

Co-production of furfural and wood composite products from bio-based processing residues

By

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Declaration

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Summary

There is an increased environmental concern to move from a petroleum-based economy to a more bio-based economy. Lignocellulosic materials have been shown to be a good source of building blocks for value-added products such as furfural. The integration of lignocellulosic material in a biorefinery concept proves to be necessary and beneficial in the industry and global context.

The lignocellulosic material was sourced locally and included sugarcane (*Saccharum officinarum*) bagasse, Blue gum (*Eucalyptus globulus*) and Long-leaved wattle (*Acacia longifolia*). The lignocellulosic materials were pre-treated with NaOH aimed at enhancing the flexural and physical properties of the manufactured panels as well as extracting hemicelluloses. The effect of the treatment on fibres and resultant by-products were evaluated using wet chemical and instrumental methods, such as high-performance liquid chromatography (HPLC), molecular weight, size-exclusion chromatography (SEM) and Fourier-transform infrared spectroscopy (FTIR).

In the present study, the co-production of composite panels and furfural was investigated. The aim was to integrate the biorefinery concept in using biomass waste and alkali pre-treatment to produce furfural. The composite panels were manufactured using untreated and alkaline treated lignocellulosic material, while furfural was produced from the pre-treated by-products.

Moreover, this study set out to simultaneously add value to the by-products from pretreated lignocellulosic material by producing furfural, which had not been done previously. In order to produce the furfural, a central composite statistical design (CCD) was used with independent variable temperatures (150-170 °C), time (30-90 min) and the response variable furfural yield, while acidic concentration (2wt%) and solid loading (14wt%) were kept constant. The experimental conditions were sourced with reference to literature to mimic the industrial

standards. The interaction of the independent variables and their effect on the produced furfural were evaluated using the Pareto analysis of variance. Response surface models were used to develop and predict the parameters yielding optimum furfural yield. The yields of furfural from the acid hydrolysis of the extracted hemicelluloses was 39, 45 and 44 mol% for sugarcane bagasse, *E.globulus* and *A.longifolia*, respectively. These values were slightly lower than the predicted values from the CCD. The low furfural yields led to a Pareto chart showing no confidence of independent variables on the furfural yield.

Furthermore, the performance of the treated materials compared to untreated materials were evaluated on the properties of the manufactured composite panels, such as modulus of elasticity (MOE), modulus of rupture (MOR), water absorption and thickness. Based on the results, the treated lignocellulosic materials enhanced the properties of the composite panels as compared to the untreated lignocellulosic materials. In the treated panels the modulus of rupture was 10.42 MPa, 11.13 MPa and 6.4 MPa for sugarcane bagasse, *E. globulus* and *A. longifolia*, respectively. The manufactured panels met the minimum requirements and are classified as low density to medium density boards according to ANSI A208.1. These panels prove useful in the wood panel industry as core material for solid doors.

Opsomming

Daar is 'n toenemende kommer oor die omgewing om van 'n petroleum-gebaseerde ekonomie na 'n meer bio-gebaseerde ekonomie te beweeg. Lignosellulosiese materiale is 'n goeie bron van boustene vir waardetoevoegende produkte soos furfural. Die integrasie van lignosellulosiese materiaal in 'n bioraffinadery-konsep blyk in die industrie en wêreldwye konteks noodsaaklik en voordelig te wees.

Die lignosellulosiese materiaal is plaaslik verkry en bevat suikerriet (*Saccharum officinarum*) bagasse, bloekom (*Eucalyptus globulus*) en langblaar-wattel (*Acacia longifolia*). Die lignosellulosiese materiaal is vooraf behandel met NaOH wat daarop gemik was om die buig- en fisiese eienskappe van die vervaardigde panele te verbeter, asook om hemiselluloses te onttrek. Die effek van die behandeling op vesels en gevolglike neweprodukte is beoordeel met behulp van nat chemiese en instrumentele metodes, soos hoëprestasie vloeistofchromatografie (HPLC), molekulêre gewig, grootte-uitsluitingschromatografie (SEM) en Fourier-transvorm infrarooi spektroskopie (FTIR).

In die huidige studie is die medeproduksie van saamgestelde panele en furfural ondersoek. Die doel was om die bioraffinadery-konsep te integreer in die gebruik van biomassa-afval en voorafbehandeling van alkali om furfural te produseer. Die saamgestelde panele is vervaardig met onbehandelde en alkaliese behandelde lignosellulosiese materiaal, terwyl furfural vervaardig is uit die voorafbehandelde neweprodukte.

Verder het hierdie studie beoog om gelyktydig waarde toe te voeg tot die neweprodukte van voorafbehandelde lignosellulosiese materiaal deur furfural te vervaardig, wat nog nie voorheen gedoen is nie. Om die furfural te vervaardig, is 'n sentrale saamgestelde statistiese ontwerp (CCD) gebruik met onafhanklike veranderlike temperature (150-170 ° C), tyd (30-90 min) en die respons veranderlike furfural opbrengs, terwyl die suur konsentrasie (2 gew.%) en vaste

belading (14 gew.%) konstant gehou is. Die eksperimentele toestande is verkry met verwysing na literatuur om die industriële standaarde na te boots. Die interaksie van die onafhanklike veranderlikes en hul effek op die geproduseerde furfural is geëvalueer aan die hand van die Pareto variansie-analise. Modelle vir responsoppervlaktes is gebruik om die parameters te ontwikkel en te voorspel wat die optimale fururale opbrengs lewer. Die opbrengste van furfural uit die suurhidrolise van die onttrekte hemiselluloses was onderskeidelik 39, 45 en 44 mol% vir suikerrietbagasse, *E. globulus* en *A. longifolia*. Hierdie waardes was effens laer as die voorspelde waardes van die CCD. Die lae furfural opbrengste het gelei tot 'n Pareto-grafiek wat geen vertroue toon in die onafhanklike veranderlikes op die furfural opbrengs nie.

Verder is die prestasie van die behandelde materiale in vergelyking met onbehandelde materiale beoordeel aan die hand van die eienskappe van die vervaardigde saamgestelde panele, soos modulus van elastisiteit (MOE), modulus van skeuring (MOR), waterabsorpsie en dikte. Op grond van die resultate het die behandelde lignosellulosiese-materiale die eienskappe van die saamgestelde panele verbeter in vergelyking met die onbehandelde lignosellulosiese-materiale. In die behandelde panele was die modulus van die skeuring onderskeidelik 10,42 MPa, 11,13 MPa en 6,4 MPa vir suikerrietbagasse, *E. globulus* en *A. longifolia*. Die vervaardigde panele het aan die minimum vereistes voldoen en word volgens ANSI A208.1 as lae digtheid tot mediumdigtheid borde geklassifiseer. Hierdie panele is nuttig in die houtpaneelbedryf as kernmateriaal vir soliede deure.

This thesis is dedicated to
God, family, friends and scientific community

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Chapter 1: Introduction

1.1 Background

The most abundant feedstock in the world for biocomposites are lignocellulosic materials (Hu and Ragauskas, 2012; Zhang, 2008). These include all the agricultural crop residues (e.g. bagasse) and non-woody forest products (e.g. rattan, bamboo) and invasive plant species. South Africa has a vast amount of alien invasive plants that are unwanted plant species brought in from other countries intentionally or unintentionally. Their presence in the environment has led to a decrease in water availability both on surface and underground (Chamier et al., 2012; Richardson and Van Wilgen, 2004). According to Sierra et al. (2007), the productivity of lignocellulosic materials per hectare is high and requires less input per unit of biomass produced. An ever-growing natural ecosystem is the most sustainable economy and is of most importance. Thus, the move from fossil fuels towards a more bio-based energy source is necessary.

The pre-treatment methods aim to fractionate lignocellulosic biomass into cellulose, hemicellulose and lignin to allow for chemical and enzymatic incubation to allow for more products to form such as sugars. Pre-treatment is necessary as the chemical structure and physical features of biomass materials make them resistant to enzymatic decomposition. Also, pre-treatment of biomasses, such as sugarcane bagasse, *Eucalyptus globulus* and *Acacia* has proven favourable in high xylan solubilisation and subsequent recovery of the liquid fraction. In the past, the use of the extracted hydrolysate, particularly xylan in producing furfural has not been significantly studied.

Alkaline pre-treatment proved to give a higher pulp yield and quality as reported by Vena et al. (2013). Moreover, the bark and wood residue of pre-treated *Acacia mearnsii* was bonded with phosphate binder in making particleboards and compared to untreated *Acacia mearnsii* (Amiandamhen et al., 2017). The modulus of rupture (MOR), modulus elasticity (MOE) and

water absorption of the manufactured treated particleboards outperformed the untreated particleboards. Pre-treated particleboards met the standards of a low-density board, showing the potential use in the wood product industry. These are some ways in which the waste from pre-treated alien invasive species can be used and made into value-added products.

The value-added product made from by-products of pre-treated biomass in this study was furfural. Furfural is a furan aldehyde compound with the potential to substitute petroleum-based products, (Yemiş & Mazza 2011). Further research and developments are increasing with the use of furfural, extracted from lignocellulosic fibre, as a possible plant-based binder has increased research and development resulting in eco-friendly composite panels. Furfural when synthesised into a binder has great thermosetting properties, it is resistant to decomposition and has high physical strength. Furthermore, furfural can also be used in the production of mastics, caulking compounds and putties.

According to Arevalo-Gallegos et al. (2017), the integration of biomass in the biorefinery concept would not only have a low-cost environmental impact, but also establish a future for sustainable production of bio-based products. Lignocellulosic biomass has great potential to meet the demands of energy, like biofuels, without the constant dependence on petroleum-based fuels that impact the environment harmfully as well as the climate.

1.2 Research aim

The overall aim of this study was to investigate the integration of pre-treatment of agricultural residues and forest waste from alien invasive species, sourced from South Africa with the production of furfural from extracted hemicelluloses, which is a by-product from the pre-treatment. Pre-treatment has been previously shown to enhance the flexural and physical properties of the composite panels. However, literature shows no record of the use of the remaining material.

To achieve this aim, the lignocellulosic biomass was pre-treated with NaOH under selected experimental conditions based on literature (Vena et al.,2013; Joubert et al.,2015). The alkali pre-treatment was selected due to its low cost and based on results from previous studies that investigated the effect of surface treatment on the properties of lignocellulosic material (Hajiha et al., 2014; Amiandamhen et al. 2018). The by-products from the pre-treatment were then used to produce furfural based on the modification of a range of reference conditions from literature (Yemiş & Mazza 2011). The central composite design was used to determine an adequate experimental design for furfural production. The effect of the operating conditions was statistically evaluated and their significance determined.

Furthermore, the use of treated fibres in composite products as investigated by Amiandamhen et al. (2016), has shown improvement in panel properties. The alkaline treated fibres in the study were used to manufacture composite panels with the sole purpose of improving the density, water absorption, thickness swelling and flexural properties. This could also be viewed as a further step in the development of adequate ways to use invasive waste species while creating value-added products is essential.

1.3 Objectives of the study

The specific objectives of this study were:

- i. To determine the effect and efficiency of the alkaline treatment on the chemical composition of lignocellulosic materials sugarcane bagasse (*Saccharum officinarum*), blue gum (*Eucalyptus globulus*) and golden wattle (*Acacia longifolia*) and to evaluate their physicochemical properties
- ii. To optimize the production of furfural within the study using commercial xylose as the starting reaction.
- iii. To produce furfural by acid catalysed dehydration of hemicelluloses present in the extracted lignocellulosic material.

- iv. To evaluate the performance of the extracted materials against the untreated materials on the density, water absorption, thickness swelling and flexural properties of the manufactured composite products.

Chapter 2: Literature review

2.1 Composite materials and Biorefinery

Composite products refer to structural materials, such as panels manufactured from lignocellulosic materials. Composite products are defined as two or multiple materials combined to form a product with more enhanced and different chemical and physical properties than those of the original materials (Gibson, 2016).

The manufacturing of composite products from wood-based materials presents specific difficulties with the lignocellulosic fibre and matrix, such as the reluctant intermolecular bonds between cellulose, hemicellulose and lignin (Hajiha et al. 2014; Amiandamhen et al., 2019). The use of treatment methods that can break intermolecular bonds and alter the morphological properties of the lignocellulosic materials is required; this will successively allow for adequate bonding of lignocellulosic material with adhesives and polymers (Amiandamhen et al., 2019).

Previous studies have shown that it is possible to produce composite products from lignocellulosic materials with comparable properties to traditional wood-based panels (Amiandamhen, 2018). Furthermore, the pre-treatment of the biomass fibres has been shown to improve the properties of composite products (Amiandamhen et al., 2017). However, the hydrolysate from the pre-treatment process is typically disposed of; thus, the integration or the conversion of the hydrolysate is necessary.

Biorefinery sets out to use renewable raw materials, such as biomass, to produce energy in a sustainable manner (Mussatto, 2016). Renewable materials are converted through different methods and treatments to produce value-added products (Figure 1) and bio-based chemicals. This integration of biomass processing within the biorefinery concept has gained considerable interest over the years and is now termed biorefinery integration.

Biorefinery integration has various benefits, because of its diversification in feedstock and value-added products. Different levels of integration allow it to add value to its sustainability, which is significantly felt economically as well as environmentally. Economic and production advantages increase with the different levels of integration (Arevalo-Gallegos et al., 2017). The biorefinery economy is very prosperous in replacing fossil fuels with bio-renewables.

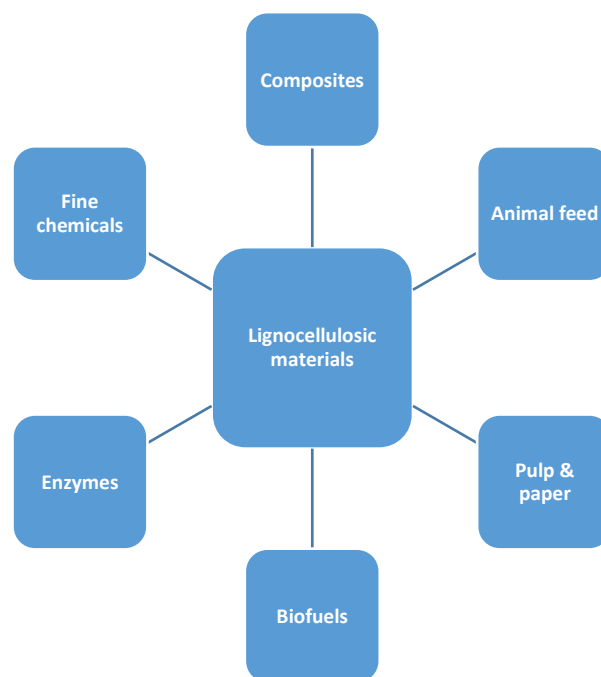


Figure 1: Bio-conversions of Lignocellulosic material into value-added bio-products (adopted from Arevalo-Gallegos et al., 2017).

2.2 Lignocellulosic material

The scientific community has gradually moved its focus to find ways to replace petroleum-derived solvents with biomass-based materials. Biomass is abundantly available and made up of hemicelluloses and makes up the non-edible component and has the potential to be used in

value-added chemical products as well as bio-based energy (Luo et al., 2019). C-5 sugars, which consist mainly of xylose, are found in hemicellulose in raw biomass, which can further be processed to produce furfural.

2.2.1 Lignocellulosic material as a biorefinery resource

The biorefinery concept uses the extracts from raw materials, such as hemicelluloses, carbohydrates, lignin and oils and converts these into fuels, high-value chemicals and other materials with the sole aim of reducing waste produced (Carvalho et al., 2008), as shown in Figure 2. These biomass conversion processes include biochemical (sugar) chemical and thermochemical (syngas) conversions, in which fractionation and separation occur.

