CHEMICAL AND PHYSICAL MODIFICATION OF WOOD BASED HEMICELLULOSES FOR USE IN THE PULP AND PAPER INDUSTRY

by

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Thesis presented in partial fulfilment
of the requirements for the Degree

of

MASTER OF SCIENCE IN ENGINEERING
(CHEMICAL ENGINEERING)

in the Faculty of Engineering
at Stellenbosch University

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March 2012

DECLARATION

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ABSTRACT

Hemicelluloses are the most abundant plant polysaccharides available next to cellulose. The industrial usage of hemicelluloses however is very limited to nonexistent. As wood is processed in the Kraft pulping process, a large fraction of these hemicelluloses is degraded to low molecular weight isosaccharinic acids, which end up in the black liquor with the degraded lignin. The extraction of hemicelluloses prior to pulping and re-introducing them as a wet-end additive has been shown to improve the paper tensile -, burst- and tear index properties. It has also been proven that the pre-extraction of hemicelluloses does not negatively affect the downstream paper products.

The objective of this project was to study the modification of extracted wood based hemicelluloses, focusing on glucuronoxylan in *Eucalyptus grandis* (*E. grandis*), by chemical and physical methods identified from literature. The methods investigated were; cationisation, carboxymethylation and ultrasound treatment. The modified hemicelluloses were applied as a wet-end additive to *E. grandis* pulp to test their effect on strength properties. An addition protocol for the new hemicelluloses additives was developed in this investigation.

The *E. grandis* glucuronoxylan was extracted by using the mild alkali extraction method of Höije *et al*. The characterization of the extracted solids from the pure *E. grandis* chips showed that 4-O-methylglucuronoxylan was extracted with an average uronic acid content of 17.3 wt.%. The hemicelluloses yield was 50.75 wt.%, based on dry biomass, containing 40.76 wt.% xylose units. The solids still contained 26.6 wt.% lignin after extraction. The presence of lignin in the extracted solids indicated that the delignification step in the extraction method used, was not sufficient for the *E. grandis* biomass. The molecular weight of the extracted glucuronoxylan was 51 589 $g.mol^{-1}$.

It was proven that the modification methods from literature are applicable to *E. grandis* glucuronoxylan, producing cationic, carboxymethyl and low uronic acid content 4-O-methylglucuronoxylan. The cationic *E. grandis* glucuronoxylan produced had a degree of substitution between 0.05 and 0.73 and an uronic acid content ranging between 6.12 and 12.70 wt.%. The carboxymethylated *E. grandis* glucuronoxylan had a degree of substitution between 0.05 and 0.11 with a uronic acid content between 10.2 and 21.4%. The sonication of *E. grandis*

glucuronoxylan resulted in products with molecular weights ranging from 54 856 to 57 347 g.mol^{-1} and uronic acid contents between 13.0 and 18.4 wt.%.

Handsheet formation with the modified hemicelluloses added, showed that the cationic *E. grandis* glucuronoxylan improved handsheet strength and surface properties the best. Cationic *E. grandis* glucuronoxylan also outperformed the industrial additive, cationic starch at a dosage level of 1.0 wt.%. The addition protocol development for cationic *E. grandis* glucuronoxylan showed it is possible to add cationic hemicellulose before refining, which results in maximum contact time with the pulp fibres without inhibiting the effect of the additive. Cationic hemicellulose additive added before refining led to a decrease in refining energy required to reach the desired strength properties.

It was concluded that the cationisation and carboxymethylation methods chosen from literature were applicable to the South African grown *E. grandis* glucuronoxylan. The cationic glucuronoxylan showed the best improvement in handsheet strength and surface properties. Cationic *E. grandis* glucuronoxylan could be added before refining in the papermaking process for maximum effectiveness of this new strength additive. The use of hemicellulosic additives will be more sustainable than starch, due to the presence of hemicelluloses in the initial biomass that enters the pulp and paper process.

OPSOMMING

Hemisellulose is die mees volopste plantpolisakkariede naas sellulose, alhoewel die industriële gebruik van hierdie hemiselluloses tans nog beperk is. In die huidige verwerking van hout met behulp van die Kraft verpulpingsproses word die hemiselluloses gedegradeer na lae molukulêre massa isosakkariniese sure wat saam met die lignien in die swartloog afvalstroom eindig. Die ekstraksie van hierdie hemiselluloses vóór die verpulpingsproses, en latere byvoeging as 'n sterktebymiddel in die papier vervaardigings proses, kan die papier treksterkte, bars-, en skeur eienskappe verbeter. Dit is aangetoon dat die ekstraksie van hemiselluloses vóór die verpulpingsproses nie die opbrengs en kwaliteit van papierprodukte negatief beïnvloed nie.

Die doelwit van hierdie projek was om die modifikasie van hemiselluloses, ge-ekstraheer uit *Eucalyptus grandis* (*E. grandis*) hout vóór verpulping, deur middle van chemiese en fisiese metodes uit literatuur te ondersoek. Die projek het spesifiek gefokus op glukuronoxilaan verkry uit *E. grandis* en wat gemodifiseer is met met behulp van kationisasie, karboksimetilering en ultraklank behandeling. Die gemodifiseerde hemiselluloses is daarna benut as 'n nat-kant bymiddel tot *E. grandis* pulp, om die sterkte eienskappe van papier te ondersoek. 'n Toevoegingsprotokol is vir die nuwe hemisellulose bymiddel ontwikkel in hierdie ondersoek.

Die glukuronoxilaan is deur middle van die matige alkali-ekstraksie metode van Höije geekstraheer. Karakterisering van die vastestof residu wat uit die suiwer *E. grandis* biomassa geekstraheer is het getoon dat 4-O-metielglukuronoxilaan geëkstraheer is, met 'n gemiddelde glukuronosuurinhoud van 17.3 massa%. Die hemisellulose opbrengs was 50.75 massa%, gebaseer op droë biomassa, en dit het 40.76 massa% xylose-eenhede bevat. Die lignieninhoud van die soliedes was 26.6 massa% na ekstraksie. Die teenwoordigheid van die lignien het daarop gedui dat die delignifikasie (van die metode) van *E. grandis* biomassa nie voldoende was nie. Die molekulêre massa van die geëkstraheerde glukuronoxilaan was 51 589 $g.mol^{-1}$.

Dit is bewys dat die modifikasiemetodes toepasbaar is op die *E. grandis* glukuronoxilaan, en dat kationiese, karboksiemetiel en lae glukuronosuur 4-0-metielglukurono-xilaan geproduseer is. Die kationiese glukuronoxilaan het 'n graad van substitusie tussen 0.05 en 0.73 gehad, met 'n glukuronosuur inhoud tussen 6.12 en 12.70 massa%. Die karboksiemetielglukuronoxilaan het 'n

graad van substitusie tussen 0.05 en 0.11 gehad, met glukuronosuurinhoude tussen 10.2 en 21.4 massa%. Die ultraklankbehandelde glukuronoxilaan het molekulêre massas tussen 54 856 en 57 347 $g.mol^{-1}$ gehad met glukuronosuurinhoude tussen 13.0 en 18.4 massa%.

Papier handvelproduksie van die pulp waar tydens die gemodifiseerde hemiselluloses toe gevoeg is, het aangedui dat die kationiese *E. grandis* glukuronoxilaan die grootste sterkte- en oppervlakeienskappe verbetering getoon het. Die kationiese glukuronoxilaan het ook, in terme van verbetering van pulpeienskappe, die industrieële kationiese stysel bymiddel oortref, by 'n doserings vlak van 1.0 massa%. Die toevoegingsprotokol ontwikkeling vir die kationiese *E. grandis* glukuronoxilaan het getoon dat hemiselluloses byvoeging tot die papiermaakproses vóór die raffinerings stadium die mees gunstige was, met dosering tussen 0.5 en 2.0 massa%. Die byvoeging van kationiese hemiselluloses vóór raffinering het gelei tot 'n afname in raffineringsenergie wat benodig word om die verlangde sterkteeienskap te verkry.

Dit is bevesting gekose kationisasie- en karboksimetilerings metodes toepasbaar op die Suid Afrikaanse *E. grandis* glukuronoxilaan was. Die kationiese glukuronoxilaan het die grootste verbetering in pulpeienskappe, in terme van handvelsterkte en oppervlakeienskappe, getoon. Kationiese glukuronoxilaan moet vóór raffinering tot die papiermaakproses bygevoeg word vir maksimum doeltreffendheid van hierdie nuwe sterktebymiddel. Die gebruik van hemisellulose bymiddels sal meer volhoubaar wees as stysel, omdat die hemiselluloses wat in die biomassa aanwesig is, in die proses teruggrplaas word.

ACKNOWLEDGEMENTS

I would like to thank following people for all their invaluable help during the course of my M.Sc.Eng degree:

- First of all my supervisors Dr. Annie Chimphango and Prof. Johann Görgens, for their support, patience, and guidance over the past two years.
- Stephen Brent, my SAPPI mentor who was invaluable in procuring knowledge from the industry and helping me whenever I asked for it.
- SAPPI, for the financial support to be able to live and study in Stellenbosch for the duration on my studies.
- PAMSA for the opportunity to do this project and the funding.
- My girlfriend, for all her help, encouragement and making all the hardships worthwhile to endure.
- My friends, old and new, for making the time in Stellenbosch pleasant.
- Phumla Vena, for all the favours and help at the beginning of the project.
- Jan-Erns Joubert, my fellow PAMSA student, for his help and friendship through out the project.
- My parents, for their support during two more years of unemployment.
- To all the people that are not mentioned here, especially the technical and analytical staff at the process engineering and forestry departments. Here I would especially like to thank Manda Rossouw for her help in developing a protocol for the SEC columns that we purchased.
- But most importantly our Heavenly Father and Jesus Christ, for without His grace I would not have been able to finish this degree.

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ABBREVIATIONS

Abbreviation	Abbreviated word
CCD	Central Composite Design
CP/MAS	Cross Polarization Magic Angle Spinning
DS	Degree of Substitution
E. grandis	*Eucalyptus grandis*
ETA	2,3-epoxypropyltri-methylammonium chlorine
F. sylvatica	*Fagus sylvatica* (Beech)
FT-IR	Fourier Transform Infrared
HPLC	High Performance Liquid Chromatography
MCA	Monochloroacetic acid
MW	Molecular weight
NMR	Nuclear Magnetic Resonance
P. abies	*Picea abies*
PHWE	Pressurised Hot Water Extraction
SEC	Size Exclusion Chromatography
SMCA	Sodium monochloroacetate
wt.%	weight percentage

CHAPTER 1

INTRODUCTION

From the first time words were put into the written form, a suitable medium to write upon has been sought after. Early cave paintings, stone tables and hieroglyphics on stone walls were the earliest writing mediums. These writing mediums lacked portability, and a new, more convenient medium was needed. This need for a more convenient writing medium led to the development of papyrus, parchment, vellum and finally paper as we know it (Ciullo, 1996). In the paper and paperboard industry there are three main categories of products; packaging, printing and writing, and absorbing and wiping (Hubbe, 2006).

Within these categories the products have different strength and other physical properties. Some of the classification properties are basis weight, tensile and burst strength, tear resistance, weight of water adsorbed, brightness and permeability of gases and liquids. These properties arise from the different inter-fibre bonding phenomena between the cellulose fibres. Virgin cellulose fibres are expensive to produce, thus non-cellulosic strength additives have been developed to get the desired properties with the minimum amount of cellulose fibres. Better inter-fibre bonding characteristics are the most important goal of strength additives which in turn results in higher quality paper (Hubbe, 2006).

Recently focus has fallen on the development of "green" additives in order to decrease the carbon foot print and improve the environmental impact of the pulp and paper industry. Development of additives from natural biomass sources are being chosen over the conventional synthetic/plastic or mineral additives (O'Byrne, 2009). One of the natural biomass additive groups that are getting much attention are native and modified hemicellulose based additives (Lima *et al.*, 2003; Ren *et al*, 2009; Rojas & Neuman, 1999; Schönberg *et al.*, 2001). Hemicelluloses are the second most abundant plant polysaccharide next to celluloses (Ren *et al.*, 2009). These polysaccharides are attractive as "green" additives because they are already present in the initial biomass that enters the pulp and paper mill (Fengel & Wegener, 2003). They should only be liberated from the biomass prior to pulping.

The biomass that is used to produce paper consists of five major components; cellulose, hemicelluloses, lignin, extractives and ash. The cellulose is used to produce paper, thus the remaining components need to be removed. During delignification in the Kraft pulping phase, the hemicellulose fraction of the biomass is degraded into isosaccharinic acids. These isosaccharinic acids end up in the black liquor and are burned in the recovery furnace (Al-Dajani & Tschirner, 2008). This is not the most efficient use of isosaccharinic acids due to their low calorific value (Al-Dajani & Tschirner, 2008). Burning of the hemicelluloses can be avoided by extracting them prior to pulping.

There are a number of advantages to the pre-extraction of hemicelluloses at a pulp and paper mill, with some of the advantages being;

- The opportunity to produce value added products in a Kraft mill integrated biorefinery from an otherwise waste material. This will improve the overall economics of the pulp and paper mill due to the production of value added products (Al-Dajani & Tschirner, 2008; Huang *et al.*, 2010; Mao *et al.*, 2009).
- Reintroduction of the extracted hemicelluloses into the wet-end of the papermaking process which has been confirmed to improve the strength properties of the paper produced (Gírio *et al.*, 2010; Kabel *et al.*, 2007; Linder *et al.*, 2003; Mao *et al.*, 2009; Satavolu & Mishra, 2010; Schönberg *et al.*, 2001).
- Improvement of yield and kinetics of delignification in the pulping section which will lead to less expensive and less intrusive pulping (Kerr & Goring, 1974; Subramaniyan & Prema, 2000).
- Reduction in the amount of white liquor used for the Kraft pulping section, since delignification is improved (Al-Dajani & Tschirner, 2008).
- The pre-extraction of hemicelluloses can be done in a manner that does not adversely affect the downstream papermaking process. It has been shown that producing paper from pre-extracted pulp delivers paper with a slightly lower tensile index but with improved brightness and shive content (Al-Dajani & Tschirner, 2008).

These advantages have only recently been applied to large scale industrial applications by Al-Dajani & Tschirner (2008).

The aim of this project was to investigate the extent to which hemicellulose additives can be improved by chemical and physical modifications. The hemicelluloses were extracted from woody biomass and then modified by cationisation, carboxymethylation or ultrasound treatments. The modified hemicelluloses were then tested as wet-end dry strength additives to handsheets. The addition method of cationic hemicellulose was investigated as well. The mind map of the thesis with a layout of the experimental work is given in Appendix A.

1.1 Research objectives

- Establish suitable chemical and physical methods from literature that are applicable for modifying the functional properties of extracted hemicelluloses.
- Determine the effect that these modification methods have on the chemical structure of the extracted hemicelluloses.
- Investigate the effect the different modified hemicelluloses have on the physical and surface properties of handsheets when they are used as wet-end additives.
- Develop an addition protocol to introducing hemicellulose as a wet-end additive to the papermaking process, by testing for the optimum position of addition.

1.2 Hypotheses

- Modification of hemicelluloses by different methods affects the paper strength properties differently.
- Different methods of introducing hemicelluloses as wet-end additives improve strength and physical properties of paper differently.
- Modified hemicelluloses as wet-end strength additives improve paper strength and other physical properties comparably to industrial additives such as cationic starch and alkylketene dimer (AKD).

CHAPTER 2

LITERATURE REVIEW

2.1 The pulp and paper industry

Woody biomass is one of the most abundant renewable raw materials available to the industrial sector, and is presently underutilised. Woody biomass is a widely classified term used for biological plant matter from trees. Woody biomass is abundant, renewable and sustainable when managed correctly. One of the oldest applications of wood based biomass is papermaking (Ciullo, 1996). The pulp and paper industry has grown to one of the most important biomass based industrial sectors. The chemical components present in woody biomass that enter a pulp and paper mill are cellulose, hemicelluloses, lignin, extractives, and inorganic matter (ash). These components differ in amount, and type, between tree species (Fengel & Wegener, 2003). The chemical composition of woody biomass can be divided into the main macromolecular cell wall - and minor low-molecular-weight components. The main macromolecular cell wall components are cellulose, hemicelluloses, and lignin. These substances are present in all woody biomass independent of type or species and only differ in the amount and type present. The minor low-molecular-weight components, which are extractives and mineral substances, are more dependent on the wood type and species. The type and quantity of the extractives and minerals varies between species (Fengel & Wegener, 2003).

The processing of the woody biomass in principle are the same at all paper mills which consist of the following stages (Holik, 2006); preparation of fibre material, sheet or web forming, pressing, drying, sizing, and calendering (Bierman, 1996; Holik, 2006). The papermaking process can be divided into different process stages which are biomass preparation, pulping, bleaching, and paper formation (Bierman, 1996; Holik, 2006). The objective of Kraft pulping is to liberate the cellulose fibres in the biomass by using chemicals, heat and pressure (Bierman, 1996). This is achieved by breaking the bonds of the lignin macromolecule and thus delignifying the biomass (Holik, 2006). The two major chemicals in the Kraft pulping process are sodium hydroxide (NaOH) and sodium sulphide (Na_2S). These two chemicals are also responsible for the dissolving of the hemicellulose fraction of the biomass. Due to this dissolving, and the harshness of the Kraft pulping process, the hemicelluloses are degraded into low molecular weight isosaccharinic acids. These isosaccharinic acids are

subsequently removed along with the black liquor from the pulping plant, which is then burnt in the soda recovery furnace (Magaton *et al.*, 2011). This hemicellulose fraction of the biomass can be extracted before pulping with little to no effect on the paper product that is produced (Al-Dajani & Tschirner, 2008). If the hemicelluloses are extracted before pulping it can produce new revenue adding streams for a pulp and paper mill (Al-Dajani & Tschirner, 2008; Magaton *et al.*, 2011)

To determine whether it is worthwhile to extract hemicelluloses from woody biomass entering a pulp and paper mill, the pulp and paper industry is investigated. The projected global consumption of paper and paperboard products for the period of 2005 to 2021 is given in Figure 2.1.

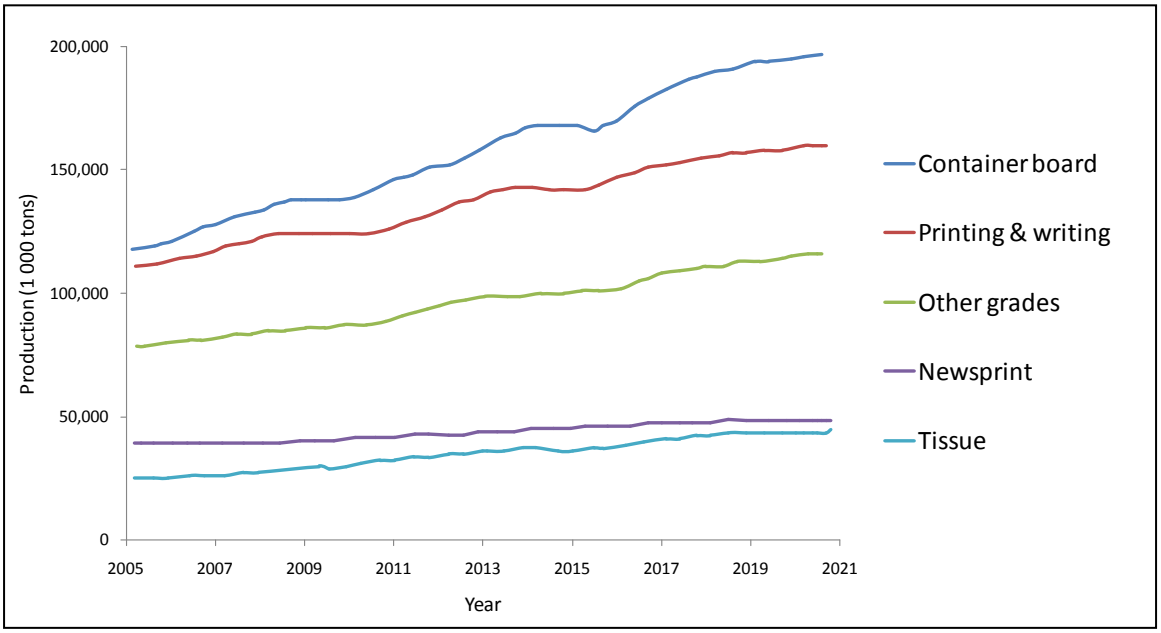


Figure 2.1: Global paper and paperboard consumption by grade for period 2005 to 2021 (redrawn from Roberts, 2007)

Figure 2.1 indicates that there is a growing trend in container board and printing & writing paper consumption through-out the world. If these growing consumption needs are to be fulfilled, process improvements and new technology developments are required to ensure that the industry is sustainable in the future. The annual 2010 production and consumption values for pulp and paper throughout the world, and more specifically for South Africa, are given in Table 2.1.

Table 2.1: Worldwide and South African pulp and paper production and consumption values for 2010 (Whiteman *et al*., 1999)

		Production (million tons)	Consumption (million tons)
Worldwide	Pulp	208.009	207.540
	Paper	392.952	390.950
South Africa	Pulp	1.888	1.693
	Paper	2.439	2.616

These values indicate that there are large quantities of hemicelluloses that can be extracted from the initial biomass of these processes. South Africa produces around 1% of all pulp and paper produced worldwide (Whiteman *et al*., 1999), with over 1.5 million hectares of South African land covered with industrial tree plantations. The pulp and paper industry is the main consumer of these plantations. The major genera's planted in these plantations are species of *Pinus*, *Eucalyptus*, and *Acacia.* These plantations consist of 54.1% *Pinus*, 37.2% *Eucalyptus*, and 8.1% *Acacia* (Paper Manufacturers Association of South Africa, 2008).

The *Eucalyptus* genera is the largest source of market pulp worldwide, with *E. grandis* becoming one the largest sources of fibres for the pulp and paper industry. This is due to its low production cost and high pulping yield (Magaton *et al*., 2009). In South Africa the most abundant species of *Eucalyptus* are *E. grandis* and *E. nitens* that are used as raw material for pulp and paper production (Meadows, 1999). *E. grandis*, also known as the flooded- or rose gum, is a hardwood native to Australia with exotic ranges growing in South Africa, Zimbabwe, Angola and Brazil (Orwa *et al*., 2009). *Eucalyptus* pulp fibres are the most desirable fibres in the market to date, since the fibres are excellent for producing tissue, printing and writing paper and the so called "new products". It is predicted that by 2015 the *Eucalyptus* genera will be providing 25% of the 70 million ton pulp market (Magaton *et al*., 2009). *E. grandis* is a suitable feedstock for hardwood hemicellulose, glucuronoxylan, extraction, since it contains approximately 20% of this plant polysaccharide (Emmel *et al*., 2003; Cotterill & Macrae, 1997).

The *Pinus* genus is the most abundant softwood in South Africa, consisting of 54.1 % of the national plantations (Paper Manufacturers Association of South Africa, 2008). *Picea abies*, which is comparable to *Pinus patula*, is one of the most abundantly grown tree species in the northern parts of Europe, where it is used for the pulp and paper industry (Nabuurs *et al*., 2002; Skrøppa, 2003; Yrjölä, 2002). The importance of *P. abies* and *Pinus,* in general, in the pulp and paper industry is due to the high quality of the timber and its long fibres (Skrøppa, 2003). *P. abies*, also known as Norway

spruce, is a softwood species which is native to predominantly Europe, Canada and the U.S.A. *P. abies* is a high quality timber which has long fibres when pulped, which is used to produce products like stencil paper and packaging material (Skrøppa, 2003). *P. abies* is one of the major wood species in the European countries, where the *Picea* genus make up 35.1% of the forests (Yrjölä, 2002), with an annual production of 80.58 million tons in 2010 (Nabuurs *et al.*, 2002). *P. abies* is a suitable feedstock for softwood hemicellulose, galactoglucomannan, extraction since it contains approximately 20% of this plant polysaccharide (Willför *et al.*, 2005; Lundqvist *et al.*, 2002), which is comparable to the hemicelluloses in *Pinus* grown in South Africa.

2.2 The papermaking process

The papermaking process hasn't changed significantly over the last couple of decades. There have been improvements in sections like pulping, which led to sulphur free pulping, microcrystalline cellulose, extended modified continuous cooking (EMCC) and low solids pulping (Bierman, 1996; Holik, 2006). In the bleaching sections improvements such as elemental chlorine free (ECF) and total chlorine free (TCF) bleaching have been made (Holik, 2006). There have also been some mechanical innovations, derived from the better understanding of the underlying principles, which improved the paper making process. This investigation focused on Kraft (sulphate) pulping, which is a chemical means of liberating the cellulose fibres from the biomass, and the Fourdrinier papermaking machine where the paper is formed (Bierman, 1996). These processes were chosen since they are predominantly used in the South African pulp and paper industry and are therefore a suitable starting point for testing hemicelluloses strength additives. A simplified block flow diagram of the papermaking process as it is used in a South African pulp and a paper mill is given in Figure 2.2 (Brent, 2010).

As discussed in Section 2.1, the hemicelluloses fraction of the biomass is degraded to isosaccharinic acids during the Kraft pulping section. The calorific value of these isosaccharinic acids are low and are therefore not an essential part of the black liquor stream that is used for steam generation (Al-Dajani & Tschirner, 2008; Marinova *et al.*, 2009). Approximately 20% of the dry biomass consists of hemicelluloses (Fengel & Wegener. 2003). These hemicelluloses can be extracted prior to pulping which improves delignification kinetics in the pulping section (Al-Dajani & Tschirner, 2008; Kerr & Goring, 1974).

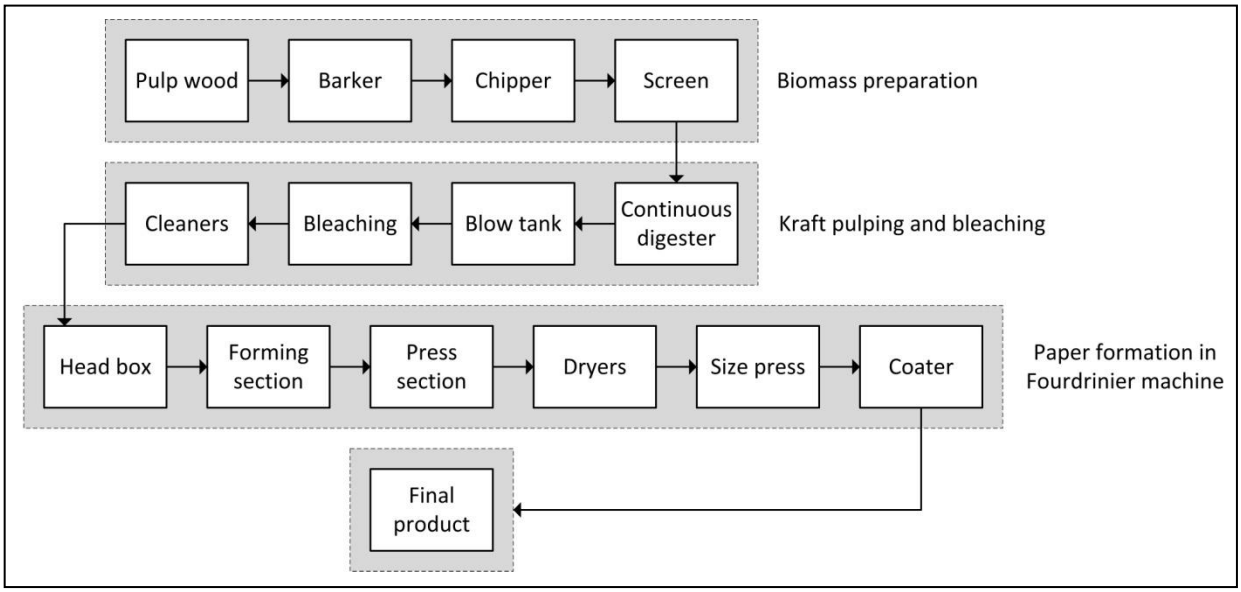


Figure 2.2: Block flow diagram of papermaking process in South Africa (Brent, 2010)

During Kraft pulping the pore size in the cell wall of the fibre and the size of the extracted lignin macromolecules increase. When hemicelluloses are removed prior to pulping, the pores and lignin macromolecules increase in size and subsequently improve the kinetics of delignification (Kerr & Goring, 1974). If an alkaline extraction method is used for hemicellulose extraction, the amount of white liquor necessary for the pulping section is reduced as well (Al-Dajani & Tschirner, 2008). The pre-extraction of hemicelluloses has been shown to have little to no effect on the paper quality that is produced from the hemicelluloses free pulp (Al-Dajani & Tschirner, 2008). The steam generation from the energy recovery furnace decreases by 10% when the isosaccharinic acids are absent from the black liquor (Al-Dajani & Tschirner, 2008; Marinova *et al.*, 2009).

The economic value of hemicelluloses is the driving force behind the recent interest in this biopolymer. When the isosaccharinic acids are burnt with the black liquor the value is R 350 per ton of hemicellulose. If it is pre-extracted and converted to value added products, such as biopolymers, the worth increases to between R 3000 and R 21 000 per ton of hemicellulose (Chimphango, 2010; Kekacs, 2007). This is a considerable increase in value, which will improve existing pulp and paper mill economics.

The Fourdrinier papermaking machine transforms the cellulose fibres into the paper product. In the Fourdrinier machine, additives and dyes are added to the cellulose pulp to give the paper or paperboard the desired properties. The machine consists of a headbox, Fourdrinier wire, presses, dryers, size press, calenders and winders (Bierman, 1996; Holik, 2006; Terblanche, 2010). The Fourdrinier machine is divided into a wet- and dry-end; the wet-end extends from the headbox to

the press section, while the dry-end stretches from the press section to the winder (Bierman, 1996; Holik, 2006; Terblanche, 2010). The paper additives are either added before the headbox or the size press depending of the type of additives that need to be added (Terblanche, 2010).

2.2.1 Additives to the papermaking process

The most important parameter in the papermaking process is the development of the strength properties during sheet formation, consolidation, and drying in the Fourdrinier machine. The strength of paper originates from the fibre-to-fibre bonds (hydrogen bonding), which occur in the sheet forming section (the wet-end) (Ahrenstedt *et al.*, 2008). The use of strength additives for the papermaking process is important to ensure that the products are fit for their specific purpose. Strength additives were developed to produce paper with specific strength and surface properties, while using the minimum amount of celluloses fibres (Hubbe, 2006). This is more economic since additives are, in most cases, less expensive to produce than virgin cellulose fibres (Goyal, 2010).

The addition of the additives can either take place before sheet formation, i.e. internally at the wet-end, or after drying, i.e. surface addition at the dry-end. The additives used in the paper industry are categorized as process- or functional additives (Othmer, 2007):

- Process additives improve the runability of the paper machine. The runability of a paper machine is improved by additives such as retention and drainage aids, biocides, dispersants, and defoamers. These additives are predominantly added at the wet-end of the paper machine.
- Functional additives are used for altering specific properties of the paper product. Materials such as fillers, sizing agents, dyes, optical brighteners, and wet- and dry-strength additives are categorised as functional additives. Some of the properties that are altered are tensile and burst strength, tear resistance, brightness, roughness, weight of water adsorbed, and the permeability of air and water. These additives can be added either at the wet- or dry-end of the paper machine.

There are a considerable number of strength additives available to the paper industry. Strength additives are classified either as wet- or dry-strength additives (Hubbe, 2010). The wet-strength of a sheet of paper implies that a sheet will maintain a high level of its strength even when it is saturated with water. It is typically necessary to maintain between 20 and 40% of its strength while wet

(Bierman, 1996). This is important for the forming section in the paper machine as the paper will be formed and pressed more easily without any breaks in the paper web during formation (Hubbe, 2010). Wet-strength additives form covalent bonds between the pulp fibres, or form their own cross linked network of covalent bonds, thus improving the wet-strength (Bierman, 1996). The dry-strength of a sheet of paper is defined as the force or energy that is required to break a paper sample; examples of this are the tensile and burst strength of a dry piece of paper (Hubbe, 2010). Dry-strength additives have a more pronounced effect on the internal bonding in paper (Bierman, 1996). A list of some commercially available wet- and dry- strength additives is given in Table 2.2 (Ahrenstedt *et al.*, 2008; Bierman, 1996; Othmer, 2007; Valton *et al.*, 2004).

Table 2.2: List of available wet- and dry-strength additives (Ahrenstedt *et al.*, 2008; Bierman, 1996; Othmer, 2007; Valton *et al.*, 2004)

Wet-strength additives	Dry-strength additives
Cationic styrene maleimide resin (SMA imide)	Natural, anionic, cationic, and amphoteric starches
Urea-formaldehyde resin (UF)	Carboxymethylcellulose (CMC)
Melamine - formaldehyde resin (MF)	Natural gums
Amino polyamide - epichlorohydrin resin	Cationic and amphoteric guar derivatives
Polymeric amine - epichlorohydrin resin	Xyloglucan
Aldehyde - modified resin	Anionic and cationic acrylamide polymers

Starches are some of the most common dry strength additives that are used in the paper industry, and the mechanism of its effect on paper is almost the same as that of hemicelluloses (Bierman, 1996). Generally starches are used as a dry strength additive and surface improvement aid; however for the alkaline papermaking process starch is a critical part of wet-end sizing (Bierman, 1996; Holik, 2006). Starch can be used in its natural- or derivatised form (Anil, 2010). Natural starch is difficult to retain on the pulp fibres, therefore cationic starch was developed. Cationic starch is currently the most commonly used dry-strength additive in the paper industry (Bierman, 1996; Cargill, 2011). Starch is more commonly known as a food source rather than a strength additive to the papermaking process (BeMiller & Wistler, 2009). For the pulp and paper industry to lower its carbon footprint, there should be a shift toward more sustainable additives.

Cellulose based paper, in its pure form, is an environmentally friendly product. This is because the cellulose fibres are liberated from renewable resources and are completely recyclable and biodegradable (O'Byrne, 2009). There are however very few paper products that aren't incorporated with the use of minerals or chemicals. These minerals and chemicals negatively affect the recyclability and biodegradation profile of the paper, but are necessary to improve the

papermaking process and products (O'Byrne, 2009). Therefore the development of "green" additives from natural biomass sources are being chosen over the conventional synthetic/plastic or mineral additives (O'Byrne, 2009). One of the natural biomass additives groups that are getting much attention are hemicelluloses based additives (Erhard & Fiedler, 2009; Kohnke *et al.*, 2009; Lima *et al.*, 2003; Ren *et al*, 2009; Rojas & Neuman, 1999; Satavolu & Mishra, 2010; Schönberg *et al.*, 2001). These polysaccharides are attractive as "green" additives because they are already present in the initial biomass that enters the pulp and paper mill (Fengel & Wegener, 2003).

2.2.1.1 Hemicelluloses as strength additives

The reason for the interest in using hemicelluloses as strength additives is due to the many free hydrogen and hydroxyl groups available in their chemical structure. When the hemicelluloses are adsorbed onto the cellulose fibres these free hydrogen and hydroxyl groups provide more hydrogen bonding sites (Espy, 1995). The more hydrogen bonding sites there are available on the cellulose fibres, the more tightly bonded the paper web will be (Bierman, 1996; Espy, 1995). Hemicelluloses are naturally interwoven in wood's micromolecular structure, which indicates a strong relationship between hemicelluloses and cellulose (Fengel & Wegener, 2003; Silva *et al.*, 2011). The molecular weight distribution of the hemicelluloses also plays an important role in the extent to which paper strength is improved (Janes, 1968). It is known that higher molecular weight hemicelluloses are more effective than low molecular weight hemicellulose additives (Megaton *et al.*, 2011). Research has shown that the presence of hemicelluloses in the paper web increase the strength properties of the paper because of the above mentioned properties (Hannuksela *et al.*, 2003; Kabel *et al.*, 2007; Linder *et al.*, 2003; Ren *et al.*, 2009; Rojas & Neuman, 1999; Schönberg *et al.*, 2001).

Hemicellulose fuctionalization can be improved by chemical, physical or enzymatic modification (Ren & Sun, 2010; Gatenholm & Tenkanen, 2004). Derivatised hemicelluloses improve paper strength properties more than unmodified hemicelluloses (Linder *et al.*, 2003). In glucuronoxylan, when the glucuronic acid side chains are removed, the solubility of this hemicellulose decreases and allows for stronger bonds within the paper web when added (Linder *et al.*, 2003). Another modification of glucuronoxylan is replacing the glucuronic acid side chains with more reactive or differently charged ion side chains that form stronger bonds than the unmodified hemicelluloses (Ren *et al.*, 2009; Kabel *et al.*, 2007).

Research indicates that the adsorption of hemicelluloses is favoured by papers produced by Kraft pulping (Hannuksela *et al.*, 2003). All the available research has been carried out for biomasses such as sugarcane bagasse, barley husk, and birch. There is however very little, to no research on hemicelluloses extracted from the hardwood species *Eucalyptus grandis* (*E. grandis*) and the softwoods *Picea abies* (*P. abies*) and *Pinus.* These three wood species are of the most abundant raw materials for the pulp and paper industry.

2.2.1.2 Application method of hemicellulose additives

The method of addition of the additives to the papermaking process is an important parameter during the process. If the additive is added in the wet-end of the papermaking machine, the internal bonding of the paper will be affected. If the additives are sprayed on at the dry-end it only affects the outer surface of the paper. The most common addition methods for hemicelluloses from literature are to either prepare a solution of the hemicellulose additive and add it in the headbox (wet-end), or to coat the dry paper produced (dry-end) by spray coating (Ren *et al.*, 2009; Ahrenstedt *et al.*, 2008; Othmer, 2007). Since hemicelluloses are not conventional strength additives to the paper making process there is a need to develop an addition protocol for these new additives.

2.2.2 Physical properties of paper

The end use of a paper product is the determining factor of its physical properties, thus different grades of paper have different physical properties. This indicates that a physical property analysis is necessary to determine the ability of hemicelluloses to manipulate paper properties. Some physical property values for three different grades of paper are given in Table 2.3. (Bierman, 1996; Goyal, 2010; Holik, 2006; Rienzo & Espy, 1996)

Table 2.3: Physical property values for selected paper grades (Bierman, 1996; Goyal, 2010; Holik, 2006; Rienzo & Espy, 1996)

Paper grade	Basis weight ($g.m^{-2}$)	Tensile index ($N.m^{-1}.g^{-1}$)	Burst index ($kPa.m^2.g^{-1}$)	Tear index (mN)	Cobb value ($g.m^{-2}$)	ISO Brightness (%)
Office / Business	80	25 - 88	3.125 - 3.750	6.25 - 7.50	22 - 26	80 - 95
Bleached Kraft	60	33 - 37	2.625 - 3.250	6.87	50	90

Before testing of paper can occur, conditioning of the paper samples is required. The conditioning is done in a temperature, and humidity, controlled room for a set period of time as set out by TAPPI (Technical Association of the Pulp and Paper Industry, 2010). The basis weight is the most fundamental property of paper and is expressed in mass per unit area (Bierman, 1996). Papermakers strive to get the desired properties of the paper with the lowest possible basis weight. This is due to economic and environmental sustainability considerations (Goyal, 2010). The accepted trade tolerance for the basis weight values given in Table 2.3 is ± 5% (Goyal, 2010). The tensile index, which is given in $N.m^{-1}.g^{-1}$, is calculated from the tensile force that is required to produce a rupture in a strip of paper with a width of 15 mm (Bierman, 1996). The tensile index is a representation of the fibre strength, bonding and length and is an indicator of the paper's resistance to web breaking during printing and converting (Goyal, 2010).

The burst index measures the amount of hydrostatic pressure it takes to rupture a piece of paper. The burst index is reported in $kPa.m^{-2}.g^{-1}$, which is acquired by constantly increasing the pressure applied on the piece of paper until it ruptures (Bierman, 1996). The tear index is a measure of the energy that is required to propagate an initial tear through several sheets of paper for a fixed distance (Bierman, 1996). The factors that influence the tear index are fibre length and inter-fibre bonding (Goyal, 2010). It is known that long fibre pulps produce papers with a high resistance to tear, as the long fibres distribute the stress over a larger area, whereas short fibre require strength additives to achieve similar properties (Bierman, 1996; Goyal, 2010; Holik, 2006). The water absorptiveness/Cobb value of paper is the amount of water that is absorbed in a specified period of time (in general 2 minutes is standard). The Cobb value is expressed as weight per unit area (Holik, 2006). The Cobb value is a function of the varying degree of porosity as well as sizing (Goyal, 2010). Paper is made up of randomly arranged fibres, thus creating pores in the structure allowing liquids to penetrate the paper web. The Cobb test is an indication of the level of sizing of the paper. If the paper product does not retain water or ink according to its specifications, sizing will need to be done to correct this (Goyal, 2010).

The ISO brightness of paper is defined as the percentage reflectance of blue light at a wavelength of 457 nm, as the industrial standard (Goyal, 2010). The brightness of paper is a measure of the whiteness (Bierman, 1996; Holik, 2006) The brightness of a paper only adds to the visual nature of the paper in question and doesn't add any strength properties to the paper (Goyal, 2010). This indicates that brightness is a consumer's choice. If the paper or board is to be used for packaging, one of the most important physical properties is the permeability of the material. The permeability

of paper is a measure of the extent it can exclude gases and vapours to pass through. Synonymous to this, it is how easily a fluid is able to move through a porous material (Holik, 2006; Pal *et al.*, 2006). The permeability of paper is dependent on its porosity (Holik, 2006; Pal *et al.*, 2006).

