Sudan University of Science and Technology

College of Graduate Studies

Conversion of Rice Husks to Chemical Compounds

تحويل قشرة الأرز إلى مركبات كيميائية

A Thesis Submitted in Fulfillment for Requirements of M.Sc Degree in Chemistry

By:
Hana Ahmed Ali Omer

Supervisor: **Dr. Adil Elhag Ahmed**

Co-supervisor: **Dr. Essa Esmail Mohammad**

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بسم الله الرحمن الرحيم

(قُلْ لَوْ كَانَ الْبَحْرُ مِدَادًا لِكَلِمَاتِ رَبِّي لَنَفِدَ الْبَحْرُ قَبْلَ أَنْ تَنْفَدَ كَلِمَاتُ

رَبِّي وَلَوْ جِئْنَا بِمِثْلِهِ مَدَدًا)

سورة الكهف الآية (١٠٩)

Dedication

This thesis is dedicated

To

My parents

My siblings and my friends

Acknowledgement

First and for the most I thank Allah so much for providing me with the strength and deep believe .

My most humble and sincere thanks to **Dr. Adil Elhag Ahmed** for his sagacity, advanced vision and special brand of leadership, I was fortunate enough to have him as my supervisor.

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Abstract

Rice husk (RH) was collected from a rice mill in central Sudan and was used as a dual source for silica and cellulose. Amorphous silica was extracted from rice husk ash (RHA) through chemical treatment with nitric acid (3M) and combustion. It was then used to extract amorphous silica through dissolution in aqueous alkali solution NaOH (1M) and subsequent gelation in acidic medium following the sol-gel process. Pure cellulose was obtained from RH after complete removal of lignin and hemicellulose by treatment with strong alkaline solution NaOH (1M) and bleaching with sodium hypochlorite solution. Silica sulfonic acid (ASO_3H) was produced by impregnating the Chlorosulfonic acid with RHA amorphous silica, Silica Aluminate (AS) was produced by mixing equal amounts of sodium aluminate and sodium silicate. The extracted silica and cellulose as well as the produced ASO_3H, AS solid acid were characterized with FT-IR, XRD, XRF and SEM-EDX. A 5% of 5-HMF was produced by a catalytic hydrolysis of extracted cellulose over ASO_3H for 8hrs at 110°C in the presence of DMF as a solvent. Also 63% furfural was produced by a catalytic hydrolysis of xylose over (AS) for 5hrs at 110°C in the presence of water as a solvent. The process is very simple and appears to be economically attractive utilizing biomass usually regarded as wasteful material.

مستخلص البحث

جُمعــت قشــرة الأرز مــن وســط الســودان و تــم اســتخدامها كمصــدر للســليلوز والســليكات. تــم اســتخلاص الســليكات مــن قشــرة الأرز مــن خــلال معالجتِها بحمــض النتريــك(3M) وحرقهــا، أُستخلصـت الســليكات النقيــة بتزويــب رمــاد قشــرة الأرز فــي محلــول قلــوى قــوي مــن هيدروكسـيد الصـوديوم(1M). اسـتخلص الســليلوز النقـي مــن قشــرة الأرز بعــد معالجتهــا بمحلــول هيدروكسـيد الصــوديوم (1M).ُ حصــل علــى ســليكات الســلفون الحمضــي بتشــريب الســليكات بحمـض ســلفون الكلوريـدو، ســليكات الالمونيــوم (الصــوداليت الزيــوليتي)، انتجــت بمــزج احجــام متســاوية مــن ســليكات الصــوديوم و ألمينــات الصــوديوم. ســليكات الســلفون، ســليكات الالمونيــوم و الســليلوز تــم تشخصــيهم بواسـطة طيـف الاشـعة تحـت الحمـراء، حيـود الاشـعة السـينية، حيـود الاشـعة السـينية المفلـورة و المسـح الالكترونـي الـدقيق. تـم الحصــول علــى5% مــن5-هيدروكسـي ميثيلالفورفيــورال مـن تحلـل الســليلوز بالحــافز (ســليكات الســلفون الحمضــية) فــي درجــة حــرارة°110المـدة 8 ســاعات فــي وجــود ثنائى ميثيـل السـلفوكسـيد كمزيـب كمـا نـتج٦٣% مــن الفورفيــورال مــن تحلـل ســكر الزيلـوز الخماســي بالحــافز (ســليكات الالمونيــوم) فــي درجــة حــرارة °110 لمـدة 5 ســاعات فــي وجــود المــاء كمزيـب. تعتبـر هـذه الطريقـة بسـيطة، اقتصـادية واعـدة فـي الاستفادة من المخلفات الحيوية.

Abbreviations

AlCL$_3$ Aluminum Chloride

rt   retention time

XRD   X-ray diffraction

XRF   X-ray fluorescents

SEM-EDEX   Scanning Electron Microscope and Energy

                               Dispersive X-ray Elements.

AS   Rice husks ash Sodaliet

ASO$_3$ Rice husks ash silica sulfuric acid

FT-IR   Fourier transform Infrared

FID   Flame ionization detector

GC   Gases chromatography

LiCl   Lithium chloride

DMF   Dimethyl formamide

Ph-Ph   phenolphthalein

NaOH   Sodium hydroxide

RH   Rice husks

RHA	Rice husks ash
HMF	5-Hydroxy methyl furfural
NaCl	Sodium chloride
HCl	Hydrochloric acid
H_2SO_4	Sulfuric acid
CNCs	Cellulose nano crystals
CNFs	Cellulose nano fibers
R_T/R_O	R_T: the radius of the elements
	R_O: the radius of the oxygen

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Introduction and litterateur review

Chapter one

Introduction and litterateur review

1. Rice husks

Rice husks (RH) and coconut shells are abundant residues in agricultural countries. Rice and coconuts are grown in many countries of the world, especially in Asia. Rice is also grown in some northern and eastern Africa countries such as Egypt and Somalia. The amount of rice straw discarded annually in Egypt is around three million tons (Hessien *et al.,* 2009). In the last decade many rice farms were established in Sudan. Rice husks are by-products from mill process of rice. A small amount of rice husks were used in biomass fuel, but the greater part of the rest were treated as waste materials. These agricultural wastes have been studied to produce raw materials such as silicon dioxide, silicon carbide, silicon nitride or new materials and pure silicon for solar cells (Amick *et al.,* 1982, Hunt, *et al.,* 1984 and Real *et al.,* 1996).Globally, approximately 600 million tons of rice paddies are produced each year. On average 20% of the rice paddy is husk, giving an annual total production of 120 million tons of rice husks (RH) which is a great environment threat causing damage to land and surrounding area where it is dumped (Mistry *et al.,* 2016).

Rice husks (RH) contain 75-90 % organic matter such as cellulose, lignin etc. and rest mineral components such as silica, alkalis and trace elements. Therefore, commercial use of RH and its ash is the alternative solution to disposal problem. RH contain about 13-29 % inorganic constituents, of which 87-97 % is SiO_2 (silica) in an amorphous condition, the major impurities in rice husks are Na, K, Mg, Ca and Fe. Their presence as oxides and silicates can vary from 3 to 13% in ash (Shinohara *et al.,* 2004).

The present conditions of the world demand greatly for the use of durable materials which is also strong. RH is a great example of such material, because by burning the rice husks under controlled conditions at temperature below 800 °C silica in amorphous form is produced. This silica can be utilized for constructional works and for porcelain production (Mistry *et al.,* 2016).

1.1 Rice husks (RH) applications

Suitability of RH to be used for different applications depends upon the physical and chemical properties of the husk such as ash content, silica content and the cellulosic content (Mistry *et al.,* 2016).

1.1.1 Rice husks as fuel

RH is mostly used as fuel in boilers for processing paddy and generation of process steam. Heat energy is produced through direct combustion, synthesis gas (syngas) to generate energy (Beagal *et al.,* 1978). Ethanol as a biofuel has been produced from cellulose and hemicellulose fractions of agro-industrial residues can be depolymerized into fermentable sugars such as the hexoses, glucose and mannose, and the pentose's xylose and arabinose, either by enzymatic or chemical hydrolysis (Mosier *et al.,* 2005). An efficient conversion of all sugars present in lignocellulose was hydrolyzed to ethanol; ethanol is a prerequisite for maximizing the profitability of an industrial process and to improve the cost-competitiveness of bioethanol production (Fu *et al.,* 2009).

