

INTEGRATION OF XYLAN EXTRACTION FROM *E.GRANDIS*, PRIOR TO PULPING, INTO KRAFT MILLS.

by

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Declaration

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Executive Summary

Pulp and paper mills are being placed under increasing pressure to maximise the use of the biomass being processed for pulp, and move towards integrated biorefineries (IFBRs), where a diverse range of products can be produced and not just pulp exclusively. Extracting hemicelluloses prior to the pulping process could increase the profitability of the mills as the hemicelluloses could be used to produce a number of additional products. Hemicelluloses are a plant polysaccharides with the most abundant hemicellulose in hardwoods being xylan, with xylose being the primary monosaccharide constituent of xylan. The majority of pulps produced in the Southern Hemisphere are done with hardwoods as feedstock, typically with the Kraft process. The attraction of the concept of extracting hemicellulose prior to pulping is further augmented by the fact that hemicellulose is underutilised in the Kraft process. In the Kraft process the hemicellulose is dissolved during pulping and burned along with lignin for the production of energy, however, hemicellulose has about half the heating value when compared to that of lignin.

The main objective of this study was to find a pre-extraction method that is effective in releasing xylan from *Eucalyptus grandis*, the most important hardwood feedstock used for pulping in the Southern Hemisphere. The method also needs to be practical in terms of integrating it into the Kraft process and should have a minimal effect on pulp yield and subsequent paper qualities.

Xylan extractions from *E. grandis* as feedstock were carried out with white liquor, green liquor and NaOH. Green liquor is the dissolved smelt originating from the recovery boiler in the Kraft process and consists mainly sodium carbonate and sodium sulphide. White liquor's principal components include sodium hydroxide and sodium sulphide and is used in the digesters during the pulping stage of the Kraft process. NaOH is a make up chemical used in the Kraft process. These chemicals were chosen since they are all already present within the Kraft process. The suitability of these chemicals as xylan extraction methods is further bolstered by the fact that their alkalinity may actually reduce chemical usage in pulping. This provides scope for

integration of hemicellulose extraction into Kraft pulping without implementing major changes to the existing industrial process. Moreover, alkali chemicals for pre-extraction allow for minimal effect on resulting pulp and paper. In terms of the extracted product, the alkaline conditions provided by these chemicals create conditions that are suitable for a high degree of polymerisation of hemicelluloses.

Xylan pre-extracted chips from selected extraction conditions were subjected to varying pulping conditions, to replicate pulp yields and properties obtained with untreated *E. grandis* chips when using conventional pulping. Handsheets were also produced from the pulps produced under the highest pulp yield conditions, and these were tested for pulp quality properties. Furthermore, mass balances were performed to gauge the impact that hemicellulose pre-extraction would have using green liquor, white liquor and NaOH on the sodium and sulphur balances of the mill.

From the extractions performed, the highest fraction of xylan recovered was 15.15% w/w utilising 2M NaOH, at 120°C for 90 minutes extraction time. This was followed by white liquor extraction at 13.27% w/w utilising 20% AA at 140°C for 90 minutes. Green liquor extraction produced the lowest xylan recovery at 7.83% w/w with 2% TTA and 160°C with an h-factor of 800. The residues from selected extraction conditions were utilised for these pulping optimisation experiments.

Selected extraction conditions used for further pulping included 2% TTA and 160°C for green liquor, 20% AA and 120°C and 140°C extraction temperature for white liquor, as well as 2M concentration and 120°C for NaOH.

The highest yielding pulping conditions were achieved with a 35% reduction in pulping chemicals and 45 minutes pulping time in combination with green liquor pre-extraction, while for pulping combined with white liquor pre-extraction a 50% reduction in chemicals and 30 minute pulping time was preferred. For pulping subsequent to NaOH pre-extraction a 75% reduction in the NaOH dosage and a 45 minute pulp time was preferred. All pulp steps were performed at 170°C.

Unbeaten handsheets produced from the selected pulping conditions for white liquor and green liquor extracted chips showed similar physical properties (burst, tear, tensile indices) when compared to the control (pulp from non-extracted chips). However the greater quantity of xylan removed from cellulose fibres with NaOH extraction, resulted in pulps with lower xylan contents, which affected the burst and tear indices of the handsheets formed from these pulps. An increase in tear, while a reduction in the burst index, was observed for the pulp produced from NaOH extracted chips.

It was concluded that although white liquor and NaOH extraction allows for greater xylan recovery, the large chemical expenditure associated with these methods will impose significant cost impacts on the existing Kraft process. From mass balances performed, green liquor xylan extraction due to its lower alkalinity, will be more forgiving in terms of additional make up chemical costs. It also allowed for minimum effect on both the pulp and paper quality, thus making it the most practical of the pre-extraction methods. However, whether the additional make chemicals required for the green liquor extraction method will be justified by the quantity of xylan extracted will only be answered by a thorough economic assessment, which was not in the scope of this project.

Bestuursopsomming

Pulp- en papiermeule word onder toenemende druk geplaas om die gebruik van die biomassa wat vir pulp verwerk word, te maksimaliseer, en om te beweeg na geïntegreerde bioraffinaderye, waar 'n groot verskeidenheid produkte vervaardig kan word, en nie slegs uitsluitlik pulp nie. Die ekstraksie van hemisellulose voor die verpulpingproses kan die winsgewendheid van die meule verhoog, aangesien die hemisellulose gebruik kan word vir die vervaardiging van verskeie bykomende produkte. Hemisellulose is 'n plantpolisakkaried, met xilaan as die hemisellulose wat die oorfloedigste in hardehout gevind word, en met xilose as die primêre monosakkaried-bestanddeel van xilaan. Die meerderheid van die pulp wat in die Suidelike Halfrond geproduseer word, word met hardehout as voerstof gedoen, tipies met behulp van die Kraft-proses. Die aantreklikheid van die konsep om hemisellulose voor verpulping te win, word verder versterk deur die feit dat hemisellulose in die Kraft-proses onderbenut word. In die Kraft-proses word die hemisellulose tydens verpulping opgelos en saam met lignien verbrand vir die opwekking van energie, maar hemisellulose het egter ongeveer die helfte van die verhittingswaarde van dié van lignien.

Die vernaamste doelstelling van hierdie studie was om 'n pre-ekstraksiemetode te vind wat xilaan doeltreffend van *Eucalyptus grandis*, die belangrikste hardhout-voerstof wat in die Suidelike Halfrond vir verpulping gebruik word, kan vrystel. Die metode moet ook prakties wees met betrekking tot integrering met die Kraft-proses, en dit moet 'n minimale uitwerking op pulpopbrengs en gevolglike papiergehalte hê.

Xilaan-ekstraksie uit *E. grandis* as voerstof is uitgevoer met wit loog, groen loog en NaOH. Hierdie chemikalieë is gekies omdat hulle reeds in die Kraft-proses teenwoordig is. Die geskiktheid van hierdie chemikalieë as xilaan-ekstraksiemetodes is verder ondersteun deur die feit dat hul alkaliniteit moontlik chemiese verbruik in verpulping kan verlaag, wat ruimte vir die integrasie van hemisellulose-ekstraksie in Kraft-verpulping laat sonder om grootskaalse veranderinge aan bestaande nywerheidsprosesse te implementeer. Alkali-chemikalieë vir pre-ekstraksie lei boonop tot 'n minimale uitwerking op resultante pulp en papier, terwyl die

alkalitoestande, met betrekking tot die geëkstraheerde produk, toestande skep wat geskik is vir 'n hoë mate van polimerisasie van hemisellulose.

Uit die ekstraksies wat uitgevoer is, is die hoogste fraksie xilaan gewin deur die gebruik van NaOH teen 15.15% w/w met 2M NaOH, teen 120 °C vir 90 minute ekstraksietyd. Dit is gevolg deur witloog-ekstraksie teen 13.27% w/w met die gebruik van 20% AA teen 140 °C vir 90 minute. Groenloog-ekstraksie het die laagste xilaan-winning teen 7.83% w/w met 2% TTA en 160°C met 'n h-faktor van 800 voortgebring.

Houtspaanders wat aan xilaan-pre-ekstraksie met groen loog onderwerp is, het pulp met kappanommers en opbrengste soortgelyk aan dié van nie-geëkstraheerde spaanders voortgebring toe die chemiese lading met 35% verlaag is, in verhouding tot dié wat vir nie-geëkstraheerde spaanders gebruik is. Xilaan-pre-geëkstraheerde spaanders met wit loog het 'n 50%-vermindering in verpulpingchemikalieë gelewer in verhouding tot houtspaanders wat aan konvensionele verpulping onderwerp is. Die chemiese reduksie van groen loog was minder as dié van wit loog weens die laer alkalilading wat tydens hemisellulose-ekstraksie voor verpulping gebruik is. Vir witloog-ekstraksie kon pulpopbrengste gehandhaaf word, alhoewel pre-geëkstraheerde spaanders met wit loog 'n neiging getoon het om pulp met laer kappanommers voort te bring. Alhoewel pulp wat uit houtspaanders gemaak is wat aan NaOH-ekstraksie onderwerp is, gelei het tot 'n 75%-vermindering van NaOH gebruik in verhouding tot dié van konvensionele verpulping, is verwag dat geen NaOH benodig sou word nie, aangesien die houtspaanders reeds tydens xilaan-ekstraksie aan 2M NaOH blootgestel is. Voorts, in die literatuur is verpulping uitgevoer ná 2M NaOH-ekstraksie sonder dat die toevoeging van NaOH tydens verpulping nodig was [61].

Handvelle is vervaardig uit die pulp wat in die hoogste pulpopbrengs-toestande vervaardig is, en dit is vir pulpgehalte-eienskappe getoets. Die verpulpingstoestande met die hoogste opbrengs is bereik met 'n 35%-vermindering van verpulpingchemikalieë en 45 minute verpulpingstyd in kombinasie met groenloog-pre-ekstraksie, terwyl vir verpulping met witloog-pre-ekstraksie 'n 50%-vermindering van chemikalieë en 30 minute verpulpingstyd verkies is. Vir

verpulping ná NaOH-pre-ekstraksie is 'n 75%-vermindering van die NaOH-dosis en 45 minute verpulpingstyd verkies. Alle verpulpingstappe is teen 170°C uitgevoer.

Ongeklopte handvelle vervaardig uit die gekose verpulpingstoestande vir witloog- en groenloog- geëkstraheerde spaanders het soortgelyke fisiese eienskappe getoon (bars-, skeur- en trek-indeks) in vergelyking met die kontrole (pulp uit nie-geëkstraheerde spaanders). Die grootste hoeveelheid xilaan is egter uit sellulose vesel met NaOH-ekstraksie verkry, wat gelei het tot pulp met laer xilaaninhoud, wat die bars- en skeur-indeks van die handvelle wat uit hierdie pulp vervaardig is, beïnvloed het. 'n Toename in die skeur-indeks, met 'n afname in die bars-indeks, is waargeneem vir die pulp wat uit NaOH-geëkstraheerde spaanders vervaardig is.

Die gevolgtrekking is gemaak dat alhoewel witloog- en NaOH-ekstraksie groter xilaanwinning moontlik maak, die groot chemiese uitgawe geassosieer met hierdie metode 'n aanmerklike koste-impak vir die bestaande Kraft-proses inhou. Groenloog-xilaanekstraksie sal, weens die laer alkaliniteit, meer geskik wees met betrekking tot die koste van bykomende aanvullende chemikalieë. Dit hou ook 'n kleiner uitwerking op die pulp- en papiergehalte in, wat dit dus die praktieste van die pre-ekstraksiemetodes maak. Of die bykomende chemikalieë nodig vir die witloog- en NaOH-ekstraksies egter geregverdig kan word deur die hoeveelheid xilaan wat gewin is, kan slegs deur 'n deeglike ekonomiese assessering beantwoord word, wat nie binne die omvang van hierdie projek geval het nie.

Dedication

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Table of Contents

Executive Summary	ii
Bestuursopsomming	v
Dedication	viii
Acknowledgements	ix
Table of Contents.....	x
List of Tables.....	xiv
List of Figures.....	xvi
Abbreviations and symbols.....	xix
CHAPTER 1: INTRODUCTION.....	1
CHAPTER 2: LITERATURE REVIEW	4
2.1. Woody Biomass.....	4
2.1.1. Use of woody biomass and its future.	4
2.1.2. Chemical composition of wood	6
2.1.2.1. Cellulose.....	7
2.1.2.2. Hemicellulose	8
2.1.2.3. Lignin.....	9
2.1.2.4. Extractives.....	10
2.1.3. Eucalyptus grandis	11
2.2. The Concept of a forest biorefinery.	12
2.2.1. Integrated Pulp and Paper Biorefinery	14
2.2.1.1. Integration of hemicellulose extraction into the Kraft process	18
2.2.1.1.1. Methods of hemicelluloses extraction	23
2.2.1.1.1.1 Acid Hydrolysis.....	23
2.2.1.1.1.2 Hydrothermal Pre-treatments.....	23
2.2.1.1.1.3 Alkali Treatments.....	24
2.3. Opportunities for improving performance of Kraft mills.....	29

CHAPTER 3: Objectives	30
CHAPTER 4: Extraction of Xylan from <i>Eucalyptus grandis</i> using green liquor, white liquor and NaOH.	33
4.1. Introduction.....	33
4.1.1. Materials and Methods.....	36
4.1.2. Sample Preparation of <i>E. grandis</i> Feedstock	37
4.1.3. Compositional analysis of <i>E. grandis</i> and pre-extracted wood chips.	37
4.1.3.1. Determination of Moisture Content	38
4.1.3.2. Extractives Content.....	38
4.1.3.3. Determination of Carbohydrates and Lignin.....	38
4.1.3.4. Ash content.....	39
4.1.3.5. Determination of wood weight loss of pre-extracted chips.	40
4.1.4. Compositional analysis of liquid fraction after extraction.	40
4.1.4.1. HPLC preparation for analysis of sugars and acids.....	40
4.1.4.2. Xylose Yield	41
4.1.4.3. Fourier Transform Infrared(FT-IR)	41
4.1.5. Extraction procedures using White Liquor, Green Liquor and NaOH.....	42
4.1.5.1. Mild temperature extraction of <i>E. grandis</i> using White Liquor	42
4.1.5.1.1. Experimental design	43
4.1.5.2. Pre-extraction of hemicellulose using temperatures above 100 °C.....	45
4.1.5.2.1. White Liquor Extraction	46
4.1.5.2.2. Green Liquor extraction	46
4.1.5.2.3. NaOH Extraction	47
4.2. Results	48
4.2.1. Compositional Analysis of the <i>E. grandis</i> feedstock.	48
4.2.2. Comparison of xylose recovered using green liquor, white liquor and NaOH.	49
4.2.2.1.1. Wood Weight Loss of <i>E. grandis</i> subjected to white liquor, green liquor and NaOH extraction at temperatures exceeding 100°C.....	57
4.2.2.2. Purity of extracted Liquor	61
4.3. Discussion.....	63

4.3.1.	E. grandis response to white liquor, green liquor and NaOH extraction.	63
4.4.	Conclusions.....	69
CHAPTER 5:	Pulping yields and quality from pre-extracted Material.....	71
5.1.	Introduction.....	71
5.2.	Materials and methods	73
5.2.1.	Pulping of chips subjected to hemicellulose pre-extraction.	73
5.2.2.	Kappa Number determination.....	75
5.2.3.	Formation of handsheets.....	77
5.2.4.	Testing of physical properties of handsheets formed.....	78
5.2.4.1.	Basis weight	78
5.2.4.2.	Tear Index	78
5.2.4.3.	Burst Index.....	79
5.2.4.4.	Tensile Index.....	79
5.3.	Results	81
5.3.1.	Effect of extracting xylan from E. grandis chips on pulp yield.....	81
5.3.2.	Physical properties of handsheets prepared from pulp produced from xylan pre-extracted wood chips	85
5.3.3.	Summary of best extraction and pulping combinations for each extraction chemical with corresponding xylan yields and handsheet properties.....	90
5.4.	Discussion.....	92
5.5.	Conclusions.....	98
CHAPTER 6:	Effect of hemicellulose pre-extraction on sodium and sulphur requirements of a Kraft mill.....	100
6.1.	Introduction.....	100
6.2.	Methodology.....	102
6.2.1.	Comparison of Na/S balance around Kraft mill for various extraction methods.	102
6.3.	Results	106
6.3.1.	Comparison of chemical usage during extraction and pulping.	106
6.3.2.	Effect of hemicellulose pre-extraction on the Na/S balance of a Kraft mill.....	110

6.3.3. Comparison of xylose recovery versus chemical addition between different extraction methods.	121
6.4. Discussion.....	123
6.4.1. Effect of extraction methods on sodium and sulphur balances of a Kraft mill. ...	123
6.5. Conclusions.....	128
CHAPTER 7: Conclusions and recommendations	130
7.1. Conclusions.....	130
7.1.1. Recovery and purity of xylan.	130
7.1.2. Quality of pulp and paper resulting from E. grandis subjected to green liquor, white liquor and NaOH extraction.....	131
7.1.3. Impact utilising green liquor,white liquor and NaOH extraction on sodium and sulfur balance of kraft mill.....	132
7.1.4. Most feasible extraction method for integration into the Kraft process.	133
7.2. Recommendations	133
References.....	135
Appendix A: Sulphuric acid addition to extracted hemicellulose streams for HPLC analysis.....	151
Appendix B: Data for extracted residues	152
Appendix C: Paper Properties	155

List of Tables

<i>Table 1: Productivities and recycle times of various feedstocks (Adapted from Liu [16])</i>	6
<i>Table 2: Typical Chemical composition on both Hardwoods and Softwoods (Adapted from Goldstein [34])</i>	7
<i>Table 3: Table depicting potential uses of xylan.</i>	8
<i>Table 4: The classification of extractives found in wood (Adapted from Stenius [52])</i>	10
<i>Table 5: E. grandis structural composition from literature.</i>	11
<i>Table 6: Table showing extraction conditions and corresponding results of hemicellulose pre-extraction using green liquor, white liquor and NaOH, for purpose of integrating into Kraft Mills.</i>	26
<i>Table 7: Table providing summary of chemicals used.</i>	36
<i>Table 8: Methods that were used for compositional analysis of wood chips.</i>	37
<i>Table 9: Concentrations of Na₂S and NaOH for extractions that were carried out using 16% and 20% AA. Concentrations are on an Na₂O equivalent basis.</i>	43
<i>Table 10: Table depicting both coded and uncoded levels of independent variables.</i>	44
<i>Table 11: Table showing experimental runs with corresponding coded variables. (Table format adapted from Fenech et al [69])</i>	44
<i>Table 12: Table indicating composition of green liquor used.</i>	47
<i>Table 13: The Average Compositional Analysis of the E. grandis Feedstock used on a dry basis.</i> 48	
<i>Table 14: Results of central composite design where E. grandis was subjected to white liquor extraction at temperatures between 50°C-90°C, AA concentrations between 16-20%, and extraction times ranging between 60 and 240 minutes.</i>	49
<i>Table 15: Table providing summary of chemicals used.</i>	73
<i>Table 16: Methods used for the determination of the physical properties of the handsheets.</i> ...	78
<i>Table 17: Table showing pulp conditions and properties of non-extracted E. grandis chips.</i>	81
<i>Table 18: Table showing pulp yields and corresponding Kappa Numbers of pre-extracted E. grandis chips subjected to various pulping conditions.</i>	82
<i>Table 19: Table showing conditions chosen to produce handsheets for testing of physical properties.</i>	85
<i>Table 20: Summary of results for best extraction and pulping combination, with xylan yields and handsheets properties, for each extraction chemical. Extraction conditions and subsequent pulping conditions are shown at the top and bottom of the table respectively.</i>	90
<i>Table 21: Table showing total amount of NaOH, Na₂S and Na₂CO₃ required for both extraction and pulping for 85g of oven dried wood chips.</i>	108

Table 22: Table showing mass balance of sodium and sulphur in Figure 29 for 0%,20%,50% and 90% recovery of the sodium and sulphur that exits in the extracted hemicellulose stream. (All quantities are displayed as kilograms per air dried pulp produced) 111

Table 23: Table showing mass balance of sodium and sulphur in Figure 33 for 0%,20%,50% and 90% recovery of the sodium and sulphur that exits in the extracted hemicellulose stream. (All quantities are displayed as kilograms per air dried pulp produced) 116

Table 24: Table showing mass balance of sodium and sulphur in Figure 35 for 0%,20%,50% and 90% recovery of the sodium and sulphur found in the extracted hemicellulose stream(All quantities are displayed as kilograms per air dried pulp produced) 119

List of Figures

Figure 1: Cellulose structure (Redrawn from Carlmark et al [35])	7
Figure 2: Cellulose structure (Redrawn from Carlmark et al [35])	7
Figure 3: Three monomer units making up lignin in nature: A:p-coumaryl alcohol, B:Coniferyl Alcohol, C:Sinapyl Alcohol. (Redrawn from Biermann [80]).....	9
Figure 4: Products produced from thermochemical and biochemical processing of lignocellulosic biomass. (Adapted from Menon and Rao [89])	12
Figure 5:Illustration of the Kraft process as a biorefinery receptor showing defined and undefined processes(Adapted from Moshekelani et al [3]).	15
Figure 6: Kraft process showing some possible additional processes to maximize use of woody biomass.(Redrawn from Stuart and El-Halwagi [54])	15
Figure 7: Schematic of Kraft chemical recovery cycle. (Adapted from Fengel and Wegner [13] and Tran et al [21])	19
Figure 8: Schematic showing general energy effects hemicellulose pre-extraction will have on the kraft process.	21
Figure 9: Layout of project objectives.	32
Figure 10: Figure depicting a three factor face centred central composite design with part A depicting the factorial portion while part B are the points in the axial portion of the design.(Adapted from Fenech et al [69].)	43
Figure 11: Figure displaying set up of oscillating digester used for hemicellulose extraction as well as pulping.	45
Figure 12: Standardized Pareto chart depicting the effects of temperature(°C), time(minutes) and Active Alkali charge(%) on xylose recovery.	51
Figure 13: Response surface plot for xylose recovery(%) after white liquor extraction under non-pressurised conditions at a fixed AA charge of 18%. The figure shows the impact of both extraction time(minutes) and temperature(°C).	52
Figure 14: Mass of solubilised sugars recovered in extraction liquor per 100 grams of E. grandis feedstock using white liquor. a)16% Active Alkali b) 20% Active Alkali. Temperatures ranging between 100°C and 140°C for both a) and b).	54
Figure 15: Mass of solubilised sugars recovered in extraction liquor per 100 grams of E. grandis feedstock using NaOH. a)1M NaOH b) 2MNaOH. Temperatures ranging between 100°C and 140°C for both a) and b).	55
Figure 16: Mass of solubilised sugars recovered in extraction liquor per 100 grams of E. grandis feedstock using green Liquor. a)2% Total Titratable Alkali b) 6% Total Titratable Alkali. Temperature of 160°C for both a) and b).	56

Figure 17: Wood weight losses obtained using three different extraction methods. A) White liquor extraction for 16% and 20% Active Alkali. B) NaOH extraction for 1M and 2M. C) Green liquor extraction using 2% and 6% TTA. 58

Figure 18: Variation of pH in green liquor extracts at TTA levels of 2% and 6% 59

Figure 19: Correlation between wood chip weight loss and the resulting pH of the extraction liquor obtained through green liquor extraction. 59

Figure 20: Relationship between total solids extracted and recovered xylose. For green liquor extraction: 2% and 6% TTA ,160°C, 200-800 h-factor. White liquor:16% and 20% TTA, 100 °C - 140°C, 90 minute extraction time. NaOH: 1M and 2M, 100°C- 140°C,90 minute extraction time. 60

Figure 21: FT-IR spectra of extracted liquor using different extraction methods :White Liquor (Top), NaOH (Middle) and Green liquor (Bottom) 61

Figure 22: Tear indices of handsheets produced from selected extraction and pulping conditions. 88

Figure 23: Burst indices of handsheets produced from selected extraction and pulping conditions. 88

Figure 24: Tensile indices of handsheets produced from selected extraction and pulping conditions. (Refer to Table 19)..... 89

Figure 25: Sodium and sulphur inputs and losses around a typical kraft mill (adapted from Henricson [103]) 103

Figure 26: Sodium and sulphur inputs and losses around Kraft mill with the addition of hemicellulose extraction. With the grey, green and blue streams representing NaOH, green liquor and white liquor extraction respectively. 103

Figure 27: Figure showing mass of chemicals used during both pre-extraction and pulping. ... 107

Figure 28 107

Figure 29: Diagram on which mass balance for integration of white liquor extraction into Kraft mill was based. 110

Figure 30: Mass balance showing total sodium and sulphur inputs and outputs of Kraft mill without hemicellulose pre-extraction. 112

Figure 31: Inputs and outputs of sodium and sulphur of kraft mill with the addition of hemicellulose extraction through the use of white liquor. Figure shows 0%,20%,50% and 90% recovery of sodium and sulphur that exits with extracted hemicellulose stream. 113

Figure 32: Diagram on which mass balance for integration of extraction into kraft mill was based. 115

Figure 33: Inputs and outputs of sodium and sulphur of Kraft mill with the addition of hemicellulose extraction through the use of green liquor. Figure shows 0%, 20%,50% and 90% recovery of sodium and sulphur that exits with extracted heimcellulose stream. 117

Figure 34: Diagram on which mass balance for integration of NaOH liquor extraction into kraft mill was based. 118

Figure 35: Inputs and outputs of sodium and sulphur of Kraft mill with the addition of hemicellulose extraction through the use of NaOH. Figure shows 50% and 90% recovery of sodium that exits with extracted hemicellulose stream. 120

Figure 36: Percentage xylose recovered versus total chemical addition(S + Na) for green liquor, white liquor and NaOH extraction methods with NO chemical recovery. Blue: Kraft mill Without Extraction, Green: Green Liquor, Red: White Liquor, Orange: NaOH. Values in brackets represent corresponding pulp yields for each extraction method. 121

Figure 37: Percentage xylose recovered versus total chemical addition(S + Na) for green liquor, white liquor and NaOH extraction methods with 90% chemical recovery. Blue: Kraft mill Without Extraction, Green: Green Liquor, Red: White Liquor, Orange: NaOH. Values in brackets represent corresponding pulp yields for each extraction method. 121

Figure 38: Conceptual drawing of chemicals used for hemicellulose extraction provided independently of the Kraft process. 125

Abbreviations and symbols

Abbreviation	Abbreviated Word
AA	Active Alkali
AIL	Acid Insoluble Lignin
AQ	Anthraquinone
CCD	Central Composite design
EA	Effective Alkali
<i>E. grandis</i>	<i>Eucalyptus Grandis</i>
FT-IR	Fourier Transformed Infrared
HPLC	High Performance Liquid Chromotography
kDa	Kilo Dalton
LAP	Laboratory analytical procedure
MW	Molecular Weight
O.D.W.	Oven Dry Weight
NREL	National Renewable Energy Laboratory
TAPPI	Technical association of the pulp and paper industry
TTA	Total Titratable Alkali
UV-Vis	Ultra Violet Visible
v/v	Volume per volume
wt.%	Weight Percentage

CHAPTER 1: INTRODUCTION

Currently, most Kraft mills focus exclusively on producing pulp. However, due to increasing environmental and economic pressures, it is becoming imperative that mills maximise the use of woody biomass that they process. Establishing integrated biorefineries where additional value added products can be produced from the wood source, instead of pulp alone, holds important economic and environmental advantages. Processes such as the Kraft process can already be considered as biorefineries as they generate pulp (mostly cellulose) and energy via the combustion of hemicelluloses and lignin [36]. In the case of Kraft Mills, the integrated forest biorefinery will be created by adding process units so that supplementary products can be produced, while still ensuring the maintenance of their core product, pulp [36]. Kraft Mills are especially befitted towards being converting towards IFBRs as they already have the required infrastructure, support networks and specialised manpower [1,36].

One promising concept towards establishing IFBRs is the extraction of hemicelluloses prior to pulping. Hemicelluloses have a number of potential uses in industries ranging from the pulp and paper industry itself, to the pharmaceutical and food industries. Kraft pulping is a low yield process with the yield commonly less than 50% of high quality pulp. Half of the hemicellulose, equivalent to about 15% of the wood weight, and almost all of the lignin that is located in the wood is dissolved in the spent pulping liquor [32]. On average, a Kraft Mill can process about 600000 metric tons of wood per year of which 90000 metric tons are typically dissolved as degraded hemicellulose [32]. The reactions that are generally responsible for hemicellulose degradation include the alkaline peeling and the alkaline hydrolysis reactions.

The fairly high heating value of lignin, 26.9 MJ/kg, makes it cost-effective to recycle it back to the reboiler for combustion. The heating value of hemicellulose is about 13.6 MJ/kg, thus causing it to be underutilised when it is incinerated in the reboiler, as it only provides about a quarter of the entire amount of energy that is recovered [32]. Due to its low heating value, it is

more valuable to extract and manipulate the hemicellulose into various products in lieu of passing it through the reboiler to burn as a fuel [39]. In order for hemicellulose pre-extraction to be a plausible step towards producing additional products, a compatible pre-extraction method needs to be found that:

- Results in acceptable hemicellulose yields.
- Can operate within the existing infrastructure of a Kraft mill.
- Allows for unchanged pulp yield when compared to that of the conventional Kraft process.
- That produces paper with physical properties comparable to that of a conventional Kraft process.

The phrase “acceptable hemicellulose yields” is a broad term. Literature indicates that the recovery of the hemicellulose, xylan specifically, can vary considerably during alkali extraction [25, 28, 38, 39, 61, 63]. Particularly high xylan yields included that of Al-dajani *et al* [28] as well as Jun *et al* [25] who both managed to recover approximately 25% of the original xylan fraction in the wood chips using white liquor and NaOH respectively from Aspen. An acceptable yield, however, can only be fully quantified when a full techno-economic study has been performed. The overall viability of hemicellulose extraction will depend on a complex interaction between technical feasibility and factors such as energy policies and market development of potential hemicellulose products [97]. An economic study, however, was beyond the scope of this project.

A number of hemicellulose pre-extraction methods have been investigated by researchers, ranging from hot water extraction, to more “mild” extraction methods using alkaline chemicals. Although some methods that have been proposed might be more effective in extracting hemicellulose, such as water and acid extraction, when compared to that of other methods, the severity of the extraction methods diminishes the final pulp yield as well as paper quality. These are key concerns of pulp and paper manufactures [28]. Alkaline extraction methods help to alleviate some of these concerns as they are more forgiving in terms of pulp yield reduction when compared to acid and water extraction methods. Moreover, low pH xylan extraction

means that pulping chemicals will have to be utilised for neutralisation and raising the pH, which is inefficient use of these chemicals. In terms of the xylan extracted, water and acidic extraction methods are also more prone to degrade xylan polymers to oligosachharides and monomers when compared to that of alkaline extraction methods, thus impeding the potential to produce high value chemicals. Resulting qualities of paper produced of non-extracted pulps have also been duplicated and in some instances even improved using alkaline pre-extraction methods such as NaOH, green liquor as well as white liquor[26,28,61,63]. Striving for commercial feasibility, increased attention is being directed towards using pre-existing alkaline chemicals within Kraft mills due to inherent economic advantages.

The aim of this study was to compare pre-existing chemicals in the Kraft process, which included green liquor, white liquor and NaOH in terms of:

- Their effectiveness in extracting xylan from *E. grandis*
- The effect that combined extraction, using the chemicals described, and pulping would have on the pulp and paper product produced.
- How integrating xylan extraction using these chemicals would affect the sodium and sulphur balance of the Kraft mill and in turn the make-up chemicals that would be required.

CHAPTER 2: LITERATURE REVIEW

2.1. Woody Biomass

2.1.1. Use of woody biomass and its future.

On earth there is an annual production of woody biomass of about 5.64×10^{10} Mg-C per year which makes it the most abundant organic source on earth [12]. During the prehistoric and historic periods of mankind, wood was both used as a building material and as a chemical raw material for the production of charcoal, tar and pitch and potash. Wood can also be considered, however, as a very modern raw material [13], being used for the creation of furniture and in converted forms as plywood, particleboard and fibreboard. Very importantly wood is also the basic substance for pulp and paper, fibres, films and additives.

The pulp and paper industry is one of the biggest users of woody biomass. In South Africa for example, the production of mechanical and chemical wood pulp is approximately 370000 tons and 1500000 tons per year, respectively, making the industry an integral part of the economy [14]. However, the increasing societal awareness that the current major sources of energy has on the environment coupled with the reality of problems with stability and sustainability of energy supply, has led to an increasing need for bio-based chemicals [16]. This has put pressure on the industry to make more effective utilization of woody biomass, but due to its existing infrastructure is also an opportunity for increased revenue.

The utilization of woody biomass to its full potential is imperative to ensure the sustainable supply of materials, chemicals and energy.

Two general aims of the utilization of renewable plant material include [13]:

- The production of chemical and energy products from sources that is renewable to replace existing energy sources and petrochemicals that are both expensive and whose reserves are exhausted.

- The better use of waste material from forestry, the wood and pulp industries and of discarded wood products.

Currently the world relies heavily on fossil fuels such as coal, natural gas and oil as sources of energy and chemicals. These sources take millions of years to replenish making their reserves finite [16]. Table 1 is adapted from Liu [16] and shows the various recycle times of chemical and energy feed stocks. It is shown in Table 1 that the recycle time of fossil fuels is in excess of 280 million years making alternative sources of fuels and chemicals crucial.

One manufacturing concept that converts plant biomass to chemicals and energy is the biorefinery [16]. Plant biomass can be fractionated into a number of compounds for use. Integrating a biorefinery into existing facility that makes use of woody biomass such as pulp mills, for example, have a number of benefits. Some pulp mills today are already operating as primitive forest biorefineries. By-products that are generated from the pulp mills are utilized in the recovery boilers to produce heat and energy. Sometimes other products such as tall oil and kerosene are also produced in conjunction with paper products. Optimized biorefineries will use advanced technologies to ensure that the wood used will be further converted to higher value products which includes biomaterials, chemicals and fuels that are more marketable [17]. This concept will be further discussed in section 2.2.

Table 1: Productivities and recycle times of various feedstocks (Adapted from Liu [16])

Feed Stock	Recycle Time	Standing Biomass tons/ha	Biomass production tons/(ha year)
<i>Algae</i>	<i>1 month</i>	<i>9</i>	<i>11.5</i>
<i>Agricultural crops</i>	<i>3month-1year</i>	<i>4.5</i>	<i>2.93</i>
<i>Temperate grasses</i>	<i>1 year</i>	<i>7.2</i>	<i>2.7</i>
<i>Savannah</i>	<i>1 year</i>	<i>18</i>	<i>4.05</i>
<i>Shrubs</i>	<i>1-5 years</i>	<i>27</i>	<i>3.15</i>
<i>Tropical forests</i>	<i>5-25 years</i>	<i>202.5</i>	<i>9.9</i>
<i>Tropical seasonal forest</i>	<i>5-25 years</i>	<i>157.5</i>	<i>7.2</i>
<i>Boreal forest</i>	<i>25-80 years</i>	<i>90</i>	<i>3.6</i>
<i>Temperate deciduous</i>	<i>10-50 years</i>	<i>135</i>	<i>5.4</i>
<i>Temperate Evergreen</i>	<i>10-80 years</i>	<i>157.5</i>	<i>5.85</i>
<i>Oil, gas and coal</i>	<i>280 million years</i>	<i>(38.4 x 10²⁷ J)</i>	<i>0</i>

2.1.2. Chemical composition of wood

Wood is a mixture of three naturally occurring polymers which include cellulose, hemicelluloses and lignin which occur in an approximate ratio of 50:25:25 [18]. The amount of each specific component varies extensively between hardwoods and softwoods. The distribution of these polymers also largely depends on the specific species as well as biological variations and specific growing conditions [18]. Even within the same species the components could vary due to different growing conditions. Each of these specific components contributes to the specific wood species' fibre properties, which in turn affects the characteristics of the products that are obtained. A small portion of wood also consists of low molecular-weight components such as extractives and mineral substances that make up between 2 and 5% of the entire wood composition. Table 2 shows the typical make up of both hardwoods and softwoods.

Table 2: Typical Chemical composition on both Hardwoods and Softwoods (Adapted from Goldstein [34]).

Component	Softwoods	Hardwoods
Cellulose	42 ± 2	45 ± 2
Hemicellulose	27 ± 2	30 ± 5
Lignin	28 ± 3	20 ± 4
Extractives	3 ± 2	5 ± 3

2.1.2.1. Cellulose

Cellulose is the major component of wood and makes up approximately half of both softwoods and hardwoods and is the most plentiful naturally occurring polymer on earth [35]. This polysaccharide is a homogeneous linear polymer consisting of 1,4 linked β -D-glucopyranose units and usually makes up 35-50% of lignocelluloses [4]. The total number of glucose residues will typically vary between 7000 and 10000 [34]. Hydrogen bonds link the cellulose molecules laterally allowing for the formation of linear bundles, with the very large number of hydrogen bonds resulting in a significant lateral association of the linear cellulose molecules [34]. The alignment of the cellulose molecules coupled with the strong association result in the formation of a crystalline structure [34].

Wood pulp is the most important raw cellulosic material. There is only around 2% of the cellulosic material being used for the production of regenerated and chemically modified fibres. [35]. In wood pulp the molecular weight of the cellulose varies according to the origin of the wood pulp as well as pulping conditions but, in general, has a degree of polymerization that varies between 300 and 1700 [35].

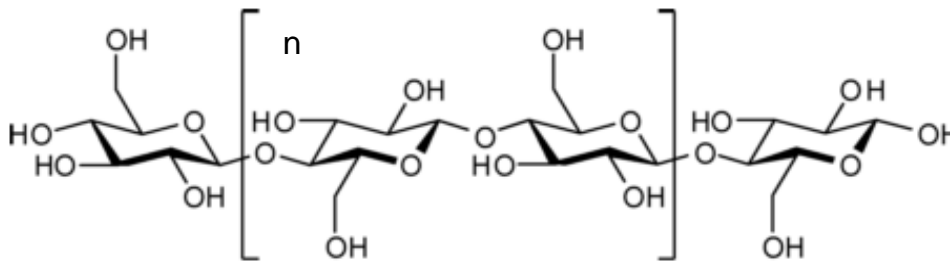


Figure 1: Cellulose structure (Redrawn from Carlmark et al [35])

2.1.2.2. Hemicellulose

Like celluloses, hemicelluloses are polymers of anhydrosugar units; however, hemicellulose may consist of several different types of sugar units [35]. In wood, hemicelluloses are almost exclusively produced from arabinose, xylose, galactose, mannose, and 4-*O* methylglucuronic acid and galacturonic acid residues [37]. Hemicelluloses interconnect other cell wall components via linkages that are covalent in nature and also through auxiliary secondary forces.

The hemicellulose platform is of particular interest due to the wide range of applications this particular platform can provide. Glucomannans and xylans are the two predominant types of hemicelluloses found in softwood and hardwood, respectively. Since hardwoods are the dominant source of biomass for Kraft Mills in South Africa, xylans are of particular interest in this study. Table 3 indicates the types of uses xylans can provide. It is clear that there are a wide variety of applications for xylan, indicating the potential benefits of extracting it before it is used in Kraft pulping

Table 3: Potential uses of xylan in industrial processes.

Pulp and Paper Industry	Pharmaceutical Industry	Chemical Industry	Food Industry	Fermentation Industry
<i>As a beater additive it improves swelling, porosity, drainage and strength</i>	<i>Anticoagulant</i>	<i>Furfural</i>	<i>Xylose</i>	<i>Enzymes, xylanase, xylose isomerise</i>
<i>Fiber Coating</i>	<i>Anti-Cancer</i>	<i>Thermoplastic material</i>	<i>Xylitol</i>	
<i>Wood resin stabiliser</i>	<i>Cholesterol-reducing</i>	<i>Polypropylene filler</i>	<i>Biodegradable polymers, plastics films, beverage packaging.</i>	<i>Biopolymers</i>
	<i>Wound Treatment agent</i>	<i>Paint Formulations</i>		
	<i>HIV Inhibitor</i>	<i>Gel-forming material</i>		

(Adapted from Christopher [32])

2.1.2.3. Lignin

Lignin is one of the most bountiful aromatic substances that are found on earth with its main function being to act as a structural material to help in strengthening the cell walls and add rigidity [42, 43]. Like with both hemicelluloses and cellulose the actual chemical composition of lignin varies greatly in wood and plants according to the species, growing conditions, the age of the specimen and even the physical location of the given lignin within a plant/wood species [43]. Softwood lignin's are predominantly based on coniferyl alcohol units, while hardwood lignin structures have a much wider range in terms of chemical composition with a number of different guaiacyl: syringyl ratios [43]. Figure 3 shows the monomer units that lignin is typically comprised of.