2.3 Hemicelluloses from woody biomass

The method of hemicellulose extraction from woody biomass is an important factor that determines the chemical structure of the isolated hemicelluloses. This will determine the functional properties of the hemicelluloses extracted. For full utilisation of the biomass, knowledge of the chemical composition is needed. The chemical composition of woody biomass can be determined using analytical standards prepared by the National Renewable Energy Laboratory (NREL) and Technical Association of the Pulp and Paper Industry (TAPPI) (National Renewable Energy Laboratory, 2010; Technical Association of the Pulp and Paper Industry, 2010).

Cellulose is the main chemical component in woody biomass consisting of 40 to 45 dry wt. % of wood. Cellulose is a homo-polysaccharide consisting of β-D-glucose monomers bonded by (1→4) glycosidic bonds. Hemicelluloses are non-cellulosic hetero-polysaccharides consisting of the sugar monomers glucose, mannose, galactose, xylose and arabinose. Hemicelluloses consist of 20 to 30 dry wt. % of woody biomass. These hetero-polysaccharides are discussed in Section 2.3.1 in more detail. Lignin, which consists of 25 to 35 dry wt. % of wood biomass, is high molecular weight polymers consisting of aromatic (phenyl propane) building blocks. Low molecular weight substances, which are extractives and ash compromise less than 11 dry wt. % of the wood biomass (Fengel & Wegener, 2003; Bierman, 1996). A representation of the general chemical composition of all woody biomass is given in Figure 2.3 (Fengel & Wegener, 2003).

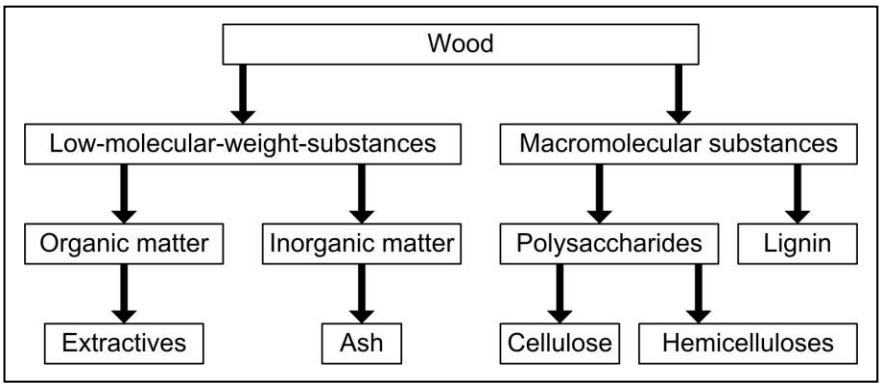


Figure 2.3: General chemical composition of all wood species (redrawn from Fengel & Wegener, 2003)

2.3.1 Hemicelluloses

Hemicelluloses are heterogeneous, non-cellulosic polysaccharidic polymers that are interconnected in the cell wall of woody biomass by covalent bonds and secondary forces (Gatenholm & Tenkanen, 2004). Hemicelluloses consist of both hexose and pentose sugar monomers, which are linked together and can be branched. The pentoses are β-D-xylose and α-L-arabinose, while the hexoses are β-D-mannose, β-D-glucose and β-D-galactose. Some hemicelluloses may contain uronic acids such as 4-O-methyl-β-D-glucuronic and galacturonic acid in the side chains (Gírio *et al.*, 2010). The chemical structures of the sugar monomers that are the building blocks of hemicelluloses are shown in Figure 2.4, with the 4-O-methyl-β-D-glucuronic acid added for convenience (Bierman, 1996).

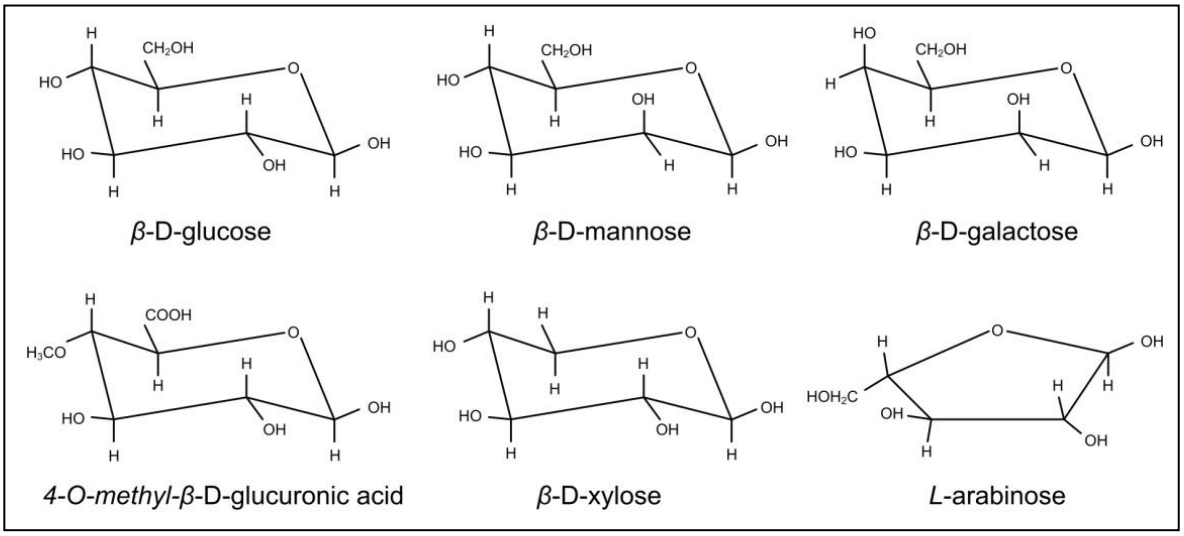


Figure 2.4: Hemicelluloses sugar monomer units (redrawn from Bierman, 1996)

Hemicelluloses are the most abundant polysaccharides in biomass next to cellulose. Hemicelluloses extracted from woody biomass are used in the hydrolyzed form to produce valuable chemicals and fuels via biological fermentation or other processes. In their polymeric form they can be used to produce sustainable films and coatings (Gírio *et al.*, 2010; Hansen & Plackett, 2008; Mao *et al.*, 2009). Hemicelluloses have great potential in the pulp and paper industry beyond being burnt in the energy recovery furnace. The two most abundant woody biomass hemicelluloses are the hardwood glucuronoxylan and softwood galactoglucomannan (Fengel & Wegener, 2003).

2.3.1.1 Glucuronoxylan

O-acetyl-4-O-methyl-glucuronoxylan (glucuronoxylan) is the main hemicellulose present in hardwoods, consisting of approximately 15 to 20 wt% of the dry mass of the wood (Emmel *et al.*, 2003; Cotterill & Macrae, 1997). Glucuronoxylan consists of a linear backbone containing β-D-xylose sugar monomer units bonded together by β-(1→4) glycosidic bonds, with one in every ten xylose units containing a 4-O-methyl-glucuronic acid side group. Glucuronoxylan has an average degree of polymerisation of 100 to 200 (Gírio *et al.*, 2010). The chemical structure of glucuronoxylan is given in Figure 2.5 (Jacobs & Dahlman, 2001).

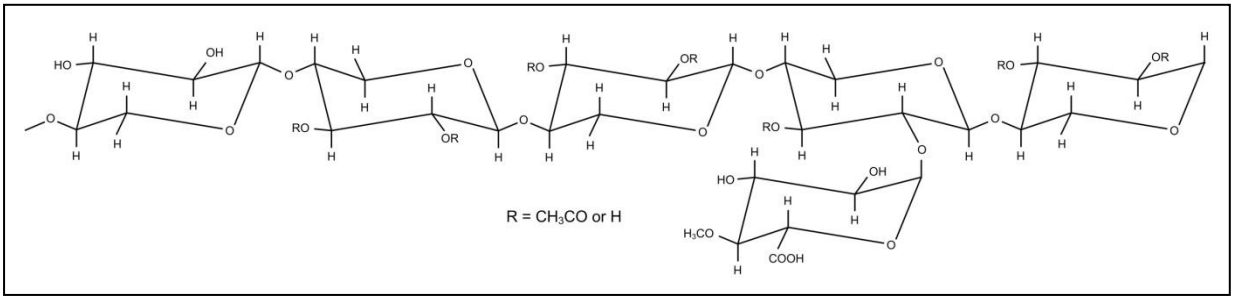


Figure 2.5: Chemical structure of O-acetyl-4-O-methyl-glucuronoxylan (redrawn from Jacobs & Dahlman, 2001)

2.3.1.2 Galactoglucomannan

O-acetyl-galactoglucomannan (galactoglucomannan) is the major softwood hemicellulose consisting of 10 to 20 wt% of the dry mass of wood (Willför *et al.*, 2005; Lundqvist, 2002). Galactoglucomannan consists of a linear backbone of β-D-glucose and β-D-mannose sugar monomers partially acetylated at positions C-2 or C-3 and α-D-galactose groups as side chains. The average degree of polymerisation of galactoglucomannan is 40 to 100, almost half that of glucuronoxylan (Gírio *et al.*, 2010). The chemical structure of galactoglucomannan is given in Figure 2.6 (Jacobs & Dahlman, 2001).

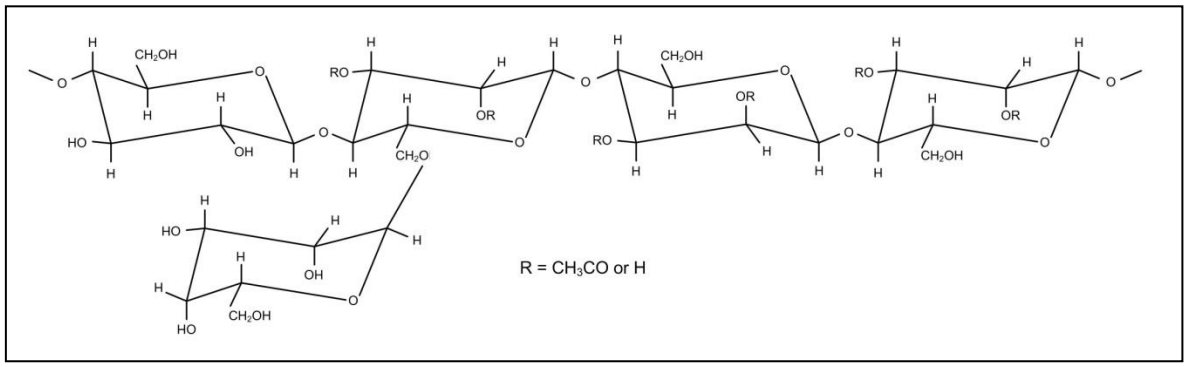


Figure 2.6: Chemical structure of O-acetyl-galactoglucomannan (redrawn from Jacobs & Dahlman, 2001)

2.3.1.3 Chemical composition of *E. grandis* and *P. abies*

The comparison of the chemical composition of the hardwood *E. grandis* and *softwood P. abies* from different literature sources is given in Table 2.4 and 2.5 (Baeza *et al.*, 1991; Cotterill & Macrea, 1997; Emmel *et al.*, 2003; Fengel & Wegener, 2003; Lundqvist *et al.*, 2002; Magaton *et al.*, 2009; Raiskila, 2008; Willför *et al.*, 2005). Table 2.4 and 2.5 show that the chemical composition values of *E. grandis* and *P. abies* from the different literature sources vary considerably. This variability is to be expected as the composition of biomass varies according to location, climate, genetics and position in the tree (Fengel & Wegener, 2003). Therefore, the chemical composition of the South African *E. grandis* feedstock needs to be completed at laboratory scale to have an exact composition that can be used for this investigation.

Table 2.4: Chemical composition comparison of *E. grandis* from literature (Baeza *et al.*, 1991; Cotterill & Macrea, 1997; Emmel *et al.*, 2003; Magaton *et al.*, 2009)

	Reference			
Chemical component	**Baeza *et al.*, 1991**	**Cotterill & Macrae, 1997**	**Emmel *et al.*, 2003**	**Magaton *et al.*, 2009**
Cellulose	53.10%	43.00%	44.65%	ND
Hemicelluloses	22.10%	ND	ND	ND
Xylan	ND	21.00%	15.33%	ND
Mannan	ND	ND	ND	ND
Lignin	24.80%	30.00%	25.77%	ND
Extractives	5.80%	ND	3.25%	0.80 - 2.90%

ND = Not determined

Table 2.5: Chemical composition comparison of *P. abies* from literature (Fengel & Wegener, 2003; Lundqvist *et al.*, 2002; Raiskila, 2008; Willför *et al.*, 2005)

	Reference			
Chemical component	**Fengel & Wegener, 2003**	**Lundqvist *et al.*, 2002**	**Raiskila, 2008**	**Willför *et al.*, 2005**
Cellulose	40.4 - 46.0%	40.0 - 45.0%	40.0 - 44.0%	35.0 - 45.0%
Hemicelluloses	15.3 - 31.1%	ND	25.0 - 29.0%	22.0 - 30.0%
Mannan	ND	20%	ND	11.0 - 17.0%
Xylan	ND	5.0 - 10.0%	ND	6 .0- 8.0%
Lignin	27.3 - 28.2%	26.0 - 32.0%	25.0 - 31.0%	ND
Extractives	1.4 - 4.0%	ND	1.0 - 5.0%	ND

ND = Not determined

2.3.2 Extraction of hemicelluloses from woody biomass

Since the early 1900's researchers have been looking at methods to liberate hemicelluloses from biomass using alkali and acidic solutions (Preece, 1944). The isolation of hemicelluloses is based on the differences in the dissolution properties of hemicelluloses in acid, alkali, water and alcohol solvents. Some of the methods that have been developed are (Chimphango, 2010):

- mild alkali extraction,
- mild acid extraction,
- solvent extraction (organosolv pulping),
- hydrothermal aquasolv extraction, and
- ionic solvents (ionic liquids) extractions.

Each of these methods results in hemicelluloses with different chemical and structural properties, such as molecular weight, galactose content, and uronic acid content. These extraction methods were summarised by Chimphango (2010) and will not be repeated here. For hemicelluloses to be functional as strength additives in the paper making process, the degree of polymerisation needs to be above 40 (Janes, 1968). Therefore it is necessary to extract polymeric hemicelluloses from the woody biomass. The preferred method of extraction for polymeric hemicelluloses is mild alkali extraction (Ren & Sun, 2010). The liberation of hemicelluloses occurs via alkaline hydrolysis of the ester linkages to liberate them from the main macromolecular web in the biomass structure (Gatenholm & Tenkanen, 2004). The liberation of hemicelluloses from this web is limited, among other factors, by the presence of lignin. The presence of lignin is limiting to the extraction process

due to ester and ether lignin-hemicelluloses linkages. With the above mentioned limitations, and the presence of hydrogen bonds between the different polysaccharide components, it becomes extremely difficult to extract hemicellulose in its pure form (Gatenholm & Tenkanen, 2004).

The alkali Höije *et al.* (2005) extraction method was chosen for this investigation due to its ability to extract polymeric hemicelluloses using a sodium hydroxide (NaOH) and sodium borohydride ($NaBH_4$) solution. The Höije *et al.* (2005) extraction method was used by Chimphango (2010) for feedstocks of *E. grandis*, sugarcane bagasse, bamboo, and *Pinus patula*. Thus the method will not be explained here again. The hemicelluloses extracted with this method resulted in polymeric hemicelluloses with a yield ranging between 50 and 83% with molecular weight range of 35 000 and 45 000 $g.mol^{-1}$ (Höije *et al.*, 2005).

2.4 Modification of hemicelluloses

Three of the most important variables that are important in modifying hemicelluloses for use as wet-end strength additives for the pulp and paper industry, are degree of substitution, surface charge and molecular weight. The degree of substitution refers to how many side chains are attached to one sugar monomer unit (Fengel & Wegener, 2003). For example the maximum degree of substitution for a sugar monomer is equal to the amount of free hydroxyl unit available. Research has shown that hemicelluloses with a high degree of substitution of uronic acid or functional groups are not easily adsorbed onto pulp fibres (Ren *et al.*, 2009; Silva *et al.*, 2011). The second variable is the surface charge of the hemicelluloses. Pulp fibres have a natural anionic charge, thus a cationic charge will result in hemicelluloses that are self-retaining on pulp fibres with a greater attraction force than neutrally charged hemicelluloses (Könke *et al.*, 2009; Ren *et al.*, 2009; Ren *et al.*, 2008; Ren *et al.*, 2007; Schwikal *et al.*, 2006). The final variable is the molecular weight; the aim is to produce modified hemicelluloses with the highest possible molecular weight (Hon, 1996; Janes, 1968; Mageton *et al.*, 2011).

2.4.1 Chemical modification methods

The functionalising of the available hydroxyl groups of hemicelluloses changes its properties, such as crystallinity, solubility, hydrophobicity or hydrophilicity (Ren & Sun, 2010). Hemicelluloses are very susceptible to chemical degradation via acid and alkali processes, and great care is required to minimize the degradation of the molecular weight during extraction/modification. This is necessary

since molecular weight plays an important role in hemicelluloses as paper strength additives (Hon, 1996; Janes, 1968; Mageton *et al.*, 2011). The first modification of hemicelluloses was to make xylan solvent soluble for molecular weight determination purposes (Ren & Sun, 2010). There are several chemical methods to modify hemicelluloses for enhanced properties, i.e. (Ren & Sun, 2010; Gatenholm & Tenkanen, 2004):

- partial hydrolysis,
- oxidation and reduction,
- etherification or esterification of the free hydroxyl groups,
- graft polymerisation, and
- cross-linking.

The two modification methods that have been receiving recent focus are etherification and esterification of the hemicelluloses (Ren & Sun, 2010). The esterification of hemicelluloses is attractive due to their easy biodegradability, which makes it compliant with "green" chemistry. Esterification of hemicelluloses can also create thermoplastic hemicellulose-based materials. Other advantages to esterification are a reduction of water absorbency of the hydrophilic hemicelluloses, increased solubility in water and reduced crystallinity (Ren & Sun, 2010, Gatenholm & Tenkanen, 2004). In this investigation the focus will fall on the etherification of hemicelluloses. Some of the reactions that fall under etherification are carboxymethylation, methylation, cationisation, benzylation and sulfoalkylation. The etherification of hemicelluloses leads to advantages such as increased solubility, stability against micro-organisms to prevent spoilage during storage, film forming ability and increased viscosity (Ren & Sun, 2010).

Cationisation and carboxymethylation are the most appealing modification methods of hemicelluloses for use as strength additives for papermaking (Ren *et al.*, 2009; Kobayashi *et al.*, 2002; Kohnke *et al.*, 2009; Tian *et al.*, 2010). The chemical structure of a cationic- and carboxymethyl hemicelluloses derivatives are shown in Figure 2.7 (Ren *et al.*, 2009).

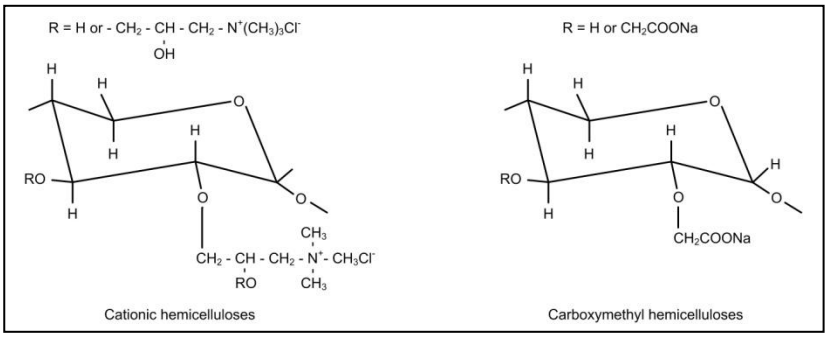


Figure 2.7: Chemical structure of cationic- and carboxymethyl hemicelluloses (redrawn from Ren *et al.*, 2009)

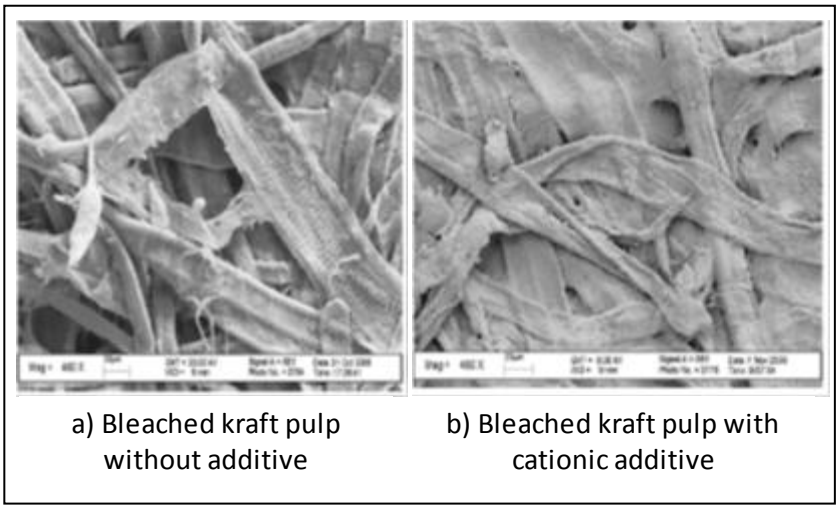
2.4.1.1 Cationisation

The cationisation of hemicelluloses takes place in a similar fashion as it does for cellulose and starch (Ren & Sun, 2010). The advantage of cationisation of hemicellulose is that it enhances solubility, and yields cationic or ampholytic polymers that have similar properties to cationic starch, cellulose and chitosan (Ren & Sun, 2010). These cationic polymers are being used as industrial additives to the papermaking process. Cationic starch is one of the most common sizing agents and strength additives in the pulp and paper industry.

The attractiveness of this modification method is that the cationic hemicelluloses are self-retaining on the anionic pulp fibres (Ren *et al.*, 2009). Research has been done on the synthesis of cationic hemicelluloses. More specifically research has been completed on the effects that different parameters such as temperature and the molar ratio of reagents to the hemicellulose have on the properties of the modified hemicelluloses (Könke *et al.*, 2009; Ren *et al.*, 2009; Ren *et al.*, 2008a; Ren *et al.*, 2007; Schwikal *et al.*, 2006). In all these research papers there is mention of using cationic hemicelluloses as strength additives for papermaking. The only research on using cationic hemicelluloses as papermaking additives were completed by Ren *et al.* (2009) and Könke *et al.* (2009) using bagasse hemicellulose and spruce Kraft pulp to produce handsheets. There is no research data available for the cationisation of hemicelluloses extracted from the hardwood *E. grandis* and softwood *P. abies* biomasses.

With the addition of cationic hemicelluloses to cellulose pulps, the strength properties of the handsheets were improved. With the strength improvement, surface smoothness and bonding strength between the cellulose fibres were improved as well (Ren *et al.*, 2009). The improvement of the surface smoothness of the handsheets is an indication that cationic hemicelluloses serve as

sizing agents as well. The Scanning Electron Microscope (SEM) photomicrographs in Figure 2.8, from the results of Ren *et al*. (2009), shows that the surface smoothness and porosity of the handsheets are lowered with the addition of cationic hemicelluloses. The difference between the two photomicrographs (Figure 2.8a and 2.8b) is that the fibres in the handsheets made with the addition of the cationic hemicelluloses are more tightly bonded and less porous, which will increase strength and decrease the roughness of the paper. The degree of substitution of the cationic side chains is an important parameter in the cationisation modification method and must be controlled correctly. Ren *et al*. (2009) found that cationic hemicelluloses with low degree of substitution values improve handsheet strength properties the most.



a) Bleached kraft pulp without additive

b) Bleached kraft pulp with cationic additive

Figure 2.8: SEM photomicrographs of handsheets with cationic hemicelluloses additives (Ren *et al.*, 2009; permission granted from Elsevier Ltd.)

2.4.1.2 Carboxymethylation

Carboxymethylation is one of the most versatile fuctionalization procedures, which provides hemicelluloses with properties such as thickening, filming, emulsification, suspension, water retaining and binding (Ren & Sun, 2010, Gatenholm & Tenkanen, 2004). Research has shown that carboxymethylated hemicellulose can be used as wet end additives to the papermaking process and that it has the same function as carboxymethyl starch and cellulose (Ren & Sun, 2010). The carboxymethylation of hemicelluloses leads to metal ion side chains. Carboxymethyl hemicelluloses as a strength additive to the papermaking process needs to be used in combination with aluminium sulphate ($Al_2(SO_4)_3$). This is because carboxymethyl hemicelluloses do not self retain on the cellulosic fibres (Ren *et al.*, 2009). The same as with cationisation, research has been done on the synthesis of carboxymethyl hemicelluloses (Kobayashi *et al.*, 2002; Petzold *et al.*, 2006a; Petzold *et*

al., 2006b; Ren *et al.*, 2009; Ren *et al.*, 2008b). The only research completed on using carboxymethyl hemicelluloses as papermaking additives was by Ren *et al.* (2009) using bagasse hemicellulose and spruce Kraft pulp for handsheet formation. The same as with cationisation, the degree of substitution of the side chains in carboxymethylated hemicelluloses is an important parameter on the strength properties of the handsheets (Ren *et al.*, 2009).

2.4.2 Physical modification methods

The use of physical modification methods on hemicelluloses to obtain strength additives for papermaking is limited. There are a number of physical modification methods available to use on hemicelluloses, and some of these methods identified from literature are (Ebringerova *et al.*, 1997; Gadhe *et al.*, 2005; Gassan & Gutowski, 2000; Haimer *et al.*, 2010; Sugiarto *et al.*, 2002):

- thermal processes,
- ultrasound treatments,
- supercritical anti-solvent precipitation,
- pulsed streamer corona discharge, and
- dielectric-barrier discharge.

The advantages of physical modification methods are that they can potentially be used to remove the side chains of hemicelluloses to affect the solubility properties. This is due to a decrease in the uronic acid content of the hemicelluloses (Walker, 1964). There is also potential for physical methods to produce nano particles from hemicelluloses as shown by Haimer *et al.* (2010) by using supercritical carbon dioxide precipitation. The largest disadvantage of physical methods is that they require expensive and specialised equipment that needs to be manufactured. The modification of hemicelluloses using ultrasound and supercritical anti-solvent precipitation methods has been described (Ebringerova *et al.*, 1997; Gadhe *et al.*, 2005; Haimer *et al.*, 2010; Haimer *et al.*, 2008; Sun *et al.*, 2002).

2.4.2.1 Ultrasound

Ultrasound has been used predominantly as an enhancement technique in the extraction of hemicelluloses from lignocelluloses (Hromádková & Ebringerová, 2003; Sun *et al.*, 2002; Sun & Tomkinson, 2002). It has been shown that using high frequency ultrasound on hemicelluloses can liberate the side chains. This is due to the formation of radicals in aqueous medium under the ultrasound conditions, which in turn oxidise the hemicelluloses (Ebringerova *et al.*, 1997; Gadhe *et al.*, 2005). One of the disadvantages of using ultrasound methods is that there is a possibility that the hemicelluloses can be degraded and that the degree of polymerisation could be decreased. This decrease in molecular weight will decrease potential use as a papermaking strength additive (Sun *et al.*, 2002). There is however no research available for using ultrasound to modify hemicelluloses intended for use as a strength additive in papermaking.

CHAPTER 3

EXTRACTION, MODIFICATION AND CHARACTERIZATION OF HEMICELLULOSES

3.1 Introduction

Recently there is a growing interest in using hemicelluloses as biodegradable polymers in similar ways such as cellulose and starch. Unfortunately, hemicellulose is not available in its pure extracted form for industrial use (Chimphango, 2010). Woody biomass contains approximately 40-45 wt.% cellulose, 25-30 wt.% lignin, and 20-30 wt.% hemicelluloses (Fengel & Wegener, 2003; Bierman, 1996). This indicates that there are large quantities of hemicelluloses present in woody biomass that can be utilised as films, coatings, pharmaceuticals, food and other industries applications, as well as additives for the papermaking industry (Ren & Sun, 2010).

Hemicelluloses are heterogeneous, non-cellulosic polysaccharide polymers which are interconnected in the cell wall of woody biomass by covalent bonds and secondary forces (Gatenholm & Tenkanen, 2004). Hemicelluloses consist of both hexose and pentose sugar monomers which are linked together and can be branched in some cases. Some hemicelluloses may contain uronic acids such as 4-O-methyl-β-D-glucuronic acid and galacturonic acid in the side chains (Gírio *et al.*, 2010). Hemicelluloses are the most complex polysaccharides in the cell wall of woody biomass. The covalent bonds that they form with lignin, as well as the extensive hydrogen bonding between the individual polysaccharide cell wall components, restrict the removal of hemicelluloses (Ren & Sun, 2010). Over the last decade, research has been done on many methods of hemicellulose extraction. Some of these methods include alkaline, alkaline peroxide, and steam explosion extraction. There is however no method that can liberate 100% pure hemicellulose from woody biomass (Gatenholm & Tenkanen, 2004; Ren & Sun, 2010).

The modification of hemicelluloses creates novel opportunities to take advantage of the various valuable properties of hemicelluloses that have been overlooked in the past. This modification can include esterification, etherification, graft polymerization, or oxidation (Gatenholm & Tenkanen,

2004; Ren & Sun, 2010). The properties that can be modified are crystallinity, solubility, surface charge, hydrophobicity, or hydrophilicity, by removing or changing the side chains of the hemicelluloses (Gatenholm & Tenkanen, 2004; Ren *et al.*, 2009; Ren & Sun, 2010). Two of the most widely used chemical modification methods for hemicelluloses are cationisation and carboxymethylation which have possible application in the pulp and paper industry (Ren *et al.*, 2009). The physical modification method includes the sonication of the hemicelluloses (Ebringerova *et al.*, 1997; Gadhe *et al.*, 2000).

In this study hemicelluloses were extracted from *E. grandis* feedstock, and then characterised to confirm whether O-acetyl-4-O-methyl-D-glucuronoxylan was extracted. Other hemicellulose samples were obtained from Sigma-Aldrich and Åbo Akademi, Finland. *Fagus sylvatica* (beech) wood glucuronoxylan was obtained from Sigma-Aldrich, and two different *P. abies* O-acetyl-galactoglucomannan samples from Åbo Akademi. These hemicelluloses were then modified using cationisation, carboxymethylation and ultrasound treatments. The modified hemicelluloses were characterised to determine the effect the modification methods had on them. The objectives for this study were:

- Establish and apply suitable chemical and physical methods from literature that are applicable for modifying the functional properties of hemicelluloses.
- Determine the effect that these modification methods have on the chemical structure of glucuronoxylan and galactoglucomannan.

3.2 Materials and methods

3.2.1 Materials

For this investigation four different hemicelluloses were used. These were *E. grandis* 4-O-methyl-D-glucuronoxylan (glucuronoxylan), *Fagus sylvatica* (beech wood) glucuronoxylan, and two differently prepared *P. abies* O-acetyl-galactoglucomannan (galactoglucomannan) samples. A summary of the different hemicelluloses used with their sources and preparation methods is given in Table 3.1. The chemical reagents with their purity as well as sources, used in the study, are given in Table 3.2.

Table 3.1: Hemicelluloses sources and preparation methods

Hemicelluloses	Source	Preparation of hemicellulose	Supplier	Reference
4-O-methyl-D-glucuronoxylan	*Eucalyptus grandis*	Alkaline extraction from *E. grandis* chips and then freeze dried with Höije *et al.* (2005) method. Completed at Stellenbosch University, South Afirca.	*E. grandis* chips from SAPPI's Ngodwana pulp and paper mill	Brent, 2010
4-O-methyl-D-glucuronoxylan	*Fagus sylvatica*	Unknown extraction completed by Sigma-Aldrich with xylose residues larger or equal to 90%.	Sigma-Aldrich	-
O-acetyl-galactoglucomannan	*Picea abies*	Pilot plant extraction using filtration and ultrafiltration and then spray drying. Completed at Åbo Akademi, Finland.	Åbo Akademi, Finland	Willför, 2010
O-acetyl-galactoglucomannan	*Picea abies*	Pressurised Hot Water Extraction (PHWE). Completed at Åbo Akademi, Finland.	Åbo Akademi, Finland	Willför, 2010

Table 3.2: Detailed list of chemicals with their purity level and sources

Chemical name	Molecular formula	Purity	Supplier company
2,3-Epoxypropyl-trimethyl-ammonium chloride	$C_6H_{14}ClNO$	> 99.7%	Sigma-Aldrich
Acetic acid	C_2H_3COOH	> 99.7%	Sigma-Aldrich
Carbazole	$C_{12}H_9N$	99%	Merck
Cellobiose	$C_{12}H_{22}O_{11}$	99%	Sigma-Aldrich
Ethanol	C_2H_5OH	99.9%	United-Scientific (Pty) Ltd.
Galactose	$C_6H_{12}O_6$	99%	Sigma-Aldrich
Galacturonic acid	$C_6H_{10}O_7$	99%	Sigma-Aldrich
Glucose	$C_6H_{12}O_6$	99%	Sigma-Aldrich
Hydrochloric acid	HCl	37%	Sigma-Aldrich
Liquid nitrogen	N_2	99%	Afrox Ltd.
Mannose	$C_6H_{12}O_6$	99%	Sigma-Aldrich
Methanol	CH_3OH	> 99.8%	Sigma-Aldrich
Monochloroacetic acid	$CH_2ClCOOH$	99%	Sigma-Aldrich
Sodium hydroxide	NaOH	> 97%	Sigma-Aldrich
Sodium monochloroacetate	$ClCH_2COONa$	98%	Sigma-Aldrich
Sulfamic acid	H_2NSO_3H	> 99%	Sigma-Aldrich
Sulphuric acid	H_2SO_4	95-98%	Sigma-Aldrich
Sulphuric acid	H_2SO_4	72%	Sigma-Aldrich
Xylose	$C_5H_{10}O_5$	99%	Sigma-Aldrich

3.2.2 Compositional analysis of woody biomass

The compositional analysis of the *E. grandis* samples received from SAPPI was done using analytical methods provided by TAPPI and the NREL (Technical Association of the Pulp and Paper Industry, 2010; National Renewable Energy Laboratory, 2010). The different analytical methods used are given in Table 3.3 and discussed below.

Table 3.3: Compositional analysis methods with analytical codes

Component analysed	Analytical method code	Reference
Size reduction and sample preparation	British Standards DD CEN/TS 14780:2005	British Standards, 2005
Moisture content	NREL/TP-510-42621	National Renewable Energy Laboratory, 2010
Ash content	NREL/TP-510-42622	National Renewable Energy Laboratory, 2010
Water & solvent extractives	TAPPI T 264 om-88	Technical Association of the Pulp and Paper Industry, 2010
Klason lignin	NREL/TP-510-42618	National Renewable Energy Laboratory, 2010
Carbohydrate composition		

3.2.2.1 Sample preparation

A representative sample of the *E. grandis* chips was obtained using the coning and quartering method as described by the British Standards DD CEN/TS 14780:2005 "Solid biofuels - Methods for sample preparation" (British Standards, 2005). Furthermore the cone-and-quartering method was applied subsequent to size reduction to obtain a more representative sample. The *E. grandis* chips were then milled using a Condux-Werk Wolfgang bei Hanau mill to reduce the chips to a size of approximately 10 mm (with the largest dimension being 10 mm). The 10mm *E. grandis* sample was milled using a Retsch ZM200 mill equipped with a 1 mm circular blade to produce samples of approximately +425 µm, which were further milled to approximately +250 µm. The sample was screened in a Retsch AS200 shaker to obtain *E. grandis* fractions between 250 and 425 µm, which were used in compositional analyses.

3.2.2.2 Moisture content

The moisture content of the biomass was determined using the NREL/TP-510-42621 method for the "Determination of total solids in biomass and total dissolved solid in liquid process samples"

(National Renewable Energy Laboratory, 2010). A biomass sample, of particle size between 250 and 425 µm, was placed in an oven at 105 °C overnight and the moisture content was calculated using Equation 3-1:

$$Moisture\ content(\%) = \frac{m_{wet} - m_{dry}}{m_{dry}} \times 100 \quad (3\text{-}1)$$

where m_{wet} is the weight of the sample before it was place in the oven and m_{dry} is the weight after it was left in the oven overnight at 105 °C. The full procedure can be found in the NREL standard.

3.2.2.3 Ash content

The NREL/TP-510-42622 method was used to determine the ash content of the biomass (National Renewable Energy Laboratory, 2010). A biomass sample in a pre-weighed crucible was placed in a Gallenkamp Muffle Furnace at 575 ± 25°C for 3 hours, after which it was cooled down to room temperature in a desiccator and then tared on a balance. The percentage ash in the sample was calculated using Equation 3-2:

$$Ash\ \% = \frac{m_{ash}}{m_{original\ sample}} \times 100 \times Moisture\ correction\ factor \quad (3\text{-}2)$$

where m_{ash} is the weight of the ash and $m_{original\ sample}$ is the weight of the original sample in the crucible. The ash content is based on dry basis of the sample, where the ash content was multiplied with a moisture correction factor which is calculated with Equation 3-3:

$$Moisture\ correction\ factor = \frac{1}{\frac{m_{dry}}{m_{wet}}} \quad (3\text{-}3)$$

where m_{dry} and m_{wet} are the same as in Equation 3-1.

3.2.2.4 Water- and solvent soluble extractives

The water- and solvent soluble extractives contents were determined using the TAPPI T 264 om-88 method (Technical Association of the Pulp and Paper Industry, 2010). The solvent extractives were obtained with a 200 mL solvent mixture of ethanol (CH_3CH_2OH) and cyclohexane (C_6H_{12}) in a 1:2 ratio

(i.e. 73 mL ethanol and 147 mL cyclohexane). The experimental setup was then left to distil over night in a Soxhlet apparatus. After the overnight distillation the solvent was evaporated till the flask was dry and the flask was place in a 105°C oven till dry and then weighed. The solvent extractives percentage was calculated by Equation 3-4:

$$Solvent\ extractives\ \ \% \ = \ \frac{m_{extractives}}{m_{wet\ sample}} \times 100 \ \times MC factor \times Ash\ factor \qquad (3\text{-}4)$$

where $m_{extractives}$ is the weight of the extractives in the flask and $m_{wet\ sample}$ is the weight of the sample placed in the cellulose thimble. The moisture correction factor was calculated with Equation 3-3. The ash correction factor corrects for the presence of ash in the sample and is calculated by using Equation 3-5:

$$Ash\ correction\ factor = \ \frac{1}{1 - oven\ dry\ ash\ content} \qquad (3\text{-}5)$$

After the solvent extractives were obtained, the water extractives were determined in a similar manner as the solvent extractives by substitution of the solvent with 220 mL distilled water. The water extractives percentage was calculated the same way as the solvent extractives, i.e. with Equations 3-3, 3-4 and 3-5.

3.2.2.5 Klason lignin and carbohydrate composition

The Klason lignin and the carbohydrate composition were determined using the NREL/TP-510-42618 method (National Renewable Energy Laboratory, 2010). A mass of 0.3 g of the extractive free, air dry, wood was placed in a glass vial where 3 mL of 72% sulphuric acid (H_2SO_4) was added while gently stirred. The mixture was placed in a Memmert water bath that was pre-set to 30°C for a duration of 1 hour with intermittent stirring every 10 minutes. The sample was then diluted to 3% sulphuric acid by adding 84 mL of distilled water. The sample was transferred to an autoclave flask and autoclaved in a Eastern EA-630 vertical autoclave for 1 hour at a temperature of 120°C and pressure of 0.12 MPa.

The sample was then transferred through a filtering crucible with 200 mL boiling water to wash of any residual reagents and sugars. The solid residue that was left on the filtering crucible was placed in the 105°C oven overnight to dry and then weighed. After this the filtering crucible was placed in

the muffle furnace for a minimum of 4 hours at 575 ± 25°C to determine the ash content left in the lignin. The acid insoluble lignin (AIL) percentage is calculated on a dry and ash free basis by Equation 3-6:

$$AIL\ \% = \frac{m_{AIL} - m_{ash}}{m_{original sample}} \times 100 \times MC\ factor \quad (3\text{-}6)$$

where m_{AIL} is the mass of the solid residue left on the filtering crucible and m_{ash} is the mass of the ash after the filtering crucible had been placed in the muffle furnace and the MC factor is calculated using Equation 3-3. The acid soluble lignin (ASL) was not determined since it was assumed to be negligible. The solution left after the filtering was used for HPLC analysis of the carbohydrate composition of the sample. The solution was neutralized using potassium hydroxide (KOH), to comply with the HPLC specifications. The sample was filtered through a 0.22 µm nylon syringe filter prior to HPLC analysis as presented in Section 3.2.6.1.

3.2.3 Extraction of *E. grandis* hemicelluloses

The extraction of glucuronoxylan from *E. grandis* was done according to the method described by Höije *et al*. (2005). The first step was the milling of the biomass for the extraction of the hemicelluloses; this entailed the size reduction of the *E. grandis* chips to the +250 to -850 µm fraction. The *E. grandis* sample was then de-waxed in 1 L of 0.05 mol.dm-3 hydrochloric acid (HCl) per 100 g of air dry biomass at room temperature for 16 hours. After this the hydrochloric acid was decanted from the biomass.