1.1.2 Rice husks ash (RHA)

Rice husks ash (RHA) produced when RH is burnt in air (Fuda *et al.,* 1975 and An *et al.,* 2011). It is the only crop by product that generates a huge quantity of ash when it is burnt in air (Zeobino *et al.,* 2011). Silica (87-99%) and minor amount of inorganic salts are the main constituents of RHA

(Magal *et al.,* 2011) with trace metal oxides (Jenkins *et al.,* 1998). Suitable substitute disposition must be scheduled to avoid undesirable environmental effect as about 70 million tons of RHA is being produced annually. Silica from RHA is an additive for rice plant itself, as it is absorbed by the roots of plant and deposited on the outer walls of epidermal cells as a silica gel and act as a physical barrier against pathogenic fungi and attacks by insects (Zhang *et al.,* 2011). In recent years, RHA is used as economically viable raw material for producing silicates and pure reactive silica because it has high silica content (Magal *et al.,* 2011).

1.1.2.1 Ceramic and refractory industry

RHA is used in the manufacture of refractory bricks because of its insulating properties. It has been used in the manufacture of low-cost, light-weight insulating boards. RHA has been used as silica source for cordierite production. Replacement of kaolinite with RHA silica in the mixture composition, yields higher cordierites with a lower crystallize temperature and decrease in activation energy of crystallization. Ceramic field showed that cenospheres provided better heat resistance and possess better thermal characteristics than the ceramics with no additives. It was found that the presence of the cenospheres prevented heat from entering the ceramic material, thus improving the thermal conductivity of the material. Thermal conductivity relates heat flowing through a sample to the temperature of the sample on opposite sides. Thermal resistance is the ability of a material to resist heat flow. Materials with a higher thermal resistance are more apt to remain at the same temperature when exposed to a change in temperature, RHA and cenospheres have the potential to become useful, heat-resistant building materials in the construction industry due to their thermal properties (Mistry *et al.,* 2016).

1.1.2.2 Cement and construction industries

Pozzolanic activity of RHA depends on (i) silica content, (ii) silica crystallization phase and (iii) size and surface area of ash particles. In addition, ash must contain only a small amount of carbon. RHA that has amorphous silica content and large surface is utilizable in many industrial applications (Makarand *et al.,* 2014). RHA is mainly used as a replacement of silica fume or as an admixture in manufacturing of low cost concrete block. Lower values of compressive strength at early ages for up to 7 days except for the mixture where the compressive strength was higher due to the increased reactivity and the filler effect of RHA. Based on that, it can be noticed that the amount of RHA present when 5% replacement used is not adequate to enhance the strength significantly. The addition of RHA is dependent on the followings:

- Percentage replacement of cement by rice husks ash
- Fineness of rice husks ash
- Chemical composition of rice husks ash
- Water to cementitious material ratio (w/b ratio)
- Type of Curing

1.1.2.3 Source of silicate

Silica from RHA can be an additive for rice plant itself, as it is absorbed by the roots of plant and deposited on the outer walls of epidermal cells as a silica gel and act as a physical barrier against pathogenic fungi and attacks by insects. Due to presence of large silica content in ash, extraction of silica is economical. Silica is also precipitated in customized forms to meet the requirements of various uses. Some of the uses of silica are in rubber

industry as reinforcing agent, in cosmetics, in toothpastes as a cleansing agent and amorphous silica as catalyst (Magale *et al.,* 2011).

1.2 Silica sulfuric acid

The silicate sulfuric acid catalyst is being used in two different forms, of which one is the silica adsorbed sulfuric acid and the other is silica sulfuric acid. Silica adsorbed sulfuric acid is very simple and economic for large scale synthesis in which it can be recovered and reused for several runs without any change in activity of the catalytic system. Studies reported it to be a safe, environment friendly, and reusable catalyst (Kiasat *et al.,* 2008).By passing certain limitations such as the destruction of acid sensitive functional groups, use of rather toxic solvents and expensive reagents or solvents, silica adsorbed sulfuric acid is an excellent candidate for sulfuric acid or chlorosulfonic acid (Eshghi *et al.,* 2007).

On the other hand, silica sulfuric acid (SSA) is another approach in the catalysis of chemical reactions. This catalyst prepared from chlorosulfonic acid has been used as an efficient reagent in chemical reactions by many international research groups. SSA is fundamentally a solid acid that has been used for different organic functional group transformations like nitration of thiols, aromatization of quinoline derivatives, stereoselective synthesis of β-amino ketones, formylation of alcohols and as a Michael addition reaction either as a reagent or as catalyst under heterogeneous conditions. Beside the use of silica as the solid support for the preparation of the catalyst, various other types of solid support media have also been utilized, of which polymers as support. Wieslaw *et al.,* [2009] studied polystyrene support on silica sulfuric acid. But due to their limitations, the use of silica as support for the catalyst system is preferred over polymer supported catalysts (Kaur *et al.,* 2015).

thermodynamic data were combined with experimental equilibrium reversals for the reaction bellow:

$$6 \ NaAlSiO_2 + 2 \ NaCl \rightarrow (NaAlSiO_2)_{12}$$

This structure has three-dimensional cage which are accessible to water molecules and some ions through relatively small windows of ~2.1 A° free diameter (Baeere 1994).It is naturally able to contain halogen salt it is also of thermal stability compared with zeolite, another advantage it is a potential candidate material for confine mental chlorinated waste (Rimodi *et al.,*2008).

1.3.1 Synthesis of sodalite

Sodalite can be successfully synthesized starting the crystallization either from gels (Hayashi *et al.*, 1984) applying hydrothermal reaction conditions to mullite and quartz (Denk *et al.,* 1971) or transformation of zeolite A. Subotić *et al.*, [1980] and Al-Azmi and Radhi [2001] found that the synthesis temperature and the amount of sodium hydroxide are the most important variables affecting the sodalite formation and the morphology when starting from gels. Furthermore, Huang *et al.,* [2011] mentioned that in zeolite a synthesis gel, which was free of structure-directing agents, Nano-crystalline sodalite could be obtained when large amounts of ethanol were added to the $NaOH–Al_2O_3–SiO_2–H_2O$ system.

1.3.1.1 Synthesis of zeolite

Silicon may be considered as the principal or key element of the framework. Elements which substitute for silicon must accept a tetrahedral coordination with oxygen. The first Pauling rule ($0.225 < R_T/Ro < 0.414$ where R_T the radius of the elements and R_O the radius of the oxygen) is useful, but it must not be applied in too strict a manner, above all when the element enters a framework with elements which accept the tetrahedral coordination easily.

Besides the coordination state, chemical factors such as condensation possibilities or the oxidation state in relation with the overall framework charge must also be considered when selecting possible T elements (T= Si, Al, Cu, ect). Aluminum is the element which replaces silicon most easily. The limits of the Si/AI ratio are 0.5 (e.g., bicchulite) and infinity (e.g., silicalite-l). However, up to now, no structure is known which can be synthesized in this whole composition range. The condensation of the silicate and aluminate anions to form aluminosilicate anions and then the zeolite framework needs the presence of hydroxide groups. In the presence of OH- oxygenated species of the T elements are formed in aqueous solution. But the OW concentration needed must be higher if the oxides of the T elements are less acidic. The main T elements in zeolites, i.e., Si and AI, are present as silicate and aluminosilicate anions in alkaline solutions (Caullet *et al.,* 1989) OH- increases the solubility of silica by ionizing the silanol groups and breaking siloxane bonds:

$$\equiv SiOH + OH\text{-} \rightarrow = SiO\text{-} + H_2O$$

$$\equiv Si\text{-}O\text{-}Si\equiv + OH\text{-} \rightarrow = SiO\text{-} + HO\text{-}Si\equiv$$
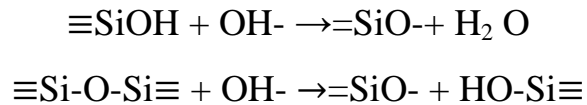
Thus, the monomeric silicic acid Si (OH) 4' which is sparingly soluble at pH 7, forms highly soluble silicate anions at high pH, but with fewer silanol groups

$$Si(OH)_4 + nOH^- \rightarrow Si(OH)_{4\_n}O_n^n + nH_2O \ (n = 1\text{-}4)$$
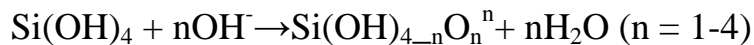
When the concentration of OH- increases, the silicate species will be less and less able to condense (the $=SiO\text{-}/=SiOH$ ratio increases), the ability of aluminate anions to condense remaining constant. This fact has several consequences (Weitkamp *et al.,* 1999):

   i.   Alumina-rich zeolites crystallize preferentially at a higher pH, a lower pH favoring silica-rich zeolites.