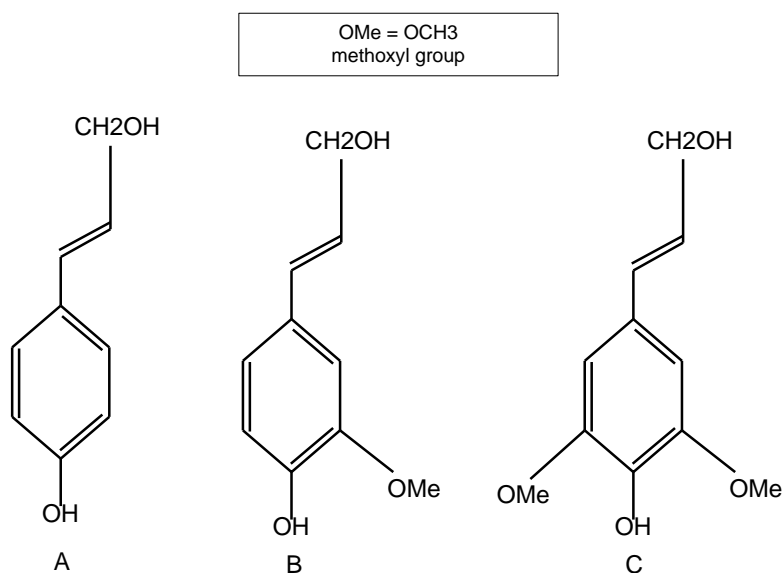


Figure 3: Three monomer units making up lignin in nature: A: *p*-coumaryl alcohol, B: Coniferyl Alcohol, C: Sinapyl Alcohol. (Redrawn from Biermann [80]).

In terms of hemicellulose extraction from wood, lignin is an unwanted presence as extraction processes can be impeded by the ester and ether lignin-hemicellulose linkages [129]. Furthermore low lignin content facilitates the delignification process during pulping [61].

2.1.2.4. Extractives

Wood extractives are low molecular weight compounds that are extractable from wood with the use of lipophilic solvents. Wood extractives can be classified into the components described in table Table 4.

Lipophilic Compounds	Phenolic Compounds	Other Compounds
<i>Alkanes</i>	<i>Simple phenols</i>	<i>Sugars</i>
<i>Fatty Acids and Alcohols</i>	<i>Stilbenes</i>	<i>Cyclitols</i>
<i>Terpenes and terpenoids</i>	<i>Lignans</i>	<i>Tropolones</i>
	<i>Isaflavones</i>	<i>Alkaloids</i>
	<i>Condensed tannins</i>	<i>Amino acids</i>
	<i>Flavonoids</i>	<i>Coumarins</i>
	<i>Hydrolyzable tannins</i>	<i>Quinones</i>

Table 4: The classification of extractives found in wood (Adapted from Stenius [52])

In wood, the total extractive fraction is normally only a small portion of the wood make-up but can create considerable problems during the pulp production processes [51]. Extractives can result in the formation of spots in pulp and paper, which can have a negative impact on a number of paper properties as well as pulp yield. Within the Kraft process the main fraction of the extractives are dissolved in the black liquor, which is then burned to produce energy or removed for the production of tall oil.

Extractives are crucial not just in terms of grasping both the taxonomy and actual biochemistry of trees, but also when looking at the impact they have from a technological viewpoint, being both a valuable raw material as well as playing a significant role in the pulping and paper-making processes [53]. During pulping extractives can impede that penetration of chemicals into the wood fibre [115] with the potential for the same problem to occur when wood chips is subjected to hemicellulose extraction.

2.1.3. *Eucalyptus grandis*

The species of wood used in this study, *E. grandis*, is the pre-dominant hardwood used by South African pulp and paper companies with about 73.8% of the commercial forestry area in South Africa comprising of *E. grandis* as well as its hybrids [84]. This species is particularly well suited for commercial planting due to its excellent silvicultural characteristics. Combining this fact with the excellent results it provides in terms of delignification, bleaching and papermaking, *E. grandis* is an extremely popular species for the production of cellulose pulp [90].

Table 5: *E. grandis* structural composition from literature.

Component	Reference				
	11	29	61	71	73
Hemicelluloses	ND	27.27	ND	ND	ND
Xylan	ND	ND	15.3	21	15.3
Mannan	ND	ND	ND	ND	ND
Arabinan	ND	ND	0.5	ND	ND
Cellulose	ND	46.16	52.7	43	44.65
Lignin	ND	14.6	21.1	30	25.8
Extractives	0.8-2.9%	2.84	4.2	ND	3.25

As with any species the composition of *E. grandis* can be varied as a result of a combination of genetics, climate conditions as well as location [13, 29]. Table 5 shows the structural composition of *E. grandis* found in literature. In this study, the xylan fraction is of particular interest with Table 5 indicating that the xylan fraction makes around a fifth of the total wood weight of *E. grandis*. Hardwoods, in general contains more xylans than that of softwoods [13], making them more suitable for subjection to xylan extraction.

2.2. The Concept of a forest biorefinery.

In many ways a biorefinery can be considered as the same as an oil refinery with the added advantage of using renewable resources that are obtained from plant materials instead of using non-renewable fossils that are derived from petroleum [7]. Unlike products which are petroleum based in nature, biorefinery products are characterised by being non-toxic, biodegradable and, very importantly, re-usable and recyclable [32].

Currently, raw petrochemical materials form the basis for a small number of basic chemicals that are used to produce a wide product range for all spheres of modern life [45]. The product range of a biorefinery includes that which is not only produced in a typical petroleum biorefinery, but also products which are unique to biorefineries. The principal products of a biorefinery include that of chemicals, biofuels, electricity and heat as well as materials such as wood, starch and fibres [126]. Figure 4 shows the types of processes that can be used to derive different components from lignocellulose.

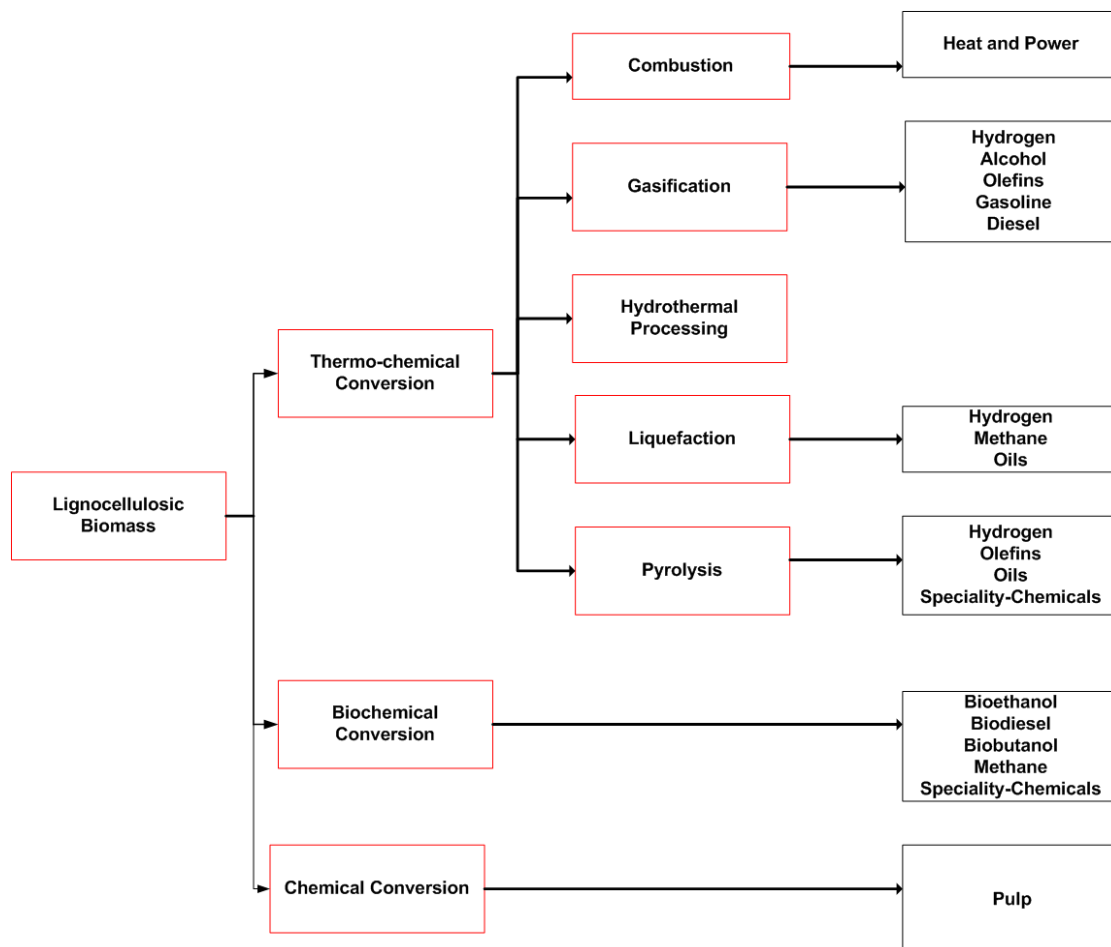


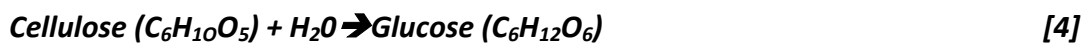
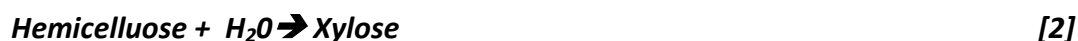
Figure 4: Products produced from thermochemical and biochemical processing of lignocellulosic biomass. (Adapted from Menon and Rao [89])

The three main biorefinery concepts include:

- Whole-crop biorefinery
- Green biorefinery
- Lignocellulose Feedstock (LCF) biorefinery

The whole-crop biorefinery utilises materials that are raw in nature such as cereals or maize. The green biorefinery makes use of inherently wet biomass such as clover, green grass or lucerne. The LCF biorefinery makes use of feedstock that are naturally dry such as biomass that contains cellulose [45]. The most promising of the three is considered the LCF biorefinery due to the fact that the material that is processed is readily available such as waste wood, straw, as well as grasses [44].

Lignocellulose has three basic components which include hemicellulose, cellulose and lignin. These components serve as platforms which can be fractionated and manipulated in order to produce biofuels and high value bio-products [32]. Equations 1-4 are a very general set of equations showing the conversion of the chemical fractions of a lignocellulose feedstock biorefinery [45].



The most valuable of the lignocellulose platforms is usually considered to be that of cellulose [54]. Cellulose is especially important in the context of the pulp and paper industry as it is the principal component of pulp.

Methods of xylan extraction that are both technically and economically feasible for integration into the Kraft process is still in its infancy phase. As a result both fundamental and applied research will be important in the coming years regarding these areas [46].

2.2.1. Integrated Pulp and Paper Biorefinery

Integrating additional processes into already existing plants that process biomass is economically far more attractive than starting a biorefinery from grass roots. The idea of forest biorefinery within the pulp and paper industry has been generating more and more interest, especially from regions that are industrially well established such as Western Europe and North America [3]. The increasing interest is mainly due to the possible diversification of the product mix which would result in an increase in revenue and more environmentally friendly utilization of woody biomass.

The integrated forest biorefinery (IFBR) in the pulp and paper context consists of implementing biorefinery units into a receptor pulping process such as the Kraft process [9]. The Kraft mill has the potential to be converted into a LCF biorefinery where all the lignocellulosic components of the wood can be optimally utilised. Kraft Mills are well poised for being converting towards IFBRs as they already have the required infrastructure, support networks and specialised manpower [1,36]. The Kraft process is also a good receptor process due to its versatility and economic benefits of its chemical recovery cycle.

Conceptually, a biorefinery based on the Kraft process consists of both the Kraft process as well as the extra unit operations needed for producing additional value added products. The Kraft process itself is well understood and well established. The extra operations needed for an IFBR however are not well defined and a large amount of research is needed to ensure that the available feedstock, product options, pathways and energy and material requirements are properly assessed to ensure that the IFBR is economically feasible [3].

Figure 5 is a simple schematic showing the Kraft process as a biorefinery receptor and emphasizes the fact that the Kraft process is well established while a considerable amount of research is needed regarding the additional biorefinery units. Figure 6, an expansion on Figure 5, shows a few selected additional biorefinery processes to the Kraft process to illustrate how supplementary operations could possibly be integrated into the Kraft process.

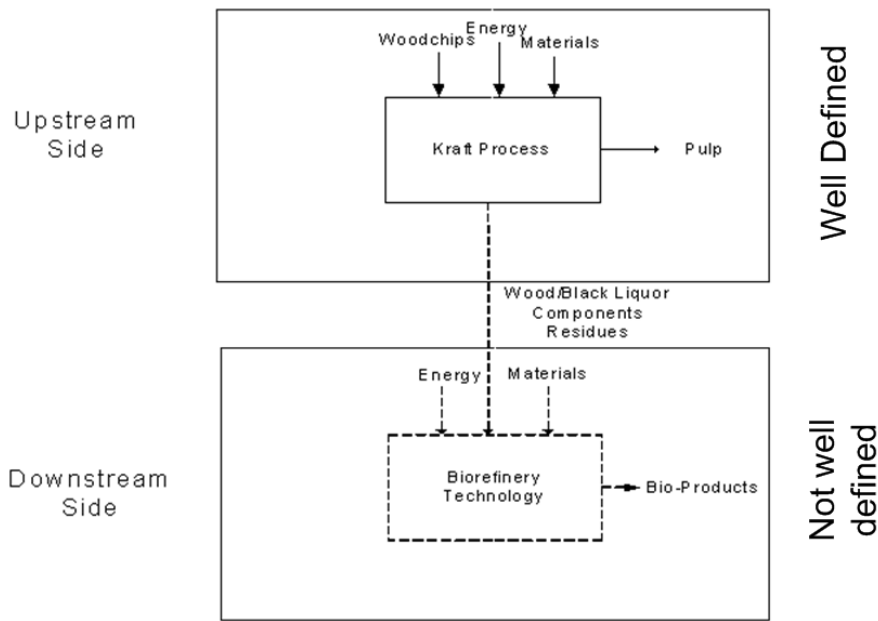


Figure 5: Illustration of the Kraft process as a biorefinery receptor showing defined and undefined processes (Adapted from Moshekelani et al [3]).

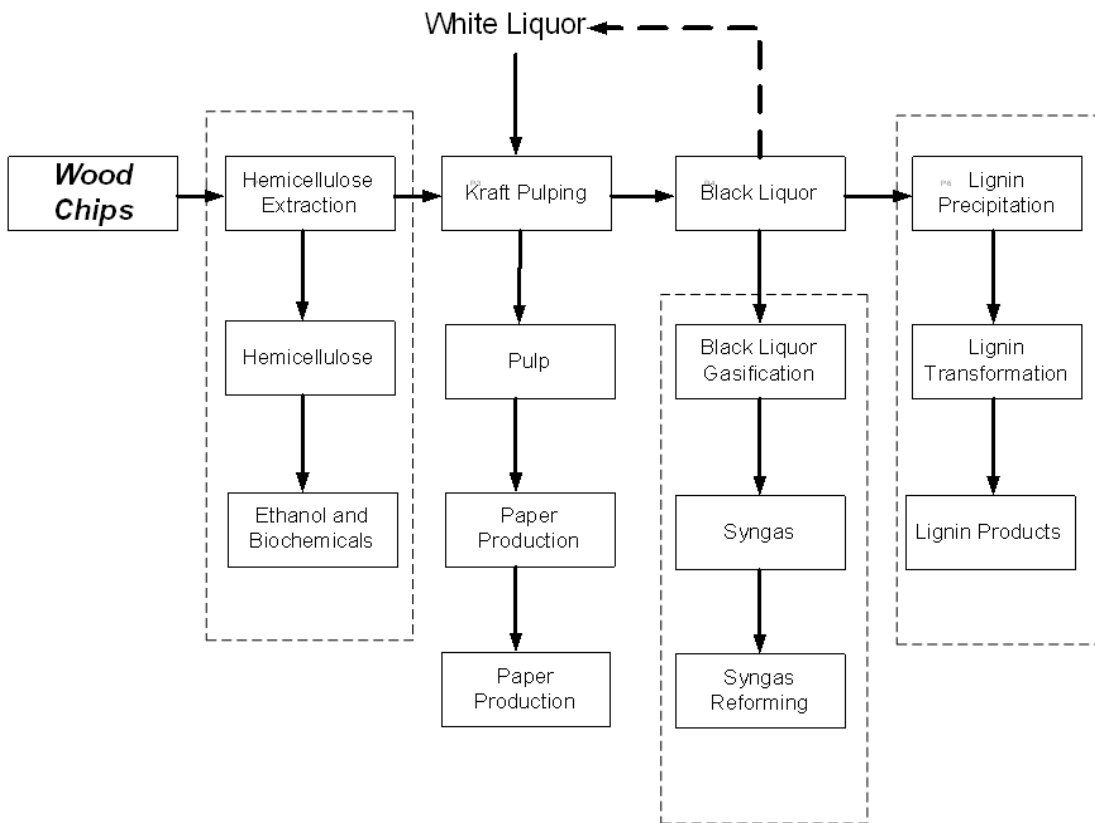


Figure 6: Kraft process showing some possible additional processes to maximize use of woody biomass. (Redrawn from Stuart and El-Halwagi [54])

A number of potential processes for the integrated Kraft biorefinery revolve around the black liquor that is formed during the pulping process. The recovery of cooking chemicals and the combustion of black liquor for energy is a crucial part of the conventional Kraft process. Black liquor gasification is one alternative form of technology which is directed at replacing the standard recovery boiler found in the Kraft process with a gasification plant [55].

In the black liquor gasification process, black liquor that is evaporated is gasified under pressure in a reactor with the resulting gas that is produced being separated from the ash and the inorganic smelt [56]. Both the gas and the smelt are then cooled and subsequently separated in the quench zone which is found below the gasifier. The smelt is dropped into quench bath in order to be dissolved forming green liquor in a manner that is analogous to the process that occurs in the dissolving tank of a recovery boiler. (The green liquor that is formed is a chemical that has also been studied as a method for the alkali extraction of hemicellulose [26, 38, and 39]. This will be further discussed in subsequent sections.) The fuel gas that is released is once again cooled, with the water vapour that is formed being condensed generating steam. The final synthesis gas products consist pre-dominantly of carbon dioxide, hydrogen as well as carbon monoxide. The gaseous fuel that is produced by black liquor gasification allows for greater end use versatility. It also allows for a reduction in air pollution and greater electricity-to-heat ratios in combined cycle systems when compared to that of the conventional systems used for the recovery boiler [57]. However commercial implication of this process proves to be difficult.

Another potential black liquor based process is the extraction of lignin from black liquor through the use of precipitation. Precipitating the black liquor could allow for the diversion of the lignin from the process to transform it into a solid biofuel which can then be used further in the mill itself or somewhere else [57]. The lignin can also possibly be transformed so that it can be used in other products such as phenols, carbon fibre composites, active carbon and binders just to name a few [59].

Hemicellulose extraction prior to pulping (also known as the value prior to pulping process [54]) is another important biorefinery concept for integration into Kraft mills. This process decreases

the wood to pulp yield but also reduces the amount of energy required during the refining process while producing an additional hemicellulose stream [54]. This is the focus of the present study, and will be discussed further in the next section.

The integrated Kraft biorefinery is an attractive business strategy that an increasing number of forestry companies are seriously considering to not just better overall financial performance but to also mitigate increasing environmental concerns such as solid waste discharge as well as liquid effluents. However, as with any new large scale engineering venture, technology as well as business risks affiliated with its implementation are inevitable [60]. Some of these risks include [127]:

- Product risks: Instability in both the demand and market prices of products.
- Feedstock risks: Fluctuation in supply and price of feedstocks.
- Technological risks: Scaling up from lab or pilot levels up to commercial level can be risky as something which functions well in the lab might cause problems on an industrial scale.

In order to mitigate these risks, to a certain extent, thorough research and simulation of the possible additional biorefinery options are pivotal.

2.2.1.1. Integration of hemicellulose extraction into the Kraft process

The Kraft process, also known as the sulphate process, is considered the most important pulping process available, as it accounts for over 90% of chemical pulps that are found worldwide [13,85]. Annually about 130 million tons of Kraft pulp is produced [21]. The chemical pulp is produced via the cooking of raw plant material in an alkaline solution with the effective chemicals being NaOH and Na₂S [86]. The purpose of the entire pulping process is the dissolution of lignin, with cellulose and some of the hemicellulose remaining in the pulp. Before the Kraft process was developed, the soda process was used, which consisted of only NaOH. Later on makeup Na₂SO₄ was added to the system prior to the recovery furnace. The furnace conditions are highly reducing resulting in the Na₂SO₄ being reduced to Na₂S. This new process was subsequently described as the Kraft process, with the word “Kraft” meaning strong in German, due to the stronger pulps produced when compared to the conventional soda process.

Due to the fact that alkaline chemicals are used within the kraft process during pulping some of the potential benefits in terms of xylan pre-extraction, should alkaline chemicals be used for extraction, include to decrease the alkaline charge whilst speeding up the delignification rate during pulping.

The process where white liquor is regenerated towards black liquor is an economically essential part of the Kraft process. The well-established chemical recovery system of the Kraft process is one of the advantages it has when compared to the conventional sulphite pulping. Severely upsetting this recovery system in terms of the sodium and sulphur balance would make hemicellulose extraction prior to pulping unfeasible.

Figure 7 shows the chemical recovery cycle of the Kraft process, which was drawn by combining features of schematics produced by Fengel and Wegener [13] and Tran *et al* [21]. In the recovery process weak black liquor from the brown stock washers are concentrated in multi-effect evaporators, so that they can be burned effectively. The concentration is usually at 65% solids or higher [21].

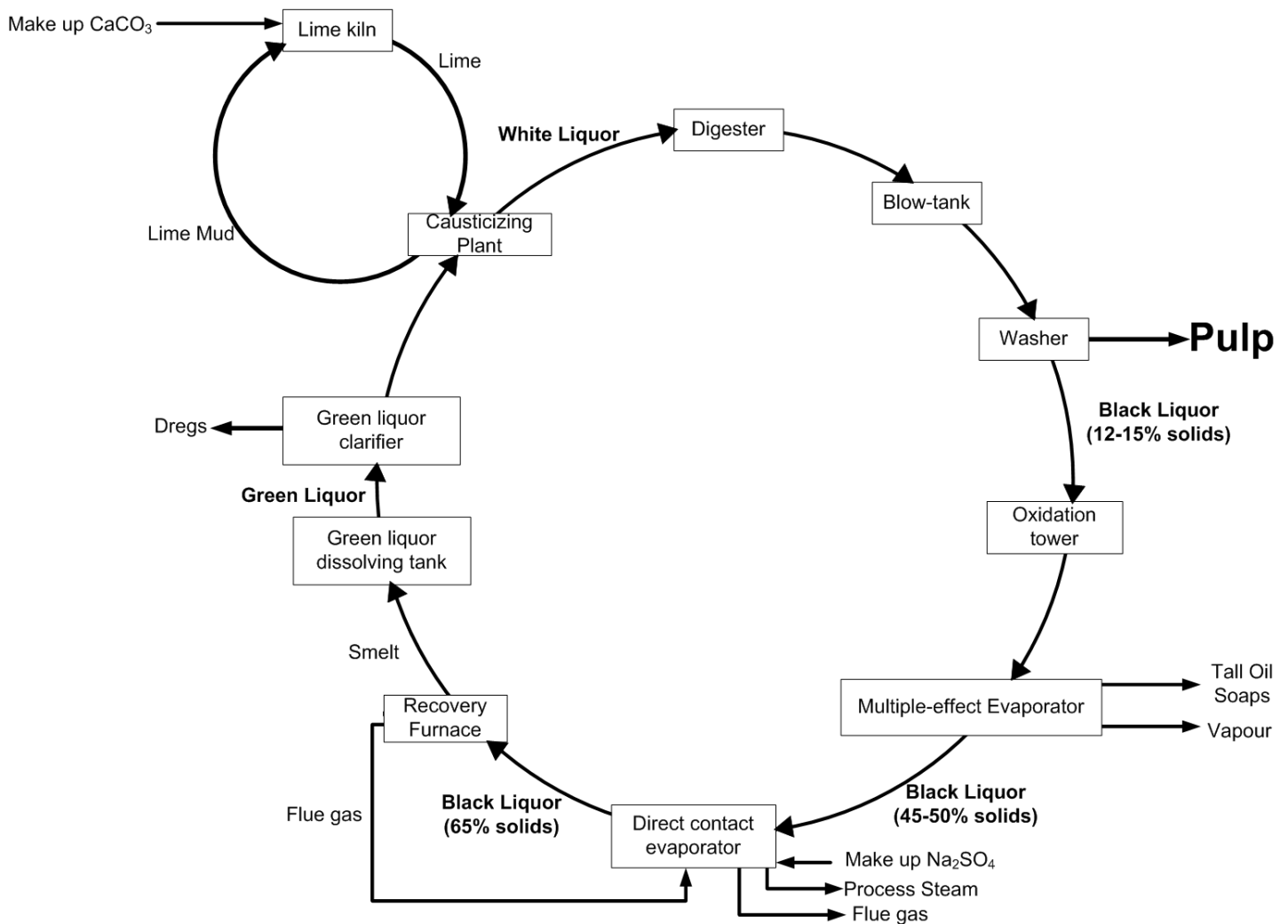


Figure 7: Schematic of Kraft chemical recovery cycle. (Adapted from Fengel and Wegner [13] and Tran et al [21])

The weak black liquor is usually concentrated in two separate evaporation processes. The first process consists of 6 evaporation stages where the vapour of the one stage is used to heat the following stage which is known as multiple-effect evaporation. The second evaporation process consists of a direct-contact evaporation procedure where flue gas from the recovery furnace is used to bring the black liquor to its final concentration.

Once the black liquor is well concentrated it is sent to the recovery furnace, which is an integral part of the Kraft recovery system and has two important functions [13]:

- To combust the organic wood material that is dissolved in the black liquor to produce heat, which in turn is transformed to process steam.

- Produce inorganic smelt which when dissolved produces green liquor.

The inorganic sodium and sulphur are recovered from the recovery boiler as smelt, consisting mainly of Na_2S and Na_2CO_3 . The molten smelt obtained from the boiler enters a dissolving tank where it is dissolved in water to form what is known as green liquor. The green liquor is sent to the causticizing plant where it reacts with lime and CaO to transform the Na_2CO_3 to NaOH . Once the green liquor is causticized it is known as white liquor, which mostly consists of NaOH and Na_2S . The white liquor is sent to the digester for reuse. The CaCO_3 that is precipitated from the causticizing process is washed and sent to the lime kiln where it is heated to a high enough temperature to produce CaO for reuse [21].

If hemicellulose is extracted, the flowrate of the black liquor as well as the organic content is decreased [125]. This will result in a reduction in the steam that is produced in the recovery boiler. The recovery boiler combusts the dissolved organic wood material that is found in the black liquor to generate heat which can be used as process steam within the mill. The addition of a hemicellulose pre-extraction unit will also require added energy; fortunately, the energy that is put into the pre-extraction vessel helps to reduce the amount of white liquor that needs to be heated in the digester. The required cooking time of the digester is also decreased which helps to save energy. The decrease in black liquor flow rate will also reduce the steam demand in the evaporation plant [125]. The lime kiln is also off loaded as less green liquor is sent to the lime kiln. This means that less calcium carbonate (CaCO_3) is needed to be removed in the white liquor clarifier and then decomposed in the lime kiln [5]. Figure 8 shows a schematic of where energy will be lost and potentially saved if hemicellulose pre-extraction is implemented into the kraft process. The extraction of hemicellulose

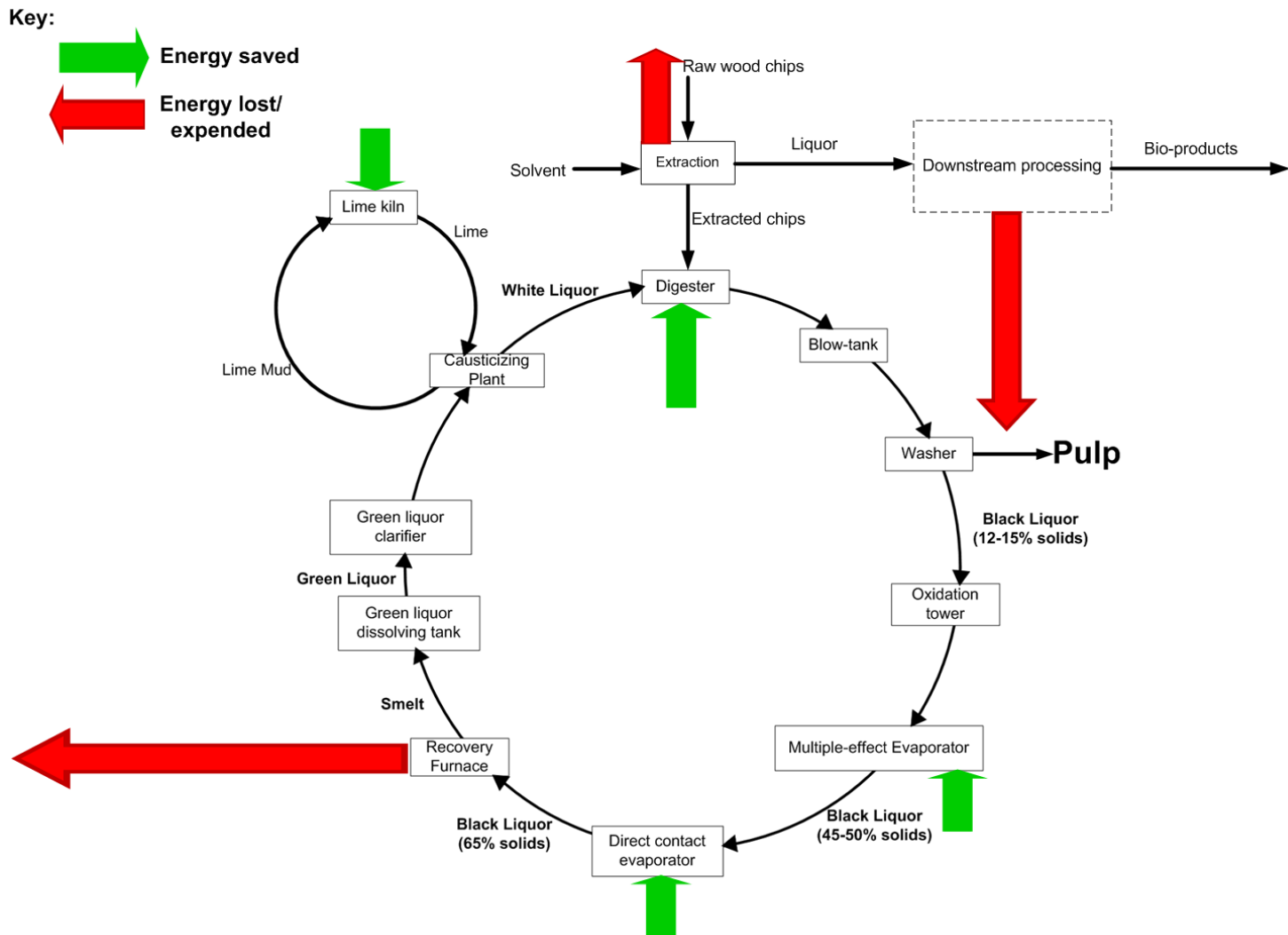


Figure 8: Schematic showing general energy effects hemicellulose pre-extraction will have on the kraft process.

The removal of hemicellulose from wood as a pre-treatment step has been done in industry for a number of years in order to produce “dissolving pulps” [28]. To produce this product, the hemicellulose component in the wood is removed so that pure cellulose can be produced. The degree of polymerization of the cellulose component is significantly lower when compared to that of the original raw wood chips [28]. The resulting cellulose yield of these processes however are low when compared to the standard Kraft pulping process.

The process of extracting hemicellulose within pulp mills is also constrained by both cellulose recovery and the inhibitors that are produced by the extraction process. The choice of hemicellulose biorefinery technology will determine the influence it has on the Kraft process such as the Na/S balance, and the pulp and paper quality. These additional technologies should both result in acceptable xylan yields as well as has a minimal effect on pulp properties while at the same time produce paper with physical properties that is comparable with that of conventional Kraft mills.

Quantifying what “acceptable xylan yield” means is difficult, as this would be closely related to the market demand and specific products that could be made. In principal the revenue returned from the extracted xylan should be greater than that of the capital utilised to extract the xylan. If a large quantity of costly chemicals is utilised and only a small fraction of xylan can be recovered the extraction method will certainly not be worthwhile. The pulp yield and corresponding paper properties such as burst, tear and tensile indices should remain within industry standard to ensure that saleable paper can still be produced. Industrially acceptable levels of pulp yield is generally 50% or greater [61]. For the product obtained from the extraction process it has to be ensured that the maximum pentose yield in non-degraded form can be obtained [10].

2.2.1.1.1. Methods of hemicelluloses extraction

2.2.1.1.1.1 Acid Hydrolysis.

Generally acid hydrolysis of hemicelluloses can be divided into two categories which include concentrated acid/low temperature and dilute acid/high temperature extraction. The extraction of monomeric sugars that involve concentrated acid hydrolysis is extremely expensive and is prone to operational difficulties [10]. For concentrated extraction, polysaccharides are dissolved by using acid concentrations such as 72% H₂SO₄, 41% HCL or a 100% trifluoroacetic acid (TFA) [10]. Concentrated acid solutions generally remove mostly cellulose and hemicelluloses into monomers and oligomers which results in a solid phase that is lignin enriched thus making the process definitely not appropriate for pulp mill integration.

Dilute acid extraction is usually carried out with sulphuric acid at concentrations and temperatures varying between 0.5-1.5% and 121-160°C respectively. However, acid hydrolysis has draw backs both in terms of the hemicellulose product produced as well as the effect it has on the pulp and paper quality. Acid extraction does not provide hemicellulose as biopolymers and has a tendency to reduce pulp yield as well as reduce subsequent paper quality [123,124].

2.2.1.1.1.2 Hydrothermal Pre-treatments

The hydrothermal biomass pre-treatment makes use of either water, steam or both for the extraction of hemicellulose. Hydrothermal treatments mainly make use of hot water and steam explosion at temperatures that are between 150°C and 230°C [10]. High temperatures for this process are crucial as below a 100°C there is no hydrolytic effect on the material [10].

In auto hydrolysis hot compressed liquid water is used to hydrolyze hemicellulose from woody biomass extremely quickly. Weak acidic conditions are initially created with water and then as well as by the formation of acetic acid [23]. The temperatures are normally in excess of 200°C and the operating pressure is carried out at a pressure that is greater than the saturation point of water [10]. This pre-treatment is a milder process when compared to acid hydrolysis and the hydrolysates obtained are generally a mixture of both oligosaccharides and monosaccharides. The hemicellulose from this process is usually in the form of oligomers due to the formation of natural wood acids [28]. At high temperatures the resulting sugar yield is reduced due to the

formation of furfural that is generated as a byproduct from side reactions. When the cellulose and lignin fractions are sent for pulping the auto hydrolysis pre-treatment increases the cooking rate but has a negative effect on overall pulp quality and yield [23].

During the process of steam explosion high pressure steam ranging between 20-50 bar and temperatures ranging between 210-290°C is used for short periods of time, which could be from a few minutes to just a few seconds. The steam condenses under the high pressures which results in the wetting of the material and the material is then driven out of the reactor through a small nozzle by an induced force [10]. This process has proven to be very effective on hardwood species. This especially so due to the fact that the high operating temperature of the process releases acetic acid which in turn hydrolyses the hemicellulose in the biomass and thus disrupts the bonding between the lignin and the cellulose [24]. Unfortunately the process results in fibre damage even at low reaction times which results in pulp yields with inferior physical properties when compared to standard Kraft pulps [24]. As a result as an integrated pre-treatment process in the Kraft process, it is not viable.

2.2.1.1.1.3 Alkali Treatments

Partially extracting hemicellulose using alkali solvents has a number of advantages in the context of integrating this step specifically in to the Kraft process. The recovery cycle (evaporation process, recovery boiler and lime kiln) of the Kraft process is off-loaded as the amount of organics in the black liquor is reduced and less white liquor is needed for the pulping process [5,27], as the pre-extracted chips has already been exposed to alkali chemicals. The effect of alkali chemicals is generally less severe on the cellulose fraction when compare to other methods that has been mentioned.

Growing attention has been given to alkali extraction methods in the pulp and paper industry, due to their synergistic potential with the Kraft process. This is especially so for pre-existing chemicals found in the Kraft recovery cycle such as green liquor and white liquor and intermediate chemicals such as NaOH. Table 6 shows some conditions using these solvents to extract hemicellulose for the purpose of Kraft mill integration.

Aldajani *et al* [25] managed to extract 40-50kg of hemicellulose per tonne of aspen chips using NaOH concentrations ranging between 1M and 2 M and temperatures ranging between 50-90°C. With these pre-extraction conditions, the pulping conditions were modified allowing for a 10 minute shorter residence time, with the final pulp yield being maintained with the absence of any effects on the fiber quality. Vena *et al* [61] used *Eucalyptus grandis* feedstock to partially extract xylan using temperatures ranging between 40°C and 90°C, extraction times between 2 and 4 hours and NaOH concentrations ranging between 1M and 2M. A xylan yield of 12.4% was obtained. The pre-extracted wood chips were subjected to further pulping with only the addition of Na₂S, to add sulfidity to the pulping cooks. Pulps were also carried out at a 15 minute shorter residence time when compared to that of the standard pulping conditions. Using these adjustments in pulping conditions pulp yield was slightly decreased with the subsequent handsheets formed indicating improvement in terms of both viscosity and breaking length properties. Both the tear and tensile indices were not affected when compared to that of the handsheets that were formed from non-extracted pulps.

Table 6: Pre-extraction of hemicellulose using green liquor, white liquor and NaOH, for purpose of integrating into Kraft Mills.

Solvent	Reference	Wood Species	Extraction Conditions	Fraction of Wood Dissolved (%)	Comment on Sugars/Hemicellulose Extracted
Green Liquor	38	Loblolly Pine	4% TTA ^a , 190°C, 90min	15.19	2% of starting wood weight recovered as xylan.
	39	Mixed Northern Hardwood	3% TTA ^a , 160°C, 800h ^b	10.80	1.7% of starting wood weight recovered as xylan. Xylan yield of 9.2%
	26	Mixed Southern Hardwood	2% TTA, 160°C, 800h ^b	ND	8 g/l as sugars
White Liquor	28	Aspen	18% AA ^c , 90°C, 240min	15.3	4.8% of starting wood weight recovered as xylan.
	63	Birch	3% EA ^d , 160°C, 160min	9	3.62 g/L as xylose, <5% Xylan yield
NaOH	25	Aspen	1.67M NaOH, 90°C, 4hours	19.3	5.26% of starting wood weight recovered as xylan.
	61	<i>E. grandis</i>	2M NaOH, 90°C, 4hours	ND	12.4% Xylan yield

^a Total Titratable Alkali^b hours(H-factor)^c Active Alkali^d Effective Alkali

Hemicellulose extraction using green liquor is normally carried out at higher temperatures coupled with lower alkali charges [26, 38, and 39]. Extraction temperatures are usually around 160°C and alkali charges ranging between 1% and 6% total titratable alkali. Extractions carried out using green liquor is often referred to as “near-neutral” extraction due to the fact that the pH of the resulting extraction liquor is close to 7, so that the oligosaccharides are not fully degraded into hydroxyl acids [26]. Yoon and Van Heiningen [38] extracted hemicelluloses from Loblolly pine wood using green liquor charges varying between 2-6% TTA and temperatures

ranging between 130°C and 160°C. They managed to extract 2% of the original wood weight as arabinoglucoroxylan. Um and Walsum [39] carried out hemicelluloses extraction on northern hardwood using 3% TTA green liquor at 160°C and at 110 min of cooking time which resulted in a xylan yield of 9.2%. Walton et al [26] extracted 8g/L of sugars using a green liquor charge of 2% TTA at 160 °C and found that pulp yield slightly increased when pulping wood chips subjected to pre-extraction.