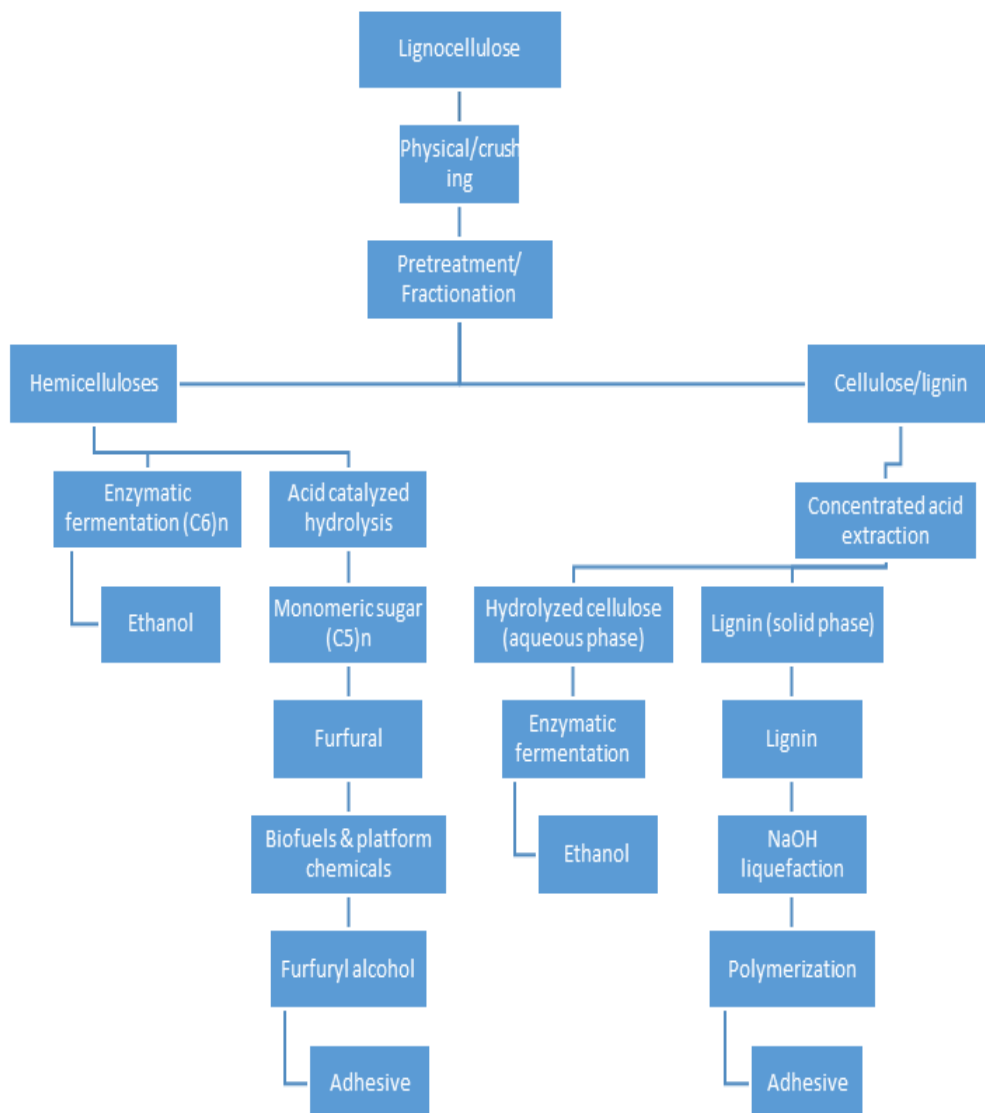


Figure 2: Different bioconversion pathways of lignocellulosic material (Demirbas 2009).

According to Giron et al. (2012), biomass is any sugar-containing material derived from forest or agricultural processes, which include wood residues and energy-producing crops.

Biomass feedstock is grouped into wood and non-woody biomass and make up the world's leading source for raw materials in the pulp production and biorefinery applications. The high demand and relatively low supply of wood has increased the cost of this material. Thus, the use of invasive species, grassy and agricultural residues has become more apparent. For instance, the planted forest has high-quality wood used in the pulp and paper industry. Moreover, they are also very productive and homogeneous, allowing better use in the biorefinery.

Also, one of the readiest available and valuable biomass worldwide is sugarcane bagasse, because of its primary use as a food source, sugar and to produce ethanol. Sugarcane bagasse used in the biorefinery concept proves to be of great advantage, as it can provide various materials that can further be processed into value-added products. These include 1) Natural polymers derived from hemicellulose, cellulose and lignin; 2) sugar from xylose, sucrose and glucose and 3) alcohols and carbon dioxide to name a few.

In the year 2015, South Africa harvested 14 million tons of sugarcane bagasse. However, deficient rainfall conditions have affected these yields. The sugarcane industry of South Africa has been ranked amongst the top 10 in the world in terms of producing sugar at cost-competitive and high quality (Pradhan and Mbohwa, 2014). The integration of biorefinery proves to be a great source of economic growth and sustainability. The use of sugarcane residue to produce ethanol is one way to achieve this integration, which has gained extensive favour, because of its low cost and high availability. However, some drawbacks, such as high energy consumption and costly pre-treatments need to be improved.

Moreover, the integration of alien invasive species in biorefinery concepts can prove advantageous. In South Africa, these species include *Acacia cyclops*, *Acacia saligna*, *Acacia mearnsii* and *Acacia longifolia*. These species have been shown to have an undesirable effect on the environment by using large amounts of water, light, land area and disrupting water stream flow, which then in turn decreases the availability of the water (Oelofse et al., 2016; Richardson and Wilgen 2004; Gorgens and Wilgen 2004). Environmental management of these species by harvest-based eradication has shown significant effect. The produced wood waste has the potential to be used to produce wood composite products.

In a study by Amiandamhen et al. (2016), bark and waste residue from alien invasive trees was used as a starting material to investigate its effect on phosphate bonded wood products. This study found that the use of these alien invasive species would be feasible in manufacturing board products as well as improving the physical properties of the boards. Amiandamhen et al. (2016) showed one of many ways to use lignocellulosic materials to produce value-added products instead of the outdated and consensual way of burning for fuel within the industry.

2.2.2 Pre-treatment of lignocellulosic material

In relinquishing our need for petroleum-based products, lignocellulosic materials serve as a great starting material for high-value products. Moreover, the carbon found in lignocellulosic material can be processed into chemical liquids (Xu and Sun, 2016), which is further integrated into available transportation fuel infrastructure.

However, the main barrier to large-scale development is biomass recalcitrance. This biomass recalcitrance disallows the effectiveness of enzymes during bioconversions process due to the inaccessibility of the enzyme caused by the complex structure of the biomass material (Xu and Sun, 2016). The biomass must first be treated to break down the complex structure and hence the salvage of multiply products making the entire process economically viable.

There are different methods to pre-treating lignocellulosic biomass, such as physicochemical, mechanical, chemical, often using acid, alkali, ionic liquids (ILs), organosolv and biological. Physical and chemical treatments are the most used methods of pre-treatment. One method in particular is the alkaline treatment of lignocellulosic material. Three streams of chemical components form a liquid fuel and lignin stream when converted into a saccharide fraction (Xu and Sun, 2016). Saccharide fraction is converted into value-added products, such as furfural (Fang, 2013; Mussatto, 2016).

The reagents used in alkali pre-treatment include calcium, ammonium anhydroxides, potassium and sodium. One of the most used pre-treatment methods in the pulp and paper industry is sodium hydroxide (NaOH) treatment and has been studied extensively in the bioconversion of lignocelluloses. NaOH treatment has a high efficiency for lignin removal with values of up to 74% (Nomanbhay et al., 2013), which increases the digestibility of hardwood and agricultural residues.

Pretreatment has also been used to improve panel properties. In this regard, pretreatment reduces the hydrophilicity of the raw material and improves the dimensional stability of the

composite products (Amiandamhen et al. 2018). Also, pre-treatment allows for better interlocking of fibre and matrix. Examples of pre-treatments (for panels) include alkalisation, acetylation, salinisation, benzylation and peroxidation.

2.2.3 Hemicelluloses from lignocellulosic biomass

Hemicelluloses are the second most abundant polysaccharide on earth (Saha, 2003; Machado et al., 2016; Phitsuwan et al., 2013; Maity, 2015). Hemicelluloses are by-products in the pulp and paper industry. Once cellulose has been isolated, the remaining lignin-hemicelluloses are combusted in the mill to recover the energy lost. From an economic and environmental perspective, it would be more desirable to exploit all valuable biomass material in the industry (Norstrom et al., 2015).

Unlike cellulose, hemicelluloses are composed of arrangements of pentoses as shown in Figure 3 and these include xylose (Xyl), arabinose (Ara), hexoses which are mannose (Man), galactose (Gal) and glucose (Glc). Hemicelluloses are frequently acetylated and have side chain groups, such as uronic acid and the 4-O-methyl ester (Hu and Ragauskas, 2012; Maity, 2015; Machado et al., 2016).

Moreover, pentoses of hemicelluloses present in hardwoods and waste residues consist mainly of xylan, while in softwoods glucomannan is present in high quantities (Pu et al., 2008; Hu and Ragauskas, 2012).

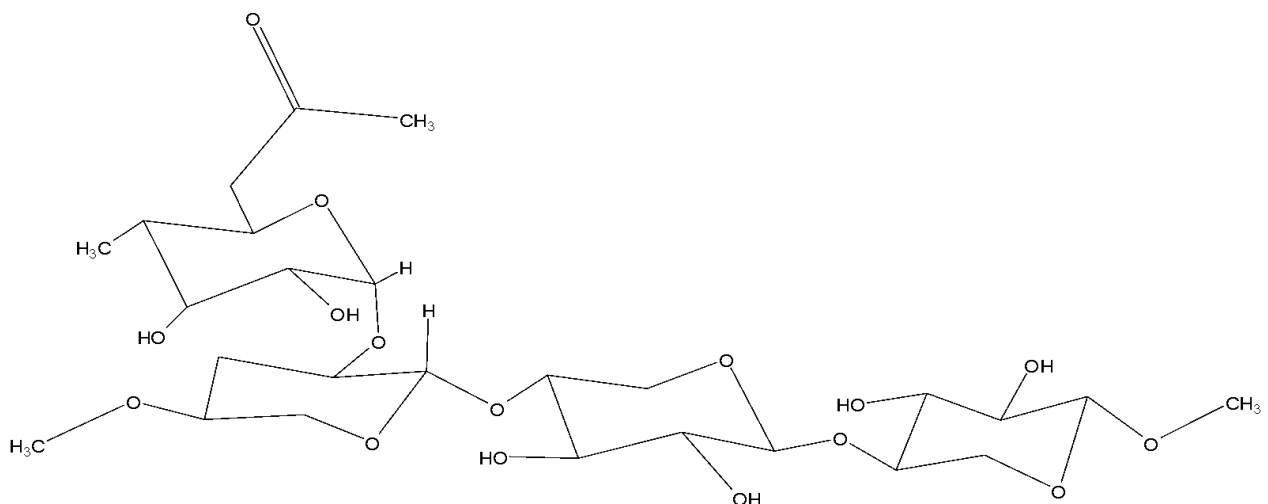


Figure 3: Basic molecular framework of hemicellulose (redrawn from Machado et al., 2016).

In the last decade, hemicelluloses have received much attention specifically for packaging, food coatings and as adhesives. The isolation of hemicellulose components with alkali-treatment has led to several pathways within the biorefinery concept to produce further value-added products. Alkali treatment is advantageous as it is cost-effective and easy to perform. Alkali pre-treatment sets out to disrupt the physical structure of the lignocellulosic material by breaking the lignin barriers attached to the hemicelluloses, disrupting the cellulose crystallinity and removing non-cellulosic components in order to increase the accessibility. Also, alkaline treatment at low temperatures contributes favourably to yield and structural features of hemicelluloses (polysaccharides) (Xu and Sun, 2016).

2.2.4 Xylans

Xylan is defined as a heteropolysaccharide with a homopolymeric backbone chain of 1, 4-linked β -d-xylopyranosyl units (Saha, 2003; Hu and Ragauskas 2012). The branches of xylan vary from species to species, which may contain arabinose, glucuronic acid, or the 4-O-methyl ether, acetic, ferulic, and p-coumaric acids (Saha, 2003). As shown in Figure 4, isolated xylan polymers can produce various chemicals, such as furfural (Sixta and Schild 2009; Vena et al., 2013).

Lee et al. (2016) created artificial enzymes to convert glucuronoxyylan, which is a hemicellulose polymer, into xylonic acid. Xylonic acid is a top-30 platform chemical (Werpy et al., 2004) which means it is of high importance in a bio-based economy. Some of the industrial benefits of xylonic acid is concrete dispersal agents, a building block of copolyamide polymers and medical precursor (Lee et al., 2016).

Xylan is present as a linear polysaccharide in both hardwoods and softwoods, and makes up about a quarter of dry biomass. The quantity and type depend on the biomass species, in

hardwoods the xylan type O-acetyl-(4-O-methylglucurono)-xylan (glucuronoxylan) are present, while in softwoods arabinoglucuronoxylan is present (Hilpmann et al., 2016). Xylans are present in grasses, cereals and herbs as well. The present study further converted the hemicelluloses extracted from sugarcane bagasse and two hardwood species into furfural.

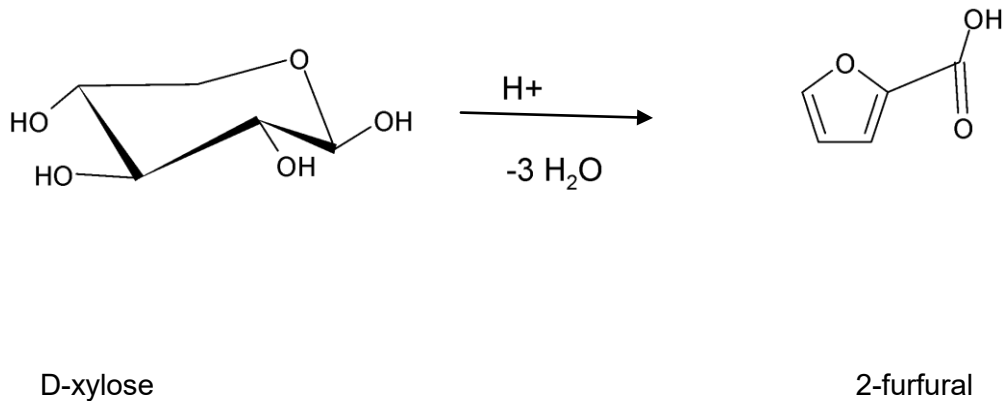


Figure 4: Acid hydrolysis of D-xylose to form 2-furfural (Binder et al., 2010).

2.3 Furfural

Furfural is described as the main dehydration product of the monosaccharide xylose present in lignocellulosic material and further classified as one of the furan derivatives (Cai et al., 2014). The quantity and quality of furfural produced are somewhat dependent on the amount of pentose (5-C sugar). Industrial produced furfural uses the acid-catalysed hydrolysis at elevated temperatures to convert monomeric sugars present in the lignocellulosic material into furfural (Zeitsch, 2000; Cai et al., 2014). The chemical structure of Furfural is shown in Figure 5 below.

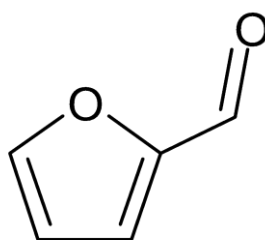


Figure 5: The chemical structure of furfural (Machado et al., 2016).

Furfural can be modified into a binder that has great thermosetting, high physical strength and resistant to decomposition properties. It can also be used in the production of mastics, caulking compounds and putties. There has been increasing growth in the furfural industrial market. Factors contributing to the growth are growing environmental concerns, use of more bio-based biomass, less dependence on petroleum-based chemicals and increasing penetration of furfural derivatives in various industry level application markets (Machado et al., 2016). It was reported that the global furfural market reached \$582.0 million in 2015. This number is said to increase to \$1.1 billion by 2021 from \$625.5 million in 2016, at an increasing compound annual growth at 11.7% (Sinha, 2016), with South Africa producing 20 000 tons/year of furfural from bagasse (Win, 2005).

