

**PRODUCTION OF FURFURAL
FROM RICE HUSK AND WATER HYACINTH**

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ABSTRACT

Agro-industrial residues are the most abundant and renewable resources on earth. Accumulation of this biomass in large quantities every year results not only in the deterioration of the environment but also in the loss of potentially valuable material which can be processed to yield a number of value added products, such as food, fuel, feed and a variety of chemicals. The use of agricultural wastes as renewable resources of chemicals and fuels is of interest from both economic and environmental point of view. Lignocellulosic biomass encompass all agricultural wastes such as straw, stem, stalk leaves, husk, shell, peel, pulp, etc. Lignocellulosic biomass can act as a potential source for the production of chemicals such as ethanol, reducing sugars, furfural, etc. Furfural is a valuable by-product that is commercially produced by dilute acid hydrolysis from lignocellulosic wastes in an aqueous medium. Furfural is an important renewable platform chemical which can be converted to bio chemicals and biofuels. This project focuses mainly on the production of furfural from Kerala's own indigenous crop waste i.e. rice husk and a local invasive floating plant commonly known as water hyacinth. The production of furfural from the above mentioned lignocellulosic biomass has been carried out via sulphuric acid catalysed hydrolysis in water solvent system. Comparison of the yield of furfural from rice husk and water hyacinth has also been investigated. The characterization of the product was carried out by FTIR, UV and ^1H NMR spectroscopy.

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CHAPTER 1
INTRODUCTION

Our current society is dependent on both renewable as well as non-renewable energy sources. The increasing demand of fuels and chemicals doesn't meet up with the declining oil reserves and increasing price of fossil fuels. The most imminent result that awaits mankind is the tremendous crisis of energy if we remain dependent on the fossil resources. The need to replace fossil resources with renewable alternatives has fostered research to enhance production of suitable biomass-based platform chemicals.

1.1 Lignocellulosic biomass

Lignocellulosic biomass is any organic matter that is available on a renewable basis which includes energy crops, agricultural residues, aquatic plants, wood and wood residues as well as other waste materials. Lignocellulosic biomass which is both sustainable and abundant can be utilized for the production of fuels and chemicals in an efficient manner. This might help in boosting the farm economy and rural development. Conversion of abundant lignocellulosic biomass to biofuels and transportation fuels presents a viable option for improving energy security and reducing greenhouse emissions.

Lignocellulose is the primary building block of plant cell walls. Lignocellulose is mainly composed of cellulose, hemicelluloses and lignin, along with smaller amounts of pectin, protein, extractives (soluble nonstructural materials such as nonstructural sugars, nitrogenous material, chlorophyll, and waxes), and ash.¹For example, hardwood has greater amounts of cellulose, whereas wheat straw and leaves have more hemicellulose. In addition, the ratios between various constituents within a single plant vary with age, stage of growth, and other conditions.

Cellulose is the natural polymer of greatest natural occurrence in the world. Cellulose is the main structural constituent in plant cell walls and is found in an organized fibrous structure. This linear polymer consists of D-glucose subunits linked to each other by (1,4)-glycosidic bonds. The long-chain cellulose polymers are linked together by hydrogen and van der Waals bonds, which cause the cellulose to be packed into microfibrils. Hemicelluloses and lignin cover the microfibrils. Cellulose microfibrils are the crystalline structure in the cell wall which makes them resistant to chemical and biological hydrolysis. Besides that, the coverage of microfibrils by lignin, hemicelluloses and cellulose amorphous regions also makes the access of catalytic enzymes to microfibrils difficult.

Hemicelluloses are complex heteropolysaccharides composed of C5 and C6 sugars such as D-glucose, D-galactose, D-mannose, D-xylose, L-arabinose, glucuronic acid and 4-O-methylglucuronic acid.² These polymers are amorphous, highly substituted with acetic acid and present branches which easily interact with cellulose, providing stability and flexibility to the aggregate. Monosaccharides connect to each other by β -1,4 and β -1,3 glycosidic bonds. The most abundant hemicelluloses structural block in hardwoods, grasses and agricultural plants is xylan, a polymer formed by xylose units. While, in softwood, the most abundant structural block is glucomannan, a polymer with a linear chain of D-mannose and D-glucose connected by β -1,4 glycosidic bonds and some branches.

Lignin is an amorphous heteropolymer which consists of three different phenylpropanoid units: p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol. Composition and structure of lignin components is not uniform and varies according to the type of biomass. In softwood lignin, the main structural block is coniferyl alcohol along with small amounts of coumaryl alcohol. In hardwood, lignin is composed by both coniferyl and sinapyl alcohols along with a small amounts of p-coumaryl alcohol.

The conversion of lignocellulosic biomass into fuels and chemicals requires effective utilization of the pentose and hexose sugars present in the hemicellulose and cellulose, respectively.

1.2 Furfural

In recent years, production of furfural from lignocellulosic biomass has received renewed attention as a sustainable platform chemical for the production of biofuels and biochemicals. According to a report by the US Department of Energy, based on factors such as manufacturing cost, market potential and its role as an intermediate for the production of other valuable

chemicals, furfural was selected as one of the top 30 platform chemicals that could be made from biomass with two of its derivatives, levulinic acid and furan dicarboxylic acid, in the top 10 of the list.³ This report was further updated in 2010. These factors have led to an increase in the demand for furfural which is expected to double in the following decade.