The white liquor that is used for the actual pulping process is also a possible method for the pre-extraction of hemicellulose. White liquor has the same advantage as green liquor as it is already present stream in the Kraft recovery cycle, and its use as a pre-extraction solvent can thus be integrated with the conventional Kraft process. Jun *et al* [28] carried out hemicellulose extraction of aspen chips using white liquor at temperatures ranging between 70°C and 90°C. They managed to extract 4.8% of the starting wood weight as xylan with the pulp yield from pre-extracted wood chips being unaffected. The resulting paper properties actually benefitted from the pre-extraction conditions. Helmerius *et al* [63] carried out hemicellulose extraction using white liquor on birch wood at higher temperatures (130°C - 160°C) and effective alkali concentrations ranging between 3 and 7%. The fraction of hemicellulose extracted under extraction conditions suitable for pulping was less than 5% of the original xylan fraction in the raw birch feedstock. Pulping of woodchips subjected to pre-extraction maintained both pulp yield and paper properties when compared to non-extracted birch feedstock [63].

It is evident that alkali solvents can be effective both in extracting hemicellulose, while being able to maintain pulp yield and paper properties; it is therefore significantly better when compared to that of pre-treatment processes such as hydrothermal pre-treatment and acid hydrolysis. However, results using alkali solvent, or any pre-extraction method, are inevitably strongly dependent on the species of wood used. Aspen wood [25, 28] seems to be especially conducive to result in significant amounts of hemicellulose extracted, while maintaining acceptable pulp and paper properties. For example, Vena *et al* [61] used similar extraction conditions to that of Al-dajani *et al* [25], while the xylan yield obtained by Vena was less than half of that of Al-dajani *et al* [25]. Finding a hemicellulose pre-extraction method will therefore

be more complex than finding one standard extraction method that fits to all Kraft processes and can be adapted to different feedstock. Due to the inherent variability within wood, the extraction method will have to be tailored according to each species and even to the type of environmental conditions a specific species has been exposed to ensure optimal results.

2.3. Opportunities for improving performance of Kraft mills.

For Kraft mills to remain as competitive as possible they need to move away from producing pulp exclusively and make full use of the lignocellulosic platforms that are inherently available in wood. Kraft mills have well established wood processing units and a knowledgeable workforce culminating in propitious circumstances for converting them into integrated biorefineries.

Hemicellulose extraction prior to pulping is a natural step towards converting Kraft mills into IFBRS due to their under-utilisation in the Kraft process and multitude of products they could potentially produce. Alkaline extraction methods seem to be the most feasible hemicellulose extraction methods due to their natural synergism with the Kraft process. Pre-existing chemicals such as green liquor, white liquor and NaOH are especially attractive alkaline extraction methods due to the opportunities for integration into the Kraft pulping process that they hold.

CHAPTER 3: Objectives

Based on the background that has been presented, the main aim of the study was to investigate and compare the feasibility of the integration of hemicellulose extraction prior to pulping into a Kraft mill utilising green liquor, white liquor and NaOH as chemicals for such hemicellulose pre-extraction. This was to be performed through the completion of the following objectives:

Objective 1:

The first objective was to investigate how green liquor, white liquor and NaOH compare in terms of the amount of xylan that is recovered in the extracted liquor under varying extraction conditions (temperature, time and alkalinity).

Objective 2:

To further investigate the effect of selected extraction conditions, based on the outcomes of objective 1, on pulp and subsequent paper properties.

These objectives were addressed by carrying out micro-pulping on woodchips that were subjected to green liquor, white liquor and NaOH extractions. Both the chemical charge as well as the pulping times was varied to try and replicate pulp properties of woodchips not subjected to pre-extraction. Pulp properties that were analysed included both pulp yield as well as kappa numbers.

Pulps from pre-extraction conditions resulting in yields and kappa numbers that were the most comparable with that of non-extracted chips were formed into handsheets so that paper properties could be tested (burst, tear and tensile indices). These paper properties were then compared to that of wood chips that were not subjected to pre-extraction.

Objective 3:

To determine the impact that using additional pre-extraction chemicals would have on a Kraft mill in terms of the sodium and sulphur balance of the mill. Mass balances were performed on extraction conditions that for green liquor, white liquor and NaOH resulted in the most comparable pulp yields and kappa numbers when compared to that of pulps produced from chips that were not subjected to pre-extraction.

This objective was addressed by performing a mass balance of the sodium and sulphur around a Kraft mill and determining the increase in make-up chemicals that would be required for certain extraction conditions. Different scenarios were investigated where varying percentages of the chemicals used during extraction are assumed to be recycled back to the Kraft process. This was then compared to that of a Kraft mill where no hemicellulose pre-extraction is implemented.

Furthermore the practicality of utilising green liquor and white liquor from an independent source was also considered and compared to that where the chemicals for hemicellulose pre-extraction are provided by the Kraft process itself. NaOH is not provided as a pure chemical by the recovery cycle as a result mass balances were done assuming NaOH is supplied independently from the start.

Objective 4:

Select a pre-extraction condition, from green liquor, white liquor or NaOH, that would be the most suitable for integration into a Kraft mill. Comparisons were drawn between xylan recovered, impact on pulp and paper properties as well as the effect on the sodium and sulphur balance of a Kraft mill. Figure 9 shows the layout of the project objectives of the thesis.

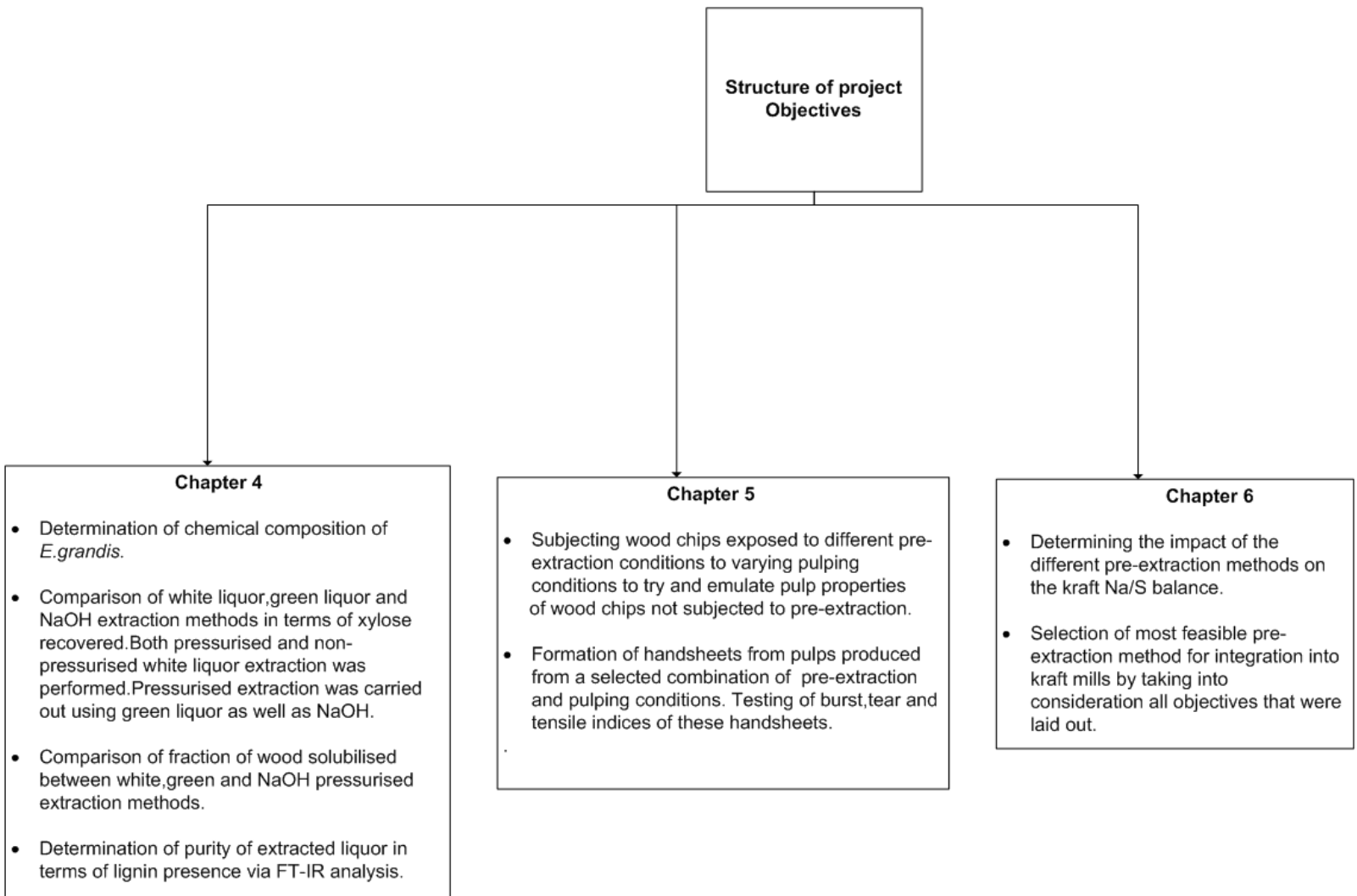


Figure 9: Layout of project objectives.

CHAPTER 4: Extraction of Xylan from *Eucalyptus grandis* using green liquor, white liquor and NaOH.

4.1. Introduction

The decrease in competitiveness of conventional pulp and paper mills, especially in temperate areas, and increasing focus on environmental awareness has created a strong incentive for pulp mills to expand the range of products they produce. Taking into account the process economics of a mill it would be the most feasible if the new products are mainly derived from hemicelluloses instead of cellulose [47]. Hemicelluloses are hetero-polysaccharides that are non-cellulosic in nature and consist of a number of different sugar units that are arranged in different portions along with different substituents [48]. Hemicelluloses are underutilised in traditional Kraft mills due to the fact that they are burned with lignin in the recovery boiler which has a much higher heating value when compared to that of hemicellulose. Due to the large amount of degradation products that is generated during the Kraft pulping process, it is not viable recovering the hemicelluloses from the black liquor waste stream [49], it would be more feasible to extract them prior to the actual pulping process. The fact that hemicelluloses are underutilised, coupled with the wide range of applications they have, make them ideal components for extraction from wood prior to the Kraft pulping process.

In order for hemicellulose pre-extraction to integrate successfully into the Kraft process an extraction method needs to be found that is both economically feasible and technically realistic. Pre-existing alkaline chemicals within the Kraft process are therefore attractive as the pulping process itself is alkaline, making them amenable to the process. The fact that these chemicals are already found within the Kraft process is also particularly convenient as they are readily available.

In this chapter the chemical compositions of the *E. grandis* feedstock was determined in terms of carbohydrates, lignin, ash and extractives content. Subsequently, xylan extractions were

performed on the *E. grandis* chips using green liquor, white liquor and NaOH which are all pre-existing chemicals in the Kraft process. Preliminary extractions based on literature conditions [28], in a form of a central composite design, were performed on *E. grandis* chips using white liquor at temperatures ranging between 50°C and 90°C coupled with extraction times between 1 and 4 hours in 500ml Schott bottles. The active alkali concentrations for these experiments ranged between 16 and 20%. Further extractions were also done using white liquor in order to obtain higher xylan recoveries by utilising more severe extraction conditions. These conditions included temperatures ranging between 100°C and 140°C coupled with active alkali concentrations of either 16% or 20%. NaOH extractions were also done at a greater severity than that generally describe in literature [25, 61] to try and bolster the quantity of xylose recovered. Extraction temperatures were also between 100°C and 140°C with molar concentrations of between 1M and 2M. “Near Neutral” green liquor extractions based on literature conditions were done at a temperature of 160°C coupled with Total Titrable alkali concentrations of between 2% and 6% [26, 38, and 39].

This chapter will focus on comparing the product obtained after extraction in terms of xylan yield as well as purity of these three extraction methods. The severity of the extraction conditions in terms of wood weigh loss on the residue will also be discussed. Furthermore, qualitative comparisons will also be drawn in terms of the possible effect these extraction methods will have on the operations of the Kraft process, with Chapters 5 and 6 providing more quantitative comparisons.

The main objectives addressed in this chapter included:

- Establishing the chemical composition of *E. grandis* feedstock utilised.
- Compare green liquor, white liquor and NaOH in terms of the amount of xylan that is recovered if these chemicals are used for pre-extraction of *E. grandis*.
- Gauge extraction severity by looking at wood weight loss for different extraction conditions.
- Compare the purity of the of the resulting extraction streams in terms of lignin content via FT-IR analysis for each extraction method.

- Evaluate how extraction conditions such as temperature and extraction alkalinity would impact the Kraft process itself.

4.1.1. Materials and Methods

Experiments were carried out using wood chips obtained from 11 year old *Eucalyptus grandis* plantation grown in Tzaneen in South Africa. The wood was chipped and the resulting wood chips were screened for size fractions ranging between 4 and 8mm. The screening was done by a six-component chip screen driven by an electric motor. Before use, the wood chips were conditioned in a conditioning room which allowed for constant temperature of 23°C coupled with 55% relative humidity.

Chemicals that were used for pre-extraction included Na₂S, NaOH, Na₂CO₃, and anthraquinone. For the characterization of wood chips as well as extracted liquor, ethanol, cyclohexane, sulphuric acid and potassium hydroxide was used. Hydrochloric Acid was used for the neutralization of extracted liquor. Analytical grade standards that were utilized for the characterization of both wood chips and extracted liquor included xylose, mannose, galactose, arabinose, cellulose and glucose. Table 7 shows a summary of the chemicals that were used as well as their corresponding purity levels, molecular weights and from which specific company they were obtained from.

Table 7: Table providing summary of chemicals used.

Name of Chemical	Chemical Purity	Chemical formula	Molecular weight (g/mol)	Supplied by
Anthraquinone	97%	C ₁₄ H ₈ O ₂	208.21	Sigma-Aldrich
Cyclohexane	>99%	C ₆ H ₁₂	84.16	Sigma-Aldrich
Cellulose	99%	C ₁₂ H ₂₂ O ₁₁	342.3	Sigma-Aldrich
Ethanol	99.9%	C ₂ H ₅ OH	46.07	United-Scientific (Pty) Ltd.
Galactose	99%	C ₆ H ₁₂ O ₆	180.17	Sigma-Aldrich
Glucose	99%	C ₆ H ₁₂ O ₆	180.17	Sigma-Aldrich
Hydrochloric Acid	37%	HCL	36.46	Sigma-Aldrich
Mannose	99%	C ₆ H ₁₂ O ₆	180.17	Sigma-Aldrich
Sodium Carbonate	> 99%	Na ₂ CO ₃	105.99	Sigma-Aldrich
Sodium Hydroxide	> 97%	NaOH	40	Sigma-Aldrich
Sodium sulfide Hydrate	> 60%	Na ₂ S·9H ₂ O	78.04	Sigma-Aldrich
Sulphuric Acid	72%	H ₂ SO ₄	98.08	Sigma-Aldrich
Xylose	99%	C ₅ H ₁₀ O ₅	150.13	Sigma-Aldrich

4.1.2. Sample Preparation of *E. grandis* Feedstock

Due to the inherent variability with in wood feedstock proper sampling procedures was imperative. Sampling was done as prescribed by the British Standards DD CEN/TS 14780:2005 “Solid biofuels - Methods for sample preparation” [83]. The coning and quartering method that is specifically used for reducing woodchips samples into smaller subsets was implemented. The entire sample of *E. grandis* feedstock was placed on a flat, clean surface and then formed into a conical pile and flattened again for a total of three times. After the final conical pile was formed and flattened it was quartered along two diagonals with each pair of opposite quarters being removed. The same coning and quartering procedure was followed for the remaining quarters.

4.1.3. Compositional analysis of *E. grandis* and pre-extracted wood chips.

The same procedure was followed for both the initial characterization of the raw *E. grandis* chips as well as the wood chips that was subjected to pre-extraction. A combination of analytical standards provided by TAPPI as well as NREL was used for the full characterization of the biomass material. The methods used for the compositional analysis of the biomass are summarized in Table 8.

Before analysis the chips were first milled using a Condux-Werk bei Hanau mill to a particle size of about ± 10 mm [49]. They were then further milled in a Retsch ZM 200 mill so that the particle size could be reduced to below $625\mu\text{m}$. The resulting particles were then sieved using a Vibratory Shaker Retsch AS200, with the $425\mu\text{m}$ and $625\mu\text{m}$ size fractions being used for analysis.

Table 8: Methods that were used for compositional analysis of wood chips.

COMPONENT	ANALYTICAL METHOD USED
<i>Carbohydrates</i>	<i>NREL/TP-510-42618</i>
<i>Extracts</i>	<i>NREL-TP 510-42619</i>
<i>Ash Content</i>	<i>NREL/TP-510-42622</i>
<i>Klason Lignin</i>	<i>NREL/TP-510-42622</i>
<i>Moisture Content</i>	<i>NREL/TP-510-42621</i>

4.1.3.1. Determination of Moisture Content

The NREL/TP-510-42621 method [30] was used in order to determine the moisture content of the biomass. The milled residue consisting of size fractions of 425µm and 625µm were placed in container of known weight in oven of 105°C for period of at least 24 hours. Equation 5 was used to determine the moisture content of the sample.

$$\% \text{ Moisture} = \frac{M_{wet} - M_{dry}}{M_{wet}} \times 100 \quad [3.1]$$

M_{wet} (g) represents the initial weight of the sample while M_{dry} (g) represents the weight of the sample after it has been dried out in the oven.

4.1.3.2. Extractives Content

The extractives content were determined by following a two-step extraction method, where both water and ethanol/cyclohexane extractives were determined as described by NREL-TP 510-42619 method [64]. The first step was to remove the water extractives by using 190 ± 5 ml of distilled water from 5 ± 0.1 mg of biomass in a tared extraction thimble [49] through reflux for a period of 24 hours in a Soxhlet apparatus. The resulting extractives was received in a flask, which was oven dried to remove the moisture. The subsequent mass of the extractives by subtracting the weight of the flask from the combined weight of the flask and extractives content. This weight was then divided by the oven dried weight of the initial sample to get the fraction of water extractives. The solvent extractives were determined in the same manner on the residue remaining after the water extractives that were done ethanol:cyclohexane (1:2 v/v) [49].

4.1.3.3. Determination of Carbohydrates and Lignin

The NREL-TP-510-42618 method [65] was used to determine both the Klason lignin and the carbohydrate fractions of the biomass through a two-step acid hydrolysis procedure. A sample of 0.3g extractive free biomass was hydrolysed using 3ml of concentrated sulphuric acid (72%) at 30 °C in a water bath. Samples were stirred intermittently every 10 minutes. The sample was then diluted to 4% (v/v) using 84 ml of distilled water and subsequently autoclaved at 121°C at a corresponding pressure of 120 kPa for period of 60 minutes. Once autoclaved, the hydrolysed

solution was filtered through a pre-weighed porcelain Coors filtering crucible, of medium porosity, with the filtrate being captured in a filtering flask.

The filtering crucibles were oven dried at 105°C for a period of 24 hours and then weighed. The crucibles were then placed in a muffle furnace for a period of at least 4 hours at a temperature of 575 ± 25 °C to determine any ash content within the lignin. The acid soluble lignin was determined with the use of equation 3.2.

$$\text{AIL (\%)} = \frac{m_{AIL} - m_{Ash}}{ODW_{sample}} \quad 3.2$$

AIL (%) represents the percentage acid insoluble lignin with m_{AIL} and m_{Ash} representing the mass of the acid insoluble lignin and the ash content respectively. ODW_{sample} represents the oven dry weight of the initial sample subjected to hydrolysis. The soluble lignin content was determined through UV-Vis spectroscopy at a wavelength of 240 nm.

The hydrolysate obtained was neutralized using KOH and filtered through a 0.22 µm nylon syringe filter before being sent for HPLC analysis. The HPLC system used consisted of a Thermo Separations Spectra system P 2000 which was equipped with both an Aminex HPX-87H column as well as an IG Cation H guard column [29] with a Shodex RI-101 refractive index detector. The mobile phase that was used was 5mM H₂SO₄ at a flowrate of 0.6 ml.min⁻¹, with the IG cation H guard column operating at 65°C.

4.1.3.4. Ash content

The ash content for the non-extracted *E. grandis* was determined using NREL/TP-510-42622 [66] by placing samples in a pre-weighed crucible in a muffle furnace at a temperature of 575 ± 25°C for a period of 5 hours until the sample was fully ashed. Due to significant chemical retention of the pre-extracted wood chips it was found that standard NREL procedures was not sufficient in fully ashing biomass subjected to green, white and NaOH pre-extractions. Due to significant chemical retention of the pre-extracted chips, ash content was determined at a temperature of 875 °C for ± 6 hours.

4.1.3.5. Determination of wood weight loss of pre-extracted chips.

Once the wood chips were subjected to pre-extraction the remaining residue fraction was air-dried and then conditioned. After conditioning the moisture content was calculated using infrared drying. The wood chips were then processed in two consecutive size reduction processes of the Condux-Werk bei Hanau mill and Retsch ZM 200 mill (section 3.2.1) for characterization and determination of ash content. The weight loss could then be determined correcting for both moisture and ash content as indicated in equation 3.3.

$$\% \text{ Wood weight loss} = \left(\frac{W_{IO} - W_{EO}(1 - Ash_E)}{W_{IO}} \right) \times 100 \quad 3.3$$

Where:

W_{IO} = The oven dry weight of the initial sample subjected to pre-extraction.

W_{EO} = The oven dry weight of the remaining residue after pre-extraction.

Ash_E = The ash fraction of the remaining residue after pre-extraction.

4.1.4. Compositional analysis of liquid fraction after extraction.

4.1.4.1. HPLC preparation for analysis of sugars and acids.

The liquor fraction from wood chips subjected to NaOH and white liquor extractions' pH was greater than 13, as a result after extraction the liquid fractions were neutralized using 37% HCL. After neutralization the samples were frozen until they were prepared for HPLC analyses. In the case where the liquid fractions obtained were from wood chips subjected to green liquor extractions, the pH was either close to that of 7 or between 5-6 depending on the initial alkali charge, therefore eliminating the need for further neutralization. These samples were also frozen before further analyses.

The sugars that were analysed included that of glucose, xylose, galactose and arabinose with acetic acid also being tested for. Both the monomer sugars and acetate composition of the liquid fraction from the pre-extracted chips were subjected directly to HPLC analyses by using the method described by the NREL/TP-510-42623 [67] which was the same method used by Helmerius *et al* [63] who subjected Birch wood to white liquor pre-extraction. The pH of the

extracted liquor was recorded and then the volume of 72% sulphuric acid that is required to bring the given sample to a 4% (v/v) acid concentration was calculated according to equation 3.3 [67]

$$V_{72\%} = \frac{[(C_{4\%} \times V_s) - (V_s \times [H^+] \times 98.08g \frac{H_2SO_4}{2} \text{ moles } H^+)]}{C_{72\%}} \quad 3.3$$

With:

$V_{72\%}$ being the volume of 72% to be added in ml.

V_s are the volume of the initial sample in ml.

$C_{4\%}$ represents the concentration of 4% w/w H_2SO_4 which is equivalent to 41 g/l.

$C_{72\%}$ represents the concentration of 72% w/w H_2SO_4 which is equivalent to 1176.3 g/l.

H^+ being the concentration of hydrogen ions in moles/L

Once the required amount of H_2SO_4 was added, the samples were autoclaved for 1 hour at 121°C. The samples were prepared for HPLC as described in section 3.2.1.3.

4.1.4.2. Xylose Yield

In order to determine the fraction of xylose recovered, the same formula was used as that by Cheng et al [94] as shown by equation 3.4.

$$Y = \frac{c \times n \times v}{m \times X_F} \quad 3.4$$

Y represents the extraction yield of the xylose (%) while c is the concentration of the xylose measured (g/L), with v (L) representing the volume of the extraction liquor. X_F and m is the fraction of xylose in the *E. grandis* feedstock and mass (g) of the *E. grandis* used for experimentation respectively. The fraction of xylan recovered can be calculated by using the stoichiometric ratio of $\frac{132}{150}$ [94].

4.1.4.3. Fourier Transform Infrared(FT-IR)

FT-IR analysis was done on selected samples of extracted liquor without any further sample preparation. The analysis was done with the use of a Thermo Nicolet Nexus 870 FT-IR system

via the ATR Golden Gate measurement device. The data analysis was done with the use of Omnic 7 software which was subsequently exported to Microsoft Excel.

4.1.5. Extraction procedures using White Liquor, Green Liquor and NaOH.

4.1.5.1. Mild temperature extraction of *E. grandis* using White Liquor

The first set of extractions that were carried out was the extraction of *E. grandis* chips using white liquor at mild temperatures. The white liquor is normally used for pulping in the digester of the Kraft process. Schott bottles (500mL) containing 50g (oven dry weight) *E. grandis* chips and white liquor were placed in a shaking hot water bath at temperatures ranging between 50°C and 90°C and times ranging between 60 and 240 minutes. The active alkali (equation 3.4) concentrations investigated were between 16% and 20% (based on oven dry weight of wood) with a fixed liquor to wood ratio of 4:1 L/kg. The liquor to wood ratio ($r_{L/W}$) is defined as initial mass of the moisture found in the wood (M_w) added to the liquor mass (M_L) divided by oven dry mass of the wood ($M_{Drywood}$), as indicated by equation 3.5 [26]. These conditions were chosen based on the results of Al-dajani *et al* [25], which showed that appreciable amount of hemicellulose can be extracted under similar conditions using Aspen wood as a feedstock.

$$\text{Active Alkali (AA) (g/L)} = \text{NaOH} + \text{Na}_2\text{S} \quad 3.4$$

$$r_{L/w} = \frac{M_L + M_w}{M_{Drywood}} \quad 3.5$$

Table 9 shows the quantity of Na₂S and NaOH used, for wood chips that were subjected to 16%, 18% and 20% active alkali charge, per 50 g (O.D.W) of *E. grandis*.

Table 9: Quantity of Na₂S and NaOH used, per 50 g of E.grandis, for extractions that were carried out using 16%, 18% and 20% AA. Concentrations are on a Na₂O equivalent basis.

Active Alkali Charge (%)	Na ₂ S (g)	NaOH (g)
16	2	6
18	2.25	6.75
20	2.5	7.5

The percentage sulfidity, defined by equation 3.6, was set to be 25% for all active alkali charges. During the pulping process, the sulfidity of the white liquor accelerates the rate of delignification [80].

$$\text{Sulfidity (S) \%} = \frac{\text{Na}_2\text{S}}{\text{NaOH} + \text{Na}_2\text{S}} \times 100 \text{ (as Na}_2\text{O)} \quad 3.6$$

Once the wood chips were subjected to pre-extraction, the 500 ml Schott bottles were cooled to room temperature after which the pre-extracted solid fraction was recovered via filtration through a 100 mesh screen. The wood chips were then washed with 5 litres of water with the wash water being added to the resulting filtrate for analysis.

4.1.5.1.1. Experimental design

For the extractions that were done using white liquor under non-pressurised conditions a 3-factor, 3 level face centred central composite design was employed consisting of three ($n_c = 3$) center points which totalled in 17 runs [68]. The experimental design is depicted geometrically in Figure 10.

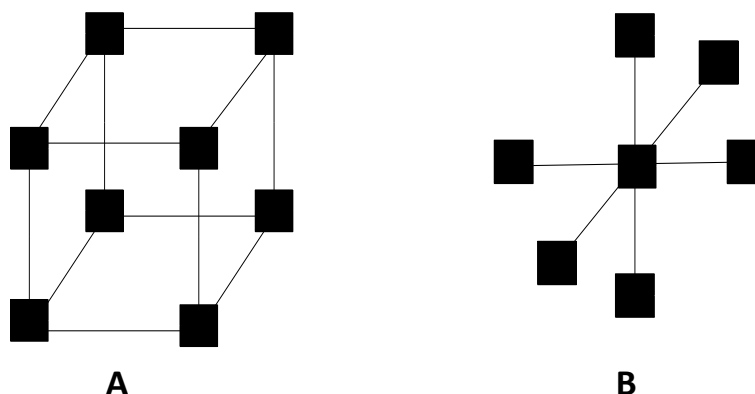


Figure 10: Figure depicting a three factor face centred central composite design with part A depicting the factorial portion while part B are the points in the axial portion of the design. (Adapted from Fence et al [69].)

Part A of Figure 10 shows the factorial fraction of the central composite design with part B depicting the axial points of the design. Together the factorial and axial portions form a CCD [69]. The three independent factors that were investigated for this experiment included temperature, extraction time and active alkali charge to determine % xylose recovered under varying conditions. For each of the independent factors three coded levels were assumed including -1, 0, and 1 [69]. Three assays were carried out at the centre point (0) for the estimation of the random error. Table 10 shows both the coded and uncoded levels of three independent factors investigated while Table 11 shows the experimental runs carried out using the face centred central composite design. The data was interpreted using Stat Soft® Statistica

Table 10: Table depicting both coded and uncoded levels of independent variables.

Factor	-1	0	1
Active Alkali Charge (%)	16	18	20
Temperature (°C)	50	70	90
Time(minutes)	60	150	240

Table 11: Table showing experimental runs with corresponding coded variables. (Table format adapted from Fenech et al [69])

Run	Alkali Charge	Temperature	Time	Point
1	-1	-1	-1	Factorial
2	1	-1	-1	Factorial
3	-1	1	-1	Factorial
4	1	1	-1	Factorial
5	-1	-1	1	Factorial
6	1	-1	1	Factorial
7	-1	1	1	Factorial
8	1	1	1	Factorial
9	-1	0	0	Axial
10	1	0	0	Axial
11	0	-1	0	Axial
12	0	1	0	Axial
13	0	0	-1	Axial
14	0	0	1	Axial
15	0	0	0	Centre
16	0	0	0	Centre
17	0	0	0	Centre

4.1.5.2. Pre-extraction of hemicellulose using temperatures above 100 °C.

Hemicellulose pre-extraction using green liquor, white liquor and NaOH were also done at temperatures exceeding 100°C; as result a pressurized vessel was required. Therefore these extractions were done in a pressurized oscillating digester with a volume of 15 dm³, the same digester that was used for subsequent pulping [122]. All extractions were carried out using 50g (oven dry weight) of screened wood chips in micro bombs, which were then placed in the digester which was half filled with water. During the extraction cycles the digester oscillated through 45° in order to ensure sufficient liquid contact with the wood chips. The temperature and pressure of the digester were monitored with the aid of a thermocouple as well as a pressure gauge fitted to the lid of the digester. A programmable logic computer (PLC) was used to control the entire extraction cycle. Pressure in the digester was liberated through the use of a blow valve with operating pressure during pulping being around 8 bar and that of the extractions varying between 2 and 7 bar.

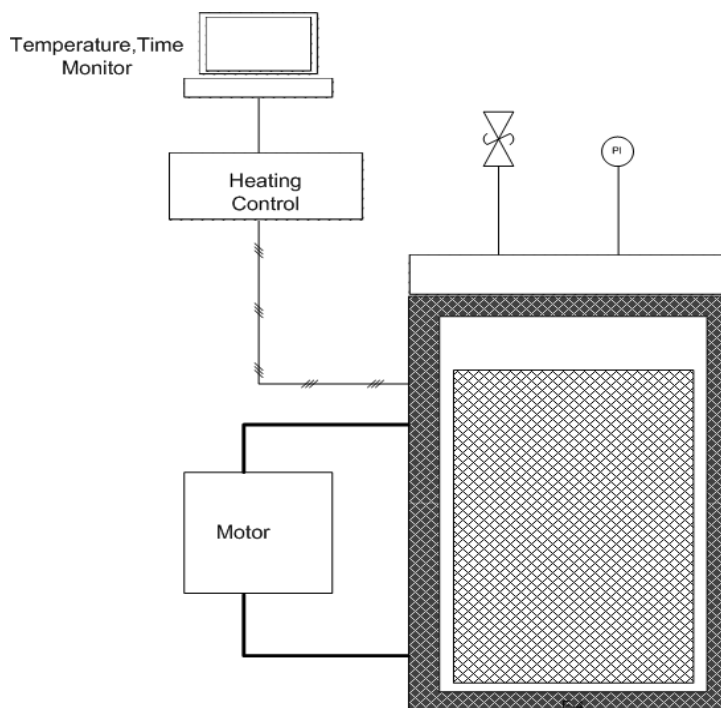


Figure 11: Figure displaying set up of oscillating digester used for hemicellulose extraction as well as pulping.

After the extraction process the micro bombs were removed and cooled to room temperature. The pre-extracted solid fraction was recovered via filtration through a 100 mesh screen. The wood chips were then washed with 5 litres of water with the wash water being added to the filtrate for subsequent analysis. White liquor extraction was carried out at temperatures ranging between 100°C and 140°C using Active Alkali charges of 16% and 20% for a period of 90 minutes at each given temperature interval. Liquor to wood ratio of 4:1 was utilised. The concentrations of each component of 16% and 20% Active Alkali that was used is described in Table 9.

4.1.5.2.1. Green Liquor extraction

The green liquor extractions were carried out at a temperature of 160°C and H-factors ranging between 200 and 800 with a liquor to wood ratio of 4:1. The H-factor [70] is a means of combining the effect that both temperature and time has on the extent of delignification on pulp during Kraft pulping into a single severity factor as described by equation 3.7. The H-factor becomes much more significant at higher temperatures. It is easier to describe the green liquor extraction conditions into a single H-factor as it takes place at high enough temperature where the H-factor becomes significant, therefore being able to avoid having to express both the temperature and time intervals.

$$H\text{-factor} = \int e^{(43.2 - \frac{16.113}{T})} dt \quad 3.7$$

A total titratable charge of both 2% and 6% was investigated. The total titratable alkali (TTA) is described in equation 3.8. The green liquor composition is described in TTA due to the fact that it also consists of Na₂CO₃.

$$TTA = NaOH + Na_2CO_3 + Na_2S \quad 3.8.$$

The conditions described used for green liquor extractions were obtained from literature [39, 26]. In addition to the NaOH, Na₂CO₃ and Na₂S that was used to make up the green liquor 0.05% (based oven dry weight) of Anthraquinone was added to the green liquor extraction step

to assist with the pulping of the pre-extracted chips .Anhraquinone has been added during the extraction step itself in a number of studies using green liquor extraction specifically, to aid as a pulping catalyst during the subsequent pulping of the pre-extracted chips [26, 27, 77]. Table 12 shows the quantity of each component of green liquor used per 50g (O.D.W.) of *E.grandis* chips.

Table 12: Table indicating quantity of each component of green liquor used per 50g (O.D.W) of *E.grandis*.

Component	Quantity of component added (g)	
	2%	6%
<i>Na2CO3</i>	0.645*	1.93*
<i>Na2S</i>	0.269*	0.80*
<i>NaOH</i>	0.085*	1.35*
<i>Anthraquinone</i>	0.025	0.025

*Indicated as equivalent amount of Na₂O

4.1.5.2.2. NaOH Extraction

The NaOH extractions were done at temperatures of 100°C,110°C,120°C and 130°C and at molar concentrations of both 1M and 2M. These extraction temperatures are higher than that that is described in literature [28,61]. From preliminary runs that were done using white liquor extraction it was deemed necessary to increase the extraction temperature using NaOH when compared to that of literature.

4.2. Results

4.2.1. Compositional Analysis of the *E. grandis* feedstock.

The chemical composition of the *E. grandis* feedstock for combined hemicellulose extraction and pulping is shown in Table 13. The cellulose fraction is expressed in terms of the glucose while the hemicellulose content, the summative combination of both xylan and arabinan, is expressed as xylose and arabinose.

Table 13: The Average Compositional Analysis of the *E. grandis* Feedstock used on a dry basis.

Component	Average
Xylose (wt %)	15.79±0.73
Glucose (wt %)	48.44±0.48
Arabinose (wt %)	0.66±0.04
Klason Lignin (wt %)	23.44±1.92
Acid Insoluble Lignin (wt %)	4.32±1
Total Extractives (wt %)	4.53±0.45
Summative Analysis (wt %)	97.17±4.05

The xylan and cellulose content, which is of particular interest in this study, is typical for the species with literature indicating that xylan content varies between 11.5% and 21% with that of the cellulose varying between 43% and 53% [11,61,71,72,73,108]. The xylan is of particular interest, as higher xylan content means that there is a larger quantity available for extraction while high cellulose content is important as it ties in closely with pulp yield.

The lignin content for the species is typical of *E. grandis* with lignin quantities in literature generally ranging between 21% and 30% [29, 72, 73]. Low lignin content is especially desirable for pulping purposes due to easier delignification. Moreover, lignin can also hinder the release of sugars during extraction processes [117].

4.2.2. Comparison of xylose recovered using green liquor, white liquor and NaOH.

Table 14: Results of central composite design where *E. grandis* was subjected to white liquor extraction at temperatures between 50°C-90°C, AA concentrations between 16-20%, and extraction times ranging between 60 and 240 minutes.

Run	Charge	Temperature	Time	% Xylose Recovery
1	16	50	60	3.54
2	16	50	240	3.79
3	16	90	60	4.88
4	16	90	240	5.09
5	20	50	60	4.18
6	20	50	240	3.79
7	20	90	60	3.72
8	20	90	240	5.63
9	16	70	150	3.93
10	20	70	150	5.03
11	18	50	150	3.47
12	18	90	150	4.44
13	18	70	60	4.13
14	18	70	240	4.36
15	18	70	150	3.90
16	18	70	150	3.99
17	18	70	150	4.20

Table 14 shows the corresponding % xylose recovered for each extraction condition that was carried out using the white liquor using mild extraction temperatures via a face-centred central composite design (Confidence level = 95%). These mild extraction conditions consisted of temperatures ranging between 50°C and 90°C, reaction times of between 1 and 4 hours and active alkali charges of between 16 and 20%.

The mild temperatures in this instance allowed for a maximum xylose recovery of 5.63% at the most severe extraction conditions (20% AA, 240 minutes, and 90°C). The recoveries shown are much lower than that that was obtained by Jun *et al* [28] who managed to obtain nearly 25% of the original fraction from the Aspen chips that they utilised using similar extraction conditions (Table 14). Jun *et al* [28] also obtained the greatest quantity of xylose recovered at the most severe extraction conditions investigated which in that case was 18% AA, 240 minutes extraction time and an extraction temperature of 90°C.

Technically, it was expected that the alkali concentration would have played a greater role in the fraction of xylose recovered during extraction. The range of Active Alkali charges investigated was small, between 16% and 20%, which could have dampened the influence of the white liquor charge in the experimental design. Furthermore, the small variability in xylose recoveries also hinders the chance of obtaining statistical significance (95% confidence level) of the extraction factors investigated with only temperature showing any statistical significance when related to xylose recovery. Figure 12 shows a clear significant ($p= 0.05$) influence of temperature on the xylose recovered.

Figure 13 shows the response surface plot of the xylose recovered. From the plot it is clear that time on its own has no influence on the xylose recovered. Temperature shows influence on the xylose recovered with the highest recovery corresponding with high temperature and longer reaction times. The figure shows extraction temperatures ranging between 45°C and 90°C, with extraction times ranging between a 40 and 240 minutes at a constant active alkali concentration of 18%.