At present bagasse and corn cobs relatively account for more than 98% of all feedstock used to manufacture furfural because they are relatively high in pentosan content, inexpensive, and readily available from sugarcane and corn processing plants, respectively (Cai et al., 2014).

Furfural has high thermosetting properties, decomposing resistance and physical strength (Mamman et al., 2008). Moreover, it is used to develop many other products from its derivatives, as shown in Figure 6. In a study by Orlova 2016, they developed a new binder based on furfural that could be used in the production of mastics, caulking compounds, putties, chemically resistant gaskets and joints. This was mainly due to the binder produced had polymerization, polycondensation and hardening characteristics.

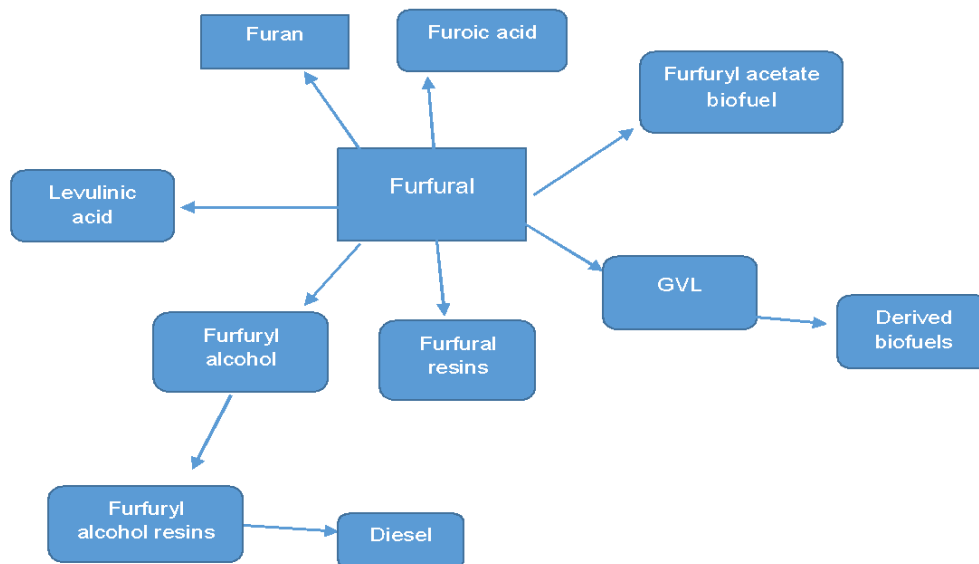


Figure 6: Potential uses of furfural derivatives in fuel and chemical products (Adopted with some modifications from Lio et al., 2019).

Researches have studied the use of xylose as a starting material to produce furfural (Luo et al. 2019). The use of pure hemicelluloses (xylan) has been investigated with xylose as the model compound. In a study done by Yemiş et al. (2011), they found that the acid catalyzed conversion of xylan, using 0.1M HCl at 180 for 30minutes in a microwave-assisted reaction, yielded 36.5wt% of furfural. Further research has been done to investigate the use of different acids, organic solvents and homogeneous catalysts in promoting the conversion of xylan into furfural (Hilpmann et al., 2016).

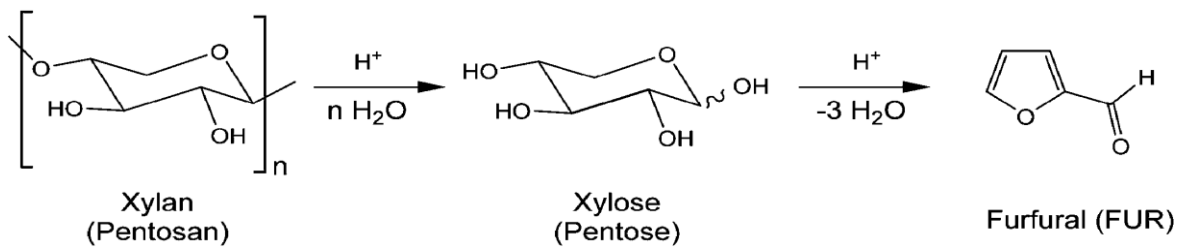


Figure 7: Chemical molecular conversion of xylan into furfural (Binder et al., 2010).

Consequently, the use of xylose and xylan to produce furfural, as shown in Figure 7, has opened doors to many advances in the biorefinery and sustainability production. The almost complete utilisation of biomass is to not only produce pulp and paper, but simultaneously furfural as well. This has subsequently led to the development of different methods to dissolve and convert hemicelluloses found in biomass into furfural, and these methods are discussed below.

2.3.1 Dissolution and conversion of hemicelluloses in raw biomass to furfural

2.3.1.1 Furfural produced from raw lignocellulosic material.

Currently, most of the industrial processes produce furfural directly from raw lignocellulosic material. The yield of furfural produced from lignocellulosic materials is dependent on the amount of pentosan present. Non-woody plants and agricultural residues have the highest pentosane content and hence higher furfural yields are dependent on the process (Gao et al., 2014). For example, O'Brien (2016) estimated that corn cob had a pentosane content of 35%, which produced furfural yields between 50-73%. Unlike the non-woody plants and agricultural

residues, the amount of xylose present in woody material is low and thus the yields produced are not as high as from non-woody biomass.

The process of producing furfural from raw lignocellulosic materials involves using acid catalysts, usually sulphuric acid, at high temperatures of 153-240°C in a batch reactor system (Cai et al., 2013). This reactor system has shown to produce low yields of furfural, which is attributed to the degradation of the furfural in the aqueous phase of the reaction (Wang et al., 2018). The common mechanism in this reaction is the hydrolysis of the xylan fragment (C5 polysaccharides) in the lignocellulosic material into xylose and subsequently the dehydration of xylose (monosaccharides) to form the furfural (Cai et al., 2013, Luo et al. 2019). Furthermore, degradation products also form, resulting in a decrease in the furfural yield and high steam-to-furfural ratio at high temperatures leads to inefficient recovery. Producing furfural in higher yields at lower energy levels, low cost and environmentally friendly acids requires more research.

2.3.1.2 Furfural produced from pre-treated and fractionated lignocellulosic material.

The process of using lignocellulosic material that has undergone pretreatment and fractionation is known as the indirect method of producing furfural. The furfural is produced from the isolated hydrolysed xylose rich hemicellulose, polymeric xylan and xylose (Mandalika & Runge 2012; Luo et al., 2019). Researchers, such as Liu et al. (2014) have shown that pre-treatment and fractionation of lignocellulosic material results in the decrease in inhibitory components, such as lignin that lowers the furfural yield formed, thus resulting in higher furfural yields (Zhang, Yu & Wang 2013). Similarly, the presence of glucose and arabinose also degraded to form furfural, thus increasing the yield even further (Mandalika & Runge 2012; Danon et al. 2014; Luo et al., 2019).

Besides, research has been done to improve the selectivity and yield of furfural (Gao et al., 2014). In a study by Luo et al. (2019) they suggested the use of organic solvents to further

breakdown the lignin-hemicellulose linkages and dissolve hemicelluloses simultaneously. It is introducing a biphasic system to compact the formed furfural from reacting with the defective products in the aqueous layer. This may seem challenging, but it is crucial in improving furfural yield and selectively and further adding to the bio-refinery economy.

Chapter 3: Experimental Design, Materials and Methods

3.1 Materials

The lignocellulosic materials used in the study are sugarcane bagasse (*Saccharum officinarum*) sourced from Illovo Sugar Ltd, blue gum (*Eucalyptus globulus*) and long-leafed wattle (*Acacia longifolia*), which was supplied by EC Biomass Fuel Pellets (Pty) Ltd, Port Elizabeth, South Africa.

In order to perform the furfural production, the xylose (kg, D-(+)-Xylose, >=99%) and sulfuric acid (ACS reagent 95.0-97.0%) were sourced from Sigma-Aldrich and used as-is. Demineralized water was sourced from the Department of Process Engineering's reverse osmosis purification plant.

3.2 Methods: Compositional analysis of lignocellulosic biomass

To perform the composition analysis, three types of biomass were milled to 1mm using a hammer mill and then further milled to 0.625 mm and 0.425 mm using Retsch ZM 200 by Haan, Germany. These were then screened through a Retsch AS200 shaker and the resultant samples were used for analysis. Micro reactors (bombs) were filled with 500mL of prepared samples and used to carry out the furfural production reaction in a 5 L stainless steel digester. The temperature (150-170 °C) was controlled throughout the reaction (Beckermann and Pickering, 2008). The experimental time started once the reactor reached the set temperature.

3.2.1 Determination of moisture content

The moisture content of the biomass was determined using the NREL/TP-510-42621 (Sluiter et al., 2008) method. A mass of 2 g of milled lignocellulosic material was placed in a weighed crucible in an oven of 105°C±3°C for at least 24 hours. After 24 hours, the container with the dry

samples was removed from the oven and transferred to a desiccator, cooled for 15 minutes and weighed. Calculation of the moisture content was done using the following equation:

$$\text{Moisture content (\%)} = \frac{W_a - W_d}{W_d} \times 100 \quad (\text{Eq. 3-1})$$

Where W_a mass of the sample before drying and W_d is mass of oven-dried sample

3.2.2 Ash determination

Ash present in the lignocellulosic material was determined by weighing a crucible and 2g of biomass, placing it into in a muffle furnace at a temperature of $575 \pm 25^\circ\text{C}$ for 5 hours until the sample was ashed. After 5 h, the crucibles were cooled, placed in the desiccator and weighed (Sluiter et al., 2012). Calculation of the ash content was done using the following equation:

$$\text{Ash (\%)} = \frac{\text{mass of ash}}{\text{mass of original sample}} \times 100 \quad (\text{Eq. 3-2})$$

3.2.3 Determination of extractives

Water and ethanol soluble extractives present in the lignocellulosic material were determined using the method described in Sluiter et al. (2012), by first weighing $5 \pm 0.1\text{g}$ of material into a thimble and placing into a Soxhlet apparatus. The initial mass of the round bottom flask was measured, once 24h had lapsed the round bottom flask with the water extractives was dried then measured. Ethanol soluble extractives were determined using the same procedure. The results of both water and ethanol extractives were calculated with the following equation:

$$\text{Extractives (\%)} = \frac{\text{Weight(flask plus extractives)} - \text{Weight(flask)}}{\text{Weight of sample}} \times 100 \quad (\text{Eq. 3-3})$$

3.2.4 Monomeric sugars and Klason lignin content

The procedure to determine the monomeric sugars and Klason lignin in the lignocellulosic material was based on the NREL-TP-510-42618 standard method. According to this method, 0.3g of extractive free biomass was hydrolysed using 72% sulphuric acid at 30 °C in a water bath. The mixture was stirred occasionally every 10 minutes. A diluted solution of 4% (v/v) was achieved by using 84 ml of distilled water and subsequently autoclaved at 121°C and 120 KPa for 60 minutes. For the extracted hemicelluloses, 1 M of sulphuric acid with 30 minutes autoclaving was required.

After autoclaving, the hydrolysed solution was filtered and oven-dried at 105°C for a period of 24hours and then weighed. The ash of the hydrolysate was determined by placing the weighed crucible in the muffle furnace for 4 hours at a temperature of 575 ± 25 °C. The soluble lignin content was determined through UV-Vis spectroscopy at a wavelength of 240 nm. The hydrolysate pH was adjusted to 7 using KOH and filtered through a 0.22 µm nylon syringe filter before HPLC analysis (Vena et al., 2013).

3.3 Alkaline Pre-treatment of lignocellulosic biomass sugarcane bagasse, *E. globulus* and *A. longifolia*

Alkaline pre-treatment was used in this study, because of its low cost and efficiency (Amiandamhen et al. 2018) with mild to harsh optimum condition. Alkaline pre-treatment of SCB was carried out using 1.5 M NaOH solution with 10 % solids, at a reaction temperature of 65 °C and 90 minutes of reaction time. The reaction took place in a water bath with the milled lignocellulosic materials placed in Schott bottles. Schott bottles were cooled to room temperature and the solid and liquid fractions were separated through filtration on 25-45 µm

filter paper under vacuum and accompanied by five distilled water washes resulting in a pH of around 7 (Vena, 2013).

E.globulus and *A.longifolia* alkaline pre-extraction were done at high temperatures in a pressurized 5L pulp digester. The temperature was set to $90 \pm 5^\circ\text{C}$ at a 10% solid loading and reaction time of 240 minutes and controlled throughout the reaction (Beckermann and Pickering, 2008). The digester rotated at a 45-degree angle, while the reaction commenced allowing for the material and alkali solution to mix well. A blow valve was used to release the pressure that built up, while the reaction procured.

The chemical compositions of solid residues and liquid fractions were determined similar to the raw materials and analysed using the NREL method. The wet solid residues were dried and kept in a temperature and humidity-controlled room for 72hrs before use in panel manufacturing. The lignin and hemicellulose present in the liquid fractions were separated using ethanol precipitation as described by Gómez-Ordóñez et al. (2012). The liquid fraction was poured into a beaker with ethanol and stored at 4°C for 48hrs to allow precipitation. The precipitated hemicelluloses were filtered and dried. The ethanol used was recovered using a rotary evaporator and remaining liquor which contained lignin were dried. The following equations (Peng et al., 2012) were used to determine the hemicelluloses precipitate and recovery:

$$\% \text{Hemicellulose precipitate} = \frac{\text{Oven dry mass of hemicellulose precipitate}}{\text{Oven dry mass non-extracted biomass}} \times 100 \quad (\text{Eq 3-3})$$

$$\% \text{Hemicellulose recovery} = \frac{\% \text{Hemicellulose precipitate}}{\% \text{Hemicellulose of biomass}} \times 100 \quad (\text{Eq 3-4})$$

3.3.1 Size Exclusion Chromatography (SEC)

SEC was used to determine the molecular weight of the extracted hemicelluloses from the lignocellulosic material and commercial xylose. Determining the molecular weight of the hemicelluloses gives insight as to its dissolution, type of saccharides and potential use (Gómez-Ordóñez et al., 2012). A concentration of 1g/L was achieved by diluting the hemicelluloses and

xylose with deionised water in a water bath set at 30°C and stirred periodically. The contents were then filtered through 0.22µm syringe filters and the molecular weights determined via HPLC. The HPLC column used consisted of Suprema column configuration of one Suprema 30 column and two Suprema 3000 columns in series and ELSD detector. Ten µL of hemicellulose was injected and the eluent used was deionised water, at 1 mL/min rate at a temperature of 30 °C. The glycan type standards for molecular weight determination were used (Gómez-Ordóñez et al., 2012). The molar mass parameters are shown in Table 6, i.e., the number-average molar mass (Mn), weight-average molar mass (Mw) and polydispersity index (Mw/Mn) of the entire hemicellulose extract and xylose (commercial) were calculated on the SEC profile.

3.3.2 FT-IR spectroscopy of lignocellulosic material (untreated & treated).

FT-IR analysis was used to monitor structural changes induced by pre-treatment on the lignocellulosic biomass and extracted hemicelluloses. Lignocellulosic feedstock (untreated and treated) and hemicelluloses extracts were ground into fine powder, as pictured in Figure 8 and then dried in the oven set at 45°C overnight. Fourier Transform Infra-Red (FT-IR) spectroscopy was used to determine and identify the functional groups in the samples. Using the method described by Naron et al. (2017), the fine grounded lignocellulosic fractions and hemicelluloses extracts were pressed down on the crystal surface using spring-loaded anvil of a Thermo Nicolet Nexus™ model 470/670/870 FT-IR spectrometer equipment with ZnSe lenses. Spectra were collected in Attenuated Total Reflectance (ATR) mode at a resolution of 4 cm⁻¹ and 64 scans per sample within the absorption bands in 4 000–630 cm⁻¹ regions. The thermo Scientific OMNIC software was used to process r the collected data further.