1.2.1 Physical-Chemical Properties of furfural

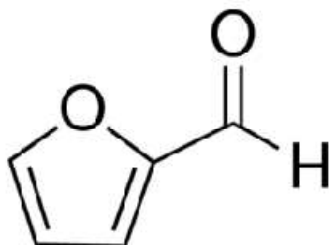


Figure 1. Furfural

Furfural (Figure 1) is a heterocyclic aromatic aldehyde derived from furan and has a molecular formula $C_5H_4O_2$. It is also known as 2-furancarboxyaldehyde, furaldehyde, 2-furanaldehyde, fural and furfuraldehyde. Furfural which has two important functional groups, an aldehyde (CHO) and a conjugated system (C=C-C=C), is a versatile compound for many applications. The two functionalities are responsible for the high chemical reactivity of furfural. The aldehyde group can undergo different types of reactions as acetylation, acylation, aldol and Knoevenagel condensation, reduction to alcohols, reductive amination to amines, decarboxylation, oxidation to carboxylic acids and Grignard reactions. The furan ring system (C=C-C=C) can undergo alkylation, hydrogenation, oxidation, halogenation, open ring reactions and nitration.⁴Due to the electron-withdrawing effect of the carbonyl group, the furan ring of furfural is less susceptible to hydrolytic ring cleavage and Diels–Alder cycloaddition reactions. Furthermore, furfural has intermediate polarity, and is therefore partially soluble in both highly polar and non-polar substances. The physical properties of furfural have been tabulated in Table 1.

Table 1. Physical properties of furfural.

Molecular formula	$C_5H_4O_2$
Molar mass ($g\ mol^{-1}$)	96.08
Appearance	Colourless oil
Odour	Almond-like

Density at 25 ⁰ C g/mL	1.16
Boiling point (⁰ C)	161.7
Freezing point (⁰ C)	36.5
Solubility % in water at 25 ⁰ C(g/L)	8.3
Acidity (mol/L)	.08-1
Viscosity at 25 ⁰ C (mPA)	1.49
Refraction index (25 ⁰ C)	1.5235
Critical pressure (MPa)	5.502
Critical temperature (⁰ C)	397
Dielectric constant (20 ⁰ C)	41.9
Vapourization heat (KJ/mol)	42.8
Combustion heat at 25 ⁰ C (KJ/mol)	234.4
Formation enthalpy (KJ/mol)	151
Surface tension mN/m (29.9 ⁰ C)	40.7
Auto-ignition temperature (⁰ C)	31.5

1.2.2 Applications of furfural

Furfural is a natural precursor to furan based chemicals. Furfural and its derivatives are strategic chemicals due to several possible applications. The derivatives of furfural are in high demand especially furfuryl alcohol, which is used as a basic component for furan resins.⁵ The importance of furfural and its derivatives has increased due to its very wide applications and this has made it imperative for the search for cheap, renewable and always available feedstock for the production of furfural.

Furfural is an important organic chemical that is used in a variety of industries such as chemical industry, refining oil industry, food industry and agricultural industry. The principal direct application of furfural is as a selective solvent. Furfural is a selective solvent for separating saturated from unsaturated compounds in petroleum refining, gas, oil and diesel fuel. The

aromatic character of the furan ring and its polarity provides good solvent selectivity towards aromatics and, in general, unsaturated compounds. It is a great selective extractant that can be used in aromatics removal from lubricant oils improving relationship between viscosity and temperature, aromatics removal from diesel to improve ignition properties, cross-linking in polymers and use as fungicide and nematocide.⁶ Furfural has a broad spectrum of industrial applications, such as the production of plastic, pharmaceuticals, and agrochemical products and numerous non-petroleum-derived chemicals from saccharides. Resins with excellent thermosetting properties and extreme physical strength can also be produced by condensation of furfural with formaldehyde, phenol, acetone, or urea. In addition to attractive thermosetting properties, physical strength, and corrosion resistance, furfural is a natural precursor to a range of furan-based chemicals and solvents, including methylfuran, furfuryl alcohol, tetrahydrofurfuryl alcohol, tetrahydrofuran, methyltetrahydrofuran, dihydropyran and furoic acid.⁷ Hydrogenation of the aldehyde group or furan ring remains the most versatile reaction to upgrade furanic components and can be employed to synthesize hydrocarbon fuels directly from furan derivatives.⁸ Cleavage of the furan ring by hydrogenolysis can produce alcohols such as 1,5-pentanediol. To synthesize longer-chain hydrocarbons from furfural, adduct formation by aldol condensation and dimerization followed by hydrodeoxygenation can produce C8 to C13+ alkanes.

1.2.3 Furfural upgrade to biofuel

The first generation of biofuels is presently produced from sugars, starches and vegetable oils. A more promising feedstock is Lignocellulose, which is more abundant, cheaper and potentially more sustainable. Some processes aim to convert the whole lignocellulose to biofuels, for example, by pyrolysis or gasification, whereas others focus on unlocking its valuable sugars to upgrade them to ethanol.⁹ Recent years have witnessed much activity to upgrade the unlocked sugars to fuels others than ethanol. For instance, glucose can be converted to hydroxymethylfurfural (HMF) and subsequently upgraded to dimethylfuran (DMF) or diesel-range hydrocarbons. Alternatively, glucose can be reformed to alkanes or converted to a mixture of light oxygenates and, subsequently, to aromatic gasoline.

Furfural can be decarbonylated to furan under reductive conditions and subsequently hydrogenated to tetrahydrofuran for blending into gasoline. However, the carcinogenic nature of

furan, combined with its high volatility prevents direct blending of this component in gasoline. Therefore for the upgradation of furfural to fuel it is important to 1) remove the polarity of the aldehyde group to blend in hydrocarbons and/or 2) reduce the volatility to blend into diesel.¹⁰ Such improvement can be achieved by hydrogenation optionally combined with acid-catalysed rearrangement or etherification, acid–base-catalysed coupling or metal-catalysed decarbonylation. Furfural upgrade can deliver either gasoline or diesel blending components. Thus furfural offers a promising rich platform for lignocellulosic biofuel, production of liquid hydrocarbons and gasoline additives such as 2-methyltetrahydrofuran (2-MTHF), methylfuran, valerate esters, ethylfurfuryl and ethyltetrahydrofurfuryl ethers as well as various C10–C15 coupling products.¹¹ Furfural upgrade technologies still require improvement to produce cost-competitive biofuels. However, the largest and most challenging step is the production of furfural itself.

