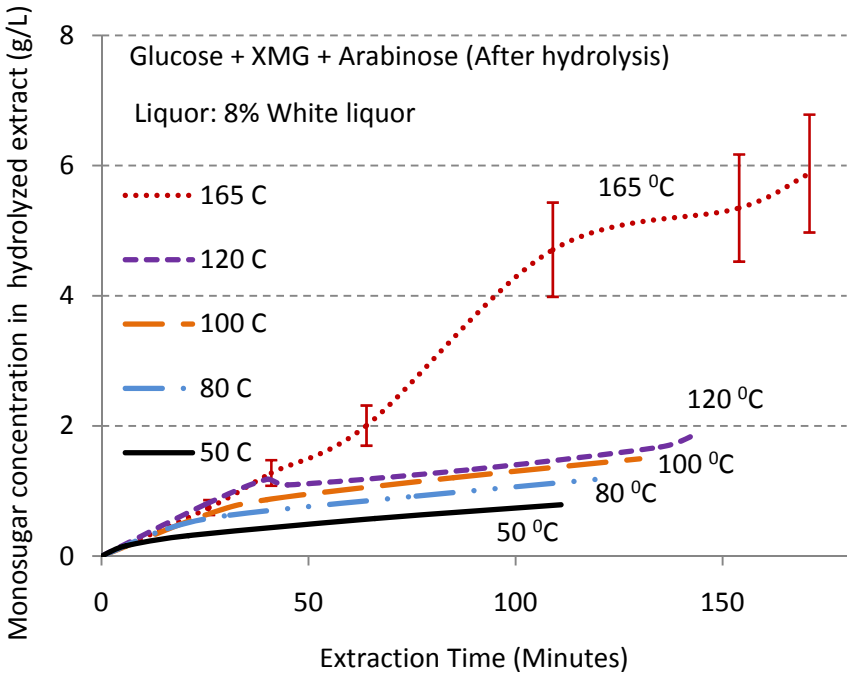


Figure 4.6 Effect of Extraction Temperature on Monosugar Concentrations

Table 4.1 shows the amount of carbohydrates sugars in the raw wood based on the basis of percent oven dry wood mass. Table 4.1 also shows the amount of carbohydrates that were extracted into the liquor at 165 ^{0}C, again on an oven dry wood mass basis

(percent). It can be concluded that most of the arabinose can be readily extracted into the liquor. Mannan and glucan almost remains unchanged during Kraft pulping. By contrast, a considerable amount of galactose and xylan are extracted from wood.

Carbohydrate	Amount remained in raw wood after 175 minutes (% O.D.)	Amount extracted into liquor after 175 minutes (%O.D.)
Arabinose	0.56	0.39
Galactose	1.22	0.25
Glucose	43	0.18
Xylose	22.8	1.64
Mannose	2.23	0.04
Total	69.81	2.50

Table 4.1 Carbohydrate Content in the Raw Wood and in the White Liquor Extract

4.3.3 Effect of Extraction Temperature on Organic Acid Concentrations

Figures 4.7 and 4.8 illustrate the effect of extraction temperature on the lactic and the formic acid concentrations in acidified extract. Both lactic and formic acids are formed by alkaline peeling reactions of wood polysaccharides [Rydholm, 1967]. Formic acid is also formed during acid degradation of glucose [Walton, 2010]. Both the formic acid and the lactic acid concentrations decreased steadily with decreasing extraction temperature. No formic and lactic acids were formed at 50 ^{0}C, which confirms that the peeling and stopping reactions do not occur until the liquor temperature is above 70-80 ^{0}C.

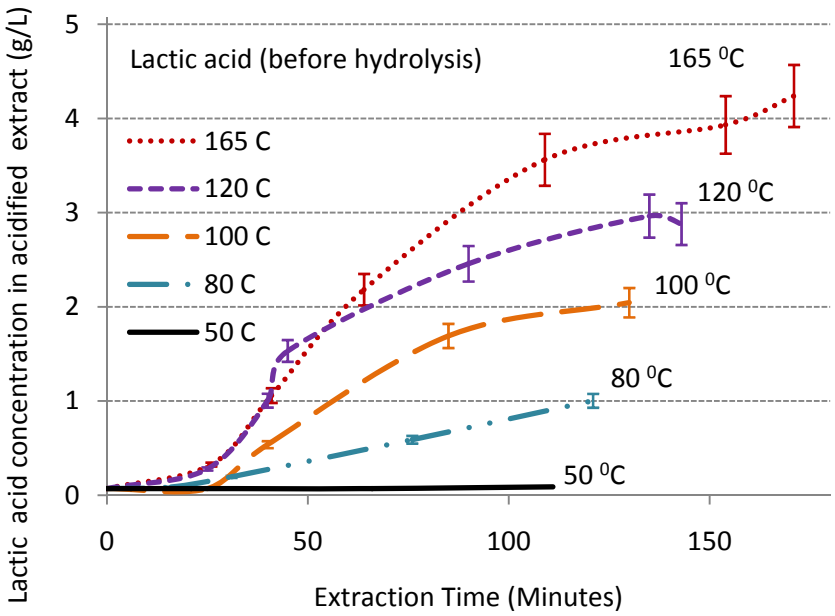


Figure 4.7 Effect of Extraction Temperature on Lactic Acid Content in Extract

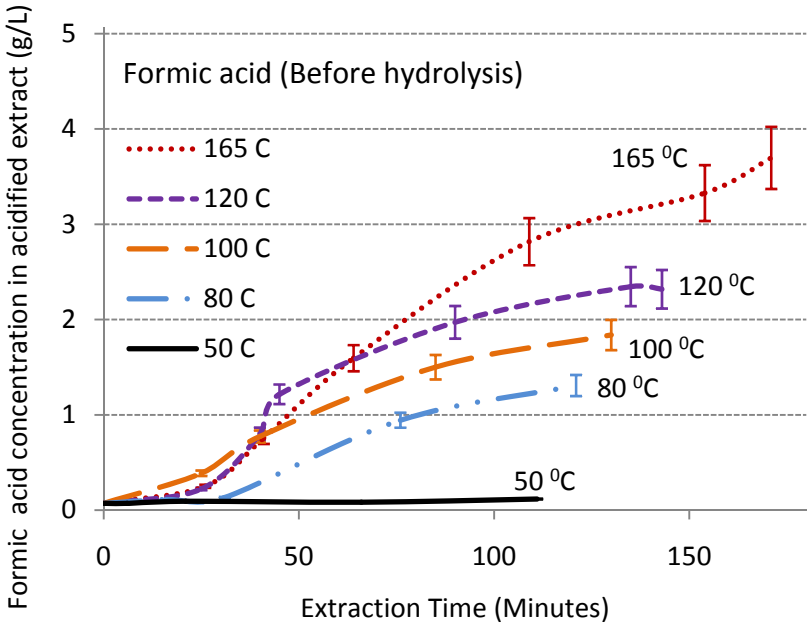


Figure 4.8 Effect of Extraction Temperature on Formic Acid Concentrations

The effect of extraction temperature on the acetic acid concentration in the acidified extract is shown in Figure 4.9. Due to a change in wood chips used to perform the experiments midway through this study, there is a reduction in the maximum acetic acid concentration when the data of Figure 4.4 are compared to the data shown in Figure 4.9. It

can be seen that for 8 % white liquor extraction, the hydrolysis rate for acetyl group remains constant over an extraction temperature range of 50 ^{0}C to 165 ^{0}C. The reason for the constant acetic acid concentration is postulated in the following section.

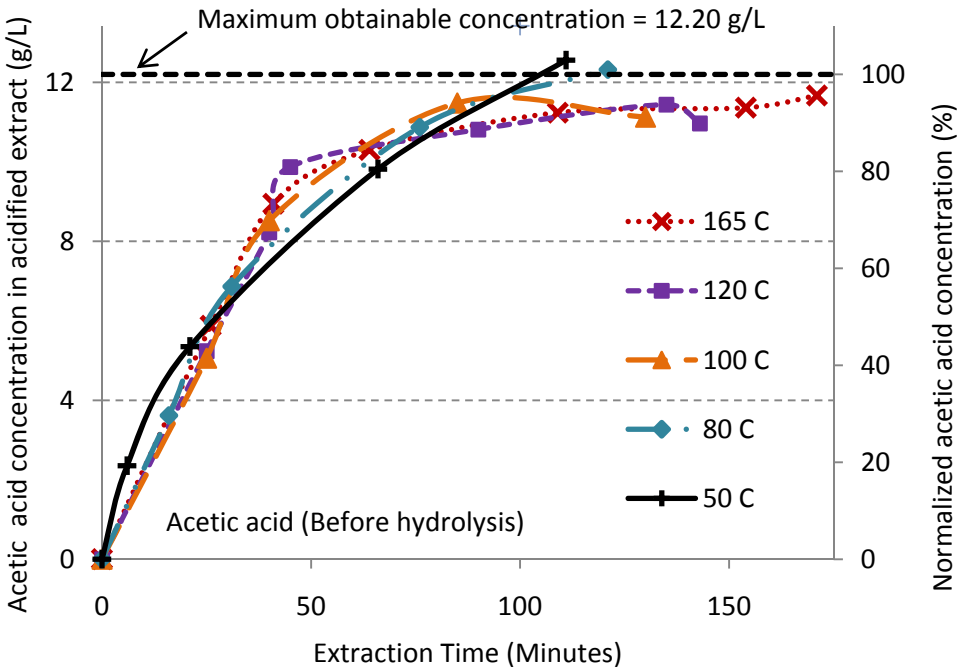


Figure 4.9 Effect of Extraction Temperature on Acetic Acid Concentrations

4.3.4 Mechanism for the Cleavage of Acetyl Groups from Xylan

Xylose is the predominant component in the hydrolyzed extracts and corresponds to about 70% of total sugars in the extract (Table 4.1). Also, most sugars in the unhydrolyzed extract are oligomers [Luo, 2012]. Consequently, the total sugar concentration in Figure 4.6 can be considered as an approximate xylan concentration in the unhydrolyzed extract. By comparing both Figure 4.6 and Figure 4.9, it can be seen that under highly alkaline conditions, the rate of hydrolysis of acetyl group is independent of the extraction temperature and the xylan hydrolysis rate. Although the extraction at 50 ^{0}C results in the cleavage of all acetyl groups, the xylan polymer remains virtually undegraded due to the low temperature. The assumption that the xylan remains undegraded at 50 ^{0}C is based on the following: Firstly, the alkaline peeling reactions start when temperature is above 70-80 ^{0}C. The negligible concentrations of formic and lactic acids in the 50 ^{0}C extract samples in

Figures 4.7 and 4.8 explain the absence of any peeling or stopping reactions at 50 ^{0}C. Secondly, the alkaline hydrolysis reactions occur at a temperature above 140 ^{0}C [Rydholm, 1967]. It is speculated that the small sugar concentrations in the 50 ^{0}C extract samples shown in Figure 4.6 correspond to the dissolution of loosely bound sugar units. Thus, in the presence of a high concentration of hydroxide ions (at least twice the acid group content on mole basis), most acetyl groups are directly hydrolyzed from solid xylan following a base (hydroxide) catalyzed mechanism for hydrolysis of ester groups [Carey, 2003]. This reaction can occur at any temperature.