The pH of 1 L distilled water, per 100 g of sample, was adjusted to 4 by using glacial acetic acid ($C_2H_4O_2$). Subsequently, 22 g of sodium chlorite ($NaClO_2$) was added to the mixture to delignify the sample which was stirred for 2 hours at a temperature of 75°C. The mixture was then left to cool down to room temperature and the solution was decanted off and the fibres subsequently washed with distilled water until the solution was clear. After the biomass was filtered and washed, a 1 L solution of 1 mol.dm^{-3} sodium hydroxide (NaOH) and 0.5 wt% of sodium borohydride ($NaBH_4$) was added to the biomass and allowed to react for 16 hours at room temperature without stirring.

The mixture was filtered using a metal mesh to remove the solid cellulose waste. The solubilised hemicellulose solution was then neutralized using a 1 mol.dm^{-3} hydrochloric acid solution. The neutralised solution was then dialysed for 2 days using distilled water with dialysis tubing made from

a cellulose membrane with a molecular weight cut-off (MWCO) of 12-14 000 $g.mol^{-1}$. The membrane was purchased from Sigma-Aldrich. The distilled water was replaced every 24 hours to ensure complete removal of the salt complexes present in the solution.

The dialysed solution was then evaporated under vacuum using a Büchi RE 121 rotary evaporator installed with an Edwards E2M8 high vacuum pump. The solution was evaporated to remove a third of the water present in the solution. After the evaporation of the water, the solution was freeze dried using liquid nitrogen (N_2). The frozen sample was placed in a VirTis Bench Top 6K model freeze dryer operating at a pressure of 100 mtorr and -60ºC for 3 days. The VirTis freeze dryer was installed with an Edwards high vacuum pump. After 3 days of freeze drying the solid hemicellulose were retrieved and weighed to determine the hemicellulose yield from the extraction run. The Höije *et al.* (2005) procedure is presented more simplified in Figure 3.1.

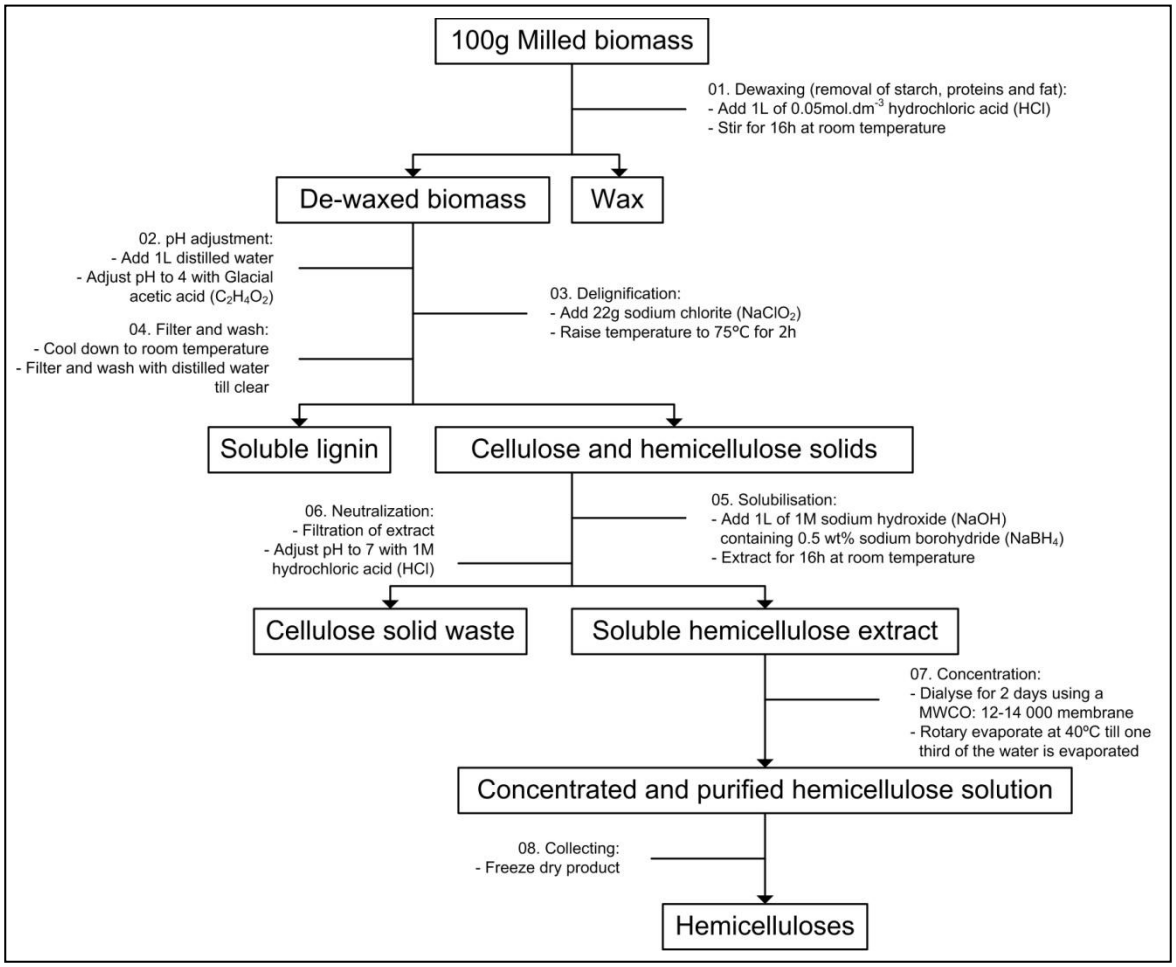


Figure 3.1: Extraction procedure for glucuronoxylan (Höije *et al.*, 2005)

3.2.4 Chemical modification methods

The procedures for the chemical modification of the different hemicelluloses were adopted from literature, however some modifications were made to accommodate for available equipment. The chemical modification methods selected were cationisation and carboxymethylation which where both done according to the following experimental design.

3.2.4.1 Experimental design

The experimental design used for the chemical modification methods was a 2^2 (levels^{factors}) Central Composite Design (CCD). The CCD is represented in Figure 3.2, which shows the different levels and factors included in the experimental design with coded values for the factors (Hinkelmann & Kempthorne, 2008).

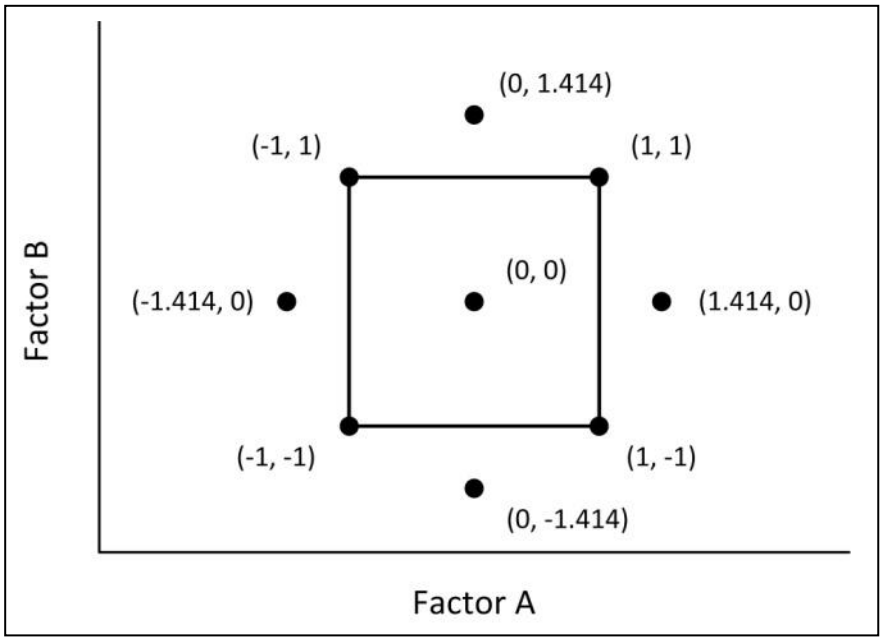


Figure 3.2: Representation of a 2^2 CCD with coded factor values (Redrawn from Hinkelmann & Kempthorne, 2008)

The centre point runs are depicted as the point (0, 0) and the experimental runs done at this point were done 5 times to determine the standard deviation of the points. The design is rotatable, which indicates that the standard deviations of all the points are the same and that the alpha value (α) is 1.414. When the design is done as mentioned above, each chemical modification method will have 13 runs for each feedstock used. The experimental design was done using the program Stat Soft®

Statistica 9.0. Table 3.4 gives a summary of the experimental design that was used for the chemical modification methods.

Table 3.4: Summary of experimental design for modification methods

Property	Description
Design type	2^2 CCD
α-type	Rotatable
α-value	1.414
Number of centre point (0, 0) runs	5
Total number of runs per experiment	13

The CCD was chosen to ensure statistically correct interpretation of the data that was generated from the experiments, by having a structured design to work from and using Stat Soft® Statistica 9.0 to interpret the data correctly. The coded and actual values used in the experimental design for cationisation and carboxymethylation are given in Table 3.5 and 6 respectively.

Table 3.5: Coded and actual values for the CCD design of cationisation

	Factor A (Molar ratio of NaOH to ETA)		Factor B (Molar ratio of ETA to xylose)	
Hemicelluloses type	**Coded**	**Actual**	**Coded**	**Actual**
Xylan and mannan	-1.414	0.10	-1.414	0.50
Xylan and mannan	-1.000	0.38	-1.000	0.87
Xylan and mannan	0.000	1.05	0.000	1.75
Xylan and mannan	1.000	1.72	1.000	2.63
Xylan and mannan	1.414	2.00	1.414	3.00

ETA = 2,3-epoxypropyltrimethylammonium chloride

The experimental setup that was used for the runs of the chemical modification consisted of a magnetic stirrer / hot plate, three necked 250 mL flask, and a condenser. The three necked flask was fitted with the condenser to reduce vapour loss during the experiment leaving 2 necks for trouble-free reagent adding. The three necked flask setup was placed on the magnetic stirrer / hot plate with a magnetic stirring bar inside. This setup allowed for effortless heating and stirring control.

Table 3.6: Coded and actual values for the CCD design of carboxymethylation

	Factor A (Ratio of ethanol to water)		Factor B (Molar ratio of SMCA to xylose)	
Hemicelluloses type	**Coded**	**Actual**	**Coded**	**Actual**
Xylan	-1.414	1.00	-1.414	0.50
Xylan	-1.000	1.15	-1.000	0.87
Xylan	0.000	1.50	0.000	1.75
Xylan	1.000	1.85	1.000	2.63
Xylan	1.414	2.00	1.414	3.00
	Factor A (Molar ratio of NaOH to mannose)		**Factor B (Molar ratio of MCA to mannose)**	
	Coded	**Actual**	**Coded**	**Actual**
Mannan	-1.414	3.38	-1.414	0.50
Mannan	-1.000	3.87	-1.000	0.87
Mannan	0.000	5.07	0.000	1.75
Mannan	1.000	6.26	1.000	2.63
Mannan	1.414	6.76	1.414	3.00

MCA = monochloroacetic acid

SMCA = sodium monochloroacetate

3.2.4.2 Cationisation

The procedure for the cationisation of hemicelluloses was adopted from Ren *et al.* (2009) and Tian *et al.* (2010). The cationisation procedure was used for both glucuronoxylan and galactoglucomannan samples using 2,3-epoxypropyltrimethylammonium chloride (ETA). The correct amount of hemicelluloses that were used for these experiments was 1.5 g glucuronoxylan accounting for 0.01 mol anhydrous-xylose units, and 0.8 g of galactoglucomannan, accounting for 0.0044 anhydrous-mannose units. The samples were first dispersed in 30 mL of distilled water at 60 °C for 20 minutes while stirring at low revolutions. This was followed by the addition of sodium hydroxide (NaOH) in a molar ratio of between 0.1 and 2.0 sodium hydroxide to ETA ($C_6H_{14}ClNO$) and gently stirred for 20 minutes at 60 °C. Then ETA was added in a molar ratio varying between 0.5 and 3.0 of ETA to the anhydrous-xylose at 60 °C, and left to react for 5 hours under gentle stirring. The solution was neutralised with 0.1 mol.dm^{-3} hydrochloric acid (HCl) to pH 7 and then precipitated with 80 % (v/v) ethanol (CH_3CH_2OH). The precipitate was filtered off using MF-Millipore™ 0.22 µm membrane filters before being washed three times with 95 % (v/v) ethanol to remove residual reagents. The precipitate was air dried for 12 hours, after which it was oven dried at 45 °C for 24 hours. The conditions of the experimental runs were calculated using the CCD design discussed in Section

3.2.4.1. Figure 3.3 is a simplified diagram of the procedure that was used for cationisation of the hemicelluloses (Ren *et al.*, 2009).

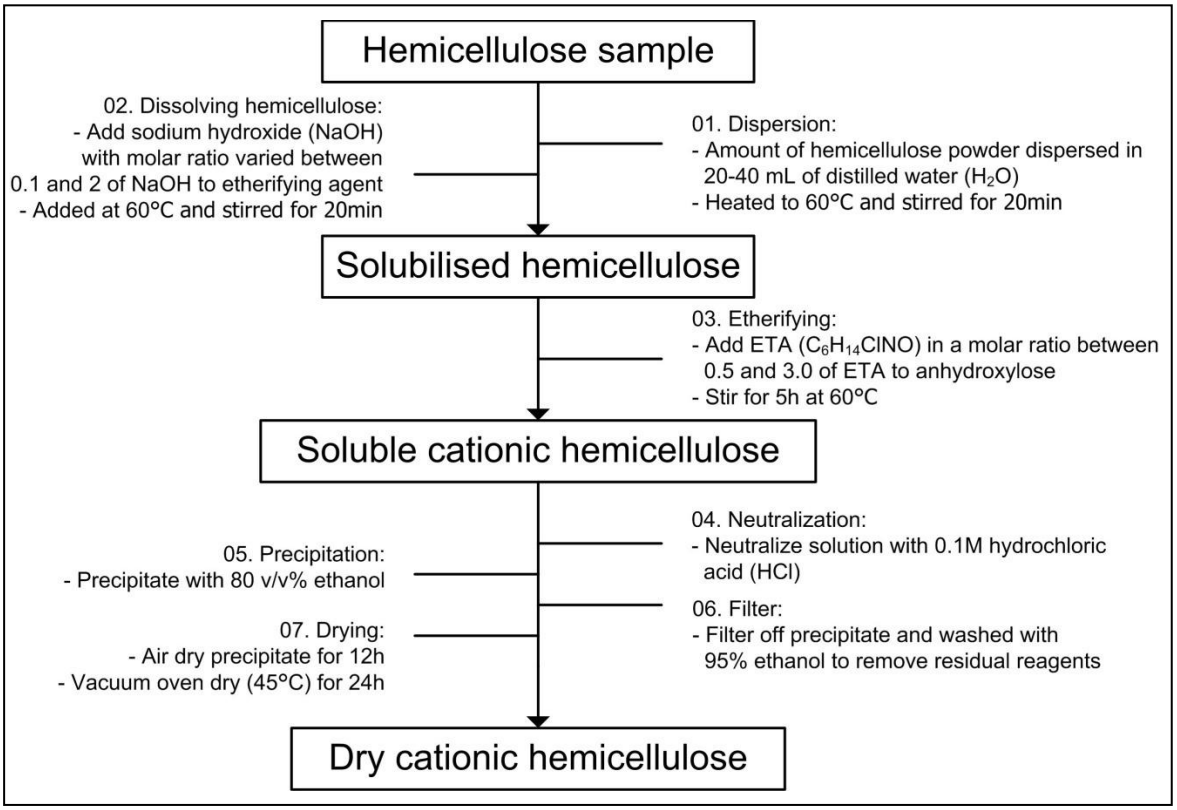


Figure 3.3: Simplified cationisation procedure (Ren *et al.*, 2009)

3.2.4.3 Carboxymethylation

The carboxymethylation processes for the hemicelluloses glucuronoxylan and galactoglucomannan use different carboxymethylation agents, namely sodium monochloroacetate (SMCA) and monochloroacetic acid (MCA), respectively. The SMCA reagent was used for glucuronoxylan samples and the procedure was adopted from Ren *et al.* (2009). For the galactoglucomannan samples the MCA reagent was used as described by the Kobayashi *et al.* (2002) procedure.

Carboxymethylated glucuronoxylan

The procedure used for carboxymethylation of glucuronoxylan was similar to Ren *et al.* (2009) with some modifications. A glucuronoxylan sample with an approximate mass of 1.5 g was dissolved in a 5% sodium hydroxide (NaOH) solution, giving a molar ratio of 1 to 1 of sodium hydroxide to anhydrous-xylose. The solution was then stirred at low revolutions for 20 minutes at 30°C. The

ethanol and water mixture was then added in the appropriate ratio of ethanol to water, as determined by the CCD experimental design (ranging between 1.0 and 2.0) to make up the sample solution to 35 mL. At the same time the appropriate amounts of sodium monochloroacetate (SMCA, $ClCH_2COONa$) was added to the mixture (in molar ratios ranging between 0.5 and 3.0 of SMCA to anhydrous-xylose). The mixture was left to react for 75 minutes at 65°C. The mixture was neutralized using a 0.1 $mol.dm^{-3}$ acetic acid (CH_3COOH) solution, and precipitation with an 80 % (v/v) ethanol (CH_3CH_2OH) solution. The resulting polymer was washed one time with 65 % (v/v) ethanol solution, and four times with 95 % (v/v) ethanol solution. The washed polymer was air dried for 12 hours, and then oven dried at 40°C for 24 hours (Ren *et al.*, 2009). The simplified experimental procedure is set out in Figure 3.4 (Ren *et al.*, 2009).

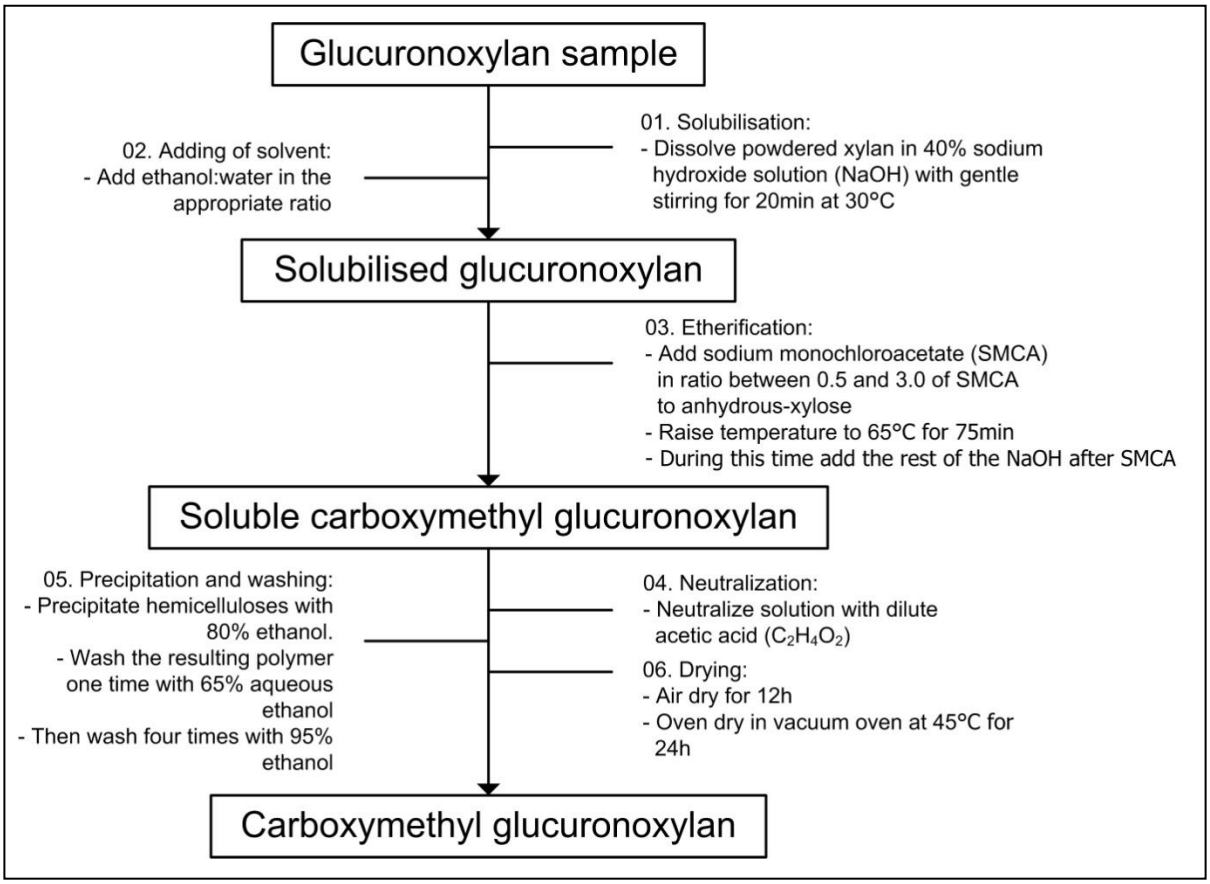


Figure 3.4: Simplified carboxymethylation of glucuronoxylan procedure (Ren *et al.*, 2009)

Carboxymethylated galactoglucomannan

The carboxymethylation of galactoglucomannan was adopted from the procedure of Kobayashi *et al.* (2002) for konjak glucomannan. Approximately 0.8 g of galactoglucomannan sample was weighed into a 250 mL three necked flask. Then 10 mL of 100 % (v/v) methanol (CH_3OH), and 10 mL of

distilled water containing sodium hydroxide (NaOH) in a molar ratio between 3.38 and 6.76 of sodium hydroxide to anhydrous-mannose according to the CCD was added. The mixture was then stirred for 30 minutes at 50°C. The monochloroacetic acid (MCA, $CH_2ClCOOH$) amount in a molar ratio of 0.5 to 3.0 of MCA to anhydrous-mannose was added and left to react for 75 minutes at 50°C. The solution was neutralized using 0.1 $mol.dm^{-3}$ hydrochloric acid (HCl) and then precipitated using 80 % (v/v) ethanol (CH_3CH_2OH). The resulting polymer was then washed with 70, 80 and 100 % (v/v) methanol (CH_3OH) successively. The polymer was air dried for 12 hours and then oven dried at 40°C for 24 hours (Kobayashi *et al.*, 2002). The simplified experimental procedure is given in Figure 3.4 (Kobayashi *et al.*, 2002).

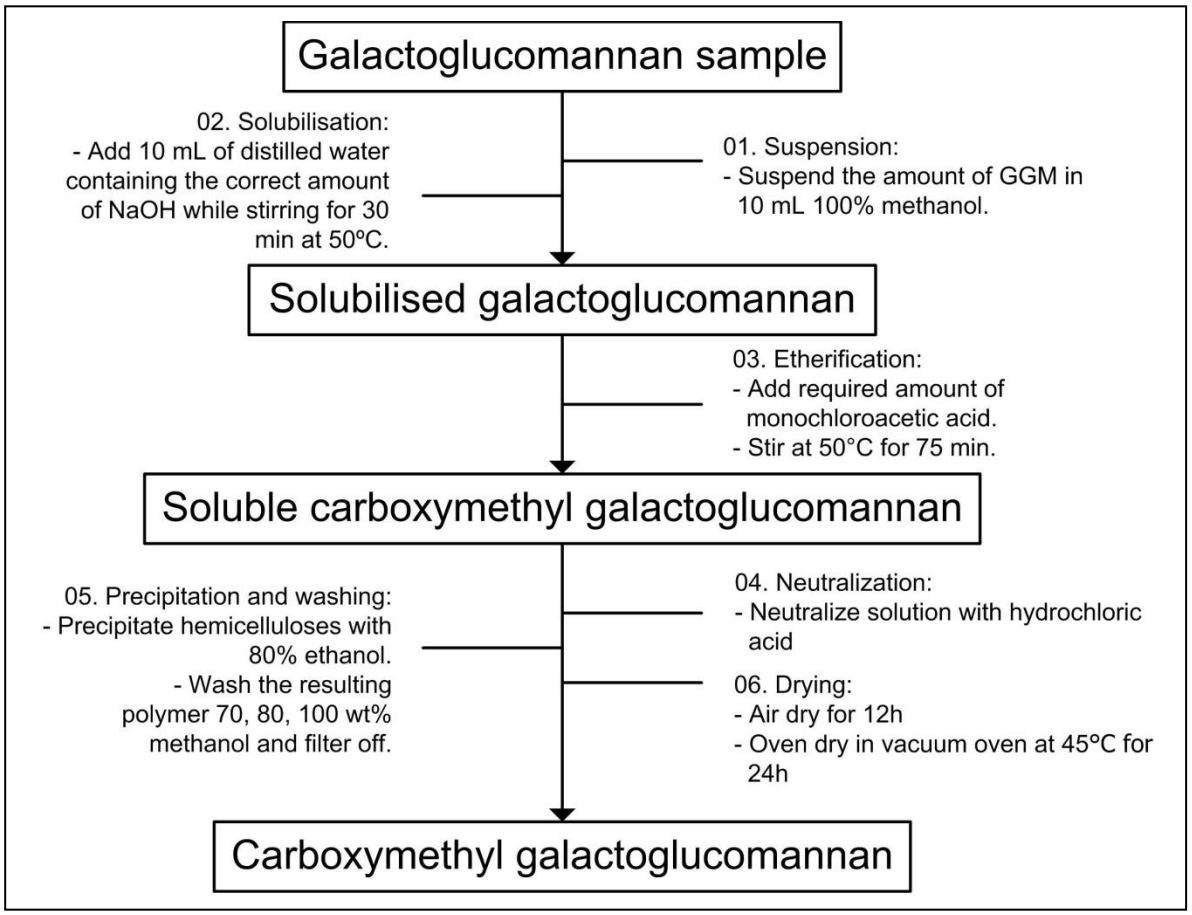


Figure 3.5: Simplified carboxymethylation of galactoglucomannan procedure (Kobayashi *et al.*, 2002)

3.2.5 Physical modification methods

There are currently no physical modification methods that are being used for producing hemicelluloses strength additives to the papermaking process. Since this is the case, a physical method was chosen from literature and the procedure was adapted for the modification of

hemicelluloses. Then testing was done to enable the observation of how the physically modified hemicelluloses behave as wet-end additives to the papermaking process. The physical method chosen was ultrasound treatment.

3.2.5.1 Experimental design

The experimental design that was used for the physical modification method was a one factor at a time design looking at only time as the variable factor. All the runs were done in duplicate or triplicate, where possible, to determine averages and standard deviations of the data points for correct statistical interpretation.

3.2.5.2 Ultrasound

Ultrasound involved the sonication of the hemicellulose sample at different time intervals. The time intervals ranged from 10 to 60 minutes. The method was adopted from Ebringerova *et al*. (1997). The ultrasound modification of hemicelluloses for use as wet-end additives in the pulp and paper industry is a relatively new approach. Therefore it is inevitable that it will be researched for its performance. The ultrasound modification of hemicellulose was done in an Elma Transsonic 460/H ultrasonic water bath. The Elma Transsonic water bath had a frequency of 35 kHz and a HF peak of 170 W. The hemicellulose was dissolved in distilled water at a temperature of 60 ^{o}C for 20 min. Sodium hydroxide (NaOH) was then added to the solution with a molar ratio of 1 to 1 of sodium hydroxide to hemicellulose. The hemicellulose samples were then placed in a 250 mL glass beaker in the Elma Transsonic water bath with the water at the same height as the sample level in the glass beaker. After the sonication period the hemicellulose sample was neutralised using 0.1 mol.dm^{-3} hydrochloric acid (HCl) and then precipitated using 80 % (v/v) ethanol. The precipitate was air dried for 12 hours and then oven dried at 45 ^{o}C for 24 hours. Figure 3.6 is a photograph of the setup used for the sonication of hemicelluloses and Figure 3.7 is the simplified sonication procedure (Ebringerova *et al.*, 1997).

Figure 3.6: Experimental setup for ultrasound treatment of hemicelluloses

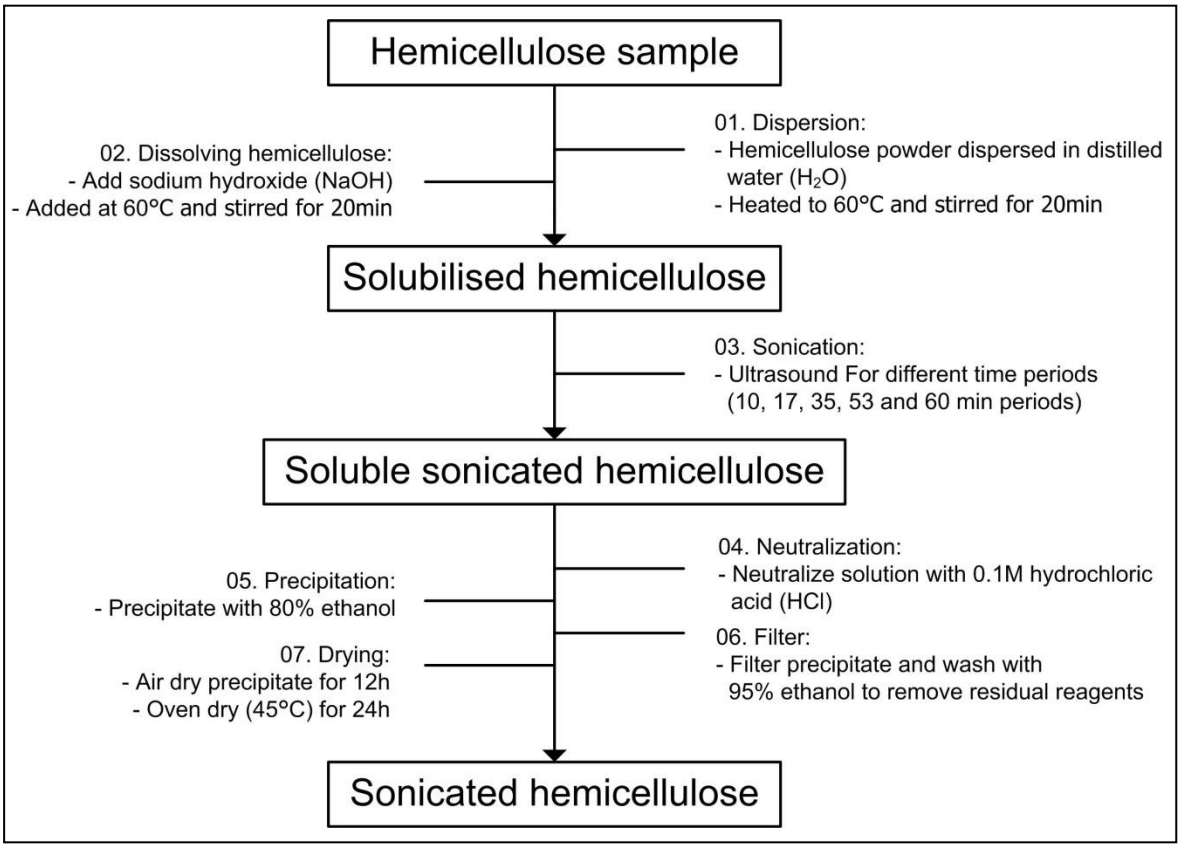


Figure 3.7: Simplified ultrasound procedure (Ebringerova *et al.*, 1997)

3.2.6 Physico-chemical analytical methods

The physico-chemical analysis of the extracted as well as the modified hemicelluloses was done by using High Performance Liquid Chromatography (HPLC), the carbazole-sulfuric acid UV-VIS method, Fourier Transform Infrared (FT-IR) spectroscopy, Nuclear Magnetic Resonance (NMR) spectroscopy, Size Exclusion Chromatography (SEC), elemental analysis, and titration methods. These methods can determine the chemical composition of the samples as well as the chemical structures.

3.2.6.1 High Performance Liquid Chromatography (HPLC)

The carbohydrate (monosaccharide) composition analysis of the *E. grandis* biomass received from SAPPI was done with HPLC and the preparation of the samples was done as described in Section 3.2.3. The HPLC equipment that was used was a Thermo Separations Spectrasystem P2000 equipped with an Aminex HPX-87H column and a IG Cation H Cartridge guard column which was kept at 65 ^{o}C. The detector that was used was a Shodex RI-101 which is a refractive index detector. The mobile phase was a 0.005 mol.dm^{-3} sulphuric acid solution with a flow rate of 0.6 mL.min^{-1}. The data capturing was done using Chromeleon® Version 6.80.

The carbohydrate composition of the extracted hemicellulose from the *E. grandis* samples were prepared according to the procedure set out in Haimer *et al*. (2010) for HPLC analysis. The samples were then analysed with the same HPLC system as above. The preparations included making a suspension of 0.1 g of hemicellulose in 8 mL of deionised water in which 2.04 mL of 0.5 mol.dm^{-1} H_2SO_4 was added while stirring for 5 minutes. The solution was hydrolysed further in an autoclave for 40 min at 120 ^{o}C and 0.12 MPa. The mixture was filtered under suction in filtering crucibles and subsequently washed with boiling deionised water. The resulting solution was filtered using 0.22 µm syringe filters before HPLC analysis.

3.2.6.2 Carbazole-sulfuric acid UV-VIS method

The carbazole-sulfuric acid UV-VIS analytical method, adopted from Li *et al*. (2007) and Brienzo *et al*. (2009), was used to determine the uronic acid content of the hemicelluloses samples. Approximately 1 mg of hemicellulose sample was dissolved in 0.4 mL of distilled water in a test tube. Subsequently, 40 µL of a 4 mol.dm^{-3} solution of sulfamic acid (H_2NSO_3H) was added, followed by 2.4

mL of 95 - 99% sulphuric acid (H_2SO_4). The mixture was allowed to stand till room temperature was reached. A 100 µL of a 0.1 w/v % carbazole ($C_{12}H_9N$) in ethanol solution was then added and the sample was placed in a water bath at 100 °C for 20 min. After the reaction in the water bath, the samples were removed and placed in an ice-water bath till room temperature was reached. The light absorbance of the samples was measured at 525 nm using a Varian Cary 50 Bio UV visible (UV-VIS) spectrophotometer. To be able to determine the uronic acid content from the absorbance values, a calibration curve was prepared beforehand using galacturonic acid standard solutions of know mass.

3.2.6.3 Fourier Transform Infrared (FT-IR) spectroscopy

The chemical structure of the hemicelluloses was studied using the Thermo Nicolet Nexus 870 FT-IR system using the ATR Golden Gate measurement device. The data analysis was done with the Omnic® 7 software and exported to Microsoft® Excel. The solid samples were directly placed on the measurement device and scanned, thus no sample preparation was needed.

3.2.6.4 Nuclear Magnetic Resonance (NMR) spectroscopy

The chemical structure of the hemicelluloses was further studied using Cross Polarization Magic Angle Spinning (CP/MAS) solid-state ^{13}C-NMR. The dry hemicellulose samples were frozen using liquid nitrogen, and subsequently ground into a fine powder. The solid powder hemicellulose samples were analysed using a 500MHz Varian VMRS Wide Bore 500 Solids system equipped with a 4 mm HX MAS probe (15N-31P). The CP-MAS data retrieved from the NMR analysis was analysed using the program SpinWorks® 3 and manipulated with OriginPro® 8.

3.2.6.5 Size Exclusion Chromatography (SEC)

The molecular weight of the hemicelluloses was determined by using Size Exclusion Chromatography (SEC). The samples were prepared by dissolving the hemicelluloses in deionised water at 30 °C under constant stirring for 2 hours. The required volume, 1.5 mL, was filtered using 0.22 µm syringe filters to remove any solids present. The concentration of the samples analysed was chosen as 1 $g.L^{-1}$, which showed the best results during calibration and testing of the SEC columns with the Pullulan (a neutral glucan) standards purchased with the columns. A cubic calibration curve was used for calibration of the columns, which resulted in the most reliable readings.

The size exclusion analysis was done on a Dionex UltiMate 3000 HPLC system with a Varian 380-LC detector which is an Evaporative Light Scattering (ELS) detector. The SEC columns were purchased from Polymer Standards Service (PSS) in Mainz, Germany. Three SEC columns with a guard column in their PSS SUPREMA analytical range were used. The particle size of all three SEC columns was 10 µm and had dimensions of 8 x 300 mm. The three columns were used in series conformation with the porosity of the first column in series being 30 Å, while the other two columns had a porosity of 3000 Å. The eluent used during analysis was a deionised water solution containing 0.05% sodium azide (NaN_3) at a flow rate of 1 mL.min^{-1}, while the columns were kept at a temperature of 25 °C.

3.2.6.6 Elemental (ultimate) analysis

The carbon (C wt.%) and nitrogen (N wt.%) content of the modified hemicelluloses were determined by elemental analysis. The elemental analysis involved the dry combustion of approximately 2 mg of hemicelluloses sample using a EuroVector EA Euro 3000 elemental analyser. The collected data was analysed on the Callidus SW® software provided with the elemental analyser. The N and C wt.% were done to determine the degree of substitution (DS_N) of the cationic hemicellulose samples. The degree of substitution was calculated according to Equations 3-7 and 8 as described by Ren *et al.* (2009) and Tian *et al.* (2009) respectively.

$$DS_{N\,(cationic\,glucuronoxylan)} = \frac{60 \times N\,wt\%}{14 \times C\,wt\% - 72 \times N\,wt\%} \qquad (3\text{-}7)$$

$$DS_{N\,(cationic\,galactoglucomannan)} = \frac{162.15 \times N\,wt\%}{1401 - 151.64 \times N\,wt\%} \qquad (3\text{-}8)$$

3.2.6.7 Titrations

The titration methods were performed to determine the degree of substitution of the carboxymethylated hemicelluloses. Two different titration methods were used for carboxymethyl glucuronoxylan and galactoglucomannan, respectively.

Carboxymethylated glucuronoxylan titration method

The titration method used to determine the degree of substitution of carboxymethyl glucuronoxylan was done as in Ren *et al.* (2009). The purity of the carboxymethylated glucuronoxylan was

estimated by re-solubilising the carboxymethylated glucuronoxylan and ethanol precipitating the sample again, as per Ren *et al*. (2009). The titration was done by placing approximately 0.2 g of sample in 50 mL of distilled water under stirring for 10 minutes after which the pH was adjusted by either using acid or alkali solutions. The solution was then titrated using 0.05 mol.dm^{-3} sulphuric acid (H_2SO_4) until the pH was at 3.74. To calculate the DS Equations 3-9 to 3-11 were used (Ren *et al*., 2009)

$$a = \frac{m^1}{m} \quad (3\text{-}9)$$

$$B = 2 \times M \times \frac{V}{a \times m} \quad (3\text{-}10)$$

$$DS_{COONa} = 0.132 \times \frac{B}{1 - 0.08 \times B} \quad (3\text{-}11)$$

Where a is the purity of the samples, m^1 is the mass of the purified sample and m is the mass of the un-purified samples used, measured in g. M is the normality of the sulphuric acid used; V is the volume of sulphuric acid used for titration in mL and B is the mmol.g^{-1} of sulphuric acid consumed per gram of sample.

Carboxymethylated galactoglucomannan titration method

The back titration method used for the determination of the degree of substitution of carboxymethylated galactoglucomannan was completed as per Stojanović *et al*. (2005). The sodium-carboxymethyl galactoglucomannan was first converted to hydrogen-carboxymethyl galactoglucomannan by replacing the sodium in the side chains with the hydrogen from hydrochloric acid. Approximately 0.5 g of hydrogen-carboxymethyl galactoglucomannan was dissolved in 20 mL of 0.2 mol.dm^{-3} sodium hydroxide (NaOH) and 50 mL distilled water. The solution was then made up to 100 mL in a volumetric flask from which 25 mL was diluted by adding 100 mL of distilled water. The diluted solution was then titrated using 0.05 mol.dm^{-1} hydrochloric acid, while using phenolphthalein as indicator. The degree of substitution was calculated by using Equations 3-12 to 3-14 (Stojanović *et al*., 2005).

$$n_{COONa} = \left(V_b - V\right) \times c_{HCl} \times 4 \quad (3\text{-}12)$$

$$m_{ds} = \left(1 - \frac{w_{water}}{100}\right) \times m_s \quad (3\text{-}13)$$

$$DS_{COONa} = \frac{180.156 \times n_{COONa}}{m_{ds} - 58 \times n_{COONa}} \quad (3\text{-}14)$$

where V_b is the volume hydrochloric acid used to titrate a blank solution, V is the volume of hydrochloric acid used to titrate the sample solution and c_{HCl} is the concentration of the hydrochloric acid used in mol.dm^{-3}.

3.3 Results and discussion

3.3.1 Compositional analysis of *E. grandis* biomass

The compositional analysis of the *E. grandis* chips was done to determine the hemicellulose content of the feedstock. The results obtained from the compositional analysis of the *E. grandis* feedstock are given in Table 3.7.