1.2.4 Production of Furfural

Furfural is perhaps the most common industrial chemical derived from lignocellulosic biomass with an annual production of 300-700 Ktonnes, China being the biggest producer. The commercial utility of furfural was first discovered at the Quaker Oats Company in 1921.¹² The company had produced vast quantities of oat hulls from the manufacture of oatmeal (at one point, Quaker Oats had produced so much of this byproduct that the leftover oat hulls were stored in a circus tent). Though they could be used as livestock feed, the hulls are only partially digestible. Quaker Oats tested a variety of processes to valorize the hulls and found that treating them with dilute sulphuric acid yielded useful amounts of furfural.

Furfural is industrially produced by acid-catalyzed hydrolysis and dehydration of pentosans in lignocellulosic feedstocks at temperatures ranging from 153⁰C to 240⁰C. Pentosaneg.xylan and arabinan, are five carbon (C5) polysaccharides contained in the hemicellulose fraction of lignocellulosic biomass.³ Biomass with higher pentosan content allows for higher mass yields of furfural and is typically favoured in commercial furfural production. Today, sugarcane bagasse and corn cobs account for more than 98% of all feed stocks used to manufacture furfural because they are relatively high in pentosan content, inexpensive, and readily available from sugarcane and corn processing plants, respectively.¹³ However, since pentosans only contribute a portion of the total composition of lignocellulose, the sole production

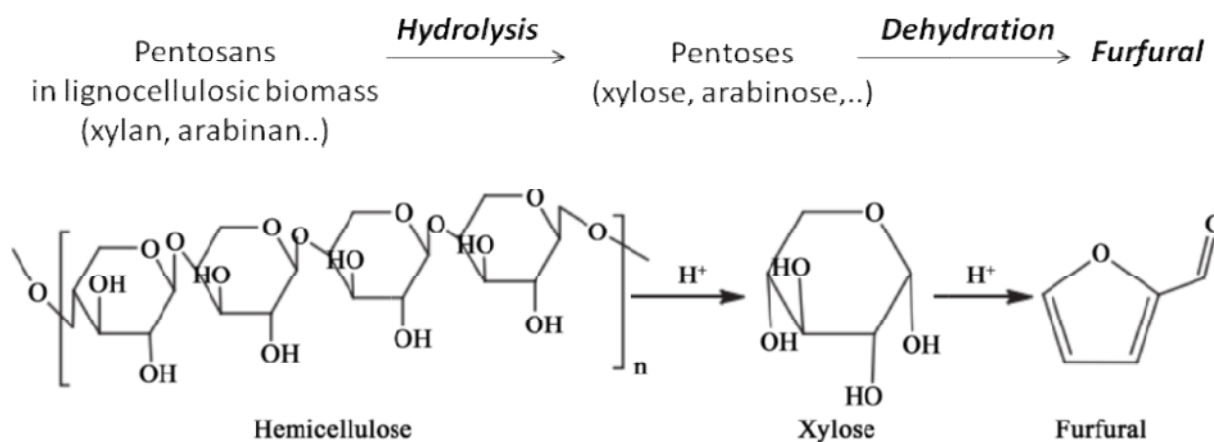
of furfural from these residues would be wasteful, inefficient and uneconomic. Cellulose is the largest fraction of lignocellulosic biomass consisting of fibrous bundles of repeating glucan units. As amorphous hemicellulose is far more acid-labile than crystalline cellulose, pentosans are hydrolyzed and dehydrated to furfural much sooner than glucans from cellulose. Thus, acid catalyzed production of furfural from biomass often leaves behind a solid residue containing glucan and lignin. Processes that can target production of valuable chemical products from all major fractions of lignocellulosic biomass will greatly improve process economics and could potentially synergistically facilitate both chemical and biological production strategies. Vedernikovs, a Latvian professor and creator of the Vedernikovs furfural process, had stated that furfural production is not economically viable without a low-cost feedstock and coproduction of other higher-value chemicals from the remaining lignin and cellulosic residues.¹⁴ For example, sugars extracted from the glucan-rich residue recovered from furfural production could be used to produce 5-HMF, levulinic acid(LA) or bioalcohol and the remaining lignin could be used for manufacture of aromatics, olefins, dibasic acids, and even carbon fiber. Acetic acid and formic acid are also secondary products from biomass which have also been shown to provide catalytic properties to furfural formation. Utilization of renewable biomass as feedstock in conversion, treatment and processing processes for obtaining high value added products have delivered the concept of biorefinery.¹⁵ In a biorefinery, the processes of biomass conversion may be integrated in such a way that a range of biofuels, bioenergy, biomaterials and biochemicals are produced together.

The conventional hydrolysis of lignocellulose proceeds with low yields and a high demand for energy. The potential of the furfural platform relies heavily on the cost-competitive production of furfural from lignocellulosic feedstock. Hence, much chemical, catalysis and engineering research is still needed to realize the potential of furfural as a platform chemical for the production of biochemicals and biofuels. With success, furfural can become a viable renewable alternative to manufacture many current petroleum-based products at a commercial scale.