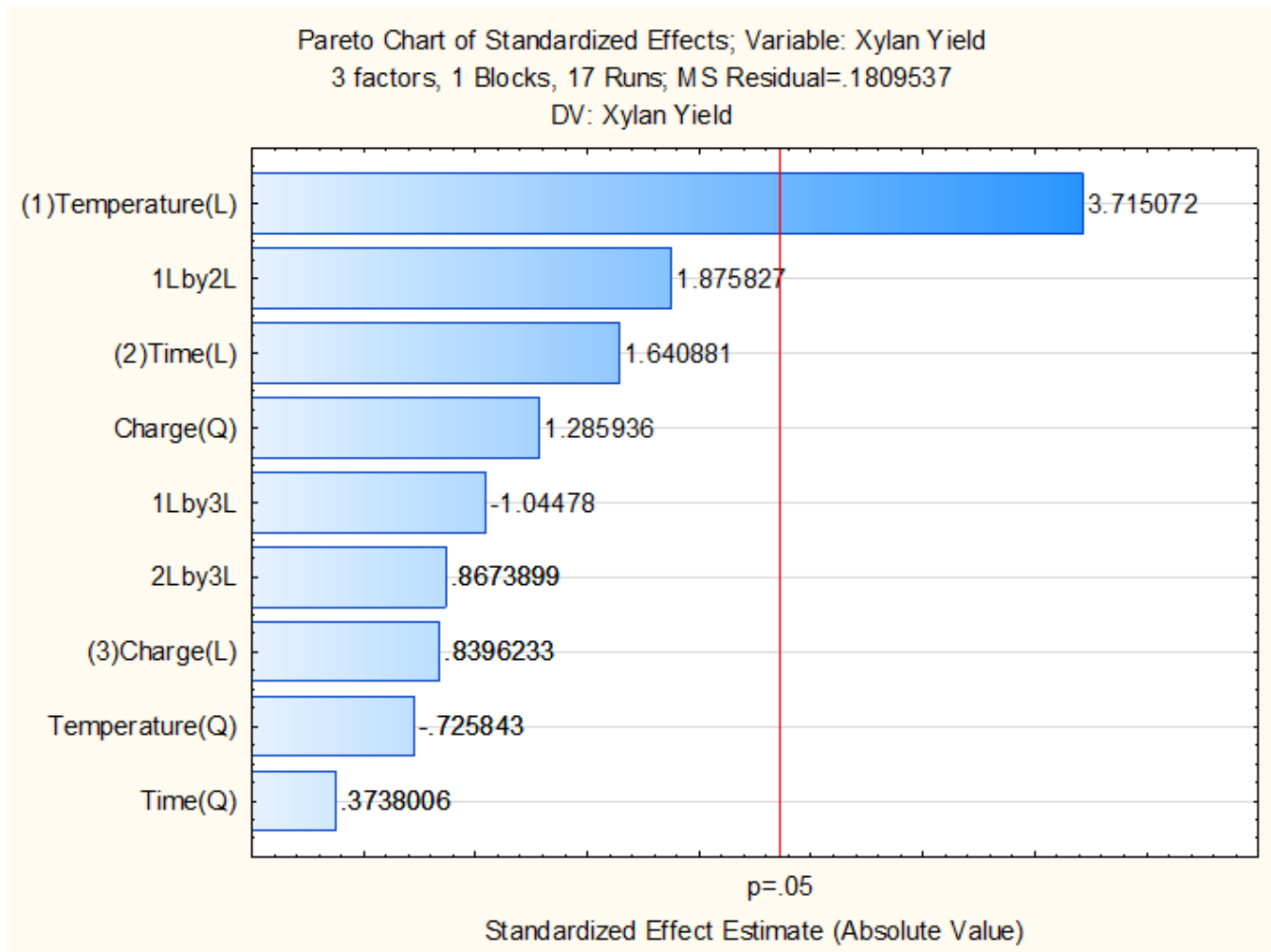


Figure 12: Standardized Pareto chart depicting the effects of temperature (°C), time (minutes) and Active Alkali charge (%) on xylose recovery.

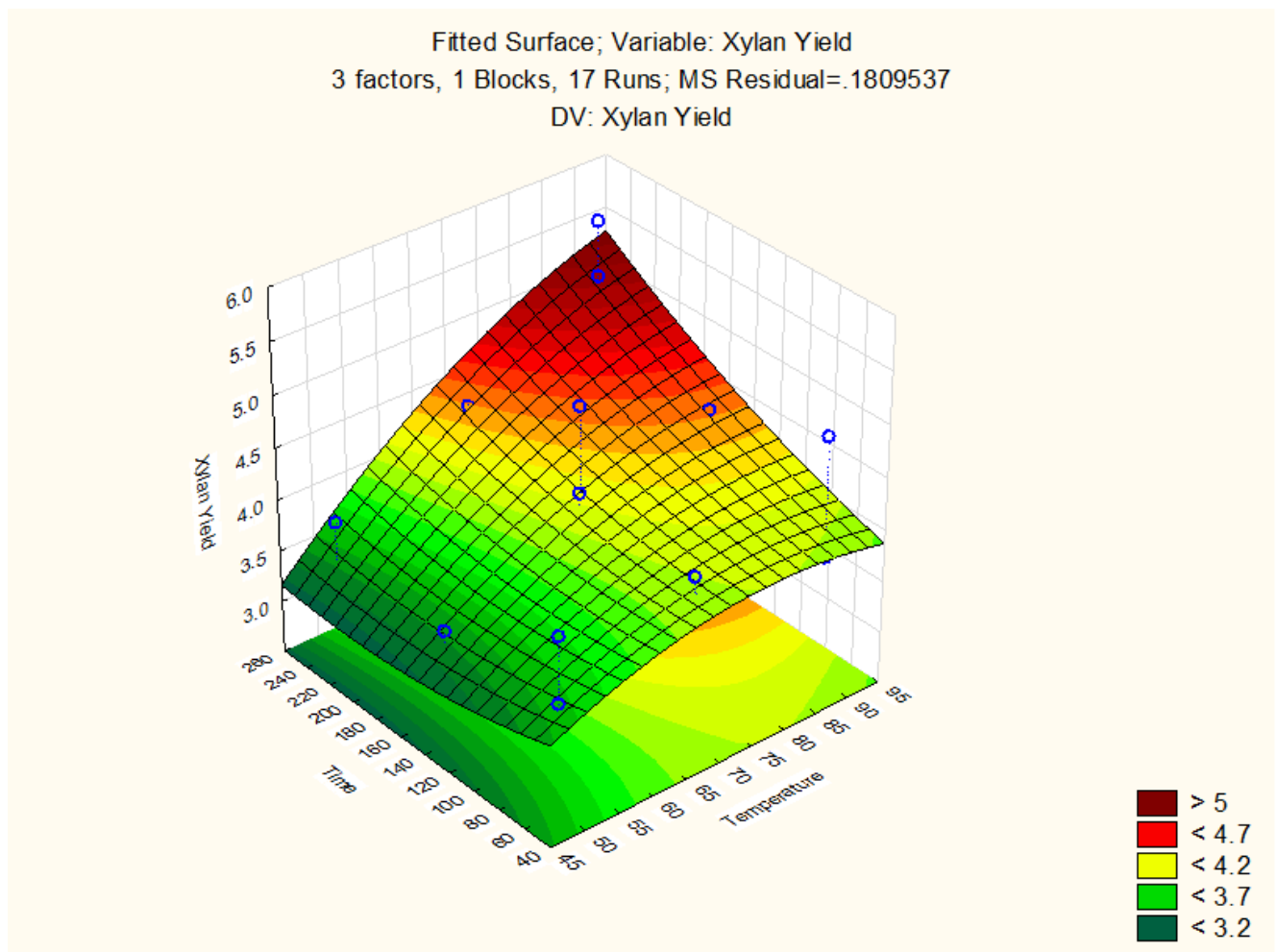


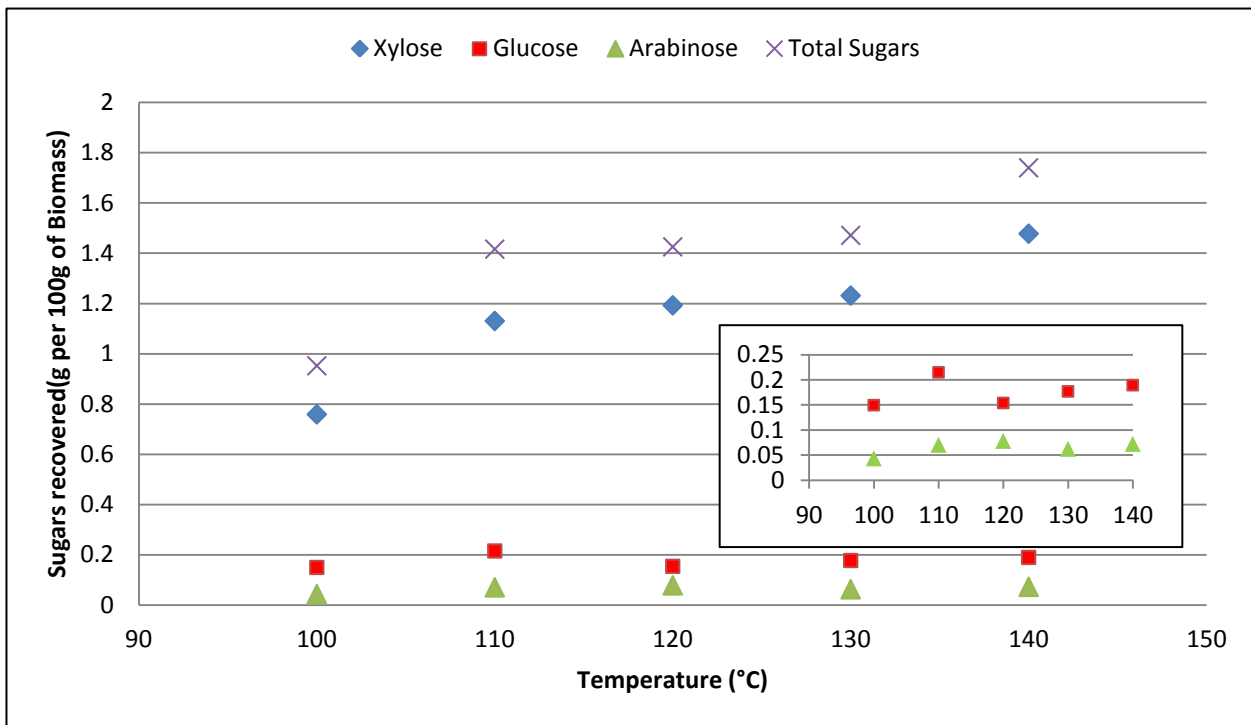
Figure 13: Response surface plot for xylose recovery (%) after white liquor extraction under non-pressurised conditions at a fixed AA charge of 18%. The figure shows the impact of both extraction time (minutes) and temperature (°C).

Xylose was the principal monosaccharide in the hydrolysed of *E. grandis* when subjected to 16% and 20%AA (Figure 14). The greatest amount of solubilised xylose recovered, based on the raw non-extracted chips, was 9.35% and 13.27% for the 16% and 20% AA white liquor extractions respectively with both obtaining highest yields at 140°C. These higher yields indicate that the increased severity in extraction temperature using white liquor helped boost the xylose recovered relative to that of the non-pressurised extractions that were carried out using white liquor.

The solubilised sugars recovered using 1M and 2M NaOH are depicted by Figure 15. Using 1M NaOH the xylose recovered increased until a temperature of 120°C where it plateaued. The same pattern was evident when using 2M NaOH albeit the xylose recovered being substantially higher for 2M NaOH than 1M NaOH (Fig. 15). The xylose recovered using 1M NaOH was lower than both the 16% AA and 20% AA charge for the white liquor, however the 2M NaOH is greater (15.15% yield) when compared to both that of 16% and 20% AA within the temperature interval investigated.

The solubilised sugars recovered using green liquor is depicted in Figure 16. The solubilised xylose that was recovered using 2% Total Titratable Alkali green liquor was greater than that of the 6% TTA green liquor, with the same behaviour observed by Walton *et al* [26]. Xylose recovered in the extraction liquors using green liquor extraction was lower when compared to that of the white liquor and NaOH extraction methods with the highest recovery being 7.83% using 2% TTA green liquor.

a)



b)

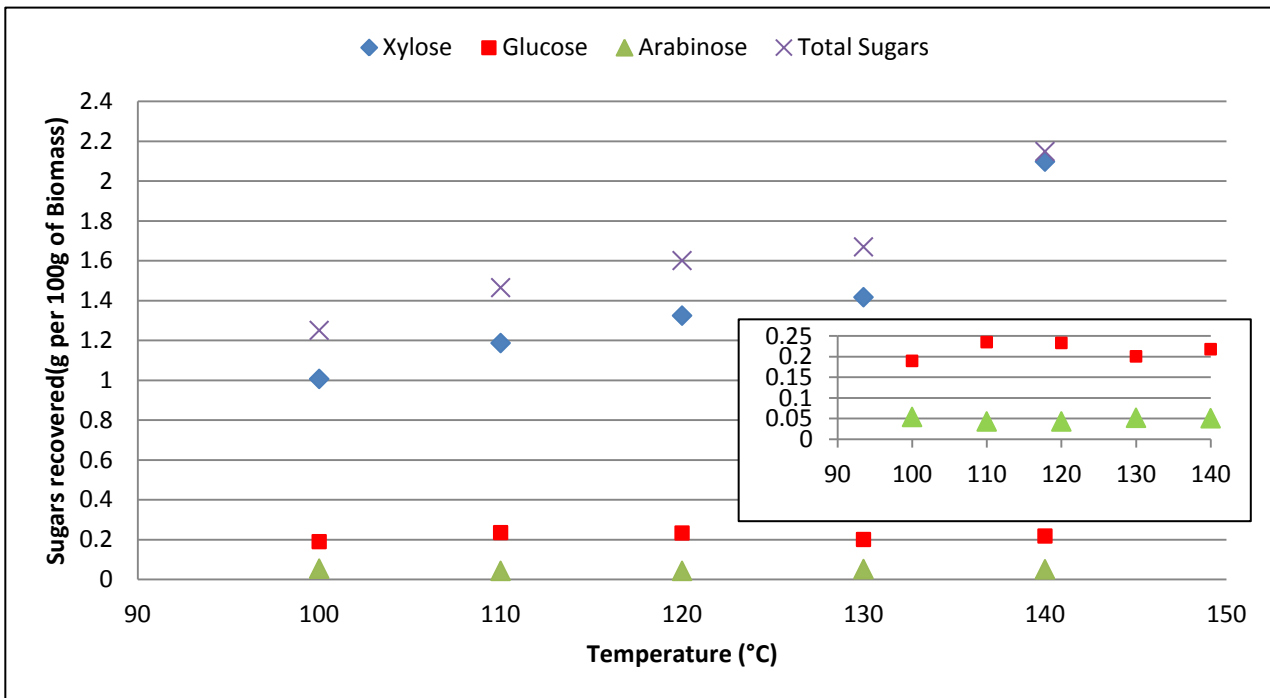
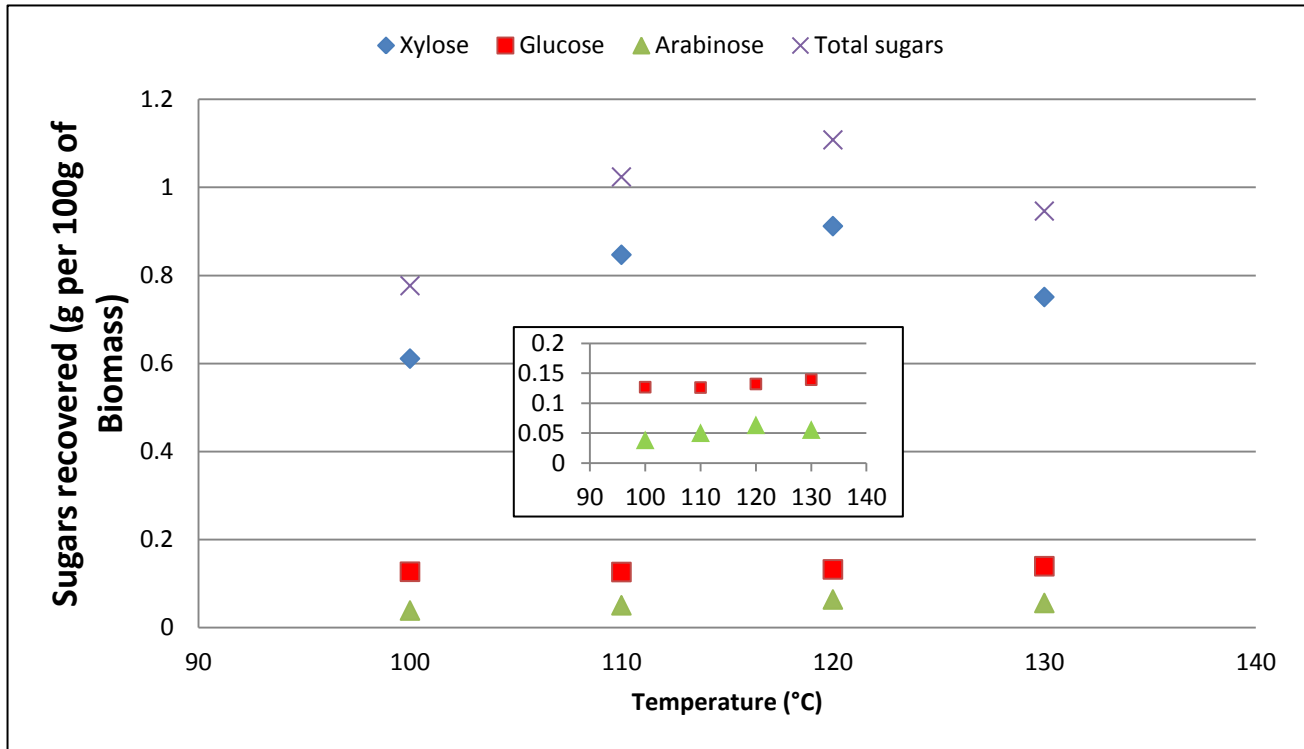


Figure 14: Mass of solubilised sugars recovered in extraction liquor per 100 grams of *E. grandis* feedstock using white liquor. a) 16% Active Alkali b) 20% Active Alkali. Temperatures ranging between 100°C and 140°C for both a) and b).

a)



b)

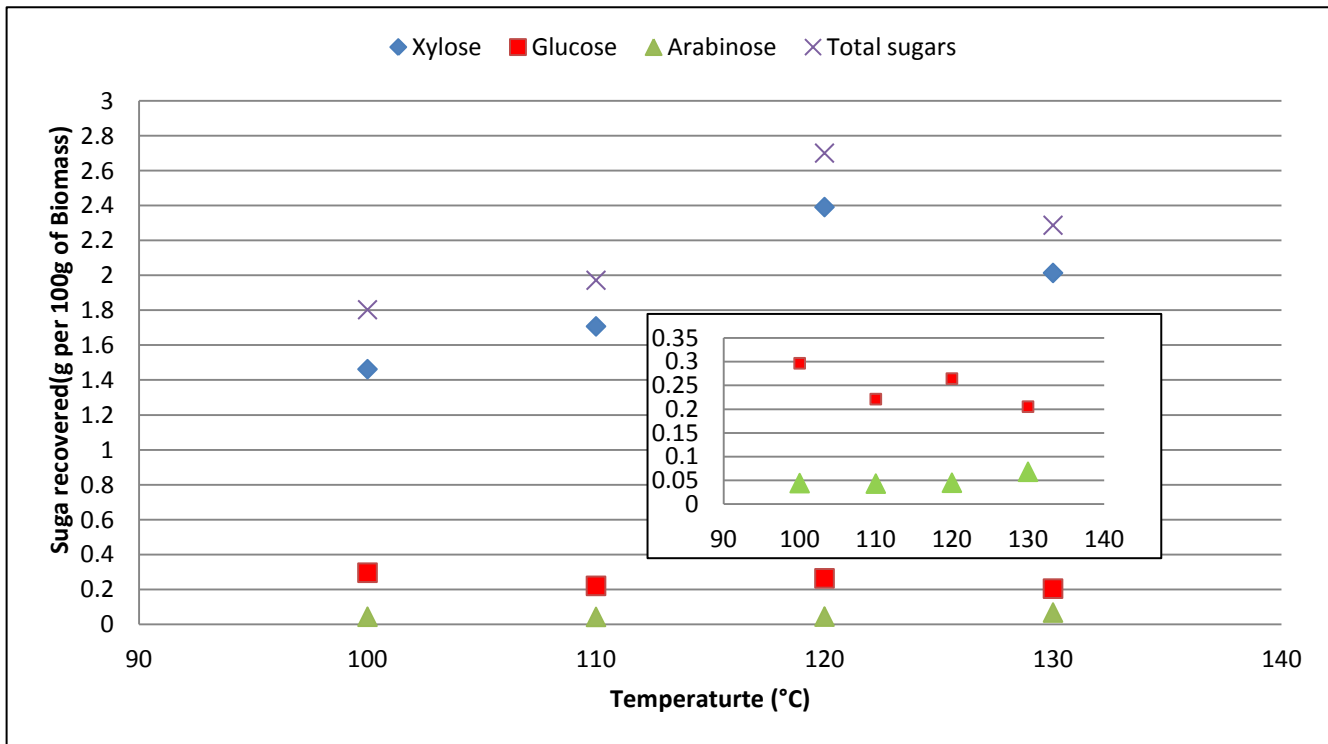
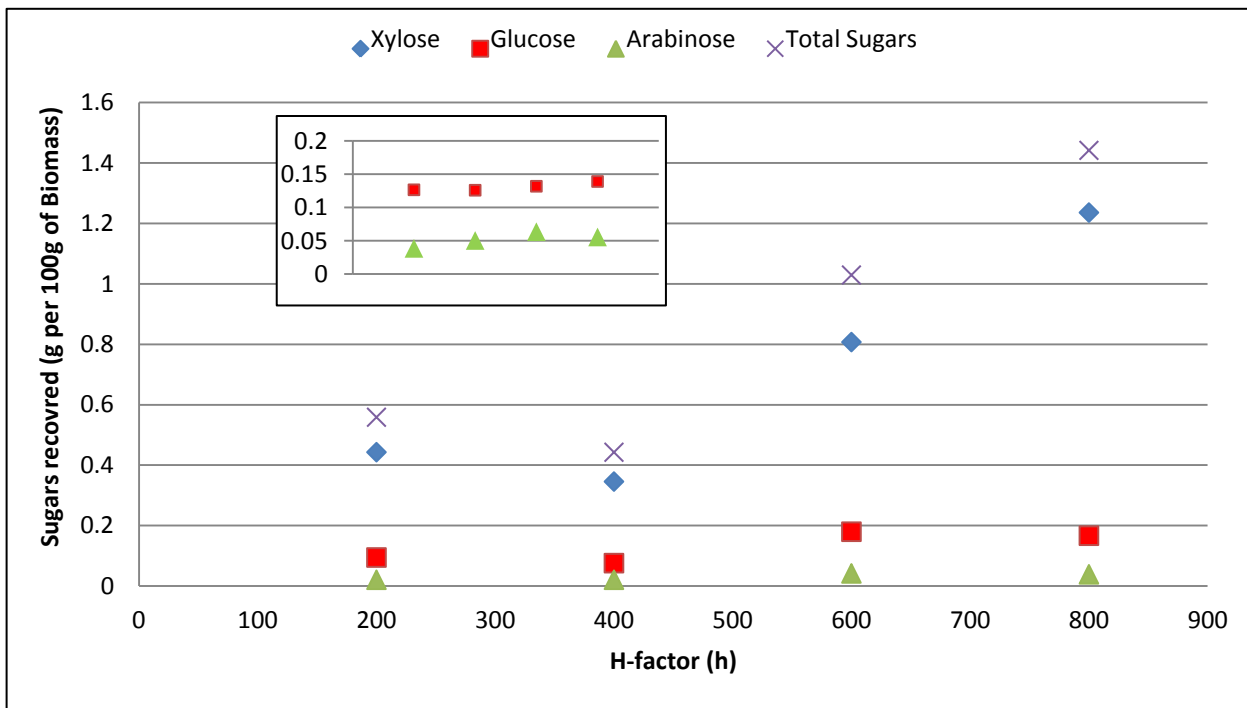


Figure 15: Mass of solubilised sugars recovered in extraction liquor per 100 grams of *E. grandis* feedstock using NaOH. A) 1M NaOH b) 2MNaOH. Temperatures ranging between 100°C and 140°C for both a) and b).

a)



b)

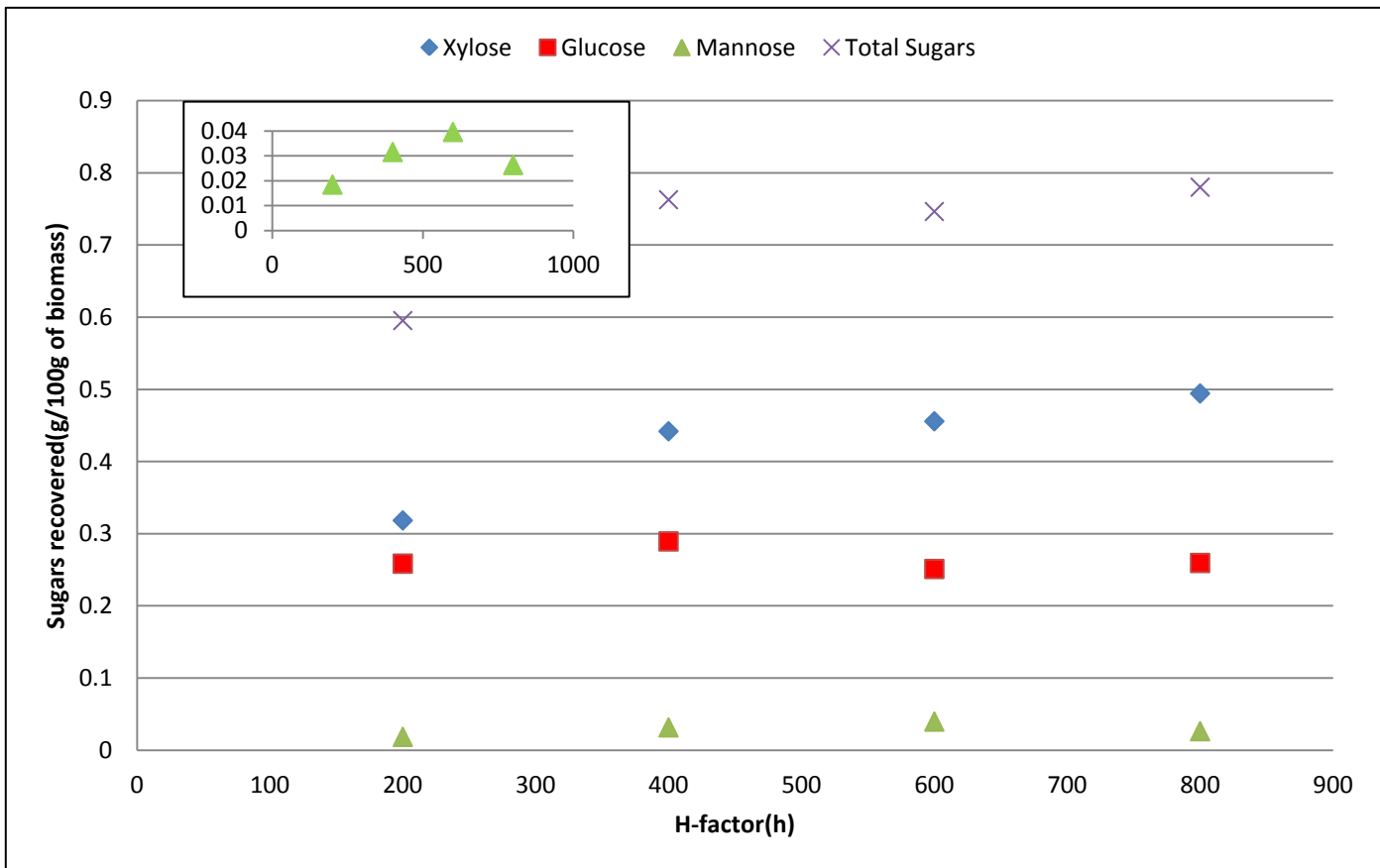


Figure 16: Mass of solubilised sugars recovered in extraction liquor per 100 grams of *E. grandis* feedstock using green Liquor. a) 2% Total Titratable Alkali b) 6% Total Titratable Alkali. Temperature of 160°C for both a) and b).

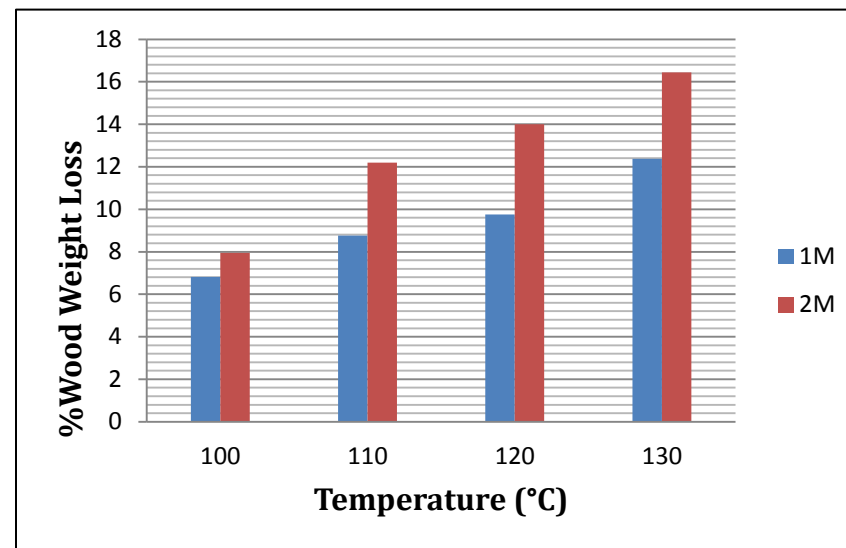
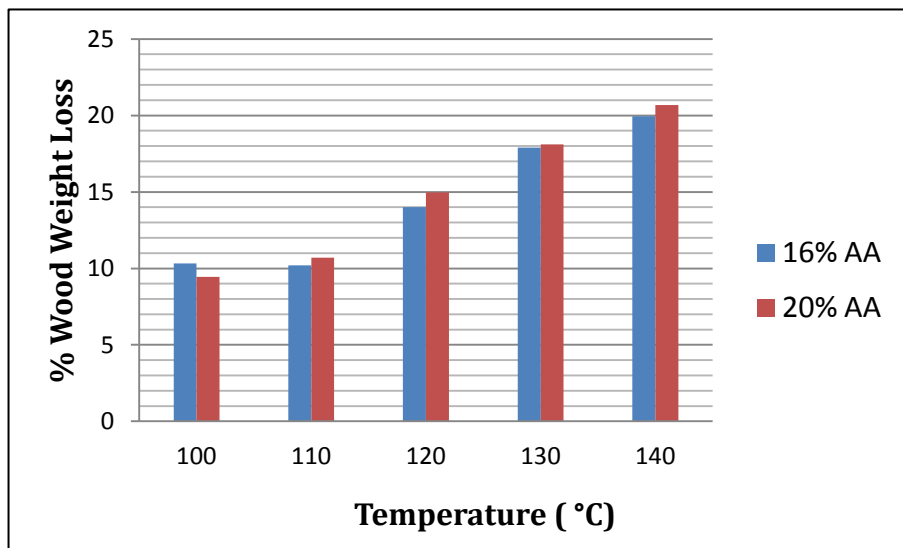
4.2.2.1.1. Wood Weight Loss of *E. grandis* subjected to white liquor, green liquor and NaOH extraction at temperatures exceeding 100°C.

Figure 17 shows the fraction of wood that was solubilised using white liquor, green liquor and NaOH at temperatures exceeding 100°C. For the white liquor extractions using 16% active alkali the wood weight loss ranged from 10.33% at 100°C to 19.95% at the most severe extraction condition investigated of 140°C. For 20% AA the wood weight loss ranged from 9.43% to 20.67% at 100°C and 140°C respectively.

For 1M NaOH, the wood weight loss ranged from 6.81% to 12.37% as the temperature increased from 100°C to 130°C. The percentage solubilised wood for 2M ranged from 7.95% to 16.44% for the temperature interval between 100°C and 130°C with the difference in solubilised wood between the two NaOH concentrations becoming more significant as the temperature increases.

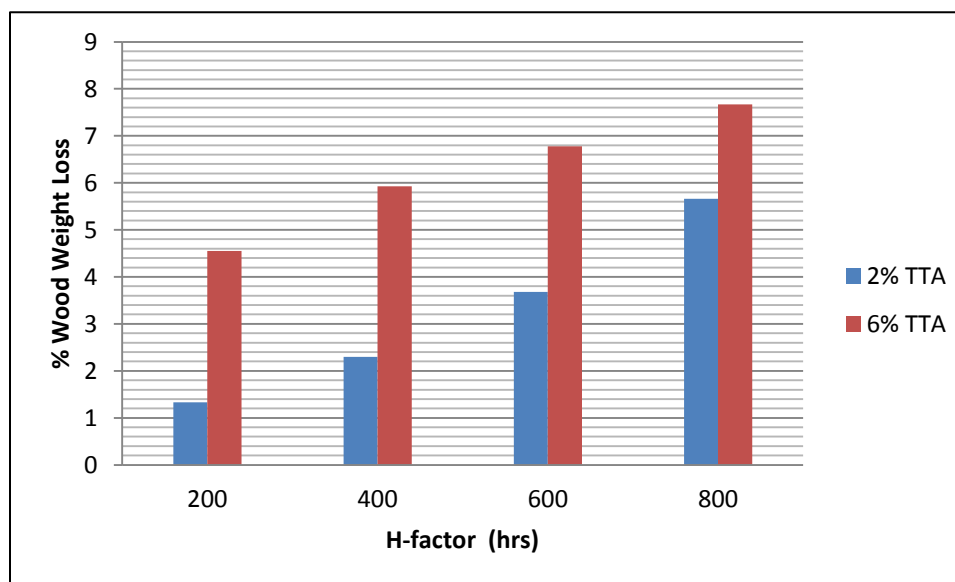
The lower alkalinities that were utilised during green liquor extraction dampened the effect on the fraction of wood that was solubilised, with the green liquor extractions resulting in lower wood weight losses when compared to that of the white and NaOH extraction methods. For 2% TTA the wood weight loss ranged from 1.32% to 5.663% for an H-factor range of between 200 and 800. The 6% TTA concentrations resulted in wood weight losses of between 4.55% and 7.67% for the same H-factor range.

Figure 18 indicates that the pH drops for both the 2% and 6% TTA extraction conditions as extraction severity increases. This is due to the increase in acetic acid found in the extracted liquor as the extraction severity continuous to increase [26]. The pH for the 6% TTA extraction conditions move to a pH of around 7, while the 2% TTA extractions, due to the lower initial alkali charge, drops to a pH of below 5. The pH of the extracted liquor, especially that of the 6% TTA charge, emulates near neutral extraction conditions thus giving rise to its name “near neutral” extraction. A plot of wood solubilisation as a function of the pH of the extract is given in Figure 19 for both 2% and 6% TTA. 6% TTA showed a strong correlation ($R^2 = 0.92$) with



A

B



C

Figure 17: Wood weight losses obtained using three different extraction methods. A) White liquor extraction for 16% and 20% Active Alkali. B) NaOH extraction for 1M and 2M. C) Green liquor extraction using 2% and 6% TTA.

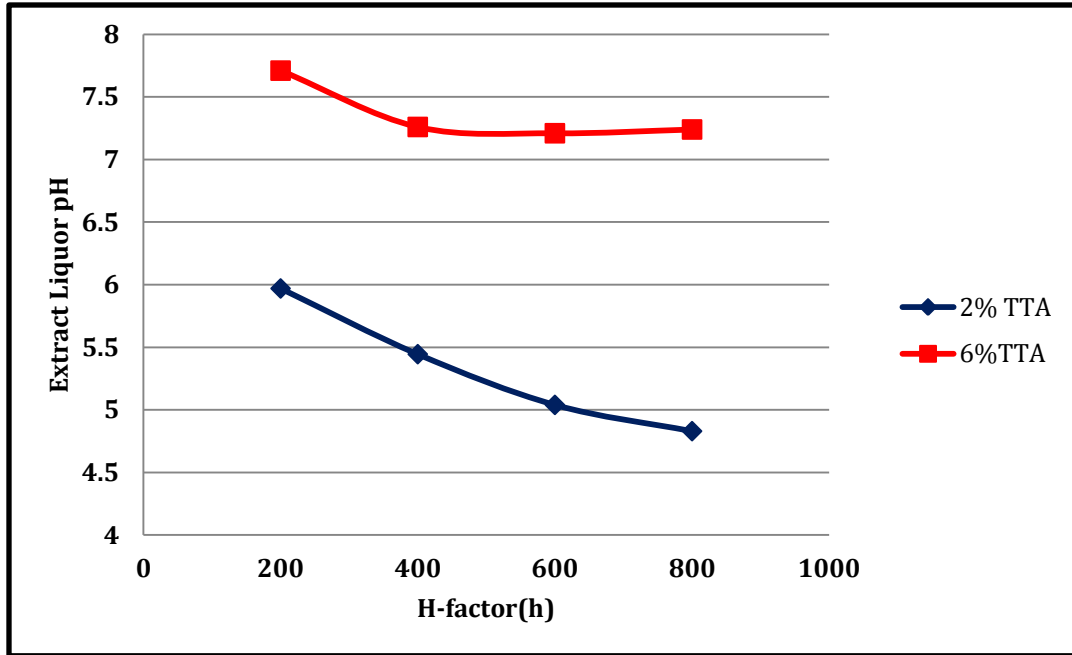


Figure 18: Variation of pH in green liquor extracts at TTA levels of 2% and 6%

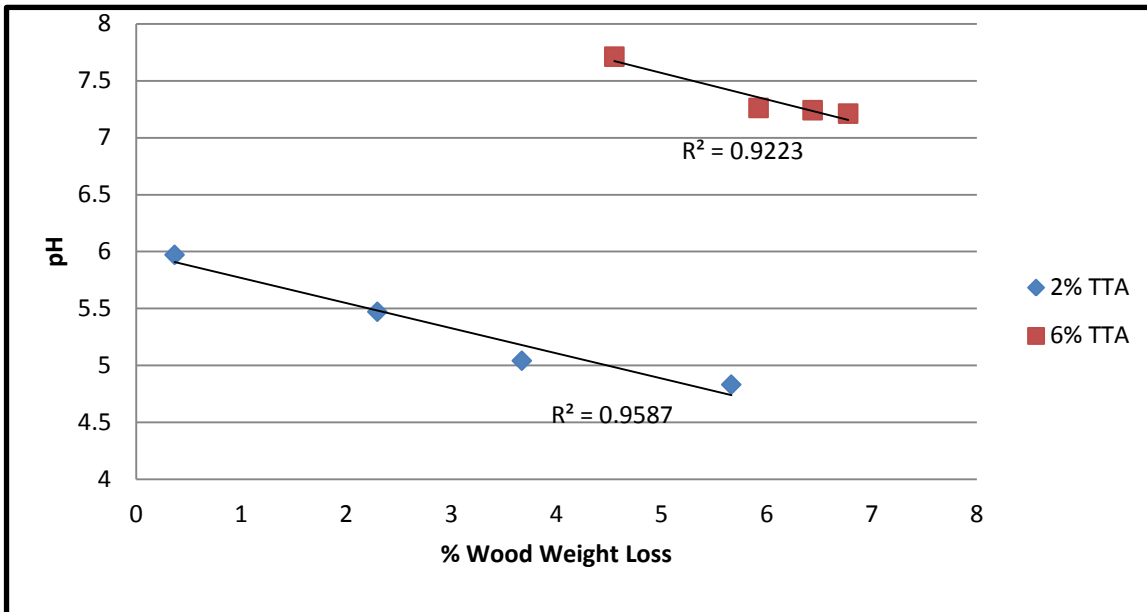


Figure 19: Correlation between wood chip weight loss and the resulting pH of the extraction liquor obtained through green liquor extraction.

2% TTA showing an even stronger correlation ($R^2 = 0.95$) indicating that the pH of the green liquor extracts can be used to predict wood weight loss [76].

The relationship between the fraction of wood solubilised and the amount of xylose recovered for each method of extraction is depicted by Figure 20. The maximum quantities of dissolved wood for 2% and 6% TTA using green liquor was 5.6% and 7.6% respectively as indicated in Figure 17. The maximum amount of dissolved wood was 16.4% and 20.67% for 20% AA white liquor and 2M NaOH extraction respectively. The lower quantities of wood dissolved for green liquor extraction relative to that of white liquor and NaOH extraction is mirrored by the lower xylose recoveries of green liquor (7.83%) relative to that of NaOH (15.15%) and white liquor (13.27%) extraction as derived from Figure 16, 15, and Figure 14 respectively.

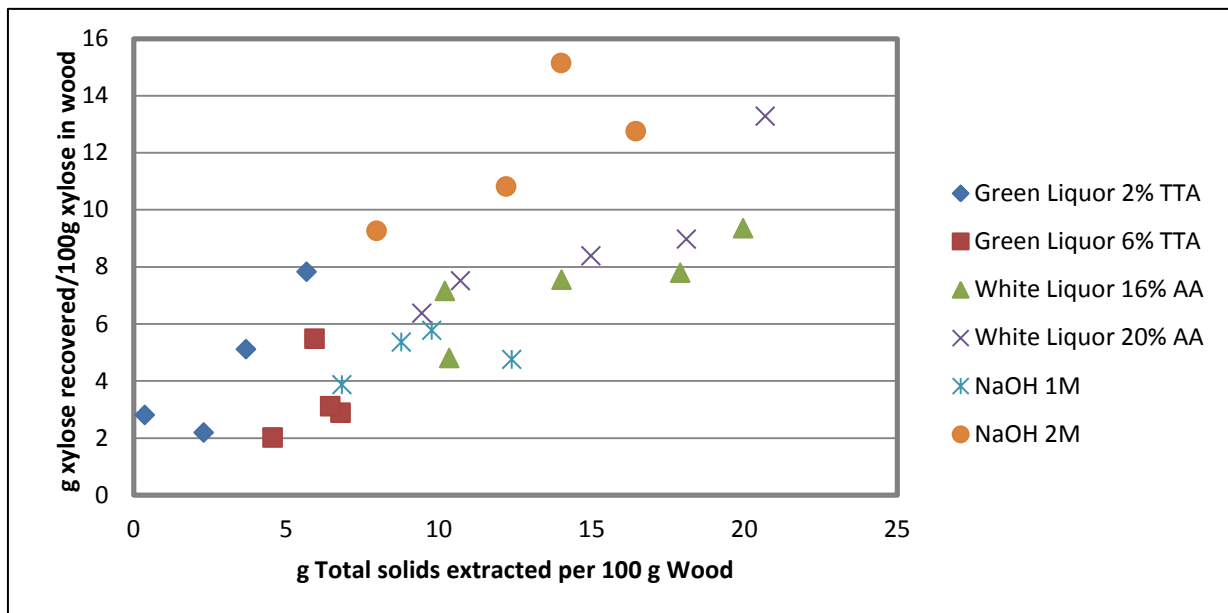


Figure 20: Relationship between total solids extracted and recovered xylose. For green liquor extraction: 2% and 6% TTA, 160°C, 200-800 h-factor. White liquor: 16% and 20% TTA, 100 °C - 140°C, 90 minute extraction time. NaOH: 1M and 2M, 100°C- 140°C, 90 minute extraction time.