Table 3.7: Compositional analysis results of *E. grandis* biomass

Component	Average	Standard deviation
Moisture content (wt.%)	6.61%	0.11%
Ash content (wt.%)	0.37%	0.07%
Water and solvent soluble extractives (wt.%)	2.84%	0.19%
Klason lignin (wt.%)	14.60%	1.12%
Cellulose (wt.%)	46.16%	0.28%
Hemicelluloses (wt.%)	27.72%	1.77%
Summative analysis (wt.%)	**98.29%**	**3.13%**

The summative analysis of the compositional analysis in Table 3.7 falls within the 5% margin of error with values ranging between 96.1% and 101.87 %. This margin of experimental error still falls inside the 95% confidence interval. The cellulose- and extractives content in this *E. grandis* sample was in accordance with the values found in literature, which were given in Table 2.4. The cellulose content in literature varied between 43.00 and 53.10 wt.%, while the extractives content varied between 0.80 and 5.80 wt.% (Baeza *et al.*, 1991; Cotterill & Macrae, 1997; Emmel *et al.*, 2003;

Magaton *et al.*, 2009). The ash content was slightly higher with an average value of 0.37 wt.% of dry biomass, while the range given in literature is between 0.06 and 0.35 wt.% of dry biomass (Da Silva *et al.*, 2010). This slightly higher ash content is attributed to the *E. grandis* sample chips not being washed properly before the compositional analysis was done, thus containing small amounts of sand. The presence of sand leads to higher silica (Si) inorganic matter in the biomass, thus higher ash content.

The lignin content was considerable lower than the values from literature (Baeza *et al.*, 1991; Cotterill & Macrea, 1997; Emmel *et al.*, 2003). The values for lignin content from literature are between 24.80 and 30.00 wt.%, but the lignin content of the *E. grandis* received from SAPPI's Ngodwana mill is 14.6 wt% of dry biomass. This deviation may be attributed to the growing conditions of the *E. grandis*, or that the species tested in this investigation is a hybrid with low lignin content (Meadows, 1999). Lower lignin content in the biomass should give rise to an increase of cellulose and hemicelluloses content (Fengel & Wegener, 2003). This is due to the loss of strength that the lignin impose on the tree while it is growing, thus the cellulose and hemicelluloses contents must increase to make up for this strength loss (Fengel & Wegener, 2003). The average hemicelluloses content from literature for *E. grandis* is approximately 22.10 wt.% of dry biomass (Baeza *et al.*, 1991; Fengel & Wegener, 2003). The hemicellulose content for the *E. grandis* from Ngodwana is 27.27 wt.% of dry biomass. This increase is due to the low lignin content as explained above. This may be a positive indication that *E. grandis* is a good candidate for hemicellulose extraction due to the increased hemicellulose content.

3.3.2 Extraction and characterisation of hemicelluloses

3.3.2.1 *E. grandis* glucuronoxylan

Glucuronoxylan was extracted from *E. grandis* chips using the Höije *et al.* (2005) method. The average yield of total solids extracted from *E. grandis* using this method, was 67.58 wt.% of dry biomass. The HPLC and Klason lignin results for the total solids extracted using the Höije *et al.* (2005) method are given in Table 3.8.

Table 3.8: Compositional analysis results of extracted *E. grandis* total solids

Component	Average	Standard deviation
Lignin (wt.%)	27.10%	4.93%
Xylose (wt.%)	40.76%	5.29%
Mannose (wt.%)	3.54%	0.29%
Glucose (wt.%)	9.77%	0.82%
Arabinose (wt.%)	0.26%	0.04%
Galactose (wt.%)	1.54%	0.21%
Uronic acid (wt.%)	15.93%	1.02%
Summative analysis (wt.%)	**98.90%**	**0.39%**

The molar ratio of anhydrous-xylose:4-O-methyl-glucuronic acid as calculated from Table 3.8, was 3.54:1, thus for every 3.54 mole of anhydrous-xylose there is 1 mole 4-O-methyl-glucuronoxylan. This molar ratio relates to a degree of substitution of 0.28, thus for every mol anhydrous-xylose there is 0.28 mol 4-O-methyl-glucuronic acid. From literature the molar ratio of anhydrous-xylose to 4-O-methyl-glucuronic acid is 10-11 to 1 (Fengel & Wegener, 2003). This indicates that the uronic acid content for the extracted xylan from this *E. grandis* sample is very high. There are also small amounts of other sugar monomers present in the total solids extracted, as seen from the mannose, glucose, arabinose and galactose contents in Table 3.8. The presence of these other sugar monomers was attributed to small quantities of arabinoxylans, mannans, solubilised cellulose and pectin complexes (Fengel & Wegener, 2003). It is however observed that xylan is the main hemicellulose present in the extracted solids with a xylose content of approximately 40.76 wt.%. This indicates that the Höije *et al*. (2005) method does not extract only glucuronoxylan from *E. grandis*, but a combination of hemicelluloses, with glucuronoxylan being the main extracted hemicellulose.

The Klason lignin results in Table 3.8 indicated that there were still substantial amounts of lignin present in the total solids extracted. Approximately 27.10 wt.% of the dry total solids extracted from the *E. grandis* was lignin. The presence of lignin in the total solids indicated that the sodium chlorite ($NaClO_2$) delignification process was not sufficient to fully delignify the *E. grandis* samples. This is also due to the higher lignin content of *E. grandis* when compared to barley husks, on which the method was based (Höjie *et al*., 2005). It is also attributed to the fact that *E. grandis* and barley husks are completely different types of biomasses, resulting in different types of lignin present (Fengel & Wegener, 2003). *E. grandis* is a hardwood, where barley husks are seeds from plants from the herbaceous/grass family. The presence of lignin may cause problems for the development of paper additives from these hemicelluloses. The oxidation of lignin is the cause of yellowing of paper

(Holik, 2006). Even though this is the case, the hemicelluloses are modified and ethanol precipitated, which will lower the lignin content considerably (Peng *et al.*, 2009; Xu *et al.*, 2007).

When corrections for the lignin content were made, the hemicelluloses yield for *E. grandis* was 50.75 wt.% of initial hemicellulose present in the biomass, as determined by compositional analysis. This hemicellulose yield is on the lower end of the yields reported by Höije *et al.* (2005) which ranged between 50 and 83%. Herbaceous biomasses have more hemicelluloses present in the macromolecular structure, which is not as tightly bonded in the physical structure as they are in hardwood biomasses (Fengel & Wegener, 2003; Krawczyk *et al.*, 2007). This difference in biomass used for the Höije *et al.* (2005) extraction method is the cause for the low hemicelluloses yield and high lignin content present in the solid extracted from *E. grandis*. The Höije *et al.* (2005) method will have to be modified to extract more pure hemicelluloses from *E. grandis* with a higher yield.

Table 3.9: Extracted *E. grandis* glucuronoxylan molecular weight and degree of polymerisation results

	Average	**Standard deviation**
Molecular weight (g.mol^{-1})	51 589	16 572
Degree of polymerisation	140	45

The molecular weight results for the extracted *E. grandis* glucuronoxylan using SEC is given in Table 3.9. The molecular weight range was between 26 000 and 68 000 g.mol^{-1}, with a degree of polymerisation ranging between 71 and 183. This degree of polymerisation is well above the minimum of 40 required for hemicelluloses to be used for paper strength additives (Janes, 1968). With a degree of polymerisation below 40, the retention and/or adsorption of hemicelluloses on the pulp fibres become very low. Hardwood hemicelluloses, predominantly glucuronoxylan, are known to have a degree of polymerisation ranging from 100 to 200 (Fengel & Wegener, 2003), thus the results for the extracted *E. grandis* glucuronoxylan fall in this range. The molecular weight range of the hemicelluloses reported by Höije *et al.* (2005) was 35 000 and 45 000 g.mol^{-1}, which is lower than the maximum of 68 000 g.mol^{-1} observed for the extracted *E. grandis* glucuronoxylan. The difference in molecular weights of the hemicelluloses extracted in this study, and that of Höije *et al.* (2005), is because the feedstock used by Höije *et al.* (2005) was barley husks. Barley husk, which is an herbaceous biomass, has lower molecular weight hemicelluloses. The FT-IR spectra of the extracted *E. grandis* glucuronoxylan as compared to commercial obtained *Fagus sylvatica* (Beech) glucuronoxylan from are given in Figure 3.8.

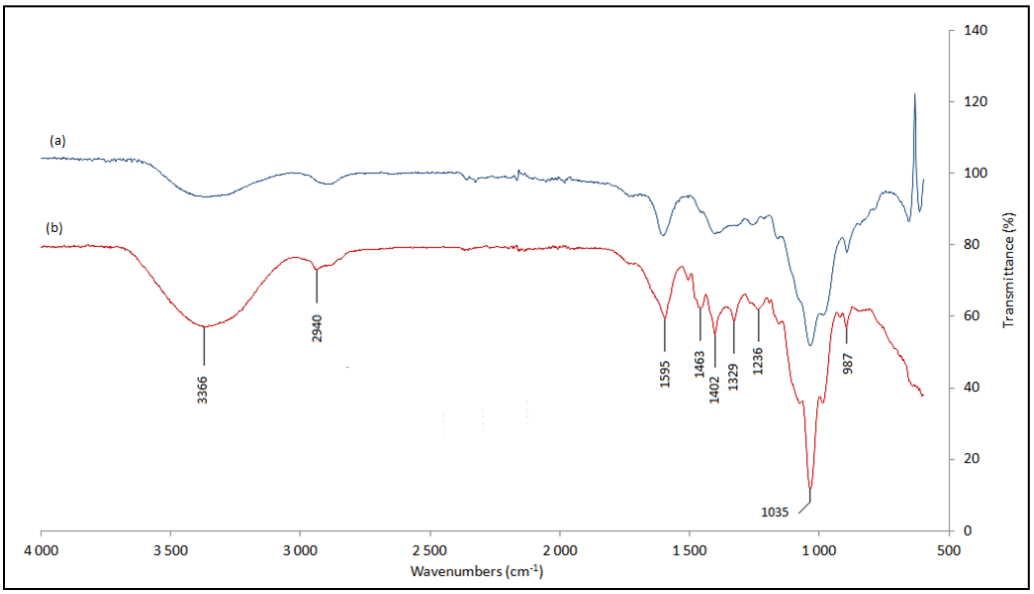


Figure 3.8: FT-IR spectra of glucuronoxylan extracted from (a) *Fagus sylvatica* and (b) *E. grandis*

The FT-IR spectra in Figure 3.8 (a), and (b), follow the same pattern, indicating similarities in their chemical structure. The sharp band at 1035 cm^{-1} is typical of xylan, indicating that xylan is the dominant hemicellulose in both the samples (Ren & Sun, 2010). The small band at 897 cm^{-1} is typical of β-anomers which show that β-glycosidic linkages are dominant between the sugar units (Ren & Sun, 2010). The bands in the carbonyl stretching region at 1573 - 1659 cm^{-1} are attributed to the adsorption of water by the hemicelluloses (Ren & Sun, 2010). The peak in the range of 1725 - 1730 cm^{-1} is attributed to the presence of C=O stretching due to the presence of acetyl - and COOH groups, which is an indication of the presence of acetyl- and uronic acid groups in the xylan in both the *E. grandis* and *Fagus sylvatica* samples (Ren & Sun, 2010). The band range between 1200 and 1600 cm^{-1} is associated with aromatic compounds which originate from lignin fractions present in the hemicelluloses (Chimphango, 2010; Fengel & Wegener, 2003). The spectra of *E. grandis* glucuronoxylan (Figure 3.8 a) show peaks at 1329 and 1595 cm^{-1}, which are attributed to syringyl ring breathing with C_{Ar}-OCH_3 and methoxyl groups in lignin. This indicates that there is lignin present in the extracted *E. grandis* glucuronoxylan (Chimphango, 2010; Fengel & Wegener, 2003). These peaks are less intense in the beech glucuronoxylan (Figure 3.8 a), which is an indication that there is less lignin present in the commercial beech xylan (Chimphango, 2010). Both the spectra also show non-polymer signals in the range of 1630 - 1640 cm^{-1}, which indicates the adsorption of water, and at 2340 - 2350 cm^{-1} for carbon dioxide (CO_2) adsorbed by the hemicelluloses (Ren & Sun, 2010).

The Solid state ^{13}C-CP/MAS NMR spectrum of the extracted glucuronoxylan from *E. grandis* is given in Figure 3.9 containing the peak assignments for the respective peaks. The NMR spectrum confirmed the findings of the FT-IR that there is lignin present in the extracted *E. grandis* hemicelluloses from the peaks at 152.91 and 55.86 ppm (Matulova *et al.*, 2005). The spectrum also confirmed that there are acetyl- and 4-O-methylglucuronic acid groups present in the xylan structure, which are indicated by the peaks at 24.86 and 85.5 ppm respectively (Matulova *et al.*, 2005). This presence of acetyl groups in the sample is contradicted by literature. This is the case due to the de-acetylation of hardwood O-acetyl-4-O-methylglucuronoxylan during the alkali solubilisation (Chimphango, 2010; Fengel & Wegener, 2003; Teleman *et al.*, 2000). A possible explanation for the presence of the acetyl group signal in the Solid state ^{13}C-CP/MAS-NMR analysis was due to contamination of the sample with the removed acetyl groups that remained in the sample solution before freeze drying. The Solid state ^{13}C-CP/MAS-NMR spectrum, with the results above, indicate that the major hemicellulose extracted from *E. grandis,* with the Höije *et al.* (2005) method, is 4-O-methylglucuronoxylan.

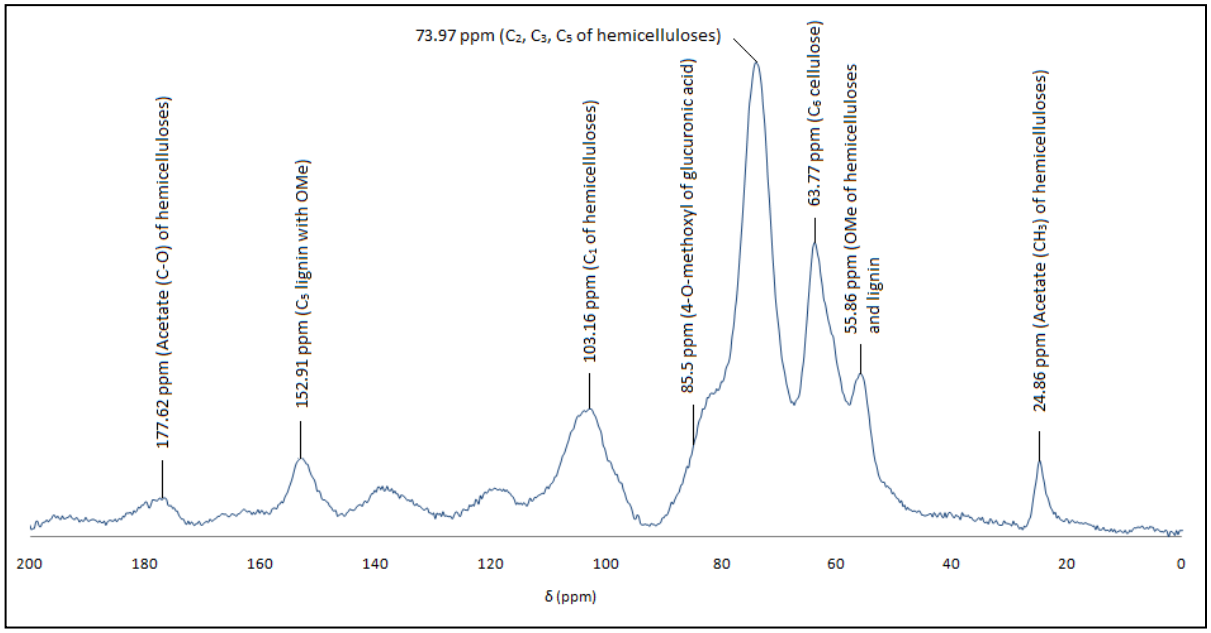


Figure 3.9: Solid state ^{13}C-CP/MAS-NMR spectrum of extracted *E. grandis* glucuronoxylan

From the above results it is clear that 4-O-methylglucuronoxylan was extracted from *E. grandis* by using the Höije *et al.* (2005) extraction method. This extracted glucuronoxylan is expected to be suitable for use as strength additive to the papermaking process since the degree of polymerisation of the glucuronoxylan is well above the minimum degree of polymerisation of 40 (Janes, 1968) that is required for use as strength additive.

3.3.2.2 *P. abies* galactoglucomannan

Two different galactoglucomannan samples were received from Prof. Stefan Willför from Åbo Akademi, Finland (Willför, 2010). The galactoglucomannan samples were extracted at Åbo Akademi, Finland, by Prof. Stefan Willför's research group, and were shipped to South Africa. No galactoglucomannan extraction experimentation was done in this study. The first method of extraction was Pressurised Hot Water Extraction (PHWE) using *P. abies* as feedstock (Leppänen *et al.*, 2010). The second method was a pilot scale method, where the process waters of a thermomechanical pulp mill in Finland, using *P. abies* as feedstock, are concentrated using filtration and ultrafiltration after which it was spray dried (Xu *et al.*, 2009).

Table 3.10: PHWE and pilot plant *P. abies* galactoglucomannan compositional analysis results (Willför, 2010)

Component	Pilot plant	PHWE
Mannose (mole %)	53.00%	56.00%
Glucose (mole %)	23.00%	16.00%
Galactose (mole %)	13.00%	9.00%
Arabinose (mole %)	4.10%	1.00%
Xylose (mole %)	1.60%	12.00%
Rhamnose (mole %)	0.10%	1.00%
Uronic acid (mole %)	5.30%	5.00%
Summative analysis (mole %)	**100.10%**	**100.00%**
Molar ratio of mannose:glucose:galactose	4 : 1 : 0.5	4 : 1 : 0.5

The HPLC results for the two different galactoglucomannan samples, as received from Finland, are given in Table 3.10 (Willför, 2010). The purity of galactoglucomannan in the solid samples was 73 mol% for the pilot plant sample and 75 mol% for the PHWE (Willför, 2010). This difference in purity is due to the re-solubilisation and precipitation step in the PHWE method (Leppänen *et al.*, 2010; Xu *et al.*, 2009). The PHWE galactoglucomannan sample would be preferred for further development of strength additives, due to this slightly higher purity when compared to the pilot plant sample. Although this is the case, the molecular mass results will provide a better indication of suitability for further additive development between the two samples.

Table 3.11: PHWE and pilot plant *P. abies* galactoglucomannan molecular weight and degree of polymerisation results (Willför, 2010)

	Pilot plant	PHWE
Molecular weight (g.mol^{-1})	39 000	8 000
Degree of polymerisation	196	45

The molecular weight results for the two different galactoglucomannan samples, as received from Finland, are given in Table 3.11 (Willför, 2010). The molecular weight of the PHWE sample was considerably lower than the pilot plant galactoglucomannan (Table 3.11). The degree of polymerisation of the PHWE sample was barely above the minimum degree of polymerisation of 40 for use as strength additive to the papermaking process (Janes, 1968). The lower molecular weight of PHWE galactoglucomannan would be attributed to the harshness of the extraction method (temperature of 170 ^{o}C for 60 min). This high temperature results in hydrolysis of the β-(1→4) glycosidic bonds, thus lowering the molecular weight of the hemicelluloses (Fengel & Wegener, 2003; Leppänen, 2010). The degree of polymerisation of the pilot plant sample is more than appropriate to be used as a strength additive in the papermaking process. The value of 196 is well above the minimum degree of polymerisation value of 40 (Janes, 1968). From this it seems that the pilot plant sample will be preferred for further modification experiments.

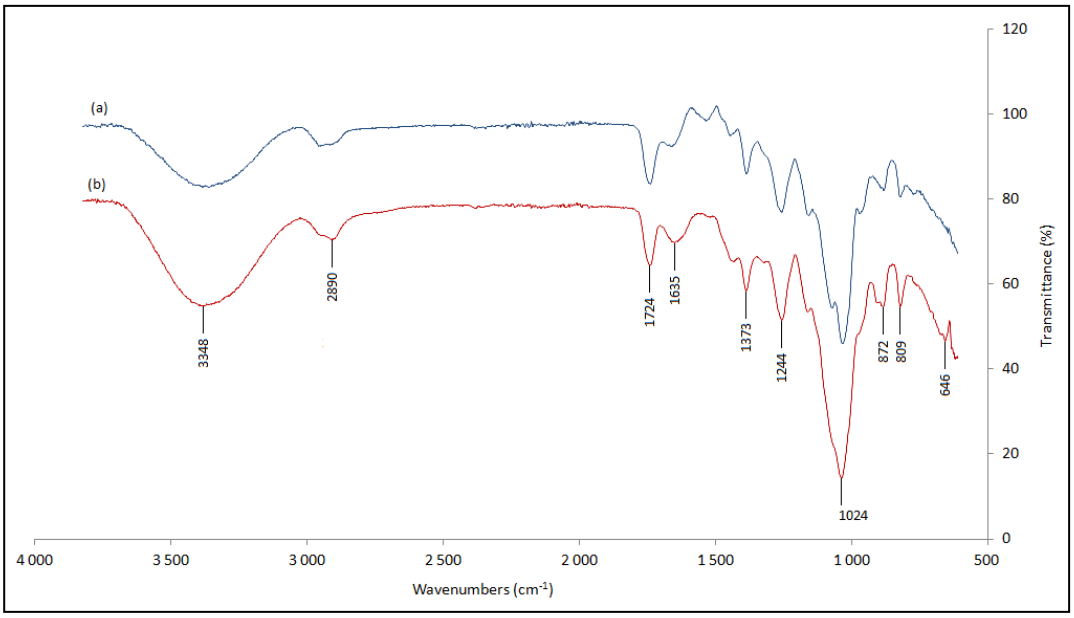


Figure 3.10: FT-IR spectra of galactoglucomannan extracted from *P. abies* with (a) pilot plant and (b) PHWE methods

The FT-IR spectra of the respective galactoglucomannan samples are given in Figure 3.10 (a) and (b). Both the spectra (Figure 3.10 a and b) show that hemicelluloses are the main component of the samples, with the sharp band at 1020 cm^{-1} (Ren & Sun, 2010). The sharp band at 950 cm^{-1} is attributed to the β-glycosidic linkages between the sugar monomers (Ren & Sun, 2010). Both the samples display a sharp peak at 1373 cm^{-1} which indicates that there are C-CH_3 acetyl bonds present (Coates, 2000). The pilot plant sample (Figure 3.10 a) displayed a band at 1519 cm^{-1}, that was absent from the PHWE sample (Figure 3.10 b). This band is a lignin associated peak, and indicates that the pilot plant sample contains a small amount of lignin, while the PHWE sample does not. The absence of lignin from the PHWE sample was due to the extra purification step that was applied to the method (Coates, 2000; Leppänen *et al.*, 2010; Ren & Sun, 2010).

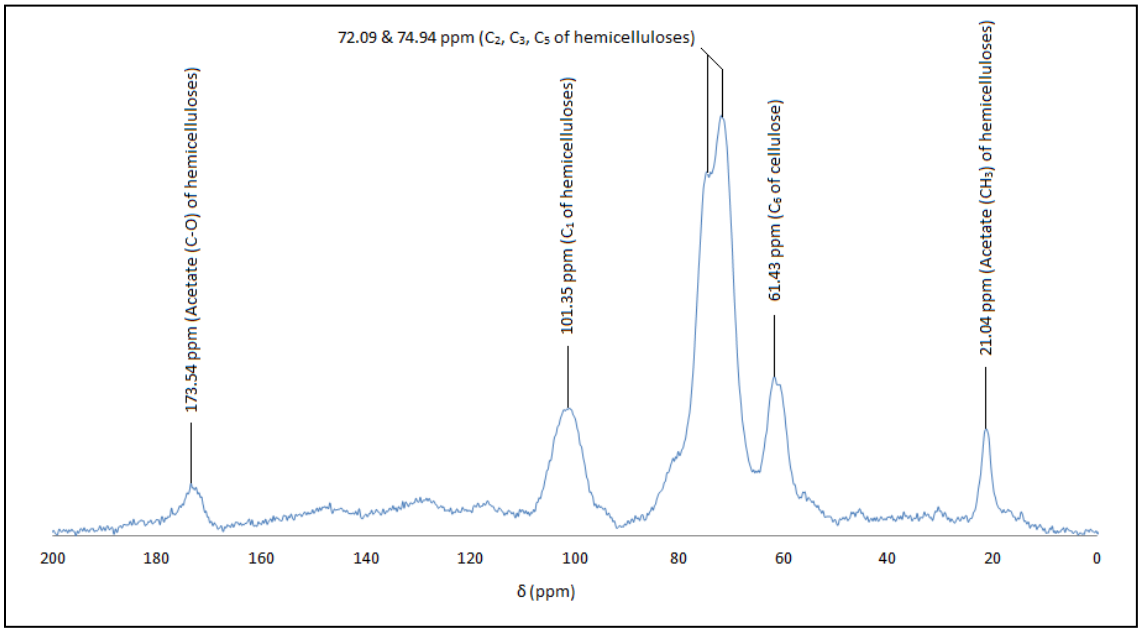


Figure 3.11: Solid state ^{13}C-CP/MAS-NMR spectrum of *P. abies* pilot plant galactoglucomannan

The Solid state ^{13}C-CP/MAS-NMR spectrum of the pilot plant extracted galactoglucomannan is given in Figure 3.11 with the peak assignments. The spectrum indicates that hemicelluloses containing acetyl groups are present in the sample (Matulova *et al.*, 2005). The acetyl groups were attributed to the peak at 21.04 ppm, and hemicelluloses to the peaks at 173.54, 101.35, 74.94 and 72.09 ppm (Matulova *et al.*, 2005). There is however some lignin present in the sample as shown by the small peaks in the range between 160 and 120 ppm. The presence of lignin in the sample was discussed in the FT-IR results above. The NMR spectra indicate that there is no uronic acid present due to the absence of the peak at 85.5 ppm (Matulova *et al.*, 2005).

The results above indicate that in both preparation methods O-acetyl-galactoglucomannan was extracted, with molecular weights suitable for strength additive development for the pulp and paper industry. Both the samples have approximately the same chemical structure, with the only difference being the molecular weights of the samples and the lignin present in the pilot plant sample. The pilot plant sample has a much higher molecular weight and will be preferred for modification, in this investigation, and use as strength additive to the papermaking process (Janes, 1968; Magaton *et al.*, 2011).

3.3.3 Modification of hemicelluloses

The modification experiments were applied to four different hemicelluloses samples, namely extracted *E. grandis* 4-O-methyl-glucuronoxylan, commercial *Fagus sylvatica* (Beech) O-acetyl-4-O-methyl-glucuronoxylan, pilot plant and PHWE *P. abies* O-acetyl-galactoglucomannan. The main focus of this investigation falls on the extracted *E. grandis* glucuronoxylan and the rest of the hemicelluloses are used as comparison materials. The important dependant outputs that were investigated for the modification of hemicelluloses were the degree of substitution of the side chains, and the uronic acid / galactose content of the hemicelluloses. The degree of substitution is defined as the moles of substituent per mole of hemicelluloses unit, which is an indication to the extent of fuctionalization of the hemicelluloses (Fengel & Wegener, 2003). The other important dependant variable was the uronic acid content which is an indication of the solubility of the hemicelluloses, with a lower uronic acid content resulting in a less soluble product (Li *et al.*, 2007, Walker, 1964). The modification methods are cationisation, carboxymethylation and sonication.

3.3.3.1 Cationisation

The cationisation of hemicelluloses results in hemicelluloses which have a cationic (positive) charge. This cationic charge originates from the positive ions that replace the uronic acid or galactose side chains on the backbone of the hemicelluloses. The resulting positive ion side chain in the method used for this investigation was $-CH_2-CHOH-CH_2-N^+(CH_3)_3Cl^-$, as shown in Figure 2.7.

Cationic glucuronoxylan

The cationisation of the extracted *E. grandis* 4-O-methylglucuronoxylan was optimised for two variables. Variable A was the molar ratio of sodium hydroxide (NaOH) to 2,3-epoxypropyltri-

methylammonium chlorine (ETA, $C_6H_{14}ClNO$) (varied between 0.10 and 2.00), while variable B was the molar ratio of ETA to anhydrous-xylose (varied between 0.50 and 3.00). The experimental conditions were carried out according to the CCD experimental design provided in Section 3.2.4.1. The analysis of the experimental results with Statistica® indicated that these variables did not impact the dependant outputs in a predictable manner, i.e. there were no statistically relevant trends in the results. The dependant outputs were cationic glucuronoxylan yield (wt.%), degree of substitution, and uronic acid content (wt.%). This lack of statistical significance may be attributed to the variability of the molecular weight of the extracted *E. grandis* glucuronoxylan sample used for the cationisation experiments. Figure 3.12 shows the molecular weight elution profile as determined by SEC. From this elution profile it is evident that there were three different molecular weight profiles in the extracted *E. grandis* glucuronoxylan sample. The elution profile with the average molecular weight of 67 322 g.mol^{-1} was attributed to the main extracted glucuronoxylan. The last two elution profiles with average molecular weights of 375 and 90 g.mol^{-1} were attributed to degraded hemicelluloses. These different molecular weights led to inconsistent results for the cationisation modification method.

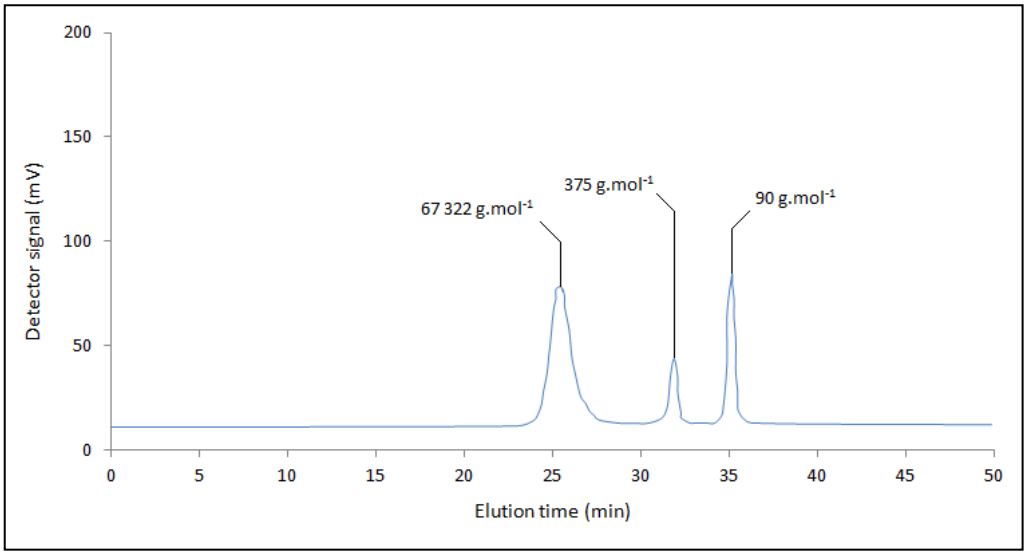


Figure 3.12: SEC elution profile for extracted *E. grandis* glucuronoxylan used for cationisation

This variability of the molecular weight made it difficult to predict the dependent outcomes for a certain modification run. This indicated that a more reliable extraction method should be used for the extraction of the *E. grandis* glucuronoxylan. Another solution will be to optimise the Höije *et al.* (2005) method for the *E. grandis* feedstock. Another reason why nothing statistically significant was observed in the results could be that one, or more, of the reagents were fed in slight excess. This, in turn, allowed for the uncertainty of the results. The lignin content present in the extracted

glucuronoxylan sample could also have a negative effect on the predictability of the cationisation. This could be due to the ester and ether lignin-hemicelluloses linkages that interfere with the replacement of the side chains (Gatenholm & Tenkanen, 2004; González Alriols *et al.*, 2010; Wallmo *et al.*, 2009). This variability of the cationic glucuronoxylan produced will make it difficult to produce paper strength additives with the specific properties (degree of substitution and uronic acid content) the producer requires.

It was noticed that all the modified cationic glucuronoxylan had uronic acid contents lower than the initial value. The modified cationic glucuronoxylan had uronic acid contents between 6.12 and 12.70 wt.%, as compared to the initial glucuronoxylan uronic acid content of 16.86 wt.%. This lowering in uronic acid content is an indication that the solubility of glucuronoxylan was modified with the cationisation method. When the uronic acid content is lowered, a decrease in solubility is noticed in the glucuronoxylan (Li *et al.*, 2007; Walker, 1964). The relationship between degree of substitution and uronic acid content is given in Figure 3.13. The graph showed that as the degree of substitution increased the uronic acid content decreased. The correlation between these two dependant outcomes was statistically significant with a p-value of 0.016. This is to be expected, as the uronic acid side chains are replaced by the cationic functionalising groups on the xylan backbone (Ren *et al.*, 2009).

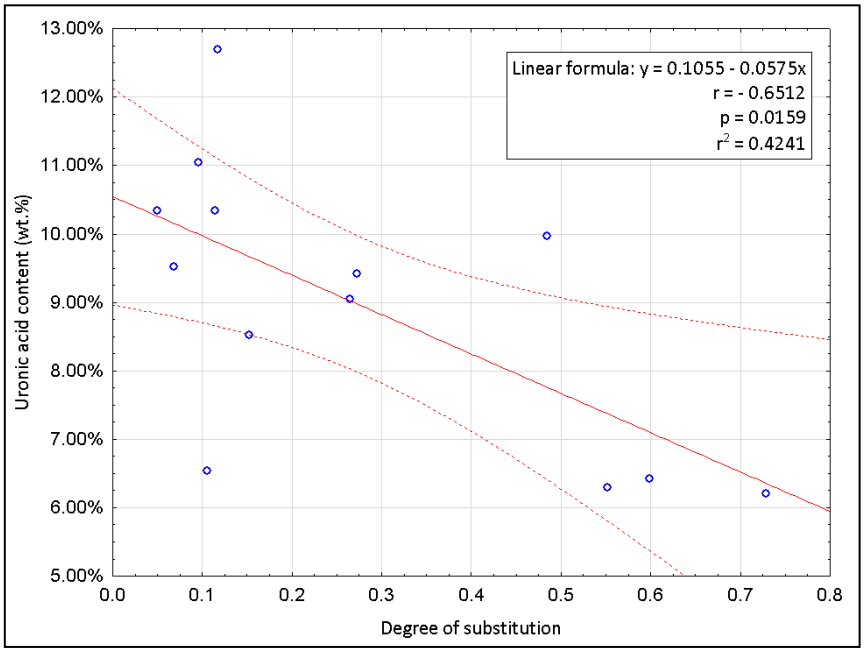


Figure 3.13: Relationship between degree of substitution and uronic acid content of cationic *E. grandis* glucuronoxylan

The modified *E. grandis* glucuronoxylan was characterised to determine whether cationic hemicelluloses were produced with the chosen method (adopted from Ren *et al.* (2009)). The FT-IR spectra of the unmodified and cationic *E. grandis* glucuronoxylan are given in Figure 3.14 (a) and (b), respectively. The two FT-IR spectra showed similar chemical structures for both samples, indicating that the basic hemicellulose structure was not modified. The cationisation caused a slight increase in intensity of the main ether bond absorbance at 1039 cm^{-1} as well as the peak at 1412 cm^{-1}, both of which are assigned to the C-N stretching vibration (Ren *et al.*, 2007; Ren *et al.*, 2008). These two changes in the spectra is an indication that the cationic side chain ($-CH_2-CHOH-CH_2-N^+(CH_3)_3Cl^-$) was attached to the back bone of the glucuronoxylan.

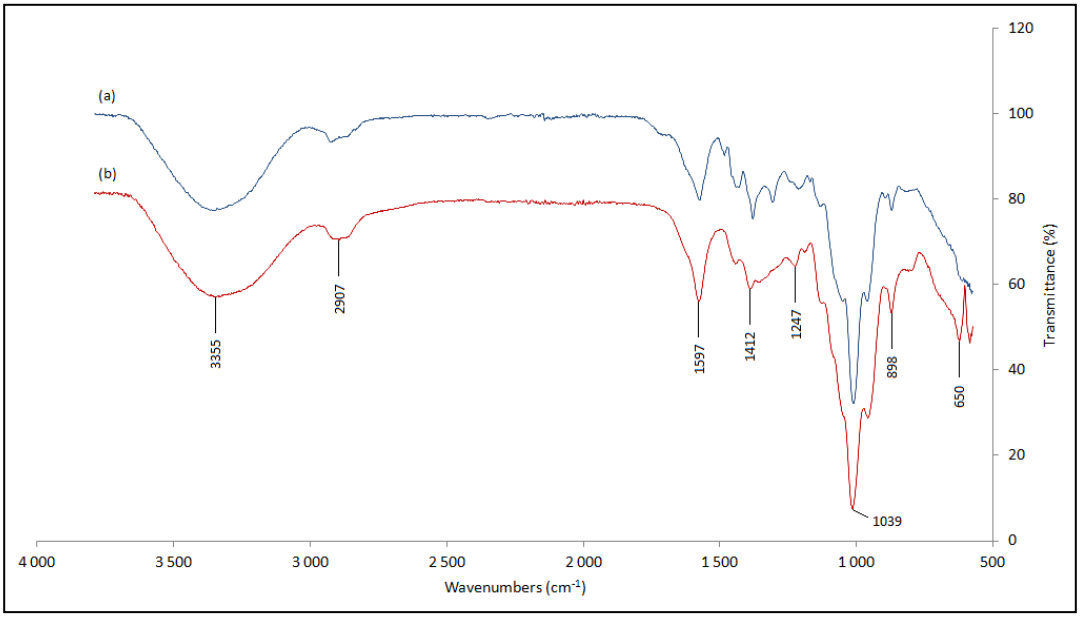


Figure 3.14: FT-IR spectra of (a) unmodified and (b) cationic *E. grandis* glucuronoxylan

The changes in the chemical structure of the hemicelluloses were verified by using Solid state ^{13}C-CP/MAS-NMR of which the spectra of the unmodified and cationic *E. grandis* glucuronoxylan are given in Figure 3.15 (a) and (b), respectively. The decrease of intensity of the peaks at 82.6 and 25.6 ppm indicated a decrease in 4-O-methylglucuronic acid and acetyl content, respectively, in the cationic glucuronoxylan. The disappearance of the peaks in the range of 160 to 110 ppm also indicated the removal of lignin during the modification. The sharp peak at 55.1 ppm is characterised by the carbon resonance of the $(CH_3)_3N^+$ moiety, confirming that cationic glucuronoxylan was produced by modification of the extracted *E. grandis* glucuronoxylan (Ren *et al.*, 2008). The minimum and maximum values obtained for the dependant outputs for the cationisation of extracted *E. grandis* glucuronoxylan are given in Table 3.12. The degree of substitution that was obtained by Ren *et al.* (2009) was between 0.09 and 0.55. The degree of substitution range for this

study was between 0.050 and 0.729. This indicated that using the Ren *et al.* (2009) cationisation method on *E. grandis* alkali extracted glucuronoxylan resulted in cationic glucuronoxylan with a higher degree of substitution.

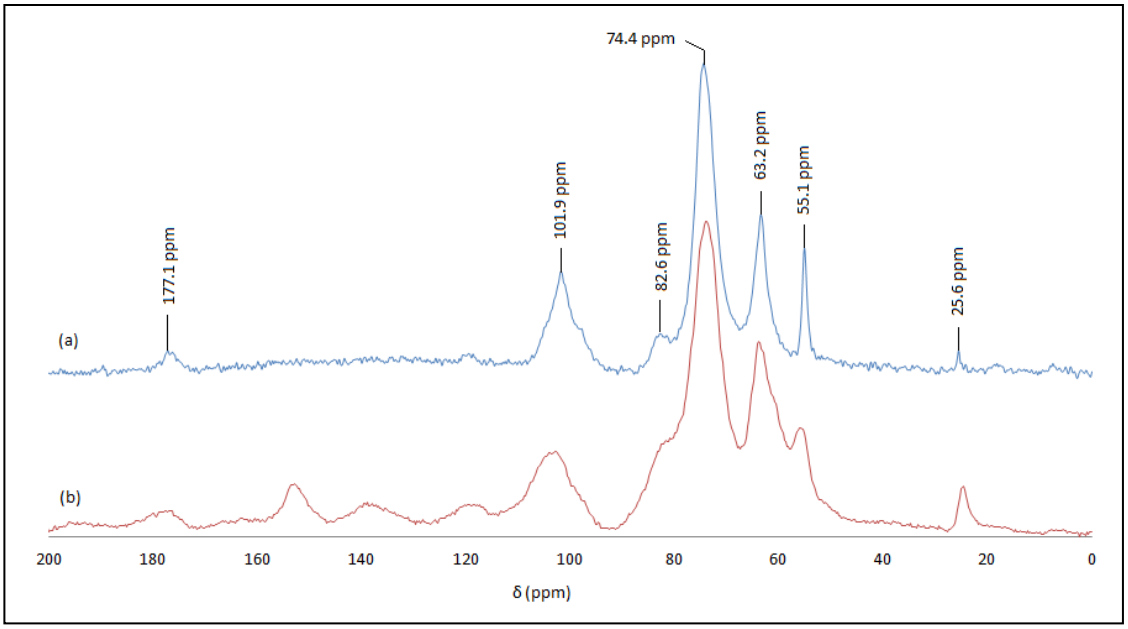


Figure 3.15: Solid state ^{13}C-CP/MAS-NMR spectra of (a) cationic and (b) unmodified *E. grandis* glucuronoxylan

Table 3.12: Dependent output ranges for cationisation of *E. grandis* glucuronoxylan

Dependent outcome	Minimum	Maximum	Standard deviation
Cationic xylan yield (wt.%)	22.36 %	46.49 %	10.00 %
Degree of substitution	0.050	0.729	0.172
Uronic acid content (wt.%)	6.12 %	12.70 %	2.39 %

Cationic galactoglucomannan

For the cationisation of O-acetyl galactoglucomannan, the galactose side chains were replaced by the cation side chain, -CH_2-CHOH-CH_2-$N^+(CH_3)_3Cl^-$ (Ren *et al.*, 2009), similar to the cationisation of *E. grandis* glucuronoxylan. The two variables were similar to *E. grandis* glucuronoxylan cationisation, with variable A being the molar ratio of sodium hydroxide to ETA (varied between 0.10 and 2.00), and variable B, the molar ratio of ETA to anhydrous-mannose (varied between 0.50 and 3.00). The dependant outputs were cationic galactoglucomannan yield (wt.%), degree of substitution, and galactose content (wt.%). The cationisation of *P. abies* O-acetyl galactoglucomannan was optimised by using the CCD experimental design given in Section 3.2.4.1. The Statistica® analysis of the

experimental results indicated some statistically significant impact of the variables on the dependant outcomes. There were no R^2 values above 0.95, but the highest model R^2 value was 0.731, for the galactose content. The p-value for the variable molar ratio of ETA to anhydrous-mannose was 0.009, which is well below 0.05. This low p-value is an indication that this variable had a significant impact on the galactose content of the cationic *P. abies* galactoglucomannan. The p-values for the both the variables for cationic galactoglucomannan yield were below 0.1, showing some statistically significant impact on this dependant outcome. All the cationic *P. abies* galactoglucomannan samples had galactose contents lower than the initial value of 13.01 wt.%.