Figure 8: Finely ground lignocellulosic material and extracted hemicelluloses

3.3.3 SEM

SEM analysis of the lignocellulosic material was performed to study the effect of alkaline treatment on the morphological characteristics of the fibres at a magnification of 1000 x. The samples were mounted on metal stubs with double-coated carbon adhesive tape. The samples were subsequently sprayed with carbon using a high vacuum S150A sputter coater before imaging. The micrographs of the treated and untreated fibres were examined using a LEO 1430VP MERLIN FE-SEM equipped with an energy dispersive X-ray spectrometer (EDS) GENESIS XM2. EDS was performed using a focussed beam of X-rays at random positions into the samples at a magnification of 500x.

3.4 Composite panel evaluation

3.4.1. Panel fabrication and testing methods

The benefits of using alkaline treatment on biomass materials for hemicelluloses extraction was evaluated on boards prepared from woody biomass as outlined in Amiandamhen et al. (2016) and Sulaiman et al. (2013) with minor modifications. The treated and untreated fibres were milled using a hammer mill, resulting in a particle size of 1mm and dried in an oven to the

moisture content of about 7%. About 10% of the oven-dried weight of wood in adhesives were thoroughly mixed manually with the wood particles until homogeneity was reached. The mixture was transferred into a rectangular steel mould and hot-pressed at 200 KPa and 165 °C for 15 minutes to obtain a final panel dimension of 218 x 75 x 13 mm. The panels were then demoulded and stored in a humidity-controlled room at 20 °C for 96 h before testing.

3.4.2. Panel evaluation

The properties of the panels were evaluated to investigate the effect of alkali treatment biomass compared to the untreated biomass, on the flexural strength and dimensional stability. Flexural test specimens with dimensions 75 x 50mm, were tested according to ASTM D1037-06a standard using an Instron testing machine, as shown in Figure 9, fitted with a 5KN load cell and operated at a rate of 5 mm/min. The specimens were tested to failure and the MOR and MOE calculated (ASTM, 2013). Samples for dimensional stability were cut using a horizontal band saw into dimensions of 75 x 50mm. The thickness of all samples used in the test was 13 ± 1.2 mm based on the set-up configuration of the steel mould. Water absorption (WA) characteristics and thickness/volume swelling (TS/VS) tests were carried out by submerging conditioned panels horizontally in freshwater for 24h. After submersion, the panels were suspended to drain for 10min, and excess water was removed from the surface. The specimens were weighed, and the thickness determined as an average of four measurements. WA was calculated from the increase in weight and expressed as a percentage of the conditioned weight, while the TS of the specimen was calculated as a percentage of the conditioned thickness.



Figure 9: Manufactured composite product and an Instron testing machine.

3.5 Experimental design and statistical analysis

A central composite design (CCD) was used to design the experiments for furfural production. CCD is a statistical method based on a multivariate nonlinear model for optimization of process variables for furfural production. CCD is also used to determine the regression model equations and optimum operating conditions from the set experiments. It is also used to study the interactions of various parameters affecting a procedure (Chattoraj et al., 2013). Using this method, the optimization process was developed using three steps: performing the statistically designed experiments, 2) estimating the independent coefficients and 3) predicting the response and examine the adequacy of the developed model with experiments (Mondal and Chattoraj, 2016, Sadhukhan et al., 2016))

The development of the CCD is defined by the number of experiments (N) shown in the equation $N = 2k-p + 2k + C_p$. Where k is the number of factors, C_p is the number of centre points, and fractionalization element $p=0$ for a full design (Ahmadi et al., 2005).

The software Statistica was used to interpret the results from furfural experiments. The interpretation was achieved by determining the analysis of variance (ANOVA) and further evaluating the significant effect of the variables in the furfural yield. Variables consisted of time (min) and temperature (°C). The Pareto analysis showed the contribution of each independent variable on the response - furfural yield. Solid loading and acid concentration were kept constant at 14%wt and 2%wt, respectively. A statistical model was formed using the data of the experimental variable and responses using a response surface model (RSM).

Moreover, the optimum experimental condition was deduced from the model and tested for fitness using regression analysis and the polynomial equation.

3.6 Experimental procedure for furfural production

Ten experimental runs were developed using 2^2 factorial experimental design with two centre variable points and evaluated in Statistica. These combinations were used in the experimental procedure to produce furfural. 14g of commercial xylose was weighed and placed in a pre-weighed dry beaker. Demineralized water was then added to give a final mass of 900g and the contents were mixed at room temperature until the xylose was wholly dissolved. A dilute acid solution was prepared by weighing the required amount of H_2SO_4 and diluting it with demineralized water.

The mixture of hemicelluloses, water and diluted acid was stirred to dissolve the hemicelluloses. The mixture was poured into microreactors and placed in the pre-prepped reactor pictured in Figure 10 that oscillates and is heated to the set temperature of 150 to 175 \pm 5°C. The total time of reaction was 60mins starting from the time set temperature is arrived at ($t=0$). At the end of the reaction, the microreactors cooled, contents filtered and stored at 4 °C for later analysis.

The furfural and xylose yield were calculated using the equations 3-5 and 3-6:

$$\text{Xylose conversion} = \frac{\text{Xylose in} - \text{Xylose out}}{\text{Xylose in}} \times 100 \quad (\text{Eq. 3-5})$$

$$\text{Furfural yield from xylose} = \frac{\text{Furfural produced}}{\text{Xylose in}} \times 100 \quad (\text{Eq.3-6})$$

3.6.1 Experimental design

In the present study, CCD was used to determine the optimum conditions for furfural production from commercial pure xylose. The design was based on dependent and independent variables, where the independent variables coded at three levels -1, 0, and 1 representing the low, middle and high level as represented in Table 1. Optimum conditions for furfural production, the independent variable, were set. The independent variables consisted of time and temperature with the acid concentration and solid loading being constant. The interactions between the variables were determined in this study.

Table 1: Experimental design for the production of furfural from commercial xylose.

Variable	Factor	Levels		
		Low (-1)	Mid (0)	High (1)
1. Temperature (°C)	X ₁	150	160	170
2. Reaction Time (min)	X ₂	30	60	90



Figure 10: Digester set up and samples of produced furfural from sugarcane bagasse, *E. globulus* and *A. longifolia*.

3.6.2 Quantification procedure for products

The furfural yield was determined using HPLC and acetic acid, sugars and by-products were quantified. The furfural samples obtained from the reactor were prepared for HPLC analysis using the following steps described below:

- I. 0.4ml of the sample were taken and diluted with 4ml of water to bring the pH to a range of 2-4.
- II. The diluted sample was filtered through a 0.22um syringe filter into the HPLC vial and capped.

The Thermo Separations Product (TSP) HPLC was fitted with an HPX-87H Biorad column with a guard cartridge, Shodex 101 RI (refractive index) detector, as well as a UV (Ultraviolet) detector with 210nm wavelength. The column operated at a temperature of 65°C with a mobile phase of 5mM sulfuric acid at a flow rate of 0.6ml/min. The UV detector was employed to monitor the furfural content, while the RI detector measured the sugars in solution.

Chapter 4: Results and Discussion

4.1 Compositional analysis of feedstock

The composition of the untreated and treated lignocellulosic materials was analysed and is presented in Table 2. The materials include sugarcane bagasse, *E. globulus* and *A. longifolia*.

Table 2: The chemical compositional of the feedstocks untreated and treated.

Composition (g/100g)						
BIOMASS	Glucose	Xylose	Arabinose	Lignin	Ash	Total Extractives
SCB*	47.32±0.31	24.46±0.2	2.31±0.02	24.50±3.24	0.7021±0.12	3.89±0.33
TREATED SCB	25.55±2.17	4.57±0.3	–	8.92±0.09	7.83±0.5	–
<i>E.GLOBULUS</i>	45.86±0.39	17.22±1.26	0.092±0.66	25.40±1.13	0.98±0.009	7.06±0.23
TREATED <i>EGLOBULUS</i>	38.17±0.38	11.05±0.11	–	16.48±4.00	3.35±0.25	–
<i>A.LONGIFOLIA</i>	47.68±0.48	22.34±0.97	1.23±0.23	24.55±2.56	0.54±0.05	7.91±0.55
TREATED <i>A.LONGIFOLIA</i>	25.70±3.90	6.12±1.08	–	1.96±0.34	16.01±2.7	–

SCB*- sugarcane bagasse

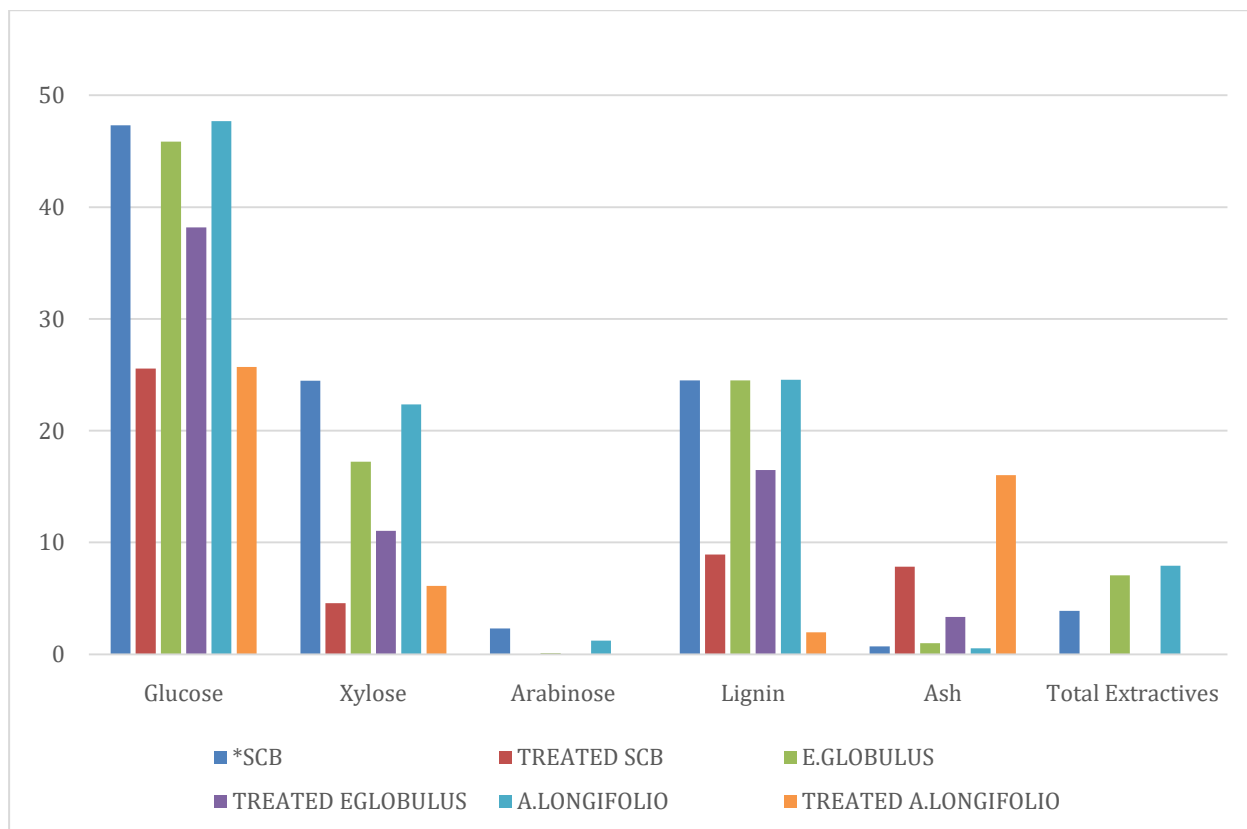


Figure 11: Chemical composition of treated and untreated lignocellulosic materials.

According to Table 2 and Figure 11, the compositional analysis of sugarcane bagasse, *E. globulus* and *A. longifolia* totals $103.1 \pm 4.4\text{g}/100\text{g}$, $95.7 \pm 3.7\text{g}/100\text{g}$ and $104.2 \pm 4.8\text{g}/100\text{g}$ of raw material, respectively. The extractives and lignin contents for *E. globulus* are 7.06 25.4 wt. %, respectively. These values are in the range reported by Joubert et al. (2015). The alkali treatment on *E. globulus* showed a decrease in the amount of xylose present from 17.22 wt. % to 11.05 wt. %, with some of the lignin being removed resulting in 16.48wt. % left in the biomass. This trend was also evident in SCB and *A. longifolia*, showing the removal of hemicelluloses (xylose) from 24.5 to 8.92 wt. % and 24.55 to 1.96wt. %, respectively, as shown in Figure 11.

The untreated sugarcane bagasse had an extractive content of 3.89 wt. %, which was slightly less than the values reported by Vena et al. (2010) and Amiandamhen et al. (2016) who reported 4.31 wt. %. High extractive content is attributed to the presence of waxes and low molecular weight. (Masarin et al. 2011), as well as free sugars or pectin and dust (Yao et al. 2015). The ash content for all biomass is within the range reported in the literature (Brienzo et

al., 2009; Castro et al., 2013; Vena et al., 2013, Joubert et al., 2015). *A. longifolia*'s ash content, 0.54 wt% , is within the range of 0.6wt. % reported by Furtado et al. (2015). High ash content in the feedstock is attributed to the presence of a high concentration of inorganic matter such as silica from sand particles (Vena, 2013).

As shown in Table 2, the lignin content of SCB was 24.50 wt. %, the same as reported by Makhetha et al. (2016). The glucose and xylose contents were 47.32 wt. % and 24.46 wt. %, respectively. These values are in line with the values reported by Vena et al. (2013). Furthermore, indications of extractives and arabinose content were not found in the treated lignocellulosic materials showing the positive effect of the alkaline treatment.

4.2 The effect of alkali pretreatment on lignocellulosic materials sugarcane bagasse, *E. globulus* and *A. longifolia*.

The effect of the alkaline treatment on structure, functional groups, morphology and hemicellulose yields of the lignocellulosic materials was investigated. The hemicelluloses precipitate, recovery and mass balance for the alkaline pretreatment is shown below in Table 3. According to Table 3, the alkaline pretreatment of sugarcane bagasse resulted in 78.4% hemicellulose recovery, which corresponds to the hemicellulose recovery stated by Vena (2013). The hemicellulose recovery of *E.globulus* was 81.2%, which is a high recovery rate compared to the 55% reported by Makhetha et al. (2016). The xylan mass balances were determined to evaluate the efficiency of the pre-treatment in extracting the hemicelluloses. From the results shown in Table 3, the mass balance of sugarcane bagasse, *E.globulus* and *A.longifolia* was 97.7%, 96.7% and 96.8% respectively; these results are within the range of 94.1 reported by Vena (2013). Based on these results, it is evident that the alkaline pre-treatment was efficient.

Table 3: Hemicelluloses precipitate, recovery, and xylan mass balance of the different lignocellulosic materials.

Lignocellulosic material	%Hemicellulose precipitate	%Hemicellulose recovery	Mass balance xylan (%)
Sugarcane bagasse	19.1	78.1	97.7
<i>E.globulus</i>	14.0	81.3	96.7
<i>A.longifolia</i>	15.3	68.5	96.8

4.2.1 Structural characterisation of lignocellulosic fractions and hemicelluloses.

Fourier transformed infrared spectroscopy was used to determine and identify the functional groups that are present in the untreated and treated biomass materials, as well as the precipitated hemicelluloses from the biomass. This analysis identifies the molecular structures present. The assignment of the wavenumber regions and functional groups for untreated and treated lignocellulosic materials are shown in Table 4.

Table 4: Assignment of the leading bands for lignocellulosic material untreated and treated from FTIR spectra.