However, the mechanism of acetyl group hydrolysis in the less alkaline and in the acidic liquor is different. The deacetylation of spruce in dilute alkali proceeds by two different mechanisms [Erins and co workers, 1976]. As per the kinetics, 70% of the total acetyl groups were removed by direct hydrolysis of acetyl groups attached to solid xylan, while the remaining was removed by deacetylation of dissolved xylan. Under dilute acidic conditions such as autohydrolysis (hot water extraction); oligomers containing acetyl groups are dissolved into the extraction liquor and then the acetyl groups are released through deacetylation of dissolved xylan oligomers [Tunc, 2008]. Thus, it can be concluded that as the concentration of hydroxide group in the liquor decreases, more acetyl groups are hydrolyzed from dissolved xylan.

4.3.5 Effect of Extraction Temperature on Lignin Concentration in Extract

Figure 4.10 shows the variation in delignification rate for the extraction temperatures ranging from 50 ^{0}C to 165 ^{0}C. Since both the effective alkali and the cooking time employed in this experiment (8% EA, 3 hrs) were significantly lower than Kraft cooking conditions (16% EA, 5-6 Hrs); only 60% of the total lignin was removed at 165 ^{0}C. The amount of lignin removed gradually decreases with decreasing the extraction temperature. Most lignin removed at low temperatures corresponds to the free phenolic lignin units, which are normally cleaved during the initial delignification phase [Sixta, 2006].

The substantial decrease in the lignin concentration at lower temperature (50 ^{o}C) helps to simplify the downstream sodium acetate separation process. The low temperature also helps to maintain high alkali concentration in the cooking liquor by reducing unwanted side reactions such as delignification and sugar degradation. High alkali concentration in turn increases the driving force for the penetration of alkali into wood chips

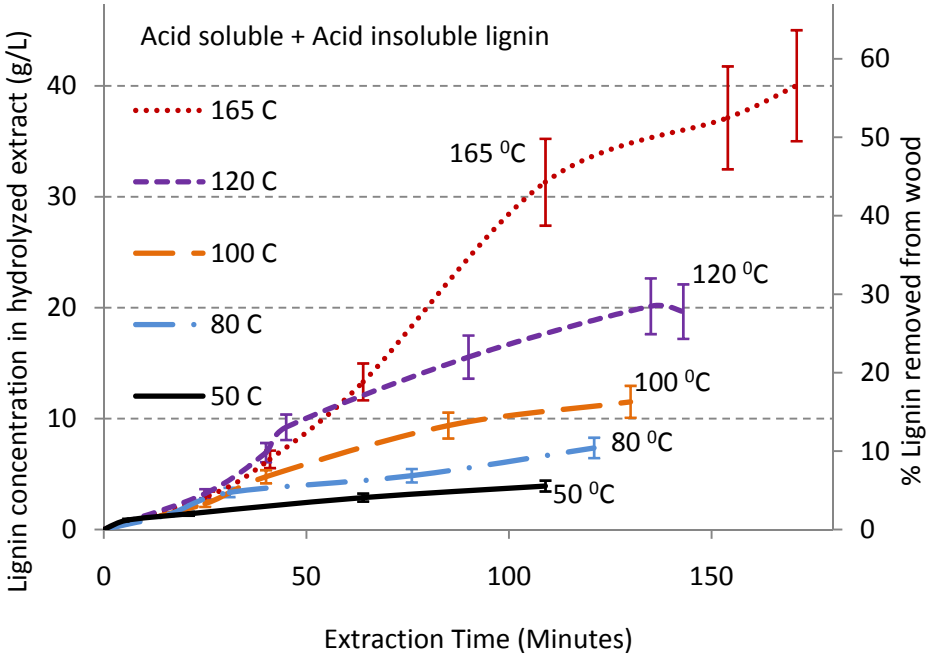


Figure 4.10 Effect of Extraction Temperature on Lignin Concentrations in Extract

4.4 Comparison of the Rate of Deacetylation of Woodmeal and Commercial Chip

The experiments were performed using samples of milled wood [Snell, 2012]. Experimental method was similar to Zanuttini's work (1997). These experiments permitted a direct comparison to the extraction data obtained for commercial hardwood chips. The extraction experiments were performed at liquor to wood ratio of 150. The alkali concentration was monitored using conductivity meter and was maintained constant by adding concentrated solution.

Figure 4.11 shows the comparison between the rate of cleavage of acetyl groups from an industrial wood chip and the milled wood at constant alkali concentration and at high liquor to wood ratio. The rate obtained for milled wood can be considered as an approximate rate of deacetylation reaction due to the absence of any diffusion effects. Also, the rate obtained for the wood chip is assumed to be the sum of diffusion effect and reaction rate. The comparison between two rates shows that the diffusion is the limiting factor for rate of cleavage of acetyl groups from thick wood chip.

It should also be noted that for an actual industrial extraction, the rate of deacetylation of thick chip may be much lower than the rate shown in Figure 4.11, due to the presence of additional limiting factors such as decreasing alkali concentration and low liquor to wood ratio.

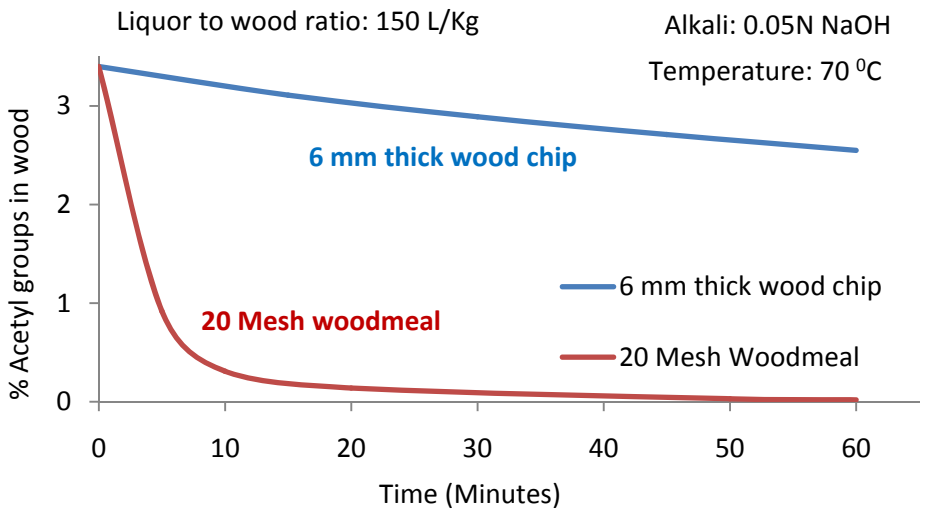


Figure 4.11 Rate of Cleavage of Acetyl Groups from Woodmeal and Wood Chip

4.5 Mass Balance and Estimation of Acetyl Groups Content in Macerated Wood

Mass balances were performed for the overall solids and the acetyl groups in the system. The acetyl group's content in the dry macerated salt free wood was calculated using two different measurements: 1] Acetic acid concentration in the drained liquor and 2] Acetyl group's content in the dry macerated wood.

4.5.1 Mass Balance on Overall Solids and Acetyl Groups

The mass balance on acetyl group was carried out by estimating the distribution of acetyl groups in the drained liquor, the macerated wood chips and for the liquor held within the chips. The results of the mass balance study are summarized in the Table 4.3. A detailed procedure for the mass balance calculations is given in Appendix E.

The average overall solids balance was found to close to within 96%; while the mass balance on the acetyl groups closed to within 98%. It was found that about 65-70% of the total acetyl groups on the raw wood were located in the liquor drained from the digester. The remaining acetyl groups (33-28%) were located in the wet macerated wood chips. This includes the acetyl groups still attached to the xylan polymers in the wood chips as well as the sodium acetate contained in the liquor held within the pores of the chips. Another 2% of the acetyl groups extracted from the wood were contained in the samples used in analytical work. In both the green liquor and the white liquor extraction experiments, the percentage of wood extracted into drained liquor increases with alkali charge and extraction temperature. The change in soaking conditions did not have a significant effect on the amount of wood extracted into the liquor.

4.5.2 Estimation of Acetyl Groups in Macerated Wood

In most cases, the residual acetyl content measured using the macerated wood agreed with the calculated value based on measurement of the sodium acetate in the extraction liquor. The agreement was within about 10%, which was about the error limit based on total acetyl content in the raw wood.

4.5.2.1 Amount of Acetyl Groups Calculated Using Macerated Wood Analysis

The amount of residual acetyl groups measured using the dry macerated wood was corrected for liquor held within chips as shown in Equation 4.6. All notations used in Equations 4.6 and 4.7 are explained in detail in Appendix E.

$$Y_{Acetyl\ in\ DMSF} = \frac{X_{Acetyl\ in\ DM} \times M_{DM} - \frac{M_{liquor\ in\ WM} \times C_{HAc\ in\ DL} \times 0.7167}{\rho_{liquor\ in\ WM}}}{M_{DMSF}} \times 100 \quad \text{.....Equation (4.6)}$$

$Y_{Acetyl\ in\ DMSF}$ = Percent acetyl groups in dry macerated salt free wood (on mass basis)

$X_{Acetyl\ in\ DM}$ = Mass fraction of acetyl groups in dry macerated wood

M_{DM} = Mass of dry macerated wood (gm)

$M_{liuqor\ in\ WM}$ = Mass of liquor held within wet macerated wood (gm)

$C_{HAc\ in\ DL}$ = Acetic acid concentration in drained liquor as measured by HPLC (gram/liter)

The conversion factor 0.7167 is the ratio of molecular weights of acetyl groups (CH_3CO) to the molecular weight of acetic acid (CH_3COOH). This factor was used to calculate an equivalent amount of acetyl groups for a given amount of acetic acid.

$\rho_{liquor\ in\ WM}$ = density of liquor held within wet macerated wood (assumed to be 1 gm/ml)

M_{DMSF} = Mass of dry macerated salt free wood (gm)

. The amount of acetyl groups in the dry macerated salt free wood was calculated as the difference between (1) the acetyl groups in wet (or dry) macerated wood and (2) the estimated amount of acetyl groups held in the liquor inside the pores of the wet macerated wood (Equation 4.6). Ideally, the amount of acetyl groups in the wet macerated wood is slightly higher than that contained in the liquor held within the pores of the wet macerated chips. Accordingly, the difference between these two values gives a positive value for the amount of acetyl groups in the dry macerated salt free wood. However, in the present study, the percent error associated with the measurement of the acetyl groups is about 6% (Appendix C). It is also expected that there may be also be an error involved in the measurement of masses of macerated wood chips and the liquor drained from the digester. All these errors may synergistically combine or cancel each other. When all errors combine, the net error is high. Thus, the calculated value of acetyl groups in dry macerated salt free wood can sometime become negative (Table 4.2).

Distribution of acetyl groups in wet macerated wood (grams)			
(A) Experiment number	(A) Mass of acetyl groups in wet macerated wood chips	(C) Mass of acetyl groups in the liquor held within the chips	(D) Mass of residual acetyl groups in dry macerated salt free wood
Ex-5	8.21	8.08	0.14
Ex-7	8.61	9.32	-0.71
Ex-6	8.91	8.66	0.25
Ex-17	9.97	8.89	1.08
Ex-18	10.06	9.63	0.43
Ex-19	8.64	9.57	-0.93
Ex-20	10.60	9.76	0.84

Table 4.2 Distribution of Acetyl Groups in Wet Macerated Wood

For practical purposes, the liquor concentration inside the chip was considered the same as that in the surrounding bulk liquid. However, the liquor concentration inside the chip should be higher than the liquid exterior to the chips. Theoretically, a concentration gradient must be maintained for diffusion of the sodium acetate product from the chip interior to the bulk of the circulating liquid. Therefore, the use of drained (external) liquor concentration to estimate the amount of the acetyl groups in the liquor held within wood chips most likely results in an overestimation of the amount of residual acetyl groups using (Equation 4.6).