ii. during crystallization from a gel, the pH increases generally (OH- is liberated

   a. by the transformation of non-bridged =SiO- groups in the gel into bridged

   b. =Si-O-Si= groups in the zeolite), thus Si/Al in the crystals may decrease from the core to the outer shell.

iii. at high pH, the low concentration of polycondensable silicate species (lower supersaturation) may favor the formation of a stable and dense phase.

iv. a high =SiO-/=SiOH ratio on the silicate and aluminosilicate anions prevents.

   a. Complete =Si-O-Si= bridging in the framework (=SiO-M+ defects are formed).

Masyoka *et al.,* [2011] and Hums *et al.,*[2017] synthesis sodalite from cool fly ash by hydrothermal treatment at 140°c for 48hrs.

Sodalite can be synthesized a silica rich source (Depmeir *et al.,* 1984). Whereas, Wei *et al.,* [2008] reported the synthesis of nanometer-size sodalite from silicate at low temperature.

Jan-Jezreel *et al,* [2011] synthesized zeolite NaY by using the Na_2SiO_3 solution from RHA, a seed gel (Al_2O_3:$10SiO_2$) was first prepared by adding Na_2SiO_3 solution into $NaAlO_2$ solution under stirring until became homogenous and left undisturbed for 24 hrs.

Novembre *et al.,* [2009] synthesized sodalite via hydrothermal conversion of kaolinite in the presence of sodium hydroxide at low temperatures, whereas he investigated the solid-state transformation of meta-kaolinite to basic sodalite in the presence of NaCl in a so-called high temperature dry process synthesis route at 850°C and ambient pressure.

Hums *et al.,* [2017] formation of zeolite sodalite (SOD) as a by-product in the synthesis of zeolite X from clear solution extracted from fused South African coal fly ash. Fly ash treated with sodium hydroxide in a weight ratio of 1/2 then fused at 550°C for 2 hrs. Crystallization temperature to 90°C.

1.3.2 Applications of zeolites

There are three main uses for zeolite in industry, the most important being catalysis, gas separation and ion exchange (pavelic *et al.,* 1980 and Sersale 1985):

- o Catalysis: zeolite is extremely useful as catalysts for several important reactions involving organic molecules. The most important are cracking, isomerization and hydrocarbon synthesis. Zeolite can promote diverse range of catalytic reaction including acid-base and metal induced reaction. The reaction can take place within the pores of the zeolite which allows more product control.

- o Gas separation: the porous structure of zeolites can be used to "sieve" molecules having certain dimension and allow them to enter the pores. The property can be fine-tuned by variating the structure by changing the size and number of cations around the pores.

- o Ion exchange: hydrated cations within the zeolite pores are bound loosely to the zeolite framework and can readily exchange with other cations when in aqueous media. Applications of this can be seen in water softening device and use of zeolite in detergents and soaps.

1.4 lignocellulosic materials

Cellulosic biomass resources are in general very widespread and abundant that covers all plant bodies produced by nature photosynthesis, represents a vast supply of renewable feedstocks to produce fuels and chemicals (Chareonlimkun *et al.,* 2010).Cellulosic materials are comprised of lignin, hemi cellulose and cellulose and are thus sometimes called lignocellulosic materials. One of the primary functions of lignin is to provide structural support for the plant. Thus, in general, trees have higher lignin contents then grasses. Unfortunately, lignin which contains no sugars encloses the cellulose and hemicellulose molecules, making them difficult to reach. Table (1.1) shows the chemical composition of different types of lignocellulosic biomass (Sun *et al.,* 2002).

While starches harvested out of plant grains and certain plant roots, and vegetable oils harvested out of certain plant seeds are known useful biomass feedstocks, their limited availability and primary life-supporting function preclude their heavy industrial utilizations without conflicting societal consequences. Cellulosic biomass, which includes agricultural residues, grasses, trees, and algae, are highly abundant as renewable alternative feedstock to produce fuels and chemicals.

Fuel ethanol that is produced from corn has been used in gasohol or oxygenated fuels since the 1980. These gasoline fuels contain up to 10% ethanol by volume. As a result, the US transportation sector now consumes about 4540 million liters of ethanol annually, about 1% of the total consumption of gasoline (Jun *et al.,* 1999).

Table 1.1: Chemical composition of different types of lignocellulosic biomas

| lignocellulosic Biomass	Cellulose %	Hemicellulose %	Lignin %
Corn cob	39	35	15
Corn fiber	15	35	8
Corn straw	40	25	17
Cotton seed hair	80-95	5-20	0
Cotton stem	31	11	30
Grass	25-40	35-50	10-30
Hard wood (hybrid poplar)	44.7	18.6	26.4
Nut shells	25-30	25-30	30-40
Paper residues	76	13	11
Rice straw	35	25	12
Soft wood (pine)	44.6	21.9	27.7
Soy straw	25	12	18
Sugarcane bagasse	40	24	25
Wheat bran	10-15	35-39	8.3-12.5
Wheat chaff	38	36	16
Wheat straw	38.2	21.2	23.4

Several technologies are known to convert biomass to fuels and chemicals. Conversion of corn starch-based feedstock by fermentation has been widely practiced, with fuel ethanol nameplate production capacity reaching 13.6 billion gallons as of January 2011. Thermo-catalytic processes for cellulosic

biomass conversion offer potential technology platforms because robust operating conditions can be used such as temperature and pH, along with flexibility in the choice of processing media. Cellulose and hemicellulose are the main polymers found in biomass. They are polymers of hexoses, mainly glucose, mannose, and galactose, and of pentoses, mainly xylose and arabinose. Developing platform chemicals from cellulosic biomass (Zhang *et al.,* 2013).

Rice husk contains 75-90 % organic matter such as cellulose, Hemicellulose and lignin (Table 1.1). These organic compounds can be used as a raw material for production of xylitol, furfural, ethanol, acetic acid, lingo sulfonic acids.