The larger degree of impact, and predictability, of the variables on the cationisation of the pilot plant *P. abies* galactoglucomannan may be due to more uniform molecular weight distribution and the low lignin content of the sample. The molecular weight elution profile of the pilot plant *P. abies* galactoglucomannan sample is given in Figure 3.16. The molecular weight elution profile shows that the main molecular weight profile was at 39 398 g.mol^{-1} average molecular weight. There were two small elution profiles with 1402 and 89 g.mol^{-1} as well, but these profiles had very small areas when compared to the main elution profile. This indicated that the galactoglucomannan sample contained hemicelluloses with molecular weight in the range of 39 398 g.mol^{-1}, with very small amounts of lower molecular weight substances. Another explanation for the more predictable results may be that the ranges chosen for the reagents were within the range applicable to the *P. abies* galactoglucomannan sample.

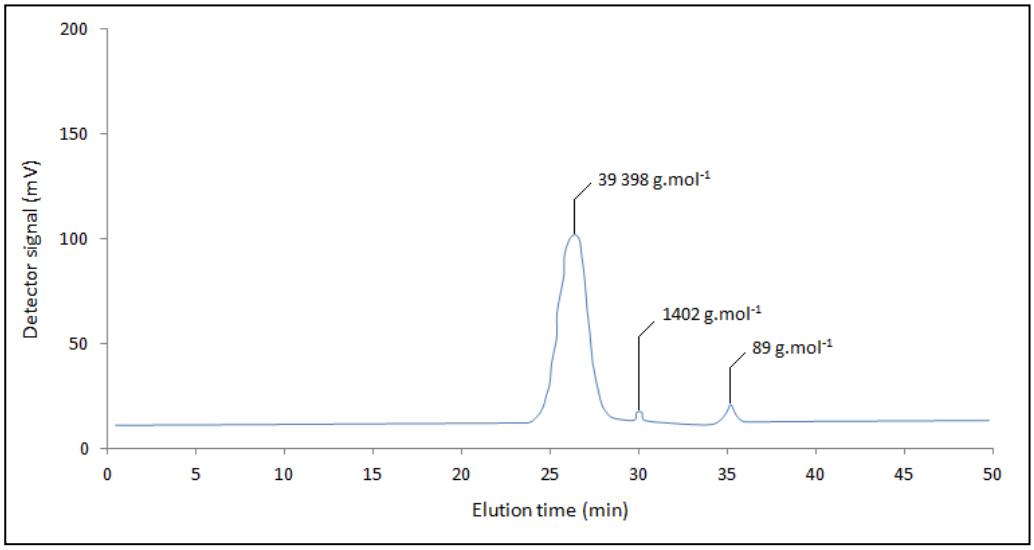


Figure 3.16: SEC elution profile for pilot plant extracted *P. abies* galactoglucomannan used for cationisation

To determine if cationic *P. abies* galactoglucomannan was produced with the chosen cationisation method, the modified products were characterised. The FT-IR spectra of the unmodified and cationic pilot plant *P. abies* galactoglucomannan are given in Figure 3.17 (a) and (b), respectively. The increase in intensity of the peak at 1374 cm^{-1} and the peak left of it is assigned to the C-N stretching vibration, which is a clear indication that the galactoglucomannan has the cationic side chain attached to it. The effect of cationisation was also shown by the increase in intensity of the peak at 1019 cm^{-1}, which indicates an increase in ether bonds (Tian *et al.*, 2010). The FT-IR spectra thus confirm that cationic *P. abies* galactoglucomannan was produced using the selected method.

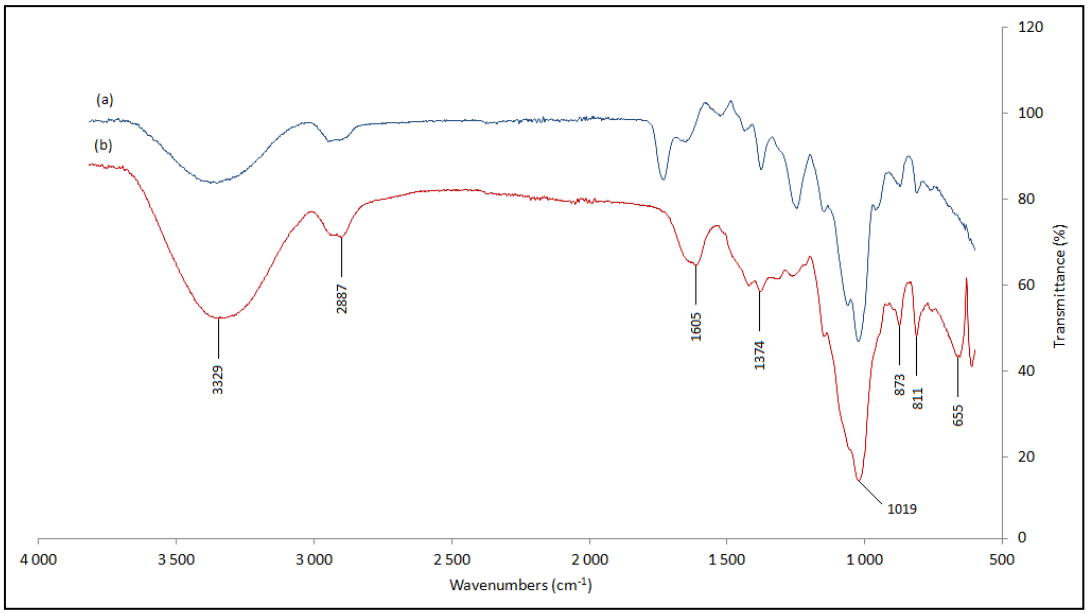


Figure 3.17: FT-IR spectra of (a) unmodified and (b) cationic galactoglucomannan from *P. abies*

From the above results it is concluded that variable A and B can be varied to produce cationic galactoglucomannan with galactose content close to the desired value, while the yield and degree of substitution will have values within a certain range. The minimum and maximum values for the dependent outputs are given in Table 3.13. The degree of substitution range that was obtained by Tian *et al*. (2009) was between 0.15 and 0.42. The maximum value of the degree of substitution for cationic galactoglucomannan, which was obtained in this investigation (0.270), was far below that of Tian *et al*. (2009).

Table 3.13: Dependant output ranges for the cationisation of *P. abies* galactoglucomannan

Dependent outcome	Minimum	Maximum	Standard deviation
Cationic mannan yield (wt.%)	47.84 %	72.74 %	8.98 %
Degree of substitution	0.029	0.270	0.084
Galactose content (wt.%)	6.76 %	11.22 %	0.85 %

3.3.3.2 Carboxymethylation

The carboxymethylation of hemicelluloses will replace the native uronic acid or galactose side chains with the metal ion group -CH_2COONa, as shown in Figure 2.7.

Carboxymethyl glucuronoxylan

The two variables that were varied for the carboxymethylation of *E. grandis* glucuronoxylan were the ratio of ethanol to water (Variable A, varied from 1.00 to 2.00), and the molar ratio of sodium monochloroacetate (SMCA, $ClCH_2COONa$) to anhydrous-xylose (Variable B, varied from 0.50 to 3.00). The dependant outputs were carboxymethyl glucuronoxylan yield (wt.%), degree of substitution, and uronic acid content (wt.%). A CCD experimental design was followed for the optimisation, as described in Section 3.2.4.1. The experimental results obtained were analysed using Statistica ®. The Statistica® analysis of the carboxymethylation of *E. grandis* glucuronoxylan yielded no model with an R^2 value of above 0.95 for any of the dependant outcomes, but gave some significant p-values. The R^2 value for the model fitted to the carboxymethyl xylan yield was 0.807, with p-values below 0.05 for both the variables. From this it was clear that the variables chosen for this method had a significant effect on the carboxymethyl xylan yield, and which can be controlled to some extent by varying both the variables. The model fitted to the degree of substitution results gave an R^2 value of 0.619 and a p-value below 0.05 for the molar ratio of SMCA to anhydrous-xylose. This shows that the degree of substitution can be controlled by this factor to some extent. All the carboxymethylated glucuronoxylan samples had uronic acid contents lower than the initial value of 18.88 wt.%. The lack of statistical significance in the Statistica® analysis is once again attributed to the lignin content (35.91 wt.%) of the initial glucuronoxylan sample (Gatenholm & Tenkanen, 2004; González Alriols *et al.*, 2010; Wallmo *et al.*, 2009). The minimum and maximum values for the dependant outputs are given in Table 3.14. The degree of substitution range that was obtained by Ren *et al.* (2009) was between 0.10 and 0.56. The maximum value is far above the maximum obtained in this investigation, which was 0.109.

Table 3.14: Dependant output ranges for the carboxymethylation of *E. grandis* glucuronoxylan

Dependent outcome	Minimum	Maximum	Standard deviation
Carboxymethyl xylan yield (wt.%)	22.40 %	31.89 %	2.18 %
Degree of substitution	0.049	0.109	0.009
Uronic acid content (wt.%)	10.21 %	21.38 %	2.57 %

The FT-IR spectra of unmodified and carboxymethylated *E. grandis* glucuronoxylan are given in Figure 3.18 (a) and (b), respectively. The sharp band at 897 cm^{-1} confirmed that the β-glycosidic linkages in the backbone of the glucuronoxylan remained after modification (Ren & Sun, 2010). The increase in intensity of the band at 1595 cm^{-1} (Figure 3.18b), confirmed the presence of the COO^- group present in the new metal ion side chain (Ren *et al.*, 2008). In addition, the results showed expansion at 1411 cm^{-1} which is assigned to -CH_2 scissoring (Ren *et al.*, 2008). These two changes confirmed the carboxymethylation of the *E. grandis* glucuronoxylan.

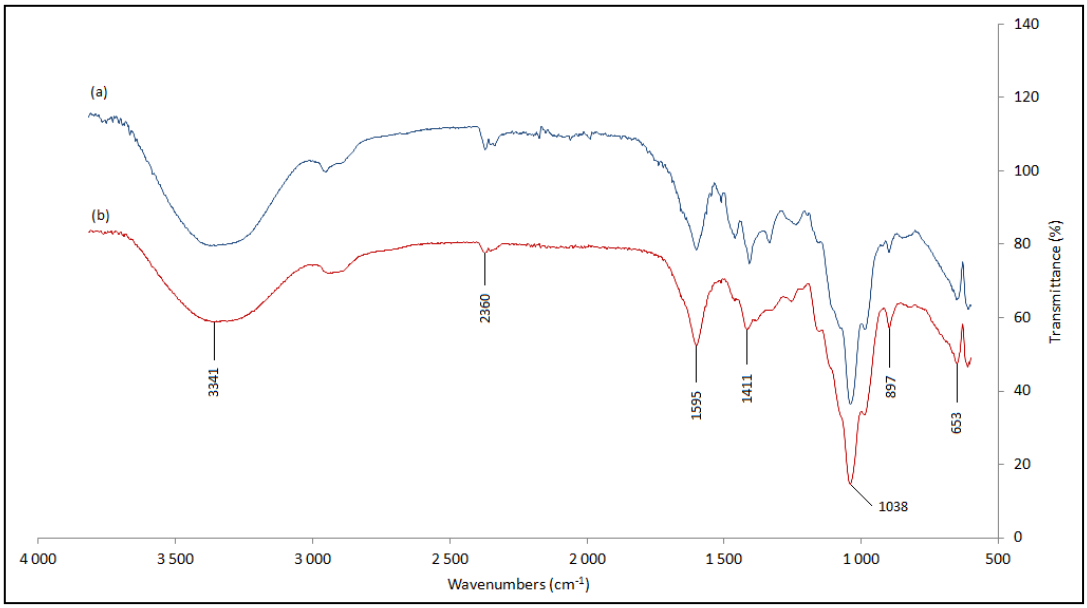


Figure 3.18: FT-IR spectra of (a) unmodified and (b) carboxymethylated glucuronoxylan from *E. grandis*

The Solid state ^{13}C-CP/MAS-NMR spectra of the unmodified and carboxymethylated *E. grandis* glucuronoxylan are presented in Figure 3.19 (b) and (a), respectively. The decrease in the peaks at 82.2 and 25.1 ppm indicated the decrease in the 4-O-methyl glucuronic acid and acetyl side groups on the backbone of the hemicellulose. The disappearance of the peaks between the range of 160 and 110 ppm shows the removal of the lignin present in the unmodified glucuronoxylan sample (Matulova *et al.*, 2005). The signal for the carboxylate groups appeared at 176.9 ppm and the peak at 73.8 ppm. These two peaks were assigned to the methylene carbon atoms of the carboxymethyl

side groups (Ren *et al.*, 2008). The NMR spectra confirmed that carboxymethyl glucuronoxylan was produced.

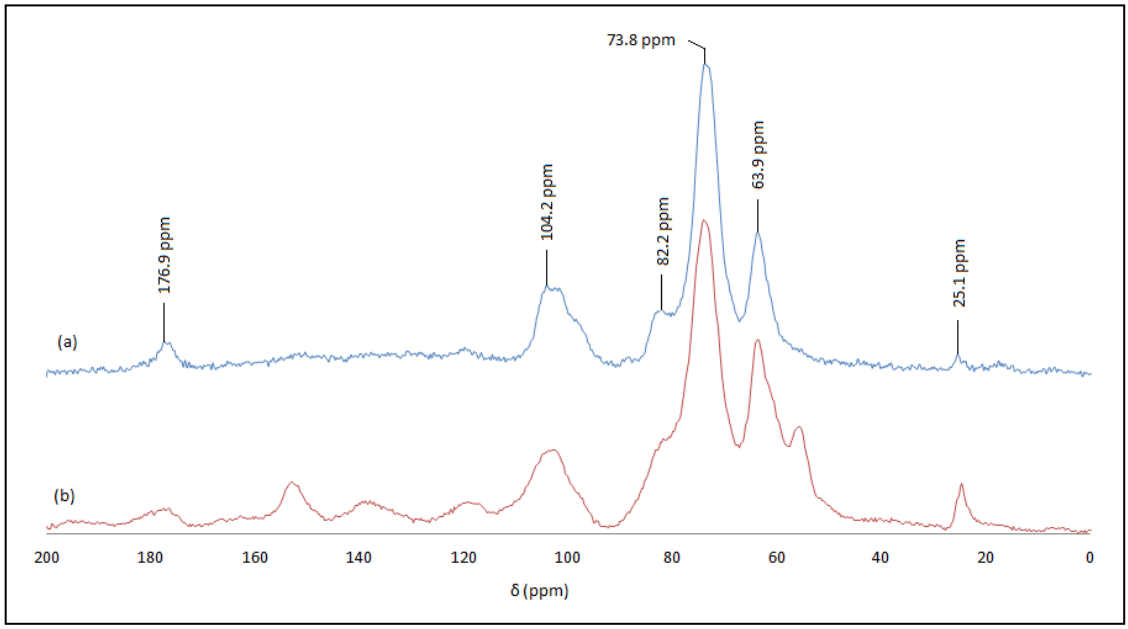


Figure 3.19: Solid state ^{13}C-CP/MAS-NMR spectra of (a) carboxymethyl and (b) unmodified *E. grandis* glucuronoxylan

Carboxymethyl galactoglucomannan

The two variables that were varied for this method were variable A, molar ratio of sodium hydroxide to anhydrous-mannose (varied between 3.38 and 6.76), and variable B, the molar ratio of monochloroacetic acid (MCA, $CH_2ClCOOH$) to anhydrous-mannose (varied between 0.50 and 3.00). The Statistica® analysis of the carboxymethylation of galactoglucomannan resulted in an R^2 value of 0.617 for the yield of carboxymethyl galactoglucomannan, and a p-value lower than 0.05 for the molar ratio of MCA to anhydrous-mannan. This indicated that the molar ratio of MCA to anhydrous-mannose had a statistically significant impact on the yield. There were no galactose content results, due to a lack of sample to determine this dependant output. This lack of statistical significance for the carboxymethylation of galactoglucomannan may be due to reagents that were present in excess. The minimum and maximum values for the dependant outputs are given in Table 3.15. The degree of substitution range that was obtained by Kobayashi *et al.* (2002) was between 0.02 and 0.32. The degree of substitution range obtained in this study was between 0.219 and 1.270. This is much higher than the range obtained by Kobayashi *et al.* (2002).

Table 3.15: Dependant output ranges for the carboxymethylation of *P. abies* galactoglucomannan

Dependent outcome	Minimum	Maximum	Standard deviation
Carboxymethyl mannan yield (wt.%)	10.80 %	77.99 %	7.43 %
Degree of substitution	0.219	1.270	0.426

The FT-IR spectra of the unmodified and carboxymethyl *P. abies* galactoglucomannan are given in Figure 3.20 (a) and (b), respectively. The new peak at 1635 cm^{-1} (Figure 3.20b) was assigned to the COO^- group, which represents the new metal ion side chains (Ren *et al.*, 2008). The new peaks at 1411 and 1375 cm^{-1} (Figure 3.20b) were assigned to -CH_2 scissoring and -OH bending vibration, respectively (Ren *et al.*, 2008). The appearance of these new peaks confirmed the carboxymethylation of the *P. abies* galactoglucomannan.

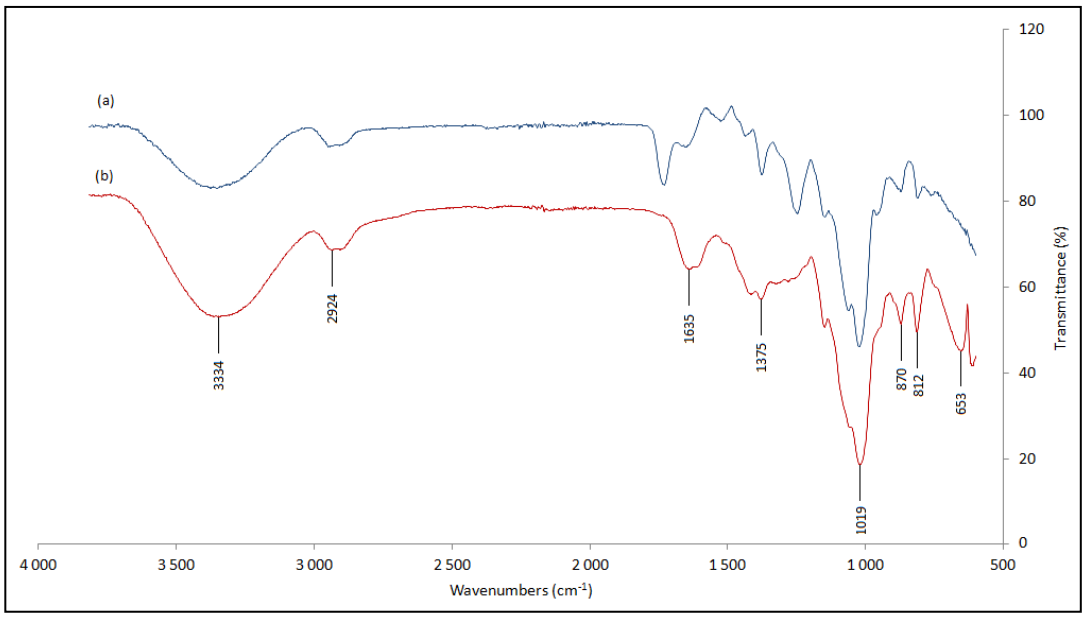


Figure 3.20: FT-IR spectra of (a) unmodified and (b) carboxymethylated *P. abies* galactoglucomannan

3.3.3.3 Sonication

Since the sonication of hemicelluloses for use as paper strength additives is a completely new method, only the sonication time was selected as independent variable.

Sonicated glucuronoxylan

The sonication of glucuronoxylan was applied to both extracted *E. grandis* and commercial *Fagus sylvatica* (*F. sylvatica*) glucuronoxylan for comparison. The sonication time was varied between 10 and 60 minutes with intervals at 17, 35, and 53 minutes. The experimental data for the one factor

experimental design was analysed with Statistica® using one way ANOVA tests. The one way ANOVA resulted in p-values of between 0.234 and 0.634 for sonicated *E. grandis* glucuronoxylan, and between 0.491 and 0.778 for *F. sylvatica*. This indicated that there were no statistically significant trends in the experimental results for the sonication of glucuronoxylan. The impact of sonication time on the dependant outcomes (sonicated xylan yield (wt.%), molecular weight ($g.mol^{-1}$), and uronic acid content (wt.%)) is presented in Figure 3.21, with the broken horizontal lines indicating the reference value of the unmodified hemicellulose. The trend lines from these graphs confirmed the lack of statistically significant trends, with all the R^2 values below 0.95. The molecular weight of the sonicated *E. grandis* glucuronoxylan was lower than the initial molecular weight, indicated by the broken horizontal line in Figure 3.21(b). For the *F. sylvatica* glucuronoxylan the molecular weight was above the initial molecular weight, and it was still rising as shown in Figure 3.21(e). This increase in molecular weight could be attributed to either new hydrogen bonds that form between larger and smaller hemicelluloses chains, or by agglomeration between the hemicellulose chains (Hendriksson & Gatenholm, 2001; Linder *et al.*, 2003). The uronic acid content was slightly lower after sonication for both the glucuronoxylan samples (Figures 21 (c) and (f)). Apart from these changes, the ultrasound treatments did not have an effect on the glucuronoxylan. The minimum and maximum values for the dependant outputs results for extracted *E. grandis* glucuronoxylan are given in Table 3.16.

Table 3.16: Dependant output ranges for the sonication of *E. grandis* glucuronoxylan

Dependent outcome	**Minimum**	**Maximum**	**Standard deviation**
Sonicated xylan yield (wt.%)	48.17 %	50.35 %	1.57 %
Molecular weight ($g.mol^{-1}$)	54 856	57 347	1 363
Uronic acid content (wt.%)	12.99 %	18.39 %	2.73 %

The FT-IR spectra of unmodified and sonicated *E. grandis* glucuronoxylan are given in Figure 3.22 (a) and (b), respectively. There were only two notable differences on the spectra, the absence of a peak at 1720 cm^{-1} in both spectra, and the intensification of the 896 cm^{-1} peak in the sonicated sample. This was an indication that the sonication did not oxidize the β-glycosidic linkages, or hydroxyl groups of the glucuronoxylan (Sun *et al.*, 2002).

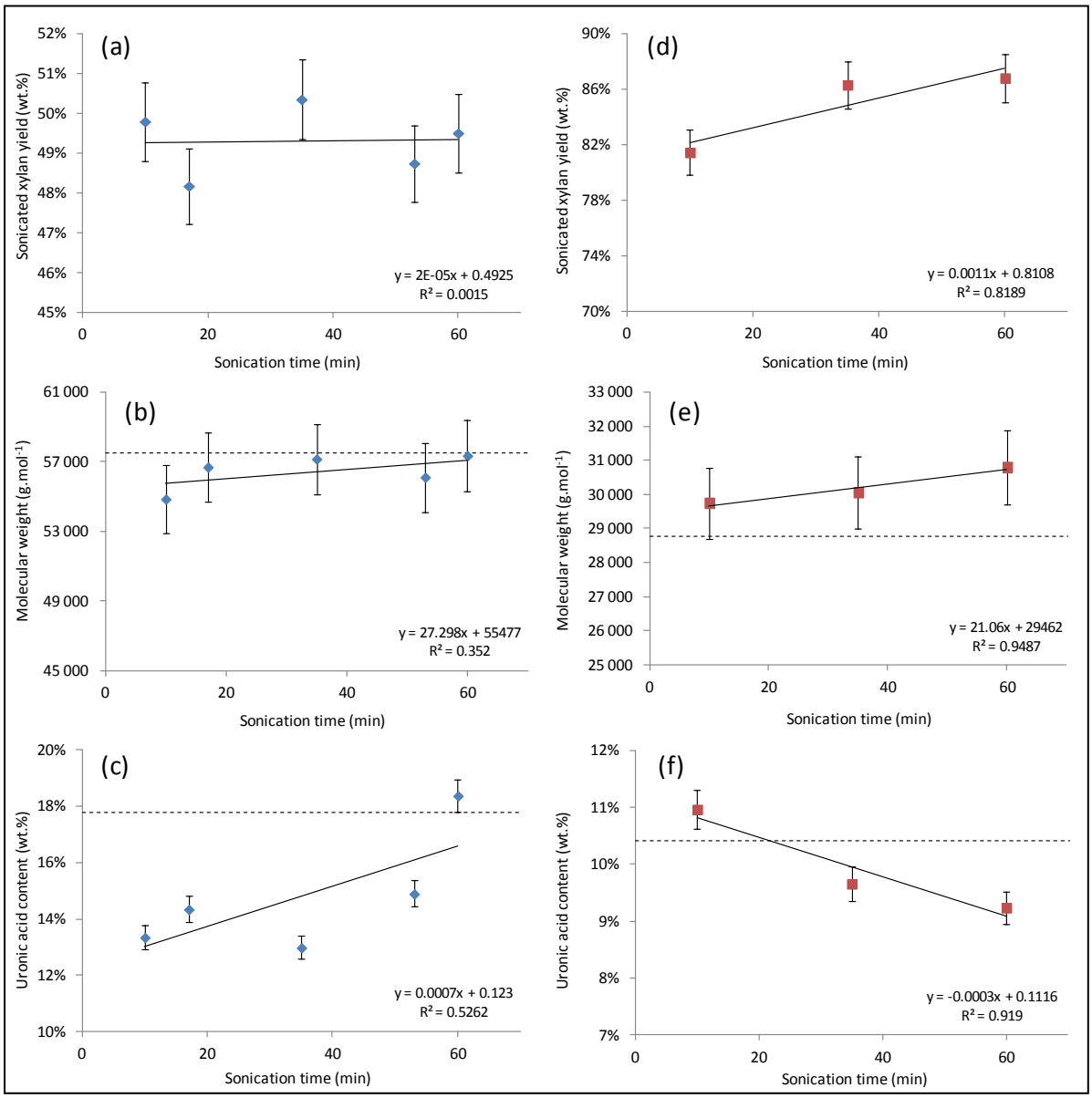


Figure 3.21: Ultrasound treatment results for *E. grandis* glucuronoxylan (a) sonicated xylan yield (wt.%), (b) molecular weight (g.mol^{-1}), and (c) uronic acid content (wt.%) and for *F. sylvatica* glucuronoxylan (d) sonicated xylan yield (wt.%), (e) molecular weight (g.mol^{-1}), and (f) uronic acid content (wt.%)

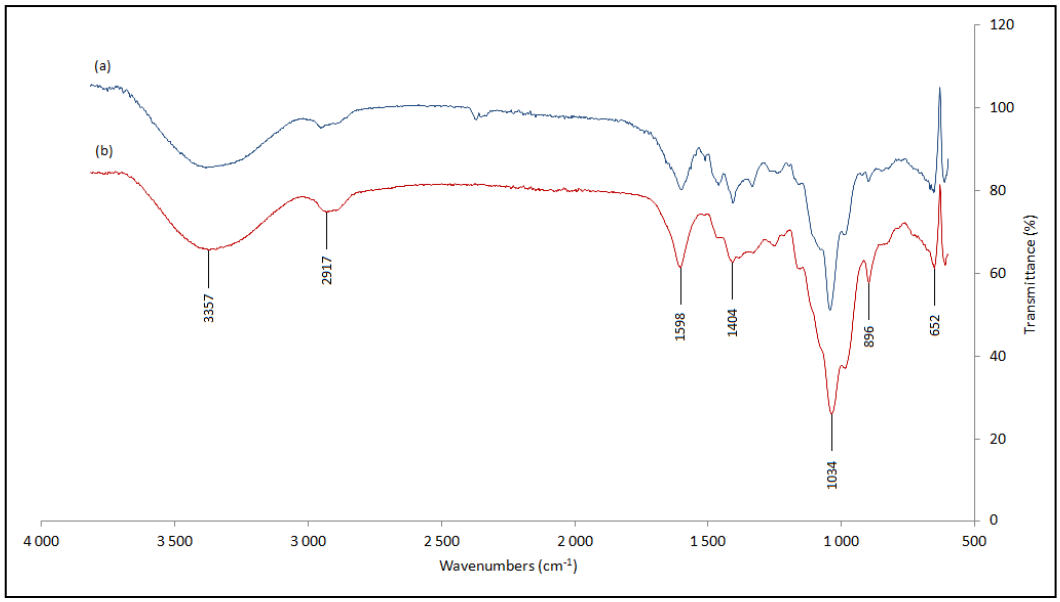


Figure 3.22: FT-IR spectra of (a) unmodified and (b) sonicated glucuronoxylan from *E. grandis*

The Solid state ^{13}C-CP/MAS-NMR spectra of the unmodified and sonicated glucuronoxylan are given in Figure 3.23 (b) and (a), respectively. The decrease of intensity of the peaks at 82.1 and 25.1 ppm showed that there was a decrease in 4-O-methylglucuronic acid and acetyl side group content respectively. The decrease in intensity and disappearance of the peaks between the range of 160 and 110 ppm, and 44.8 ppm, was an indication that the lignin content of the sonicated hemicelluloses had decreased. The Solid state ^{13}C-CP/MAS-NMR spectra thus confirmed that ultrasound treatments lower the acetyl- and 4-O-methyl glucuronic acid content of the *E. grandis* glucuronoxylan.

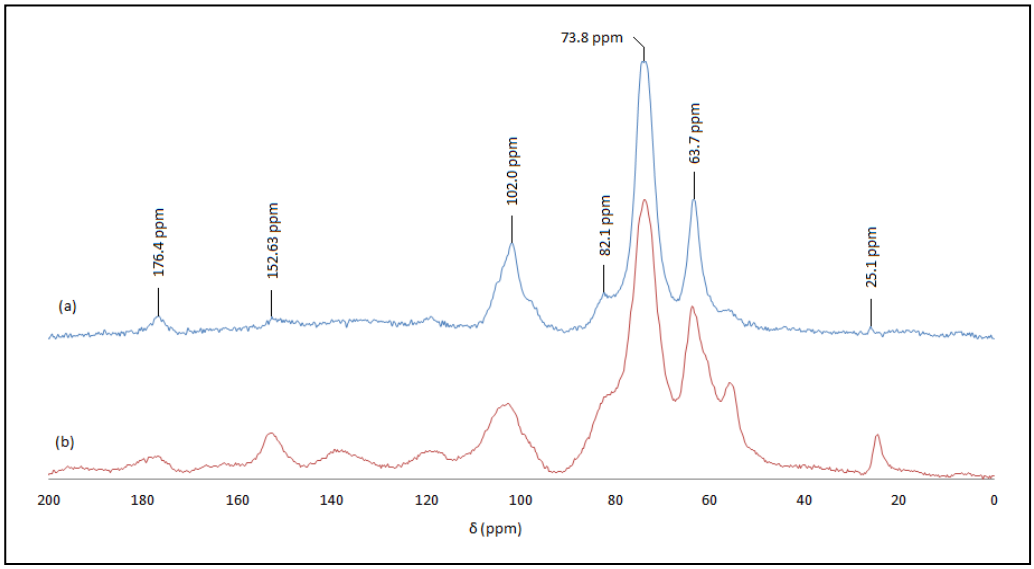


Figure 3.23: Solid state ^{13}C-CP/MAS-NMR spectra of (a) sonicated and (b) unmodified *E. grandis* glucuronoxylan

Sonicated galactoglucomannan

The sonication of galactoglucomannan was applied to both the pilot plant and PHWE *P. abies* galactoglucomannan. The one way ANOVA tests done on the experimental data, resulted in p-values of between 0.008 and 0.894, for sonicated pilot plant *P. abies* galactoglucomannan, and between 0.059 and 0.673 for PHWE *P. abies* galactoglucomannan. Almost all of the p-values showed that there is no statistical significance in the results, except for one. The p-value of the effect sonication time had on the galactose content of the pilot plant *P. abies* galactose was 0.008. This low p-value indicated statistical significance between these two variables. The graphs of the experimental data are given in Figure 3.24, with the broken horizontal lines indicating the reference values for the unmodified hemicellulose. The graphs confirmed that there are no statistically significant trends with all of the R^2 values below 0.95. The only effects that the ultrasound had on galactoglucomannan was slightly lower molecular weight and galactose content. The minimum and maximum values for the dependant outputs results for pilot plant *P. abies* galactoglucomannan are given in Table 3.17.

Table 3.17: Dependant output ranges for the sonication of *P. abies* galactoglucomannan

Dependent outcome	Minimum	Maximum	Standard deviation
Sonicated mannan yield (wt.%)	65.06 %	67.38 %	4.26 %
Molecular weight ($g.mol^{-1}$)	32 261	33 027	986
Galactose content (wt.%)	7.80 %	9.61 %	0.20 %

The FT-IR spectra of unmodified and sonicated pilot plant *P. abies* galactoglucomannan are given in Figure 3.25 (a) and (b), respectively. The major changes in the FT-IR spectra of the sonicated galactoglucomannan (Figure 3.25b) were the appearance of the peaks at 1610 and 1375 cm^{-1}. The peak at 1610 cm^{-1} was associated with the absorption of water, while 1375 cm^{-1} was associated with CH deformation due the lowering of the lignin content.

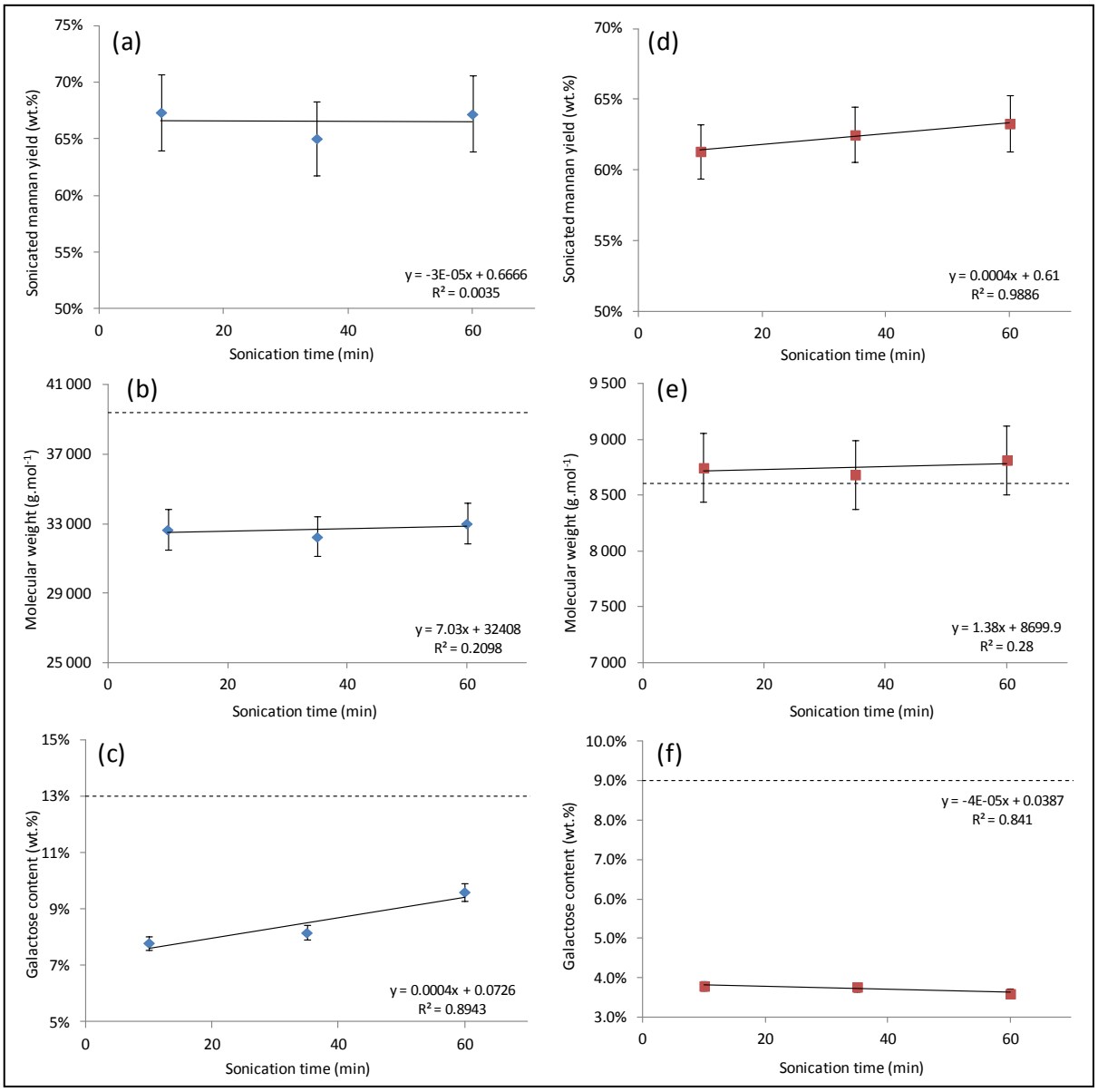


Figure 3.24: Ultrasound treatment results for *P. abies* pilot plant galactoglucomannan (a) sonicated mannan yield (wt.%), (b) molecular weight (g.mol^{-1}), and (c) galactose content (wt.%) and for *P. abies* PHWE galactoglucomannan (d) sonicated xylan yield (wt.%), (e) molecular weight (g.mol^{-1}), and (f) uronic acid content (wt.%)

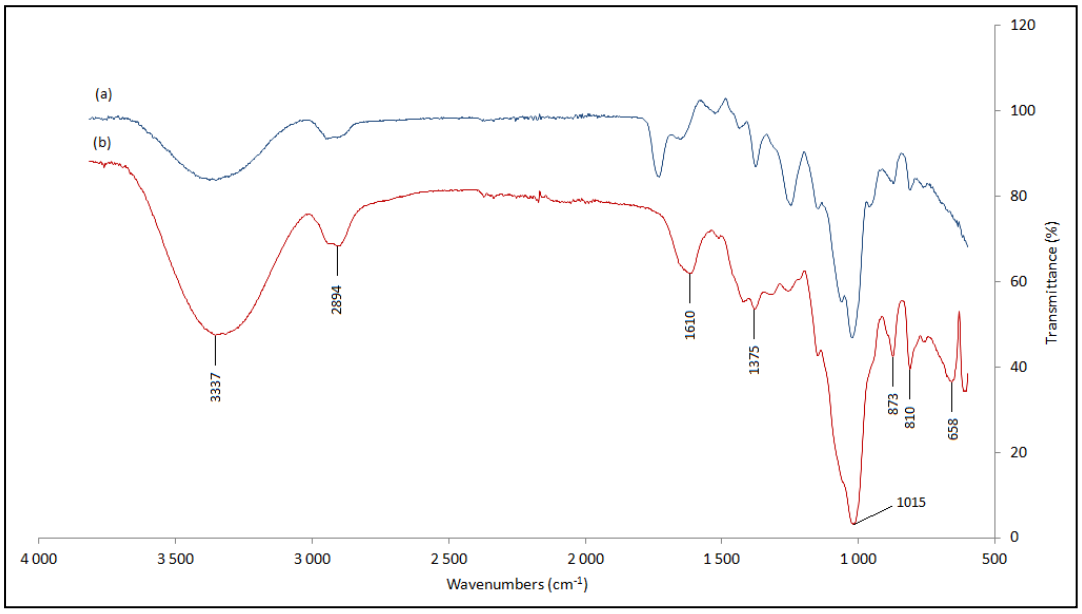


Figure 3.25: FT-IR spectra of (a) unmodified and (b) sonicated galactoglucomannan from *P. abies*

3.4 Conclusions

The modification of hemicelluloses by cationisation, carboxymethylation and ultrasound treatments produced cationic, carboxymethyl and more pure hemicelluloses, respectively. It can be concluded that the chemical modification methods (cationisation and carboxymethylation) chosen from literature were suitable for the modification of the extracted *E. grandis* 4-O-methylglucuronoxylan, *F. sylvatica* 4-O-methylglucuronoxylan, and *P. abies* galactoglucomannan. The ultrasound treatments did not modify the properties, or chemical structure, of the hemicelluloses, and it was therefore concluded that the ultrasound treatment used for this investigation were not suitable for hemicellulose modification.