1.2.5 Chemistry of furfural synthesis

There is no laboratory route for the synthesis of furfural. Furfural is exclusively produced from acid hydrolysis and dehydration of pentoses contained in lignocellulosic biomass, mainly

xylose. The acid hydrolysis of xylan into xylose (a monosaccharide) and successive dehydration of xylose yields furfural (Scheme 1).¹⁵



Scheme 1. Furfural production from lignocellulosic biomass.

In the hydrolysis of hemicelluloses, selective cleavage of the C–O bonds present between adjacent sugar units is very important to yield intact monomer sugar molecules. Mineral acids and enzymes are generally used as catalyst to hydrolyze these polymeric carbohydrates. All lignocellulosic biomass containing pentosans could in theory be used as a raw material for furfural production; however industrial production of furfural requires a minimum content of 18–20% of pentosans. Only about one third of the pentosans in the raw materials can be converted into furfural by means of existing production processes.

The current technology for furfural production is inefficient and suffers from low yields (<50 mol % of theoretical) owing to undesired side reactions. Furfural once produced undergoes self-coupling or resinification reaction with itself or with the sugars or with the intermediates formed during the reaction, leading to the formation of dark, resinous insoluble material (humins) or soluble polymers. The undesired products produced as a by-product with furfural are humins, which are a solid carbonaceous species. Furfural yields in industrial batch processes are between 45 % and 50 % due to formation of degradation products like humins.¹⁶ It has been proposed that the humins are produced by a reaction between furfural and xylose. Furfural can also undergo fragmentation to smaller molecules such as formic acid, formaldehyde, acetaldehyde, pyruvaldehyde, glyceraldehydes, glycolaldehyde and lactic acid. Several studies

have suggested ways to inhibit the formation of humins and subsequently increase the furfural yield. Various strategies have been employed to prevent decomposition of furfural and to improve furfural yields, including conventional distillation, removal of furfural into the vapor phase using steam and the extraction of furfural from the catalytically active aqueous phase using biphasic solvent systems. In biphasic reactions, the furfural, as it is produced, is selectively transferred into the organic phase avoiding furfural decomposition in the aqueous phase via rehydration or condensation with xylose, etc.¹⁷ Among many organic solvents tested in biphasic systems that can increase the yield and selectivity of furfural, 2-methyltetrahydrofuran has been showing to be a good option.

1.3 Lignocellulosic biomass from Kerala for furfural production

Kerala is a green state with a wide variety of trees and plants. Agriculture is one of the major occupations in Kerala. Since farms have become highly mechanized and reliant on synthetic fertilizers and pesticides, the crop residues, which were once recycled, are now largely wastes whose disposal presents a continuing problem for the farmer. The reuse of organic wastes is an appropriate method of environment management. It converts unwanted, low-value agricultural residues to useful and high-value feedstocks for chemicals such as ethanol, reducing sugars and furfural. The native lignocellulosic biomass which we studied in this project is discussed below.

1.3.1 Rice husk

Rice hulls (or rice husks) a major by-product of the rice milling industry, is one of the most commonly available lignocellulosic materials that can be converted to different types of fuels and chemical feedstocks through a variety of thermochemical conversion processes. Rice husk are the hard protecting coatings of seeds, or grains, of rice. The husk protects the seed during the growing season, since it is formed from hard materials, including opaline silica and lignin. The hull is mostly indigestible to humans. India being the second largest rice producer in the world, a systematic approach to this material can give birth to a new industrial sector of rice husk ash in India.¹⁸ Having a relatively higher silica content (>10 %) than the other lignocellulosic waste materials makes it useless for many applications. Despite the massive amount of annual production worldwide, so far rice husks have been recycled only for low-value applications. In recent years, many rice mills in rice producing countries have started using rice husk for the

energy production for mill operations as well as household lighting in rural regions. Additionally, rice hulls can be put to use as building material, fertilizer, insulation material, or fuel.

1.3.2 Water hyacinth

Water hyacinth (*Eichhornia crassipes*) was originated in Amazon basin and distributed throughout the tropics due to its Attractive purple flower. Mature plants consist of roots, rhizomes, stolon, leaves and inflorescence. Its Leaves are thick, waxy and glossy with bulbous and spongy stalk. The inflorescence is spike of 8-10 Flowers. The flowers are purplish blue. Each flower has 6 petals, the upper most petals with a yellow blue Bordered central splotch. Its shoots consist of branched, stoloniferous rhizome. Roots are adventitious, Fibrous and dark in colour. Water hyacinth reproduces both sexually and vegetative. However, sexual Reproduction is limited. Vegetative reproduction occurs by stolon under favourable condition. It has become the most problematic weed in many tropical and subtropical fresh water habitats worldwide.

Scientific name: *Eichhornia crassipes* (Martias) solms.

Common name: Water hyacinth

Originated from Rich and diverse rain forests of the Amazon river basin.

Biological description: An aquatic macrophyte, a monocotyledon.

Family: Pontederiaceae.

Ideal condition for water hyacinth:

- High air temperature
- High relative humidity
- Long sun exposure
- pH of between 4.0 and 8.0

In Indonesia, water hyacinth biomass has been utilized as furniture and handicraft. Also, water hyacinth has been fermented to produce bioethanol .Recently, research on the synthesis of Carboxymethyl Cellulose (CMC) from water hyacinth has been proposed. Carboxymethyl Cellulose (CMC) is a derivated cellulose that is used in food and non-food products for examples as a thickener agent, detergents, and paints. However, thousand tons of this biomass still unutilized properly. A study proven that water hyacinth biomass contains pentosans as much as 23.7%. It's mean that water hyacinth can be used as the promising precursor in the synthesis of furfural.