4.5.2.2 Amount of Acetyl Groups Calculated from Extract Analysis

The calculated value of acetyl groups using acetic acid concentration in the drained liquor is shown in Equation 4.7

$$Y_{\text{Acetyl in DMSF}} = \frac{M_{\text{Acetyl in raw wood}} - \frac{M_{\text{total liquor in the system}} \times C_{\text{HAc in DL}} \times 0.7167}{\rho_{\text{liquor in WM}}}}{M_{\text{DMSF}}} \times 100 \quad \text{.....Equation (4.7)}$$

$M_{\text{Acetyl in raw wood}}$ = Mass of total acetyl groups in raw wood (gm)

$$M_{\text{total liquor in the system}} = \begin{pmatrix} \text{amount of liquor charged} \\ \text{at the begining of cook} \end{pmatrix} - \begin{pmatrix} \text{amount of liquor} \\ \text{withdrawn as samples} \end{pmatrix}$$

All other symbols have their meanings as explained previously.

As per the mass balance studies, macerated wood chips contain about 45% moisture and this moisture corresponds to the 1/3rd of the total liquor in the reaction system. As explained previously, the liquor concentration inside the wood chip is slightly higher than the external liquor concentration. Therefore, 1/3rd of the total liquor in Equation 4.7 has a concentration higher than the external liquor concentration. Thus, the second term in the Equation 4.7 remains underestimated and gives rise to the higher value for the amount of acetyl groups in the macerated wood.

It should be noted that the values for the amount of acetyl groups calculated using the extract analysis are never negative (Table 4.3); whereas the ones calculated using macerated wood may be negative. One possible reason for this discrepancy is that the value of acetyl groups calculated using the analysis of the liquid extract is based on only one measured value for the acetic acid concentration; whereas, the content of residual acetyl groups estimated using the analysis of the macerated wood is based on two measured values of acetic acid concentration. Thus, the estimate made based on Equation 4.7 is thought to be more accurate than the analysis based on Equation 4.6.

However, the residual acetyl content in the pores of the chips can be more accurately measured by washing the macerated wood chips with an excess quantity of water to separate the liquor which is held within wood chips.

Experiment number and experimental conditions		% Overall mass balance closure	% Wood extracted into drained liquor		% Solid content in drained liquor	% Organic content in drained liquor	% Solid in Wet macerated hips	% Organic in wet macerated chips		Acetyl groups mass balance closure (%)		% distribution of total acetyl groups of raw wood (at the end of cook)				% Acetyl groups in dry macerated salt free wood	
												in drained liquor	% in liquor within chips	in dry macerated Salt free wood	% in extract samples	Calculated from macerated wood	Calculated from extract analysis
1	0.5N NaOH, Soaking at 27 ^{0}C	96.38	13.26		5.36	3.16	42.98	41.30		86.09		57.54	25.24	0.43	2.88	0.02	0.93
2	0.5N NaOH, Soaking 120 ^{0}C	99.74	13.72		5.52	3.30	44.43	42.43		96.11		65.82	29.14	**-2.22**	3.37	**-0.12**	0.30
3	0.5N NaOH, No soaking	98.14	11.72		4.72	2.82	45.97	44.23		101.64		70.96	27.05	0.78	2.85	0.04	0.26
4	2% Green Liquor, 165 ^{0}C	96.80	11.95		3.62	2.86	45.32	44.95		83.50		54.09	20.34	7.33	1.74	0.35	1.24
12	6% Green Liquor, 165 ^{0}C	95.57	13.03		5.40	3.10	43.16	41.61		102.53		69.99	30.77	**-1.31**	3.08	**-0.06**	0.07
5	8% Green Liquor, 165 ^{0}C	98.22	17.42		7.21	4.12	42.77	40.35		98.22		59.46	27.81	3.59	3.07	0.19	0.69
6	15.9% White Liquor, 165 ^{0}C	95.27	40.91		16.98	9.14	39.76	28.43		104.82		63.92	31.90	5.62	3.38	0.54	0.81
7	8% White Liquor - 165 ^{0}C	100.3	27.77		11.00	6.43	41.80	36.76		103.77		69.37	33.58	**-2.27**	3.09	**-0.14**	0.02
Error analysis	[1] 8% White Liquor - 165 ^{0}C	-	-		11.55	-	41.73	36.69		-		-	-	-	-	-	-
	[2] 8% White Liquor - 165 ^{0}C	90.27	19.83		11.39	4.56	42.22	37.51		99.15		65.00	28.65	2.02	3.47	0.11	0.46
	[3] 8% White Liquor - 165 ^{0}C	93.82	23.51		10.34	5.41	41.35	37.20		106.02		69.76	30.24	3.04	2.99	0.17	0.27
	[4] 8% White Liquor - 165 ^{0}C	95.53	22.76		10.52	5.27	42.90	38.78		92.29		62.20	25.76	3.72	0.61	0.20	0.80
8	8% White Liquor - 120 ^{0}C	93.49	14.60		8.41	3.48	45.06	41.12		99.04		64.56	28.24	3.43	2.82	0.15	0.43
9	8% White Liquor - 100 ^{0}C	103.51	13.98		8.29	3.38	46.34	42.79		103.06		69.30	30.57	1.36	1.84	0.05	0.11
10	8% White Liquor - 80 ^{0}C	96.12	8.98		6.75	2.18	45.40	40.76		96.74		67.40	30.37	**-2.94**	1.92	**-0.12**	0.22
11	8% White Liquor - 50 ^{0}C	98.75	6.65		5.79	1.65	47.83	42.79		106.72		70.50	30.99	2.67	2.56	0.10	0.003
	Average	96.80	-		-	-	-	-		98.65		65.32	28.71	1.68	2.64	-	-

Table 4.3 Overall and Acetyl Group Mass Balance

4.6 Expected Acetic Acid Production Rates in Kraft Pulp Mills

Acetic acid production rates were calculated using the formula given below,

$$P_{HAc} = \left[\frac{P_{pulp} \left(1 - x_{water}\right)_{pulp} \left(x_{Ac}\right)_{wood} \left(f_{Ac}\right)_{wood}}{y_{pulp} * (0.7167)} \right] \text{----------Equation(4.8)}$$

where

$(x_{water})_{pulp}$ = Fraction water content in the pulp = 0.05,

y_{pulp} = Pulp yield or fraction of original dry wood mass extracted into pulp = 0.45,

$(x_{Ac})_{wood}$ = % acetyl groups in dry wood which is an average value for hardwood and softwood = 3%

0.7167 = Ratio of the molecular weight of acetyl groups (CH_3CO = 43) to the molecular weight of acetic acid (CH_3COOH = 60), and

f_{Ac} = 0.60 = Fraction of total acetyl groups in the raw wood that are present in the liquor drained from the digester

Figure 4.12 shows the expected acetic acid production rates for Kraft pulp mills of various sizes.

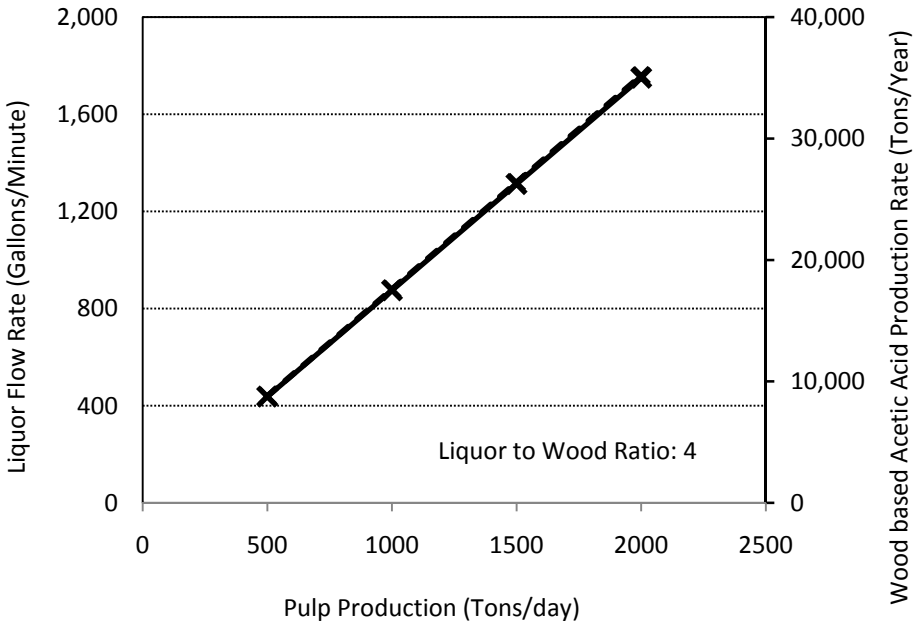


Figure 4.12 Expected Acetic Acid Production Rates and Liquor Flow Rates

The capacity of a modern synthetic acetic acid plant is about 550,000 Tons/year; whereas the acetic acid production rate resulting from cleavage of acetyl groups is 8,000 to 32,000 Tons/year depending upon the size of the pulp mill. Thus, the production capacity from any one Kraft mill, even one of substantial size, would be small and would not disrupt the acetic acid market. Although the wood derived acetic acid production rates are about 15-50 times smaller than that of commercial plant, it still represents positive revenue to the pulp mill owner provided a cost effective separation method can be developed.

. The maximum possible production rate for acetic acid produced from Kraft mill all over the world is estimated to be approximately 6.2 million tons per year. This value is based on a global chemical pulp production rate of 130 million tons per year and a consideration that Kraft pulp corresponds to 90% of the total chemical pulp production. In 2010, the global demand for acetic acid was approximately 9.56 million tons per year [Massingham, J., 2011]. Thus, the Kraft mills have a potential to become a sustainable source for the acetic acid production for the chemical process industry provided a cost effective separation method can be developed.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

Experimentally, the rate of cleavage of acetyl groups from wood hemicelluloses is a function of chip soaking temperature, extraction temperature, alkali concentration and the type of the alkali used in the extraction process.

Soaking at 120 ^{0}C is more effective than no soaking or soaking at 27 ^{o}C. Because wood chips are used in commercial Kraft pulp production, the alkali must penetrate into the pores of the wood and thus into the walls of the cells before it can react with the acetyl groups in the wood. The increase in the effectiveness of soaking with temperature is attributed to an increase in the rate of reaction with temperature [Zanuttini, 1997] and also to a reduction in the viscosity of the alkali solution which facilitates alkali penetration.

The rate of cleavage of acetyl groups from wood hemicelluloses is a direct function of the initial hydroxide ion concentration in the extraction liquor. Both white liquor and 0.5 N NaOH have faster rates of hydrolysis of acetyl groups when compared to green liquor, which contains considerably less hydroxide ions.