The cationisation modification of the hemicelluloses in this investigation resulted in derivatives with $-CH_2-CHOH-CH_2-N^+(CH_3)_3Cl^-$ side chains, which was confirmed with FT-IR and Solid state ^{13}C-CP/MAS-NMR, making the hemicelluloses cationic. The range of the degree of substitution for the cationic *E. grandis* glucuronoxylan was between 0.050 and 0.729. It was between 0.029 and 0.270 for the cationic *P. abies* galactoglucomannan. The uronic acid content of the glucuronoxylan and the galactose content of the galactoglucomannan were all lowered during the modification process. The side chain that was attached to the hemicellulose backbones during carboxymethylation was the metal ion group $-CH_2COONa$. This was confirmed with FT-IR and Solid state ^{13}C-CP/MAS-NMR analyses of all the modified hemicelluloses. The minimum and maximum values for the degree of

substitution for the carboxymethyl *E. grandis* glucuronoxylan were 0.049 and 0.109. It was 0.219 and 1.270 for the *P. abies* galactoglucomannan. Once again the uronic acid and galactose content of the modified hemicelluloses were lower than their initial values.

Ultrasound treatments did not have the expected effect on the hemicelluloses for the samples tested in this study. The hemicelluloses were not oxidized by radicals formed in the aqueous medium. This may be attributed to insufficient sonication power of the equipment used. The methods in literature used high frequency ultrasound at a power levels ranging from 100 to 250 W at a frequency of 610 kHz, while the power of the apparatus used in this investigation was 170 W at 35 kHz. The lignin content lowered after sonication and ethanol precipitation. The molecular weight range for the sonicated *E. grandis* glucuronoxylan was between 54 856 and 57 347 $g.mol^{-1}$, while the range for *P. abies* galactoglucomannan was between 32 261 and 33 027 $g.mol^{-1}$. The molecular weight increase as the sonication time increases may be attributed to either new hydrogen bonds formed between the hemicelluloses backbone chains, or agglomeration within the sample.

CHAPTER 4

HANDSHEET FORMATION WITH HEMICELLULOSES ADDITION AND ADDITION PROTOCOL DEVELOPMENT

4.1 Introduction

In the pulping process hemicelluloses are degraded into low molecular weight isosaccharinic acids. These isosaccharinic acids end up in the black liquor along with the degraded lignin. This black liquor is concentrated and burnt for steam generation (Al-Dajani & Tschirner, 2008). These hemicelluloses can be pre-extracted from the biomass prior to pulping with little to no downstream effect on the paper quality (Al-Dajani & Tschirner, 2008; Marinova *et al.*, 2009). This pre-extraction of the hemicelluloses speed up the kinetics of the delignification during the Kraft pulping process if an alkaline extraction method is used, thus lowering the initial volume of white liquor that is required (Al-Dajani & Tschirner, 2008; Kerr & Goring, 1974).

Along with improved delignification during the pulping section, alkaline pre-extraction of hemicelluloses will result in value added products that can be produced from the hemicelluloses. One of the possible uses of the hemicelluloses is as wet-end strength additive in the papermaking process (Ren *et al.*, 2009; Rojas & Neuman, 1999; Schönberg *et al.*, 2001). It has been proven that the presence of native, or modified, hemicelluloses in the paper web improves paper physical and surface properties (Ren *et al.*, 2009; Rojas & Neuman, 1999; Schönberg *et al.*, 2001). If these hemicellulosic strength additives can perform as efficiently as the conventional strength additives, the use of synthetic additives will decline. The development of hemicellulosic strength additives will be a movement toward more “green” strength additives for the paper industry (O’Byrne, 2009).

No investigation has been done to determine the most appropriate time or stage to add the hemicellulose additives to the papermaking process. There has however been some investigation in using hemicelluloses as a refiner/beater additive (Bhaduri *et al.*, 1995). There is thus a need for an

investigation to determine how the hemicellulosic additives behave during some of the processes of the papermaking process such as, dosage level, bleaching, and refining/beating.

In this study, modified hemicelluloses were used as additives to produce handsheets. This was done to investigate the effect differently modified hemicelluloses had on the physical and surface properties of paper. The addition protocol for cationic hemicelluloses was investigated as well, to determine the optimum addition point to the papermaking process, i.e. before bleaching, during refining, or in the headbox (wet-end) of the papermaking machine, as well as to determine the optimum dosage level of cationic hemicelluloses. The objectives for this study were:

- Investigation of the effect the different modified hemicelluloses had on the physical and surface properties of handsheets when they were used as wet-end additives and compared to commercially available wet-end additives.
- Development of an addition protocol for introducing hemicellulose as wet-end additives to the papermaking process, by testing for the optimum stage when add them.

4.2 Materials and methods

4.2.1 Materials

Pure *E. grandis* pulp from the Kraft process was used for handsheet formation in this study. The pulp was provided by SAPPI's Ngodwana mill in the Mpumalanga Province, South Africa. Both un-bleached, and bleached, pulps were obtained from this mill. The pulp was sampled from the pulping process at the appropriate sampling points. Both pulp samples had a consistency of approximately 25% (Grobler, 2011).

The hemicellulose types used in this study were the same as those listed in Table 3.1. The industrial wet-end additives were supplied by SA Paper Chemicals (Pty) Ltd. Two different additives were supplied namely CatStarch 134 and Aquapel 312. CatStarch 134 is a cationic starch derivative, while Aquapel 312 is an alkylketene dimer (AKD) additive. Both of these additives are in the sizing category of additives and CatStarch 134 has the added advantage of adding strength to the paper web. A detailed list of other chemical reagents used in this study is given in Table 4.1.

Table 4.1: Detailed list of chemicals with their purity level and sources

Chemical name	Molecular formula	Purity	Supplier company
Aluminium sulphate	$Al_2(SO_4)_3$	99.99%	Sigma-Aldrich
Hydrogen peroxide	H_2O_2	30%	Sigma-Aldrich
Sodium hydroxide	NaOH	> 97%	Sigma-Aldrich

4.2.2 Bleaching

Hydrogen peroxide (H_2O_2) bleaching was conducted on the un-bleached pulp. The procedure used for the laboratory bleaching of the pulp was adopted from Süss *et al*. (1997) and Hubbe (2010). Un-bleached pulp samples with a consistency of 30% were used. The pulp was placed in a plastic bag, which was placed in a water bath for pre-heating to 70 ^{o}C. When the temperature was 70 ^{o}C, 0.6 % sodium hydroxide was added on an oven dry basis of the pulp, while the hydrogen peroxide was added at 2 % on an oven dry basis of the pulp. The mixture was allowed to react for 30 min at the desired temperatures ranging between 70 and 90 ^{o}C under constant mixing. The pulp was then removed from the plastic bag, and the reaction solution was filtered off. The remaining pulp was washed several times to remove any reactants from the pulp. The bleached pulp was then placed in an oven at 45 ^{o}C to dry the pulp overnight. The oven dry bleached pulp was then used for handsheet formation. A summary of the bleaching conditions are given in Table 4.2 (Hubbe, 2010; Loureiro *et al*., 2011; Sundara, 1998).

Table 4.2: Hydrogen peroxide bleaching conditions (Hubbe, 2010; Loureiro *et al*., 2011; Süss *et al*., 1997; Sundara, 1998)

Variable	Chosen value
Hydrogen peroxide charge	2 % based on oven dry pulp
Sodium hydroxide charge	0.6 % based on oven dry pulp
Temperature	70 - 90 ^{o}C
Reaction time	30 min

4.2.3 Refining

The refining/beating of the pulp samples was done with the well established analytical method TAPPI T 200 om-89 “Laboratory beating of pulp (beater method)” was used (Technical Association of the Pulp and Paper Industry, 2010). A representative sample from the pulp was placed in a beater

with a controlled bedplate and beaten at different time intervals. The refining time was done over a range of 60 minutes with representative samples being taken at times 0, 5, 10, 20, 40 and 60 minutes. The refining time was then converted to refining energy (kilowatt hours per ton of pulp that was being refined, $kWh.ton^{-1}$) for better comparison. The freeness of the pulp was measured before and after beating, to determine the draining rate of the pulp. The dosage level of the cationic *E. grandis* glucuronoxylan additive was 1.0 wt.% based on dry pulp.

4.2.4 Freeness of pulp

The freeness of the pulp was measured with the analytical method TAPPI T 227 om-92 "Freeness of pulp (Canadian standard method)" (Technical Association of the Pulp and Paper Industry, 2010). A 2L, 1.2 wt% consistency pulp was prepared. This was done by weighing 24 g of dry pulp sample, and allowing it to soak in a small quantity of water for 4 hours. The mixture was then diluted up to 2 L. The pulp was then disintegrated at 3000 rpm to 50 000 revolutions in a British Pulp Evaluation Apparatus standard disintegrator. It was then diluted to 7.2 L to a consistency of 0.3 wt%. A 1000 mL sample was taken from the stock in a measuring cylinder. This was inverted three times to mix the pulp sample thoroughly. The 1000 mL pulp sample was then poured into the freeness tester, and the procedure for the tester was followed. The volume discharged from the side orifice was recorded in millilitres (mL).

4.2.5 Repeatability of pulp consistency

The properties of handsheets prepared from different pulp slurries might be different. Therefore for each test that was done, reference handsheets had to be made. However, a method was used to gain sufficient control over the inherent variability between pulp consistencies. Whenever a pulp solution was prepared, it was done in a 20 L container with adequate stirring. The solution was made up of a quantity of wet pulp, and the container was filled with tap water to a volume of 20 L. After adequate mixing a volume of 1000 mL was extracted from the container and a handsheet was made from this volume. The handsheet was placed on a heating table to reach a bone dry state. The handsheet was then weighed, and an algorithm was used to calculate the mass of pulp, or volume of water, that had to be added to the container to get the consistency of the pulp to 0.30 %. The algorithm used is given in Appendix C. This procedure was applied to all the pulp slurries

prepared for the handsheet formation to ensure uniform stock consistency throughout experimentation.

4.2.6 Hand sheet formation

The TAPPI T 205 om-88 standard method was used for the "Formation of handsheets for physical testing of pulp" (Technical Association of the Pulp and Paper Industry, 2010). The pulp test specimen was weighed to 24 g, to the nearest 0.5 g, dry weight. The test specimen was soaked in cold water for at least 4 hours. The wetted fibre was then diluted to 2000 mL (1.2 % consistency) with cold water and then disintegrated in a British Pulp Evaluation Apparatus standard disintegrator at 3000 rpm for 50 000 revolutions. The disintegrated pulp was diluted to 7200 mL (0.30% consistency) with cold water and thoroughly mixed by stirring. This ensured adequate contact time for adsorption of the hemicelluloses onto the pulp fibres. Then 400 mL of the stock was poured into separate containers for handsheet formation.

The British Pulp Evaluation Apparatus sheet machine, shown in Figure 4.1, was filled halfway with cold tap water, and then the 400 mL stock was added. The sheet machine was filled up to 349.3 mm above the wire surface, and the perforated stirrer was moved up-and-down five times within the pulp solution. After the water surface stabilized, the drain cock of the machine was fully opened to drain the water and form the handsheet. After the formation of the handsheet, blotting paper was used to remove the sheet from the wire with a couching apparatus. The removed handsheet, placed between the two blotting papers, was placed in an Agfa-Gevaert wire drying press for 24 hours to dry. This procedure was repeated ten times for the same pulp sample to form ten handsheets for the physical testing.

For the handsheets that were prepared with hemicelluloses additives, a dosage of 1.00 wt.% (on the dry weight of the pulp) was chosen from literature (Ren *et al.*, 2009). The pulp slurry with the hemicelluloses additives was then stirred for 10 minutes after addition. Then the handsheet formation procedure was followed as stated above.

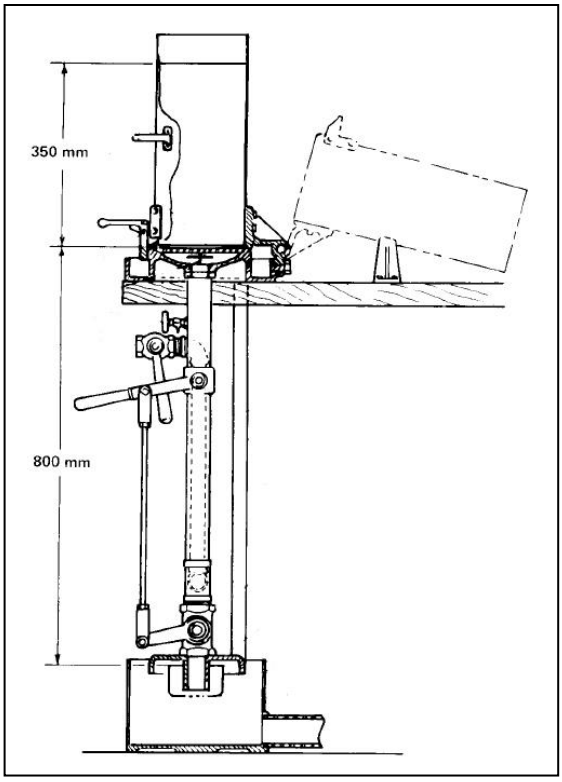


Figure 4.1: Standard 159 mm diameter British sheet machine (Technical Association of the Pulp and Paper Industry, 2010)

4.2.7 Physical and surface properties of handsheet

The physical- and surface properties are used by industry to determine paper quality. These properties were measured to determine the impact of additive addition. Before any testing could commence, the handsheets had to be conditioned according to the TAPPI T402 standard for "Standard conditioning and testing atmospheres for paper, board, pulp handsheet, and related products" (Technical Association of the Pulp and Paper Industry, 2010). The handsheets were placed in a temperature and humidity controlled dark room for 48 hours at a temperature of 23 °C and a relative humidity of 50%, after which the properties of the handsheets were then tested. The physical properties of importance are; basis weight, tensile strength, breaking length, burst- and tear index and the Cobb test. The surface- and other properties are; ISO brightness, air permeability, roughness and photographs taken with Scanning Electron Microscope (SEM). These physical properties were measured with the standard methods given in Table 4.3, while the surface- and other properties were measure with standard equipment.

Table 4.3: Standard methods used for physical property determination of handsheets

Physical property tested	Analytical standard	Additional standard required
Conditioning	TAPPI T402 om-08	-
Basis weight	TAPPI T 220 om-88	-
Tensile strength and breaking length	TAPPI T 220 om-88	TAPPI T 494 om-96
Burst index	TAPPI T 220 om-88	TAPPI T 403 om-08
Tear index	TAPPI T 220 om-88	TAPPI T414 om-98
Water absorptiveness (Cobb test)	TAPPI T 441 om-98	-

4.2.7.1 Basis weight

The basis weight of paper is defined as the mass per unit area of the paper in $g.m^{-2}$. The TAPPI T 220 om-88 standard method was used for basis weight determination (Technical Association of the Pulp and Paper Industry, 2010). Five handsheets were weighed on a balance to the closest 0.01 g, and the total mass was then multiplied by 10. The area of each sheet was 200 cm^2, from the handsheet apparatus that was used. Equation 4-1 is the equation that was used to determine the basis weight:

$$Basis\ weight = Mass\ of\ the\ 5\ handsheets \times 10 \quad (4\text{-}1)$$

4.2.7.2 Tensile index

The tensile index of the handsheets were tested by using the TAPPI standards coded T 220 om-88 and T 494 om-96, which used a constant rate of elongation apparatus (Technical Association of the Pulp and Paper Industry, 2010). The Instron TM-M elongation apparatus was used with the Hottinger Baldwin Messtechnik GmbH MVD2510 measurement amplifier. The tensile strength for a 15 mm width piece of handsheet is calculated by using Equation 4-2. The tensile strength was then used to calculate the tensile index given in Equation 4.3:

$$Tensile\ strength = 0.6538 \times Tensile\ break\ load \quad (4\text{-}2)$$

$$Tensile\ index = 1000 \times \frac{Tensile\ strength}{Basis\ weight} \quad (4\text{-}3)$$

where the tensile break load is measured in kg and the tensile strength is given in $kN.m^{-1}$.

4.2.7.3 Burst index

The burst index of the handsheets was determined with the TAPPI standards coded T 220 om-88 and T 403 om-08 (Technical Association of the Pulp and Paper Industry, 2010), using the Mullen C Burst Tester. The burst index is calculated by Equation 4-4:

$$Burst\ index = \frac{Bursting\ strength}{Basis\ weight} \quad (4\text{-}4)$$

where the units for bursting strength is kPa and basis weight $g.m^{-2}$, making the units of burst index $kPa.m^2.g^{-1}$.

4.2.7.4 Tear index

The tear index of the handsheets was measured with the TAPPI standards coded T 220 om-88 and T 414 om-08, which are Elmendorf-type methods (Technical Association of the Pulp and Paper Industry, 2010). The apparatus used was the Elmendorf tear tester. The tear index was calculated using Equation 4-5:

$$Tear\ index = \frac{\frac{Force\ to\ tear\ 5\ sheets \times 16 \times 9.81}{5}}{Basis\ weight} \quad (4\text{-}5)$$

where the force to tear a single sheet is measured in gram and basis weight in $g.m^{-2}$, making the units of the tear index $mN.m^2.g^{-1}$.

4.2.7.5 Water absorptiveness (Cobb test)

The TAPPI T 441 om-98 standard method for determining the "Water absorptiveness of sized (non-bibulous) paper, paperboard, and corrugated fibreboard (Cobb test)" was applied to handsheets using the equipment depicted in Figure 4.2 (Technical Association of the Pulp and Paper Industry, 2010). The Cobb value was calculated by multiplying the weight of the water absorbed by a 100 to get the grams water absorbed per square meter of paper ($g.m^{-2}$), this calculation is given in Equation 4-6.

$$Cobb\ value = \ Final\ weight_{wet\ handsheet} - Initial\ weight_{dry\ handsheet} \times 100 \qquad (4\text{-}6)$$

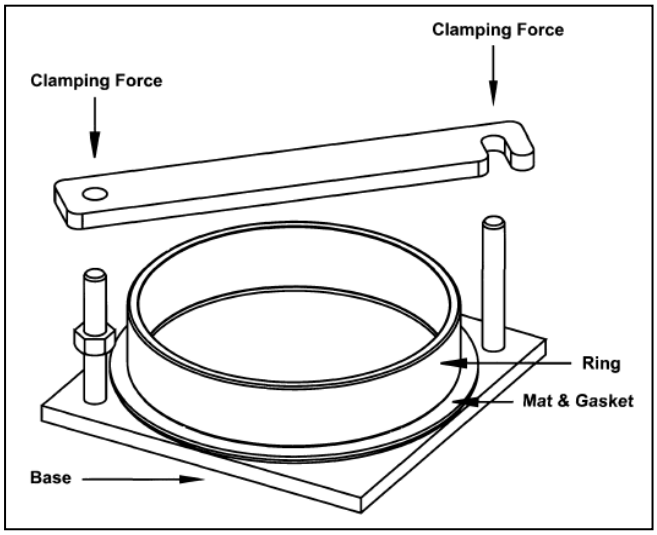


Figure 4.2: Equipment used during Cobb test (Technical Association of the Pulp and Paper Industry, 2010)

4.2.7.6 ISO Brightness

The ISO brightness of the handsheet samples were measured using a Zeiss Elrepho 65843 reflectance photometer, according to the manufacturer's specifications.

4.2.7.7 Air permeability

The air permeability was measured at SAPPI's Technology Centre in Pretoria on a Messmer Büchel Roughness & Air Permeance Tester. The instrument has a range of measurement between 0 and 5000 mL.min^{-1} and was designed especially for the measurement of paper samples. The handsheets were placed in the measurement head and a reading was taken for the air permeance of the handsheet. For samples where the air permeance exceeded the 5000 mL.min^{-1} limit, the differential pressure was noted. The differential pressure relates to the air permeability of a sample.

4.2.7.8 Roughness

The roughness of the handsheets was measured in µm using a Mahr - MarSurf PS1 instrument. Measurements were taken over a length of 5.6 mm of the handsheet and measured 3 times in the vertical direction and 3 times in the horizontal direction at different sites on the handsheet.

4.2.7.9 Scanning electron microscope

Scanning Electron Microscopy (SEM) was performed with a ZEISS LEO 1430 VP. The handsheet samples were coated with gold using a S150A Sputter Coater and the photos were taken at a magnification of 50 times.

4.3 Results and discussion

The aim of this study was to determine whether hemicellulosic additives are suitable for replacing industrial additives that are currently being used in the paper industry. Since hemicelluloses are wood polymers it might be a suitable, and more "green", replacement for synthetic additive s in the paper industry (O'Byrne, 2009). Over the decades it has been assumed that the dry strength of paper was achieved by hydrogen bonding between the overlapping fibres in the paper web. Recent studies have indicated that inter-fibril entanglement also plays a significant role in the development of paper's physical properties (Schall *et al.*, 2008). It was proven that an increase in fibre-to-fibre bonding in the paper web has led to an increase in strength properties of the paper. The use of fillers during the wet-end of the papermaking process leads to reduced fibre-to-fibre bonding due to the introduction of non-polymer additives which leads to weaker strength properties of the paper (Almgren *et al.*, 2009; Drouin *et al.*, 2001).

The scope of this study was to investigate the effect that the differently modified hemicelluloses had on the handsheet physical and surface properties. The hemicelluloses were added to the handsheet pulp slurries at a loading of 1.00 wt.%, based on the dry weight of the pulp. The modified hemicellulose that showed the best improvement in handsheet properties was then further used to develop an addition protocol. The addition protocol was developed by comparing the downstream impacts the various addition points had on the handsheet properties. This modified hemicellulose was then compared to industrial additives.

4.3.1 Handsheet formation with hemicelluloses additives

The modified hemicelluloses from Chapter 3 were used for handsheet formation. The hemicelluloses were cationic, carboxymethyl and sonicated *E. grandis* glucuronoxylan and *P. abies* galactoglucomannan.

4.3.1.1 Cationic hemicelluloses additives

The handsheet properties were compared against the degree of substitution and the uronic acid / galactose content of the glucuronoxylan / galactoglucomannan additives using Statistica®. The Statistica® analysis of the experimental data yielded no model with R^2-value greater the 0.95. All the p-values were above 0.05 as well. This is an indication that there were no statistically significant trends in the data. This variability in the results makes predicting the handsheet properties for a certain degree of substitution, or uronic acid / galactose content, difficult. This variability is again attributed to the varying molecular weight of the modified hemicelluloses as discussed in Section 3.3.3.1. This occurs since higher molecular weight hemicelluloses improve paper strength properties more (Megaton *et al.*, 2011).

Graphs of the strength properties of the handsheets are given in Figure 4.3 for qualitative analysis. The broken horizontal lines represent the reference handsheet properties. The reference handsheets were prepared from pulp to which no additives were added and no sizing was done, i.e. handsheets that were made from pulp alone. Both the cationic *E. grandis* glucuronoxylan and *P. abies* galactoglucomannan were given in the graphs for comparison purposes. The most significant observation from all the graphs (Figure 4.3 (a) to (f)) is that the majority of the experimental data points are above the reference lines. This indicated that cationic glucuronoxylan and galactoglucomannan improved the strength properties of the handsheets; however the cationic *E. grandis* glucuronoxylan improved the properties slightly more. The hemicelluloses attached to the cellulose fibres in the pulp created more hydrogen bonding sites on the fibres. This in turn increased the fibre-to-fibre bonding strength between the cellulose fibres, and thusly increasing the strength properties of the handsheets (Almgren *et al.*, 2009; Drouin *et al.*, 2001; Hendriksson & Gatenholm, 2001; Linder *et al.*, 2003).

This increase in handsheet strength with cationic hemicelluloses addition was confirmed by Ren *et al*. (2009). They also concluded that as the degree of substitution increased, so did the extent of strength property improvement. This was not observed for this investigation, with too much variability in the results. The increase in the degree of substitution leads to a decrease in uronic acid content for glucuronoxylan. This decrease in uronic acid content leads to more insoluble glucuronoxylan, which can aggregate better and form larger particles in solution. These larger particles are attached more easily to the cellulose fibres and produce more hydrogen bonding sites (Linder *et al*., 2003; Ren *et al*., 2009). This indicated that cationic glucuronoxylan with lower uronic acid content is more suitable for use as wet-end strength additive for the paper industry.

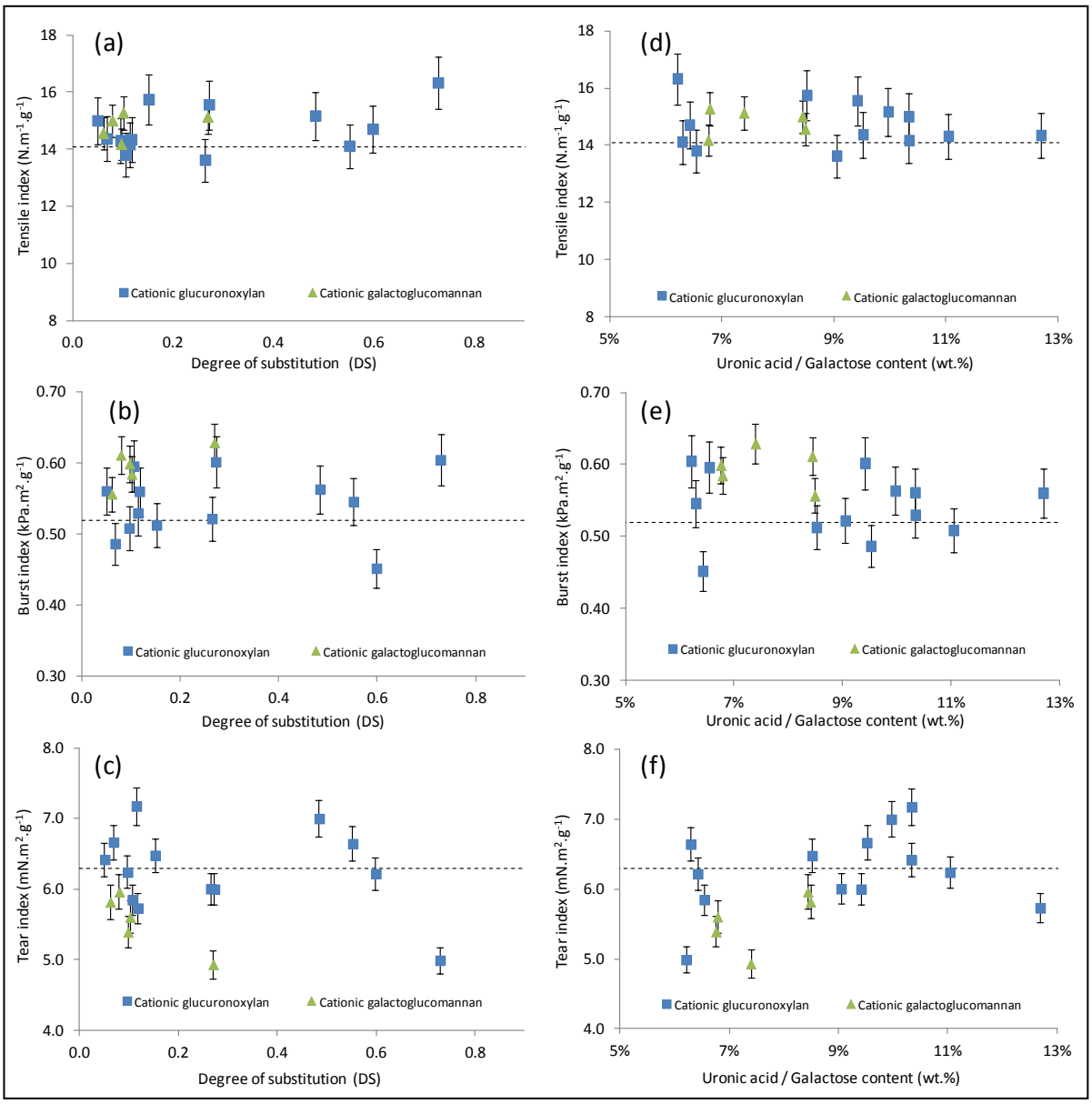
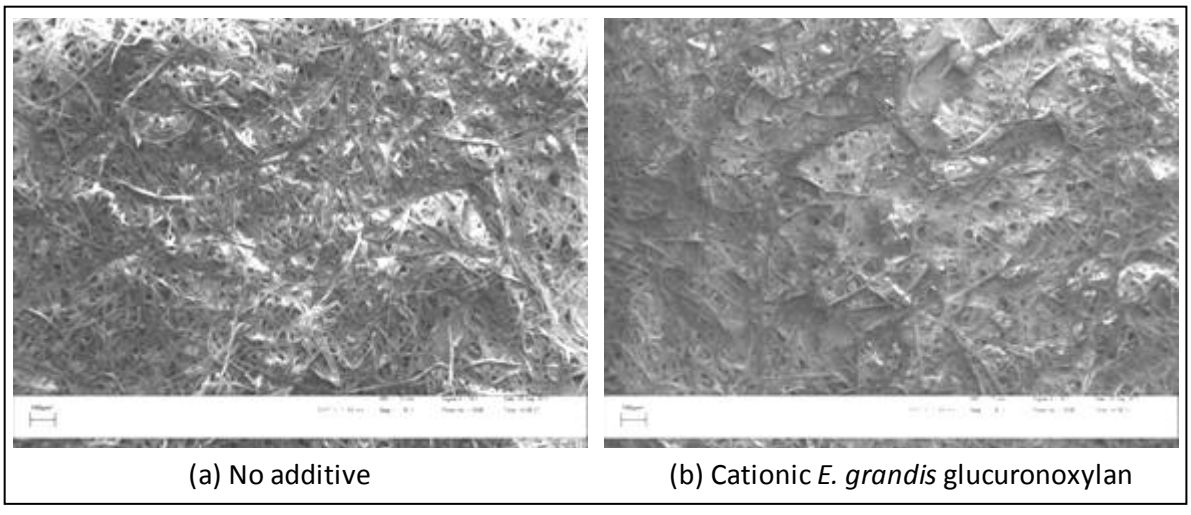


Figure 4.3: Cationic *E. grandis* glucuronoxylan and *P. abies* galactoglucomannan additives degree of substitution against (a) tensile index, (b) burst index, and (c) tear index and uronic acid / galactose content against (d) tensile index, (e) burst index, and (f) tear index of handsheets

The graphs of the other properties of the handsheets are given in Figure 4.5 for qualitative analysis. From Figures 4.5 (a) and (d) it was observed that most of the experimental data points are above the reference line (broken horizontal line). This could be due to the hygroscopic (water loving) nature of hemicelluloses, which indicate that the water absorptiveness of the paper produced with the addition of hemicelluloses additives will be increased (Bierman, 1996; Holik, 2006). There are however experimental data points underneath the reference line. This could be due to the surface pores that are decreased by the stronger fibre-to-fibre bonds, resulting in lower water

absorptiveness (Ren *et al*., 2009). The majority of the experimental data points for the ISO brightness of the handsheets are below the reference line. This decrease in brightness may be attributed to the small amount of lignin that was present in the hemicelluloses when added (Holik, 2006), as well as the light brown colour of the cationic hemicelluloses. The light brown colour of the cationic hemicelluloses was caused by the oxidation of the lignin during the hemicelluloses cationisation process (Fengel & Wegener, 2003). Figures 4.5 (c) and (f) are representative of the air permeability of the handsheets given as a pressure difference over the handsheet, since the handsheets are too porous to give relevant air permeability values in $mL.min^{-1}$. The pressure difference values for the handsheets with cationic hemicelluloses added are above the reference line, indicating reduced air permeability. The porosity of the handsheets apparently declined due to cationic hemicelluloses addition, possible due to stronger fibre-to-fibre bonding causing reduced void volume (Ren *et al*., 2009).

The analysis of the surface texture of the handsheets formed with cationic *E. grandis* glucuronoxylan was done with the SEM photomicrographs given in Figure 4.4. The handsheet with no additives (Figure 4.4 (a)) showed a large amount of interspaces among the fibres. These interspaces declined when cationic glucuronoxylan was added, as observed in Figure 4.4 (b). This was also observed by Ren *et al*. (2009) as shown in Figure 2.8. The decrease in interspaces was attributed to enhanced hydrogen bonding created by the cationic hemicellulose additive. This confirms that cationic hemicellulose improves the fibre-to-fibre bonding within the paper web.



(a) No additive (b) Cationic *E. grandis* glucuronoxylan

Figure 4.4: SEM photomicrographs of (a) reference handsheet and (b) handsheet with cationic *E. grandis* glucuronoxylan added

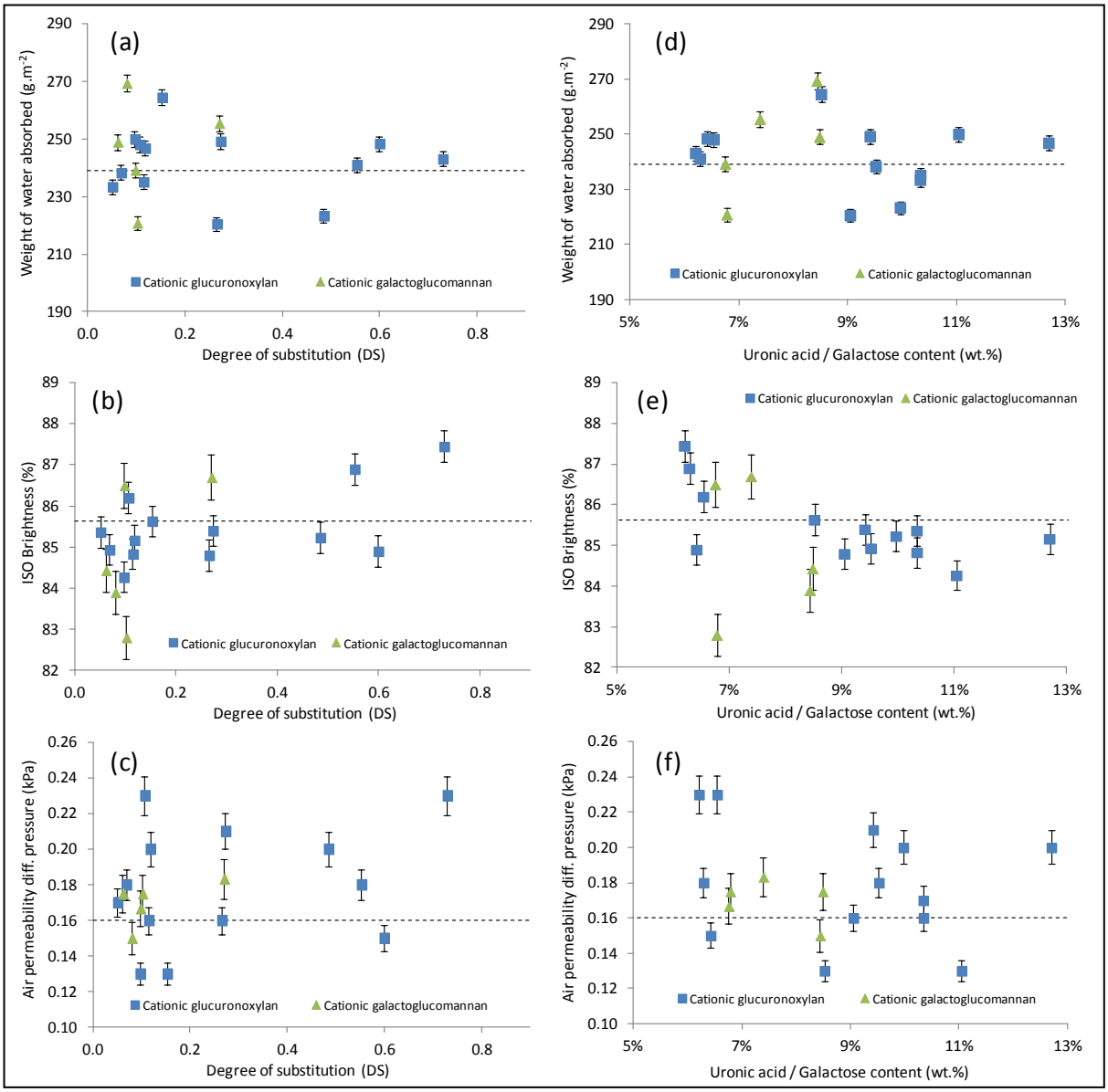


Figure 4.5: Cationic *E. grandis* glucuronoxylan and *P. abies* galactoglucomannan additives degree of substitution against (a) weight of water absorbed, (b) ISO brightness, and (c) pressure difference and uronic acid / galactose content against (d) weight of water absorbed, (e) ISO brightness, and (f) pressure difference

4.3.1.2 Carboxymethyl hemicelluloses additives

The degree of substitution and uronic acid content of the carboxymethylated *E. grandis* glucuronoxylan and *P. abies* galactoglucomannan additives was analysed against the handsheet properties using Statistica®. The experimental data was not analysed against the galactose content of the *P. abies* galactoglucomannan due to a lack of sample mass to determine it. The same carboxymethyl hemicelluloses from Chapter 3 were used as additives for handsheet formation. There were no R^2 values greater than 0.95 for models to fit the experimental data. There was however one p-value lower than 0.05, for the uronic acid content of carboxymethyl *E. grandis* glucuronoxylan on the burst index of the handsheets with this additive added. This shows that the uronic acid content of the carboxymethyl glucuronoxylan had a statistically significant effect on the burst index of the handsheets. The graphs of the experimental results for the strength properties of the handsheets are given in Figure 4.6 for qualitative analysis. The broken horizontal lines represent the reference handsheet properties with the absence of additives. Both the cationic *E. grandis* glucuronoxylan and *P. abies* galactoglucomannan were given in the graphs for comparison purposes.

From the graphs (Figures 4.6 (a) to (f)) it was observed that the majority of the data points were on or below the reference line for both carboxymethyl hemicellulose additives. This indicated that the carboxymethyl hemicelluloses additives did not improve the handsheet strength properties significantly, if at all. The lack of improvement in the strength properties could be due to a shortage of aluminium sulphate [$Al_2(SO_4)_3$] that was added with the carboxymethyl hemicellulose. Carboxymethyl hemicelluloses are ionic chemicals, which need to be incorporated with aluminium sulphate (Ren *et al.*, 2009). The aluminium sulphate forms absorption points on the cellulose fibres with positive charges. These positive sites then act with the ionic groups by forming coordination bonds, and improve the paper strength properties (Holik, 2006; Ren *et al.*, 2009). The loading of the carboxymethyl hemicelluloses were 1.00 wt.% on the dry weight of the pulp, and 2.5 wt.% for the aluminium sulphate. This indicated that a higher loading for the aluminium sulphate may be required. This was also noticed by Ren *et al.* (2009).