No	Peaks(cm^{-1})						Assignment of functional groups*
	SCB	TSC B	Eg	TEg	Al	TAI	
1	3335	3332	3336	3333	3337	3329	O-H and N-H stretch of Amide II / Intermolecular bonded OH of cellulose, carbohydrate
2	2893	2891	2897	2894	2889	2898	C-H stretch
3	1729	1720	1730	1728	1730	1729	Unconjugated C=O stretch of acetyl, ester or

							carboxylic acid groups
4	-	-	-	-	1636	1630	Conjugated C=O stretch of acetyl, ester or carboxylic acid
5	1602	-	1601	-	1603	-	C=C stretch of the aromatic ring (lignin)
6	-	1591	1593	1591	1593	1593	Uronic acid carboxylate vibration
7	1450	1452	1457	1458	-	-	Asymmetric bending in CH ₃ (lignin)
8	-	-	-	-	1369	1369	C-H stretch (Cellulose)
9	-	-	-	-	1321	1318	C=O stretching of Guaiacyl
10	1240	1231	1233	1228	1235	1226	C-O stretch vibration (lignin, xylans and ester group)
11	1032	1029	1031	1030	1031	1031	C-O-C pyranose ring stretch vibration (arabinoxylans)
12	897	900	896	896	897	896	β-glycosidic linkages between xylopyranose (xylan chains)
13	832	830	833	832	830	831	C-H bending lignin
14	661	661	652	652	661	659	N/A

Key: T-treated; SCB-sugarcane bagasse, EG- *E.globulus*; AL-*A.longifolia*

*All assignments of functional groups were sourced from literature: Hu et al., 2012; Mostaçõ-Guidolin and Bachmann 2011; Wang et al., 2012a; Sun et al., 2014 and finally Naron et al. 2017.

As shown in Table 4, the broad bands 3329-3337cm⁻¹ of the treated fibres were narrower in the untreated fibres. According to Kobayashi et al. (2009), this band is associated with the intermolecular bonded hydrogen, the OH- group of carbohydrate. This indicates that the alkali treatment removed the OH group's present in the lignocellulosic materials, thus leading to better bonding of the adhesive with the fibres as there are fewer hydroxyl groups, which the fibres more resistant to the water molecules. The C-H symmetrical stretch around 2890-2910 cm⁻¹ is present in all the species (Sawpan et al. 2011). The peak at 1730 cm⁻¹ is present in all the untreated and treated fibres of all the species. This peak is typically credited to the C=O stretching of the acetyl groups of hemicelluloses (Liu et al., 2004). However, the intensity of this peak slightly decreased when treated with alkali, implicating that hemicelluloses were partially removed (Pelaez-Samaniego et al. 2014).

In addition, the C=C stretch at $1601\text{-}1603\text{ cm}^{-1}$ is not evident in the untreated and treated biomass materials of all the species (Table 4). This suggests that the alkali treatment was able to remove some of the lignin from the raw biomass. However, the asymmetric bending in CH_3 , which is associated with lignin, at $1450\text{-}1458\text{ cm}^{-1}$ is present in all the untreated and treated species, except for *A. longifolia* (untreated and treated). This could be a failure of the spectroscopy in detecting these peaks.

Furthermore, the peaks for C-H stretch and C=O assigned cellulose and guaiacyl, respectively (Hajiha et al., 2014), were only detected in the *A. longifolia* species both untreated and treated. As shown in Figure 12, the peaks at $1231\text{-}1240\text{ cm}^{-1}$ had high absorbance of all the fibres, which represent the C-O stretch of lignin, xylans and ester groups (Kaczmar et al., 2011). According to Figure 12, the C-O-C stretching was also present at the peaks $1029\text{-}1032\text{ cm}^{-1}$, this relates to the pyranose ring stretch present in arabinoxylans. Moreover, the β -glucosidic linkages between the sugar units in hemicelluloses and cellulose were present in all the fibres indicated by the band $896\text{-}900\text{ cm}^{-1}$ (Hajiha et al., 2014).

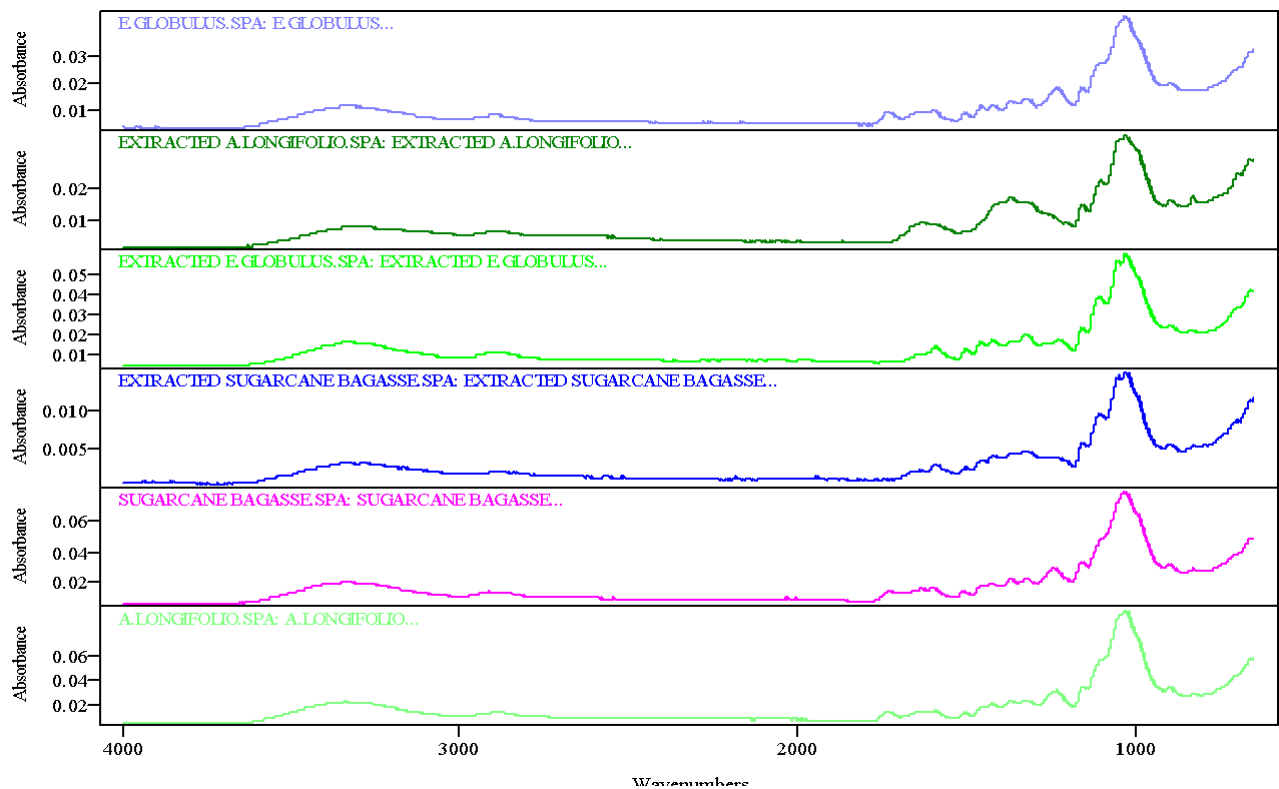


Figure 12: FTIR spectra of untreated and treated lignocellulosic samples.

As shown in Table 5 below, the C-O-C stretching was present at the peaks 1101-1098 cm^{-1} in the hemicelluloses extracted from the lignocellulosic materials, this relates to the pyranose ring stretch present in arabinoxylans (Hajiha et al. 2014). The commercial xylose sample did not show this peak, indicating it was mostly pure xylose present. The commercial xylose and extracted hemicelluloses from the lignocellulosic all had peaks at 1627-1643 cm^{-1} associated with conjugated C=O stretch present in carboxylic acids (Sun et al., 2014).

Table 5: Assignment of the leading bands for commercial xylose and hemicelluloses samples from FTIR spectra.

No	Peaks (cm^{-1})				Assignment of functional groups
	Xylose commercial	SCB Hemi	EG hemi	Al hemi	
1	3324	3329	3333	3330	O-H and N-H stretch of Amide II / Intermolecular bonded OH of carbohydrate
2	2889	2881	2930	2930	C-H stretch
3	-	-	-	-	Unconjugated C=O stretch of acetyl, ester or carboxylic acid groups
4	1642	1643	1627	1639	Conjugated C=O stretch of acetyl, ester or carboxylic acid
5	1602	1600	1600	1600	C=C stretch of the aromatic ring (lignin)
6	-	-	-	-	Uronic acid carboxylate vibration
7	1450	1453	1457	1462	Asymmetric bending in CH_3 (lignin)
8	1383	1362	1399	1359	C-H stretch (Cellulose)
9	1338	-	-	-	C=O stretching of Guaiacyl
10	1126	-	-	-	N/A
11	-	1098	1103	1101	C-O-C pyranose ring stretch vibration (arabinoxylans)
12	901	982	-	-	β -glycosidic linkages between xylopyranose (xylan chains)

13	-	-	-	-	C-H bending lignin
14	664	664	660	656	N/A

Key: SCB Hemi - Sugarcane bagasse hemicelluloses; EG Hemi - *E.globulus* hemicelluloses; AI Hemi - *A.longifolia* hemicelluloses.

*All assignments of functional groups were sourced from literature: Hu et al., 2012; Mostaço-Guidolin and Bachmann 2011; Wang et al., 2012a; Sun et al., 2014 and finally Naron et al. 2017.

Moreover, the broad bands $3329\text{-}3330\text{cm}^{-1}$ of the extracted hemicelluloses were less broad and intense as the commercial xylose sample as shown in Figure 13 and this could have further added to the low yield of furfural in the study. This band is associated with the intermolecular bonded hydrogen, OH- group, of carbohydrate (Kobayashi et al. 2009).

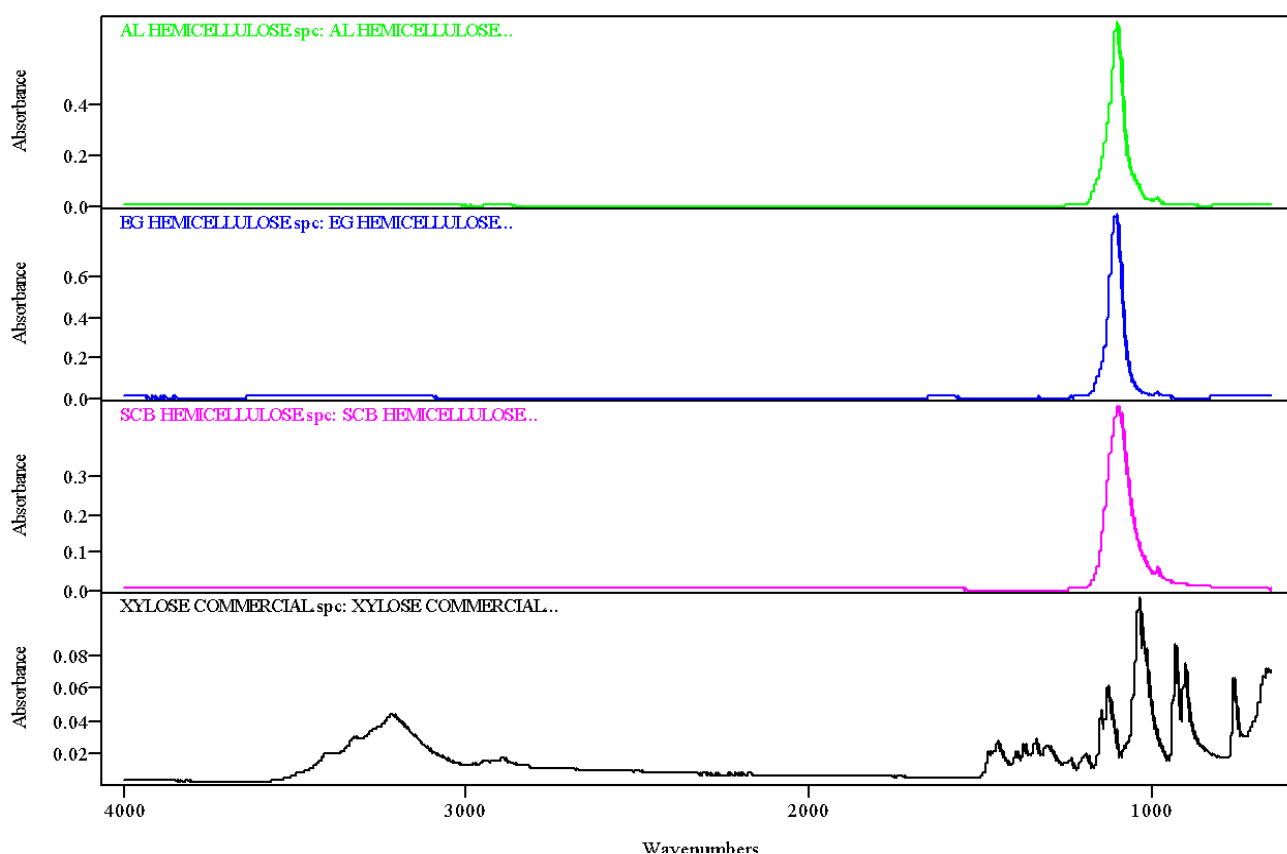


Figure 13: FTIR spectra of hemicelluloses and xylose commercial samples.

4.2.2 Molecular weight of the alkaline extracted hemicelluloses from different lignocellulosic materials.

The weight-average (Mw) and number-average (Mn) molecular weights of commercial xylose and extracted hemicelluloses were determined using size-exclusion chromatography (SEC) According to Table 6, the molecular weights of the extracted hemicelluloses from Sugarcane bagasse, *E. globulus* and *A. longifolia* were 1868, 1858 and 1852 Da, respectively and the commercial xylose was 1885 Da. Vena et al. (2013) and Peng et al. (2012) reported molecular weights (Mw) of 54,400 to 85540 Da for alkali-soluble hemicellulose.

Table 6: Molecular properties of the commercial xylose and extracted hemicelluloses.

Hemicelluloses	Mw (Da)	Mn (Da)	Polydispersity (Mw/Mn)
Xylose Commercial	1885	1841	1.02
SCB NaOH extraction	1868	1826	1.02
<i>E.globulus</i> NaOH extraction	1858	1822	1.02
<i>A.longifolia</i> NaOH extraction	1852	1820	1.02

On the other hand, molecular weights found in this study were lower when compared to other researchers. Peng et al. (2012) suggest that low molecular weight of alkali-soluble hemicellulose is the result of using highly concentrated ethanol (90-95%) during precipitation. Thus, it is recommended to gradually precipitate the hemicellulose subfractions using ethanol concentrations between 15 % and 75%. Furthermore, this significant decrease in molecular weight of the extracted hemicelluloses is caused by the cleavage of lignin-carbohydrates bonds and depolymerisation of hemicellulose during alkali extraction (Yang et al., 2013). The lower molecular weight of the hemicelluloses could have given rise to the low furfural yields attributed

to the fact that a lower molecular weight of alkali-soluble hemicelluloses relates to a less branched fraction (Peng et al., 2012).

4.2.3 Scanning Electron Microscopy

Scanning electron microscopy was used to investigate the lignocellulosic surface and morphology. The obtained micrographs can be seen in Figure 14 and Figure 15.

As shown in Figure 14, the untreated sugarcane bagasse (a), *E. globulus* (c) and *A. longifolia* (e) had large amounts of extractives evident on the surface pit aperture, cell cavities and between the microfibril of the pit membrane. The treated lignocellulosic materials (b, d, f) show that the extractives were leached out, and the pits of the cell wall opened up. Moreover, the treated lignocellulosic materials had a smoother surface, which is a result of the removal of waxy substances and lignin from the fibre surface during treatments. Amiandamhen et al. (2016) found that the treated samples with smoother surfaces bonded well with the adhesives. Similar results were also found in Hajiha et al. (2014). The cell microstructure was slightly altered after treatment due to the removal of some of the hemicelluloses, as can be seen by the holes in the cell wall. The decomposition of the fibres suggests the severity of the alkali treatment and similarly more fragmentation.