The initial hydroxide ion in the extraction liquor also determines the mechanism by which acetyl groups are hydrolyzed from the hemicellulose backbone. If the extraction liquor contains excess hydroxide ions (at least twice the acid group content), then most acetyl groups are directly hydrolyzed from the xylan polymer to form sodium acetate, and the xylan remains in the wood provided the temperature is low [Erin and co-workers, 1976]. At elevated temperature, the xylan oligomers would be dissolved and they would undergo peeling reactions and contribute to the solids content of the extract. However, when the extract pH is below 7, first xylose oligomers containing acetyl groups are dissolved into the

liquor and then the acetyl groups are slowly released through successive deacetylation of dissolved xylan oligomers [Tunc, 2008].

The extraction temperature has a minor effect on cleavage of acetyl groups provided that the extraction liquor contains excess hydroxide ions. But, it is expected that the extraction temperature affects the rate of cleavage of acetyl groups if the pH of the extraction liquor is below 7. Low extraction temperature helps in minimizing unwanted side reactions such as peeling and delignification reactions. Minimization of the unwanted side reactions reduces the burden on the separation process and helps in maintaining high alkali concentration which in turn increases the driving force required for deacetylation reaction and for diffusion of caustic into the pores of the wood.

The hydroxide ion concentration in the extraction liquor and the extraction temperature should be optimized to recover acetyl groups in such way that the extracted liquor will have the lowest possible concentration of lignin and sugars so that they do not affect the acetic acid separation process. The proposed white liquor charge and extraction temperature appears to be about 6-8% and 50-80 ^{o}C, respectively for commercial wood chips. Under these conditions virtually all of the acetyl groups are cleaved off from the xylan while less than 5% of the lignin and 1% of the sugars in the wood are dissolved. Lastly, virtually no formic and lactic acids are produced from peeling of carbohydrates.

The wood derived acetic acid production rates from individual pulp mill are about 15 to 50 times smaller than that of a modern synthetic acetic acid plant. However, the total possible acetic acid production rate from the worldwide Kraft pulp industry is comparable to the total annual consumption rate for acetic acid. Thus, Kraft pulp mills appear to have the potential to become a sustainable source for acetic acid production, provided that a suitable separation process can be developed.

5.2 Recommendations for Future Work

Identification of cost effective sodium acetate separation process: It is imperative that separation experiments be performed to identify a cost effective separation process for removal of sodium acetate from the alkaline extract. The following separation methods are thought to be applicable: Ion exchange, membrane separation and liquid- liquid extraction. It is expected that the proposed separation process may not be limited to these methods. Using the appropriate separation process, there should be minimal reductions in the residual effective alkali content of the liquor to permit the residual alkali to be sent back to the cooking process.

Additional extraction experiments: Additional extraction experiments should be performed to estimate the rate of cleavage of acetyl groups at lower effective alkali charges on wood. It is recommended that concentrations such as 6% or 4% be evaluated. The sodium acetate separation process should become easier as the effective alkali charge is lowered.

Techno-economic analysis: Once the possible separation processes have been identified, it is recommended that a techno-economic analysis be performed in a manner similar to the study described by Mao and co-workers (2010). The objective of this work would be to determine the economic feasibility of recovering acetic acid from hardwood by alkali extraction.

Chip washing Study: Approximately 1/3rd of the total acetyl groups on raw wood remain in the liquor within the wet macerated wood chips and are burned in the recovery boiler. It is recommended that chip washing experiments be performed to estimate the feasibility of recovery of additional acetyl groups which otherwise would be burned in the recovery boiler.

Modelling of diffusion of alkali and deacetylation reaction: It is further recommended that the experiments be performed to evaluate the shrinking core model to

describe the deacetylation of hardwood using alkali. In these experiments, milled wood should be used to eliminate diffusion effects. This would permit a kinetic expression to be developed for the true reaction rate, much like what was done by Zanuttini and co-workers (1997). Using the reaction rate determined in the wood meal experiments, a diffusion model could then be developed to more accurately predict the deacetylation process in commercial wood chips; which is thought to be controlled by diffusion of caustic into the chips.

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APPENDICES

APPENDIX A

ESTIMATION OF ACETYL GROUPS IN WOOD

The acetyl content in the raw and the macerated wood samples was determined by extraction with caustic following a method described by Song[2]. The following procedure was used.

Procedure

About 0.25 gm (on oven dry basis) of extractive free wood meal was placed in a test tube which had a cap. About 5 ml of 0.5 N NaOH solution was then added to the test tube and the cap applied. The pH was between 12 and 13. The test tube and its contents was shaked well and heated for 3 hours in a 70 ^{0}C water bath. This result in the cleavage of all the acetyl groups bound to the xylan backbone[1].

A 2.5 ml sample of clear solution was removed from the top and the pH was adjusted to 1 by adding 1.5 ml of 1N HCl. The final volume was adjusted to 5 ml by adding 1 ml of water. The resulting solution was then filtered using a 0.45 micrometer filter. The 1 ml of the filtered solution was then placed in an HPLC vial. The percentage acetyl content in the biomass was calculated by following Equation (A.1).

$$\%\ \text{Acetyl}_{\text{Extractive-free}} = \left(\frac{C_{\text{HAc,HPLC}}\,(\text{g/ml}) \times \text{Volume}_{\text{final}}\,(\text{ml}) \times \text{conversion factor}}{\text{Oven dry weight of wood sample (gm)}} \right) \times 100 \quad \text{.....Equation(A.1)}$$

where,

$C_{AcOH,\ HPLC}$ = Concentration of acetic acid in the sample when determined by the HPLC (g/ml).

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[1] Song T.et al., "Extraction of galactoglucomannan from spruce wood with pressurised hot water," 10th European Workshop on Lignocellulosics and Pulp, Royal Institute of Technology, KTH, Stockholm, Sweden. (2008)

$Volume_{final}$ = Final volume of the liquid solution after the pH was adjusted and the addition of 1 ml of water.

Conversion factor = 0.7167 (Ratio of molecular weights of acetyl groups (CH_3CO) to acetic acid (CH_3COOH))

APPENDIX B

ANALYSIS OF RESIDUAL EFFECTIVE ALKALI

As explained previously, the 8% white liquor was considered to the most appropriate alkali concentration evaluated for the recovery of acetyl groups. Consequently, the effect of extraction temperature was studied using 8% white liquor to identify an optimum extraction temperature. For each of these experiments, the liquor drained from the digester at the end of extraction was analyzed for residual effective alkali content (REA). The REA analysis is relevant to estimating the amount of make-up white liquor, that is sodium hydroxide (NaOH) and sodium sulfide (Na_2S), required to complete the pulping process. Both high and low REA can lead to corrosion of carbon steel digesters[3]. Thus, it is important to monitor the alkali concentration.

The residual alkali is usually measured by following the ABC titration method as given in TAPPI Standard method (TAPPI T 625 cm-85). Generally, the ABC method involves a manual acid-base titration procedure with three equivalence points at different pH values. The equivalence point A (pH=10-11) detects hydroxide plus one-half sulphide; equivalence point B (pH=7.5-8.5) detects another one-half of the sulphide concentration; and equivalence point C (pH=4.014 5.5) detects carbonate. The presence of borate interferes with the conventional ABC method because borate is an effective buffer at a pH of 9 and thus obscures the equivalence point B[2].

In the present study, an automated titration system developed by Metrohm was used in performing the ABC titration for residual alkali. This automated titration system was developed for use when sodium borohydride is added to the pulping liquor to inhibit peeling reactions. This equipment follows a modified three point titration method, which takes into

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[2] Hsu, Wy-hwa Wesley, " Methods for analyzing boron-containing alkaline pulping liquors", U.S. Patent 6,913,672. (Jul 5, 2005)

account the presence of boron in the liquor[3]. This method can also be used in the analysis of the liquor samples which do not contain boron.

Extraction temperature (^{0}C)	**120**	**80**	**50**
Initial effective alkali charge based on dry wood (% Na_2O)	8	8	8
Initial effective alkali based on liquor volume (grams of Na_2O/L)	20	20	20
Residual effective alkali (grams of Na_2O/L)	6.2	8.5	9.85
Residual active alkali (grams of Na_2O/L)	7.15	10.8	14.15
Total titratable alkali (grams of Na_2O/L)	14.45	20.2	18.3
Causticity (%)	42.1	39.9	57

Table B.1 Residual Effective Alkali Contents of White Liquor Extracts

Property	**Value**
pH	13.64
% Solid Content (dissolved)	6.75
% Organics (dissolved)	2.18
% Inorganics (dissolved)	4.57
Acetate (g/L)	11.65
Lignin (g/L)	8.57
Sugars (g/L)	1.23
Na_2CO_3(g/L)	8.33
Na_2S(g/L)	5.79
NaOH (g/L)	4

Table B.2 Composition of Final Liquor in Experiment 10- 8% White Liquor- 80 ^{0}C

APPENDIX C

ERROR ANALYSIS EXPERIMENTS

The 8% white liquor extraction experiment which was conducted at an extraction temperature of 165 ^{0}C was repeated four times to assess the reproducibility of the analytical measurements. The results of the four replicate experiments are summarized in Figures C.1 thru C.8 for all of the response variables evaluated in the current work.