Water hyacinth (*Eichhornia crassipes*) was chosen as it is a representative of the aquatic plant species and due to its attractive feature. Water hyacinth (Figure 2) is a free floating aquatic plant, which is originating from the Amazon in South America. Water hyacinth is an aquatic plant which can grow fast especially in rich nutrient water area. This aquatic plant species has relatively low cost and it is characterized by extremely high growth rates in fresh water, depends on the location and season¹⁹. Its fast growth rate causes many problems such as losses of water in irrigation systems, obstruction of shipping routes, interference with hydroelectric power generation systems and increased sedimentation by trapping slit particles. These are the main reason behind why water hyacinth growth needs to be kept under control. It has been recently found to be valuable for lignocellulosic content based sugar production, due to its high growth rate, huge availability, its biodegradability and high holocellulose content. 140 millions of water hyacinth can increase every year and these plants cover 140 km² water areas with a fresh biomass. They cause an enormous ecological and economic disaster worldwide, and they must be removed every year²⁰.



Figure 2. Water Hyacinth

CHAPTER 2
LITERATURE REVIEW

Barbosa et. al.²¹ (2014) investigated furfural production from corn stalk, sugarcane bagasse and eucalyptus wood using different concentrations of several types of mineral acids (HCl, H₂SO₄, etc.). They also investigated the potential of using auto-hydrolyzates from auto-hydrolysis kraft process done in eucalyptus wood. The auto- hydrolyzate extracted in the process first phase is rich in xylose oligomers and monomers, which have potential for furfural production. Hydrochloric acid was the one which presented higher yield, efficiency and productivity of furfural. The most promising biomass was corn stalk, however it was also proved that the use of eucalyptus liquor from auto-hydrolysis is feasible, what had never been used before as source of xylose for furfural production.

Kauret. al.²² (2015) studied the use of pre-hydrolysis liquor from kraft process for furfural production. Hemicelluloses in the liquor were concentrated through membrane separation and converted to furfural using reactors in monophasic and biphasic systems, proving the feasibility of the process.

Li et. al.²³ (2016) investigated the effect of hemicellulose characteristics of corn stalk in alkaline medium for furfural production. It was found that a higher amount of xylose, lower number of branches, higher polydispersity and crystallinity of hemicelluloses contributed for furfural production.

Molina et. al.²⁴ (2015) compared activity and stability of using pure niobium and niobium supported on silica-zirconia and proved that immobilization of niobic acid makes it a more stable catalyst, which can be recycled and operated in continuous process during the reaction, yet activity presented is lower when compared to pure niobium.

Gebreet. al.²⁵ (2015) used sugarcane bagasse as a potential source for furfural production. This paper deals with the production of furfural from sugarcane bagasse via the sulphuric acid catalysed hydrolysis of sugarcane bagasse in an aqueous medium using NaCl as an additive. The

effect of temperature, pH and the concentration of NaCl on the furfural yield was investigated. It was found that the furfural yield increased with temperature, acidity and NaCl concentration.

Wankasiet. al.²⁶ (2013) found that the peels of ripe English mango could be used as a source for the production of furfural. The method employed the acid catalysed hydrolysis of the peels of mango. The use of HCl in this work and the distillation employed was found as a better way for the production of the product furfural. The distillates were then tested further for furfural using UV/Visible and IR spectroscopic methods in addition to other physico chemical parameters. The study revealed the best production of furfural from the peels of *Mangifera indica*.

Cai et. al.³ (2013) gave a critical analysis of past and current progress for the production of furfural from the lignocellulosic biomass. In this review, the chemistries of furfural formation and furfural destruction are discussed to gain an insight into effective strategies that could improve furfural yields. Potential co-products from lignocellulosic biomass are identified. Finally, several competing technologies relevant to integrated production of furfural with other products from biomass are described. The importance of developing integrated production strategies to co-produce furfural with other valuable products is discussed.

Dashtbanet. al.²⁷ (2012) reviewed various processes developed for producing furfural at industrial and laboratory scales. Generally, furfural production yield was higher in bi-phasic systems than in aqueous systems. However, furfural production in bi-phasic systems encounters certain technical challenges, including solvent recovery, process complexity, and environmental issues, which prevent its practical implementation at industrial scales. This study also reviews the advantages and disadvantages of various furfural production processes proposed in the literature. Attempts at chemical conversion of mono-sugars derived from biomass hemicelluloses to fuels and chemicals have been extensively reported in the literature. For example, 5-hydroxymethylfurfural (HMF) can be produced from glucose and can be further converted to 2,5-dimethylfuran (DMF).²⁸ This review focuses on various processes which have been developed for producing furfural from woody biomass, agricultural residues, and commercially available sugars. It also addresses the challenges and technical problems associated with laboratory- and commercial-scale furfural production processes.

Machado et. al.² 2016 focussed on analyzing applications and different production methods for furfural from lignocellulosic biomass. A review about the chemical composition of lignocellulosic biomass along with the potential chemical, thermochemical and biochemical processes of lignocellulosic biomass conversion in bioproducts in the biorefinery context was accomplished. Routes of furfural production from biomass are exposed. Several furfural applications are highlighted, as well as furfural properties and economic aspects. The main route for furfural production consists of an acid hydrolysis of hemicelluloses present in lignocellulosic biomass to obtain xylose, which goes through a dehydration reaction to produce furfural. Due to the presence of an aldehyde group and a conjugated system of double bounds, furfural can go through several reactions, allowing the production of a range of value added products. In this sense, this article performs a review about mechanisms of furfural production from lignocellulosic biomass, highlighting its chemical properties which enable its utilization in different industrial applications of economic interest.