1.4. 1. Cellulose

Cellulose is an organic compound with the formula $(C_6H_{10}O_5)_n$. It is a polysaccharide consisting of a linear chain of several hundred to many thousands of β $(1{\rightarrow}4)$ linked D-glucose (figure 1.2) units (Updegraff *et al.,* 1969). Cellulose is water insoluble compound normally found in plant cell walls, especially in branches, stems, other woody parts. It plays an important role in the integrity of plant cell walls. Cellulose can be produced by a fermentation process. Bacteria that can be used to produce cellulose are Acetobacter strains, Gluconacetobacter, Agrobacter, Sarcina, among others which includes non-pathogenic bacteria and is known as cellulose bacteria (Ross *et al.,* 1991; Klemm *et al.,* 2005).Cellulose is the most abundant organic polymer on Earth. In the table above different cellulose content in biomass for example of cotton fiber is 90%, wood is 40–50%, Grass 20-40% and so on.
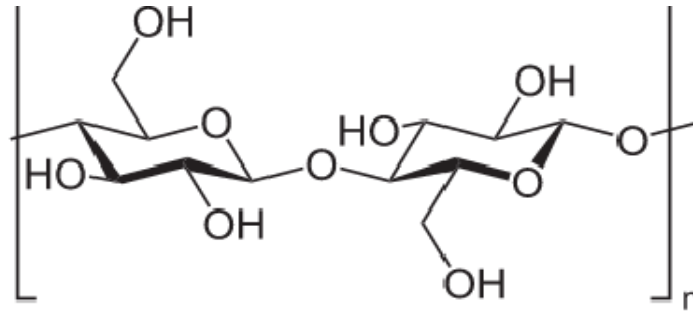
Figure 1.2: β(1→4) linked D-glucose units

Cellulose is derived from D-glucose units, which condense through β(1→4)-glycosidic bond. This linkage motif contrasts with that for α(1→4)-glycosidic bonds present in starch and glycogen. Cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. Cellulose fibers from plants are known as micro-fibrils that are 2-20 nm in diameter and form a strong network within the cell wall of the plant. Groups of polysaccharides are arranged in parallel to form cellulose micro-fibrils that cluster into macro-fibrils. Cellulose molecules can be arranged up to thousands of micro-fibrils chain units of D-glucose linked by hydrogen bonding (Nishiyama *et al.,* 2002). This confers tensile strength in cell walls, where cellulose micro fibrils are meshed into a polysaccharide matrix. Compared to starch, cellulose is also much more crystalline. Whereas starch undergoes a crystalline to amorphous transition when heated beyond 60–70 C in water. Amorphous cellulose obtained by treating cellulose in strong alkali solution Garima *et al.*, [2016] study populous plant cellulose when treated by NaOH 17.5% at 25 to 2h, for Hemicellulose isolation used mixture of ethanol: acetic acid (70:30).

Various crystalline structures of cellulose are known, corresponding to the location of hydrogen bonds between and within strands. Natural cellulose is cellulose I, with structures I_α and I_β. Cellulose produced by bacteria and algae is enriched in I_α while cellulose of higher plants consists mainly of I_β. Cellulose in regenerated cellulose fibers is cellulose II. The conversion of cellulose I to cellulose II is irreversible, suggesting that cellulose I is metastable and cellulose II is stable. With various chemical treatments it is possible to produce the structures cellulose III from cellulose I. Perez *et al.*, [2003] produced cellulose III from cellulose I by treatment with ammonia solution.

1.4.1.1 Cellulose fibers and crystals

Cellulose fibers are extracted from wood through a process known as pulping, where the wood is disintegrated, and fibers can be obtained. Pulping can be performed either mechanically or chemically. In mechanical pulping, the fibers are extracted through grinding and have lower strength compared to other fibers and are, therefore, used in applications that require a lower strength, such as newsprint. However, only around 40 % of wood is cellulose, where the other major constituents are, as previously mentioned, hemicelluloses and lignin (Timell *et al.,* 1967).Therefore to extract fibers with higher purity with respect to cellulose content different chemical processes, i.e., chemical pulping can be applied to remove lignin and part of the hemicelluloses. There are two main processes: The Kraft, or sulfate, process, is the dominating process (Chakar *et al.,* 2004) while the sulfite process is applied to produce high-cellulose content dissolving pulp. For the extraction of nanosized fibrils, chemical pulp is preferred over mechanical pulp, due to its higher cellulose content. Since fibrils grow as bundles in cellulose fibers, disintegration of fibers is required in order to obtain

individualized fibrils. In the 1980s, Turbak *et al.,* [1983] managed to disintegrate cellulose fibers into cellulose nanofibrils (CNFs) through mechanical disintegration.

Nanocellulose is a general term for the cellulosic particles with Nano-scale structural dimensions. Recently, the preparation of nanocellulose has garnered interest for being biodegradable and nontoxic, and the extraordinary properties brought by the Nano-size effect (Kargarzadeh *et al.,* 2012). Nanocellulose can be further divided into three types of materials, namely cellulose nanocrystals (CNCs), cellulose nanofibrils (CNFs), and bacterial cellulose (BC). Each of the three types of nanocellulose requires different methods of extraction from the cellulose sources and possesses distinct properties, which dictate their applicability and functionality (Abitbol *et al.,* 2016). The production of CNCs from the source fibers consists of three main parts: pretreatment of the fibers, isolation of CNCs, and post-treatment of hydrolyzed celluloses. Pretreatment of fibers includes the alkali treatment and bleaching treatment. Isolation of CNCs usually involves acid hydrolysis. Other methods include enzymatic hydrolysis, TEMPO oxidation and the use of ionic liquid for the isolation of CNCs. The post-treatment of hydrolyzed celluloses includes purification and sonication (Nechyporchuk *et al.,* 2016).

1.4.1.2 Cellulose isolation

Cellulose obtained from plant in which the cellulose fibrils are embedded with lignin and hemicelluloses. As already known, the lignin and hemicellulose that make up the cell wall components of plants is difficult to remove in the purification process (Klemm *et al.,* 2005). Cellulose can be isolated from lignocellulosic materials via various pretreatment methods,

such as mechanical, physiochemical, and chemical treatments, often using alkali, acid, organosolv, ionic liquids, or steam, have been developed with the goal of increasing the enzymatic digestibility of biomass(Kumar *et al.,*2009 and Brodeur *et al.,*2011).

a- Acid method

Wide variable acid can use to delignification cellulosic plant acetic acid, sulfuric acid and hydrochloric acid are suitable solvent. The diglyme-HCl method developed by Wallis *et al.,* [1997] and modified by Macfarlane *et al.,* [1999] is probably the simplest method for producing cellulose from whole wood. The method involves a single processing step that removes most extractives, hemi-cellulose and lignin, takes less than 24 h to complete and does not require specialized glassware (Macfarlane *et al.* 1999). The CNC isolated from oil palm trunk (OPT) using acid hydrolysis method has been reported by Lamaming *et al.,* [2015] and Mazlita *et al.,*[2016].

b- Alkyl method

Some bases can also be used for pretreatment of lignocellulosic materials and the effect of alkaline pretreatment depends on the lignin content of the materials (Fan *et al.,* 1987 and McMillan1994). The mechanism of alkaline hydrolysis is believed to be saponification of intermolecular ester bonds crosslinking xylan hemicelluloses and other components, for example, lignin and other hemicellulose. The porosity of the lignocellulosic materials increases with the removal of the crosslinks (Tarkow and Feist 1969). Dilute NaOH treatment of lignocellulosic materials caused swelling, leading to an increase in internal surface area, a decrease in the degree of polymerization, a decrease in crystallinity, separation of structural linkages between lignin and carbohydrates, and disruption of the lignin structure (Fan *et al.,* 1987). The digestibility of NaOH-treated hardwood increased from 14% to 55%

with the decrease of lignin content from 24–55% to 20%. However, no effect of dilute NaOH pretreatment was observed for softwoods with lignin content greater than 26% (Millet *et al.,* 1976). Dilute NaOH pretreatment was also effective for the hydrolysis of straws with relatively low lignin content of 10–18% (Bjerre *et al.,* 1996).

c- Physical method

Extraction technique that included the isolation of water soluble fiber fractions from various food sources. Southgate *et al.,* [1979] outlined and updated an extraction and fractionation procedure for lignocelluloses, crude lignin and cellulose fractions. In addition, numerous researchers have determined the cellulose, hemicelluloses and lignin contents of dietary fiber from food sources, physical treatment centrifuged at 1500 g or 3000 rpm in alkaline water (pH 7.0- 7.5) for 2 h at 20°C (Laufenberg *et al.,*2003).

d- Organosolv process

In the organosolv process, an organic or aqueous organic solvent mixture with inorganic acid catalysts (HCl or H_2SO_4) is used to break the internal lignin and hemicellulose bonds. The organic solvents used in the process include methanol, ethanol, acetone, ethylene glycol, triethylene glycol and tetrahydrofurfuryl alcohol (Chum *et al.,* 1988; Thring *et al.,* 1990). Organic acids such as oxalic, acetylsalicylic and salicylic acid can also be used as catalysts in the organosolv process (Sarkanenet *et al.,* 1980). At high temperatures (above 185° C), the addition of catalyst was unnecessary for satisfactory delignification (Sarkanen, 1980, Aziz and Sarkanen, 1989).

e- Oxidative delignification

Lignin biodegradation could be catalyzed by the peroxidase enzyme with the presence of H_2O_2. The pretreatment of cane bagasse with hydrogen peroxide greatly enhanced its susceptibility to enzymatic hydrolysis. About 50%

lignin and most hemicellulose were solubilized by 2% H_2O_2 at 30° _C within 8 hrs (Azzam 1989).

f- Biological pretreatment

In biological pretreatment processes, microorganisms such as brown-, white- and soft-rot fungi are used to degrade lignin and hemicellulose in waste materials (Schurz 1978). Brown rots mainly attack cellulose, while white and soft rots attack both cellulose and lignin. White-rot fungi are the most effective basidiomycetes for biological pretreatment of lignocellulosic materials (Fan *et al.,* 1987).