Furthermore, micrographs b, d, and f showed a reduced contrast of the cell walls, which indicates the removal of lignin (Karp et al. 2015; Chundawat et al. 2011).

Moreover, alkaline treated fibres result in depolymerized cellulose and increased fibre defibrillation thus allowing for more contact between reaction sites, fibre and matrix (Hajiha et al., 2014).

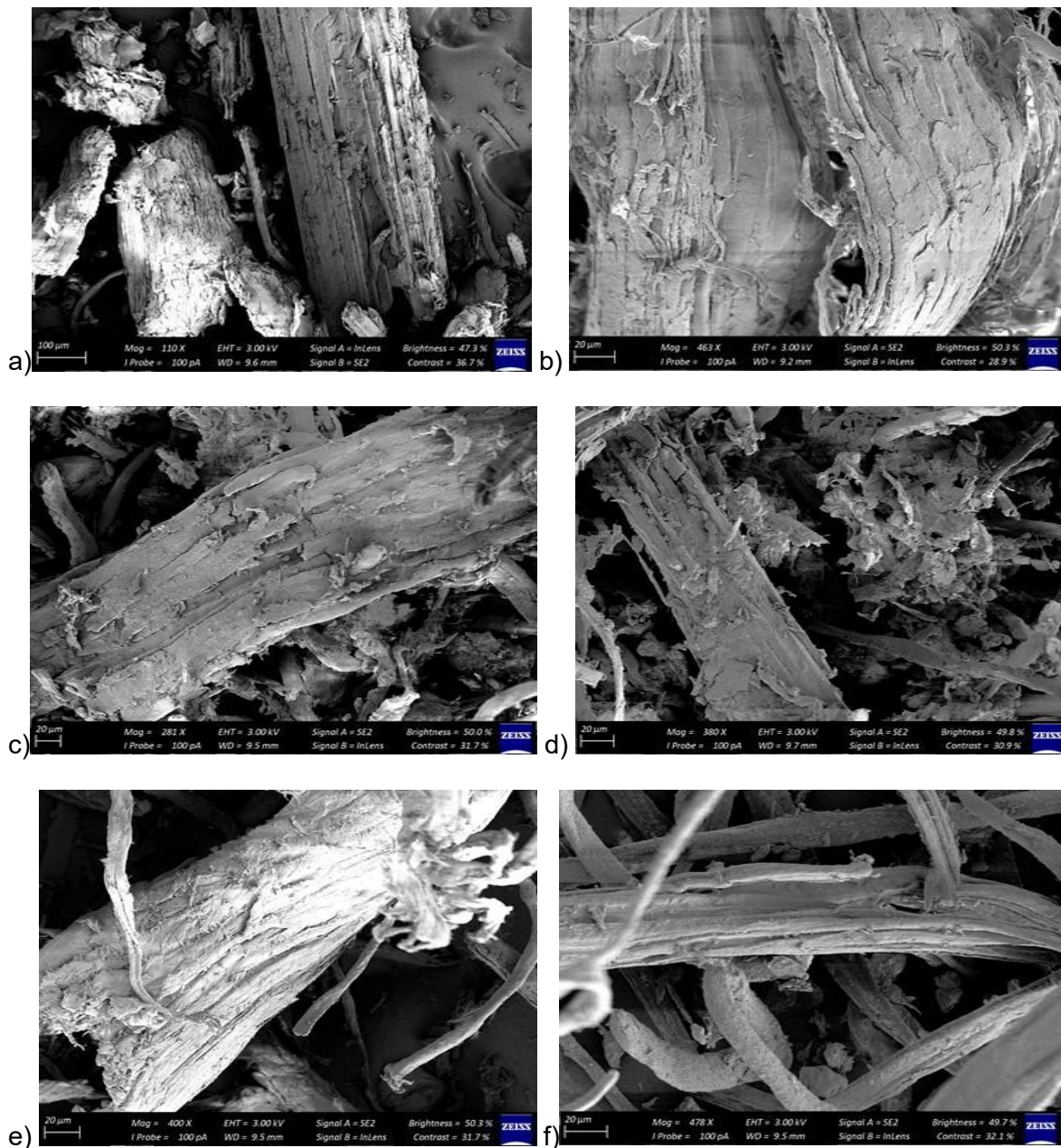


Figure 14: SEM of Sugarcane bagasse a) untreated and b) treated; *E. globulus* c) untreated and d) treated; *A. longifolia* e) untreated and f) treated.

According to Figure 15, the crystalline structure of the hemicelluloses (h, i, j) are better viewed at magnifications of 795X to 3.30KX as opposed to the commercial xylose (g) viewed at 128X magnification. These result show that the small size of extracted hemicelluloses is consistent with the measured molecular weights (Table 5). In addition, the crystalline shapes of the hemicelluloses (h, i, j), are irregular and serves as an indication of its impurity as compared to

the homogenous shape of the commercial xylose. This agrees with the FT-IR spectra in Figure 13 and in Table 5.

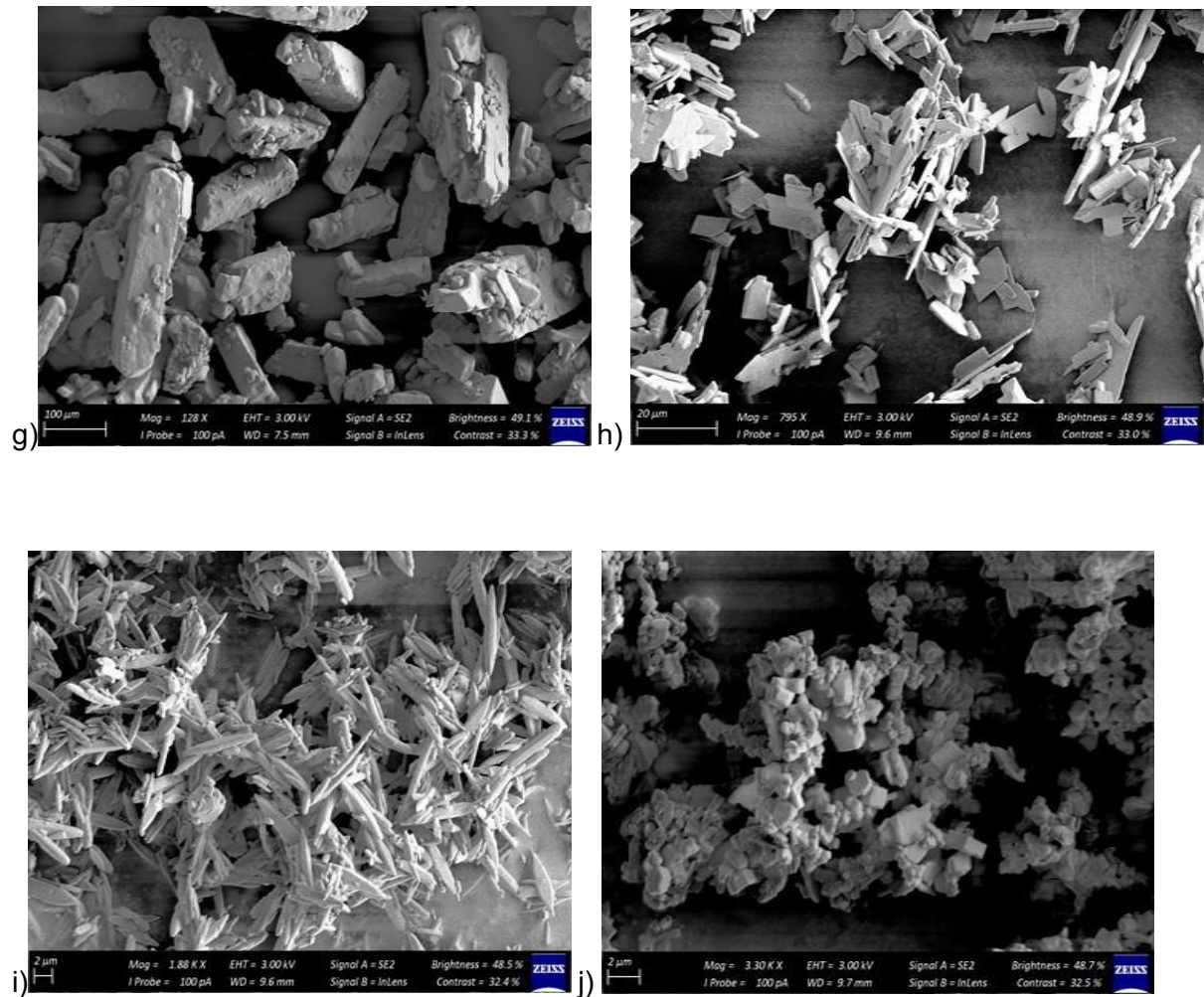


Figure 15: SEM of extracted hemicelluloses from different lignocellulosic materials and commercial xylose.

g= Xylose commercial

h= Sugarcane bagasse hemicellulose

i= *E.globulus* hemicelluloses

j= *A.longifolia* hemicelluloses

4.3 Panelboards

The panels were manufactured using the untreated and alkali pretreated lignocellulosic material. The use of alkali pre-treatment was aimed at enhancing the wood panel properties. The properties of the manufactured wood panels are shown in Table 7.

Table 7: Properties of manufactured untreated and treated wood panels.

	Wood panels	MOR	MOE	Density			
		(MPa)	(MPa)	(g/cm ³)	WA%	TS%	VS%
Untreated	SCB	6,4	1030	0,67	55	17,6	20
	<i>A. longifolia</i>	3,4	497	0,74	61	9,07	14,8
	<i>E. globulus</i>	3,5	318	0,71	59	9,2	13,2
Treated	SCB	10,42	1702	0,82	40	12,4	11,8
	<i>A. longifolia</i>	11,13	1665	0,78	44	8,88	12
	<i>E. globulus</i>	6,4	802	0,8	38	7,83	3,33

4.3.1 Density

The density of a manufactured panel is crucial as it affects the flexural properties, as well as its dimensional stability. As shown in Table 7, the density of the manufactured boards increased to some extent with alkali treatment compared to the untreated panels for sugarcane bagasse, *A. longifolia* and *E. globulus*.

In the untreated panels, the mean density ranged from 0.67 to 0.74, while in the alkaline treated panels, the mean density ranged from 0.78 to 0.82g/cm³. The increase in the density could be a result of better interlocking between the fibres and the commercial urea-formaldehyde adhesive Bondtite®, which is the result of less-porous solid biomass material (Amiandamhen et al. 2017). According to the American National Standard (ANSI 2016), particleboards with a density of between 0.60–0.8 g/cm³ are classified as medium-density panels and above 0.8 g/cm³ as high-density panels. Both the treated and untreated panels mean density fell within the range of the

medium density boards. Furthermore, the treated panels SCB, *E. globulus* and *A. longifolia* showed an improvement of 22, 5.4 and 13%, respectively. From the results, it is evident that the alkali pretreatment of the lignocellulosic material enhanced the properties compared to the untreated panels.

4.3.2 Dimensional stability (WA and TS)

Water absorption (WA) and Thickness swelling (TS) of the composite panels are shown in Table 7. Both WA and TS showed a decreasing trend from untreated panels and treated panels concerning their species, as seen in Figure 16. The WA of untreated panels were 55, 61 and 51% for bagasse, *A. longifolia* and *E. globulus*, respectively, while the WA of alkali-treated panels were 40, 44 and 38% showing improvement of 27, 28 and 35%, respectively. However, the water absorption of the panels did not meet the minimum standard for furniture grade particleboard for use in humid conditions according to ISO 16893:2016 (E), standard being $\leq 25\%$. Contrarily, the thickness swelling of the boards met the requirements, $\leq 18\%$, for furniture grade particleboard according to ISO 16893:2016 (E).

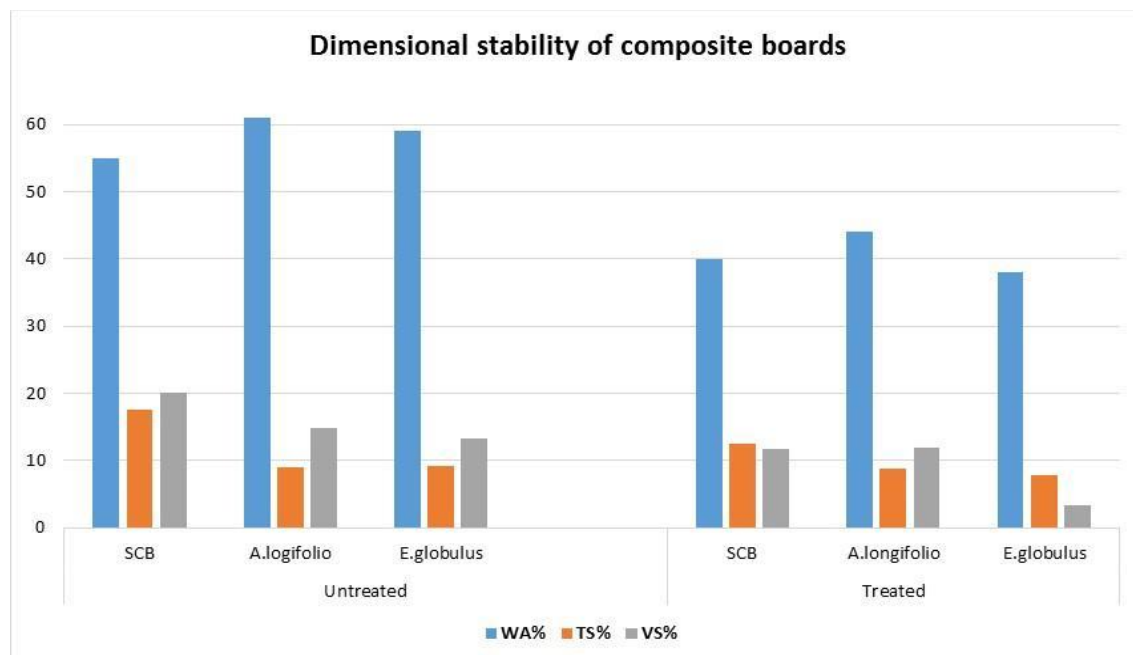


Figure 16: Water absorption (WA), thickness swelling (TS) and volume swelling (VS) of various composite boards.

4.3.3 Modulus of rupture (MOR) and Modulus of Elasticity (MOE)

MOR and MOE are essential properties to determine the application of the composite boards. MOR is the maximum strength a composite panel can endure before failure and the MOE is the tensile elasticity or rigorousness. According to Table 7, the alkali-treated panels showed significant improvement in strength and elasticity. The MOR of untreated panels was 6.4, 3.4 and 3.5 MPa for bagasse, *A. longifolia* and *E. globulus*, respectively, while the MOR of alkali-treated panels was 10.42, 11.13 and 6.4 MPa.

The MOE of untreated panels was 1030, 497 and 318 MPa, while the MOE of alkali-treated panels was 1702, 1665 and 802 MPa for bagasse, *A. longifolia* and *E. globulus*, respectively.

The modulus of rupture (MOR) of the panels produced met the minimum requirement of 3.0 MPa for LD1 according to ANSI A208.1.1999 and 11 MPa for M-1. The modulus of elasticity (MOE) of panels produced met the minimum requirement of 550 MPa for LD1 according to ANSI A208.1.1999

The composite panels that are M-1 density boards are the alkali-treated panels with bagasse and *A. longifolia*. These properties allow for the boards to be used for floor underlayment, industrial furniture, to name a few. LD-1 and LD-2 boards are the untreated panels with bagasse, *A. longifolia*, *E. globulus* and alkali-treated *E. globulus* panels. These LD panels are manufactured for sidings and partitioning like in solid doors as the amount of load is not significant or required. Improvements on the boards, in terms of strength, can be made by increasing the binder content.