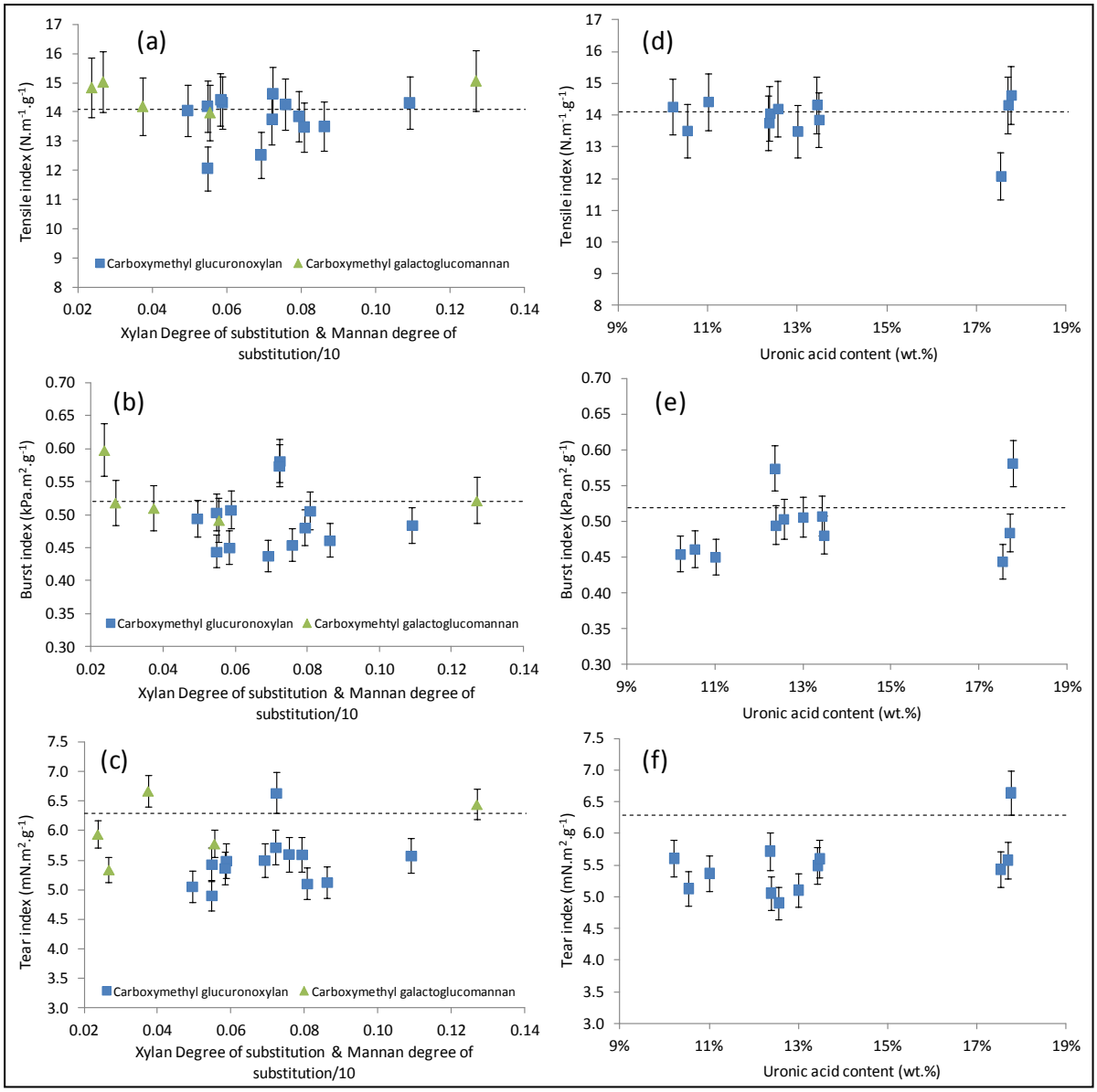
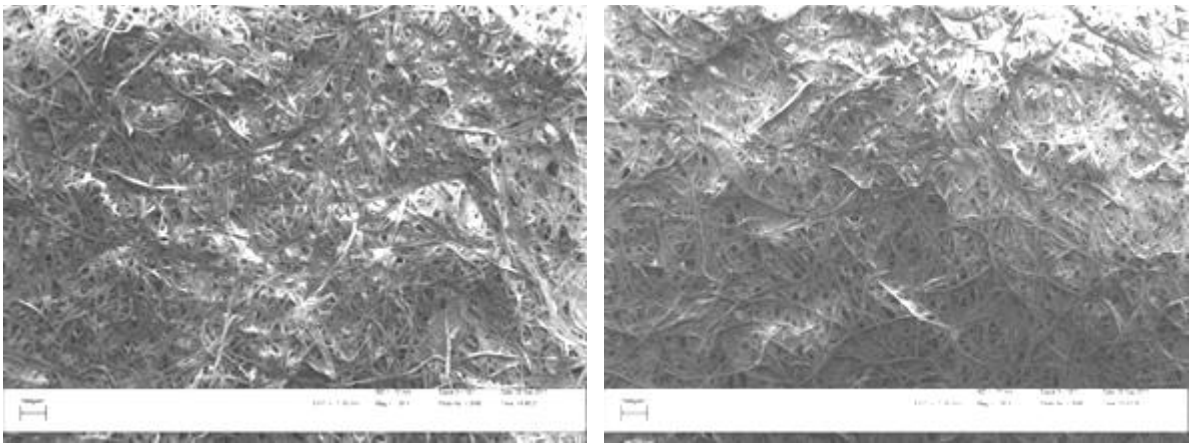


Figure 4.6: Carboxymethyl *E. grandis* glucuronoxylan and *P. abies* galactoglucomannan additives degree of substitution against (a) tensile index, (b) burst index, and (c) tear index and uronic acid content against (d) tensile index, (e) burst index, and (f) tear index of handsheets

Figure 4.8 contains the graphs of the other properties of the handsheets against the degree of substitution and uronic acid content of the carboxymethyl hemicelluloses added. From the graphs for the weight of water absorbed (Figures 4.8 (a) and (d)) it was observed that the majority of the results for both the carboxymethyl hemicelluloses were above the reference line. This was due to the hygroscopic (water loving) nature of the carboxymethyl hemicelluloses retaining more water (Bierman, 1996; Holik, 2006). The ISO brightness (Figures 4.8 (b) and (e)) values were below the reference line, which indicated that the carboxymethyl hemicelluloses lowered the handsheets

brightness. The lower brightness may be attributed to the light brown colour of the carboxymethyl hemicelluloses. The light brown colour was probably caused by the oxidation of lignin in the hemicelluloses during the carboxymethylation process (Fengel & Wegener, 2003).

The SEM photomicrographs of handsheets with, and without carboxymethyl *E. grandis* glucuronoxylan are given in Figure 4.7. From the SEM photomicrographs no significant differences were observed. There was however a few less interspaces in the presence of carboxymethyl *E. grandis* glucuronoxylan in Figure 4.7 (b). The fibres also appeared to be more flattened onto each other in Figure 4.7 (b) when compared to the reference handsheet in Figure 4.7 (a).



(a) No additive (b) Carboxymethyl *E. grandis* glucuronoxylan

Figure 4.7: SEM photomicrographs of (a) reference handsheet and (b) handsheet with carboxymethyl *E. grandis* glucuronoxylan added

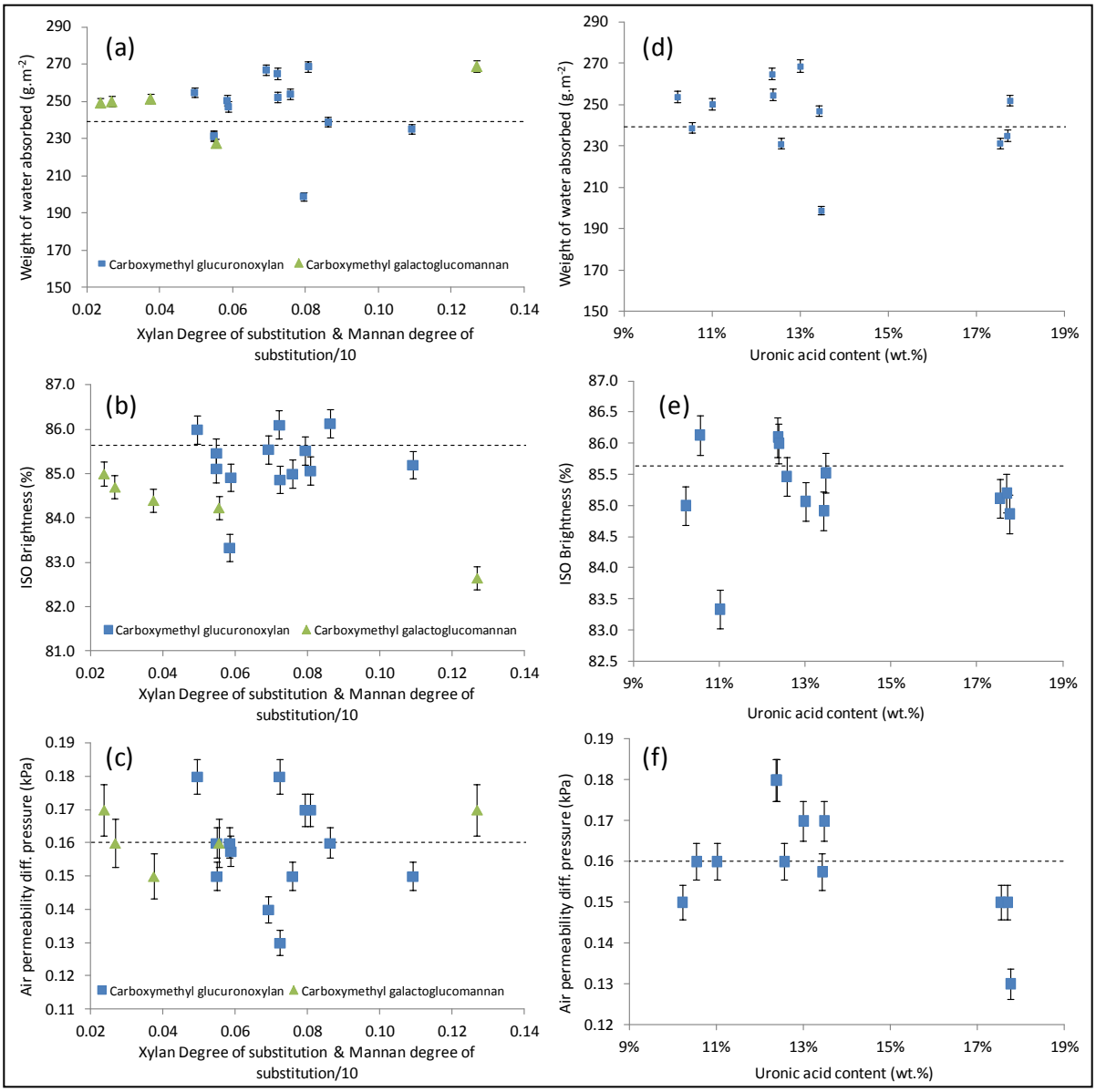


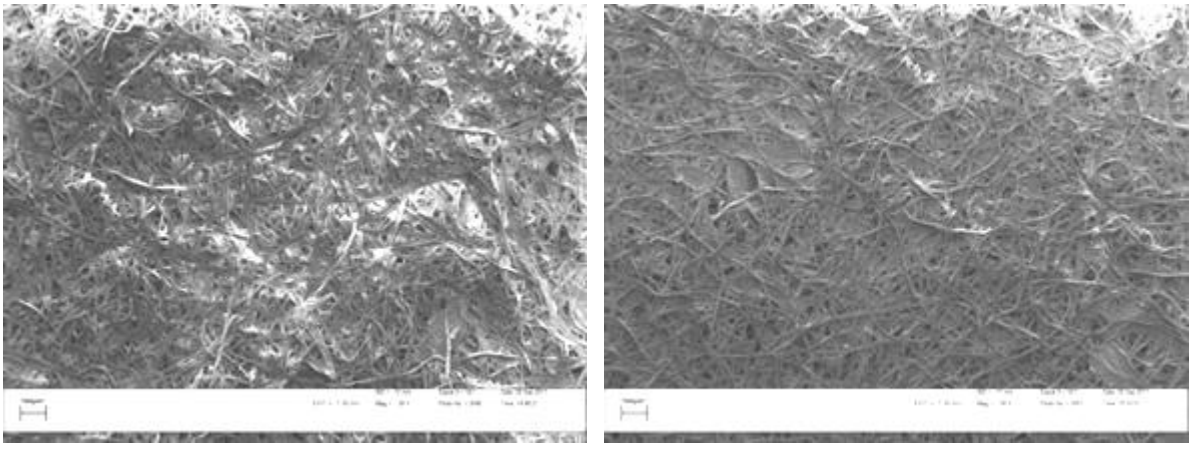
Figure 4.8: Carboxymethyl *E. grandis* glucuronoxylan and *P. abies* galactoglucomannan additives degree of substitution against (a) weight of water absorbed, (b) ISO brightness, and (c) pressure difference and uronic acid content against (d) weight of water absorbed, (e) ISO brightness, and (f) pressure difference

4.3.1.3 Sonicated hemicelluloses additives

The analysis of the handsheet strength and surface properties was done against the sonication time applied to the different hemicelluloses. The analysis was done in Statistica® using a one way ANOVA test since there was only one independent variable (sonication time). The one way ANOVA tests yielded p-values below 0.05 for some of the handsheet properties. This indicated that there were

statistically significant trends between some of the handsheet properties and the sonication time. The sonication time against the strength and surface properties of the handsheets graphs are given in Figure 4.10 (a) to (f). The trend lines in graphs (a) to (e) are the trends that had showed statistical significance from the one way ANOVA tests. The R^2 values and the p-values were given on the graphs. From the graphs in Figure 4.10 it was observed that the majority of the experimental data points were below the broken horizontal reference lines. This was an indication that the sonicated hemicelluloses did not improve the handsheet properties sufficiently. This lack of handsheet property improvement could be due to the sonicated hemicelluloses not self retaining on the celluloses fibres (Ren *et al.*, 2009). If this was the case, sonicated hemicelluloses should be incorporated with aluminium sulphate addition (Holik, 2006; Ren *et al.*, 2009).

To investigate the effect the sonicated *E. grandis* glucuronoxylan had on the surface of the handsheets, SEM photomicrographs were taken and provided in Figure 4.9. From the SEM photographs there were no visible signs of improvement. There was no visible change in the interspaces between the celluloses fibres. It does however seem as if the sonicated *E. grandis* glucuronoxylan handsheet (Figure 4.9 (b)) was smoother that the reference (Figure 4.9 (a)). This improvement of surface smoothness was attributed to the process used to produce the handsheets, rather than the sonicated hemicelluloses additives.



(a) No additive (b) Sonicated *E. grandis* glucuronoxylan

Figure 4.9: SEM photomicrographs of (a) reference handsheet and (b) handsheet with sonicated *E. grandis* glucuronoxylan added

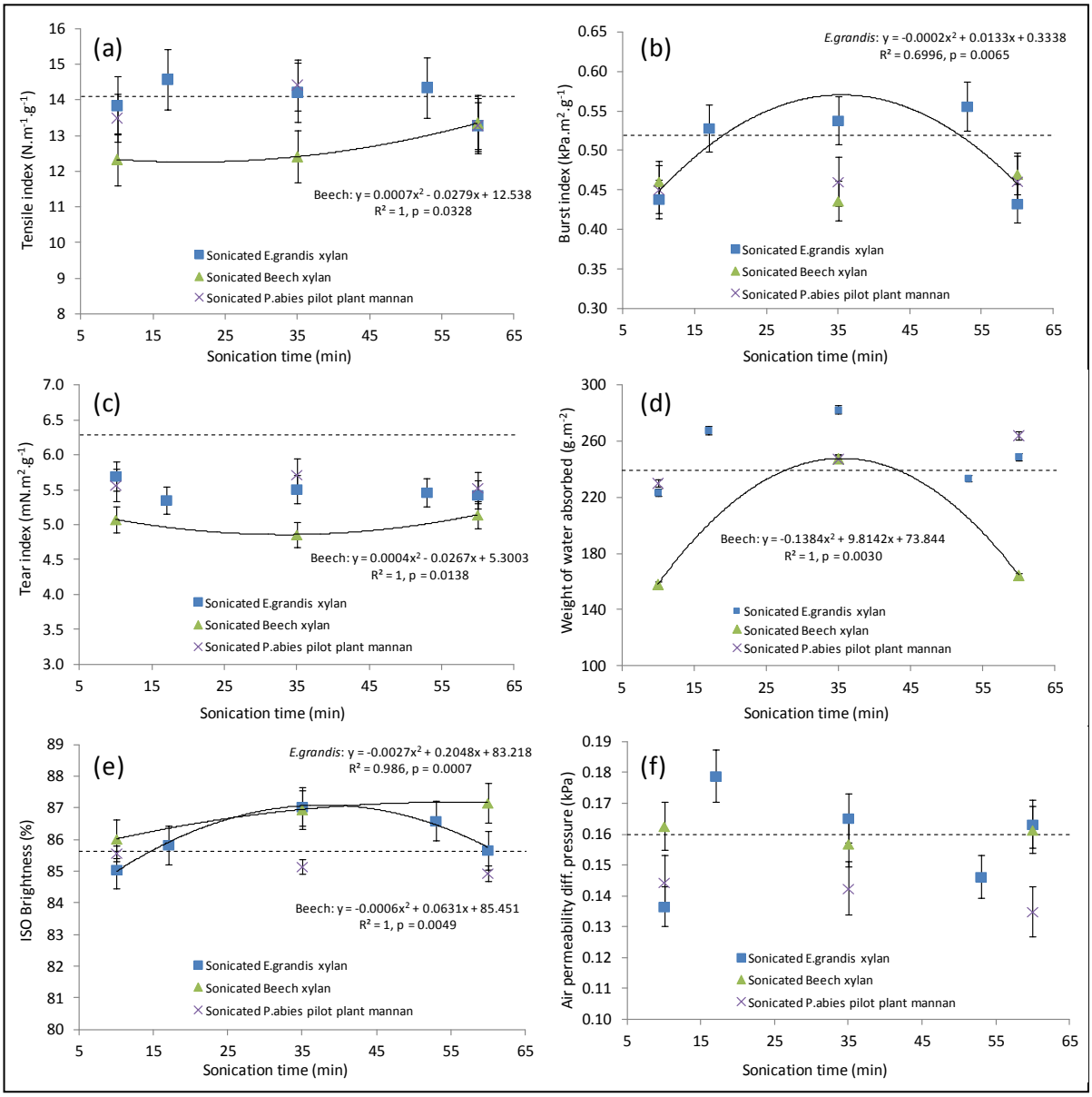


Figure 4.10: Sonication time of *E. grandis* and Beech glucuronoxylan and *P. abies* galactoglucomannan against (a) tensile index, (b) burst index, (c) tear index, (d) weight of water absorbed, (e) ISO brightness, and (f) pressure difference of handsheets

4.3.1.4 Comparison of all modified hemicelluloses additives at 1% dosage

For the comparison between all the additives used in this study, handsheets were made with an additive dosage of 1 wt.% on the dry weight of pulp. The pulp used was bleached pure *E. grandis* Kraft pulp. The additives had a contact time of 10 minutes after which the handsheets were produced. The handsheet properties that were compared are tensile index ($N.m^{-1}.g^{-1}$), burst index ($kPa.m^2.g^{-1}$), tear index ($mN.m^2.g^{-1}$), Cobb (weight of water absorbed) ($g.m^{-2}$), ISO brightness (%), air permeability (pressure difference over the handsheets) (kPa), and roughness (µm). The comparison of the additives was not part of the addition protocol development. It was completed to provide an overall picture of all additives in this study. Figure 4.11 (a) to (g) contains the comparison graphs, where the horizontal broken lines represent the reference handsheets properties. Table 4.4 provides the additive that improved each handsheet property the most.

Table 4.4: Additives which showed the most improvement of handsheet property

Handsheet property	Best additive
Tensile index ($N.m^{-1}.g^{-1}$)	Cationic *E. grandis* glucuronoxylan
Burst index ($kPa.m^2.g^{-1}$)	Cationic *P. abies* galactoglucomannan
Tear index ($mN.m^2.g^{-1}$)	Cationic *E. grandis* glucuronoxylan
Cobb (weight of water absorbed) ($g.m^{-2}$)	Aquapel 312
ISO brightness (%)	Cationic *E. grandis* glucuronoxylan
Air permeability (pressure difference over the handsheets) (kPa)	Cationic *E. grandis* glucuronoxylan
Roughness (µm)	Unmodified *P. abies* galactoglucomannan

From Figure 4.11 and Table 4.4 it was observed that the additive which showed the most improvement of the properties at a dosage of 1 wt.% was cationic *E. grandis* glucuronoxylan. This hemicellulosic additive improved handsheet properties more than the industrial strength additives. This improvement of handsheet properties when cationic hemicelluloses additives were added was confirmed by Liu *et al.* (2011) and Ren *et al.* (2009). Cationic hemicelluloses perform the best due to their cationic nature. Pulp fibres have a natural anionic charge, making cationic hemicelluloses self retaining on the pulp fibres (Könke *et al.*, 2009; Ren *et al.*, 2009; Ren *et al.*, 2008; Ren *et al.*, 2007; Schwikal *et al.*, 2006). Hemicelluloses are also present in the raw biomass with cellulose, indicating that hemicelluloses have a strong attraction to cellulose (Fengel & Wegener, 2003). These factors make cationic hemicelluloses a preferred additive.

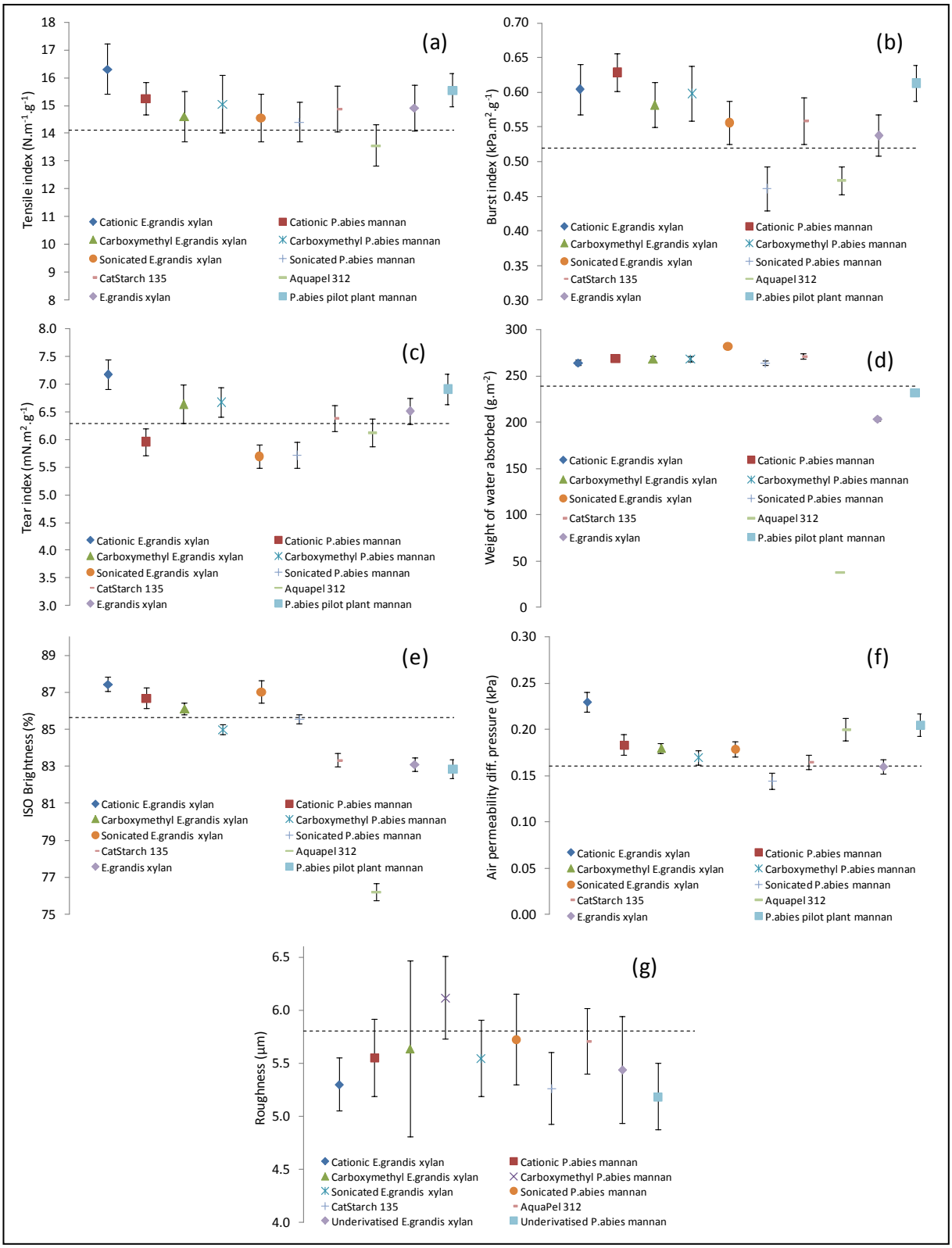


Figure 4.11: Effect of all selected additives on handsheet strength and surface properties

A comparison of all the selected additives showed that cationisation of *E. grandis* glucuronoxylan was the most effective modification method of hemicelluloses for use as strength additive in the paper industry. It also indicated that this hemicellulose have the possibility of performing better than the current industrial additives, such as cationic starch. The cationic *E. grandis* glucuronoxylan was therefore selected for the addition protocol development.

4.3.2 Hemicelluloses additive addition protocol development

The aim of the addition protocol was to maximize the contact time of the hemicellulose additives with the cellulose fibres by adding it as early as possible to the paper making process. This is however a difficult task as pulp consistency should be taken into account as well (Bierman,, 1996; Holik, 2006). If the hemicellulose additives are added to a high consistency pulp (10 to 15%) there will not be adequate mixing, and the contact area of the hemicelluloses will be insufficient. The addition protocol will determine where the optimum stage in the paper making process will be to add the hemicellulose additives for maximum utilisation of these new additives.

The approach to develop the addition protocol was to first determine the optimum dosage level to the dry weight of the pulp. Then a bleaching testing was completed with and without hemicellulose additives. The refining of the pulp fibres with hemicelluloses additives was investigated as well. Then finally the hemicellulose additives were compared to industrial strength additives. The hemicellulose that was used for the addition protocol development was cationic glucuronoxylan, alkali extracted from *E. grandis* biomass. The FT-IR and Solid state ^{13}C-CP/MAS-NMR characterisation of the cationic *E. grandis* glucuronoxylan was provided in Section 3.3.3.1. The cationic *E. grandis* glucuronoxylan selected had a degree of substitution of 0.1996, and uronic acid content of 8.39 wt.%.

4.3.2.1 Dosage

The dosage of the cationic *E. grandis* glucuronoxylan was done in the range between 0.5 wt.% to 10.0 wt.% based on the dry weight of the pulp with intermediate dosage values of 1.0 and 5.0 wt.%. The cationic glucuronoxylan was added to the disintegrated pulp stock with a consistency of 0.30% and left for a contact time of 15 minutes under constant stirring. All the dosage points were done in duplicate to obtain average values and error values. The experimental results were analysed using Statistica®, by using one way ANOVA tests for single independent variables. The p-values for all the handsheet properties against the dosage level of the hemicelluloses were below 0.05. This indicated that statistical significant trends were present in the results. The graphs of the handsheet properties against the dosage of the hemicelluloses are provided in Figure 4.12 (a) to (g).

From Figure 4.12 (a) it was observed that an increase in dosage percentage led to an increase in basis weight. This increase was attributed to the fact that the addition of hemicelluloses add to the carbon loading of the paper. There was however a maximum loading capacity at a dosage level of approximately 8.0 wt.%. This may be due to the saturation of the cellulose fibre bonding sites, or inadequate contact time for all of the cationic *E. grandis* glucuronoxylan to get adsorbed onto the cellulose fibres (Albersheim *et al.*, 2010; Ren *et al.*, 2009; Zhang *et al.*, 2011). This maximum loading capacity was reflected in the tensile and tear index graphs as well (Figure 4.12 (b) and (d)), which showed that these strength properties start to decline after a dosage of approximately 7.0 wt.%. The burst index (Figure 4.12 (c)) however, decreased as the tear index increased. The burst and tear index is inversely proportional, which explained this occurrence (Caulfield & Gunderson, 1988). From these results it was concluded that the optimum dosage of cationic *E. grandis* glucuronoxylan was 4.0 wt.% based on dry weight of pulp. This dosage level provided the maximum increase in both tensile and tear index with minimal decrease of the burst index. In the paper industry, cationic starch additives are added at a dosage between 2.0 and 4.0 wt.% based on dry pulp (Bierman, 1996), which indicated that a dosage of 4.0 wt.% of hemicellulose was not unrealistic.

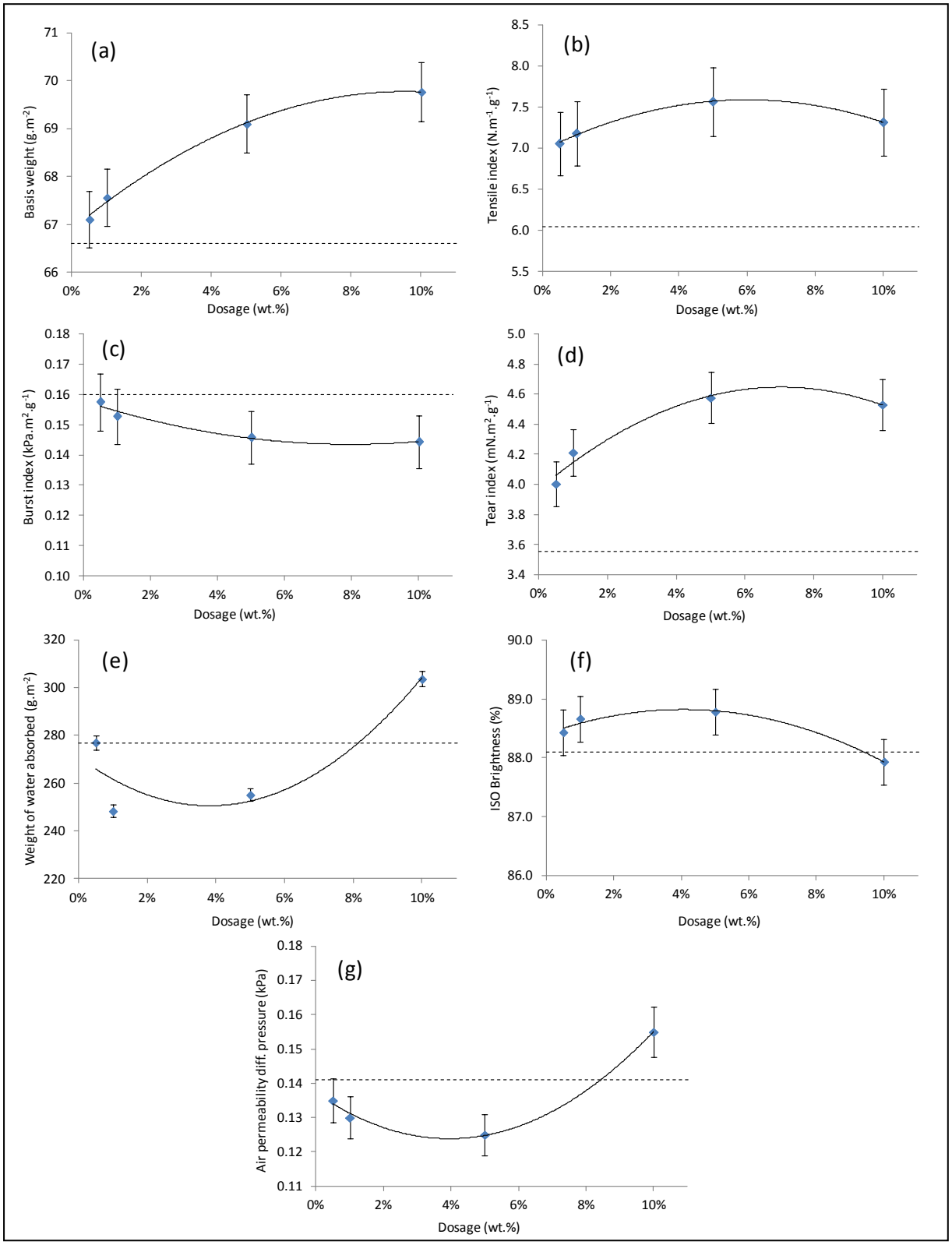


Figure 4.12: Dosage levels of cationic *E. grandis* glucuronoxylan effect on handsheet strength and surface properties

4.3.2.2 Bleaching

Hydrogen peroxide (H_2O_2) bleaching was applied in this addition protocol to resemble mild bleaching conditions. The two temperatures that were chosen from literature for this investigation were 65 and 85 ^oC (Hubbe, 2010; Loureiro *et al.*, 2011; Sundara, 1998). The dosage of the cationic *E. grandis* glucuronoxylan was 1.0 wt.% on dry pulp basis. The results that were obtained are displayed as bar graphs in Figure 4.13. There was an increase in the tensile index (Figure 4.13 (a)) when cationic *E. grandis* glucuronoxylan was present at 65^oC bleaching. There was however no effect on the other handsheet properties at 65^oC (Figure 4.13 (b) to (f)), which indicated that the cationic *E. grandis* glucuronoxylan had no effect during bleaching. This lack of handsheet property improvement may be attributed to the cationic *E. grandis* glucuronoxylan being degraded during the bleaching process (Fang et al., 1999). Another possible explanation for the lack of handsheet property improvement may have been the consistency of the pulp during bleaching. The pulp consistency during bleaching was 30%, which could have made the hemicelluloses contact area insufficient, due to low homogeneity of the mixture. The conclusion was made that cationic *E. grandis* glucuronoxylan was not a suitable additive during bleaching due to the high consistency of the pulp during bleaching, as well as the bleaching chemicals degrading the hemicelluloses.

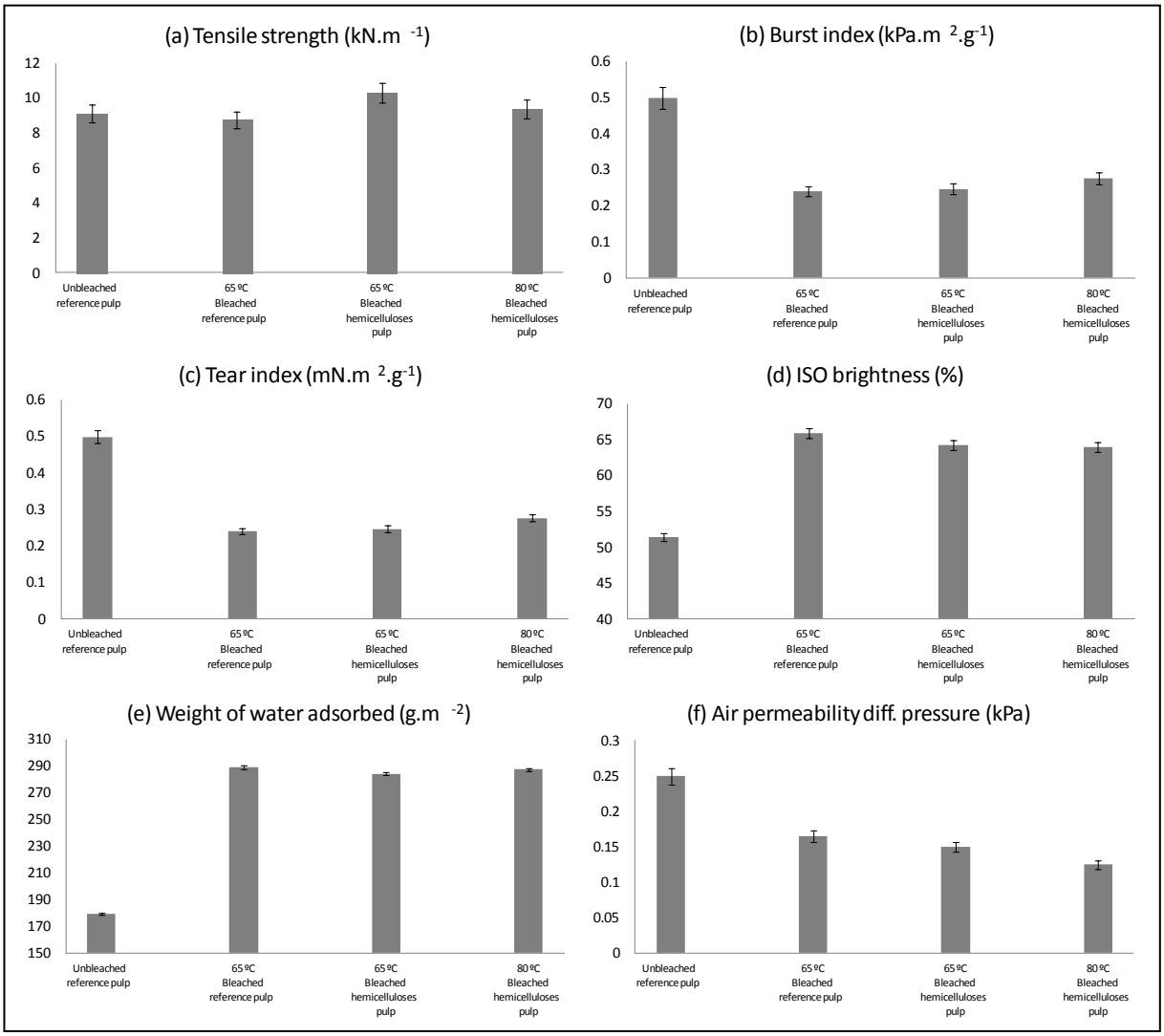


Figure 4.13: Handsheet results for bleaching with cationic *E. grandis* glucuronoxylan additive present

4.3.2.3 Refining

The cationic *E. grandis* glucuronoxylan additive's behaviour during refining was tested to determine whether it was able to withstand the abrasive forces that act on the fibres during refining. The cellulose fibres get fibrillated during the refining process, which increases the amount of hydrogen bonding sites. This increase in hydrogen bonding sites leads to increase hydrogen bonding between the pulp fibres and thus increasing the paper strength and surface properties (Bierman, 1996). This process can only be taken to a certain level, as the freeness (Canadian Standard Freeness) of the pulp declines with increasing refining. A lower freeness level leads to slower drainage of the water from the paper web, which slows down the paper machine speed (Bierman, 1996; Holik, 2006).

There is no industry standard for freeness, but freeness's less than 400 are seldom used as the drainage of the pulp would be too low on the paper machine wire (Nash, 2011).

The refining experimental results were analysed in Statistica® using one way ANOVA tests for single independent variables (refining energy). The p-values for the reference, and cationic *E. grandis* glucuronoxylan containing refining experiments were below 0.05 for the following dependant outputs; Canadian Standard Freeness (mL), basis weight ($g.m^{-2}$), burst index ($kPa.m^2.g^{-1}$), Cobb (weight of water absorbed) ($g.m^{-2}$), ISO brightness (%), and air permeability (pressure difference) (kPa). The low p-values indicated that there are statistically significant trends present in these dependant outputs. The p-values for the tensile ($N.m^{-1}.g^{-1}$) and tear ($mN.m^2.g^{-1}$) indexes were above 0.05. This indicated that these dependant outputs trends are not statistically significant. The graphs of the handsheet strength and surface properties against the refining energy are given in Figure 4.14. The horizontal broken lines are the reference handsheet strength and surface properties values. The vertical broken line represents a freeness value of 400 mL. Refining energies to the left of this line correspond to freeness's above 400 mL, and vice versa.

The basis weight (Figure 4.14 (b)) of the handsheets with the cationic *E. grandis* glucuronoxylan additive was higher than the reference refined handsheets. This was an indication that the cationic glucuronoxylan stayed adsorbed onto the cellulose fibres during refining. The tensile index (Figure 4.14 (c)) and pressure difference (Figure 4.14 (h)) showed higher values with the cationic *E. grandis* glucuronoxylan added. This indicated that there could be a reduction in refining energy to achieve the same strength properties. Bhanduri *et al.* (1995) also investigated using hemicelluloses as refining additives. Their research confirmed that hemicelluloses can reduce refining energy by increasing strength and surface properties during refining. The higher strength properties are attributed to the inter-fibre bonding that was improved by hemicelluloses due to their hydrophilic properties. These properties cause swelling of cell walls in water imparting fibre flexibility. Hemicelluloses also contribute to more hydrogen bonding points increasing fibre-to-fibre bonding (Bhanduri *et al.*, 1995). It was concluded that the addition of cationic *E. grandis* glucuronoxylan before refining can give the desired strength properties with less refining energy per ton of pulp. Therefore cationic hemicelluloses can be used as refining additives in addition to strength additives.