1.4.2 Hemicellulose

Hemicelluloses (figure 1.3) a heterogeneous polymer constructed with C5 and C6 sugars (such as xylose, arabinose, glucose, galactose, mannose, etc.), is typically the second-most-abundant component of biomass, after cellulose (Dumitriu *et al.,* 2005). In most grasses and hardwoods, xylan a polymer of xylose is often found as the primary hemicellulose. As a result, xylan conversion is critical for utilization of important biomass feedstocks such as corn Stover, Miscanthus, switchgrass, and poplar. Major hemicelluloses aremanna's, xylan, arabinans, and galactans among which most important in softwoods (coniferous trees) are galactoglucomannans (20%) and arabinoglucurunoxylans (10%) (Sjo *et al.,* 2005).
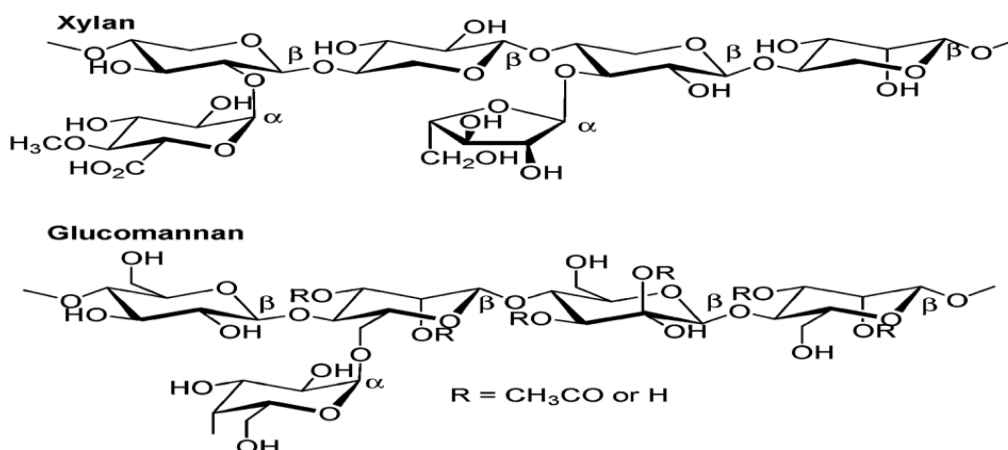
Figure 2.3: Hemicellulose chemical structures

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. Selective acid hydrolysis of hemicellulose substrates produces xylose in good yield which essentially depends on the hydrolysis kinetics (Zhang *et al.,* 2013).

1.5 . 5-Hydroxymethylfurfural (5-HMF)

5-Hydroxymethylfurfural (5-HMF) or "5-(hydroxymethyl) furan-2-carbaldehyde, 5-HMF"(figure 1.4) is an organic compound formed by dehydration of certain sugars. The molecule consist of hetero furanic ring (which consist of five atoms when four carbon member an oxygen atom) besides two functional group are aldehyde and alcohol.
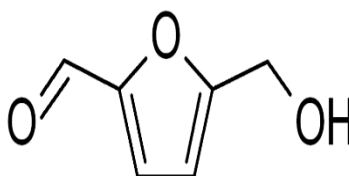
Figure1.4: The Chemical structure of 5-HMF

Since the last decade of the 19th century, 5-HMF had been of great interest, 5-HMF It is an intermediate for pharmaceutical products (Sriwilaijaroen *et al.,* 2011) flavor-enhancers in food, polymer synthesis, and biofuel production (Gan *et al.,* 2013 and Yin *et al.,* 2011) 5-HMF can be produced in compressed hot water, organic solvents (Moreau *et al.,* 2004 and Yuan *et al.,* 2011), and ionic liquids (Zhao *et al.,* 2007).

1.5.1 5-HMF in the natural products

The furan derivative 5-hydroxymethylfurfural (5-HMF) is present in a wide variety of foods. Formation of 5-HMF occurs during thermal processing, non-enzymic browning reactions or prolonged storage of food. The compound is produced from reducing sugars (fructose, sucrose and to a lesser degree glucose) either via the Maillard reaction in the presence of proteins. Example for some foods including HMF like milk, fruit juice and alcoholic drinks especially the sweet wines (Antal *et al.,* 1990).

Bakery products food form HMF substances during heat treatment. HMF is also produced in the food in canalization process during the storage. Upon toasting bread the amount increasing from 14.8 (5min) to 2024.8mg/kg (60min).Honey contains certain minor constituents like minerals, saccharides (75% fructose and glucose disaccharides 3–10% sucrose), proteins, enzymes, amino acids, vitamins, organic and phenolic acids, flavonoids, carotenoids, volatile substances and products of the Maillard reaction (Celechovska 2002; Serrano *et al.,* 2007). During processing, honey is usually warmed to lower its viscosity, and to prevent crystallization or fermentation. Temperatures of 32 - 40 °C do not affect honey quality. However, the use of higher temperatures leads to the formation of an important degradation product, 5-hydroxymethylfurfural 15mg/kg (Anklam1998; Turhan *et al.,* 2008). HMF is a natural product component in

heated food but usually present in low concentration. Physiologic, pharmacologic and/or toxicological effects caused by 5- HMF in mammals generally ranged from 50 to 500 mg/ kg body weight while lethal amounts generally ranged from 500 to 5000mg/ kg body weight (Hatim, 2004).
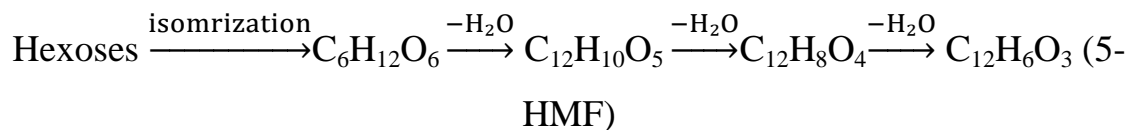
1.5.2 Synthesis of 5-HMF

From the commercial point of view, 5-HMF is a versatile and multi-functional compound. It is a good starting point for the synthesis of precursors of pharmaceuticals, thermo-resistant polymers, and macrocyclic compounds, and particularly for the synthesis of dialdehydes, ethers, amino alcohols, and other organic intermediates. These may lead to the possibility of numerous chemical. 5-HMF as the derivative of furan is mainly derived from petrochemicals at present, but it also could be obtained by dehydration of three water molecules from hexose Starch and cellulose can be hydrolyzed into glucose under acidic conditions or enzymatic conditions (Zhang *et al.,* 2013).

Starch hydrolyzes into glucose in hot water at 453-513K, and produces 5-HMF, maltose and fructose. Hydrolyzate glucose is the most abundant monosaccharide; the reaction of glucose dehydration is an important and attractive chemical reaction, because it produces two valuable derivatives, anhydroglucose and 5-HMF (Nagamori *et al.,* 2004).

As glucose is the monomer unit of cellulosic biomass, a high-speed and high-selectivity process for glucose conversion will strongly be demanded. Until recently, an ionic liquid system demonstrated that glucose even cellulose could be effectively converted to HMF in the presence of Lewis acids (Zhao *et al.,* 2007; Yu *et al.,* 2009; Stahlberg *et al.,* 2010).