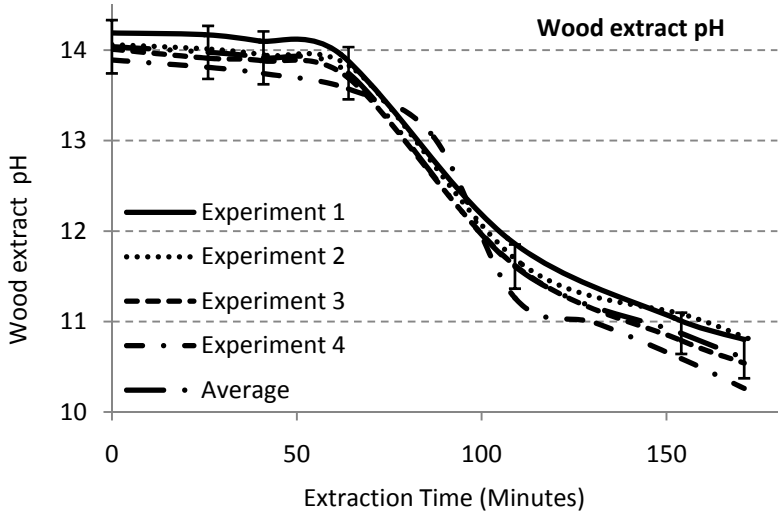

Figure C.1 Reproducibility of Extract pH Measurement

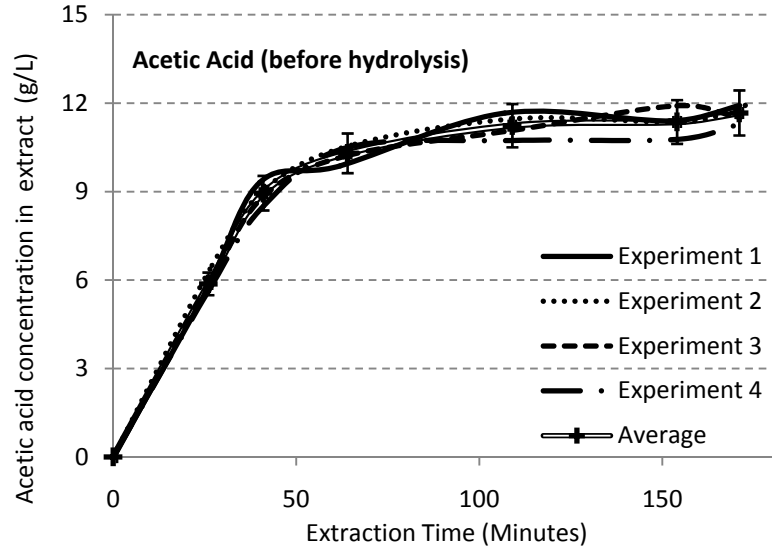

Figure C.2 Reproducibility of Acetic Acid Concentration Measurement

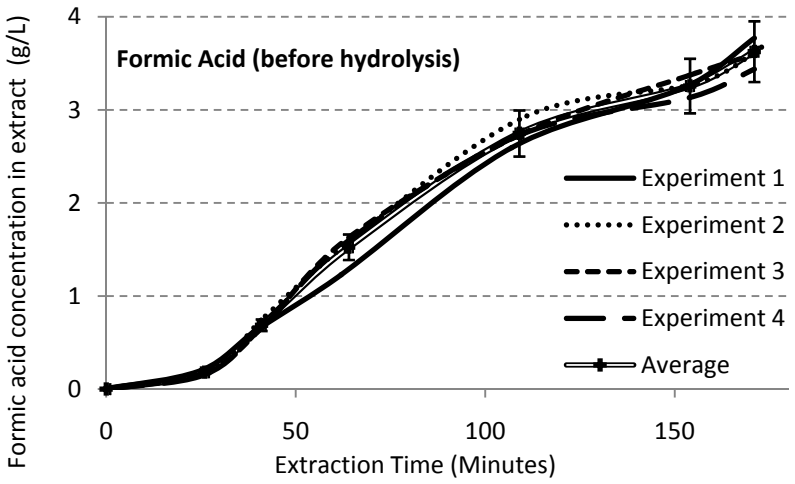

Figure C.3 Reproducibility of Formic Acid Concentration Measurement

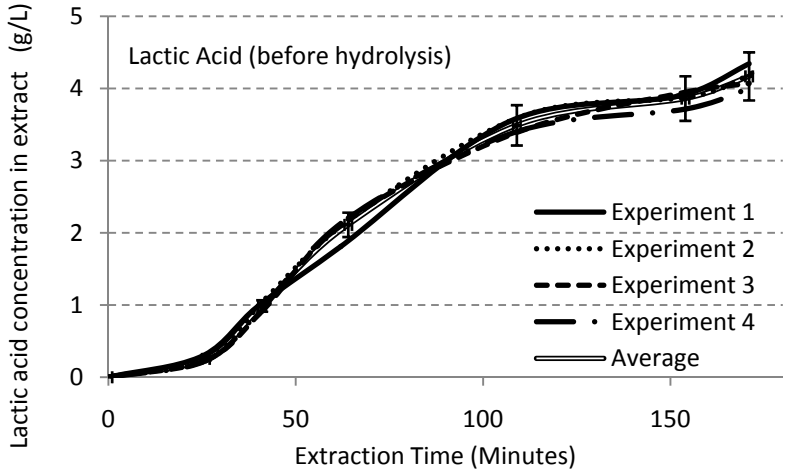

Figure C.4 Reproducibility of Lactic Acid Concentration Measurement

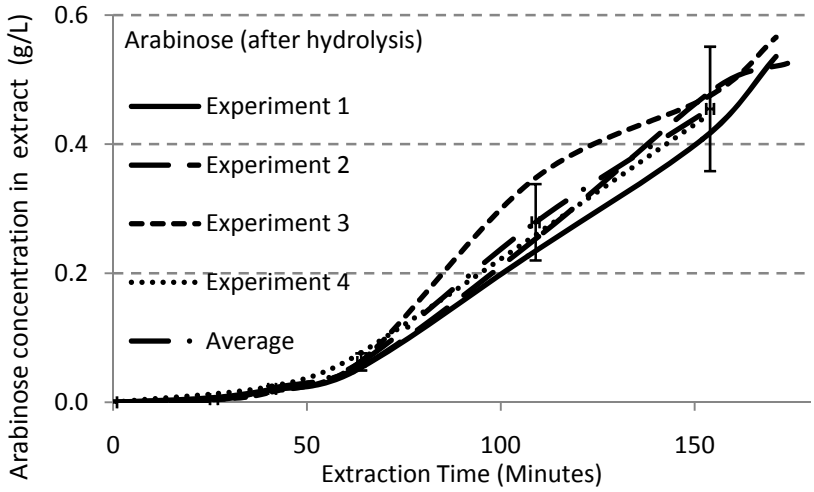

Figure C.5 Reproducibility of Arabinose Concentration Measurement

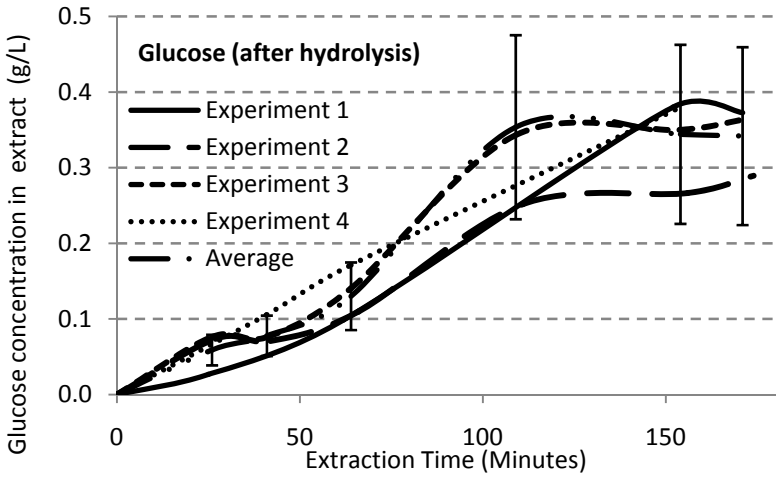

Figure C.6 Reproducibility of Glucose Concentration Measurement

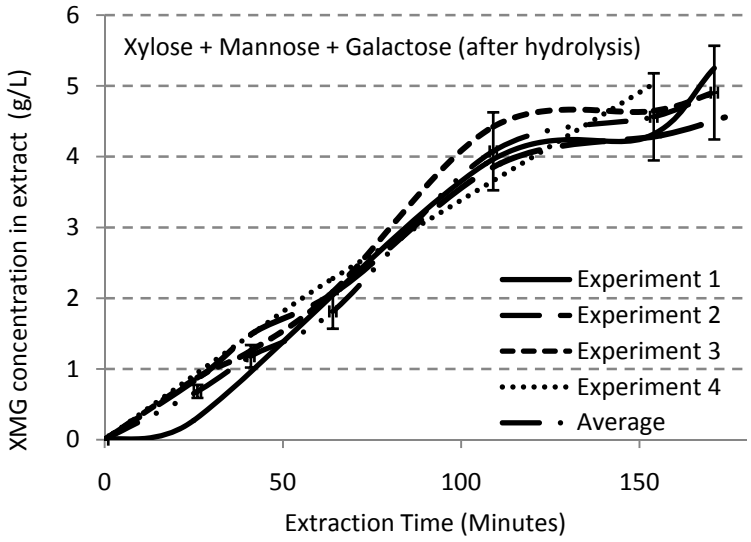

Figure C.7 Reproducibility of XMG Concentration Measurements

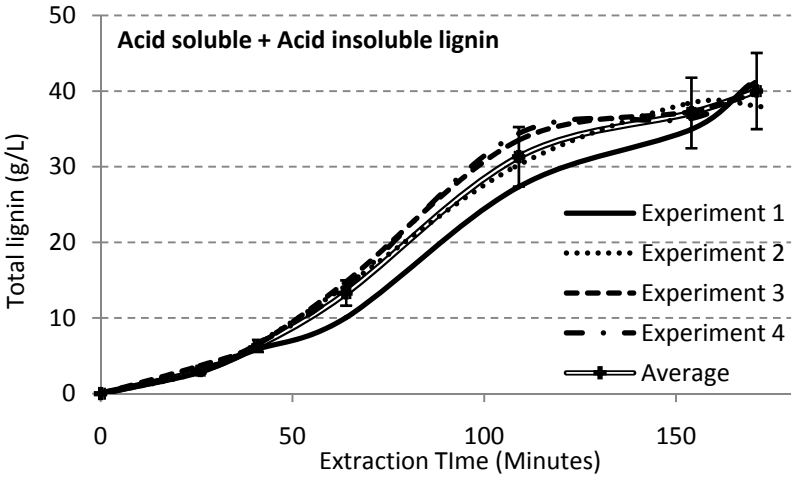

Figure C.8 Reproducibility of Lignin Concentration Measurements

Owing to the small sample size (4), the student's t-distribution was used to calculate the confidence interval for the mean value of a normal random variable. The method outlined by Mendenhall and Sincich[3] was used to estimate the 95% confidence limits on the data (Equation C.1). This was done using the measured mean value (X), the standard deviation (s), the number of data points (n) and the t-statistic ($t_{\alpha/2,(n-1)}$) for a confidence limit of α. By using the $t_{\alpha/2,\,(n-1)}$ statistic, the total error α, represents a two-tail test with an α/2 error on each side of the mean in the distribution.

$$X - t_{\alpha/2,n-1} \times \frac{s}{\sqrt{n}} < \mu < X + t_{\alpha/2,n-1} \times \frac{s}{\sqrt{n}} \quad \text{.....Equation(C.1)}$$

For each type of measurement, the percent error was calculated at different time interval by dividing the absolute value of the error limit by the absolute value of mean as shown in the equation C.2. The average percent error (Equation C.3) for each type of measurement was then calculated by averaging the percent error obtained at the different times. The results of the error analysis are summarized in Table C.1.

$$\text{Percent error}(\%) = \frac{t_{\alpha/2,n-1} \times \frac{s}{\sqrt{n}}}{\mu} \times 100 \quad \text{.....Equation(C.2)}$$

$$\text{Average percent error}(\%) = \frac{\sum_{i=0}^{n} \text{Percent error for } i^{th} \text{ time interval}}{n} \times 100 \quad \text{.....Equation(C.3)}$$

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[3] Mendenhall, William; Sincich, Terry, *Statistics for engineering and the sciences*; Prentice - Hall: New Jersey. 1995.

Type of measurement	**Average percent error (%)**
Wood extract pH	2.10
Acetic acid concentration before hydrolysis (g/L)	6.55
Formic acid concentration before hydrolysis (g/L)	9.03
Lactic acid concentration before hydrolysis (g/L)	7.90
Arabinose concentration after hydrolysis (g/L)	21.2
Glucose concentration after hydrolysis (g/L)	34.4
XMG concentrations after hydrolysis (g/L)	13.5
Acid insoluble lignin after hydrolysis (g/L)	11.2
Acid soluble lignin after hydrolysis (g/L)	17.1

Table C.1 Estimated Average Percent Error Limit on Various Analytical Measurements

APPENDIX D

CHEMICAL CHARGE FOR EXTRACTION EXPERIMENTS

Table D.1 shows the chemical charge for various alkali streams that are used this study.