4.2.2.2. Purity of extracted Liquor

FT-IR spectroscopic analysis was carried out on the extracted liquor that resulted from the highest xylose yielding conditions. As a result samples were sent for FT-IR analysis at extraction conditions of 140°C and 20% AA, 120°C and 2M as well as 800H and 2% TTA, for the white liquor, NaOH and green liquor respectively. Figure 21 shows the spectra of the extraction liquor obtained from the conditions described.

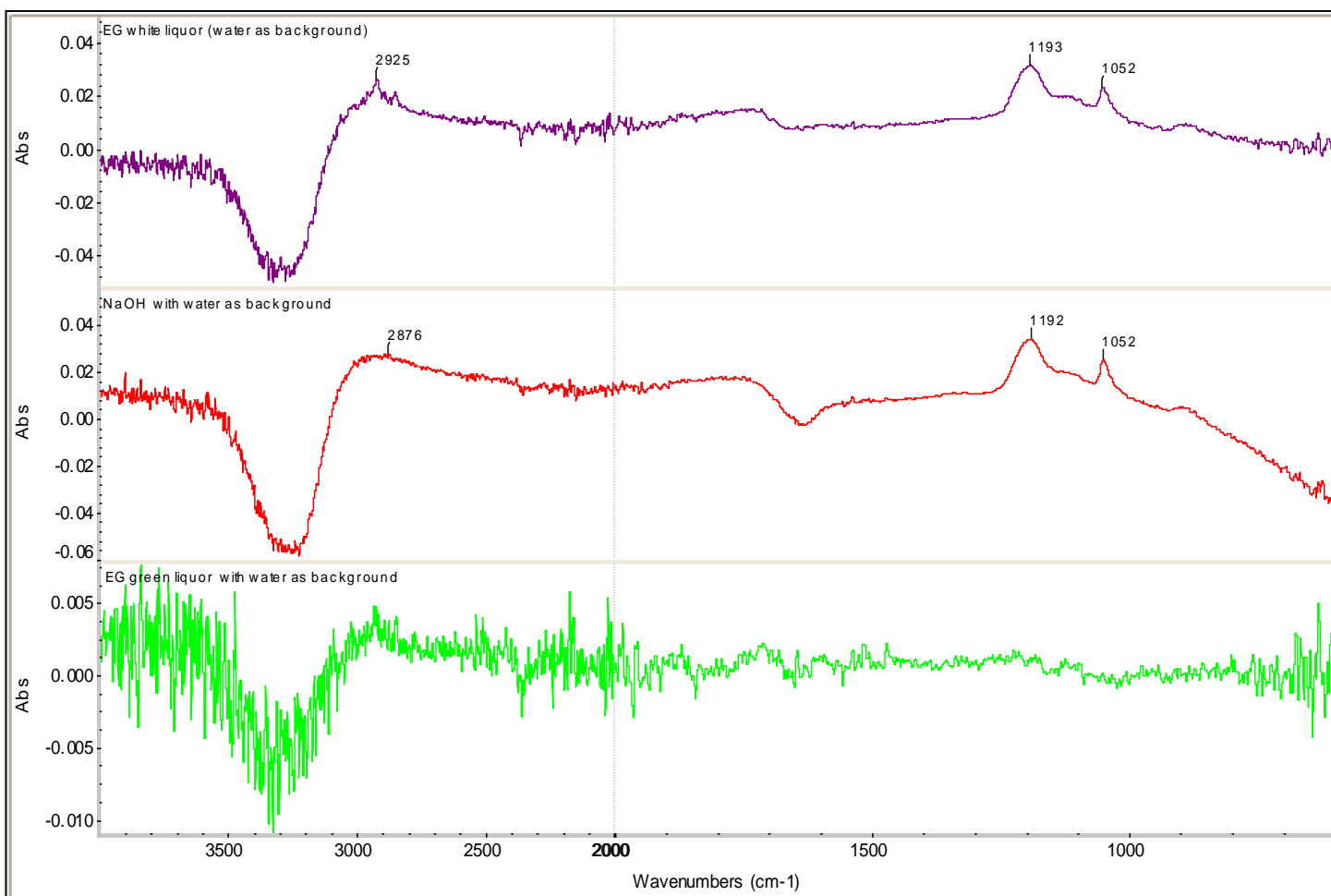


Figure 21: FT-IR spectra of extracted liquor using different extraction methods: White Liquor (Top), NaOH (Middle) and Green liquor (Bottom)

Both the extracted liquor obtained from chips subjected to white liquor and NaOH extraction displayed peaks at 1193/1192 cm^{-1} as well as at 1052 cm^{-1} , which are absent in the extraction

liquor that was obtained from the chips subjected to green liquor extraction. The samples that were sent for FT-IR analysis were extracted liquor samples that had been diluted through the addition of wash water which made picking up components via FT-IR more difficult. However, one can still observe a distinct similarity between that of the white liquor and NaOH. The deformation of C-O coupled with the deformation of aromatic C-H has been reported for lignin model compounds in the 1052 cm^{-1} region [101,102] with the 1192 cm^{-1} and 1193 cm^{-1} peaks possibly being associated with $\text{C}_{\text{aryl}}\text{-O}$ in lignin model compounds [101]. Thus, indicating that both these peaks are very likely lignin derived.

4.3. Discussion

4.3.1. *E. grandis* response to white liquor, green liquor and NaOH extraction.

Although extraction of hemicellulose utilising green liquor, white liquor and NaOH has been done in literature [26, 28, 61] literature does not provide a comparison of these extraction methods on the same feedstock. From data that has been provided in this chapter, comparisons can be drawn between green liquor, white liquor and NaOH as extraction chemicals on the same feedstock of *E. grandis* in terms of :

- Xylan Yield (Fraction of xylan recovered in extracted liquor from feedstock)
- Purity of extracted product

The most successful extraction method, in terms of the quantity of xylan that was recovered in the extraction liquor, was that of utilising NaOH. As derived from Figure 15, the maximum quantity of xylan that was recovered in the extraction stream was a 15.15% w/w of the xylan found in the feedstock (2M, 120°C, 90 minute extraction time). This was followed by white liquor extraction with 13.27% (20% AA, 140°C, 90 minute extraction time) and green liquor extraction with 7.83% (2% TTA, 160°C, 800h) as derived from Figure 14 and Figure 16 respectively. White liquor and NaOH extraction have comparable xylan recoveries, however the *E. grandis* feedstock subjected to green liquor extraction was notably less than that of white liquor and NaOH extraction. Although green liquor extraction utilised higher temperatures the considerably lower alkalinity utilised during extraction hampered the release of xylan from the given *E. grandis* feedstock. The more severe alkalinities of the NaOH and white liquor extraction conditions results in an increase in the disruption of cellulose crystallinity as well as promotes the breaking of ester linkages between lignin and hemicellulose which in turn promotes the dissolution of hemicellulose [111].

The lower quantities of xylan released from using green liquor is corroborated by the lower quantities of wood that was solubilised when compared to that of white liquor and NaOH extraction. Maximum wood weight losses included 20, 67%, 16, 44% and 7.67% for white liquor, NaOH and green liquor extractions respectively as shown in Figure 17. The majority of the

wood material that is released in the case of green liquor extract is expected to be acetyl groups which are subject to a rapid release in alkaline conditions [28]. Figure 18 indicates a clear drop in pH as the extraction severity increases for both the 2% and 6% TTA.

When looking at the process conditions utilised for xylan extraction and corresponding xylan yields, it is evident that the feedstock of *E. grandis* utilised in this study showed particular recalcitrance to xylan release when compared to that of other feedstocks utilised in literature. In order to achieve xylan yields in excess of 10%, extraction conditions had to be more severe when compared to that utilised in literature. Vena *et al* [61] managed to extract 12.4% of the xylan present in an *E. grandis* feedstock utilising mild alkali conditions which included an extraction temperature of 90°C and 1M NaOH. Only with extraction temperatures greater than 100°C could comparable xylan yields be obtained using NaOH in this study.

For white liquor, for example, both mild (50°C - 90°C) extraction temperatures and more severe extraction temperatures (100°C – 140 °C) were investigated in this study. From Table 14 the maximum recovery of xylan utilising mild extraction temperatures was 5.09%, significantly less than that was observed by Jun *et al* [28] who used white liquor extraction on Aspen under similar conditions and managed to recover approximately 25 % the xylan in the feedstock. Aspen, as a species appears to be particularly well suited to xylan extraction with Al-dajani *et al* [25] managing to recover almost 30% of xylan in the feedstock with temperatures ranging between 50°C and 90°C and NaOH concentrations ranging between 1M and 2M.

Factors that could have hampered the release of xylan in this particular feedstock of *E. grandis* include:

- Extractives content
- Lignin content

As indicated in Table 13, the extractives content of the *E. grandis* used in this study is around 4.5%. The extractives content for this feedstock of *E. grandis* was fairly high when compared to that of other species of *E. grandis* in literature [11, 29, 61, and 73]. The extractives found in literature ranges between 2.9% [11] and 4.2% [61]. Moreover ,the Aspen utilised by Jun *et al*

[28] had an extractives content of less than 1%. Within individual species of wood the extractive content is fairly variable and are also site specific with the extractives content of two genetic clones having the potential to vary quite substantially according to where the trees are placed [75]. A high extractives content can hinder both wood and fiber processing [75], and it is known to impede pulp yield as it hinders the penetration of pulping chemicals [115]. Certain components making up the composition of extractives are hydrophobic and can aggregate on the surface of the fiber which can both block the penetration of chemicals and the diffusion of lignin fragments from the fiber wall [112].

Lignin content of the feedstock could also obstruct the release of xylan. The xylan yields obtained by Vena *et al* [61] further illustrates the role lignin content can play in the release of xylan during alkali extraction. The feedstock Vena *et al* [61] utilised had a particularly low lignin content for *E. grandis*, with a lignin content of only 21.1 % compared to the lignin content of 27.7% (Table 14) of the *E. grandis* used in this study. This indicates that the low lignin content of the feedstock utilised by Vena *et al* [61] made the feedstock particularly amenable to hemicellulose extraction. The release of sugar tends to decrease with increasing lignin content [117]. Higher lignin content allows for a more significant formation of lignin-carbohydrate complexes taking the form of α -benzyl ether linkages [49].

As the extraction temperature was increased to above 100°C, however, utilising white liquor, as indicated by Figure 14, there was a marked improvement in the recovery of xylan (expressed as xylose) when compared to that of temperatures below 100 °C. *E. grandis* chips was subjected to white liquor extraction at temperatures between 100°C and 140°C at active alkali concentrations of either 16% or 20% at extraction times of 90 minutes. From Figure 14, one can infer that the highest fraction of xylan recovered was 13.27% and 9.37% for 20% and 16% AA respectively. As indicated in Figure 14, the effect of alkali concentration became more apparent at these higher temperatures as the higher alkali concentration of 20% active alkali produced a higher xylan recovery at each temperature interval when compared to that of the 16% active alkali. During Kraft pulping, it is known that the dissolution of xylan is strongly dependent on cooking conditions [110] with the same being observed for the extractions that were carried

out in this study. The higher temperatures used during pressurised extraction promoted the dissolution and recovery of a greater amount of xylan when compared to the extractions using white liquor that were done at temperatures below 100°C.

For the white liquor extractions that were carried out at temperatures exceeding 100°C, as indicated in Figure 14, there was no peak in xylose recovery, indicating that process conditions were not severe enough. It is known that during Kraft pulping (where white liquor is also utilised for pulping) that as the temperature increases xylan degradation increases due to an increase in the rate of alkaline hydrolysis of glycosidic bonds [110]. However, at temperatures below 140°C the 4-O-methylglucuronic acid substituents, as well as arabinose that are present in xylan provides a certain amount of stability against the primary peeling reaction that takes place. The 4-O-methylglucuronic acid substituents are mainly found within the C-2 position whereas the arabinose is found in the C-3 position [110]. The higher temperatures utilised during extractions that exceeded 100°C was severe enough to allow for greater xylan solubilisation in relation to that of mild temperature extractions, however was mild enough to still allow for higher recovery in the extracted liquor.

Figure 21 gives insight into the purity of the xylan product that is extracted utilising green liquor, white liquor and NaOH. The absence of the 1052 cm⁻¹, 1192 cm⁻¹ and 1193 cm⁻¹ (Figure 21) bands in the green extraction liquor accentuates the fact that the green liquor extraction conditions is less severe when compared to that of the white liquor and NaOH extraction conditions as the lignin extracted was not significant enough to be signalled in the FT-IR results. Green liquor extraction conditions were less severe than that of white liquor and NaOH extractions, in terms of alkalinity, which was corroborated by the lower wood weight loss of *E. grandis* chips subjected to green liquor extraction when compared to that of white liquor and NaOH extractions (Figure 17). The lower extraction severity allowed for a purer extracted product as less lignin would naturally end up in the extracted liquor.

It has been determined that NaOH > white liquor > Green liquor in terms of xylan yields. The first step in selecting the best extraction method for integration into the Kraft process would be to look at the product yield as this is the motivation for subjecting the feedstock to alkaline chemicals. From this perspective NaOH extraction has an advantage over the other extraction methods. However, in terms of the final product it has also been shown that green liquor extraction allows for a purer a product when compared that of white liquor and NaOH extraction in terms of lignin content. A purer product would naturally offset costs as subsequent purification steps would be less intense.

Product yield and purity, however, also needs to be weighed against the implication the extraction chemicals and corresponding extraction conditions will have on the Kraft process. The higher quantity of wood weight losses induced by white liquor and NaOH extraction when compared to that of green liquor would allow for greater production through put ,barring pulp yield is maintained, as a greater quantity of woodchips subjected to pre-extraction can be processed in the digester when compared to a scenario where woodchips has not been subjected to pre-extraction. Moreover, green liquor extraction requires higher temperatures would which naturally increase energy costs. However, one important inherent advantage of green liquor extraction is the significant lower alkalinity utilised during extraction when compared to that of white liquor and NaOH extraction. This would have significant cost benefits in terms of make up chemicals required when compared to that of white liquor and NaOH extraction.

To further answer the question of the implication of integrating hemicellulose extraction into the Kraft process, pre-extracted *E. grandis* residues need to be subjected to pulping. In this study, for green liquor pre-extraction as well as that of the NaOH pre-extraction, the highest yielding xylan extraction conditions was selected for further pulping. The extraction conditions included 2% TTA, 160°C and an h-factor of 800 for green liquor while for NaOH it included 2M NaOH, 120°C as well as a 90 minute extraction time. However, for white liquor extraction two extraction conditions were utilised for further pulping. This included the highest yielding extraction condition which was 20% AA, 140°C and extraction time of 90 minutes as well a less

severe extraction condition which included 120°C, 20% and an extraction time of 90 minutes. Two extraction conditions were utilised for white liquor as the highest yielding extraction condition resulted in a wood weight loss of 20.67% indicating the extraction severity resulted in a high quantity of wood solubilised which could impact resulting pulp yield. As a result both the highest yielding extraction condition as well as an extraction condition which was less severe was investigated. The less severe extraction condition resulted in a wood weight loss of 15 %. For the highest yielding green liquor and white liquor extraction conditions the wood weight losses were 7.67% and 16.44% respectively. Pulping of the pre-extracted residues is further discussed in the succeeding chapter.

4.4. Conclusions

The specific *E. grandis* feedstock was resistant towards releasing any significant amount of xylan (reported as xylose), when compared to that of literature at extraction temperatures less than 100°C. Factors that could have influenced this is the relatively high extractives content of the feedstock which could result in the prevention of penetration of chemicals into the fiber wall. Furthermore, the lignin content of the species was higher than that of feedstocks studied in literature [61, 28] that was subjected to alkaline extraction at mild (50°C -90°C) temperatures.

It can be concluded, that the most effective extraction conditions in terms of maximising xylan recovery for the *E. grandis* feedstock utilised, is through the use of NaOH with corresponding extraction conditions of 2M NaOH, 120°C as well as an extraction time of 90 minutes. The high alkali concentration of the extraction method allowed for a significantly greater xylan release compared to that of green liquor extractions that resulted in a maximum recovery of 7.83% xylan. White liquor with its alkalinity of 20% AA allowed for a maximum xylan recovery of 13.27%.

In terms of product purity it can be concluded that green liquor allows for the purest xylan product when considering the lignin residual content in the extracted liquor. FT-IR analysis registers lignin in the liquor resulting from white liquor and NaOH pre-extraction and not that of green liquor.

When comparing the potential of the green liquor, white liquor and NaOH extraction methods for integrating into the Kraft process, the high xylan recovery of the NaOH extraction method is an obvious advantage and this was also at a lower temperatures when compared to both that of the white liquor and NaOH extraction methods. The high wood weight loss during extraction is also an opportunity for increased production throughput. However, the alkalinity was higher than that of both the white liquor and NaOH extraction methods. The green liquor extraction method had an advantage as the extractions took place at much lower alkalinity, this was

coupled with that fact that the purity of the extraction stream was greater than that of the white liquor and NaOH extraction methods in terms of lignin content.

For a full understanding of the most feasible extraction method one has to look at both the effect on the pulp and paper properties as well as the chemical mass balance which will be addressed in subsequent chapters.

CHAPTER 5: Pulping yields and quality from pre-extracted Material

5.1. Introduction

A large part in evaluating the feasibility of hemicellulose pre-extraction within the Kraft process rests on the effect it has on the pulp and the subsequent paper quality. It is imperative that the quality of the pulp as well as the paper strength properties mirrors that of conventional pulping processes, where no hemicellulose pre-extraction is implemented prior to pulping. Alkaline methods are more suited to pre-extraction of hemicellulose biopolymers, due to its natural synergism with the Kraft process, and less severe effect on pulp and paper quality when compared to alternative extraction methods.

As indicated Chapter 4, extractions performed using white liquor at temperatures below 100°C resulted in xylan recoveries that were lower than the extractions performed using white liquor, green liquor and NaOH at temperatures exceeding 100°C. A white liquor concentration of 20% AA at a temperature of 140°C produced the highest xylan (13.27%) recoveries. It was found that the highest fraction of xylan that was recovered in the extracted liquor (15.15%) from all the extraction methods resulted from the use of NaOH at temperature of 120°C coupled with an alkali concentration of 2M. Green liquor extraction resulted in xylan recoveries that were lower compared to that of both the white liquor and NaOH extractions (7.83%).

Pulping of wood residues resulting from wood chips subjected to green liquor, white liquor and NaOH has been performed in literature [62, 28, 61] on different feedstocks. In this study, however, a more definitive comparison can be drawn between the extraction methods as extractions coupled with subsequent pulping was performed on the same feedstock of *E. grandis*.

For both the green liquor and NaOH extractions that were performed, as reported in Chapter 4, extraction conditions selected for further pulping included residues resulting from the highest

xylan yielding extraction conditions. For the highest xylan yielding green liquor and NaOH extraction conditions the wood weight losses were 5.5% and 14% respectively with the corresponding xylan yields being 15.15% and 7.83% respectively. For the highest yielding white liquor extraction condition the extraction severity resulted in a wood weight loss of about 20%. As a result, for the white liquor extractions pulping was performed on both the highest yielding extraction condition (140°C, 20% AA) and at a less severe extraction condition (120°C, 20% AA). The pulping that was performed on the residue resulting from the green liquor extraction was done by reducing the alkali charge to try and obtain kappa numbers that are the same as that of non-extracted chips subjected to pulping. Due to the more severe extraction conditions of the white liquor and NaOH extractions both the alkali charges and pulping times were reduced to try and emulate pulp properties of non-extracted chips. Pulps produced that resulted in yields and kappa numbers similar to that produced from non-extracted chips, were used to make handsheets. These handsheets were tested for their burst, tear and tensile indices. The objectives for this study included:

- Optimising of pulping conditions for cellulignin residues after hemicellulose pre-extraction using green liquor, white liquor as well as NaOH.
- Compare the best combinations of pre-extraction with pulping to that of unextracted pulped *E. grandis* in terms of the resulting handsheet properties.

5.2. Materials and methods

Table 15: Table providing summary of chemicals used.

Name of Chemical	Chemical Purity	Chemical formula	Molecular weight(g/mol)	Supplied by
Potassium Iodide	99%	KI	166	Merck
Potassium Permanganate	99%	KMnO ₄	158.03	Merck
Sodium Hydroxide	> 97%	NaOH	40	Sigma-Aldrich
Sodium Thiosulfate	0.2M	Na ₂ S ₂ O ₃	158.11	Sigma -Aldrich
Sodium sulfide hydrate	> 60%	Na ₂ S·9H ₂ O	78.04	Sigma-Aldrich
Starch Solution	indicator, 1% in H ₂ O	–	–	Sigma -Aldrich
Sulphuric Acid	95-98%	H ₂ SO ₄	98.08	Sigma -Aldrich

5.2.1. Pulping of chips subjected to hemicellulose pre-extraction.

In order to have an adequate amount of sample to produce handsheets, extractions were carried out using selected pre-extraction conditions using 85g (O.D.W) chips with the use of the micro-bombs. After pre-extraction the chips were removed from the bombs and the resulting liquor drained from the chips through a 100 Mesh screen. The pre-extracted chips were not washed once extraction was carried out. The chips were air dried after which it was placed in the conditioning room. The chips were weighed and correcting for both moisture and ash content, the oven dry weight of the chips were obtained. Higher ash content also allows for a lower chemical loading during pulping as a larger portion of chemicals would have remained on the chips themselves. Less pulping chemicals was added to wood chips resulting from white and NaOH extraction when compared to that of wood chips resulting from green liquor extractions. With the oven dry weight determined the correct amount of water could be added to ensure a liquid to wood ratio of 4.5:1, with the required volume of water needed being calculated with equation 3.5.

As a benchmark non-extracted *E. grandis* were also subjected to pulping by simulating batch cooking conditions. Pulping conditions including a liquor to wood ratio of 4.5:1, 170°C pulping

temperature, 18% AA coupled with 25% sulfidity. Cooking conditions were based on suggested pulping conditions of South African *E. grandis* [129]. Pulping time at 170°C was set to 45 minutes to achieve a kappa number of 20.

For green liquor, extraction conditions of 2% TTA coupled with an H-factor of 800 was used for further pulping as these conditions resulted in the highest xylose recovery for that particular solvent, which was 7.83% as derived from Figure 16. Furthermore, due to the low alkali charge used during extraction, the wood weight loss was only 5.6% as indicated in Figure 17.

Solid residues that were selected resulting from the white liquor extractions included that resulting from 20% AA extractions for both 120°C and 140°C. The 140°C extraction condition was used as it culminated in the greatest xylose recovery for that particular solvent. Wood chips subjected to a more moderate pre-extraction temperature of 120°C was also used for pulping as the 140°C extraction condition was severe and a more mild extraction condition also needed to be investigated that resulted in reasonable xylose recovery relative to the maximum at 140°C.

For the NaOH extractions the condition of maximum xylose recovery was used which was 120°C, as the weight loss was not significant (16%), at that particular extraction condition. Table 18 shows the chemical charge that was used relative to the amount of chemicals used for the non-extracted *E. grandis* chips (Standard Conditions) for all the extraction conditions.

Pulping of cellulignin residues was performed by using the same severity as when pulping untreated woodchips, and then the pulping chemicals dosage and process severity was progressively reduced until pulp yield close to the conventional process with untreated woodchips could be obtained.

For the pulping of solid residues from the green liquor pre-extraction of xylan that was performed the pulping time at 170°C was kept at 45 minutes due to the low extraction severity of the initial extractions and low alkali charged used. 10%, 20% as well as 35% reduction of pulping chemicals was investigated, during the pulping that was performed on the green liquor pre-extracted *E. grandis* chips [62]. Johakimu *et al* [62] performed green liquor extractions on *E.*

grandis using between 0% and 3% TTA. During subsequent pulping of pre-extracted residue the target kappa number could be obtained using a 20% reduction in pulping chemicals.

Due to the high chemical charge used for the white liquor extraction conditions the cooking time at 170°C was reduced for both the extractions that were carried out at 120°C and 140°C. For the 120°C extractions the cooking time was reduced to 30 minutes, while 25 minutes was used for the 140°C extraction conditions. For the 120°C extraction conditions, the chemical charge was reduced by 10%, 50% and 85%. After xylan extraction using white liquor, Helmerius *et al* [63] reduced the chemical charge during pulping by only 3%. However, the effective alkali charge used during extractions was significantly lower relative to this study.

At the end of the pulping processes the fibers were separated from the resulting black liquor by washing it through a 10 mesh screen with running water until all the pulp has passed through with uncooked fibers (rejects) remaining on the 10 mesh screen. After washing the pulp was screened with a packer slotted laboratory screen. Freeness of the pulps was not determined. Excess water from the pulp was removed through spin drying, with the spin dried pulps having an approximate moisture content of 70%. The pulp yield after screening was determined as the percentage of the original oven dry mass of the *E. grandis* chips. The pulp yield was determined with the use of equation 5.1 [61].

$$\text{Pulp Yield (\%)} = \frac{\text{Oven dry Mass of Pulp} \times 100}{\text{Initial Oven dry Mass of wood chips.}} \quad 5.1.$$

5.2.2. Kappa Number determination

Once the pulp was subjected to screening and spin drying, the kappa number of the pulps was determined using the method that is outlined by ISO 302:2004 (E) [82]. The kappa number of a given pulp indicates the lignin content of the pulp as well as how bleachable the pulp is. 50 ml (± 0.1) of both potassium permanganate solution and sulphuric acid were mixed in a beaker. A disintegrated pulp specimen of between 1.2g and 1.5g (O.D.W.) was then reacted in the potassium permanganate and sulphuric acid solution for a period of exactly 10 minutes with

the reaction terminated using a potassium iodide solution of 10 ml. The free unreacted iodine within the mixture was then titrated with 0.2 mol/L sodium thiosulphate solution with the volume of sodium thiosulphate consumed at the inflection point recorded. The same procedure as described above was carried out with a “blank” where no sample was added to determine the amount of sodium thiosulphate consumed during titration when no lignin is present. The kappa number was then determined using equations 4.1 through 4.3 [82].

$$V_a = \frac{(V_1 - V_2)c}{0.1} \quad 4.1$$

$$X_1 = \frac{V_a d}{m} \quad 4.2$$

$$X_2 = \frac{V_a d}{m} [1 + 0,013(25-t)] \quad 4.3$$

Where:

- V_a is the volume of potassium permanganate that was consumed in millimeters.
- V_1 and V_2 is the volume of sodium thiosulfate consumed in the blank and with pulp sample respectively.
- c is the sodium thiosulphate concentration in moles per litre.
- X_1 and X_2 are the kappa numbers with and without temperature correction factors respectively.
- d represents the correction factor to a permanganate consumption of 50% on a mass/mass basis.
- m is the pulp specimen oven dry mass in grams.
- t is reaction temperature in degrees Celcius.

5.2.3. Formation of handsheets

In order to gauge the effect hemicellulose pre-extraction has once the pre-extracted chips are pulped, handsheets from selected extraction and pulping conditions (Please refer to Table 18 for extraction and pulping conditions), were made and the physical properties of these sheets tested. The handsheets were formed from unbeaten pulp according the method outlined by TAPPI T 205 om-88 [50]. A test specimen of 24g (\pm 0.5 g) was soaked in 2L distilled water for a period of at least 4hours and was then disintegrated in a British Pulp Evaluation Apparatus standard disintegrator for 50000 revolutions at 3000 rpm. Once the disintegration of the pulp specimen was completed it was then diluted to a stock of 8000ml with an equivalent consistency of 0.3%.

The actual formation of the hand sheets was done using The British Pulp Evaluation Apparatus sheet machine. The sheet formation machine was filled up to the halfway mark with tap water after which 400ml of stock, drawn from the 8000ml stock, was added. Once the stock was added, the machine was filled with water. The perforated stirrer was inserted while ensuring the perforated disc remained below the liquid level while it was moved up and down 5 times. Once the water surface returned to a motionless state, after the mixing with the perforated stirrer, the drain cock was opened. This allowed for the water to drain from the machine with draining resulting in the handsheet formed on the surface of the wire. The formed handsheet was then removed with the aid of blotting paper and a couching apparatus. The handsheet, wedged between two blotting papers, was positioned in an Agfa-Gevaert drying press to remove the bulk of the moisture. In total at least ten handsheets were made from an unbeaten pulp sample to ensure a sufficient amount was made so that handsheets with deformations can be discarded while still ensuring there is enough for physical testing.

5.2.4. Testing of physical properties of handsheets formed.

The impact of the hemicellulose pre-extraction was determined by looking at the physical properties of the handsheets formed from the resulting pulps. The properties that were investigated included the burst, tear and tensile indices, with the basis weight being used in the determination of each of these properties. Table 16 shows the physical properties that were tested and the corresponding analytical methods that were utilised. The handsheets were cut with the aid of a jig that is specially designed to give the required dimensions of paper specimens, as specified by TAPPI T 220 om-88 in order to perform the tensile, tear and burst

Table 16: Methods used for the determination of the physical properties of the handsheets.

Physical Property	Analytical standards used
<i>Burst Index</i>	<i>TAPPI T 220 om-88/TAPPI T 403 om-08</i>
<i>Tear Index</i>	<i>TAPPI T 220 om-88/TAPPI T414 om-98</i>
<i>Tensile Strength</i>	<i>TAPPI T 220 om-88/TAPPI T 494 om-96</i>
<i>Basis weight</i>	<i>TAPPI T 220 om-88</i>

5.2.4.1. Basis weight

The basis weight, which is defined as the mass per unit area ($\text{g}\cdot\text{m}^{-2}$) of a given paper sample was determined according to the methodology outlined by the TAPPI T 220 om-88 Standard [50]. Five conditioned handsheets were weighed together on a balance sensitive to 0.001g. The area of each handsheet formed was 200 cm^2 . The basis weight was calculated by multiplying the weight of the 5 handsheets by 10.

5.2.4.2. Tear Index

The force required to tear multiple plies perpendicular to the plane of paper is quantified through the tear index. This particular property was tested by following the methods described in both Tappi T 220 om-88 and Tappi T414 om-98 [50] which are the Elmendorf specific methods. As the name suggests the Elmendorf tear tester was used. The average tearing force was calculated through the use of equation 4.4.

$$\text{Average Tearing Force} = \frac{\text{Force required to tear 4 sheets} \times 16 \times 9.81}{4}$$

4.4

Equation 4.4 is specific to the standard 1600-gf instrument, which is scaled from 0-100, which was the one used for testing. The constant 9.81 is used to convert the result from grams-force (gf) to milliNewtons (mN). The tear index was then obtained through the use of equation 4.5.

$$\text{Tear Index} = \frac{\text{Average Tearing Force}}{\text{Basis weight}} \quad \mathbf{4.5}$$

Where the units of the tear index is $\text{mN}\cdot\text{m}^2\cdot\text{g}^{-1}$.

5.2.4.3. Burst Index

The burst index gives an indication of resistance to rupture of a particular test specimen and was tested through the use of both TAPPI standards coded T 220 om-88 and T 403 om-08. The test specimen is ruptured via the increasing pressure of a rubber diaphragm which expands as hydraulic pressure is increased. The particular machine that was used is known as the Mullen C burst tester. This particular property was calculated through the use of equation 4.6.

$$\text{Burst Index} = \frac{P}{\text{Basis Weight}} \quad \mathbf{4.6}$$

Where P is the bursting strength, in kPa, measured with the Mullen C burst tester with the units for the burst index being $\text{kPa}\cdot\text{m}^2\cdot\text{g}^{-1}$.

5.2.4.4. Tensile Index

Tensile strength is the maximum force per unit width with that a particular test specimen can withstand before rupturing. While the tensile index is the tensile strength of a particular specimen divided by its grammage. The tensile index can used to help ascertain fibre strength properties as well as bonding. TAPPI standards coded T 220 om-88 and T 494 om-96 [50] were followed to determine the tensile indices. The equipment that was used included an Instron TM-M elongation apparatus coupled with a Hottinger Baldwin Messtechnik GmbH MVD2510 measurement amplifier. The tensile strength and tensile indices is given by equations 4.7 and 4.8 respectively.

$$\text{Tensile Strength} = 0.6538 \times \text{Tensile Break Load} \quad \mathbf{4.7}$$

$$\text{Tensile Index} = \frac{\text{Tensile Strength}}{\text{Basis Weight}} \quad \mathbf{4.8}$$

The units for tensile strength are given in kg while that of the tensile index is given in terms of kN.m^{-1} .

5.3. Results

5.3.1. Effect of extracting xylan from *E. grandis* chips on pulp yield

The average screened pulp yield of raw virgin *E. grandis* chips was 41.67% with average rejects being 1.02%. The chips were pulped to a kappa number of 20.3. Table 17 shows the pulping conditions as well as the corresponding pulp properties of *E. grandis* chips that were not subjected to pre-extraction, which served as the control conditions.

Table 17: Table showing pulp conditions and properties of non-extracted *E. grandis* chips.

Cooking Conditions						
Temperature	Time at set temperature	Ramp Time	H-factor	AA Charge	Liquor to wood ratio	Sulfidity
170°C	45 minutes	90 minutes	866	18%	4.5:1	25%
Pulp Properties						
Screened Pulp Yield %	Kappa Number	% Rejects				
41.67±0.02	20.3±2.2	1.02±0.27				

The average yield of 41.67%, indicated in Table 17, for the pulp obtained from virgin *E. grandis* chips was low when compared to that of yields obtained industrially, with desired industrial levels being above 50% [92]. Again, as was discussed with the xylan extractions that were performed in Chapter 4, the extractives content might have played a role in the lower pulp yield due to the part extractives play in preventing chemical penetration during pulping. A low extractives content as possible is desirable for pulping purposes [113]. Significant variations in wood properties between *E. grandis* trees even with trees that grow within the same location are known to occur making the deviation of pulp yield of this particular feedstock of *E. grandis* not particularly exceptional [91].

From the hemicellulose extractions that were carried out selected extraction conditions were used for further pulping (Table 18). For the green liquor, the solid residue resulting from extractions that were carried out using 2% TTA and an H-factor of 800 was selected for further pulping.

Table 18: Pulp yields and corresponding Kappa Numbers of pre-extracted *E. grandis* chips subjected to various pulping conditions.

Solvent	Extraction Conditions			Pulping Conditions			
	Alkali Charge	Temperature(°C)	Time/H-factor	Chemical Charge	Time at 170°C(minutes)	Screened Pulp Yield (%)	Kappa Number
Green Liquor	2% TTA	160	800(h-factor)	10% Reduction*	45	37.20	12.84
	2% TTA	160	800(h-factor)	20% Reduction*	45	40.60	16.01
	2% TTA	160	800(h-factor)	35% Reduction*	45	43.19	18.70
White Liquor	20%AA	120	90 minutes	10% Reduction*	30	37.40	ND
	20% AA	120	90 minutes	50% Reduction*	30	41.60	12.86
	20% AA	120	90 minutes	85% Reduction*	30	Uncooked**	-
	20% AA	140	90 minutes	40% Reduction*	25	34.00	10.83
	20% AA	140	90 minutes	60% Reduction*	25	37.00	15.92
NaOH	2M	120	90minutes	No chemicals added ^a	30	Uncooked**	-
	2M	120	90minutes	Half standard amount ^b of Na ₂ S added	30	Uncooked**	-
	2M	120	90 minutes	Standard Amount ^c Na ₂ S added	30	Uncooked**	-
	2M	120	90 minutes	Standard Amount ^c Na ₂ S added	45	Significant amount of rejects	-
	2M	120	90 minutes	Standard Amount ^d Na ₂ S and 25% Standard Amount NaOH	45	40	18.85

^a No additional chemicals were added to chips after extraction.

^b Only half the amount of Na₂S required for 85g(O.D.W.) of non-extracted chips was added. No NaOH added.

^c Same amount of Na₂S as is required for 85g (O.D.W.) of non-extracted chips was added. No NaOH added.

^d Same amount of Na₂S and 25% of NaOH as is required for 85g (O.D.W.) of non-extracted chips was added.

*Represents percentage reduction of Na₂S and NaOH relative to Na₂S and NaOH required for 85g(O.D.W.) of non-extracted chips.

**Wood chips after pulping were not in pulp form as they weren't sufficiently pulped.

Rows highlighted pink are conditions that were used for the testing of handsheet properties.

For the pulping that was performed using chips subjected to white liquor extraction at 120°C, a 10% reduction in chemical charge produced a pulp yield of 37.40%, which was too severe in combination with the pre-extraction conditions, thus resulting in a lower pulp yield. A 50% reduction in chemical charge resulted in a pulp yield of 41.6%, very similar to the yield obtained with conventional pulping of untreated woodchips, with a kappa number of 12.86, which was lower than with conventional pulping. Even a 50% reduction in chemical charge as well as a 15 minute reduction in cooking time resulted in a significantly lower kappa number when compared to that of the kappa number that was obtained under standard pulping conditions. These results are depicted Table 18. This indicates that the white liquor extraction of hemicellulose from virgin wood chips at 120°C, 20% AA and 90 minutes extraction time is a significant delignification process. Pulp yield was still maintained despite of the lower kappa number indicating that lignin extraction is fairly selective during the pre-extraction process, using white liquor, relative to the cellulose fraction found in the wood. The addition of Na_2S during pre-extraction is able to accelerate the process of delignification without concurrently elevating the rate at which carbohydrates are dissolved, resulting in a low kappa number but still maintaining pulp yield.

For the pulping of solid residues from white liquor extraction at 140°C, the cooking time at 170°C was reduced from 45 minutes to 30 minutes. Two conditions were investigated which included 40% reduction in chemical charge as well as a 60% reduction. A 40% reduction produced a pulp yield of 34% with a corresponding kappa number of 10.21, as is indicated Table 18. The low kappa number again illustrates the fact that white liquor pre-extraction serves as pre-delignification process thus allowing for a fairly significant reduction in chemical charge during pulping relative to the standard pulping conditions. From Table 18, a 60% reduction in chemical charge increased the pulp yield to 37% as well as the kappa number to 15.92. Due to the significant chemical charge used for the white liquor during the pre-extraction processes the chemical charge during the actual pulping process could be significantly reduced, more so than that of the green liquor and at a 15 minute shorter cooking time when compared to that of the green liquor.

Initially, due to the significant NaOH concentration that the *E. grandis* chips were subjected to during NaOH pre-extraction, the pulping time was also reduced to 30 minutes while no additional chemicals were added during pulping (Table 18). These pulping conditions were inadequate with the result being that the pre-extracted chips did not transform into a pulp, thus remaining in a wood residue form. The pre-extracted chips using NaOH was subsequently pulped using Na₂S to add sulfidity to the pulp without any additional NaOH. Even with the addition of the Na₂S the cooking conditions were not severe enough to produce a pulp. At a 45 minute pulping time using the standard amount of Na₂S still a significant amount of rejects were produced indicating that chemical addition during pulping was not adequate. With the addition of 25% of the NaOH that was used during control pulping conditions for the non-extracted *E. grandis*, an acceptable pulp was produced. A pulp of 40% and a kappa number very close to the 20.57 that was obtained for non-extracted chips as is indicated Table 18 was obtained.

5.3.2. Physical properties of handsheets prepared from pulp produced from xylan pre-extracted wood chips

The pulps obtained from the residues of hemicellulose pre-extractions, under the preferred pulping conditions, were tested for physical properties, as presented in Table 19. These handsheet properties were compared to those of handsheets made from pulps obtained through conventional pulping of non-extracted *E. grandis* woodchips, which served as the control. No beating was applied to the pulps prior to handsheet formation.