1.5.2.1 Dehydration of glucose

Glucose is a hexoses sugar converting glucose to 5-HMF is a critical step in the utilization of cellulosic biomass because β-d-glucose is the fundamental building block of cellulose polymer. The ability to produce 5-HMF in high yield from fructose implies low oligomers and humins produced from glucose, an isomerization product of fructose. Acidic medium dehydrates three molecules of water from glucose forming 5-hydroxymethylfurfural. The catalytic reaction has wide range in dehydrated glucose to 5-HMF. The synthesis mechanism of preparation of 5-HMF from hexose is shown in equation below (Xien *et al.,* 2010):

$$\text{Hexoses} \xrightarrow{\text{isomrization}} C_6H_{12}O_6 \xrightarrow{-H_2O} C_{12}H_{10}O_5 \xrightarrow{-H_2O} C_{12}H_8O_4 \xrightarrow{-H_2O} C_{12}H_6O_3 \text{ (5-HMF)}$$

Therefore, selective conversion of glucose to 5-HMF implies that a reaction system comprised of a reaction medium and a suitable catalyst can effectively suppress the formation of oligomers and humins as waste products. For glucose as a starting material to be selectively converted to 5-HMF, it is essential to the followings: (Zhang *et al.,* 2013).

- o Limit the oligomerization and huminization of glucose.
- o Catalyze facile isomerization of glucose to fructose.
- o Convert fructose to 5-HMF in high efficiency.
- o Limit the degradation of 5-HMF to levulinic acid and formic acid.

1.5.3 Application of purified 5-HMF

5-Hydroxymethylfurfural (5-HMF), which contains a hydroxymethyl group and an aldehyde group also the reaction of furanic ring, has potential applications in the syntheses of many useful compounds and novel polymer materials, including medicines, plastic resins, and diesel fuel additives

through hydrogenation, oxydehydrogenation, esterification, halogenation, polymerization, hydrolysis, and other chemical reactions (Roman *et al.,* 2006).

1.5.3.1Reactions of the hydroxymethyl group

Hydroxyl methyl group in 5-HMF typical behavior of primer alcohol other compound can produced throw esterification, ethers, halogenation, alkylation, oxidation and reduction as illustrated in Table 1.2 (Roman *et al.,* 2006).

Table 1.2: Reactions of hydroxymethyl group

Reaction	Compound
Formation of esters	5,5′-diformylfurfurylether,(triphenylmethoxy) methylfurfural,α-D-glycosylmethylfurfurals ,benzyloxymethylfurfural and tert-butyldimethylsyliloxymethylfurfural
Formation of halides	5-chloromethylfurfuralm and 5-bromomethylfurfural
Oxidation	2,5-furandicarbaldehyde, dialdehyde

1.5.3.2 Reactions of the formyl group

The formyl group in the 5-HMF is reaction through oxidation, condensation and reduction as listed in Table 1.3 (Roman *et al.,* 2006).

Table 1.3 Reactions of the formyl group

Reaction	Compound
Oxidation	5-hydroxymethyl-2-furancarboxylic, 2,5-furandicarboxylic and 5-formyl-2-furancarboxylic
Condensation	5-acetoxymethyl-furfurylideneacetic, ethyl 5-hydroxymethylfurfurylideneacetate and 2-(5-hydroxymethylfurfuryl)-benzothiazole
Reduction	2,5-Bis-(hydroxymethyl) furan, 5-hydroxymethyl-2-Methyl furan, 5-hydroxymethyl-2-tetrahydrofurfurylamine and 2,5-bis-(hydroxymethyl)tetrahydrofuran

1.5.3.3 Reactions of the furan ring

Cleavage of the furan ring occurs in acidic medium (Choudury *et al.,* 1957) to give levulinic acid, formic acid and various polymeric substances. Recently, Horvat *et al* has proposed the mechanism of HMF degradation. The reaction proceeds via two possible routes (path 'a' and 'b'), which depend on the position of water addition (Horvat *et al.,* 1985).

- ✓ The reaction via mechanism 'a' leads to the formation of 2,5-dioxo-3-hexenal, which undergoes the decomposition to levulinic and formic acids.
- ✓ Reaction through the path 'b' results in the formation of polymers.

1.5.3.4 5-HMF as fuel

2,5-DMF produced from the partial or deep hydrogenation of HMF, 2,5-DMF is a very promising liquid fuel in the future, with a high energy density, 31.5 MJ/L, which is similar to that of gasoline (35.0 MJ/L), and is 40% higher than that of ethanol (23.0 MJ/L) Moreover, 2,5-DMF (bp 92–94 °C) is less volatile than ethanol (bp 78 °C) and is immiscible with water, so that it is especially suitable to be used as a transportation fuel(Tong *et al.,* 2010).

1.6 Furfural

Furfural is an organic compound formed by dehydration of certain sugars. The molecule consist of hetero furanic ring was discovered already in about 1821 by Johann Wolfgang Döbereiner, officially reported in 1832 (Dunlop and Peters 1953). In 1840 John Stenhouse, a Scottish chemist, discovered that furfural could be produced by distilling food crop materials like corn and oats using sulfuric acid. He also determined the chemical formula (figure 1.5) and in the early years of the 20th century the chemical structure was elucidated.
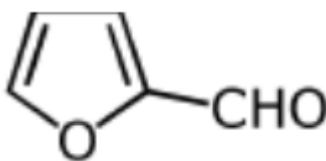
Figure 1.5: The chemical structure of furfural

Its name was derived from the Latin word "furfur" meaning bran, an early source of the product. Already from 1922 Quaker Oats Company started to produce furfural from oat hulls, based on a batch process using concentrated sulfuric acid. Nowadays, most of the furfural on the world market, about 280 kton/yr was produced in China, representing more than half of the global

capacity. This Chinese production capacity is characterized by widespread, inefficient (~50% of the theoretical furfural yield) small-scale fixed bed processes (Win 2005).
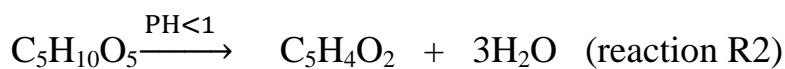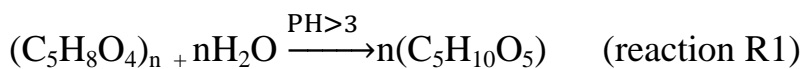
1.6.1 Furfural in the natural products

Heterocyclic compound furfural is commonly found in varying amounts in various foods rich in carbohydrates because of improperly monitored thermal processing which hexoses respectively pentose's it is dehydrated by the acid catalysis (Antal *et al.,* 1990).

Jianu *et al.,* [2011] study the presence of furfural 5g/ml in the apricot and peach juice proceeded thermally at temperature above 110°C soaking in water.

1.6.2 Xylose dehydration

The hydrolysis of hemicellulose by acidic solution residual xylose which dehydrated, hemi-cellulose part of biomass is first hydrolyzed by a (light) acid catalyzed step to form xylose (reaction R1). Under more severe acidic conditions, xylose is instantaneously cyclo-dehydrated to furfural (reaction R2). Besides furfural, also small amounts of carboxylic acids, mainly acetic acid and formic acid, are produced. These are formed by the hydrolysis of formyl and acetyl side groups of the hemi-cellulose.

$$(C_5H_8O_4)_n {}_+ nH_2O \xrightarrow{\text{PH>3}} n(C_5H_{10}O_5) \quad \text{(reaction R1)}$$

$$C_5H_{10}O_5 \xrightarrow{\text{PH<1}} C_5H_4O_2 + 3H_2O \quad \text{(reaction R2)}$$

Several authors have evaluated this reaction using as catalysts HCl, CrClx using mono or biphasic system. Marcotulio and De Jong [2010] proved that the use of NaCl and HCl results in up to 80% selectivity, using similar catalysts than the ones used by Pagan-Torres *et al.,* [2012] for glucose. Actually, the furfural selectivity increases from 12.6% to 80.7% as the HCl /

Xylose molar ratio increases from 0.6 to 2.4. This suggests that high acid concentration is necessary to obtain high selectivity of furfural. However, further increasing the ratio of HCl to xylose to 3:1 improves the selectivity by only 3% (Xing *et al.,* 2010). Different organic phases have also been reported, most of them are the same as the ones used when dehydrating hexoses. The operating temperature ranges from 160ºC to 200ºC. Note that this range is also similar to the one used for the dehydration of the hexoses.