Type of alkali	White Liquor		Green Liquor		0.5N NaOH
Alkali charge (based on dry wood)	15.9% EA	8% EA	8% TTA	2% TTA	6.2 % as N_2O
NaOH (100%, gram)	16.3	8.2	0.9	0.2	8.0
Na_2S (61.5%, gram)	13.4	6.7	4.4	1.1	0
Na_2CO_3 (100%, gram)	6.7	3.4	8.9	2.2	0
Wood chips (on dry basis, gram)	100	100	100	100	100
Water in chips (gram)	66.67	66.67	66.67	66.67	66.67
L/W Ratio	4	4	4	4	4
Additional water to adjust L/W ratio to 4	297	315.1	319.21	329.8	325.33

Table D.1 Chemical Charge for Different Alkali Streams

The reader should refer to the Material and Methods section for detailed expressions for estimating the alkali charged to the extraction vessel.

APPENDIX E

MASS BALANCE PROCEDURE

Figure E.1 shows the approximate amount of various solid and liquid streams generated during extraction. The first column of the figure shows input streams to the digester' whereas the second column shows the output streams from the digester. Figure E.1 also shows the type of solid and liquid streams that are obtained after drying the wet macerated wood chips The detailed analytical scheme is available in the Materials and Methods section (Figure 3.6)

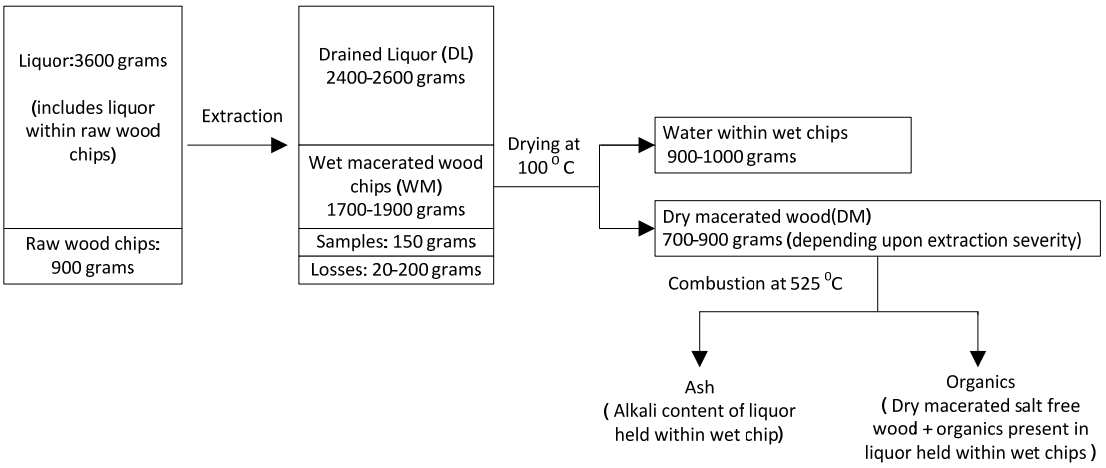

Figure E.1 Solid and Liquid Streams Generated during Extraction Experiments

Table E.1 lists the notations that are used in the mass balance equations

Notation	Meaning
M	Mass of a particular stream
X	Mass fraction of a particular component in the designated stream
WM	Wet macerated wood chips
DM	Dry macerated wood chips
DMSF	Dry macerated salt free wood
DL	Liquor drained from the digester at the end of extraction

Table E.1 Notations Used in the Mass Balance Equations

Inputs

Following the extraction, both the wet macerated wood chips and the residual liquor were removed from the digester and their masses (M_{WM} & M_{DL}) measured gravimetrically.

The mass fraction of solids in both the wet macerated wood chips ($X_{solids\ in\ WM}$) and the drained liquor ($X_{solids\ in\ DL}$) was estimated by drying the samples at 100 ^{0}C until a constant mass residue was obtained.

$X_{solids\ in\ DL}$ = Mass fraction of solids (ogranic + inorganic) in the drained liquor

$X_{solids\ in\ WM}$ = Mass fraction of solids (ogranic + inorganic) in wet macerated wood

The mass fraction of the inorganic ash in both the wet macerated wood chips and the drained liquor was estimated by combustion of dry solids of drained liquor and wet macerated wood at 525 ^{0}C until constant mass residue was obtained. Consequently, the organic content was also calculated using equations given below.

$$X_{organics\ in\ WM} = X_{solids\ in\ WM} \times \left(1 - X_{ash\ in\ DM}\right)$$

$$X_{organics\ in\ DL} = X_{solids\ in\ DL} \times \left(1 - X_{ash\ in\ solids\ within\ DL}\right)$$

$C_{HAc\ in\ DL}$ = Acetic acid concentration in drained liquor as measured by HPLC (gram/liter)

$X_{acetyl\ groups\ in\ DM}$ = Mass fraction of acetyl groups in dry macerated wood

Assumptions in the Mass Balance Study

1. The concentrations of liquor contained within the wood chips, liquor lost in the piping system and liquid samples were the same as that of the drained liquor.
2. The density of the all extract samples withdrawn at different time intervals as well as the liquor drained from the digester at the end of extraction was assumed to be same as that of water (1 gm/mL). Therefore, the volumes of these liquid streams must be same as their masses and this allows using both volume and mass interchangeably as has been done in Equation E.5.

Overall Mass (Solids) Balance

The overall mass balance was performed by following the methods outlined by Luo (2010).

$$M_{liquor\ within\ WM} = \frac{M_{WM} \times \left(1 - X_{solids\ in\ WM}\right)}{\left(1 - X_{solids\ in\ DL}\right)} \quad \text{.....Equation(E.1)}$$

$$M_{organics\ in\ WM} = X_{organics\ in\ WM} \times M_{WM}$$

$$M_{organics\ in\ liquor\ within\ WM} = X_{organics\ in\ DL} \times M_{liquor\ within\ WM}$$

$$M_{DMSF} = M_{organics\ in\ WM} - M_{organics\ in\ liquor\ within\ WM} \quad \text{.....Equation(E.2)}$$

$M_{In\ digester} = M_{raw\ wood\ on\ dry\ basis} + M_{liquor} + M_{water\ in\ chips}$ ..... (Total mass added in the digester)

$M_{recovered} = M_{drained\_liquor} + M_{wet\_macerated\_wood}$ ..... (Total mass recovered from digester)

$M_{lost\ liquor} = M_{In\_digester} - M_{Recovered}$ ..... (Total mass lost in piping system or as a steam)

The mass of the wood extracted into liquor was taken to be the organic contents in the masses of (1) drained liquor, (2) liquor within the wet macerated wood, (3) liquor losses and lastly (4) the liquid samples.

$$M_{\substack{wood\ extracted \\ into\ liquor}} = \left(M_{DL} + M_{\substack{liquor \\ within\ WM}} + M_{\substack{lost \\ liquor}} + M_{\substack{liquor \\ samples}} \right) \times X_{organics\ in\ DL} \quad \text{.....Equation(E.3)}$$

$$\text{Overall mass balance closure (\%)} = \frac{M_{wood\_extracted\_into\_liquor} + M_{DMSF}}{M_{raw\_wood\_chips\_on\_dry\_basis}} \times 100 \quad \text{.....Equation(E.4)}$$

Mass Balance on Acetyl Groups

The component mass balance on the acetyl groups was performed by estimating the amount of acetyl groups in the raw and macerated wood, the drained liquor, the liquor lost in the piping system and in the samples used in the HPLC analysis for organic acids. Closure on the material balance was done by comparing the measured quantity of acetyl groups in the raw wood to that in macerated wood and the various liquor streams.

Acetyl groups in drained liquor

$$M_{\text{acetyl groups in DL}} = C_{\text{HAc in DL}} \times \text{volume of drained liquor} \times 0.7167$$

$$M_{\text{acetyl groups in DL}} = C_{\text{HAc in DL}} \times M_{DL} \times 0.7167 \quad \text{.....Equation(E.5)}$$

The conversion factor 0.7167 is the ratio of molecular weights of acetyl groups to the molecular weight of acetic acid. This factor is used here to calculate equivalent amount of acetyl groups for a given amount of acetic acid

Acetyl groups in liquor within wet macerated wood chips

$$M_{\text{acetyl groups in liquor within WM}} = C_{\text{HAc in drained liquor}} \times M_{\text{liquor within WM}} \times 0.7167 \quad \text{.....Equation (E.6)}$$

Acetyl groups in dry macerated salt free wood

$$M_{DM} = X_{\text{solids in WM}} \times M_{WM}$$

$$M_{\text{acetyl groups in DM}} = X_{\text{acetyl groups in DM}} \times M_{DM}$$

$$M_{\text{acetyl groups in DMSF}} = M_{\text{acetyl groups in DM}} - M_{\text{acetyl groups in liquor within WM}} \quad \text{.....Equation(E.7)}$$

Acetyl groups in the extract samples and in the lost liquor

$$M_{\text{acetyl groups in extract samples \& in lost liquor}} = C_{\text{HAc in DL}} \times \left(M_{\text{extract samples}} + M_{\text{lost liquor}}\right) \times 0.7167 \quad \text{.....Equation (E.8)}$$

$$\begin{pmatrix}\text{acetyl group}\\ \text{mass balance}\\ \text{closure (\%)}\end{pmatrix} = \frac{M_{\text{acetyl groups in DL}} + M_{\text{acetyl groups in liquor within WM}} + M_{\text{acetyl groups in DMSF}} + M_{\text{acetyl groups in extract samples \& in lost liquor}}}{M_{\text{acetyl groups in raw\_wood}}} \times 100$$

.....Equation (E.9)

APPENDIX F

ANALYTICAL DATA

Sample No	Time (minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	27	13.70 ± 0.29	0.00 ± 0.00	4.00 ± 0.26	10
2	30	27	13.20 ± 0.28	4.67 ± 0.31	2.66 ± 0.17	25
3	50	104	13.18 ± 0.28	5.66 ± 0.37	2.40 ± 0.16	25
4	70	160	13.09 ± 0.27	8.56 ± 0.56	1.59 ± 0.10	25
5	90	160	12.90 ± 0.27	9.46 ± 0.62	1.36 ± 0.09	25
6	150	160	11.29 ± 0.24	11.52 ± 0.75	0.81 ± 0.05	25
7	210	160	10.10 ± 0.21	11.62 ± 0.76	0.93 ± 0.06	25

Table F.1 Analytical Data of Experiment 1 – Soaking at 27 ^{0}C

Sample No	Time (minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	27	13.70 ± 0.29	0.00 ± 0.00	4.00 ± 0.26	10
2	13	80	13.34 ± 0.28	2.51 ± 0.16	3.28 ± 0.21	25
3	26	120	13.28 ± 0.28	7.27 ± 0.48	1.94 ± 0.13	25
4	56	120	13.06 ± 0.27	11.70 ± 0.77	0.71 ± 0.05	25
5	71	160	12.69 ± 0.27	11.83 ± 0.77	0.70 ± 0.05	25
6	131	160	9.47 ± 0.20	13.27 ± 0.87	0.33 ± 0.02	25
7	191	160	8.56 ± 0.18	13.64 ± 0.89	0.30 ± 0.02	25

Table F.2 Analytical Data of Experiment 2 – Soaking at 120 ^{0}C

Sample No	Time (minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	27	13.70 ± 0.29	0.00 ± 0.00	4.00 ± 0.26	10
2	20	104	13.11 ± 0.28	6.63 ± 0.43	2.10 ± 0.14	25
3	40	160	13.03 ± 0.27	8.18 ± 0.54	1.68 ± 0.11	25
4	60	160	12.47 ± 0.26	10.33 ± 0.68	1.10 ± 0.07	25
5	120	160	10.78 ± 0.23	12.07 ± 0.79	0.63 ± 0.04	25
6	180	160	9.06 ± 0.19	13.63 ± 0.89	0.26 ± 0.02	25