The conversion of raw sugarcane bagasse into C5-sugars and furfural was demonstrated with the one-pot method using Brønsted acidic ionic liquids (BAILs) without any mineral acids or metal halides by Matsagar et, al. Various BAILs were synthesized and characterized using NMR, FT-IR, TGA, and CHNS microanalysis and were used as the catalyst for raw biomass conversion. The remarkably high yield (i.e. 88%) of C5 sugars from bagasse can be obtained using 1-methyl-3(3-sulfopropyl)-imidazolium hydrogen sulfate ($[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$) BAIL catalyst in an aqueous medium. Similarly, the $[\text{C}_3\text{SO}_3\text{HMIM}][\text{HSO}_4]$ BAIL also converts the bagasse into furfural with very high yield (73%) in one-pot method using a water/toluene biphasic solvent system.

CHAPTER 3
OBJECTIVES

The primary focus of this project is to study the potential of native waste lignocellulosic biomass in the production of furfural using sulphuric acid catalysed water solvent system.

The following are the objectives of the project:

1. To carry out a literature survey on the production of furfural from lignocellulosic biomass and to study the advantages and disadvantages of the various processes in literature.
2. To investigate the potential of a few easily available and abundant native waste lignocellulosic biomass such as rice husk and water hyacinth for the production of furfural using sulphuric-acid catalysed monophasic solvent systems.
3. To quantify and characterize the product using ^1H NMR, IR and UV-Vis spectroscopy.
4. To propose future studies.

CHAPTER 4
MATERIALS AND METHODS

4.1 Materials used

4.1.1 Raw materials

The native waste lignocellulosic biomasses used in the production of furfural in this project were rice husk and water hyacinth (*Eichhornia crassipes*). Rice husk was obtained locally from a farm in Alappuzha district of Kerala in India. Water hyacinth was collected from water bodies near Mavelikara, located in Alappuzha district.

4.1.2 Reagents and Solvents

Sulphuric acid, sodium chloride, dichloromethane, aniline and glacial acetic acid were the reagents used for the experimental study. The reagents and solvents that were used in the experiments were of analytical grade.

4.1.3 Equipments and instruments

The equipments that were used for the experiment are oven, Grinder, Round bottom flask, condenser, condenser tubes, beaker, thermometer, oil bath, separating funnel, hot plate. The instruments that were used for analysis are BrukerAvance III 400 MHz FT-NMR spectrometer, Agilent UV-Vis-NIR spectrophotometer and Perkin Elmer 400 FTIR spectrometer.

4.2 Methodology

4.2.1 Sample preparation

The raw materials, rice husk and water hyacinth were chopped into small pieces and then washed thoroughly with water to remove the contaminants. After washing they were sun dried and then placed in an air circulating oven for 48 hours. After drying they were crushed into fine powder in a grinder. The powder was further dried for another 15 minutes in the oven after which it was used in the experiments (Figure 3).



Figure 3: (a) Dried rice husk powder (b) Dried water hyacinth powder

4.2.2 General Procedure for Furfural production:

(a) Digestion

15 g of ground biomass and 15 g of NaCl were weighed into a 500 mL conical flask. Along with this 20 ml of concentrated H_2SO_4 and 80 ml of water were added into the conical flask. The mixture was left to stand overnight for digestion.

(b) Hydrothermal Production of Furfural

The furfural production was carried out using the domestic pressure cooker as a hydrothermal reactor (Figure 4).



Figure 4: Experimental setup for hydrothermal production of Furfural

The conical flask which was left to stand overnight was placed inside a 20 L pressure cooker and cooked on high heat with the weight on the pressure cooker. After the first whistle the heat was reduced to low and the contents of the pressure cooker were left to simmer for the next 60 minutes. The heat was turned off after 60 minutes and the pressure cooker was allowed to cool down. After cooling the pressure cooker is opened and the conical flask is carefully taken out. The spot test for furfural is conducted to test for the presence of furfural. The mixture was then filtered via vacuum filtration and the filtrate which was golden yellow, was transferred into a separating funnel. The solvent extraction was carried out three times with dichloromethane as extracting solvent using 15 mL of the solvent each time (Figure 5). As the density of furfural is more than that of water, the fufural layer is below the water layer as shown in Figure 4. The exteacted organic layer was left overnight for the solvent dichloromethane to evaporate. The

resultant reddish brown product liquid was weighed and the yield calculated. The product was analysed using ^1H NMR, IR and UV-Vis spectroscopy.



Figure 5. Solvent extraction

(c) Spot test for furfural

A mixture of aniline and glacial acetic acid is used as the testing reagent. A filter paper is dipped into this mixture and is then held at the mouth of the conical flask after the hydrothermal treatment in the pressure cooker. The presence of furfural is indicated by the formation of a pink colour (Figure 6).



Figure 6. Spot test for Furfural

CHAPTER 5
RESULTS AND DISCUSSION

Furfural formation from raw materials containing pentosans consists of two steps. The first step involves acid-catalyzed hydrolysis where the pentosans are hydrolysed at high temperatures to monomeric pentoses in aqueous media. In the second step, pentoses are converted into furfural by the elimination of water. While the first reaction step proceeds rapidly and at high yield, considerable decomposition of furfural occurs during the dehydration step. Hence the synthesis of furfural from lignocellulosic biomass was carried out using water solvent system to prevent the decomposition of furfural and thereby improve the furfural yield. The synthesis of furfural was carried out via the hydrothermal method using a domestic pressure cooker.

5.1 Production of Furfural

Among the two raw materials that were used in this project, rice husk was more promising as a potential lignocellulosic biomass for furfural production. Approximately 15g of the ground biomass together with 15g of sodium chloride and 20 ml sulphuric acid as catalyst was cooked using a domestic pressure cooker as a hydrothermal reactor. The results of these two experiments are tabulated in Table 2.