In acidic medium, the furfural formed can decompose into resins and formic acid. Resins are formed in two types of reaction: furfural reacting with intermediates in the xylose-to-furfural conversion, or furfural reacting with itself. With O_2 present, furfural can be oxidized to some acidic products that are not specified yet. Acetic acid is derived from acetyl groups in hemi-cellulose at ~120° C in acidic medium. 5-methylfurfural (5-MF) is also detected in the furfural product stream in industrial production (Arnold and Buzzard 2003).

Vinit *et al.,* [2012] obtained furfural by using Bronsted acid such as HCl as a catalyst to dehydrate Xylulose and xylose under similar reaction conditions. They yielded 39% and 29% of furfural, respectively. However, when they introduced combination of Lewis and Brønsted acids catalysts for the dehydration of xylulose and xylose at moderated reaction temperature (~418K) extremely higher yield of furfural was obtained (≈76%).

1.6.3 Applications of purified furfural

Furfural due to their high reactivity, these compounds require further upgrading to more stable products if the goal is to incorporate them to the gasoline/diesel pool. Several approaches for furfural conversion have been attempted. Aldol condensation of furfural with small ketones is a promising approach to produce larger compounds (C_8-C_{15}) that may fall in the fuel

range (Surapas *et al.,* 2011). High yields of condensation products by direct condensation of furfural with acetone have been obtained in the presence of basic catalysts. However, condensation is only the first step. Selective deoxygenation is necessary to obtain compounds acceptable as components of transportation fuels. A highly desirable outcome of this deoxygenation step is preserving C-C bonds while effectively breaking the C-O bonds. The possible reaction pathways include medicines, plastic resins, and diesel fuel additives through hydrogenation, oxydehydrogenation, polymerization, hydrolysis, and other chemical reactions (Roman *et al.,* 2006).

Table1.4: Reaction Aldehyde group and furanic ring on the furfural (Roman *et al.,* 2006)

Reaction when	The reaction type					
	Reduction	Oxidation	Substitution	hydrolysis	Addition	Polymerization
Aldehyde group	Methyl furan, Furfural alcohol	Furanic acid	Furfural amine, 5-nitro furfural	Levulinic acid	Furfuryll den ketone, 2-furanacry llic acid, 2-furanacry lo nitrilic	-
Furanic	THF,Tetra hydrofuran yl alcohol	Muleic acid	Pyrroles, Thiofuran	Succinic acid, Succinic anhydride	-	Polyols, Polyester resin

1.7 Literature review

Trevor *et al.,* [2004] studied the preparation of 5-HMF by ionic liquids from fructose. They pointed out that when the reaction was carried out in 1-butyl 3-methyl imidazolium tetrafluoroborate（$BMIM^+BF_4^-$）as solvent and Amberlyst-15 as catalyst, the yield of 5-HMF up to 50%. But when the reaction was carried out in 1-butyl 3-methyl imidazolium tetrafluoroborate ($BMIM^+BF_4^-$) and 1-butyl 3-methyl imidazolium hexafluorophosphate ($BMIM^+PF_6^-$) as solvents, DMSO was used as a co-solvent and Amberlyst-15 as catalyst, the yield of 5-HMF was nearly 80%.

Qi *et al.,* [2008] obtained 5-HMF from glucose in high-temperature liquid water (HTLW) at temperatures of 180 to 220°C under a pressure of 10 MPa. The maximum yielded was found to 32.0% after conducting the reaction 30 min.

Fu-Rong *et al.,* [2014] synthesized 5-hydroxymethylfurfural (HMF) from D-glucose under mild reaction conditions, using SO_3H-functionalized acidic ionic liquids as catalysts and H_2O-4-methyl-2- pentanone (MIBK) biphasic systems as solvent. High glucose conversion of 97.4% and HMF yield of 75.1% were registered in 360 min at a reaction temperature of 120 ℃.

Takagaki *et al.,* [2009] used a combination of Amberlyst-15 (a solid acid) and Mg–Al hydrotalcite (a solid base) in N, N'-dimethylformamide (DMF) for synthesizing 5-HMF from glucose; they achieved 5-HMF with selectivity of 58% and the glucose conversion of 73% when the reaction was run at 80℃.

Zhao *et al.,* [2007] demonstrated that the use of $CrCl_2$ in 1-ethyl-3-methylimidazolium chloride [EMIM]Cl gave 5-HMF selectivity of 72% and glucose conversion of 94% at 80 ℃.

Huang *et al.*, 2010 showed that combining enzymatic and acid catalysts to synthesize 5-HMF from glucose gave 5-HMF a selectivity of 70% and glucose conversion of 85%.

Otomo *et al.,* [2014] used dealuminated Beta-zeolite as an effective bifunctional catalyst for the direct transformation of glucose to 5-HMF.They achieved 55% selectivity for 5-HMF and 78% glucose conversion.

Zhang *et al.,* [2011] studied the production of 5-hydroxymethylfurfural (HMF) through dehydration of glucose in ionic liquids in the presence of hydroxyapatite supported chromium chloride (Cr-HAP) using oil-bath heating and microwave irradiation (MI). A maximum HMF yield of 40% was obtained from the dehydration of glucose under MI in 2.5 min.

Lavarack *et al.,* [2002] obtained 80%furfural from sugarcane bagasse used dilute acid to hydrolysis of bagasse. The reaction conditions varied were; temperature (80 – 200°C), mass ratio of solid to liquid (1:5–1:20), type of bagasse material (i.e. bagasse or bagacillo), concentration of acid (0.25–8 wt% of liquid), type of acid (hydrochloric or sulphuric) and reaction time (10–2000 min). The reaction also produced xylose, arabinose, glucose, acid-soluble lignin (ASL) as side products.

Dewi *et al.,* [2013] obtained 5-HMF using sugarcane bagasse as a raw material. These experiments were performed in a batch-type reactor containing slurry of 10 ml of water and 1.2 g of solids. The effect of temperature (200°C and 300°C) and reaction times (3 to 30 min) on 5-HMF yield was investigated. An optimum yield of 3.09% was produced at 270°C after10 min.

Xiaohui *et al.,* [2018] produced furfural and levulinic acid (La) over solid acid–induced hydrothermal treatment of bagasse. In the first stage, hydrothermal treatment of hemicellulosic bagasse was carried outin the

biphasic system for 2.5 hours over Sn-MMT/SO$_4^{\ominus 2}$ solid acid catalysts at optimum temperature of 170°C.A furfural yield of 88.1% was produced . In the second stage, an amount of 61% levulinic acid was obtained at 180°C after 3hours reaction time.

Telleria *et al.,*[2013] obtained furfural from the cyclodehydration of xylose using Lewis (Nb$_2$O$_5$) and Bronsted (Amberlyst 70) acidsas catalysts.The reaction was conducted at 175 ℃ in a biphasicsystem water /toluene.The conversion of xylose over Lewis acid catalyst was found to be 46%, whereas that over Bronsted acid catalyst was registered to be 35%.

1.8 Objectives

The main objectives of this study were:

- To synthesize RHSO$_3$ and Sodalite from rice husks ash.
- To extract cellulose from rice husks.
- To convert the extracted cellulose to 5-HMF using RHSO$_3$ as catalyst.
- To convert xylose to furfural using sodalite as catalyst.
- To optimize the dehydration conditions to produce 5-HMF.
- To investigate and characterize the isolated cellulose, 5-HMF, furfural, RHSO$_3$, sodalite.

Chapter Two

Materials and methods

Chapter two
Materials and methods

2.1 Collection and pretreatments of rice husks

Rice Husks (RH) was collected from Aljazeera State (Sudan) in season 2014. It was washed with tape water, rinsed with distilled water and dried at room temperature for 24 h.