Table F.3 Analytical Data of Experiment 3 - No Soaking

Sample No	Time (Minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	24	12.23 ± 0.26	0.00 ± 0.00	4.00 ± 0.26	10
2	25	113	9.97 ± 0.21	1.37 ± 0.09	3.61 ± 0.24	25
3	40	113	9.37 ± 0.20	2.43 ± 0.16	3.31 ± 0.22	25
4	63	165	8.94 ± 0.19	3.10 ± 0.20	3.13 ± 0.20	25
5	108	165	7.22 ± 0.15	5.23 ± 0.34	2.54 ± 0.17	25
6	153	165	4.64 ± 0.10	8.27 ± 0.54	1.71 ± 0.11	25
7	175	111	4.38 ± 0.09	10.60 ± 0.69	1.24 ± 0.08	25

Table F.4 Analytical Data of Experiment 4 - 2% Green Liquor, 165 ^{0}C

Sample No	Time (Minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	24	13.30 ± 0.28	0.00 ± 0.00	4.00 ± 0.26	7
2	24	113	12.47 ± 0.26	3.97 ± 0.26	2.87 ± 0.19	25
3	39	113	11.35 ± 0.24	5.38 ± 0.35	2.47 ± 0.16	25
4	61	165	10.05 ± 0.21	8.23 ± 0.54	1.68 ± 0.11	25
5	106	165	9.63 ± 0.20	10.06 ± 0.66	1.19 ± 0.08	25
6	151	165	8.40 ± 0.18	13.58 ± 0.89	0.24 ± 0.02	25
7	173	111	8.21 ± 0.17	13.61 ± 0.89	0.26 ± 0.02	25
DL	-	-	-	12.57 ± 0.82	0.69 ± 0.05	-

Table F.5 Analytical Data of Experiment 5 - 8% Green Liquor, 165 ^{0}C

Sample No	Time (Minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	24	14.34 ± 0.30	0.00 ± 0.00	4.00 ± 0.26	5
2	25	113	14.34 ± 0.30	5.67 ± 0.37	2.38 ± 0.16	25
3	40	113	14.32 ± 0.30	9.61 ± 0.63	1.27 ± 0.08	25
4	63	165	14.28 ± 0.30	12.01 ± 0.79	0.61 ± 0.04	25
5	108	165	14.11 ± 0.30	13.50 ± 0.88	0.22 ± 0.01	25
6	154	165	13.97 ± 0.29	13.83 ± 0.91	0.15 ± 0.01	25
7	168	111	13.90 ± 0.29	13.30 ± 0.87	0.32 ± 0.02	25
DL	-	-	13.15 ± 0.28	12.83 ± 0.84	0.81 ± 0.05	-

Table F.6 Analytical Data of Experiment 6 - 15.9% White Liquor, 165 ^{0}C

Sample No	Time (Minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	24	14.19 ± 0.30	0.00 ± 0.00	4.00 ± 0.26	5
2	25	113	14.17 ± 0.30	4.36 ± 0.29	2.75 ± 0.18	25
3	40	113	14.10 ± 0.30	8.44 ± 0.55	1.60 ± 0.10	25
4	62	165	13.95 ± 0.29	10.87 ± 0.71	0.93 ± 0.06	25
5	107	165	12.92 ± 0.27	12.15 ± 0.80	0.59 ± 0.04	25
6	156	165	11.04 ± 0.23	13.36 ± 0.87	0.28 ± 0.02	25
7	172	111	10.80 ± 0.23	12.93 ± 0.85	0.43 ± 0.03	25
DL	-	-	10.27 ± 0.22	14.52 ± 0.95	0.02 ± 0.00	-

Table F.7 Analytical Data of Experiment 7 - 8% White Liquor, 165 ^{0}C

Sample No	Time (Minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	24	13.98 ± 0.29	0.00 ± 0.00	3.50 ± 0.23	7
2	26	113	13.88 ± 0.29	5.23 ± 0.34	2.00 ± 0.13	22
3	41	113	13.82 ± 0.29	8.29 ± 0.54	1.14 ± 0.07	27
4	66	165	13.75 ± 0.29	9.74 ± 0.64	0.75 ± 0.05	20
5	111	165	13.61 ± 0.29	11.06 ± 0.72	0.40 ± 0.03	22
6	156	165	13.37 ± 0.28	11.10 ± 0.73	0.40 ± 0.03	25
7	175	111	13.31 ± 0.28	10.25 ± 0.67	0.66 ± 0.04	18
DL	-	-	13.03 0.27	11.37 ± 0.74	0.43 ± 0.03	-

Table F.8 Analytical Data of Experiment 8 - 8% White Liquor, 120 ^{0}C-Part I

Sample No	Time (Min)	Concentration after pH adjustment (g/L)		Concentrations after acid hydrolysis (g/L)				
		Formic acid	Lactic acid	Glucose	Arabinose	XMG	Acid insoluble lignin	Acid soluble lignin
1	0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
2	26	0.15 ± 0.01	0.21 ± 0.02	0.04 ± 0.01	0.00 ± 0.00	0.75 ± 0.16	1.88 ± 0.21	1.35 ± 0.23
3	41	0.73 ± 0.07	0.93 ± 0.07	0.03 ± 0.01	0.01 ± 0.00	1.14 ± 0.24	4.30 ± 0.48	2.63 ± 0.45
4	66	1.15 ± 0.10	1.46 ± 0.12	0.01 ± 0.00	0.02 ± 0.00	1.06 ± 0.22	5.52 ± 0.62	3.70 ± 0.63
5	111	1.90 ± 0.17	2.39 ± 0.19	0.01 ± 0.01	0.07 ± 0.01	1.25 ± 0.27	9.62 ± 1.08	5.93 ± 1.01
6	156	2.27 ± 0.21	2.89 ± 0.23	0.04 ± 0.01	0.10 ± 0.02	1.54 ± 0.33	12.84 ± 1.44	7.29 ± 1.24
7	175	2.25 ± 0.20	2.81 ± 0.22	0.05 ± 0.02	0.10 ± 0.02	1.71 ± 0.36	12.12 ± 1.36	7.52 ± 1.28
DL	-	2.41 ± 0.22	3.03 ± 0.24	0.03 ± 0.01	0.12 ± 0.03	1.49 ± 0.32	14.18 ± 1.59	8.79 ± 1.50

Table F.9 Analytical Data of Experiment 8 - 8% White Liquor, 120 ^{0}C – Part II

Sample No	Time (Minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	24	13.96 ± 0.29	0.00 ± 0.00	3.50 ± 0.23	7
2	25	100	13.81 ± 0.29	5.06 ± 0.33	2.05 ± 0.13	22
3	40	100	13.74 ± 0.29	8.52 ± 0.56	1.08 ± 0.07	22
4	85	100	13.58 ± 0.29	11.48 ± 0.75	0.26 ± 0.02	25
5	130	100	13.52 ± 0.28	11.12 ± 0.73	0.38 ± 0.02	20
DL	-	-	13.35 ± 0.28	12.19 ± 0.80	0.11 ± 0.01	96

Table F.10 Analytical Data of Experiment 9 - 8% White Liquor, 100 ^{0}C – Part I

Sample No	Time (Min)	Concentration after pH adjustment (g/L)		Concentrations after acid hydrolysis (g/L)				
		Formic acid	Lactic acid	Glucose	Arabinose	XMG	Acid insoluble lignin	Acid soluble lignin
1	0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
2	25	0.32 ± 0.03	0.00 ± 0.00	0.02 ± 0.01	0.00 ± 0.00	0.61 ± 0.13	1.13 ± 0.13	1.20 ± 0.20
3	40	0.70 ± 0.06	0.47 ± 0.04	0.02 ± 0.01	0.01 ± 0.00	0.84 ± 0.18	2.75 ± 0.31	2.01 ± 0.34
4	85	1.43 ± 0.13	1.62 ± 0.13	0.02 ± 0.01	0.03 ± 0.01	1.16 ± 0.25	5.75 ± 0.64	3.63 ± 0.62
5	130	1.77 ± 0.16	1.97 ± 0.16	0.03 ± 0.01	0.04 ± 0.01	1.42 ± 0.30	7.15 ± 0.80	4.36 ± 0.74
DL	-	1.71 ± 0.15	2.46 ± 0.19	0.05 ± 0.02	0.06 ± 0.01	1.67 ± 0.35	8.73 ± 0.98	4.97 ± 0.85

Table F.11 Analytical Data of Experiment 9 - 8% White Liquor, 100 ^{0}C – Part II

Sample No	Time (Minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	24	13.82 ± 0.29	0.00 ± 0.00	3.50 ± 0.23	6
2	25	80	13.77 ± 0.29	3.62 ± 0.24	2.46 ± 0.16	30
3	40	80	13.79 ± 0.29	6.86 ± 0.45	1.55 ± 0.10	21
4	85	80	13.74 ± 0.29	10.87 ± 0.71	0.43 ± 0.03	26
5	130	80	13.68 ± 0.29	12.32 ± 0.81	0.05 ± 0.00	25
DL	-	-	13.64 ± 0.29	11.85 ± 0.78	0.23 ± 0.01	-

Table F.12 Analytical Data of Experiment 10 - 8% White Liquor, 80 ^{0}C-Part I

Sample No	Time (Min)	Concentration after pH adjustment (g/L)		Concentrations after acid hydrolysis (g/L)				
		Formic acid	Lactic acid	Glucose	Arabinose	XMG	Acid insoluble lignin	Acid soluble lignin
1	0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
2	25	0.04 ± 0.00	0.02 ± 0.00	0.04 ± 0.01	0.00 ± 0.00	0.38 ± 0.08	0.85 ± 0.10	0.68 ± 0.12
3	40	0.06 ± 0.01	0.13 ± 0.01	0.07 ± 0.02	0.00 ± 0.00	0.56 ± 0.12	1.90 ± 0.21	1.48 ± 0.25
4	85	0.87 ± 0.08	0.52 ± 0.04	0.11 ± 0.04	0.01 ± 0.00	0.81 ± 0.17	3.17 ± 0.36	2.31 ± 0.39
5	130	1.24 ± 0.11	0.93 ± 0.07	0.14 ± 0.05	0.01 ± 0.00	1.04 ± 0.22	5.02 ± 0.56	3.34 ± 0.57
DL	-	0.64 ± 0.06	1.09 ± 0.09	0.15 ± 0.05	0.01 ± 0.00	1.08 ± 0.23	5.13 ± 0.57	3.45 ± 0.59

Table F.13 Analytical Data of Experiment 10 - 8% White Liquor, 80 ^{0}C – Part II

Sample No	Time (Minutes)	Temperature (^{0}C)	pH	Acetic acid concentration after pH adjustment (g/L)	Calculated % acetyl groups in macerated wood (using extract concentration)	Sample volume (mL)
1	0	24	13.94 ± 0.29	0.00 ± 0.00	3.50 ± 0.23	7
2	6	50	13.95 ± 0.29	2.35 ± 0.15	2.83 ± 0.19	25
3	21	50	13.95 ± 0.29	5.35 ± 0.35	1.98 ± 0.13	25
4	64	50	13.90 ± 0.29	9.82 ± 0.64	0.73 ± 0.05	50
5	109	50	13.81 ± 0.29	12.56 ± 0.82	0.01 ± 0.00	35
DL	-	-	13.79 ± 0.29	12.70 ± 0.83	0.00 ± 0.00	142