Table 2: Furfural production via the reflux and distillation method.

S. No	Biomass	Weight of biomass (gm)	Weight of NaCl (gm)	Con. H ₂ SO ₄ (ml)	Water (ml)	Crude Yield (gm)
1	Rice Husk	15.0565	15.0500	20	80	0.3453
2	Water hyacinth	15.0366	15.0375	20	80	0.0408

The product yields given in the tables are crude yields, ie. the weight of solvent residues in the product have not been deducted. Table 2 shows that rice husk gave higher product yields than water hyacinth. Saturation of the aqueous solution with NaCl was necessary as halide ions, especially chloride, appear to promote enolization and improve the selectivity and yield of furfural.³⁷

5.2 Instrumental Analysis

5.2.1 ^1H NMR spectrum

The ^1H NMR spectrum of the product was recorded on the Bruker Avance III 400 MHz FT-NMR spectrometer using CDCl_3 as the solvent. The spectrum shows the signals for both furfural and toluene (Figure 7). ^1H NMR spectrum of furfural is quite complex. There are four protons in furfural which gives four different signals in the ^1H NMR spectrum. The aldehydic proton signal appears in the downfield region at 9.66 ppm as a singlet. The three ring protons give three different signals because of the asymmetry of the molecule. Out of the three ring protons, the α proton H_2 , i.e. the proton on the carbon directly attached to the oxygen is the most downfield due to the inductive effect of oxygen. This proton appears at 7.71 ppm as a doublet because the H_2 proton couples with the H_3 proton. The H_3 proton has two neighbouring vicinal protons H_2 and H_4 . The H_3 proton couples with both these protons and resonates as a doublet of a doublet at 6.61 ppm. The H_4 proton gives a doublet as a result of coupling with the H_3 proton at 7.26 ppm. The coupling constants were difficult to calculate as a result of poor resolution. The singlet at 5.32 ppm is of the residual solvent dichloromethane. The area for the dichloromethane peak integrates to 14 which suggests seven dichloromethane molecules. This shows that the molar ratio of furfural to dichloromethane in the product is 1:7.

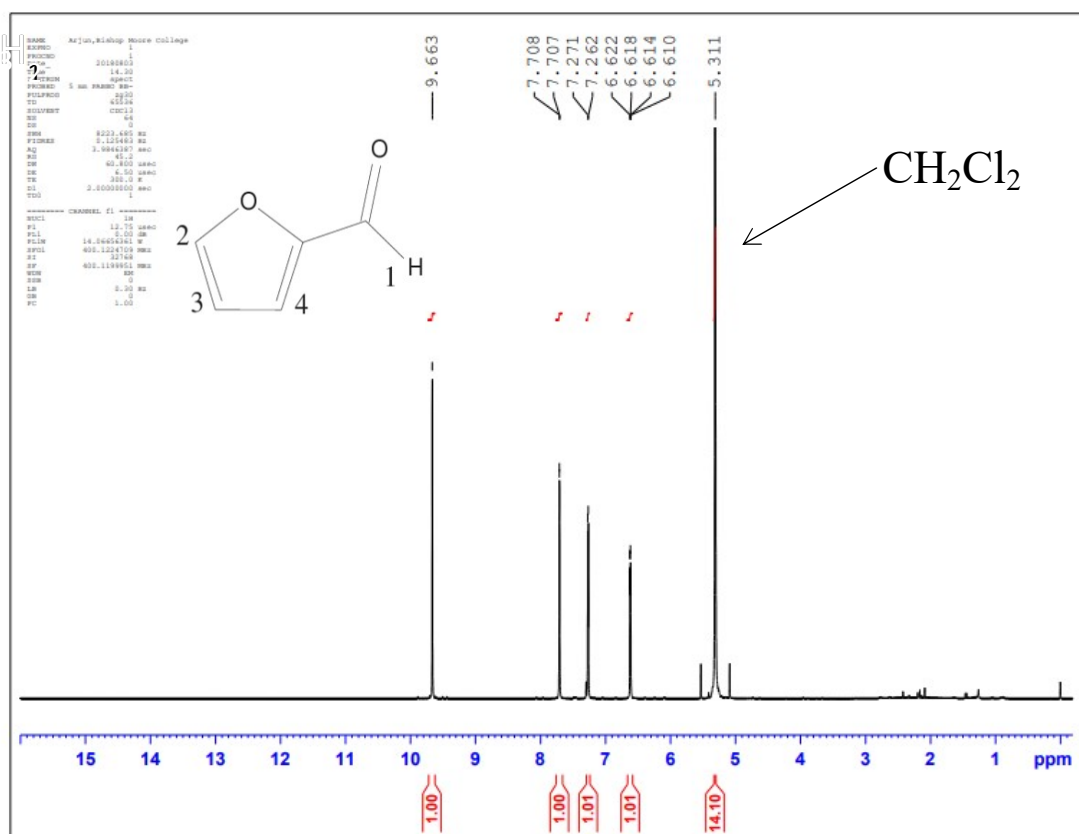


Figure 7: ¹H NMR spectrum of the product obtained from rice husk.

5.3.2 UV-Vis Spectroscopy

The absorption intensity of the sample was tested using UV-Vis spectrophotometer. A dilute solution of the product with distilled water was prepared. The analysis was done using Agilent UV-Vis-NIR spectrophotometer in the range from 200 to 800 nm. The maximum absorption obtained for the product is at 277 nm with a smaller absorption peak at 230 nm (Figure 8). This is characteristic of furfural.²⁹ The strong absorption peak at 277 nm is due to the carbonyl group conjugated to unsaturated bonds. This also further confirms the presence of furfural as the broad band may be due to the conjugation in the furfural.