4.4 Furfural production

The experiments for the conversion of the extracted hemicelluloses to furfural were performed using micro bombs in a 5L pulp digester. The experimental design (Table 8) had a total of 10 runs with two repeated centre points for the furfural production from commercial xylose.

Table 8: Results of the (CCD) experimental design for the conversion of commercial xylose into furfural.

Experimental variables			Response variables	
Experimenta			Furfural yield	Xylose conversion
I Runs	Time(s)	Temperature (°C)	(mol %)	(mol %)
1	30	160	39,9	53
2	30	170	37,8	34
3	90	160	58,84	71
4	90	170	35,7	92
5	17,3	165	0	89
6	102,4264	165	7,14	55
7	60	157,9289	1,49	97
8	60	172,0711	0	0
9	60	165	35,7	91
10	60	165	63	83

The analysis of variance (ANOVA) procedure was used to analyse the effects of the independent variables on the furfural yield. Table 9 shows the lack of significance ($p > 0.05$) of time and temperature on furfural yield, according to the experimental conditions set in this study. The RSM (response surface method) was used to analyse the interaction between variables and to predict the desired furfural yield further.

Table 9: ANOVA of the effect of temperature and reaction time.

ANOVA of the effect temperature and reaction time.

Properties	Dependent variables (p values)	
	Temperature	Time
Xylose consumed	0.294987*	0.684066*
Furfural yield	0.381047*	0.424605*

* Denotes significant values at $p < 0.05$

4.4.1 Effect of independent variables on furfural yield

The relationship between temperature and reaction time taken to produce furfural from commercial xylose is shown in Figure 17. The maximum furfural yield of 63 mol% recorded at 59 minutes, at a temperature of 165 °C. Once this maximum was reached the yield slowly decreased with time and temperature.

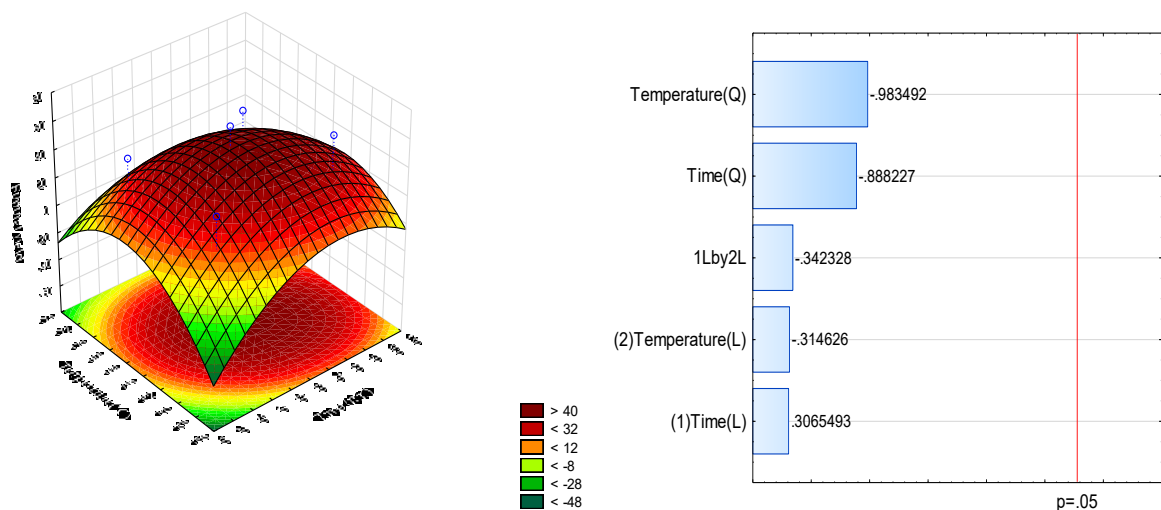


Figure 17: Pareto chart and Response surface plot showing the effects of variables on furfural yield.

Figure 17 above, shows the response surface plot representing the interactions of the independent variables and response result, furfural yield. As the temperature and reaction time increase or decrease, the furfural yield changes. As shown in the same figure, at a temperature of 140°C (x-axis) and a reaction time of 90 minutes (z-axis), the corresponding furfural yield on the y-axis is 60.43%. As a result, several plots for other runs of varying parameters against furfural yield in the same graph resulted in the 3D surface plots.

Further, the produced yield of furfural increases with increase in temperature (Figure 17). This agrees with the result of Wenjuan et al. (2016) who recorded 61.06% yield of furfural from corncob. However, at higher temperatures, it was observed that the furfural yield begins to decrease. These trends may be because at high temperatures; furfural cannot be recovered from the reactor due to its degradation, since, as temperature increases, the furfural degradation rate also increases, which agrees with findings by Zhang et al. (2017). Also, at high temperatures, much of the furfural produced in the reactor reacts with intermediates, such as formic acid or other furfural monomers and is instantly converted to longer polymers.

The increase in furfural yield was observed with an increase in reaction time from 30 – 90 min, keeping all other factors constant. Shaukat et al. (2012) reported that an increase in percentage yield of furfural increased with time. Figure 17 shows that at prolonged reaction times, the furfural yield started decreasing, which was also observed by Yemiş and Mazza (2011). It is suggested that the xylose could have already been converted to furfural, thus by extending the reaction time the formed furfural reacts with the contents in the liquid and forms side products. This results in a decreased furfural yield.

4.4.2 Optimisation process for furfural production

The confirmation experiments were done to determine the sufficiency of the model for furfural yield. The optimisation process for furfural production was done by selecting the software profile

and desirability option. Desirability is an objective function that ranges from 0 to 1 with the sole purpose of maximizing a process with its selected parameters. In summary, to obtain this desirability the prediction profile for the dependent variable (furfural yield %), a series of graphs were plotted one for each independent variable. From this, the prediction profile will show the predicted variables that would give the most desirable response, furfural yield%.

The individual desirability scores of each parameter are illustrated in Figure 18. After optimisation of the level of each factor and with their corresponding furfural yield, a confirmation study was performed using the optimised parameters. From the CCD, the desirability score of 0.78 was selected, and the best-optimised conditions were found to be at a reaction time of 59 minutes and a temperature of 165 °C. Moreover, the results of the confirmation experiments (Table 10) were done in three replicates under the optimal conditions calculated using the desirability function and model equation (RSM). The furfural yield obtained from the confirmation study is closely related to the data obtained from desirability optimisation by using CCD.

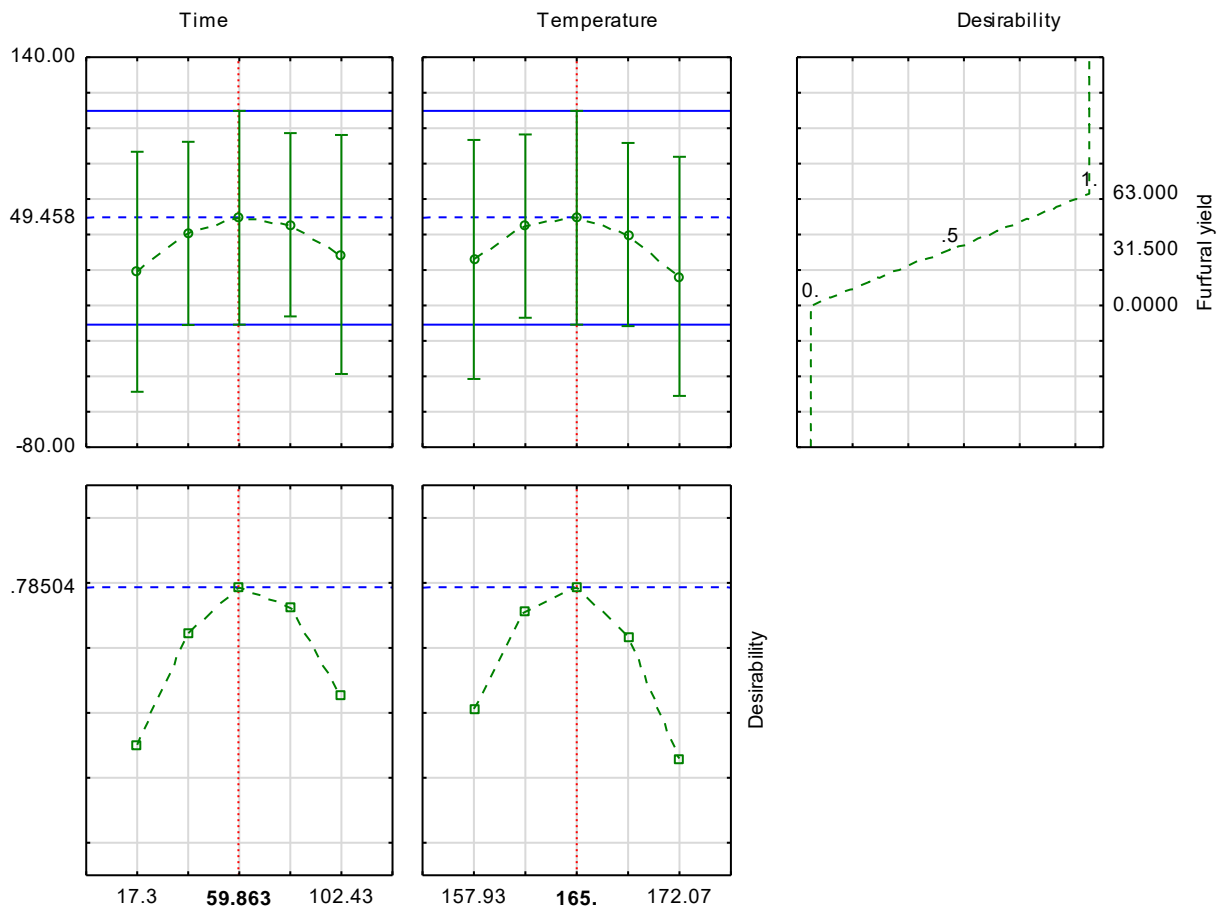


Figure 18: Profiles for the RSM predicted values and desirability function for the production of furfural using commercial xylose.

Additionally, a polynomial model was developed from the CCD which represents the relationship of the yield of furfural produced from xylose:

$$Z = -15646.70 + 7.59079x - 0.101412x^2 + 188.14y - 0.5658y^2 - 0.03507(xy) \quad (\text{Eq 4-7})$$

Where Z = furfural yield; x = time; y = temperature

The positive coefficient values indicate that factors increase furfural yield in the test range, whereas negative coefficient values indicate that factors decrease the furfural yield. The equation revealed that temperature (y) was the factor that had the most influence on the furfural yield than the reaction time (x). Other researchers (Agirrezabal-Telleria et al.2011; Yemiş & Mazza 2011) have reported that a high reaction temperature usually results in a high xylose

conversion and simultaneous a high furfural yield, however in this study, both variables were not as significant, described by p-value < 0.05, within the experimental design.

The experimental values (Table 10) of furfural yield from commercial xylose, sugarcane bagasse, *E. globulus* and *A. longifolia* were found to be 48.001, 39.6472, 45.1258 and 43.8942mol% respectively, which are close to the predicted value of 49.4729mol%.

Table 10: Confirmation experiments based on the RSM model for the produced furfural.

Sample	X_1	X_2	Furfural (mol %)	
			Predicted	Measured
Xylose commercial	60	165	49.4729	48.001
SCB hemicellulose				39.6472
EG hemicellulose				45.1258
Al hemicellulose				43.8942

X_1 - time (min); X_2 - temperature ($^{\circ}$ C)

According to Table 10, the furfural conversion yield of *E. globulus* was the highest. Yang *et al.* (2005) reported that the furfural produced decreased with increasing pentose concentration. Considering the chemical composition of the different biomass materials in this study, *E. globulus* had a lower pentose concentration, which could explain its higher furfural yield. The commercial pure xylose had a higher furfural yield compared to the rest of the biomass materials, even though studies, such as Yemiş & Mazza (2011) reported that pure xylose had a lower furfural yield than hemicellulose from biomass materials.

The reasons for the low furfural yield could be:

1) Acetic acid present in the hemicelluloses samples could have added to the acidity of the reaction, causing a faster reaction rate thus increasing furfural loss.

- 2) The formation of side reactions, such as char, fragmentation of pentose and the resinification of the furfural formed.
- 3) Inadequate mixing of the contents during the reaction in the digester.
- 4) The cross-polymerization reactions that caused a decrease in the furfural yield with the increase in undesired by-products (Sievers et al. 2009; Yemiş & Mazza, 2011; Yang et al. 2012; Zhang 2013; Barbosa 2013).

Furthermore, the model presented a suitable regression coefficient of $R^2 = 0.82$. The value of the adjusted determination coefficient is $R^2 = 0.76$, indicating that 76% of the total variation on furfural production data can be described by the selected model, which is quite reasonable, indicating a high level of significance for the model (Tanyildizi et al. 2005).

Chapter 5: Conclusions and Recommendations

Conclusions

The overall objective of this study was to pre-treat woody biomass with the aim of improving panel properties and integrating this with furfural production.

The NREL methods were used to determine the chemical composition of the lignocellulosic materials - untreated and treated. The results showed that the alkaline treatment method was useful in extracting hemicelluloses (xylose) from the lignocellulosic materials, giving precipitation yields of 19.1, 14 and 15% for sugarcane bagasse, *Eucalyptus globulus* and *Acacia longifolia*, respectively. The FT-IR analyses further showed the effectiveness of the alkali treatment in removing the lignin of the lignocellulosic materials. The yield of the extracted hemicelluloses was sufficient enough to be used for furfural production and the SEM micrographs showed smoother surface of the treated fibres indicating possible improvements to panel properties when used.

Furthermore, this study set out to evaluate the performance of panels made with the extracted materials and untreated material on the density, water absorption, thickness swelling and flexural strength. The produced panels manufactured from NaOH treated lignocellulosic materials showed improved mean density over the panels made from untreated lignocellulosic material. Similarly, the mechanical properties expressed as MOR and MOE of the treated panels showed improvements over the untreated panels. Also, water absorption and thickness swelling significantly improved with the alkali treatment. The formed panels met the minimum requirement set by ANSI A208.1 in classifying the panels as low density to medium density boards. The use of the produced panels in the wood panel industry is possible.

Moreover, this study investigated the use of commercial xylose to optimize the production of furfural via acid hydrolysis. Experimental variables selected were temperature (150-170 °C),

time (30-90 min), acidic concentration (2wt%) and solid loading (14wt%). The experimental data was modelled in Statistica using the Central Composite Design (CCD). The interaction of the independent variables and their effect on the produced furfural were evaluated using Pareto analysis of variance. Response surface models were used to develop and predict the parameters yielding optimum furfural yield. The parameters selected for optimum furfural yield of 63 mol% were a temperature of 165 °C, a reaction time of 59 minutes, while acidic concentration and solid loading were kept constant.

Based on these results, the extracted hemicelluloses from the alkaline pre-treated lignocellulosic materials were used to produce furfural in a batch reactor through acid hydrolysis. The yields of furfural produced from the extracted hemicelluloses were 39, 45 and 44 mol% for sugarcane bagasse, *E. globulus* and *A. longifolia*, respectively. These values were slightly lower than the predicted values from CCD, which can be mainly attributed to the loss of furfural evident from low molecular weight of the hemicelluloses, char formation and reduced collected volume from the reactor. The low furfural yields led to a Pareto chart showing no confidence of independent variables on the furfural yield.

From this study, we can conclude that the furfural was co-produced with composite products by using biomass residues that undergone alkali treatment. Further modifying the produced furfural from pre-treatment by-products, such as hemicelluloses extracts, into fuels and chemicals could add to the integrated biorefinery and economic feasibility.