Table 19: Conditions chosen to produce handsheets for testing of physical properties.

Solvent	Extraction Conditions			Pulping Conditions	
	Alkali Charge	Temperature	Time at set temperature/ H-factor	Chemical Charge	Time at 170°C (minutes)
NaOH	2M	120	90 minutes	Standard Amount Na ₂ S and 25% NaOH ^a	45
Green Liquor	2% TTA	160	800 h	35% Reduction [*]	45
Control	NA	NA	NA	Standard ^{**}	45
White Liquor	20% AA	120	90 minutes	50% Reduction [*]	30

^a Same amount of Na₂S and 25% of NaOH as is required for 85g (O.D.W.) of non-extracted chips was added.

^{*} Represents percentage reduction of Na₂S and NaOH relative to Na₂S and NaOH required for 85g(O.D.W.) of non-extracted chips.

^{**} Standard cooking conditions as described in Table 17.

Selecting a pulp produced from a residue that was subjected to NaOH xylan pre-extraction, was straight forward as the selection was limited to one condition which resulted in a useable pulp. The resulting pulp that was produced resulted in a pulp yield of 40%, with only a slight reduction in kappa number to 18.85 compared to a kappa number of 20.3 of non-extracted chips, as indicated in Table 18.

From the pulps that were produced from the green liquor pre-extracted chips (2% TTA, 800h) the pulp resulting from a chemical charge reduction of 35% was selected. This pulp resulted in a

favourable pulp yield with a kappa number of 18.74 that was close to that of the standard non-extracted pulps' 20.3.

For pulps produced from the white liquor pre-extracted wood chips, the kappa numbers were lower with the kappa numbers ranging from 10.83 to 15.94 as is indicated in Table 18. It was decided to select a combination of pre-extraction and pulping conditions that culminated in the highest pulp yield. The pre-extraction condition that was chosen was that of 120°C, 20% AA and 90 minute extraction time. The corresponding pulping conditions that were chosen were that of 50% reduction in chemical charge and 30 minutes cooking time (15 minute reduction in cooking time). Using the extraction and pulping combination described resulted in a pulp yield of 41.6% which compares well to that of non-extracted residue which was 41.67% (Table 18). The xylan yield using an extraction condition of 120°C, 20% AA and 90 minute extraction time, however, was 8.35% which is lower than the maximum yield for white liquor extraction which was 13.27%, as derived from Figure 14. The maximum xylan yield for white liquor extraction was obtained using 140°C, 20% AA and 90 minute extraction time (Figure 14). However, the pulp yield of *E. grandis* residue that was subjected to these extraction conditions was 34% and 37% for a 40% and 60% reduction in chemical charge respectively, as indicated in Table 18. Ultimately the focus is on maintaining production of the principal product which is pulp, as a result 120°C, 20% AA and 90 minute extraction time was deemed more favourable than 140°C, 20% AA and 90 minute extraction time even though the latter resulted in a greater xylan yield.

When selecting pulping conditions for the solid residue from white liquor pre-extraction, it was possible to achieve the same pulp yield as with the conventional process, but with significantly lower kappa numbers in comparison to both the conventional pulping process and the pulps obtained from solid residues of the NaOH and green liquor pre-extractions.

Figure 22 through to Figure 24 show the tear, tensile and burst indices of the handsheets that were produced. There was a distinct increase in the tear index for the handsheets made from the NaOH pre-extracted pulp relative to handsheets from conventional pulps (Figure 22). The tear indices of the handsheets made from unbeaten pulps, obtained from solid residues of green liquor and white liquor extractions, were similar to that of the conventional pulps and did not increase as what was seen in the NaOH extracted chips.

For white liquor and green liquor pre-extraction, the combination of pre-extraction with modification of pulping conditions for the solid residues had no effect on the burst indices. The burst indices presented in Figure 23 show that the burst indices of handsheets made from pulp produced from wood chip residues of green liquor and white liquor xylan extractions were similar to that of the reference handsheets.

Figure 24 summarises the tensile indices that were obtained from the handsheets that were formed. Again the tensile indices of the green liquor and white liquor extracted pulps are similar to that of the reference. The NaOH extracted pulps show a reduction in the mean tensile strength properties relative to the reference pulp, however from the t-test performed it was not statistically significant with the corresponding p-value being greater than 0.05.

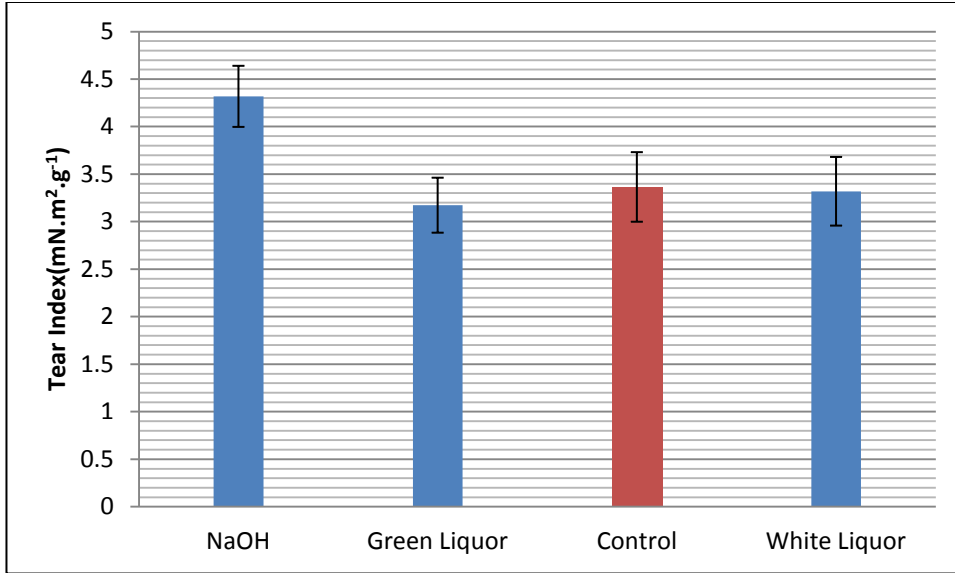


Figure 22: Tear indices of handsheets produced from selected extraction and pulping conditions.
 (Refer to Table 19)

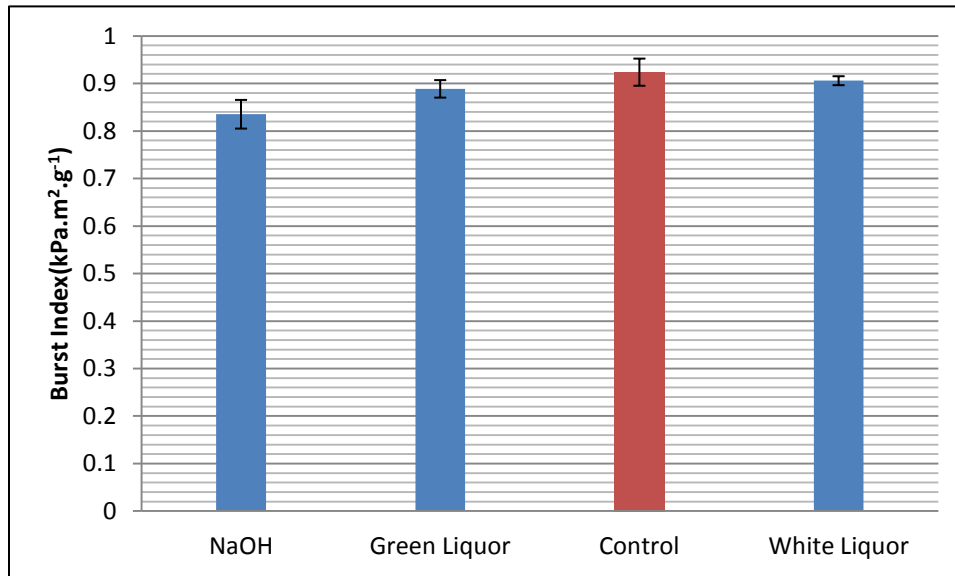


Figure 23: Burst indices of handsheets produced from selected extraction and pulping conditions.
 (Refer to Table 19)

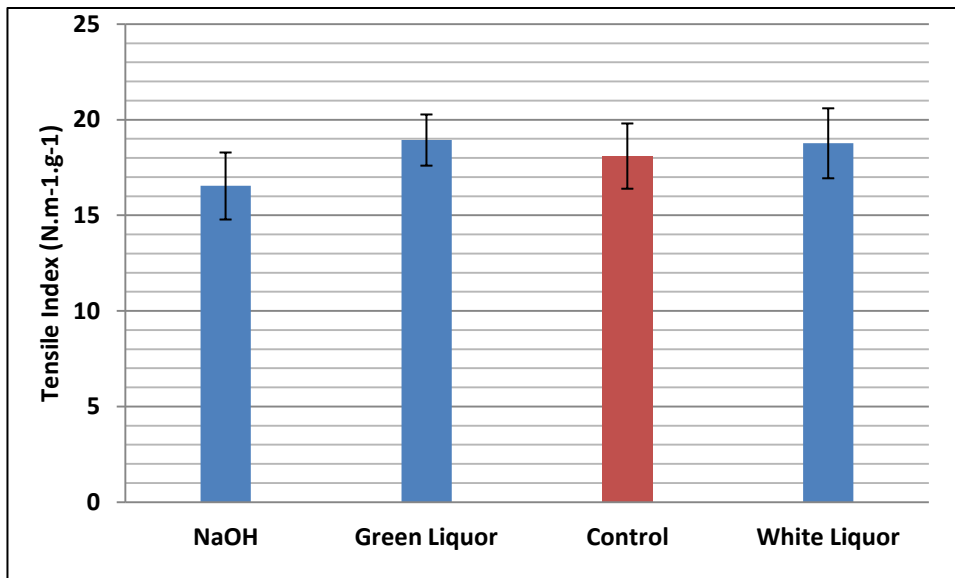


Figure 24: Tensile indices of handsheets produced from selected extraction and pulping conditions. (Refer to Table 19)

5.3.3. Summary of best extraction and pulping combinations for each extraction chemical with corresponding xylan yields and handsheet properties.

An integrated summary is given by Table 20 which compares selected extraction conditions and pulping combinations that have been deemed the best for each extraction method in terms of xylan yield/pulp yield/kappa numbers.

Table 20: Summary of results for best extraction and pulping combination, with xylan yields and handsheets properties, for each extraction chemical. Extraction conditions and subsequent pulping conditions are shown at the top and bottom of the table respectively.

<i>Solvent</i>	<i>Extraction Conditions</i>			<i>Xylan Yield (%)</i>
	<i>Alkali Charge</i>	<i>Temperature (°C)</i>	<i>Time /H-factor</i>	
<i>Control</i>		NA		
<i>Green Liquor</i>	2% TTA	160	800(h-factor)	7.83
<i>White Liquor</i>	20% AA	120	90 minutes	8.35
<i>NaOH</i>	2M	120	90 minutes	15.15

<i>Solvent</i>	<i>Pulping Conditions and Pulp Yield</i>			<i>Handsheet Properties</i>		
	<i>Chemical Charge</i>	<i>Time at 170°C (minutes)</i>	<i>Pulp Yield (%)</i>	<i>Burst kPa.m².g⁻¹</i>	<i>Tear mN.m².g⁻¹</i>	<i>Tensile N.m⁻¹.g⁻¹</i>
<i>Control</i>	18% AA	45	41.67	0.924	3.365	18.106
<i>Green Liquor</i>	35% Reduction*	45	43.19	0.889	3.173	18.944
<i>White Liquor</i>	50% Reduction*	30	41.6	0.906	3.32	18.774
<i>NaOH</i>	25% Reduction in NaOH used*	45	40	0.835	4.319	16.541

The results displayed in Table 20 shows that NaOH extraction results in the highest xylan yield when using 2M NaOH at 120°C and 90 minutes extraction at 15.15%. It is almost double that than the 8.35% which results from the use of white liquor at 120°C, 20% AA and 90 minute extraction time. However, NaOH resulted in the lowest reduction in chemicals used during pulping as depicted in Table 20, with a 25% reduction only in the NaOH quantity used during pulping. This was even though 2M NaOH was used during the initial extraction process. Green liquor and white liquor allowed for 35% and 50% respectively in the reduction of chemicals used as indicated Table 20. From Table 20 one can also see that the high xylan yield obtained by NaOH extraction is also marred by the fact that there was a 9.6% decrease in the burst index of unbeaten handsheets produced from NaOH extracted chips. Whereas although the xylan yields resulting from green liquor and white liquor pre-extracted chips are substantially lower than that of NaOH, the unbeaten handsheets did not have any statistical variation from handsheets produced from non-extracted chips (Figure 22, Figure 23 , Figure 24 and Table 20).

From Table 20, pulp yield resulting from green liquor extracted chips were 43.19% which in fact was an increase from pulps produced from non-extracted chips which was 41.67%. White liquor pre-extracted chips produced a pulp yield of 41.6% showing no change from the control, while NaOH resulted in a slight pulp yield reduction to 40%.

5.4. Discussion

Pre-extraction of *E. grandis* with the use of green liquor improved the subsequent efficiency of the pulping process by reducing the chemical requirement during pulping without compromising on the yield as well as the quality of the pulp. As the reduction in chemical charge increased during pulping, both the yield and kappa numbers increased. A 35% reduction in chemical charge, resulted in a pulp yield of 43.19% and a corresponding kappa number of 18.70, as indicated in Table 18. From Table 17, pulp yield of the non-extracted chips was 41.67% with a corresponding kappa number 20.3 which demonstrates that pulp yield can be maintained and even increased. Pulp yield is a good indicator of how the extraction of hemicellulose has affected the cellulose fiber quality which in turn is an indicator of how the process economics would be affected [26]. For pulps derived from green liquor extracted chips, the unbeaten handsheets that were produced resulted in tear, burst and tensile indices that were almost identical to that of the reference non-extracted pulp (Figure 22, Figure 23 and Figure 24 respectively). The tensile, tear and burst indices obtained for handsheets produced from pulps resulting from non-extracted chips were $18.2 \text{ N.m}^{-1}.\text{g}^{-1}$, $3.2 \text{ mN.m}^2.\text{g}^{-1}$ and $0.924 \text{ kPa.m}^2.\text{g}^{-1}$ respectively. Green liquor extracted chips showed no statistically significant deviations from those values, as indicated in Figure 22, Figure 23 and Figure 24 respectively.

The maintenance of pulp yield after green liquor extraction on *E. grandis* is corroborated by the results obtained by Johakimu *et al* [62]. Green liquor extraction was performed by Johakimu *et al* [62] on *E. grandis* using between 0% and 3% TTA. Johakimu *et al* [62] found that during subsequent pulping of pre-extracted residue, pulp yield could be preserved and the target kappa number could be obtained using a 20% reduction in pulping chemicals. However, the strength properties of the handsheets produced showed deviation from that produced from pulps of non-extracted chips. Johakimu *et al* [62] assessed handsheets produced from pulps that were subjected to a refining (beating) level of 3000 RPM. It was found that at this refining level the tensile index decreased by 16% relative to the reference with a slight decrease in burst strength, coupled with a slight increase in tear strength. The results observed by Johakimu *et al* [62] highlights the effect beating can have on the paper properties of handsheets produced from pulp with reduced hemicellulose content. Beating helps to enhance inter-fiber bonding

which helps to improve both tensile and bursting strength. In this study no beating was performed on any pulps that were produced.

The combined extraction and pulping process utilising green liquor has the potential to give a definite advantage when compared to that of the Kraft pulping process alone. Exposing *E. grandis* to green liquor extraction prior to pulping not only provides an additional product stream in the form of xylan, but also has the potential to not only maintain pulp yield but increase it. Furthermore, from Table 18, the 35% reduction in chemicals used during pulping when compared to that of non-extracted chips is especially encouraging as the initial alkaline concentration of the green liquor used for extraction was only 2% TTA. This is lower when compared to the 20% AA and 2M utilised for the white liquor and NaOH extractions respectively. This indicates that the impact on the sodium and sulphur balance of a pulp mill will be reduced when compared to that of the other extraction methods utilised such as white liquor and NaOH. The fact that the unbeaten handsheet properties mirrored that of unbeaten handsheets produced from non-extracted chips is also promising, although beating of pulps might induce greater variability between the handsheet properties arising from pulps of green liquor pre-extracted and non-extracted *E. grandis* chips.

The greater alkalinity used during white liquor extractions, when compared to that of green liquor, allowed for a greater reduction in chemical charge when compared to that of green liquor extraction during the subsequent pulping of the white liquor pre-extracted residue. An extraction and pulping combination that resulted in a favourable pulp yield (43.19%) was that where *E. grandis* was subjected to white liquor pre-extraction at 120°C and 20% AA with 90 minutes extraction time. Subsequent pulping conditions included that where the white liquor pre-extracted chips was pulped at a chemical reduction, relative to the standard cooking conditions, of 50% as indicated in Table 18. This was coupled with a 15 minute reduction in cooking time when compared to that of non-extracted chips. This resulted in a pulp yield of 41.60%, comparable with that of the reference pulp of 41.67% (Table 18). Another distinguishing feature between the pulps from *E. grandis* subjected to white liquor pre-extraction and green liquor extraction, is the tendency of white liquor pulps to have low kappa

numbers. For the white liquor extraction condition that resulted in a favourable pulp yield (41.6%), a kappa number of 12.86 was produced. This is substantially lower than that of the kappa number of 20.3 of the pulp produced from non-extracted *E. grandis*, as indicated in Table 18. The fact that the pulp yield could be maintained while still producing low kappa numbers indicates that the white liquor extractions coupled with pulping conditions where both cooking time and chemical charge is reduced results in selective dissolution of lignin ,thus increasing pulping efficiency.

As indicated in Figure 22 to Figure 24 , no statistical significance was observed in terms of burst, tear and tensile indices of handsheets produced from green liquor and white liquor pre-extracted residues when compared to that of the non-extracted *E. grandis*. Again, one has to bear in mind that beating could potentially result in more significant deviations being exhibited from that of handsheets produced from pulps resulting from non-extracted *E. grandis* chips.

Subjecting *E. grandis* chips to the white liquor pre-extraction conditions described in Table 20, does allow for a slightly higher xylan yield (8.35%) when compared to that of green liquor extraction (7.83%). As an extraction method for integration into the Kraft process, one of the obvious advantages of white liquor extraction over that of green liquor extraction would be the higher xylan yield. Also there is a 50% reduction in the chemicals utilised during pulping when compared to that of pulping of non-extracted chips. However, one has to bear in mind that the initial alkalinity of the white liquor used during extraction was 20% AA which is which is significantly greater than the 2%TTA utilised for green liquor extraction. The impact on the sodium and sulphur balance of a Kraft mill will most likely be higher than that of green liquor as a result of the high alkalinity even though the reduction in the use of pulping chemicals was 50%.

Adjusting pulping conditions for NaOH extracted chips was more problematic than expected, as the chips were not as conducive to producing acceptable pulps, even with a reduction in cooking time and chemical charge, as white liquor pre-extracted chips. This was surprising as NaOH extracted chips was subjected to a higher chemical charge when compared to that of the white liquor. This could be due to the fact that the remaining Na₂S on the white liquor pre-

extracted wood chips played a significant role in helping to dissolve lignin during the actual pulping process. From Table 18, chips that were subjected to NaOH pre-extraction using 2M NaOH at 120°C and that were then subjected to cooking conditions of 45 minutes at 170°C with the same Na₂S and 25% of NaOH used for standard conditions resulted in comparable pulp yields and kappa numbers when compared to that of the non-extracted chips.

Vena *et al* [61] extracted xylan from *E. grandis* chips at temperatures ranging between 40°C and 90°C, using between 1M and 2M NaOH concentrations coupled with extraction times of between two and four hours. During subsequent pulping of selected extraction conditions the cooking time at 170°C could be reduced from 45 minutes to 30 minutes with the addition of only Na₂S during pulping. Both the pulp yield and kappa numbers could be maintained. Both the fact that the pulping time could be reduced as well the fact that no additional NaOH was required could have been facilitated by the lower lignin content of the chips utilised by Vena *et al* [61]. The klason lignin content was only 16% compared to the 23% of the *E. grandis* chips utilised in this study. Al-dajani *et al* [28] performed NaOH extraction on Aspen chips under similar conditions to that of Vena *et al* [61] after pre-extraction with no additional NaOH added, with a 10 minute reduction in cooking time at 170°C. Again, both pulp yield as well as kappa numbers were maintained. The aspen wood chips utilised had a slightly lower klason lignin content (21%) however it also had an extractives content of almost half that of the *E. grandis* chips in this study at 2.1%. Certain components making up the composition of extractives are hydrophobic and can aggregate on the surface of the fiber which can both block the penetration of chemicals and the diffusion of lignin fragments from the fiber wall [112].

Disparities were observed in terms of both the tear and burst indices of pulps resulting from NaOH pre-extracted chips when compared to that of the non-extracted chips. An increase of 28% was observed for the tear index of pulps derived from NaOH extracted chips, however, a reduced burst index of 9.6% was also observed as indicated in Table 20. This indicates that quantity of xylan removed from the NaOH pre-extracted chips was significant enough to start impacting the paper produced. The reduction in xylan of the NaOH pre-extracted chips promoted fibre stiffness which in turn increased tear strength [93]. As hemicellulose content of

pulp is reduced there is reduction in accessible fibril surfaces for water molecules. This results in dried pulps being less conducive to swelling when soaked in water as a result of fiber separation being more challenging and less contact area with water [93]. This reduced flexibility has a positive effect on the tear strength properties of the paper [63] up to a certain point of extraction.

The relationship between the burst and tear indices is generally inverse [95], which was observed for the burst and tear indices of the handsheets produced from the pulp of NaOH xylan pre-extracted chips. There was a statistically significant reduction in burst index relative that of the reference ($p=0.021$) tested at 95% confidence level (Figure 24). The reduction in xylan content in *E. grandis* chips subjected to NaOH extraction reduced the flexibility and the contact area between given fibres by assisting swelling and internal fibrillation that hemicelluloses provide, hence the reduced burst indices [63]. Helmerius *et al* [63] reported a reduction in the burst index of white liquor extracted birch chips thus, an inverse relationship between burst and tear indices.

Figure 24 summarises the tensile indices that were obtained from the handsheets that were formed. The NaOH extracted pulps show a reduction in the mean tensile strength properties relative to the reference pulp, but is not statistically significant as was confirmed with a t-test with the p-value being greater than 0.05. As a result the tensile indices are all statistically similar to that of the reference. One has to bear in mind that the handsheets that were made in this study were handsheets produced from unbeaten pulps. Beating helps to enhance interfiber bonding which helps to improve both tensile and bursting strength. With beating it is possible that the discrepancy between tensile indices between that of the NaOH extracted pulps and that of the reference might increase due to the low hemicellulose content of the NaOH extracted pulps.

The fact that NaOH extraction results in a xylan yield of 15.15% indicates that this extraction method is definitely superior to that of white liquor and green liquor pre-extraction when only considering the extraction product. However, when the quantity of chemicals utilised as well as the effect on handsheet properties that are produced from the *E. grandis* chips subjected to

NaOH extraction are considered, the method does not give the same potential as a hemicellulose extraction method. For the 2M NaOH that was utilised during the extraction process, the reduction in chemicals utilised was only 25% of the NaOH used during the pulping of non-extracted chips but with no reduction in Na₂S (Table 18) . Due to the high alkalinity utilised during the actual extraction the impact on the sodium balance will be severe. This will be further analysed in the succeeding chapter. The fact that there is a 9.6 % reduction in burst index of handsheets produced from *E. grandis* chips that has been subjected to NaOH extraction also takes away from high xylan yield that was obtained utilising this extraction method (Table 20). Companies will most likely be attracted to extraction processes that will maintain or improve current paper standards.

Pulping of wood residues resulting from wood chips subjected to green liquor, white liquor and NaOH has been performed in literature [62, 28, 61] on different feedstocks. In this study, however, a more definitive comparison can be drawn between the extraction methods as extractions coupled with subsequent pulping was performed on the same feedstock of *E. grandis*. From the results that have been discussed in both Chapter 4 and this chapter, green liquor extraction appears to be the most feasible method of pre-extraction of xylan from *E. grandis*. This is mainly due to:

- Low alkalinity during extraction, which means less sodium and sulphur lost from the process when compared to white liquor and NaOH extraction.
- Purer extracted xylan product, when compared to that of white liquor and NaOH extraction.
- Increased pulp yield relative that of pulps obtained from non-extracted chips.
- No significant impact on burst, tear and tensile properties of unbeaten handsheets produced, compared to that of handsheets obtained from pulps resulting from non-extracted *E. grandis*.

Although green liquor pre-extraction resulted in the lowest xylan yield, 7.83% as indicated in Table 20, the low alkalinity used during the initial extraction is what especially sets this extraction method apart from white liquor and NaOH extraction. The low alkalinity will offset

the need for additional make-up chemicals required due to sodium and sulphur lost during extraction.

5.5. Conclusions

Manipulation of the pulping conditions of woodchips that has been subjected to xylan pre-extraction results in pulp yields within range of that of *E. grandis* pulps obtained from non-extracted chips. Reducing chemical load during pulping as well as the actual pulping time is effective means of adjusting for extractions performed using alkaline chemicals. Kappa numbers could also be maintained for pulps resulting from green liquor and NaOH extracted chips, however, this proved to be more difficult for pulps produced from white liquor pre-extracted chips. White liquor is used as a pulping chemical due to its ability to dissolve as much lignin as possible while dissolving as little as possible of cellulose [114]. As a result it was still possible to maintain pulp yield even if kappa numbers were lower.

The properties of unbeaten handsheets that were produced from pulps of green and white liquor extracted chips did not show any variation from that of the control. The control being handsheets produced from pulps of non-extracted chips. However, deviations were observed from handsheets produced of pulps resulting from NaOH extracted chips. This indicates that the larger fraction of hemicellulose removed started affecting the paper properties of pulps produced from NaOH extracted chips, with an observed increase and reduction in tear and burst indices respectively.

Beating the pulps produced before handsheet formation might induce an increase in the variation of paper properties relative to that of the control. Beating affects the structure of the inter-fibre bonds, thus strengthening those bonds, a reduction in hemicellulose will influence the strengthening affect beating has.

In terms of selecting an extraction method with the greatest overall combined benefit when compared to that of Kraft pulping alone, green liquor extraction appears to give the greatest benefit. The xylan recovery with this method is 7.83%, less than the 8.35% and 15.15% of white

liquor and NaOH respectively. However, the overall benefit using this method will be greater due to its low alkalinity during extraction as well as improved pulp yield and minimal effect on subsequent unbeaten handsheet properties. However, a proper mass balance needs to be performed to try and ascertain the total chemical usage when taking into account both the extractions performed and the subsequent pulping for each extraction method. This will give a fuller understanding of the benefit green liquor will have in terms of chemical usage when compared to that of the other extraction methods. This will be addressed in the following chapter.

CHAPTER 6: Effect of hemicellulose pre-extraction on sodium and sulphur requirements of a Kraft mill.

6.1. Introduction

Research into modifying Kraft mills into integrated biorefineries has gained increasing momentum. Increasing product portfolio by maximising the woody biomass processed in Kraft mills has a number of advantages both economically and environmentally. The pre-existing infrastructure as well as knowledgeable workforce makes Kraft mills well suited towards converting them into integrated biorefineries. Extracting hemicellulose prior to pulping in lieu of burning them in the reboiler is an attractive option towards converting Kraft mills into biorefineries due to the number products that can be produced

Alkali extraction is the most suitable for extracting hemicellulose prior to pulping in the Kraft process. This is because the pulping process in the Kraft process is an alkali process, and the properties of the fibres are best preserved during extraction using alkali solvents when compared to others methods such as acid/water extraction. Using intermediate or make up chemicals that are available in the Kraft process is even more attractive due to its economic benefits. . From the results reported in Chapter 5 it was observed that pulp properties of chips not subjected to pre-extraction could be emulated by reducing the chemical loading and cooking time of wood chips that were subjected to pre-extraction. It was also found that physical properties of unbeaten handsheets produced from pulps resulting from green and white liquor extracted chips were unaffected when compared to that of the control. NaOH extracted chips, however, showed an increase in tear index coupled with a reduction in burst index relative to that of the control. Further analysis was required on the chemical quantities required for both the extraction and pulping processes using green liquor, white liquor and NaOH.

This chapter provides mass balance of the sodium and sulphur around the extraction point as well the pulping processes for selected extraction and pulping conditions. These selected pulping and extraction conditions include those that were eventually selected for the formation of handsheets as indicated in Table 18. As a result a mass balance was done for one green liquor, white liquor as well as NaOH extraction/pulping combination. This was all compared to a scenario where no extraction takes place. Additionally, the practicality of supplying green liquor and white liquor independently of the Kraft process was also considered and compared to where these chemicals are supplied by the Kraft process itself. NaOH, although a chemical utilised by the Kraft cycle, is not directly produced by the Kraft recovery cycle itself as an independent pure chemical.

Separating the extracted hemicellulose from the chemicals used for extraction will be pivotal, both in ensuring a pure hemicellulose stream as well as returning chemicals that were used for extraction back to the system. A brief discussion regarding this concept is also provided in this chapter.

The objectives of this chapter include:

- Present a mass balance of sodium and sulphur around the extraction point and pulping process for green liquor, white liquor and NaOH extraction/pulping combinations.
- Compare these balances to that of a Kraft mill without hemicellulose extraction.
- Consider the scenario where green liquor and white liquor are provided independently of the Kraft cycle for hemicellulose pre-extraction.

6.2. Methodology

6.2.1. Comparison of Na/S balance around Kraft mill for various extraction methods.

The cooking chemicals that are made up of sulphur and sodium are crucial for Kraft pulp mills [103]. The sulfidity of the liquor must be kept at the required level and the balance of both the sodium and sulphur must be maintained. Hemicellulose pre-extraction could result in a significant disruption of the Na/S balance of the Kraft mill [104]. Figure 25 shows the losses and inputs of sodium and sulphur that are typically found within Kraft mills, while Figure 26 shows the Na/S balance around the mill with the addition of hemicellulose pre-extraction. The disturbance of the Na/S balance of the mill as a result of increased sodium and sulphur losses during extraction could impede the implementation of hemicellulose pre-extraction into Kraft mills. This is especially so if the chemicals used for extraction are not recovered. As a result this would have to be compensated for via additional make up chemicals which could prove to be significant, even compared to the additional revenue produced from supplementary products resulting from hemicellulose extraction [104].

The sodium and sulphur mass balances were done using the results from the extraction and pulping conditions that were selected for the formation of handsheets, without recovery of pulping chemicals from the extracted hemicellulose products. For the actual Kraft chemical recovery cycle it was assumed that the recovery for the pulping chemicals was 97% [21]. The amount of sodium and sulphur used in the balances are expressed as kilograms of both sodium and sulphur used per air dry ton of pulp that is produced.

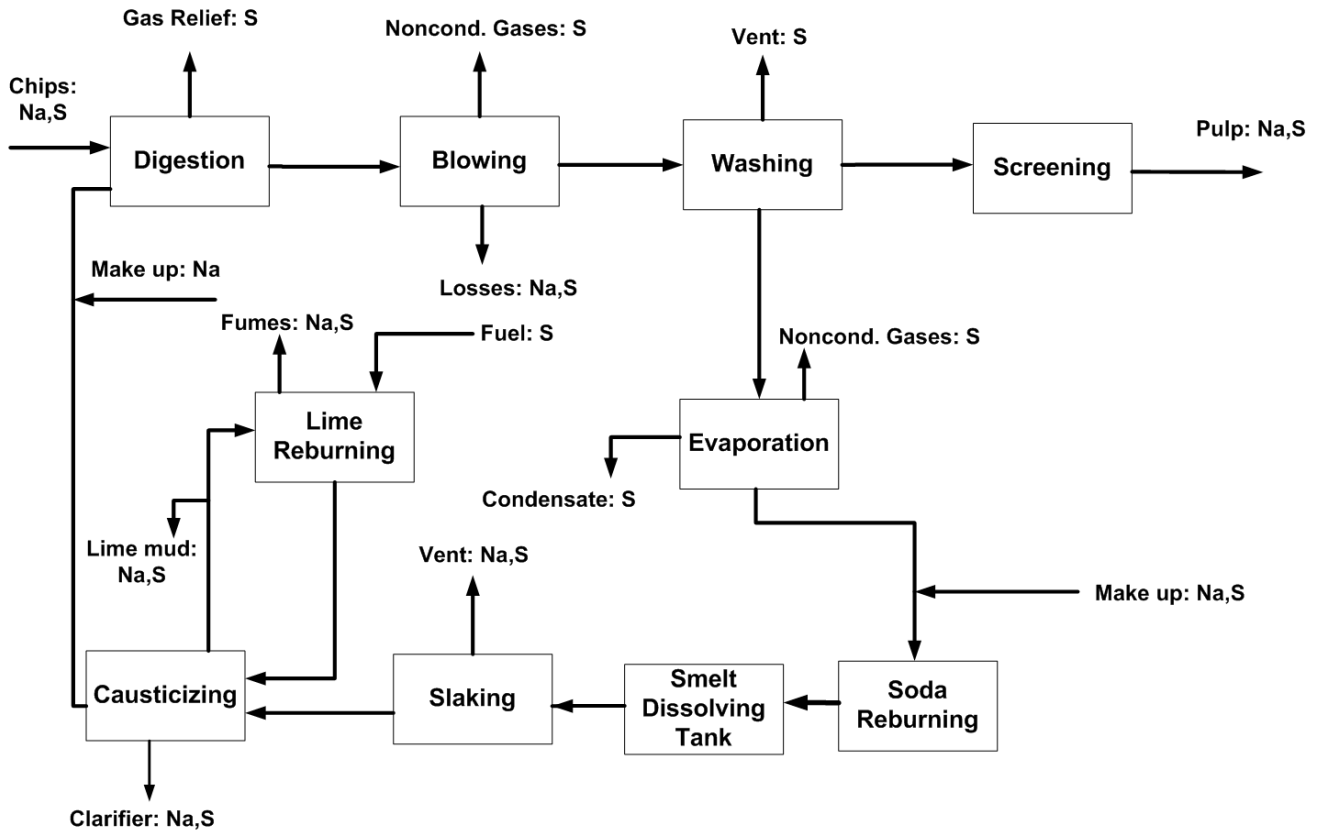


Figure 25: Sodium and sulphur inputs and losses around a typical kraft mill (adapted from Henricson [103])

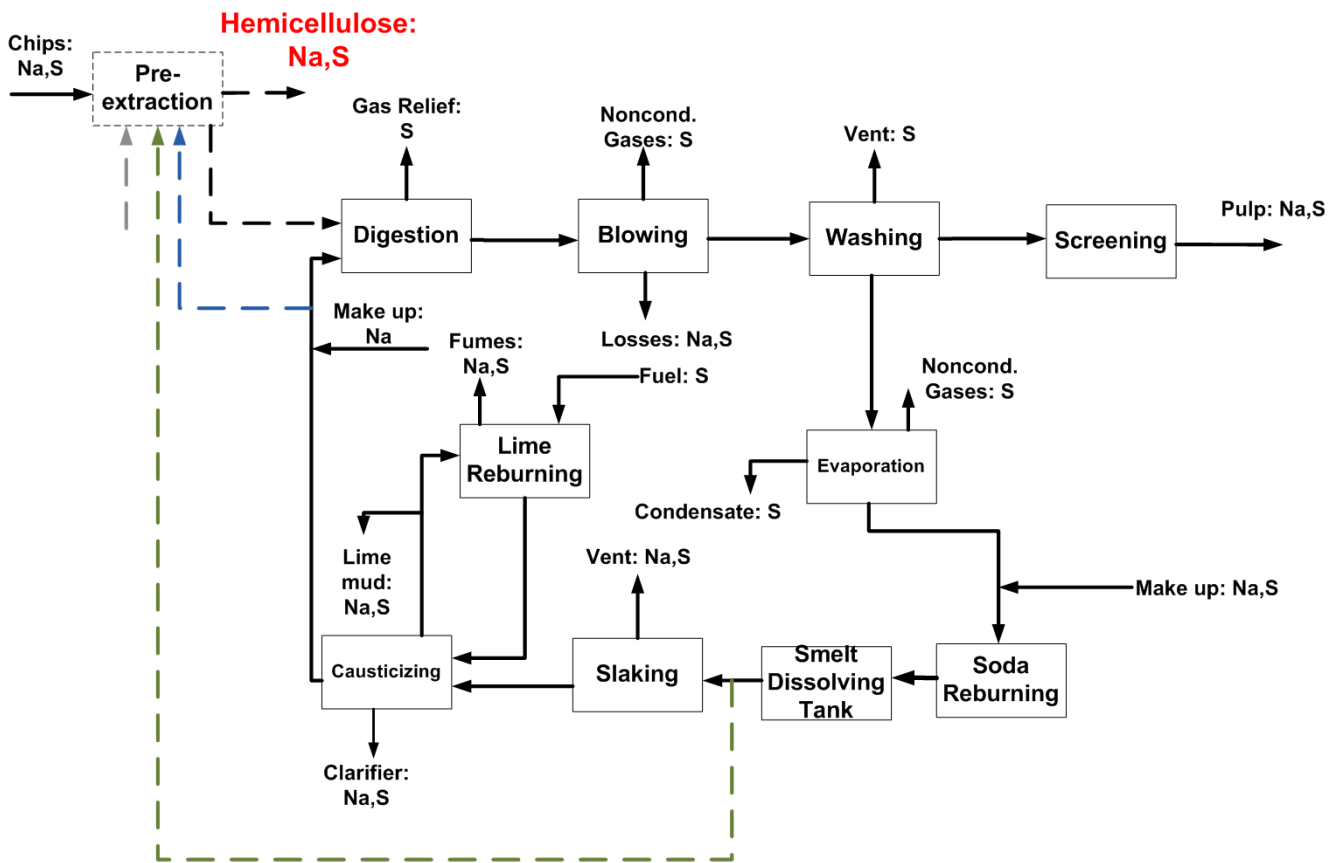


Figure 26: Sodium and sulphur inputs and losses around Kraft mill with the addition of hemicellulose extraction. With the grey, green and blue streams representing NaOH, green liquor and white liquor extraction respectively.

The amount of sodium and sulphur used for each specific hemicellulose extraction condition, where enough wood is processed to produce 1 ton of air dried pulp, was calculated through the aid of equations 5.1 through to 5.4.

$$Na_{Na_2S} = ((M_{Na_2S} \times 2 \times (23/78.1)) \times \frac{1000}{0.085 \times Y \times (1+P_M)}) \quad 5.1$$

$$Na_{NaOH} = ((M_{NaOH} \times (23/40)) \times \frac{1000}{0.085 \times Y \times (1+P_M)}) \quad 5.2$$

$$Na_{Na_2CO_3} = ((M_{Na_2CO_3} \times 2 \times (23/106)) \times \frac{1000}{0.085 \times Y \times (1+P_M)}) \quad 5.3$$

$$S_{Na_2S} = ((M_{Na_2S} \times 2 \times (32/78.1)) \times \frac{1000}{0.085 \times Y \times (1+P_M)}) \quad 5.4$$

Na_{Na_2S} , Na_{NaOH} , $Na_{Na_2CO_3}$ represents the mass (kg) of sodium, if one ton of air dried pulp is to be produced, from Na_2S , $NaOH$ and Na_2CO_3 respectively. S_{Na_2S} represents the mass (kg) of sulphur used during hemicellulose extraction, if a ton of air dried pulp is to be produced, from Na_2S . In order to calculate the total amount of sodium used during white liquor extraction the sodium used from Na_2S and $NaOH$ was added together, while, as green liquor consists of all three Na_2S , $NaOH$ and Na_2CO_3 , the Na from all these components were added together. With $NaOH$ extraction, only the Na from the $NaOH$ used required calculation. The only component containing sulphur was Na_2S , which is only found in white and green liquor. The values 23, 32, 78.1, 40, 106, are the molecular weights (g/mol) of sodium, sulphur, Na_2S , $NaOH$ and Na_2CO_3 respectively. The value 0.085 is the oven dry mass (kg) of the wood chips used during extraction while Y represents the pulp yield. P_M is the moisture fraction for air dried pulp which was assumed to be 10%. Pulp is normally dried to about 10% as this helps to reduce fiber bonding making the pulp more conducive to being dispersed in water for further paper making [105]. M_{Na_2S} , M_{NaOH} , $M_{Na_2CO_3}$ and M_{Na_2S} is the mass (kg) of the Na_2S , $NaOH$, Na_2CO_3 and Na_2S used during the actual extractions during experimentation.