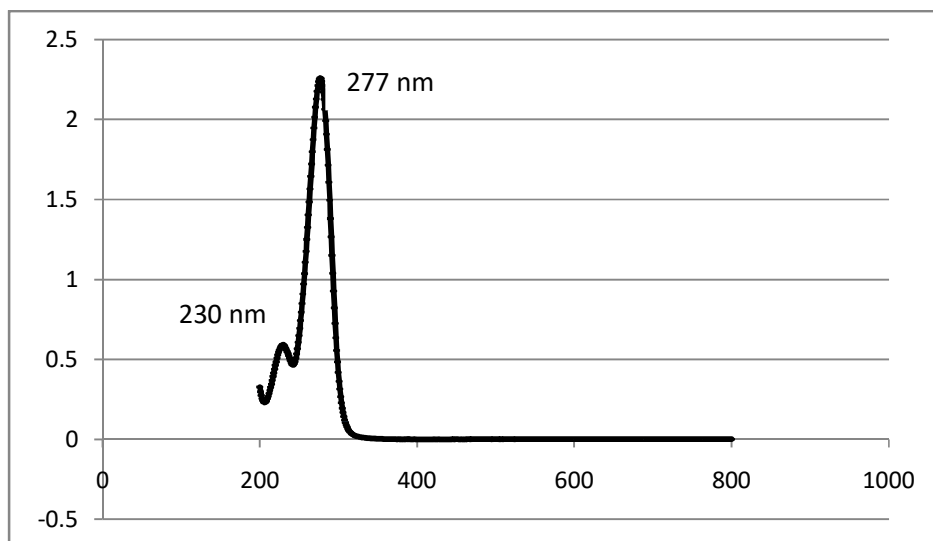


Figure 8: UV-Vis spectrum of the product obtained from rice husk.

5.3.3 IR Spectrum

FTIR spectra with ATR of the products were recorded in a Perkin Elmer 400 instrument with spectrum software. 32 scans were done at a resolution of 4 cm^{-1} . Spectrum was recorded from $400\text{--}4000\text{ cm}^{-1}$. The IR spectrum shows a strong absorption at 1742 cm^{-1} which is characteristic of a carbonyl group (Figure 9). The two weak bands in the $2700\text{--}2775\text{ cm}^{-1}$ and around $3000\text{--}3100\text{ cm}^{-1}$ is indicative of aldehydic group.

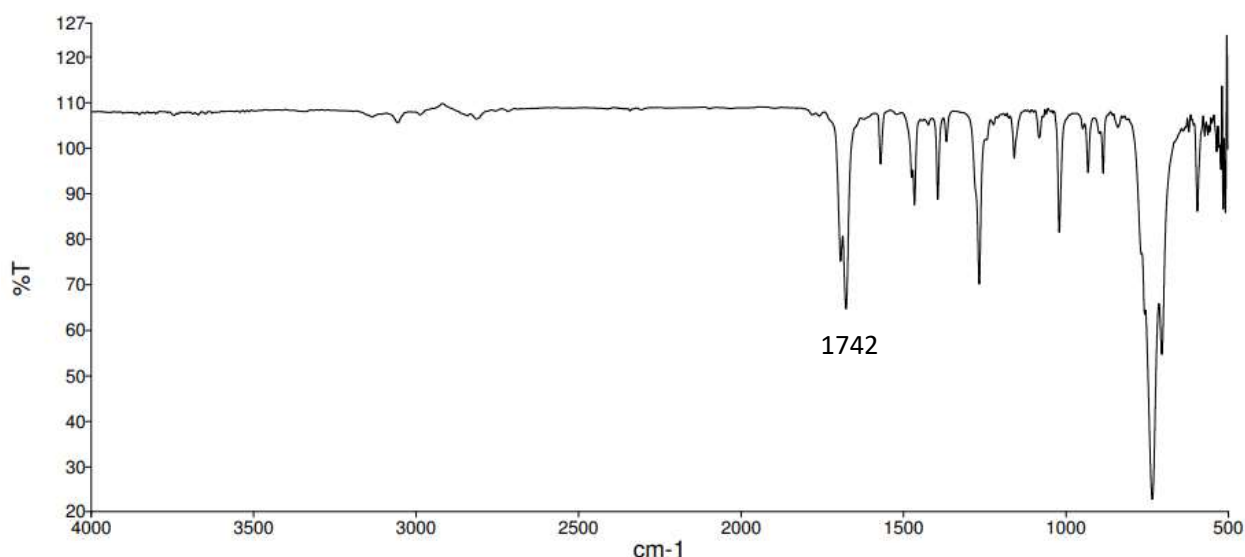


Figure 9: FTIR spectrum of the product obtained from rice husk.

CHAPTER 6
CONCLUSIONS AND FUTURE WORK

The primary research objective of this M. Sc. project was to investigate the potential of the two lignocellulosic biomasses which were chosen for the production of furfural via the sulphuric acid catalysed hydrolysis reaction in the water solvent system. Pursuing this objective we have successfully produced furfural from rice husk and water hyacinth. Comparing the two lignocellulosic biomass that was investigated, rice husk appeared to be the most promising and could be potentially used as a native lignocellulosic biomass for production of furfural.

The production of furfural was carried out using the hydrothermal method in a domestic pressure cooker. The characterization of the product was carried out by FTIR, UV-Vis and ^1H NMR spectroscopy.

As future work, development of environmentally friendly catalysts that will replace the conventional corrosive mineral acid catalysts is proposed.

CHAPTER 7
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