Table F.14 Analytical Data of Experiment 11 - 8% White Liquor, 50 ^{0}C – Part I

Sample No	Time (Min)	Concentration after pH adjustment (g/L)		Concentrations after acid hydrolysis (g/L)				
		Formic acid	Lactic acid	Glucose	Arabinose	XMG	Acid insoluble lignin	Acid soluble lignin
1	0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
2	6	0.00 ± 0.00	0.00 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.15 ± 0.03	0.42 ± 0.05	0.44 ± 0.08
3	21	0.02 ± 0.00	0.00 ± 0.00	0.03 ± 0.01	0.00 ± 0.00	0.29 ± 0.06	0.58 ± 0.07	0.84 ± 0.14
4	64	0.01 ± 0.00	0.00 ± 0.00	0.07 ± 0.02	0.00 ± 0.00	0.51 ± 0.11	1.42 ± 0.16	1.46 ± 0.25
5	109	0.05 ± 0.00	0.02 ± 0.00	0.09 ± 0.03	0.00 ± 0.00	0.70 ± 0.15	2.08 ± 0.23	1.84 ± 0.31
DL	-	0.04 ± 0.00	0.02 ± 0.00	0.09 ± 0.03	0.00 ± 0.00	0.78 ± 0.16	2.14 ± 0.24	1.77 ± 0.30

Table F.15 Analytical Data of Experiment 11 - 8% White Liquor, 50 ^{0}C – Part II

Experiment No	Raw wood properties		Mass added to digester (gram)		Mass recovered from the digester (gram)			Losses (gram)
	Moisture content in raw wood (%)	% Acetyl Content	Wood (dry basis)	Total liquor (including moisture in raw wood)	Drained liquor (gm)	Wet macerated wood chips (gram)	Total mass of all extract samples removed	
1	40	4	800	3200	2211	1610	160	19
2	40	4	800	3200	2155	1622	160	63
3	40	4	800	3200	2325	1563	135	-23
4	40	4	800	3200	2279	1510	160	51
5	40	4	800	3200	2112	1602	157	129
6	40	4	900	3600	2502	1721	155	122
7	40	4	900	3600	2400	1777	155	168
8	40	3.5	900	3600	2495	1819	141	45
9	40	3.5	900	3600	2498	1883	96	23
10	37.5	3.5	900	3600	2500	1924	108	-32
11	37.5	3.5	900	3600	2440	1937	142	-19
Error Analysis -1 (E-1)	40	3.5	900	3600	-	-	-	-
Error Analysis-2 (E-2)	40	3.5	900	3600	2500	1690	157	153
Error Analysis-3 (E-3)	40	3.5	900	3600	2567	1701	139	93
Error Analysis-4 (E-4)	40	3.5	900	3600	2603	1689	158	50

Table F.16 Masses of Wood Chips and Liquor Added and Recovered From the Digester

Time (Minutes)	Extract pH			
	Error analysis-1	Error analysis-2	Error analysis -3	Error analysis -4
0	14.19 ± 0.30	14.06 ± 0.30	14.01 ± 0.29	13.89 ± 0.29
26	14.17 ± 0.30	14.01 ± 0.29	13.91 ± 0.29	13.81 ± 0.29
41	14.10 ± 0.30	13.94 ± 0.29	13.88 ± 0.29	13.74 ± 0.29
64	13.95 ± 0.29	13.77 ± 0.29	13.69 ± 0.29	13.57 ± 0.28
109	11.92 ± 0.25	11.63 ± 0.24	11.62 ± 0.24	11.26 ± 0.24
154	11.04 ± 0.23	11.06 ± 0.23	10.79 ± 0.23	10.59 ± 0.22
179	10.80 ± 0.23	10.78 ± 0.23	10.54 ± 0.22	10.26 ± 0.22
Extract Concentrations after Acid Hydrolysis				
Time (Minutes)	Acid soluble lignin (g/L)			
	Error analysis-1	Error analysis-2	Error analysis -3	Error analysis -4
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
26	1.01 ± 0.17	1.16 ± 0.20	1.61 ± 0.27	1.41 ± 0.24
41	1.82 ± 0.31	2.65 ± 0.45	2.61 ± 0.45	2.67 ± 0.46
64	3.16 ± 0.54	5.58 ± 0.95	5.63 ± 0.96	6.03 ± 1.03
109	9.16 ± 1.56	9.85 ± 1.68	10.98 ± 1.87	12.18 ± 2.08
154	11.20 ± 1.91	12.58 ± 2.14	11.34 ± 1.93	12.02 ± 2.05
179	12.69 ± 2.16	12.21 ± 2.08	12.86 ± 2.19	14.11 ± 2.41
Time (Minutes)	Acid insoluble lignin (g/L)			
	Error analysis-1	Error analysis-2	Error analysis -3	Error analysis -4
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
26	1.69 ± 0.19	1.44 ± 0.16	2.12 ± 0.24	1.76 ± 0.20
41	3.92 ± 0.44	3.74 ± 0.42	3.98 ± 0.45	3.92 ± 0.44
64	6.91 ± 0.77	8.72 ± 0.98	9.18 ± 1.03	8.04 ± 0.90
109	18.19 ± 2.04	20.12 ± 2.26	22.54 ± 2.53	22.22 ± 2.49
154	23.74 ± 2.66	25.78 ± 2.89	25.96 ± 2.91	24.36 ± 2.73
179	28.11 ± 3.15	25.71 ± 2.88	26.88 ± 3.01	27.12 ± 3.04

Table F.17 Analytical Data of Error Analysis Experiments –Part I

Extract Concentrations after Adjusting pH to 1				
Time (Minutes)	Acetic acid concentrations (g/L)			
	Error analysis-1	Error analysis-2	Error analysis -3	Error analysis -4
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
26	5.54 ± 0.36	6.50 ± 0.43	5.82 ± 0.38	5.63 ± 0.37
41	9.31 ± 0.61	9.15 ± 0.60	8.83 ± 0.58	8.50 ± 0.56
64	9.87 ± 0.65	10.61 ± 0.69	10.22 ± 0.67	10.50 ± 0.69
109	11.66 ± 0.76	11.48 ± 0.75	11.07 ± 0.73	10.73 ± 0.70
154	11.40 ± 0.75	11.37 ± 0.74	11.91 ± 0.78	10.77 ± 0.71
179	11.92 ± 0.78	11.97 ± 0.78	11.50 ± 0.75	11.28 ± 0.74
Time (Minutes)	Formic acid concentrations (g/L)			
	Error analysis-1	Error analysis-2	Error analysis -3	Error analysis -4
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
26	0.20 ± 0.02	0.19 ± 0.02	0.17 ± 0.02	0.16 ± 0.01
41	0.64 ± 0.06	0.78 ± 0.07	0.66 ± 0.06	0.66 ± 0.06
64	1.23 ± 0.11	1.64 ± 0.15	1.63 ± 0.15	1.60 ± 0.14
109	2.59 ± 0.23	2.94 ± 0.27	2.73 ± 0.25	2.73 ± 0.25
154	3.23 ± 0.29	3.29 ± 0.30	3.37 ± 0.30	3.13 ± 0.28
179	3.77 ± 0.34	3.70 ± 0.33	3.60 ± 0.32	3.44 ± 0.31
Time (Minutes)	Lactic acid concentrations (g/L)			
	Error analysis-1	Error analysis-2	Error analysis -3	Error analysis -4
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
26	0.29 ± 0.02	0.27 ± 0.02	0.23 ± 0.02	0.23 ± 0.02
41	0.99 ± 0.08	1.09 ± 0.09	0.92 ± 0.07	0.95 ± 0.08
64	1.81 ± 0.14	2.25 ± 0.18	2.19 ± 0.17	2.21 ± 0.17
109	3.54 ± 0.28	3.63 ± 0.29	3.39 ± 0.27	3.40 ± 0.27
154	3.90 ± 0.31	3.89 ± 0.31	3.95 ± 0.31	3.72 ± 0.29
179	4.34 ± 0.34	4.26 ± 0.34	4.07 ± 0.32	4.00 ± 0.32

Table F.18 Analytical Data of Error Analysis Experiments- Part II

Extract Concentrations after Acid Hydrolysis				
Time (Minutes)	Glucose (g/L)			
	Error analysis-1	Error analysis-2	Error analysis -3	Error analysis -4
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
26	0.03 ± 0.01	0.07 ± 0.03	0.08 ± 0.03	0.00 ± 0.00
41	0.06 ± 0.02	0.07 ± 0.02	0.08 ± 0.03	0.11 ± 0.04
64	0.10 ± 0.03	0.11 ± 0.04	0.14 ± 0.05	0.17 ± 0.06
109	0.47 ± 0.16	0.25 ± 0.09	0.34 ± 0.12	-
154	0.38 ± 0.13	0.27 ± 0.09	0.35 ± 0.12	0.38 ± 0.13
179	0.37 ± 0.13	0.29 ± 0.10	0.36 ± 0.13	-
Time (Minutes)	Arabinose (g/L)			
	Error analysis-1	Error analysis-2	Error analysis -3	Error analysis -4
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
26	0.01 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
41	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.01
64	0.05 ± 0.01	0.06 ± 0.01	0.06 ± 0.01	0.08 ± 0.02
109	0.23 ± 0.05	0.26 ± 0.06	0.35 ± 0.07	-
154	0.41 ± 0.09	0.49 ± 0.10	0.48 ± 0.10	0.45 ± 0.10
179	0.54 ± 0.11	0.53 ± 0.11	0.57 ± 0.12	-
Time (Minutes)	XMG [Xylose + Mannose + Galactose] (g/L)			
	Error analysis-1	Error analysis-2	Error analysis -3	Error analysis -4
0	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00
26	0.27 ± 0.04	0.90 ± 0.12	0.88 ± 0.12	0.00 ± 0.00
41	0.46 ± 0.06	1.52 ± 0.21	1.26 ± 0.17	1.48 ± 0.20
64	0.75 ± 0.10	2.13 ± 0.29	2.09 ± 0.28	2.28 ± 0.31
109	3.90 ± 0.53	3.90 ± 0.53	4.42 ± 0.60	-
154	4.27 ± 0.58	4.30 ± 0.58	4.65 ± 0.63	5.03 ± 0.68
179	5.25 ± 0.71	4.56 ± 0.62	4.91 ± 0.66	-

Table F.19 Analytical Data of Error Analysis Experiments- Part III

BIOGRAPHY OF THE AUTHOR

Ravikant Amogisidha Patil was born on 16th November 1985 in Solapur, India. He was raised in Mumbai where he completed his elementary and high school education. He graduated with a Bachelor of Chemical Technology degree from the Institute of Chemical Technology, Mumbai in 2007. After graduation, he worked as a process engineer at the Paxchem Ltd, Mumbai for one year. Then, he moved to the Indian Institute of Technology, Kharagpur, where he earned his Master of Technology degree in Chemical Engineering in May 2010. He enrolled into Chemical Engineering graduate program at the University of Maine in Fall-2010. The author plans to continue his studies toward his PhD degree in Chemical Engineering at the University of Maine. Ravi is a candidate for the Master of Science degree in Chemical Engineering from The University of Maine in December 2012.