Concerning the recovery of the sodium and sulphur used during extraction, several scenarios were investigated including 0%, 20%, 50% and 90% recovery. These percentages represents the

fraction of sodium and sulphur that is recovered from the stream leaving with the hemicellulose and does not include the sodium and sulphur that still remains on the woodchips after extraction. The fraction of sodium and sulphur that is retained on the chips was calculated by using the experimental ash contents that were obtained from the chips after extraction and was included in the mass balance. In the case of green liquor and white liquor that consist of multiple chemicals, one assumption that had to be made for the sake of the mass balance was that the ratio of sodium to sulphur remaining on the wood chips after extraction is the same ratio as in the initial green liquor and white liquor mixtures.

6.3. Results

6.3.1. Comparison of chemical usage during extraction and pulping.

The mass of NaOH, Na₂S and in the case of green liquor, Na₂CO₃ as well, required for both the extraction and pulping conditions is displayed in Figure 27. The PFD is based on the chemical requirement of 85g (O.D.W.) of *E. grandis* chips. The chemical requirement for pulping non-extracted chips is also displayed as a reference. All masses are on a Na₂O equivalent basis. Table 21 shows the total amount of Na₂S, NaOH and Na₂CO₃ that was required for both pulping and extraction.

From Figure 27 and Table 21 the greatest chemical expenditure during the initial extraction and the subsequent pulping process is that of the NaOH extracted chips. A significant amount of NaOH was used during the initial extraction process, this was further exacerbated by the fact 25% of the standard amount of NaOH used for pulping non-extracted chips also had to be utilised. When comparing the amount of chemicals used for *E. grandis* chips that was subjected to both NaOH extraction and subsequent pulping (From woodchips to pulp) to that of *E. grandis* chips that was only subjected to pulping chemicals (reference) there is a 117% increase in the quantity of NaOH used. The same amount of Na₂S was utilised when compared to that of the reference conditions.

Extraction Condition							Pulping	
Solvent	Alkali Charge	Temperature	Time/H-factor	Na ₂ S(g)	NaOH(g)	Na ₂ CO ₃ (g)	Na ₂ S(g)	NaOH(g)
<i>No Extraction</i>							3.82	11.47
<i>White Liquor</i>	20%	120	90 minutes	4.25	12.75		1.91	5.74
<i>NaOH</i>	2M	120	90 minutes		21.08		2.87	3.82
<i>Green Liquor</i>	2% TTA	160	800 H	0.46	0.14	1.1	2.483	7.4555

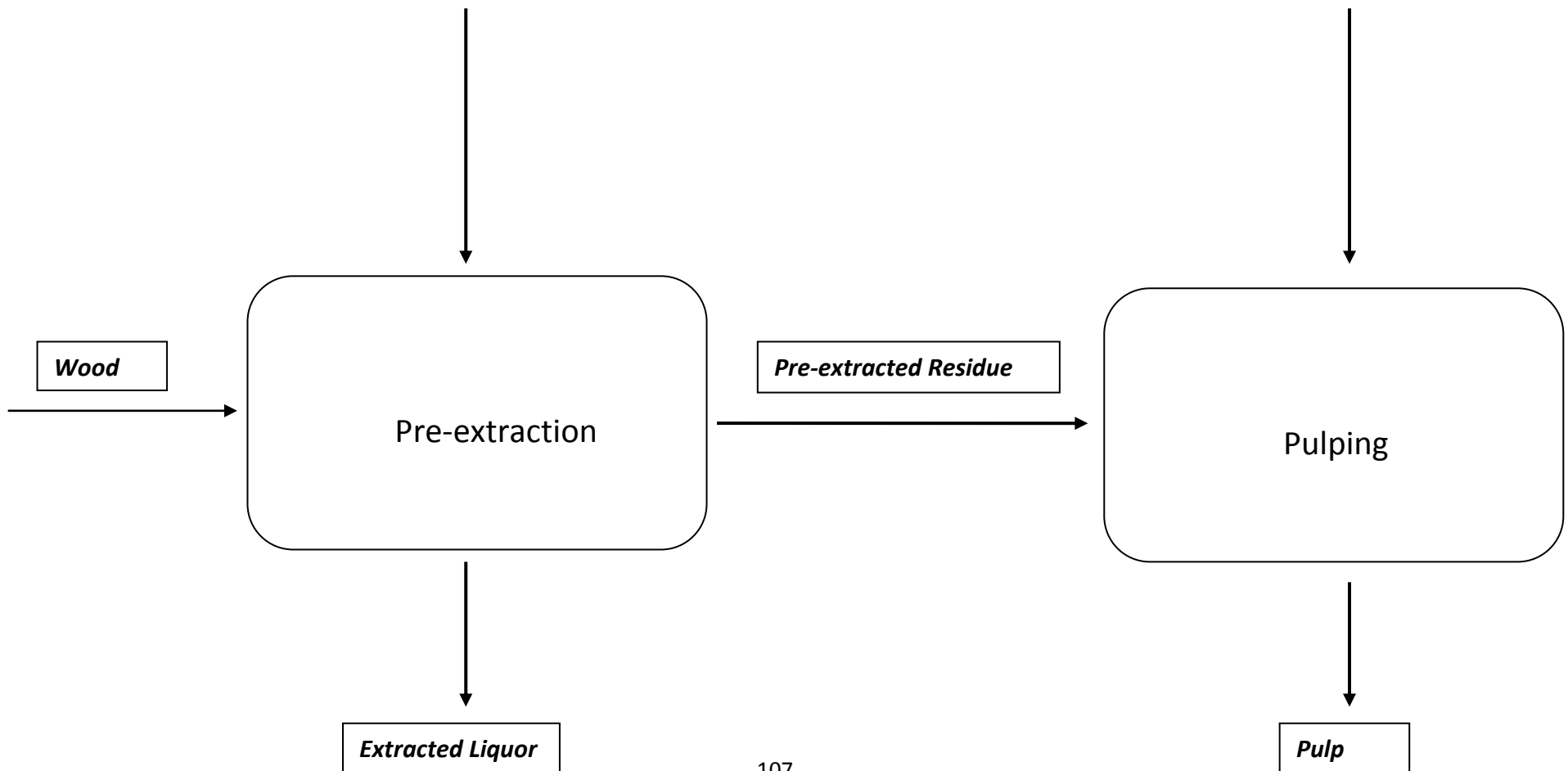


Figure 27: Figure showing mass of chemicals used during both pre-extraction and pulping.

Extraction Condition				Total(Extraction + Pulping)		
Solvent	Alkali Charge	Temperature	Time/H-factor	Na ₂ S(g)	NaOH(g)	Na ₂ CO ₃ (g)
<i>No Extraction</i>				3.82	11.47	
<i>White Liquor</i>	<i>20%</i>	<i>120</i>	<i>90 minutes</i>	<i>6.16</i>	<i>18.49</i>	
<i>NaOH</i>	<i>2M</i>	<i>120</i>	<i>90 minutes</i>	<i>3.82</i>	<i>24.90</i>	
<i>Green Liquor</i>	<i>2% TTA</i>	<i>160</i>	<i>800 H</i>	<i>2.94</i>	<i>7.60</i>	<i>1.1</i>

Table 21: Table showing total amount of NaOH, Na₂S and Na₂CO₃ required for both extraction and pulping for 85g of oven dried wood chips.

For the white liquor extractions that were carried out a 50% reduction in chemicals was used during pulping, however, when combining the quantity of chemicals used during both the extraction and pulping processes (From woodchips to pulp) there was a 61% increase in both the use of NaOH and Na₂S relative to that of the reference as calculated from Table 21. Again a large quantity of Na₂S and NaOH was used during the initial extractions. One consolidation that can be taken away from the fact that a higher total chemical charge was used for the white liquor extractions when compared to that of the reference is that a shorter cooking time was used. This was not done during the NaOH extractions.

As calculated from Table 21, for the chips that were subjected to green liquor extraction a 35% reduction in both Na₂S and NaOH during the pulping phase relative to that of the reference was used. Due to the low alkalinity that was used during the initial green liquor extractions there was actually a net reduction relative to that of the reference pulp when both the extractions and pulping was taken into consideration. There was a 23% reduction in the amount of Na₂S coupled with a 33% reduction in the amount of NaOH used. When adding in the Na₂CO₃ that was used during the green liquor extractions there was a total reduction of 24% in mass of chemicals used relative to the amount of chemicals that was used for the reference pulp on the non-extracted *E. grandis*.

Figure 27, coupled with Table 21, give some insight into the possible economic effects of integrating hemicellulose extraction into a Kraft process. It helps to paint a picture of how

hemicellulose extraction could offset the total amount of chemicals needed for physical fiber processing relative to that of standard Kraft process. However, a total mass balance is needed to gain a fuller understanding of the economic consequences as the total amount of sodium and sulphur lost from the system via extraction will play a pivotal role in determining the feasibility of the process. This will be discussed in the section which follows.

6.3.2. Effect of hemicellulose pre-extraction on the Na/S balance of a Kraft mill.

Figure 29 is a schematic on which the mass balance using white liquor extraction was based. Of particular interest are streams 10, 11, and 12. From stream 10 the sodium and sulphur is removed from the Kraft system via the extracted hemicellulose, while stream 11 is the sodium and sulphur that is hypothetically recovered from the extraction stream. Stream 12 is the make-up sodium and sulphur that is fed to the Kraft recovery cycle. Although the diagram of the Kraft process is very simplified and a balance around each unit operation is not given a good overall balance of the sodium and sulphur that is lost from the system is still provided. Table 22 shows the sodium and sulphur in each stream depicted in Figure 29 for 0%, 20%, 50% and 90% recovery of the sodium and sulphur used during extraction.

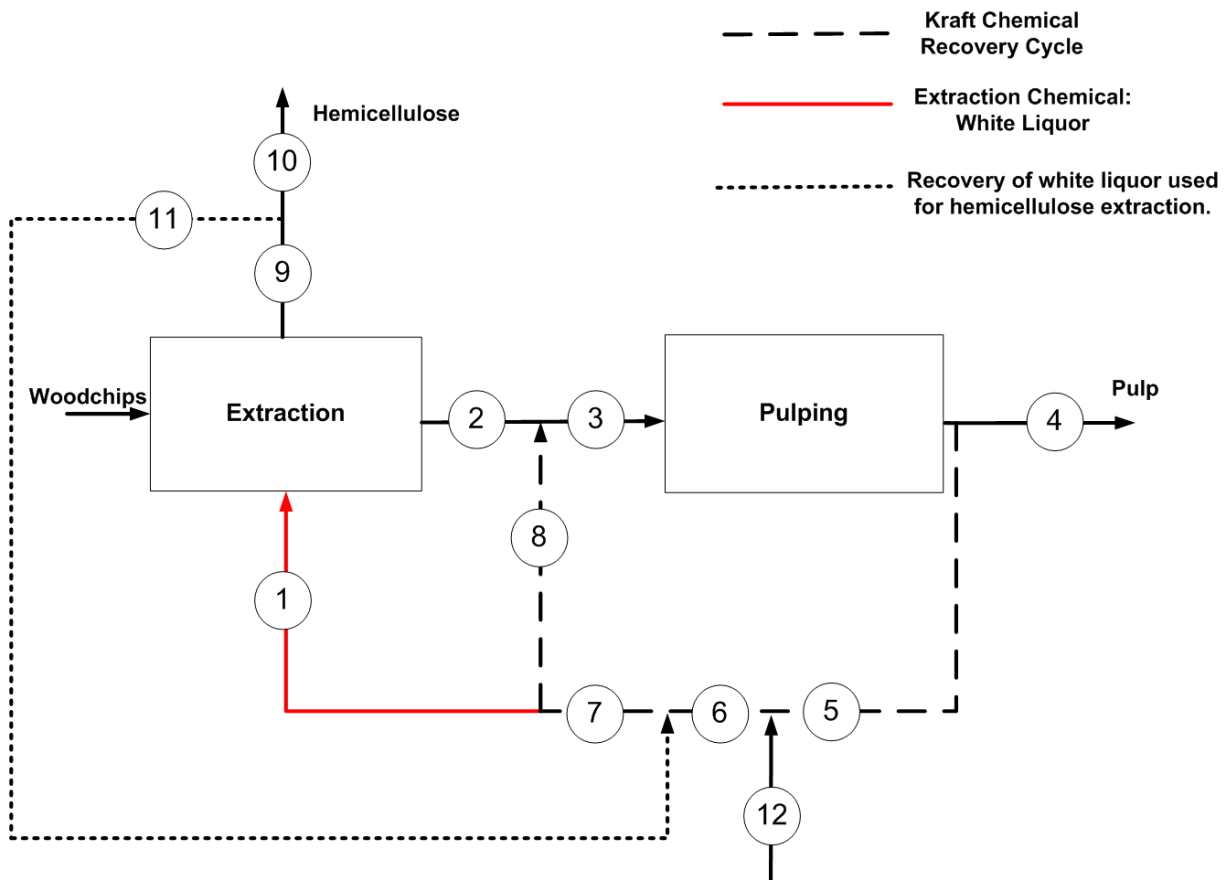


Figure 29: Diagram on which mass balance for integration of white liquor extraction into Kraft mill was based.

Table 22: Table showing mass balance of sodium and sulphur in Figure 29 for 0%, 20%, 50% and 90% recovery of the sodium and sulphur that exits in the extracted hemicellulose stream. (All quantities are displayed as kilograms per air dried pulp produced)

Stream	Percentage Recovery	Na (kg/adt)	S (kg/adt)	Stream	Percentage Recovery	Na (kg/adt)	S (kg/adt)
1	0	324.27	44.77	7	0	470.20	64.89
	20	324.27	44.77		20	470.20	64.89
	50	324.27	44.77		50	470.20	64.89
	90	324.27	44.77		90	470.20	64.89
2	0	110.17	15.21	8	0	145.92	20.12
	20	110.17	15.21		20	145.92	20.12
	50	110.17	15.21		50	145.92	20.12
	90	110.17	15.21		90	145.92	20.12
3	0	256.09	35.33	9	0	214.10	29.56
	20	256.09	35.33		20	214.10	29.56
	50	256.09	35.33		50	214.10	29.56
	90	256.09	35.33		90	214.10	29.56
4	0	7.68	1.06	10	0	214.10	29.56
	20	7.68	1.06		20	171.28	23.65
	50	7.68	1.06		50	107.05	14.78
	90	7.68	1.06		90	21.41	2.96
5	0	248.41	34.27	11	0	0.00	0.00
	20	248.41	34.27		20	42.82	5.91
	50	248.41	34.27		50	107.05	14.78
	90	248.41	34.27		90	192.69	26.60
6	0	470.20	64.89	12	0	221.79	30.62
	20	427.37	58.98		20	178.96	24.71
	50	363.14	50.11		50	114.73	15.84
	90	277.50	38.29		90	29.09	4.02

In order to help inspect the losses of sodium and sulphur visually as well to help determine the amount of Na_2SO_4 and NaOH that will be needed to compensate for the lost sodium and sulphur, simple vector diagrams were drawn up. Vector diagrams were drawn depicting the total sodium and sulphur losses as well as the sodium and sulphur that is added to the system via Na_2SO_4 as well as NaOH . Figure 30 shows the mass balance of sodium and sulphur of a

hypothetical Kraft mill without hemicellulose extraction. The sodium and sulphur losses (Figure 30) and make-up streams are based on the standard pulping conditions that were used during experimentation. The sodium and sulphur lost was calculated as 3% of the sodium and sulphur used for pulping, as the Kraft chemical recovery was assumed to be 97%. The sulphur lost from the Kraft system is made up via the use of Na_2SO_4 . However, the addition of Na_2SO_4 will inevitably add sodium to the system via ratio of 1.42 kilograms of sodium per kilogram of sulphur. Therefore one can compensate for the loss of sulphur through Na_2SO_4 and then calculate the amount on sodium added to the system through the ratio of 1.42kg/kg, and add the remaining sodium through the addition of NaOH. Na_2SO_4 , albeit a cheaper alternative to NaOH, will add excess sulphur to the system if it is used to account for all of the lost sodium [104].

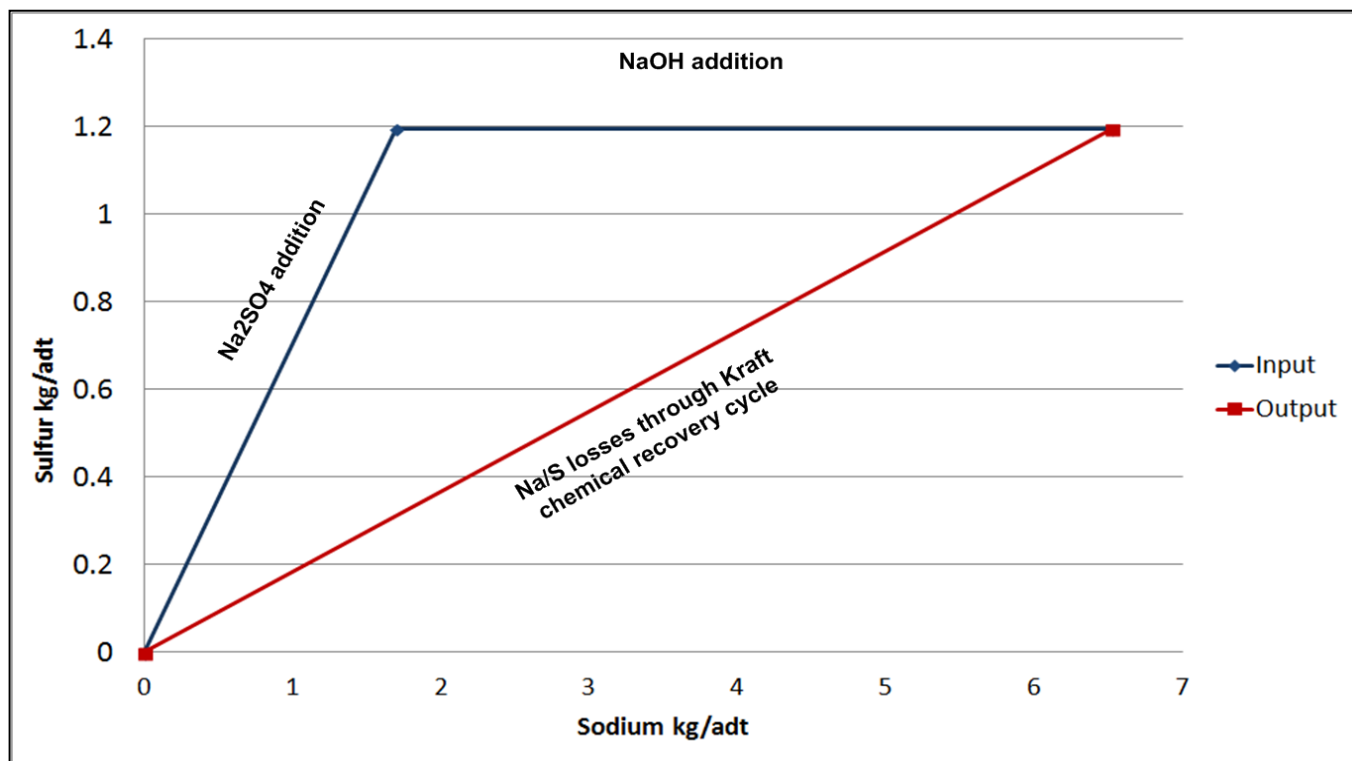


Figure 30: Mass balance showing total sodium and sulphur inputs and outputs of Kraft mill without hemicellulose pre-extraction.

Table 22 depicts the losses of sodium and sulphur when white liquor extraction is implemented into the Kraft system using the amount of sodium and sulphur that were used during pulping and extraction experimentally. The natural losses of sodium and sulphur observed from the Kraft

recovery cycle is dwarfed by the losses obtained through hemicellulose extraction, this is especially so if none of the white liquor used for extraction is recovered. The sodium and sulphur that needs to be accounted for is 221.79 kg/adt and 30.62 kg/adt respectively when none of the sodium and sulphur used for extraction is recovered. In contrast to the 6.51kg/adt and 1.2 kg/adt of sodium and sulphur respectively that has to be re-added to the Kraft system with no hemicellulose pre-extraction. Even if up to 90% of the sodium and sulphur that exits with the extracted hemicellulose stream is recovered, 29.09kg/adt of sodium and 4.02kg/adt of sulphur is lost.

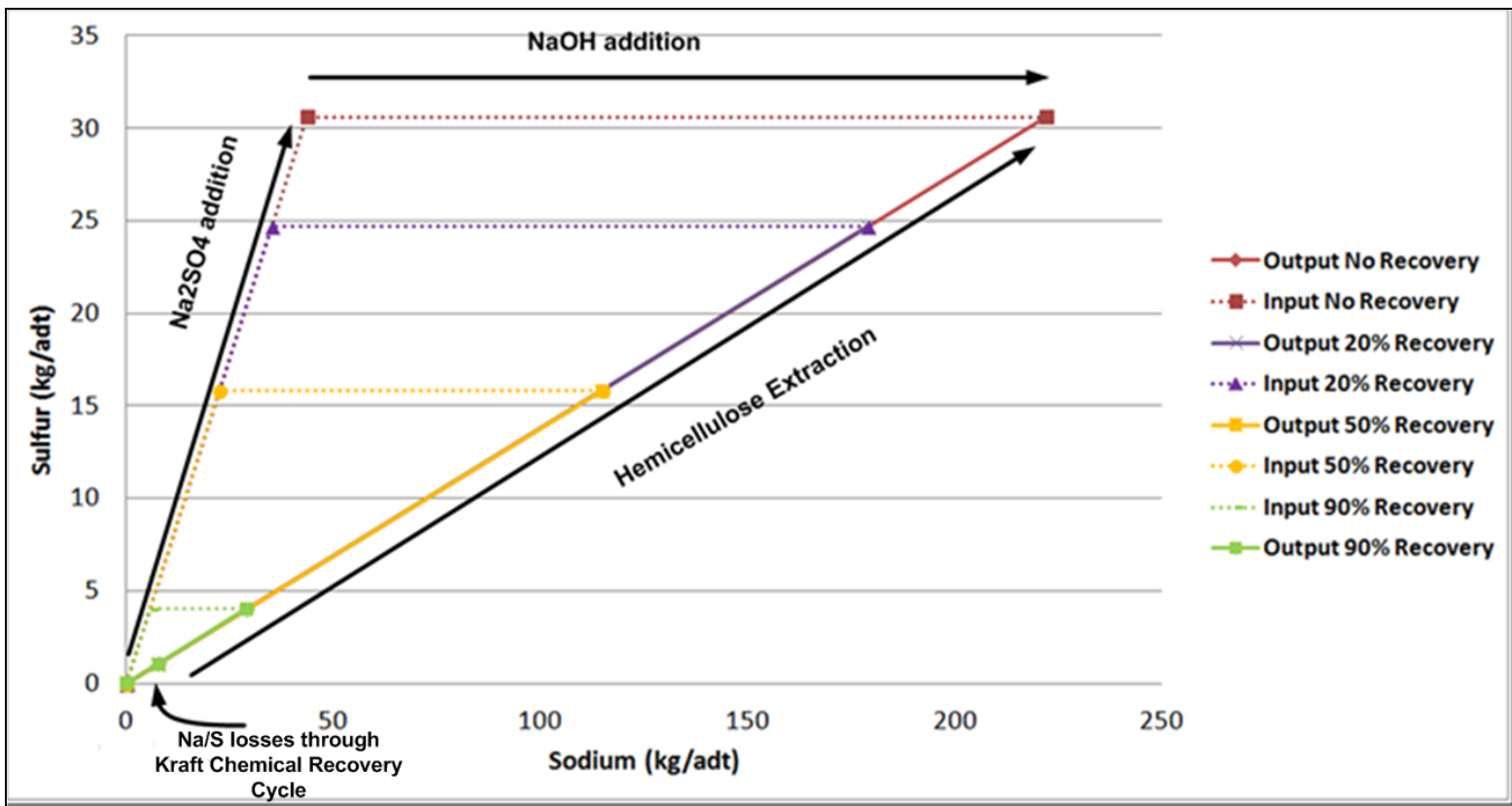


Figure 31: Inputs and outputs of sodium and sulphur of kraft mill with the addition of hemicellulose extraction through the use of white liquor. Figure shows 0%, 20%, 50% and 90% recovery of sodium and sulphur that exits with extracted hemicellulose stream.

The quantity of white liquor that is utilised for hemicellulose pre-extraction has a significant impact on both the sodium and sulphur balance of the mill, especially if the sodium and sulphur is not at all recovered back to the system. The feasibility of using white liquor to extract hemicellulose will strongly depend on the recovery of chemicals back to the system. Even if a significant portion can be recovered the feasibility will still strongly rely on whether the products produced from the hemicellulose justify the expenditure on additional make-up chemicals economically.

The drawing that was utilised for the sodium and sulphur balance (Figure 32) using green liquor is essentially the same as that that was used for the white liquor extraction, except conceptually a green liquor stream is drawn from the recovery cycle. This is instead of a white liquor one for the hemicellulose extraction. Table 23 shows the sodium and sulphur found in each stream per kilogram of air dried pulp that is produced, with Figure 33 being the corresponding vector diagram showing the total sodium and sulphur balance with green liquor extraction. It shows the scenarios where 0%, 20%, 50% and 90% of the sodium and sulphur in the extracted hemicellulose stream is recovered.

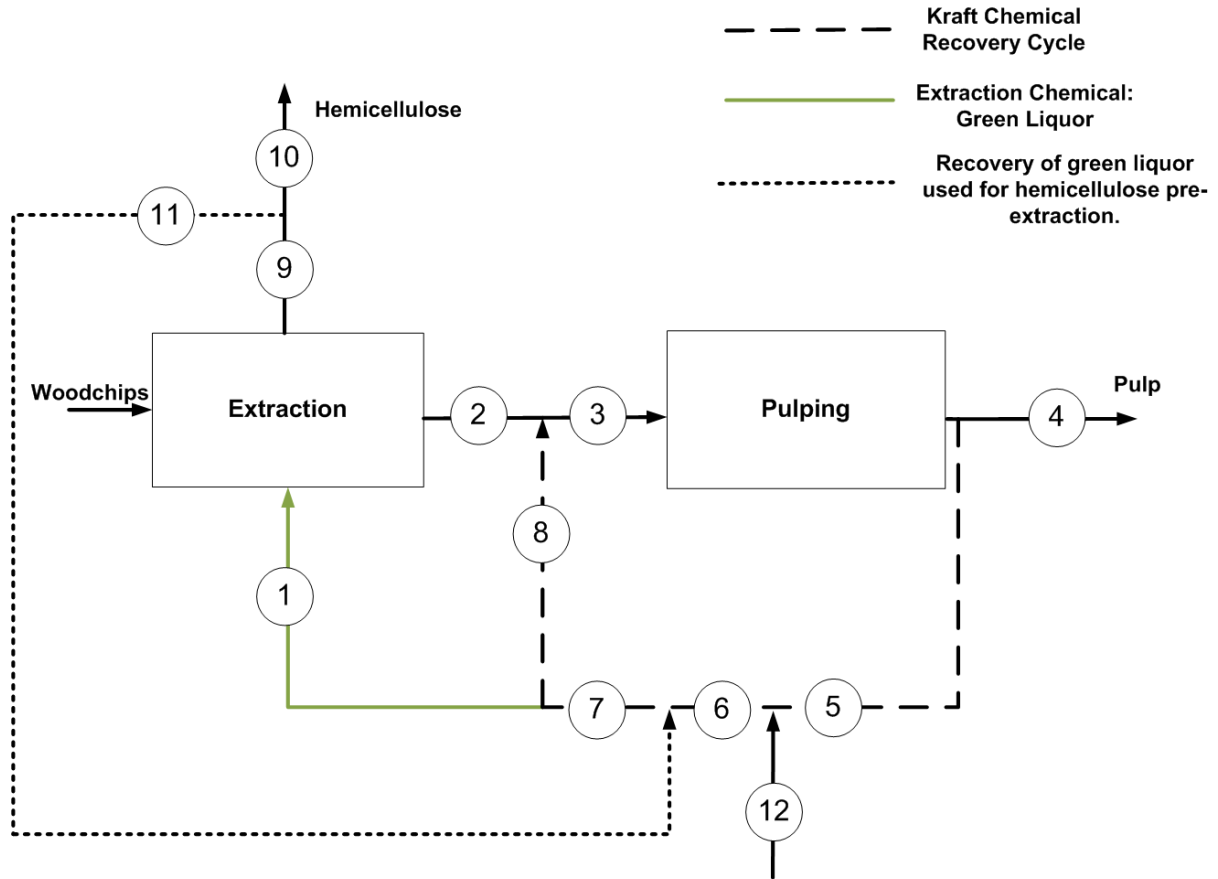


Figure 32: Diagram on which mass balance for integration of extraction into kraft mill was based.

Table 23: Table showing mass balance of sodium and sulphur in Figure 32 for 0%, 20%, 50% and 90% recovery of the sodium and sulphur that exits in the extracted hemicellulose stream. (All quantities are displayed as kilograms per air dried pulp produced)

Stream	Percentage Recovery	Na (kg/adt)	S (kg/adt)	Stream	Percentage Recovery	Na (kg/adt)	S (kg/adt)
1	0	51.44	44.77	7	0	197.37	24.79
	20	324.27	44.77		20	197.37	64.89
	50	324.27	44.77		50	197.37	64.89
	90	324.27	44.77		90	197.37	64.89
2	0	8.40	0.76	8	0	145.92	20.12
	20	8.40	0.76		20	145.92	20.12
	50	8.40	0.76		50	145.92	20.12
	90	8.40	0.76		90	145.92	20.12
3	0	154.32	20.88	9	0	43.05	3.91
	20	154.32	20.88		20	43.05	3.91
	50	154.32	20.88		50	43.05	3.91
	90	154.32	20.88		90	43.05	3.91
4	0	4.63	0.63	10	0	43.05	3.91
	20	4.63	0.63		20	34.44	3.12
	50	4.63	0.63		50	21.52	1.95
	90	4.63	0.63		90	4.30	0.39
5	0	149.69	20.26	11	0	0.00	0.00
	20	149.69	20.26		20	8.61	0.78
	50	149.69	20.26		50	21.52	1.95
	90	149.69	20.26		90	38.74	3.51
6	0	197.37	24.79	12	0	47.67	4.53
	20	188.76	24.01		20	39.07	3.75
	50	175.84	22.83		50	26.15	2.58
	90	158.63	21.27		90	8.93	1.02

The effect on the sodium and sulphur balances relative to that where no hemicellulose extraction was implemented is significantly less severe using green liquor extraction when compared to that of white liquor extraction. In the case where none of the sodium or sulphur exiting with the hemicellulose is recovered (stream 11) the amount of sodium and sulphur lost is 47.67 kg/add and 4.53 kg/adt of pulp produced. With 90% recovery only 8.93 kg/adt and 1.02

kg/adt of sodium and sulphur respectively is lost which is very similar to the case of the Kraft mill where no hemicellulose is extracted. Due to the lower alkaline concentration of the green liquor significantly less sodium and sulphur is lost from the kraft system when compared to white liquor extraction. Even though less sodium and sulphur is used during the pulping portion of chips that were subjected to pre-extraction when compared to green liquor extraction, significantly more sodium and sulphur is lost with the extracted hemicelluloses during white liquor extraction. The reduction in chemicals used during pulping of chips that were subjected to pre-extraction does not seem to be of significant advantage due to the fact that the Kraft recovery cycle is already very efficient. Once chemicals are used for pulping whether it is less or more relative to that of the standard Kraft system, the sodium and sulphur are maintained in the system and do not need to be appreciably replenished. The point of concern is clearly where the sodium and sulphur leaves with the extracted hemicelluloses as there can be significant losses.

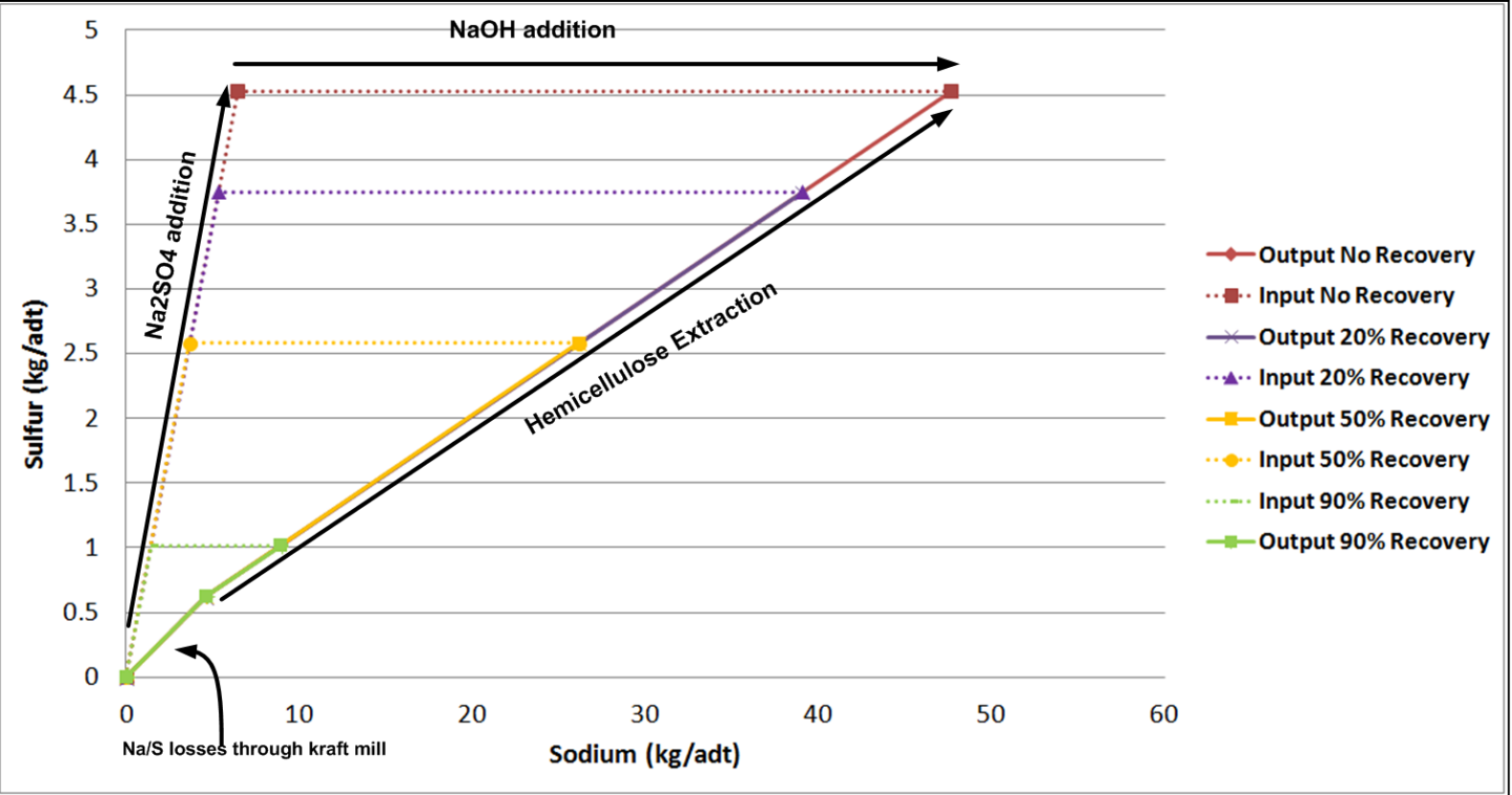


Figure 33: Inputs and outputs of sodium and sulphur of Kraft mill with the addition of hemicellulose extraction through the use of green liquor. Figure shows 0%, 20%, 50% and 90% recovery of sodium and sulphur that exits with extracted hemicellulose stream.

Due to the fact that the NaOH used is not drawn from the Kraft chemical recovery cycle the PFD (Figure 34) used for the mass balance is different to that used for green liquor and white liquor extraction. As there is no sodium and sulphur drawn from the recovery cycle for extraction, there is excess sodium that builds up in the recovery cycle from the sodium that enters with the pre-extracted chips (stream 2) that needs to be removed from the recovery recycle. The sodium that is drawn from the recovery cycle would naturally be sent back to the extraction point to save on the addition of make-up NaOH, which was done through stream 10.

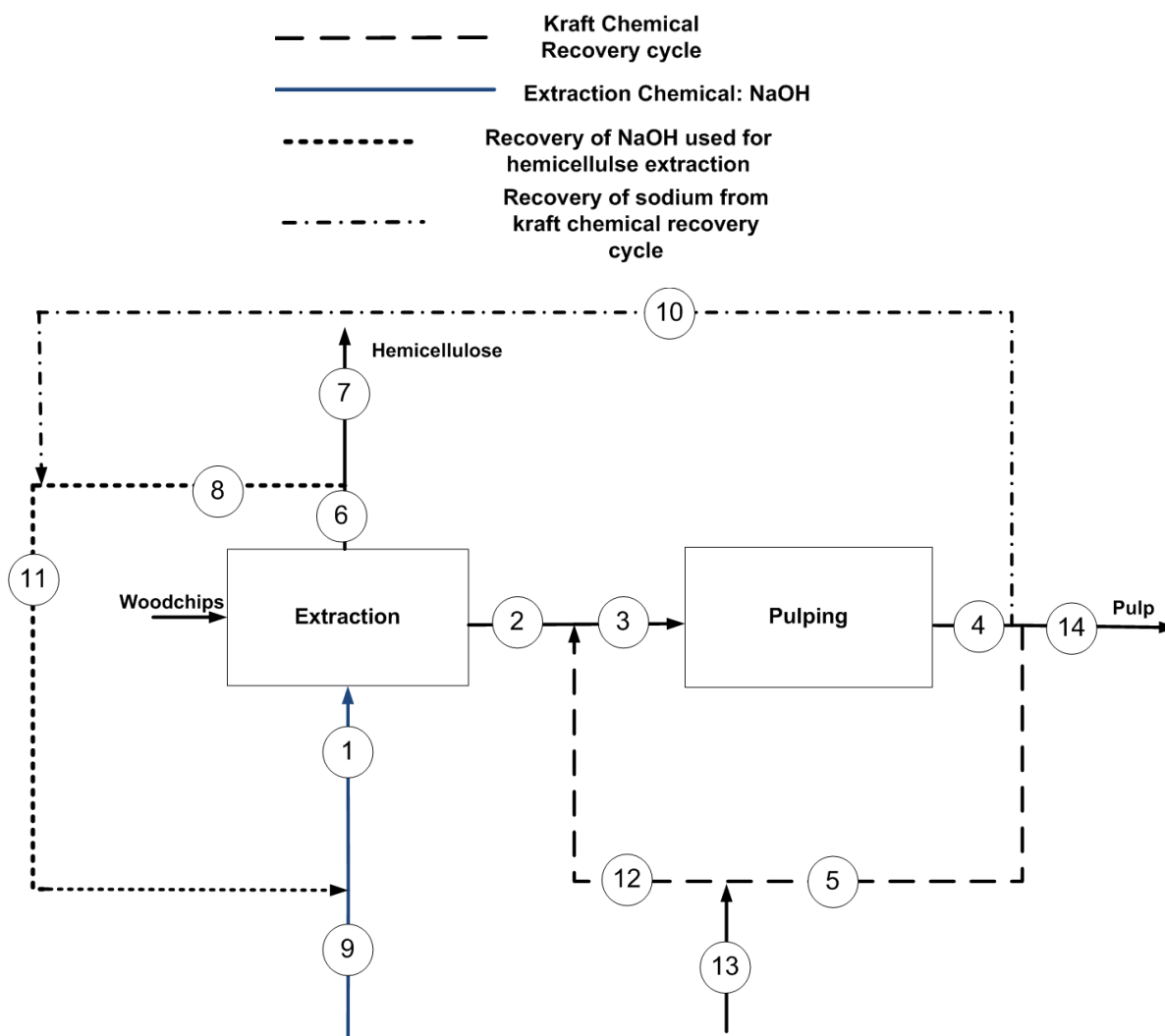


Figure 34: Diagram on which mass balance for integration of NaOH liquor extraction into kraft mill was based.