Recommendations

Increase the furfural yield, the reactor set up, and the design needs to be improved. The furfural needs to be collected in its vapour phase, thus avoiding it reacting with the degraded products in the solution.

The possibility of producing a biobased furfural binder could be investigated. Such a binder could replace traditional fossil based binding materials.

Moreover, an economic study needs to be done to assess the scalability and feasibility of the co-production of furfural and composite products in its entirety in South Africa. This can be achieved by using the techno-economic analysis.

References

Agirrezabal-Telleria, I., Larreategui, A., Requies, J., Güemez, M.B. and Arias, P.L., 2011. Furfural production from xylose using sulfonic ion-exchange resins (Amberlyst) and simultaneous stripping with nitrogen. *Bioresource technology*, 102(16), pp.7478-7485.

Ahmadi, M., Vahabzadeh, F., Bonakdarpour, B., Mofarrah, E. and Mehranian, M. (2005) 'Application of the central composite design and response surface methodology to the advanced treatment of olive oil processing wastewater using Fenton's peroxidation', *Journal of Hazardous Materials*, 123(1–3), pp. 187–195. doi: 10.1016/j.jhazmat.2005.03.042.

Amiandamhen, S.O., Meincken, M. and Tyhoda, L., 2016. Magnesium based phosphate cement binder for composite panels: A response surface methodology for optimisation of processing variables in boards produced from agricultural and wood processing industrial residues. *Industrial Crops and Products*, 94, pp.746-754.

Amiandamhen, S.O., Montecuccoli, Z., Meincken, M., Barbu, M.C. and Tyhoda, L., 2017. Phosphate bonded wood composite products from invasive Acacia trees occurring on the Cape Coastal plains of South Africa. *European Journal of Wood and Wood Products*, pp.1-8.

Amiandamhen, S.O., Meincken, M and Tyhoda, L., 2018. The effect of chemical treatments of natural fibres on the properties of phosphate-bonded composite products. *Wood science and technology*, 52(3), pp.653-675

Amiandamhen, S.O., Meincken, M and Tyhoda, L., 2019. Natural fibre modification and Its influence on fibre-matrix interfacial properties in biocomposites materials. *Fibers and Polymers* 0000, Vol.0, No.0, 1-13.

ANSI A208.1-1999, Particleboard, American National Standard, Composite Panel Association, Gaithersburg, 1999

ANSI A208.1-1999, Particleboard, American National Standard, Composite Panel Association, Gaithersburg, 1999

Arevalo-Gallegos, A., Ahmad, Z., Asgher, M., Parra-Saldivar, R. and Iqbal, H.M., 2017. Lignocellulose: a sustainable material to produce value-added products with a zero waste approach—a review. *International Journal of Biological Macromolecules*, 99, pp.308-318.

ASTM (2013) ASTM D1037-13 Standard test methods for evaluating properties of wood-base fiber and particle, Annual Book of ASTM Standards. doi: 10.1520/D1037-06A.1.2.

Binder, J.B., Blank, J.J., Cefali, A.V. and Raines, R.T., 2010. Synthesis of furfural from xylose and xylan. *ChemSusChem*, 3(11), pp.1268-1272.

Cai, C.M., Zhang, T., Kumar, R. and Wyman, C.E., 2014. Integrated furfural production as a renewable fuel and chemical platform from lignocellulosic biomass. *Journal of Chemical Technology & Biotechnology*, 89(1), pp.2-10.

Carvalho, F., Duarte, L.C. and Gírio, F.M., 2008. Hemicellulose biorefinery: a review on biomass pretreatments. *Journal of Scientific & Industrial Research*, pp.849-864.

Chamier, J., Schachtschneider, K., Le Maitre, D.C., Ashton, P.J. and Van Wilgen, B.W., 2012. Impacts of invasive alien plants on water quality, with particular emphasis on South Africa. *Water SA*, 38(2), pp.345-356.

Demirbas, M.F., 2009. Biorefineries for biofuel upgrading: a critical review. *Applied Energy*, 86, pp.S151-S161.

Ebringerová, Anna, Zdenka Hromádková, and Thomas Heinze. "Hemicellulose." In *Polysaccharides i*, pp. 1-67. Springer, Berlin, Heidelberg, 2005.

Fang, Z., 2013. Pretreatment techniques for biofuels and biorefineries (pp. 417-432). Berlin: Springer.

Furtado, C.M., Stolz, A.D.S., Pinto, F.L., Moura, A.B., Morisso, F.D.P., Pitarelo, A.P., Ramos, L.P., Mühlen, C.V. and Riegel-Vidotti, I.C., 2015. Pyroligneous liquor produced from acacia mearnsii de wild wood under controlled conditions as a renewable source of chemicals. *Química Nova*, 38(8), pp.1068-1074.

Gao, H., Liu, H., Pang, B., Yu, G., Du, J., Zhang, Y., Wang, H. and Mu, X., 2014. Production of furfural from waste aqueous hemicellulose solution of hardwood over ZSM-5 zeolite. *Bioresource technology*, 172, pp.453-456.

Gibson, R.F., 2016. Principles of composite material mechanics. CRC press

Girón, R.P., Suárez-Ruiz, I., Ruiz, B., Fuente, E. and Gil, R.R., 2012. Fly ash from the combustion of forest biomass (*Eucalyptus globulus* bark): composition and physicochemical properties. *Energy & Fuels*, 26(3), pp.1540-1556.

Girón, R.P., Suárez-Ruiz, I., Ruiz, B., Fuente, E. and Gil, R.R., 2012. Fly ash from the combustion of forest biomass (*Eucalyptus globulus* bark): composition and physicochemical properties. *Energy & Fuels*, 26(3), pp.1540-1556.

Gómez-Ordóñez, E., Jiménez-Escrig, A. and Rupérez, P., 2012. Molecular weight distribution of polysaccharides from edible seaweeds by high-performance size-exclusion chromatography (HPSEC). *Talanta*, 93, pp.153-159.

Gorgens, A.H.M. and Van Wilgen, B.W., 2004. Invasive alien plants and water resources in South Africa: current understanding, predictive ability and research challenges: Working for Water. *South African Journal of Science*, 100(1-2), pp.27-33.

Hajiha, H., Sain, M. and Mei, L.H., 2014. Modification and characterization of hemp and sisal fibers. *Journal of Natural Fibers*, 11(2), pp.144-168.

Hilpmann, G., Becher, N., Pahner, F.A., Kusema, B., Mäki-Arvela, P., Lange, R., Murzin, D.Y. and Salmi, T., 2016. Acid hydrolysis of xylan. *Catalysis Today*, 259, pp.376-380.

Hu, F. and Ragauskas, A., 2012. Pretreatment and lignocellulosic chemistry. *Bioenergy Research*, 5(4), pp.1043-1066.

Hu, F. and Ragauskas, A., 2012. Pretreatment and lignocellulosic chemistry. *Bioenergy Research*, 5(4), pp.1043-1066.

Joubert, A.J., Chimphango, A.F. and Görgens, J.F., 2016. Effect of Integrating Xylan Extraction from *E. grandis* into the Kraft Pulping Process on Pulp Yield and Chemical Balance. *BioResources*, 11(1), pp.2417-2437.

Lee, C.C., Kibblewhite, R.E., Paavola, C.D., Orts, W.J. and Wagschal, K., 2016. Production of D-xylonic acid from hemicellulose using artificial enzyme complexes. *Journal of microbiology and biotechnology*.

Luo, Y., Li, Z., Li, X., Liu, X., Fan, J., Clark, J.H. and Hu, C., 2019. The production of furfural directly from hemicellulose in lignocellulosic biomass: A review. *Catalysis Today*, 319, pp.14-24.

Machado, G., Leon, S., Santos, F., Lourega, R., Dullius, J., Mollmann, M.E. and Eichler, P., 2016. Literature review on furfural production from Lignocellulosic biomass. *Natural Resources*, 7(03), p.115.

Maity, S.K., 2015. Opportunities, recent trends and challenges of integrated biorefinery: Part I. *Renewable and Sustainable Energy Reviews*, 43, pp.1427-1445

Makhetha, M.R.A., 2016. Fractionation of Lignocellulosic Biomass for production of materials and chemicals (Doctoral dissertation, Stellenbosch: Stellenbosch University).

Mamman, A.S., Lee, J.M., Kim, Y.C., Hwang, I.T., Park, N.J., Hwang, Y.K., Chang, J.S. and Hwang, J.S., 2008. Furfural: Hemicellulose/xyloseederived biochemical. *Biofuels, Bioproducts and Biorefining*, 2(5), pp.438-454

Mostaço-Guidolin, L.B. and Bachmann, L., 2011. Application of FTIR spectroscopy for identification of blood and leukemia biomarkers: A review over the past 15 years. *Applied Spectroscopy Reviews*, 46(5), pp.388-404.

Mussatto, S.I. ed., 2016. Biomass fractionation technologies for a lignocellulosic feedstock based biorefinery. Elsevier.

Naron, D.R., Collard, F.X., Tyhoda, L. and Görgens, J.F., 2017. Characterisation of lignins from different sources by appropriate analytical methods: Introducing thermogravimetric analysis-thermal desorption-gas chromatography-mass spectroscopy. *Industrial crops and products*, 101, pp.61-74.

Norström, E., Fogelström, L., Nordqvist, P., Khabbaz, F. and Malmström, E., 2015. Xylan–A green binder for wood adhesives. *European Polymer Journal*, 67, pp.483-493.

O'Brien P., 2006. Furfural chemicals and biofuels from agriculture by Wonda Business and Technology Services, in RIRDC Publication no 06/127. Rural Industries Research and Development Corporation, Barton, A.C.T.

Oelofse, M., Birch-Thomsen, T., Magid, J., de Neergaard, A., van Deventer, R., Bruun, S. and Hill, T., 2016. The impact of black wattle encroachment of indigenous grasslands on soil carbon, Eastern Cape, South Africa. *Biological invasions*, 18(2), pp.445-456.

Oguche, J.E., Ameh, A.O., Tanimu, Y. and Egu, S.A., 2017. Determination and optimization of effect of process parameters on furfural yield from microalgae. *FUW Trends in Sci. & Techn J*, 2(2), pp.782-787.

Pelaez-Samaniego, M.R., Yadama, V., Lowell, E. and Espinoza-Herrera, R., 2013. A review of wood thermal pretreatments to improve wood composite properties. *Wood Science and Technology*, 47(6), pp.1285-1319.

Peng, F., Peng, P., Xu, F., & Sun, R. C. (2012). Fractional purification and bioconversion of hemicelluloses. *Biotechnology advances*, 30(4), 879-903.

Phitsuwan, P., Sakka, K. and Ratanakhanokchai, K., 2013. Improvement of lignocellulosic biomass in planta: a review of feedstocks, biomass recalcitrance, and strategic manipulation of

ideal plants designed for ethanol production and processability. *Biomass and bioenergy*, 58, pp.390-405.

Pradhan, A. and Mbohwa, C., 2014. Development of biofuels in South Africa: Challenges and opportunities. *Renewable and Sustainable Energy Reviews*, 39, pp.1089-1100.

Richardson, D.M. and Van Wilgen, B.W., 2004. Invasive alien plants in South Africa: how well do we understand the ecological impacts?: working for water. *South African Journal of Science*, 100(1-2), pp.45-52.

Sadhukhan, B., Mondal, N.K. and Chatteraj, S., 2016. Optimisation using central composite design (CCD) and the desirability function for sorption of methylene blue from aqueous solution onto *Lemna major*. *Karbala International Journal of Modern Science*, 2(3), pp.145-155.

Saha, B.C., 2003. Hemicellulose bioconversion. *Journal of Industrial Microbiology and Biotechnology*, 30(5), pp.279-291.

Sawpan, M.A., Pickering, K.L. and Fernyhough, A., 2011. Effect of fibre treatments on interfacial shear strength of hemp fibre reinforced polylactide and unsaturated polyester composites. *Composites Part A: Applied Science and Manufacturing*, 42(9), pp.1189-1196.

Sierra, C.A., Harmon, M.E., Moreno, F.H., Orrego, S.A., VALLE, D. and JORGE, I., 2007. Spatial and temporal variability of net ecosystem production in a tropical forest: testing the hypothesis of a significant carbon sink. *Global Change Biology*, 13(4), pp.838-853.

Sixta, H. and Schild, G., 2009. A new generation Kraft process. *Lenzinger Berichte*, 87(1), pp.26-37.

Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D. and Crocker, D. (2012) 'NREL/TP-510-42618 analytical procedure - Determination of structural carbohydrates and lignin in Biomass', Laboratory Analytical Procedure (LAP), (April 2008), p. 17. doi: NREL/TP-510-42618

Sulaiman et al. (2013) Evaluation of the Properties of Particleboard Made Using Oil Palm Starch Modified With Epichlorohydrin."Particleboard adhesive,"BioResources 8(1), 283-301.

Tabarsa, T., Jahanshahi, S. and Ashori, A., 2011. Mechanical and physical properties of wheat straw boards bonded with a tannin modified phenol–formaldehyde adhesive. *Composites Part B: Engineering*, 42(2), pp.176-180.

Taherzadeh, M.J. and Karimi, K., 2008. Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. *International journal of molecular sciences*, 9(9), pp.1621-1651.

Van Wilgen, B.W. and Gorgens, A.H.M., 2004. Invasive alien plants and water resources in South Africa: current understanding, predictive ability and research challenges: Working for Water. *South African Journal of Science*, 100(1), pp.27-33.

Vena, P.F., 2013. Integration of xylan extraction prior to kraft and sodaAQ pulping from South African grown *Eucalyptus grandis*, giant bamboo and sugarcane bagasse to produce paper pulps, value added biopolymers and fermentable sugars (Doctoral dissertation, Stellenbosch: Stellenbosch University).

Vena, P.F., García-Aparicio, M.P., Brienzo, M., Gørgens, J.F. and Rypstra, T., 2013. Effect of alkaline hemicellulose extraction on kraft pulp fibers from *Eucalyptus grandis*. *Journal of Wood Chemistry and Technology*, 33(3), pp.157-173.

Wang, Q., Zhuang, X., Wang, W., Tan, X., Yu, Q., Qi, W. and Yuan, Z., 2018. Rapid and simultaneous production of furfural and cellulose-rich residue from sugarcane bagasse using a pressurized phosphoric acid-acetone-water system. *Chemical Engineering Journal*, 334, pp.698-706.

Wenjuan X, Suping Z, Junjie L &Qinjie C 2016. Furfural production from corncobs using thiourea as additive. *Environmental Progress & Sustainable Energy*

Win, D.T. (2005) Furfural—Gold from Garbage. *AU Journal of Technology*, 8, 185-190

Xu, J.K. and Sun, R.C., 2016. Recent Advances in Alkaline Pretreatment of Lignocellulosic Biomass. In *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery* (pp. 431-459). Elsevier.

Xu, J.K. and Sun, R.C., 2016. Recent Advances in Alkaline Pretreatment of Lignocellulosic Biomass. In *Biomass Fractionation Technologies for a Lignocellulosic Feedstock Based Biorefinery* (pp. 431-459). Elsevier.

Yemiş, O. and Mazza, G., 2011. Acid-catalyzed conversion of xylose, xylan and straw into furfural by microwave-assisted reaction. *Bioresource technology*, 102(15), pp.7371-7378.

Zeitsch, K.J., 2000. *The chemistry and technology of furfural and its many by-products* (Vol. 13). Elsevier.

Zhang, L., Xi, G., Yu, K., Yu, H. and Wang, X., 2017. Furfural production from biomass-derived carbohydrates and lignocellulosic residues via heterogeneous acid catalysts. *Industrial crops and products*, 98, pp.68-75.

Zhang, Y.H.P., 2008. Reviving the carbohydrate economy via multi-product lignocellulose biorefinery. *Journal of industrial microbiology & biotechnology*, 35(5), pp.367-375.