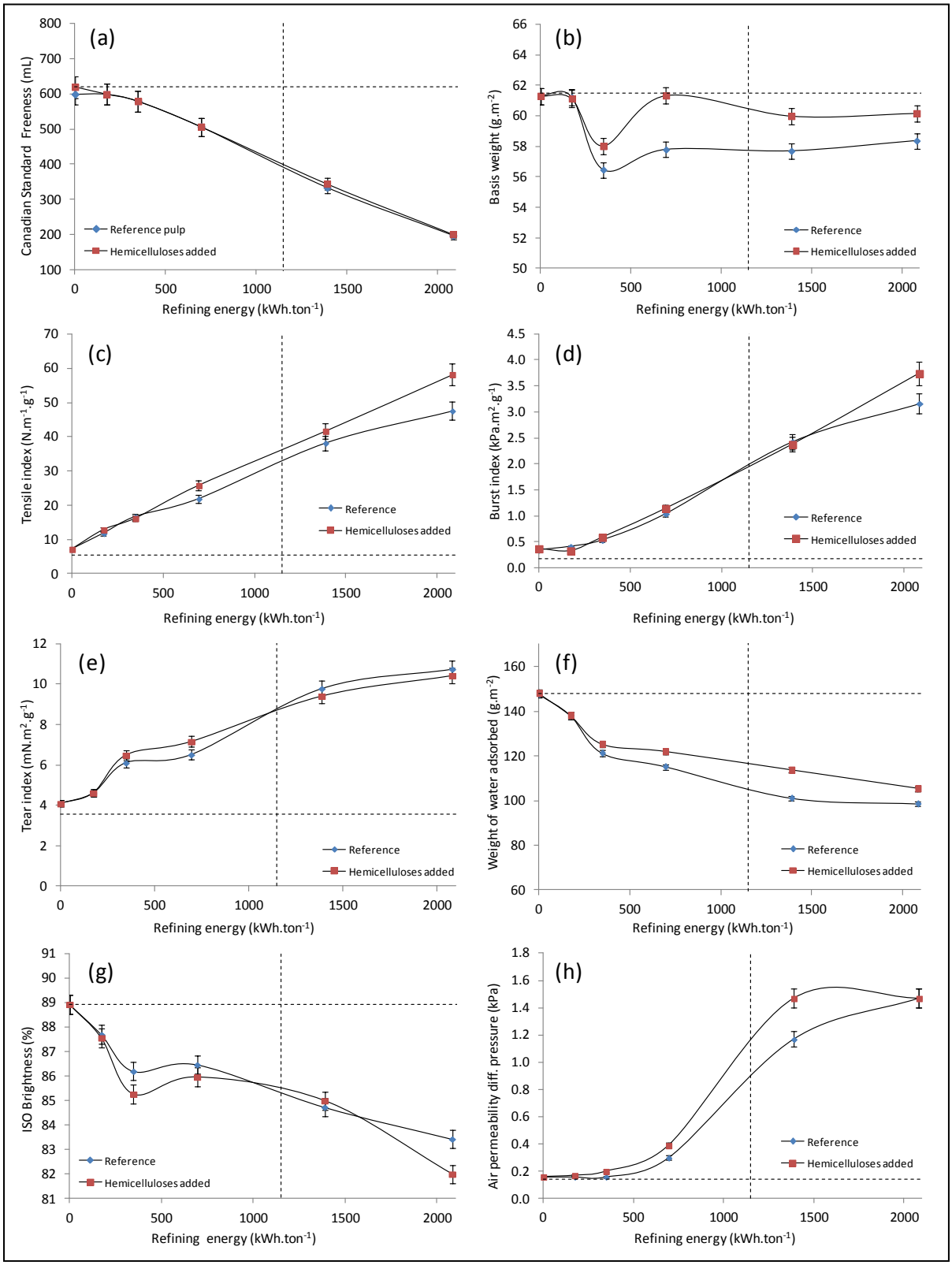


Figure 4.14: Refining of pulp with- and without cationic *E. grandis* glucuronoxylan additives and the effect it had on handsheet strength and surface properties

4.3.2.4 Comparison between dosage of hemicelluloses and industrial additives

The industrial additive that was used for the comparison with cationic *E. grandis* glucuronoxylan was cationic starch (CatStarch 134). For the characterisation of the cationic starch the FT-IR spectrum of it is given in Figure 4.15. The characteristic peaks at 1150 and 1079 cm^{-1} were attributed to the C-O bond-stretching vibration of the anhydrous glucose units, which confirmed that starch is the main component (Wang *et al.*, 2009). Furthermore a characteristic peak was observed at 3282 cm^{-1}, which was attributed to the vibration of the hydroxyl groups. The peaks at 2931 (C-H) and 1421 cm^{-1} (C-N) showed that the quaternary ammonium groups are attached to the backbone of starch (Wang *et al.*, 2009). These characteristic peaks confirmed that CatStarch 134 is in fact cationic starch.

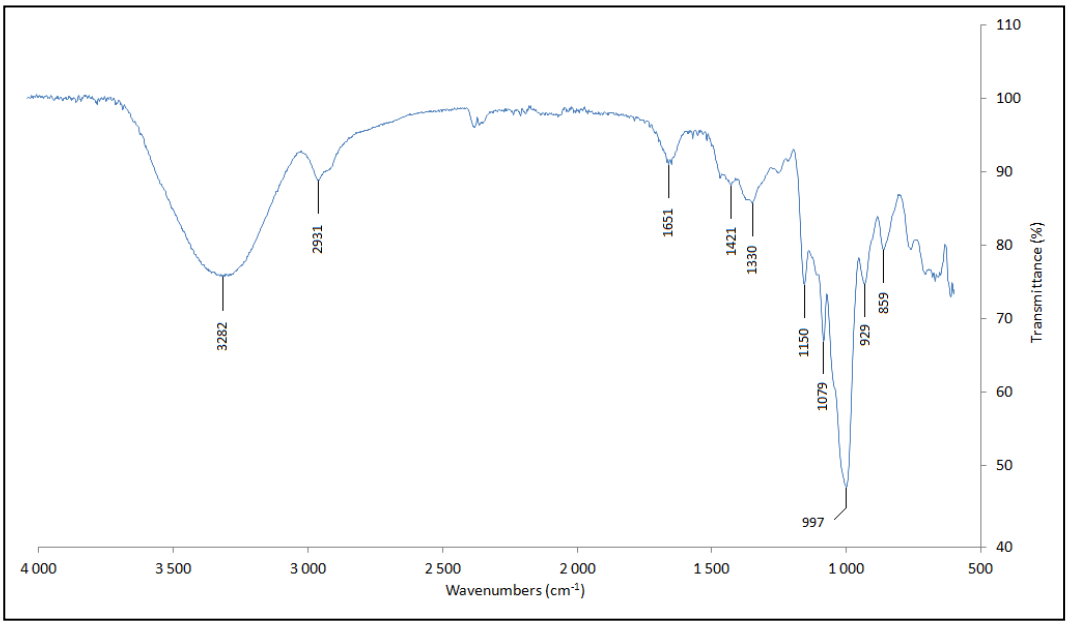


Figure 4.15: FT-IR spectra of industrial cationic starch additive (CatStarch 134)

The dosage comparison was completed on pure cationic *E. grandis* glucuronoxylan, pure cationic starch (CatStarch 134) and a 50-50 wt.% mixture of these two additives. The dosage comparison was done using bleached *E. grandis* Kraft pulp with a contact time of 15 minutes for all the additives. The experimental results were analysed in Statistica® using one way ANOVA tests for single independent variables (refining energy). All the p-values were below 0.05, which indicated statistical significance for the resulting trends. The graphs of all the handsheet strength and surface properties against the refining energy are presented in Figure 4.16.

From the graphs in Figure 4.16 it was observed that all the additives behave similarly up until a dosage level of approximately 2.0 wt.%, except for the tensile index. The similar behaviour was attributed to the fact that hemicelluloses and starch additives have approximately the same mechanisms for paper strength improvement (Bierman, 1996). Beyond the 2.0 wt.% dosage level the cationic starch improves the strength and surface properties much more efficiently than cationic *E. grandis* glucuronoxylan and the 50-50 mixture. This could be due to larger molecular weight or higher degree of substitution of the CatStarch 134 additive as compared to the hemicelluloses based additives. The CatStarch 134 production process has been optimised, whereas cationic *E. grandis* glucuronoxylan is still in the testing phase. Optimization of the production process of the cationic *E. grandis* glucuronoxylan additive is necessary, as cationic hemicelluloses with a higher degree of substitution improve paper strength properties more (Ren *et al.*, 2009). The degree of substitution for the cationic *E. grandis* glucuronoxylan used in this investigation was 0.1996, which is on the lower side of what is possible (Ren *et al.*, 2009; Schwikal *et al.*, 2006). Cationic *E. grandis* glucuronoxylan however showed potential to be a strength additive to the paper making process.

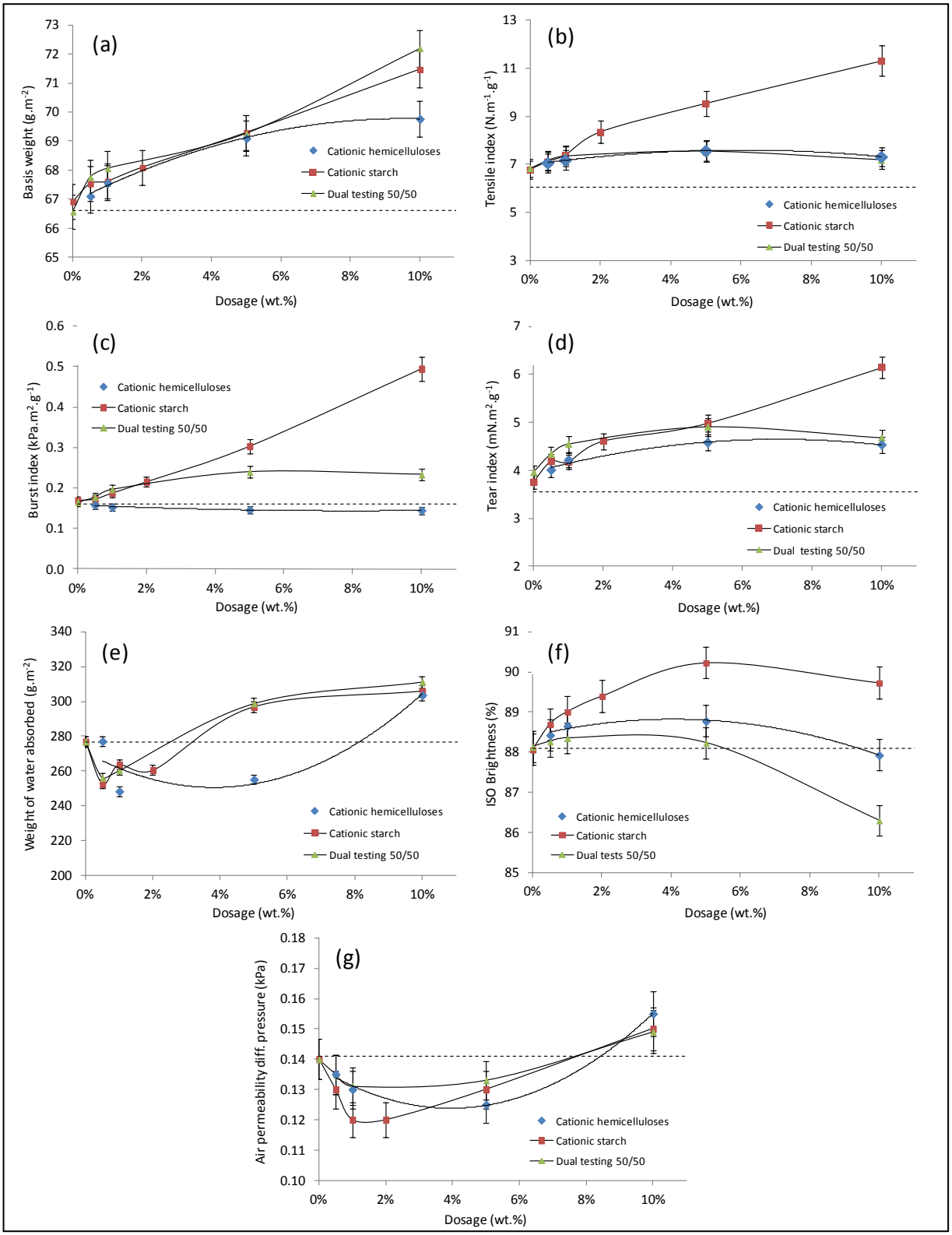


Figure 4.16: Dosage comparison of cationic *E. grandis* glucuronoxylan and cationic starch (CatStarch 134)

4.4 Conclusions

Between the three modification methods that were investigated, it was concluded that the cationic *E. grandis* glucuronoxylan additive showed the best improvement in handsheet strength and surface properties. It showed the best improvement in the tensile and tear index, Cobb (weight of water adsorbed), brightness, air permeability and roughness properties of the handsheets. There was however no statistically relevant handsheet properties trend between the degree of substitution or uronic acid content of the cationic *E. grandis* glucuronoxylan. The lack of a statistically relevant trend was also observed for the other hemicelluloses additives, with no p-values below 0.05 from Statistica® analyses. The lack of statistically relevant results was attributed to the variability of the hemicelluloses additives molecular weight and the lignin still present. It was concluded that cationic *E. grandis* glucuronoxylan was the best strength additive produced during this investigation. The cationic *E. grandis* glucuronoxylan was therefore chosen for the addition protocol development.

From the addition protocol it was concluded that it is possible to add the cationic *E. grandis* glucuronoxylan to the paper making process before the refining section. This will allow for maximum contact time with the pulp and reduce the refining energy required for the pulp. A dosage of between 1.0 and 2.0 wt.% on the dry weight of the pulp was observed to be the best for the cationic *E. grandis* glucuronoxylan. This dosage was chosen from the comparison between the hemicelluloses and industrial additives. It was observed that at dosage levels between 0.5 and 2.0 wt.%, the cationic *E. grandis* glucuronoxylan had approximately the same improvements in handsheet strength and other properties as the cationic starch (CatStarch 134) industrial additive. This indicated that cationic *E. grandis* glucuronoxylan can perform in competition with cationic starch additives at low dosage levels. Since cationic starch additives are applied at dosage levels of between 2.0 and 4.0 wt.%, cationic hemicelluloses can replace cationic starch additives when they are to be used at 2.0 wt.%. The cationic *E. grandis* glucuronoxylan production process needs to be optimised to produce a higher degree of substitution, which in turn will lead to better improvement of paper strength and surface properties.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

The focus of this investigation was to investigate chemical and physical modification methods of hemicelluloses from literature and apply them to the South African hardwood hemicellulose, *Eucalyptus grandis* 4-O-methylglucuronoxylan, and apply this modified hemicellulose as a strength additive to paper.

5.1 Conclusions

- The modification methods chosen from literature were applied to the South African *E. grandis* hardwood 4-O-methylglucuronoxylan extracted with an alkali extraction method. From the chemical modification methods cationic- and carboxymethyl glucuronoxylan were produced in which the glucuronic acid side chains were replaced by more functional groups. For the ultrasound physical modification method hemicelluloses with lower uronic acid content were produced.

- The CCD experimental design for the modification methods revealed little to no control over the modification of the *E. grandis* glucuronoxylan with none of the R^2 values above 0.95 for the models and very few p-values below 0.05. This was attributed to the variability in the extracted *E. grandis* glucuronoxylan samples performed in the laboratory, and the fact that the method that was used for extraction was not optimised for the *E. grandis* feedstock.

- From the handsheet formation experimentation, it was found that the cationic *E. grandis* glucuronoxylan showed the best improvement in handsheet strength and surface properties. When the cationic *E. grandis* glucuronoxylan was compared to an industrial cationic starch additive, it was observed that the cationic hemicelluloses improved the paper strength and other properties more than the industrial cationic starch additive. This indicated that cationic hemicellulose additive has the potential of outperforming current industrial additives, such as cationic starch.

- It was concluded that it is possible to add cationic *E. grandis* glucuronoxylan additives before the pulp enters the refining section. This allowed maximum contact time between the additive and pulp. At a dosage level of 0.5 to 2.0 wt.%, the cationic *E. grandis* glucuronoxylan performed just as well, and in some cases, better than the cationic starch industrial additive. However, after 2.00 wt.% dosage, the cationic starch outperformed the cationic *E. grandis* glucuronoxylan additive. The addition of cationic hemicelluloses can also lower the refining energy required to reach the required paper strength properties.

The overall, and most important, conclusion of this investigation is that modified wood based hemicelluloses are able to perform as well as industrial strength additives in low dosages when producing paper. These hemicellulosic additives can be used as a processing aid, as it was observed that the refining energy can be lowered with the addition of cationic hemicelluloses before the refining of pulp. This will lead to a decrease in the usage of additives like cationic starch that could rather be used as a food source instead of a paper strength additive. The extracted hemicelluloses will be a more environmentally "green" solution and will promote maximum utilization of the initial biomass entering the pulp and paper mill.

5.2 Recommendations

- Further research on the extraction of hemicelluloses from *E. grandis* is required to determine the optimum extraction conditions for maximum hemicellulose yield with minimum lignin content. When the optimum conditions have been determined, pilot scale trials should be considered to test the feasibility of the pre-extraction of hemicelluloses from *E. grandis* on an industrial scale. This pilot scale extraction will also provide more consistent hemicellulose for further investigations.

- Further experimentation on the cationisation of *E. grandis* glucuronoxylan is required to optimise the cationisation of alkali extracted *E. grandis* glucuronoxylan. This will provide cationic hemicelluloses with high degree of substitutions that will provide better improvement of paper strength and physical properties.

- Handsheet testing should be done with *E. grandis* pulp from which the hemicelluloses were pre-extracted, and then re-introduced to the pulp mixture as unmodified and cationic hemicelluloses. This will provide an overall picture of the pre-extraction and re-introduction process.

- Pilot scale testing of the cationic *E. grandis* glucuronoxylan should be done on a pilot scale paper machine to determine whether the cationic hemicellulose will have the same improvement in paper properties as it did with the handsheets.

- Further studies are required to determine the economic aspects of hemicelluloses pre-extraction and modification for use as strength additive on industrial scale.

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APPENDIX A

MIND MAP OF THESIS

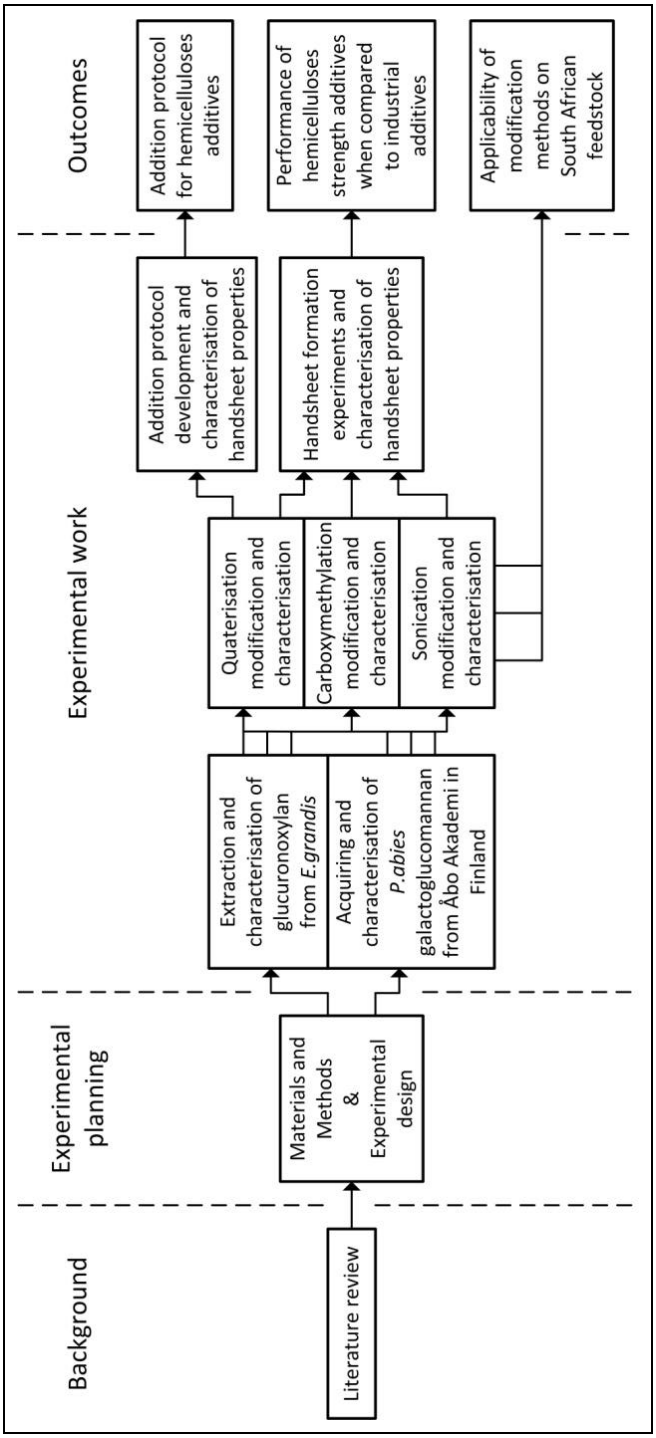

Figure A.1: Mind map of thesis with experimental work

APPENDIX B

ERROR CALCULATIONS

For the measurements that were done in replicate the standard deviation was taken of the replicates and the error was calculated as a percentage of the average and then added to the graphs as error bars with this percentage error. An example is given in Table B.1.

Table B.1: Example of replicate measurements error calculation

	Uronic acid replicate measurements				Statistics	
Run ID	1	2	3	Average	Standard deviation / Error	Error percentage (%)
CAT-01	6.42%	6.72%	6.48%	6.54%	0.1587%	2.43%
CAT-03	12.62%	12.81%	12.67%	12.70%	0.0985%	0.78%
CAT-04	9.41%	10.10%	9.05%	9.52%	0.5334%	5.60%
CAT-08	9.25%	8.92%	8.98%	9.05%	0.1758%	1.94%
CAT-10	9.56%	9.82%	10.53%	9.97%	0.5021%	5.04%
Average				0.0956	0.2937%	3.16%

The deliverables where only a mass was weighed a different method of error calculation was done. For every time the scale was tared an error of 0.1, 0.01, 0.001 or 0.0001 needs to be take into account depending on the mass of the sample being weighed. An example of the method used is given below.

$$Error_{yield} = {}^{\pm 0.1}m_{biomass} + {}^{\pm 0.1}m_{hemicelluloses} \times yield\ \%$$

$$Error_{yield} = {}^{\pm 0.1}105.4586 + {}^{\pm 0.1}10.3417 \times 62.40$$

$$Error_{yield} = 0.6626\ \%$$

$$Percentage\ or\ Error_{yield} = 0.88\ \%$$

APPENDIX C

ALGORITHM TO GET CONSTANT CONSISTENCY OF PULP

The method used to calculate a constant consistency of the stock used for handsheet formation is given in Table C.1.

Table C.1: Calculation of constant consistency for handsheet formation experiments

	A	B	
1	Comments on calculations:		
2	The blue cells are the input cells that you need to fill in. The green cells are the outputs of how much water or fibre you need to add depending on the mass of the 1000 mL handsheet to acquire the correct consistency		
3	Calculating the consistency of the stock is done in cell B6, and you can determine the mass of the 1000 mL handsheet you need to get the consistency you want by changing cell B11 and see what effect it has on the consistency in cell B6.		
4	After you have determined the mass of the 1000 mL handsheet you need for your specific handsheet you can change the formulas to suit your needs. You need to input the bone dry weight of your 1000 mL handsheet into cell B7 for the formulas to be changed.		
5			
6	Consistency of stock =	=B11/1000	
7	Mass that 1000 mL handsheet should be =	3	g
8			
9	Volume water & fibre in the vessel after the stock has been made	20	L
10	Volume of fibre suspension put into the vessel (mL of disintegrated pulp)	2400	mL
11	Mass of 1000 mL handsheet made (bone-dry mass)	3	g
12	Correction: Add water (L)	=IF(B11>B7,(B18-B7*(B9-1))/B7,0)	L
13	Correction: Add water (mL)	=(IF(B11>B7,(B18-B7*(B9-1))/B7,0))*1000	mL
14	Correction: Add bone-dry fibres (g)	=IF(B11<B7,B7*(B9-1)-(B18),0)	g
15	Correction: Add more fibre suspension (mL)	=IF(B11<B7,A20*1000,0)	mL
16			
17	BEGIN: Fibre content	=(B11/1)*B9	g
18	END: Fibre content	=B17-B11	
19	Concentration	=B18/(B9-1)	g/L
20	=(B7*(B9-1)-B18)/(A21-B7)	Lit	
21	=B17/(B10/1000)	g/L	

APPENDIX D

RAW DATA FOR MODIFICATION AND HANDSHEET FORMATION

The tables in Appendix D are the raw experimental results that were generated for the modification of hemicelluloses and the handsheets that were made with the addition of the modified hemicelluloses.

Table D.1: Cationisation experimental results for glucuronoxylan samples

		Factors (actual values)		Characterisation results			Handsheet results							
Run ID	Hemicelluloses sample	A (Molar ratio of NAOH to ETA)	B (Molar ratio of ETA to xylose)	Yield (%)	Degree of substitution	Uronic acid content (%)	Basis weight ($g.m^{-2}$)	Tensile index ($N.m^{-1}.g^{-1}$)	Breaking length (km)	Burst index ($kPa.m^2.g^{-1}$)	Tear index ($mN.m^2.g^{-1}$)	Weight of water adsorbed ($g.m^{-2}$)	% ISO Brightness	Air permeability shown as pressure difference (kPa)
CAT-01	*E. grandis* xylan	1.05	1.75	45.32%	0.106	6.54%	64.35	13.7995	1.41	0.60	5.85	248.1	86.2	0.23
CAT-02	*E. grandis* xylan	1.05	3.00	39.16%	0.152	8.52%	65.36	15.7440	1.61	0.51	6.48	264.5	85.6	0.13
CAT-03	*E. grandis* xylan	1.05	1.75	45.40%	0.117	12.70%	62.94	14.3403	1.46	0.56	5.73	246.8	85.2	0.2
CAT-04	*E. grandis* xylan	1.05	1.75	43.74%	0.068	9.52%	61.17	14.3661	1.46	0.49	6.67	238.3	84.9	0.18
CAT-05	*E. grandis* xylan	1.05	0.50	45.78%	0.050	10.34%	61.07	14.9959	1.53	0.56	6.42	233.4	85.4	0.17
CAT-06	*E. grandis* xylan	0.10	1.75	37.69%	0.096	11.04%	60.32	14.3078	1.46	0.51	6.24	250.0	84.3	0.13
CAT-07	*E. grandis* xylan	0.38	0.87	36.91%	0.599	6.42%	60.52	14.7064	1.50	0.45	6.22	248.4	84.9	0.15
CAT-08	*E. grandis* xylan	1.05	1.75	46.49%	0.265	9.05%	60.07	13.6210	1.39	0.52	6.01	220.5	84.8	0.16
CAT-09	*E. grandis* xylan	1.72	2.63	22.36%	0.114	10.34%	59.01	14.1622	1.44	0.53	7.18	235.1	84.8	0.16
CAT-10	*E. grandis* xylan	1.05	1.75	22.98%	0.484	9.97%	62.74	15.1671	1.55	0.56	7.00	223.3	85.2	0.2
CAT-11	*E. grandis* xylan	2.00	1.75	32.22%	0.272	9.42%	62.74	15.5587	1.59	0.60	6.00	249.2	85.4	0.21
CAT-12	*E. grandis* xylan	0.38	2.63	28.36%	0.729	6.21%	62.84	16.3261	1.66	0.60	4.99	243.1	87.5	0.23
CAT-13	*E. grandis* xylan	1.72	0.87	40.82%	0.552	6.29%	61.38	14.1088	1.44	0.55	6.65	241.1	86.9	0.18
CAT-14	Beech xylan	0.38	0.87	88.22%	0.058	13.64%	62.43	15.1753	1.55	0.54	6.28	201.1	86.3	0.14
CAT-15	Beech xylan	1.05	1.75	98.21%	0.096	5.92%	62.43	15.3578	1.57	0.55	6.53	231.9	85.9	0.15
CAT-16	Beech xylan	1.72	2.63	83.56%	0.098	9.39%	62.43	14.5786	1.49	0.58	5.28	239.5	87.4	0.16

Table D.2: Cationisation experimental results for galactoglucomannan samples

		Factors (actual values)		Characterisation results			Handsheet results							
Run ID	Hemicelluloses sample	A (Molar ratio of NAOH to ETA)	B (Molar ratio of ETA to xylose)	Yield (%)	Degree of substitution	Galactose content (%)	Basis weight ($g.m^{-2}$)	Tensile index ($N.m^{-1}.g^{-1}$)	Breaking length (km)	Burst index ($kPa.m^2.g^{-1}$)	Tear index ($mN.m^2.g^{-1}$)	Weight of water adsorbed ($g.m^{-2}$)	% ISO Brightness	Air permeability shown as pressure difference (kPa)
CAT-17	Pilot plant mannan	0.38	0.87	69.85%	0.18	6.91%								
CAT-18	Pilot plant mannan	0.1	1.75	72.74%	0.06	7.27%								
CAT-19	Pilot plant mannan	2	1.75	54.67%	0.07	6.79%								
CAT-20	Pilot plant mannan	1.05	1.75	65.69%	0.10	6.76%	64.00	14.1744	1.45	0.60	5.39	239.2	86.5	0.17
CAT-21	Pilot plant mannan	1.05	1.75	47.84%	0.27	7.39%	63.59	15.1277	1.54	0.63	4.93	255.5	86.7	0.18
CAT-22	Pilot plant mannan	1.05	1.75	65.37%	0.10	6.78%	61.58	15.2728	1.56	0.58	5.61	220.8	82.8	0.18
CAT-23	Pilot plant mannan	0.38	2.63	61.16%	0.11	8.36%								
CAT-24	Pilot plant mannan	1.05	1.75	71.70%	0.08	8.44%	60.52	14.9995	1.53	0.61	5.96	269.4	83.9	0.15
CAT-25	Pilot plant mannan	1.72	0.87	66.75%	0.05	8.46%								
CAT-26	Pilot plant mannan	1.05	1.75	65.18%	0.06	8.49%	59.31	14.5605	1.48	0.56	5.82	249.0	84.4	0.18
CAT-27	Pilot plant mannan	1.05	3	57.24%	0.10	9.80%								
CAT-28	Pilot plant mannan	1.72	2.63	51.08%	0.07	7.30%								
CAT-29	Pilot plant mannan	1.05	0.5	67.85%	0.03	11.22%								
CAT-30	PHWE mannan	0.38	0.87	53.85%	0.01	7.98%								
CAT-31	PHWE mannan	1.05	1.75	26.22%	0.10	8.49%	60.42	14.1183	1.44	0.56	5.19	216.9	85.0	0.15
CAT-32	PHWE mannan	1.72	2.63	22.57%	0.09	10.73%								

Table D.3: Carboxymethylation experimental results for glucuronoxylan samples

		Factors (actual values)		Characterisation results			Handsheet results							
Run ID	Hemicelluloses sample	A (Ratio of ethanol to water)	B (Molar ratio of SMCA to xylose)	Yield (%)	Degree of substitution	Uronic acid content (%)	Basis weight ($g.m^{-2}$)	Tensile index ($N.m^{-1}.g^{-1}$)	Breaking length (km)	Burst index ($kPa.m^2.g^{-1}$)	Tear index ($mN.m^2.g^{-1}$)	Weight of water adsorbed ($g.m^{-2}$)	ISO Brightness (%)	Air permeability shown as pressure difference (kPa)
CM-01	*E. grandis* xylan	1.50	1.75	31.89%	0.07	17.76%	61.43	14.6284	1.49	0.58	6.64	252.2	84.9	0.13
CM-02	*E. grandis* xylan	1.85	0.87	29.15%	0.08	10.21%	61.58	14.2634	1.45	0.45	5.61	254.0	85.0	0.15
CM-03	*E. grandis* xylan	1.85	2.63	22.40%	0.07	12.36%	63.09	13.7549	1.40	0.57	5.72	265.0	86.1	0.18
CM-04	*E. grandis* xylan	1.50	1.75	30.07%	0.06	13.43%	62.99	14.3258	1.46	0.51	5.49	247.2	84.9	0.16
CM-05	*E. grandis* xylan	1.15	2.63	24.05%	0.08	13.00%	67.62	13.4901	1.38	0.51	5.10	268.8	85.1	0.17
CM-06	*E. grandis* xylan	1.50	1.75	30.82%	0.05	12.38%	65.15	14.0533	1.43	0.49	5.06	254.8	86.0	0.18
CM-07	*E. grandis* xylan	1.00	1.75	25.29%	0.08	13.47%	64.45	13.8537	1.41	0.48	5.60	199.0	85.5	0.17
CM-08	*E. grandis* xylan	1.15	0.87	28.84%	0.09	10.54%	64.25	13.5085	1.38	0.46	5.13	238.9	86.1	0.16
CM-09	*E. grandis* xylan	1.50	1.75	26.36%	0.05	12.56%	64.00	14.1998	1.45	0.50	4.90	231.2	85.5	0.16
CM-10	*E. grandis* xylan	1.50	0.50	31.61%	0.05	17.53%	63.54	12.0798	1.23	0.44	5.43	231.6	85.1	0.15
CM-11	*E. grandis* xylan	2.00	1.75	23.99%	0.07	21.38%	62.74	12.5372	1.28	0.44	5.50	267.0	85.6	0.14
CM-12	*E. grandis* xylan	1.50	3.00	27.16%	0.11	17.69%	61.88	14.3173	1.46	0.48	5.58	235.2	85.2	0.15
CM-13	*E. grandis* xylan	1.50	1.75	31.21%	0.06	11.00%	61.38	14.4216	1.47	0.45	5.37	250.5	83.3	0.16
CM-14	Beech xylan	1.15	0.87	89.68%	0.63	7.45%	60.07	13.9100	1.42	0.37	6.01	193.5	82.3	0.12
CM-15	Beech xylan	1.50	1.75	97.09%	0.86	9.21%	59.16	14.2780	1.46	0.44	6.63	213.9	82.8	0.13
CM-16	Beech xylan	1.85	2.63	92.24%	0.88	7.06%	59.91	13.9831	1.43	0.47	6.81	219.5	84.4	0.144

Table D.4: Carboxymethylation experimental results for galactoglucomannan samples

		Factors (actual values)		Characterisation results			Handsheet results							
Run ID	Hemicelluloses sample	A (Molar ratio of NaOH to mannose)	B (Molar ratio of MCA to mannose)	Yield (%)	Degree of substitution	Galactose content (%)	Basis weight ($g.m^{-2}$)	Tensile index ($N.m^{-1}.g^{-1}$)	Breaking length (km)	Burst index ($kPa.m^2.g^{-1}$)	Tear index ($mN.m^2.g^{-1}$)	Weight of water adsorbed ($g.m^{-2}$)	ISO Brightness (%)	Air permeability shown as pressure difference (kPa)
CM-17	Pilot plant mannan	5.07	1.75	61.08%	0.37	ND	58.76	14.1952	1.45	0.51	6.68	251.4	84.4	0.15
CM-18	Pilot plant mannan	5.07	1.75	77.99%	0.55	ND	59.71	13.9813	1.43	0.49	5.78	227.6	84.2	0.16
CM-19	Pilot plant mannan	6.26	0.87	51.11%	0.54	ND								
CM-20	Pilot plant mannan	5.07	3.00	10.80%	0.54	ND								
CM-21	Pilot plant mannan	6.26	2.63	48.32%	0.66	ND								
CM-22	Pilot plant mannan	5.07	0.50	65.63%	0.72	ND								
CM-23	Pilot plant mannan	5.07	1.75	65.95%	0.27	ND	61.68	15.0335	1.53	0.52	5.34	250.0	84.7	0.16
CM-24	Pilot plant mannan	3.38	1.75	55.76%	0.66	ND								
CM-25	Pilot plant mannan	3.87	0.87	53.80%	0.50	ND								
CM-26	Pilot plant mannan	5.07	1.75	71.40%	0.24	ND	60.72	14.8385	1.51	0.60	5.94	249.3	85.0	0.17
CM-27	Pilot plant mannan	3.87	2.63	61.67%	0.42	ND								
CM-28	Pilot plant mannan	5.07	1.75	60.31%	1.27	ND	60.82	15.0680	1.54	0.52	6.45	268.9	82.7	0.17
CM-29	Pilot plant mannan	6.76	1.75	58.25%	0.22	ND								
CM-30	PHWE mannan	3.87	0.87	52.41%	0.60	ND								
CM-31	PHWE mannan	5.07	1.75	46.24%	0.07	ND	60.02	13.6370	1.39	0.47	6.80	274.8	83.1	0.15
CM-32	PHWE mannan	6.26	2.63	43.01%	0.45	ND								

ND = Not determined due to shortage of sample mass

Table D.5: Ultrasound experimental results for glucuronoxylan samples

			Characterisation results			Handsheet results							
Run ID	Hemicelluloses sample	Sonication time (min)	Yield (%)	M_w (g/mol)	Glucuronic acid content (%)	Basis weight ($g.m^{-2}$)	Tensile index ($N.m^{-1}.g^{-1}$)	Breaking length (km)	Burst index ($kPa.m^2.g^{-1}$)	Tear index ($mN.m^2.g^{-1}$)	Weight of water adsorbed ($g.m^{-2}$)	ISO Brightness (%)	Air permeability shown as pressure difference (kPa)
US-01	*E. grandis* xylan	10	50.21%	50 130	12.68%	58.81	14.3353	1.46	0.41	5.60	209.5	85.1	0.14
US-02	*E. grandis* xylan		49.33%	57 113	13.32%	59.06	13.2079	1.35	0.47	5.85	261.2	85.1	0.13
US-03	*E. grandis* xylan		49.83%	57 325	14.06%	58.40	13.9773	1.43	0.43	5.64	200.5	85.0	0.15
US-04	*E. grandis* xylan	17	47.64%	56 622	14.33%	65.86	14.9664	1.53	0.52	5.48	260.8	86.5	0.18
US-05	*E. grandis* xylan		49.39%	57 433	18.05%	65.82	14.5124	1.59	0.56	5.15	284.2	85.5	0.17
US-06	*E. grandis* xylan		47.48%	56 020	10.68%	65.81	14.2510	1.51	0.51	5.43	259.1	85.5	0.19
US-07	*E. grandis* xylan	35	48.26%	57 238	11.26%	65.86	14.1807	1.45	0.52	5.48	280.9	87.0	0.16
US-08	*E. grandis* xylan		49.91%	57 105	14.77%	65.89	14.5412	1.51	0.51	5.43	275.3	87.1	0.15
US-09	*E. grandis* xylan		52.87%	57 130	12.94%	65.15	13.9155	1.41	0.58	5.62	291.5	87.1	0.19
US-10	*E. grandis* xylan	53	49.66%	54 484	9.87%	65.19	14.2512	1.50	0.59	5.51	241.5	86.7	0.15
US-11	*E. grandis* xylan		50.16%	57 312	21.41%	65.12	14.1553	1.41	0.56	5.34	234.1	86.5	0.13
US-12	*E. grandis* xylan		46.39%	56 535	13.44%	65.10	14.6353	1.49	0.52	5.54	225.9	86.6	0.16
US-13	*E. grandis* xylan	60	48.32%	57 060	17.54%	63.79	12.4083	1.27	0.44	5.41	252.1	85.7	0.17
US-14	*E. grandis* xylan		48.40%	57 903	20.26%	63.71	13.5123	1.21	0.45	5.51	231.5	85.6	0.16
US-15	*E. grandis* xylan		51.78%	57 078	17.37%	62.81	13.9152	1.39	0.41	5.36	264.2	85.7	0.17
US-16	Beech xylan	10	76.92%	28 132	10.12%	65.15	12.1317	1.24	0.49	5.06	164.7	86.0	0.16
US-17	Beech xylan		85.94%	31 355	11.81%	65.46	12.5241	1.26	0.43	5.09	151.6	86.1	0.17
US-18	Beech xylan	35	83.64%	30 582	11.96%	64.14	12.2451	1.25	0.43	4.83	241.5	87.0	0.16
US-19	Beech xylan		88.96%	29 534	7.35%	64.25	12.5697	1.28	0.44	4.88	254.2	86.9	0.16
US-20	Beech xylan	60	88.06%	31 053	7.52%	63.59	13.4455	1.37	0.45	5.18	159.9	87.1	0.16
US-21	Beech xylan		85.54%	30 540	10.94%	63.12	13.2551	1.35	0.49	5.1	169.3	87.3	0.17

Table D.6: Ultrasound experimental results for galactoglucomannan samples

			Characterisation results			Handsheet results							
Run ID	Hemicelluloses sample	Sonication time (min)	Yield (%)	MW (g/mol)	Galactose content (%)	Basis weight ($g.m^{-2}$)	Tensile index ($N.m^{-1}.g^{-1}$)	Breaking length (km)	Burst index ($kPa.m^2.g^{-1}$)	Tear index ($mN.m^2.g^{-1}$)	Weight of water adsorbed ($g.m^{-2}$)	ISO Brightness (%)	Air permeability shown as pressure difference (kPa)
US-22	Pilot plant mannan	10	65.13%	34 616	7.55%	59.61	13.6656	1.39	0.49	5.79	220.1	85.3	0.14
US-23	Pilot plant mannan		69.63%	30 735	8.04%	59.54	13.3124	1.34	0.42	5.34	240.5	85.9	0.15
US-24	Pilot plant mannan	35	61.83%	32 186	8.28%	59.71	14.4145	1.47	0.45	5.78	231.9	85.6	0.14
US-25	Pilot plant mannan		68.30%	32 335	8.05%	61.07	14.4198	1.47	0.47	5.65	263.0	84.7	0.15
US-26	Pilot plant mannan	60	70.78%	32 951	9.55%	59.46	13.6547	1.39	0.44	5.81	266.3	85.0	0.12
US-27	Pilot plant mannan		63.68%	33 103	9.67%	59.76	12.9049	1.32	0.49	5.25	262.3	84.9	0.15
US-28	PHWE mannan	10	60.52%	8 709	4.01%								
US-29	PHWE mannan		61.54%	8 971	3.77%								
US-30	PHWE mannan		61.93%	8 557	3.62%								
US-31	PHWE mannan	35	62.31%	8 517	3.56%	60.26	15.2351	1.52	0.56	5.71	261.6	86.6	0.14
US-32	PHWE mannan		61.77%	8 786	4.11%	60.12	15.5548	1.59	0.53	5.74	267.8	86.4	0.13
US-33	PHWE mannan		63.42%	8 750	3.66%	60.15	15.6525	1.56	0.61	5.62	256.2	85.9	0.14
US-34	PHWE mannan	60	62.40%	8 675	3.75%								
US-35	PHWE mannan		63.96%	8 781	3.56%								
US-36	PHWE mannan		63.53%	8 988	3.50%								