Table 24: Table showing mass balance of sodium and sulphur in Figure 34 for 0%,20%,50% and 90% recovery of the sodium and sulphur found in the extracted hemicellulose stream(All quantities are displayed as kilograms per air dried pulp produced)

Stream	Percentage Recovery	Na (kg/add)	S (kg/adt)	Stream	Percentage Recovery	Na (kg/adt)	S (kg/adt)
1	0	418.18	0.00	8	0	0.00	0.00
	20	418.18	0.00		20	56.62	0.00
	50	418.18	0.00		50	141.54	0.00
	90	418.18	0.00		90	254.78	0.00
2	0	135.10	0.00	9	0	283.09	0.00
	20	135.10	0.00		20	226.47	0.00
	50	135.10	0.00		50	141.54	0.00
	90	135.10	0.00		90	28.31	0.00
3	0	267.81	31.44	10	0	135.10	0.00
	20	267.81	31.44		20	135.10	0.00
	50	267.81	31.44		50	135.10	0.00
	90	267.81	31.44		90	135.10	0.00
4	0	267.81	31.44	11	0	135.10	0.00
	20	267.81	31.44		20	191.71	0.00
	50	267.81	31.44		50	276.64	0.00
	90	267.81	31.44		90	389.87	0.00
5	0	128.73	30.50	12	0	132.72	31.44
	20	128.73	30.50		20	132.72	31.44
	50	128.73	30.50		50	132.72	31.44
	90	128.73	30.50		90	132.72	31.44
6	0	283.09	0.00	13	0	3.98	0.94
	20	283.09	0.00		20	3.98	0.94
	50	283.09	0.00		50	3.98	0.94
	90	283.09	0.00		90	3.98	0.94
7	0	283.09	0.00	14	0	3.98	0.94
	20	226.47	0.00		20	3.98	0.94
	50	141.54	0.00		50	3.98	0.94
	90	28.31	0.00		90	3.98	0.94

Table 24 shows the corresponding sodium and sulphur quantities for the streams found in Figure 34. The total amount of sodium that needs to be added to the system when none of the NaOH in the extracted hemicellulose stream is recovered is 287.07 kilograms per ton of air dried pulp produced. This is improved to 32.29 kg/adt of pulp produced if 90% of the NaOH in the stream is hypothetically recovered. With the NaOH extraction no additional sulphur is lost from the system as no sulphur is present during the initial extraction. This is depicted by Figure 35 which shows the sodium and sulphur inputs of a Kraft mill for 50% and 90% recovery of the sodium leaving with the extracted hemicellulose.

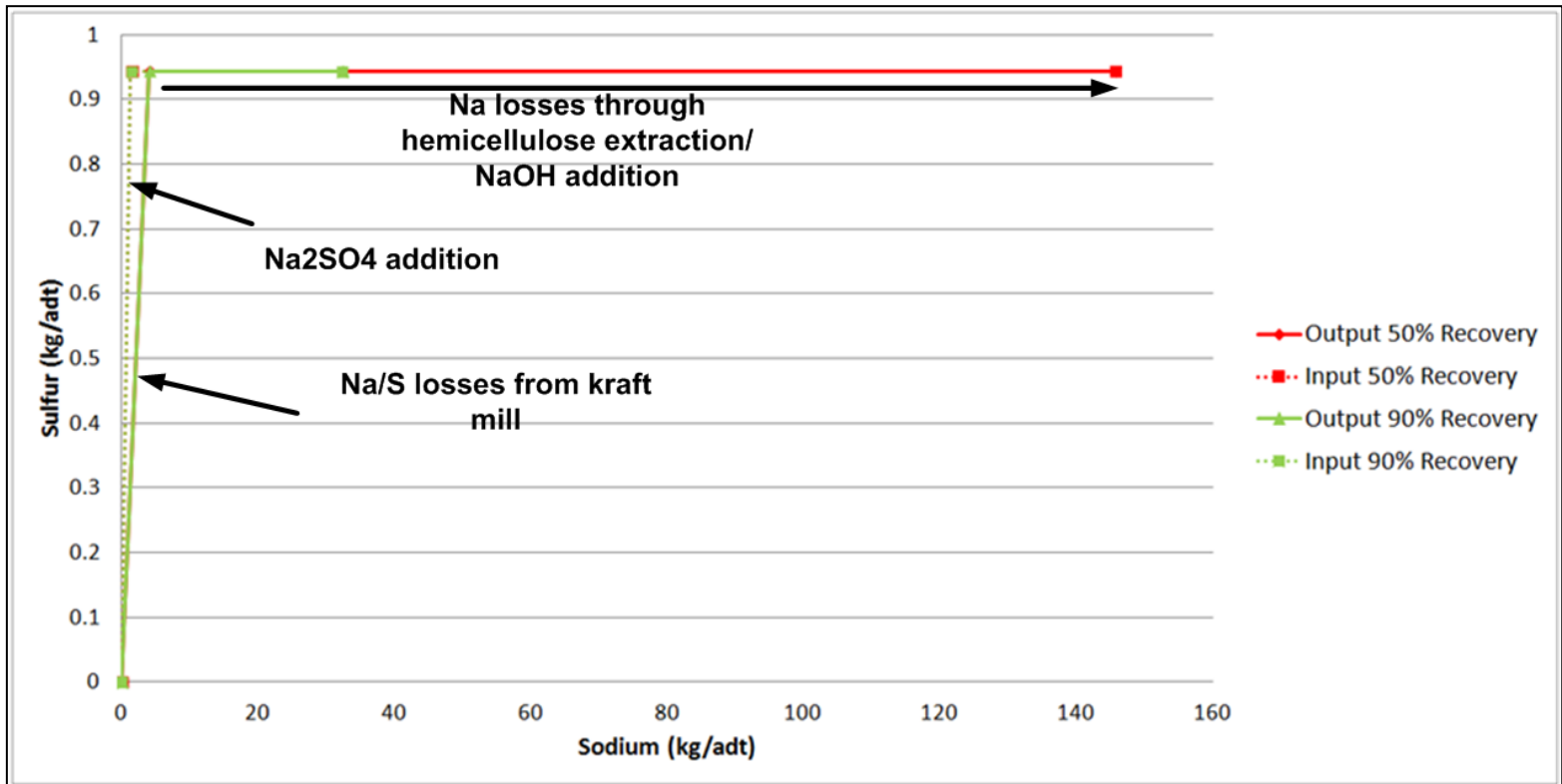


Figure 35: Inputs and outputs of sodium and sulphur of Kraft mill with the addition of hemicellulose extraction through the use of NaOH. Figure shows 50% and 90% recovery of sodium that exits with extracted hemicellulose stream.

6.3.3. Comparison of xylose recovery versus chemical addition between different extraction methods.

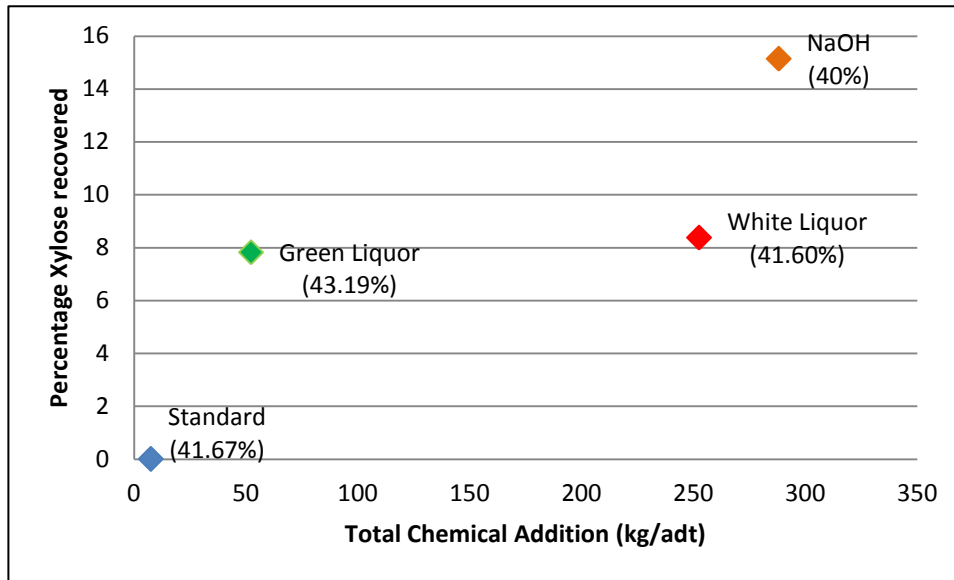


Figure 36: Percentage xylose recovered versus total chemical addition (S + Na) for green liquor, white liquor and NaOH extraction methods with NO chemical recovery. Blue: Kraft mill Without Extraction, Green: Green Liquor, Red: White Liquor, Orange: NaOH. Values in brackets represent corresponding pulp yields for each extraction method.

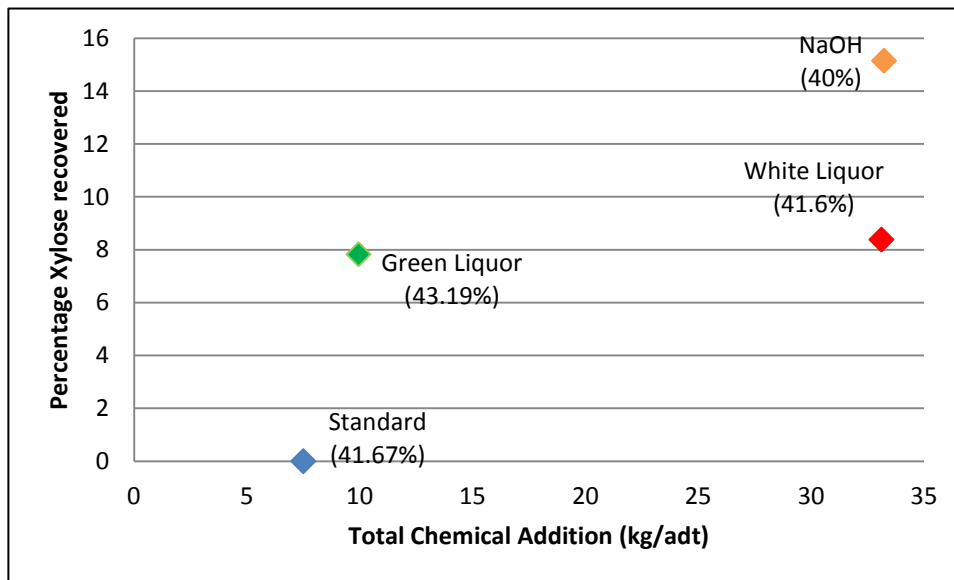


Figure 37: Percentage xylose recovered versus total chemical addition(S + Na) for green liquor, white liquor and NaOH extraction methods with 90% chemical recovery. Blue: Kraft mill Without Extraction, Green: Green Liquor, Red: White Liquor, Orange: NaOH. Values in brackets represent corresponding pulp yields for each extraction method.

In order to summarise the chemical addition required versus the fraction xylose recovered, for each extraction method, Figure 36 and Figure 37 were drawn up. The corresponding pulp yields have been added in brackets. Two cases are shown; one where no chemicals have been recovered from the hemicellulose carrying stream (Figure 36) and the other where 90% of the chemicals are recovered (Figure 37). The fraction of xylose recovered using green liquor and white liquor is similar, however the chemical addition required for the white liquor extraction method is substantially greater than that of the green liquor extraction method. This is evident for both the scenarios where no chemicals are recovered and where 90% of the chemicals are recovered. The sodium hydroxide extraction method produced the greatest amount of recovered xylose, but this advantage is dampened by the high amount chemicals used during both the extraction and pulping processes.

Further adding to the green liquor extraction process' greater attractiveness, compared to the other methods, is that the pulp yield was slightly higher than pulp produced from the wood chips that was not subjected to extraction. Also, when the chemical recovery approaches 90% the amount of chemicals that needs to be added to the system per kg of air dried ton of green liquor pulp produced is similar to that of the non-extracted chips with the added advantage that an additional products stream is produced.

6.4. Discussion

6.4.1. Effect of extraction methods on sodium and sulphur balances of a Kraft mill.

In the Kraft process only about half of all the technical equipment is physically used for pulping. The remaining equipment is used for chemical recovery due to the high cost of the chemicals, with the alkaline chemicals having to be recovered to almost 100%, thus meaning total removal of the cooking liquor from the pulp [86]. It is unambiguously clear that for hemicellulose extraction to be feasible there has to be a significant recovery of the chemicals from the extracted hemicellulose product back to the Kraft process itself. This is especially so for the white liquor and NaOH extraction methods, due to the high alkalinity during the initial extraction phase prior to pulping. Maintaining profitability alone, using these extraction methods, might be difficult due to additional operational costs that might be incurred to make up for lost chemicals. Even if 90% of the sodium and sulphur exiting with the hemicellulose stream can be recovered, the white liquor extraction method will still result in 4.46 and 5.08 times as much sodium and sulphur lost respectively, compared to a mill with no hemicellulose extraction. If 90% of the sodium in the hemicellulose extraction stream, from NaOH extraction, is recovered back to the extraction point it will still result in 4.96 times as much sodium lost from the system when compared to a Kraft mill with no extraction. As a result chemical recovery would have to be close to a 100% of the chemicals used during extraction for both white liquor and NaOH extraction methods.

The most forgiving extraction method on the sodium and sulphur balance was that of the green liquor extraction due to the low alkali concentration used during the initial extraction process. With 90% of the sodium and sulphur recovered the sodium and sulphur that needs to be accounted for starts mirroring in quantity that of a Kraft process without hemicellulose extraction, with only a 1.73 and 1.29 increase in the amount of sodium and sulphur that needs to be replenished in terms of make-up chemicals. However, although green liquor extraction results in the lowest sodium and sulphur losses during extraction the recovery of chemicals will

also be necessary to ensure the feasibility of this extraction method. It is evident that the practicality of hemicellulose extraction will not just lie in the extraction technology itself but also will be heavily dependent on hemicellulose separation and chemical recovery technologies.

Technologies that will most likely be looked towards for the task of recovering chemicals will be membrane processes. Due to the low energy requirements as well as low chemical consumption, membrane processes are expected to play an integral part in integrated biorefineries like that of Kraft mills [96]. The purification of streams using membranes can be controlled with the pore size of membranes and operating parameters without having to adjust temperature or pH. Schlesinger et al [98] found that nano-filtration to be particularly effective in terms of recovering hemicellulose from highly caustic streams.

Arkell *et al* [106] carried out an investigation using nano-filtration where the focus was more placed on the recovery of the alkali solvent used rather than the purification of extracted hemicellulose. A residual stream resulting from the alkaline extraction of wheat bran which had already been purified through ultrafiltration was further treated with the use of nano-filtration. It was found that using a 200 MCWO polymeric membrane that 99.9% of the sugars are retained, however, this was coupled with a 30% retention of the NaOH. With a 1000 MCWO polymeric membrane 80% sugars could be retained with retention of 10% NaOH. A compromise would naturally have to be reached between sugar retention and alkaline recovery through rigorous economic analysis. Studies regarding the purification of highly caustic streams containing hemicellulose are limited and studies focussed on recovering the caustic fraction even more so. Thus a substantial amount of research will have to be focussed in this area.

An important question that also needs to be taken into account is whether using green liquor, white liquor and NaOH originating from the Kraft process is more beneficial when compared to supplying these chemicals independently from the Kraft process. Figure 38 is a conceptual schematic showing hemicellulose extraction where the extraction chemicals are not derived from the recovery cycle.

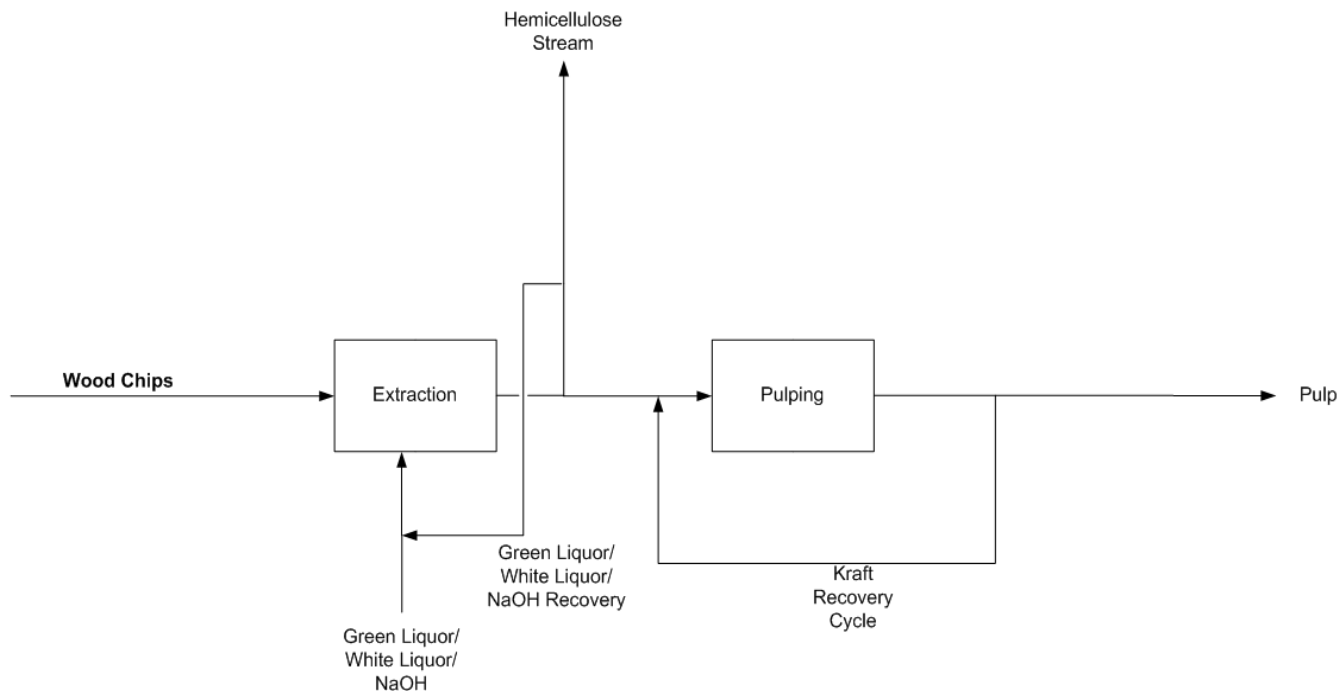


Figure 38: Conceptual drawing of chemicals used for hemicellulose extraction provided independently of the Kraft process.

Green liquor and white liquor are chemicals that are inherent to the Kraft chemical recovery cycle. Supplying these chemicals independently would mean that these chemicals would be supplied by another Kraft cycle or produced onsite with the use of Na₂S, NaOH and, in the case of green liquor, Na₂CO₃. This would prove to be unpractical and costly in comparison to that where the chemicals are drawn directly from the Kraft chemical recovery cycle as which is the case in Figure 29 and Figure 32. As a result deriving green liquor and white liquor directly from the recovery is more beneficial than supplying them independently of the Kraft process.

Green liquor and white liquor are intermediate chemicals within the Kraft recovery cycle, while NaOH is a make up chemical. Green liquor serves as a pre-cursor to white liquor while white liquor is utilised in the digester for pulping. NaOH, on the other hand, is used in a number of processes in the Kraft mill where there is a need for sodium hydroxide, which includes the digester as well as the bleaching plant [97]. Although NaOH is a chemical used in the Kraft process it is not produced as a pure chemical in the recovery cycle. Figure 34 shows hemicellulose extraction with NaOH being drawn from an independent source and not the Kraft cycle itself and the mass balance was done based on that fact.

Jun *et al* [28] suggests that because a chemical such as white liquor, for example, is a pre-existing chemical within the recovery cycle itself, its use as extraction solvent is more realistic than that of NaOH. The same would also account for green liquor as it is also a chemical originating from the Kraft chemical recovery cycle. The cost of the NaOH will also depend on the source from where it is provided.

It has been established that the magnitude of the impact that the white liquor and NaOH extraction methods will have on a conventional Kraft mill will be more severe than that of the green liquor extraction method in terms of the sodium and sulphur balance. From analysing Figure 36 and Figure 37 the benefits of this increased impact from the white liquor pre-extraction method is marginal to negligible. This is due to the fact that the selected white liquor extraction condition that was utilised only results in a fractional increase in terms of xylose that is recovered. The lower pulp yield of the white liquor extracted method relative of the green liquor extraction method also further disadvantages this method. One has to bear in mind that pulp will still be the principle product and that a slightly higher pulp yield will most likely be more beneficial than a slightly higher xylose recovery.

The xylose recovered using the NaOH extraction method is almost double that when compared to that of the green liquor extraction method. However, the chemical addition required is about 6 and 3 times that of the green liquor when no chemical recovery and 90% recovery takes place respectively. It is doubtful that the market demand for hemicellulose will be enough to justify the costs incurred by the large chemical consumption, even though the xylose recovered is

double that of the green liquor extraction method. The NaOH extraction method is further marred by the fact that the pulp yield is lower than both that of the pulp produced from non-extracted chips as well as the green liquor extracted chips. Also the paper produced from pulp resulting from NaOH extracted chips has a lower burst index, although higher tear index relative to that of paper produced from pulps resulting from chips where no extraction took place. Greater discrepancies in terms of paper properties from pulps resulting from NaOH extracted chips relative that of non-extracted chips are also more likely to increase when beating is done as these pulps have a lower hemicellulose content.

From the study that has been done, in order to select the most feasible extraction method for integration into the Kraft process, one has to take all available data into consideration. From the discussion in Chapter 5 green liquor was selected as the most feasible extraction method due to the following points:

- Low alkalinity during extraction, which means less sodium and sulphur lost from the process when compared to white liquor and NaOH extraction.
- Greater purity of the xylan product when compared to white liquor and NaOH.
- Increased pulp yield relative that of pulps obtained from non-extracted chips.
- No statistical impact on burst, tear and tensile properties of unbeaten handsheets produced, compared to that of handsheets obtained from pulps resulting from non-extracted *E. grandis*.

From the results obtained in this section the presumption that the low alkalinity of green liquor extraction will have a smaller effect on the resulting sodium and sulphur balance of the mill when compared to that of white liquor and NaOH was correct. As a result, from the results obtained in this study, green liquor extraction is the most feasible extraction method for integration into Kraft mills. However, the success of the implementation of integrating green liquor extraction will still depend on the recovery of extraction chemicals utilised, which means the feasibility of the integration of hemicellulose extraction into the Kraft process is still heavily dependent on the further development of process technologies. These technologies have to be able to successfully and economically separate the hemicellulose product from the chemicals

utilised for extraction. Another potential issue with the use of green liquor is that it reacts with the calcium in the wood resulting in the formation of calcium carbonate scale. Additional assessments will also have to be done to see how this problem can be mitigated before green liquor extraction can be fully integrated into the Kraft process [62]. Clean out operations might have to be implemented periodically such as using steam shock during a water boil out or high temperature washing with the use of acid [130].

6.5. Conclusions

As expected, implementing hemicellulose pre-extraction using pre-existing chemicals from the Kraft process will definitely impact on the sodium and sulphur balance of the mill. Even though there might be a reduction in the quantity of chemicals used during pulping relative to that of a Kraft mill without extraction, the loss of chemicals through the extracted hemicellulose stream will be significant. This is particularly so for the higher alkali extraction methods such as that of the white and NaOH extraction methods, principally because of their high alkali concentrations during the extraction process itself. The lower alkalinity of the green liquor “near-neutral” extraction method allows for less chemicals to be lost with the hemicellulose stream, but recovery of the chemicals used will still be necessary to make the extraction process feasible. Membrane processes that recover the chemicals used during extraction will play a pivotal role in ensuring the feasibility of alkali pre-extraction processes that is integrated into the Kraft process. Thus, significant focus will have to be directed in that area if alkali hemicellulose pre-extraction is to be realistic.

Supplying green liquor and white liquor from the Kraft chemical recovery cycle itself will be more practical than supplying it independently of the process. This is due to the fact that these chemicals are inherent to the recovery cycle and producing these chemicals independently would serve to be more costly. NaOH is not produced as chemical on its own in the recovery cycle, therefore supply would inevitably be independent of the Kraft recovery cycle.

In terms of an extraction method that compromises the best between xylose recovery, effect on pulp and paper quality and quantity of chemicals used for extraction, the green liquor

extraction method outperforms that of the white and NaOH extraction methods. The minimal effect on the paper properties of pulps produced from green liquor pre-extracted chips coupled with the maintenance of pulp yield further lends to it being the most suitable method for integrating into the Kraft process.

CHAPTER 7: Conclusions and recommendations

7.1. Conclusions

The main focus of this study was to compare using green liquor, white liquor and NaOH, which are all pre-existing chemicals in the Kraft process, in terms of the amount of xylan that is recovered. The effect on pulp and paper properties should *E. grandis* be subjected to these chemicals for xylan pre-extraction were also to be investigated. The study also focussed on evaluating the effect these different extraction methods would have on both the sodium and sulphur balance of the mill. From this, the end focus was to select an extraction method that would be the most suitable for integration into the Kraft process. From the study carried out the following conclusions can be drawn:

7.1.1. Recovery and purity of xylan.

- The feedstock of *E. grandis* utilised displayed recalcitrance towards releasing significant amounts of xylan, using 20% AA white liquor for extraction, at temperatures below 100°C when compared to that of literature [28]. The lower recoveries might be attributed to a high extractives content, with extractives inhibiting chemical penetration during the extraction process.
- The feedstock did respond to higher temperatures with xylan recoveries (expressed as xylose) increasing as temperatures moved beyond 100°C. From the three extraction chemicals utilised NaOH extraction was the most successful in terms of quantity of xylan recovered, followed by white liquor and green liquor extraction respectively. NaOH extraction using 2M, 120 °C and 90 minute extraction time resulted in 15.15 % w/w of the original xylan fraction recovered from the *E. grandis* feedstock. The highest xylan

recovery with the use of white liquor was 13.27% w/w of the xylan found in the original feedstock. Corresponding extraction conditions were 20% AA, 140°C and 90 minute extraction time. Green liquor extraction produced the lowest maximum xylan recovery (7.83%) utilising 2% TTA, 160°C and a corresponding H-factor of 800, with the higher alkalinities utilised for the white liquor and NaOH extractions allowing for greater xylan recoveries in comparison to that of green liquor.

- FT-IR analysis indicated that from the extractions performed the purist extracted xylan product in terms of lignin content resulted from green liquor extraction. The lower alkalinities utilised by green liquor extraction allowed for less severe extraction conditions minimising lignin being released from the feedstock.

7.1.2. Quality of pulp and paper resulting from *E. grandis* subjected to green liquor, white liquor and NaOH extraction.

- Pulp yields produced from chips subjected to white liquor and NaOH extraction compared well to that of pulps produced from chips not subjected to extraction, the kappa numbers of pulps from white liquor pre-extracted chips, however, had a tendency to be lower than that of *E. grandis* chips not subjected to pre-extraction.
- Deviations were observed in terms of the paper properties of handsheets produced from unbeaten pulps resulting from chips subjected to NaOH extraction due to the higher amount of xylan extracted when compared to that of the white liquor and green extraction methods. No deviations were observed using green liquor and white liquor.
- Pulps resulting from *E. grandis* subjected to green liquor extraction, allowed for an increase in pulp yield coupled with no deviations in the properties of unbeaten handsheets produced when compared to that of non-extracted *E. grandis*.

7.1.3. Impact utilising green liquor, white liquor and NaOH extraction on sodium and sulfur balance of Kraft mill.

- The high alkalinities utilised for white liquor and NaOH extraction will have significant impacts on the sodium and sulfur balances of a Kraft mill. These extraction processes would require significant amount of make up chemicals to keep the extraction processes sustainable. For the white liquor extraction method, even if 90% of the sodium and sulphur exiting with the hemicellulose stream can be recovered the extraction method will still result in 4.46 and 5.08 times as much sodium and sulphur lost respectively, when compared to a mill with no hemicellulose extraction. Similarly, for NaOH extraction, if 90% of the sodium in the hemicellulose extraction stream is recovered back to the extraction point it will still result in 4.96 times as much sodium lost from the system when compared to a Kraft mill with no extraction. This will have severe economic implications as one of the Kraft mills main advantages is that it has a closed chemical recovery cycle with almost 100% of the chemicals utilised during pulping being recovered.
- The lower alkalinity utilised during the green liquor extraction proved to be a definite advantage. If 90% of the sodium and sulphur used for extraction can be recovered the sodium and sulphur that needs to be accounted for starts mirroring in quantity that of a Kraft process without hemicellulose extraction. With only a 1.73 and 1.29 times increase in the amount of sodium and sulphur respectively that needs to be replenished in terms of make-up chemicals.
- It is evident that in order for hemicellulose extraction to be feasible focus needs to be directed towards technologies that can separate hemicellulose from the alkali chemicals used for extraction, in an economic manner.

7.1.4. Most feasible extraction method for integration into the Kraft process.

- From the three chemicals and corresponding extraction conditions investigated, green liquor extraction is the most feasible due to the following points:
 - Compared to the white liquor and NaOH extraction method the make up chemicals required would be significantly less due to the lower alkalinity used during extraction.
 - Greater purity of the xylan product when compared to white liquor and NaOH, which means less cost on downstream processes in terms of purifying the product.
 - Increased pulp yield relative that of pulps obtained from non-extracted chips.
 - No statistical impact on burst, tear and tensile properties of unbeaten handsheets produced, compared to that of handsheets obtained from pulps resulting from non-extracted *E. grandis*.

It has to be noted that green liquor extraction is the most feasible extraction method *relative* the white liquor and NaOH extraction methods. As mentioned before, the feasibility of the extraction method will still rely on whether there are technologies available that can feasibly recover the chemicals utilised for extraction.

7.2. Recommendations

Due to variability between the same species of wood as a result of different growing conditions, it is recommended that extractions using green liquor, white liquor and NaOH under the same conditions with *E. grandis* obtained from different locations be carried out to observe the extent this effect has on the variation of results. The particular feedstock of *E. grandis* used, resulted in particularly low pulp yields, which could possibly be attributed to its high extractive

content. It would also be interesting to observe how pulp results would be affected using a feedstock of *E. grandis* that allowed for normal pulp yields.

It is recommended that for future testing of pulp samples resulting from pre-extracted chips, that refining (beating) be performed on the pulp before handsheets are formed. Refining the pulp will intensify the variation in paper properties between wood chips subjected to different pre-extraction conditions as the role hemicellulose plays with inter fibre bonding will be increased. This will allow for more conclusive results in terms of the how the different extraction methods compare in how they affect paper properties. For enough pulp to be produced to allow for refining it would mean that the mass of wood chips subjected to pre-extraction would have to be increased.

For a fuller understanding of the feasibility of the implementation of hemicellulose extraction into Kraft mills, it would be imperative that simulations be performed to observe how the energy balance of the mill would be impacted. The impact on the water balance of the mill is also of extreme importance and needs to be studied. A significant amount of water would also be required to wash the extracted chips which need to be taken into consideration [104].

Further investigation needs to be carried out on both the purification of the hemicellulose stream once fractionated as well as the recovery of chemicals used during the extraction process. Technologies involved in these processes will form a fundamental part of any integrated Kraft mill with hemicellulose pre-extraction. Further analysis also have to be carried out to see how scaling will affect the process if an extraction method such as green liquor is implemented due to the carbonate loading.

An intensive market analysis would have to be carried out on the demand for hemicellulose related products so that a full economic assessment can be performed to ascertain the quantity of extracted hemicellulose that would be required to justify the implementation of hemicellulose pre-extraction.

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Appendix A: Sulphuric acid addition to extracted hemicellulose streams for HPLC analysis

Table a 1: Table showing quantity of sulphuric acid added, depending on pH, for a volume of 20 ml of extracted hemicellulose in preparation for HPLC analysis.

<i>pH</i>	<i>H⁺ Ions (moles/L)</i>	<i>Volume of Sulphuric Acid Required (ml)</i>	<i>pH</i>	<i>H⁺ Ions (moles/L)</i>	<i>Volume of Sulphuric Acid Required (ml)</i>
4.3	0.0000501187	0.69706	6.2	0.000000631	0.69710
4.4	0.0000398107	0.69707	6.3	0.000000501	0.69710
4.5	0.0000316228	0.69707	6.4	0.000000398	0.69710
4.6	0.0000251189	0.69708	6.5	0.000000316	0.69710
4.7	0.0000199526	0.69708	6.6	0.000000251	0.69710
4.8	0.0000158489	0.69709	6.7	0.000000200	0.69710
4.9	0.0000125893	0.69709	6.8	0.000000158	0.69710
5	0.0000100000	0.69709	6.9	0.000000126	0.69710
5.1	0.0000079433	0.69709	7	0.000000100	0.69710
5.2	0.0000063096	0.69710	7.1	0.000000079	0.69710
5.3	0.0000050119	0.69710	7.2	0.000000063	0.69710
5.4	0.0000039811	0.69710	7.3	0.000000050	0.69710
5.5	0.0000031623	0.69710	7.4	0.000000040	0.69710
5.6	0.0000025119	0.69710	7.5	0.000000032	0.69710
5.7	0.0000019953	0.69710	7.6	0.000000025	0.69710
5.8	0.0000015849	0.69710	7.7	0.000000020	0.69710
5.9	0.0000012589	0.69710	7.8	0.000000016	0.69710
6	0.0000010000	0.69710	7.9	0.000000013	0.69710
6.1	0.0000007943	0.69710	8	0.000000010	0.69710

Table a 1 shows the quantity of sulphuric acid added to 20 ml of extracted hemicellulose liquor in preparation for HPLC analysis. The values were obtained via the use of equation 3.3. The pH of the liquors produced from white liquor and NaOH extraction were generally around a pH of 7 as they were neutralised through the use of 37% HCL after extraction. That of the green liquor streams was between 4.5 and 7.6. It can be seen from the table that the addition of sulphuric acid remains consistent for the pH range shown at 0.697 m of 72% sulphuric acid for 20 ml of sample.

Appendix B: Data for extracted residues

Table B 1: Table showing data for pre-extracted residues using white liquor. (90 minute extraction time)

Chemical Charge	Temperature(°C)	Starting Weight(g)	Weight after extraction(g)	Moisture fraction after Extraction	Dry weight of wood(g)	Ash fraction	% Wood Weight Loss
16%	100	56.5	53.5	0.11	48.20	0.09	10.33
	110	56.5	52.6	0.11	47.43	0.08	10.35
	110	56.5	53.6	0.13	47.64	0.08	10.03
	120	56.5	49.1	0.11	44.43	0.09	16.86
	120	56.5	53	0.12	47.47	0.09	11.17
	130	56.4	54.7	0.11	44.54	0.09	16.85
	130	56.7	53.29	0.11	43.73	0.09	18.65
	140	56.9	47.3	0.14	41.49	0.08	22.44
	140	56.1	49.2	0.13	43.53	0.08	17.47
20%	100	56.7	55.2	0.13	49.02	0.09	9.44
	110	56.5	53.7	0.11	48.40	0.09	9.86
	110	56.5	52.7	0.11	47.50	0.09	11.54
	120	56.5	53	0.11	47.83	0.11	12.85
	120	56.5	51.2	0.13	45.51	0.11	17.10
	130	56.6	51.2	0.12	45.68	0.11	16.87
	130	56.5	49.2	0.11	44.24	0.11	19.33
	140	56.2	49.7	0.14	43.79	0.11	19.88
	140	56.6	48.8	0.13	43.22	0.11	21.48

Table B 2: Table showing data for pre-extracted residues using NaOH. (90 minute extraction time)

Chemical Charge	Temperature(°C)	Starting Weight(g)	Weight after extraction (g)	Moisture fraction after Extraction	Dry weight of wood(g)	Ash fraction	% Wood Weight Loss
1 M	100	56.6	53.4	0.093	48.87	0.07	6.82
	110	56.1	52.23	0.130	46.22	0.08	12.11
	110	56.5	52.51	0.128	46.55	0.08	12.11
	120	55.7	51.7	0.137	45.47	0.07	12.55
	120	55.6	50.59	0.110	45.58	0.07	12.18
	130	56.4	50.2	0.088	46.14	0.07	12.38
2 M	100	56.5	56.7	0.110	53.4	0.12	7.95
	110	55.4	56.69	0.170	52.23	0.13	11.92
	110	56.5	57.31	0.167	52.51	0.13	12.47
	120	56.3	55.1	0.144	51.7	0.12	13.29
	120	56.9	56.02	0.170	50.59	0.12	14.71
	130	56.5	53.4	0.137	50.2	0.13	16.44

Table B 3: Table showing data for pre-extracted residues using green liquor.

Chemical Charge	Temperature(°C)	Starting Weight(g)	Weight after extraction(g)	Moisture Frac after Extraction	Dry weight of wood(g)	Ash fraction	% Wood Weight Loss
2%	200	56.5	53.3	0.095	48.68	0.01	1.33
	400	56.5	51.8	0.078	48.05	0.00	1.96
	400	56.5	51.3	0.075	47.72	0.00	2.63
	600	56.5	51.5	0.071	48.09	0.01	2.27
	800	56.5	50.4	0.075	46.88	0.02	5.66
	800	56	50.4	0.0847	46.46	0.02	5.67
	200	56.5	53.2	0.112	47.84	0.03	5.09
6%	200	56.8	52	0.069	48.64	0.03	4.01
	400	56.5	51	0.082	47.13	0.03	6.21
	400	56.5	51.2	0.0796	47.42	0.03	5.63
	600	56.5	51.1	0.0807	47.28	0.04	6.78
	800	56.5	50.7	0.083	46.81	0.03	7.37
	800	56.1	51.82	0.0929	47.42	0.03	5.51

Appendix C: Paper Properties

Table C 1: Table showing extraction conditions with corresponding basis weights of handsheets that were made.

Extraction Conditions			Pulping		Handsheets		
Alkali Charge	Temperature	Time at set temperature/ H-factor	Chemical Charge	Time at 170°C(minutes)	Number of Handsheets made	Average Weight of 5 handsheets(g)	Basis Weight(g.m ⁻²)
2M*	120	90 minutes	Standard Amount Na2S and 25% NaOH	45	14	1.37	69.035
2% TTA**	160	800 h	35% Reduction	45	14	1.24	62.635
NA***	NA	NA	Standard	45	14	1.20	60.615
20% AA****	120	90 minutes	50% Reduction	30	14	1.22	61.448

*NaOH extraction

**Green Liquor extraction

***Control

**** White Liquor extraction

Table C 2: Table showing raw data used to determine tensile indices.

<i>Solvent</i>	<i>Test Number</i>	<i>Tensile break load (kg)</i>	<i>Tensile strength (kN.m⁻¹)</i>	<i>Tensile index (N.m⁻¹.g⁻¹)</i>	<i>Average tensile index (N.m⁻¹.g⁻¹)</i>	<i>Standard Deviation</i>
NaOH	1	1.960	1.281	18.561	16.541	1.753
	2	1.738	1.137	16.463		
	3	1.896	1.240	17.960		
	4	1.514	0.990	14.342		
	5	1.624	1.062	15.379		
Green Liquor	1	1.873	1.225	19.554	18.944	1.339
	2	1.776	1.161	18.535		
	3	1.983	1.297	20.704		
	4	1.807	1.181	18.859		
	5	1.635	1.069	17.067		
Control	1	1.506	0.984	16.240	18.106	1.706
	2	1.871	1.224	20.186		
	3	1.807	1.181	19.488		
	4	1.657	1.084	17.878		
	5	1.552	1.014	16.737		
White Liquor	1	1.814	1.186	19.303	18.774	1.830
	2	1.803	1.179	19.184		
	3	1.868	1.221	19.873		
	4	1.875	1.226	19.952		
	5	1.462	0.956	15.556		

Table C 3: Table showing raw data used to determine tear indices.

<i>Solvent</i>	<i>Test Number</i>	<i>Force to tear 4 sheets (g)</i>	<i>Tear resistance (mN)</i>	<i>Tear index (mN.m².g⁻¹)</i>	<i>Average tear index (mN.m².g⁻¹)</i>	<i>Standard Deviation</i>
NaOH	1	10	313.824	4.546	4.319	0.321
	2	9	282.442	4.091		
Green Liquor	1	6	188.294	3.006	3.173	0.289
	2	7	219.677	3.507		
	3	6	188.294	3.006		
Control	1	6	188.294	3.106	3.365	0.366
	2	7	219.677	3.624		
White Liquor	1	7	219.677	3.575	3.320	0.361
	2	6	188.294	3.064		

Table C 4: Table showing raw data used to determine burst indices

Solvent	Test Number	Bursting strength (kPa)	Burst index (kPa.m ² .g ⁻¹)	Average burst index (kPa.m ² .g ⁻¹)	Standard Deviation
NaOH	1	60	0.869	0.835	0.030
	2	56	0.811		
	3	57	0.826		
Green Liquor	1	57	0.910	0.889	0.018
	2	55	0.878		
	3	55	0.878		
Control	1	58	0.957	0.924	0.029
	2	55	0.907		
	3	55	0.907		
White Liquor	1	56	0.911	0.906	0.009
	2	56	0.911		
	3	55	0.895		