2.2 Chemicals

All chemicals used were pure and they were used without further purifications. Sodium hydroxide NaOH (Oxford, 98%); acetone (Alpha, 99%); chlorosulfonic acid (Alpha, 99%); dimethyl formamide DMF (Labtech, 99.5%); nitric acid (Alpha, 65%); lithium chloride (Sigma Aldrich, 99); aluminium chloride $AlCl_3$ (Labtech, 97%), methanol (Alpha, 99%); ethanol (Alpha, 99%); toluene (Alpha, 99%) and Benzene (Alpha, 99%).

2.3 Ashing of rice husks

The clean rice husks were stirred with 1.0 M nitric acid at room temperature for about 24 hours (to reduce all metallic impurities to negligible levels). It was thoroughly washed with distilled water until the pH of the rinse became constant. The wet RH was subsequently dried in an oven at 100 ˚C for 24 hours. The acid-leached RH was burned in a furnace at 800 ˚C for 6 hours for complete combustion (Kalapathy *et al.,* 1995). The white rice husks ash (RHA) obtained was used for silica extraction and modification.

2.4 Synthesis of aluminosilicate material

5.0 g of the RHA sample was added to 250 mL of 1.0 M NaOH in a plastic container and stirred for about 18 h at room temperature to extract the silica as sodium silicate. The solution was filtered through Whatman No. 41 ash less filter paper. 50 ml sodium aluminate solution was prepared from

ALCL$_3$, dissolved in NaOH 8% and was added dropwise to the sodium silicate. The gel began to form with continuous stirring. The gel was aged for 72 h at a room temperature and the gel/precipitate was filtered, washed thoroughly with distilled water and dried at 100 ˚C for 18 h. The silica xerogel was ground to powder and washed again with distilled water several times then filtered and dried at 100 ˚C for 18 h and labeled AS.

2.5 Synthesis of silica from RHA

5.0 g of the RHA sample was added to 250 mL of 1.0 M NaOH in a plastic container and stirred for about 18 h at room temperature to extract the silica as sodium silicate. The solution was filtered through Whatman No. 41 ashless filter paper. The extracted sodium silicate was titrated with 3.0 M HNO$_3$. The acid solution was added at a slow rate of ca. 1.0 mL min^{-1} with constant stirring. Silica gel started to precipitate when the pH decreased to less than 10. The titration was continued until the solution pH reached 5.0. The silica gel/precipitate was aged for 24 h. The silica gel/precipitate was filtered, washed thoroughly with distilled water and dried at 100 ˚C for 18 h. The silica xerogel was ground to powder and washed again with distilled water several times then filtered and dried at 100°C for 18 h. This extra washing enabled the nitrate ions present to be washed off completely. The silica obtained was labeled as RHASiO2.

2.5.1 Synthesis of silica sulphuric acid

6g of silica were transferred to a 250 ml three-necked flask. 3.0 ml (55 mmole) of chlorosulfonic were added a dropwise (HCL gas evolved from the reaction vessel immediately). After the addition was completed the mixture was stirred for 30 min. A white solid (silica sulfuric acid) material was obtained and weighed (Rajendran *et al.,* 2011; Ganeshpure *et al.,* 2007 and Sahoo *et al.,* 2006).

2.6 Isolation of cellulose from RH

Rice husks were crushed to a powder, washed by sodium hydroxide NaOH (1M) in water bath at 50°C for 60 minutes with constant stirring to remove lignin and hemicellulose. This step repeated five times. The residue was washed by distilled water and again by sodium hydroxide (1M) in a water bath at 80° C for 90 minutes to remove any remaining hemicellulose. This step as repeated three times and finally the contents were washed by hot distilled water to remove the hydroxide (Phenolphthalein was used to give an indication of complete removal of NaOH) and dried. A bleaching step was performed to remove the brown color. The bleaching agent was prepared by mixing equal parts of an acetate buffer solution with sodium hypochlorite solution (27g of NaOH were added to 75ml concentrated glacial acetic acid and completed to the mark in one litre volumetric flask with distilled water. One litre of sodium hypochlorite solution (1.7%) was prepared). The bleaching process was carried in a water bath 80 C to 90 minutes with constant stirring. This step repeated five times and finally washed with hot distilled water several times. The obtained cellulosic material was dried and weighed.

2.7 Conversion of cellulose into HMF

The cellulose hydrolysis was carried out in liquid-phase in a 50 mL round bottom flask equipped with magnetic stirrer and water condenser. 20 mL of DMF, 0.2 g of LiCl and 0.18 g cellulose, were separately transferred to a round bottom flask containing 0.2 g of silica sulfonic acid (catalyst). The temperature during the hydrolysis was fixed at 110°C. The hydrolysis mixture was refluxed for 8 hrs and the conversion process was tested by GC.

2.8 Conversion of xylose into furfural

The xylose dehydration was carried out in liquid-phase in a 50 mL round bottom flask equipped with magnetic stirrer and water condenser. 20 mL of distilled water and 2g of xylose were separately transferred to a round bottom flask containing 0.2 g of aluminosilicates (AS). The hydrolysis temperature was fixed at 110 °C. The hydrolysis mixture was refluxed for 5 h, the solution was filtered and the filtrate was kept to determine the content of furfural by GC. The whole process was repeated using methanol, ethanol, benzene and toluene in each experiment. FTIR analysis was performed to characterize the obtained furfural.

2.9 FT-IR measurements

The Infrared spectroscopic analysis was carried out for the isolated cellulose, 5-HMF, Silica Sulfuric acid and aluminosilicates (Sodalit). Few milligrams of each of the above materials were mixed thoroughly with few milligrams of KBr and compressed to form transparent disk. The Infrared spectra of samples were recorded in a Fourier transform infrared Spectrometer FT-IR Shimadzu (model 8400 S-Japan) between 400-4000 cm^{-1}.

2.10 XRF method

The sample was first crushed into a fine powder and then was pressed into a pellet using 15 ton pressing machine. The diameter of pellet was about 2.5 cm and the mass was about 1g. The pellet was exposed to the XRF spectrometer system where it was measured for 2000 sec. The concentration of the elements was determined using AXIL XRF software. A plant standard was used to ensure reliability of the results (soil hay standard obtained from the IAEA, Vienna).

2.11 XRD method

An analytical X-Ray Diffraction instrument model X`Pert PRO with Monochromator Cu- radiation (λ= 1.542 Å) at 45 K.V., 35 M.A and scanning speed 0.03 o/sec was used. The reflection peaks between $2\Theta = 20$ and 60, corresponding spacing (d, Å) and relative intensities (I/I_o) was obtained. The diffraction charts and relative intensities are obtained and compared with ICDD files.

2.12 SEM-EDX method

The scanning electron microscopy (SEM) photographs for samples were achieved using SEM model Quanta FEG 250 attached with EDX Unit with accelerating voltage 0.2 KV to 30 KV magnification 14x up to 1000 000x.

2.13 G C method

The furfural sample was determined using GC-2010 Shimadzu with high polar column. The flow rate of nitrogen gas was 0.8 cm³min⁻¹ and the column is attached to FID detector. The injector temperature was 200C and the temperature of the column was programmed between 100 to 150°C. The heating rate was programmed at 10 C/min. The injection volume was 2.0 μliter. Under these conditions furfural has a retention time of 1.89 min. In a typical manner, the process was repeated for HMF and the retention time was found to be 1.94 min. The concentrations of furfural and HMF were calculated using the following equation (Abou-Yousef *et al.,* 2014):

$$\text{Product moles} = \frac{[\text{Product concentration}\left(\frac{\text{mg}}{\text{ml}}\right) \times \text{filtrate volume(ml)}]/1000}{\text{Product molecular weight}}$$

$$\text{Product yield \%} = \frac{\text{Product moles}}{\text{moles of initial material}} \times 100$$

Chapter Three

Results and discussion

Chapter three

Results and discussion

3.1 FT-IR analyses of silica sulphuric acid, aluminosilicate and cellulose

FT-IR spectroscopy was utilized to identify the functional groups in the catalyst AS, ASO_3H and cellulose. Figures (3.1) to (3.3) display the spectra of these materials.
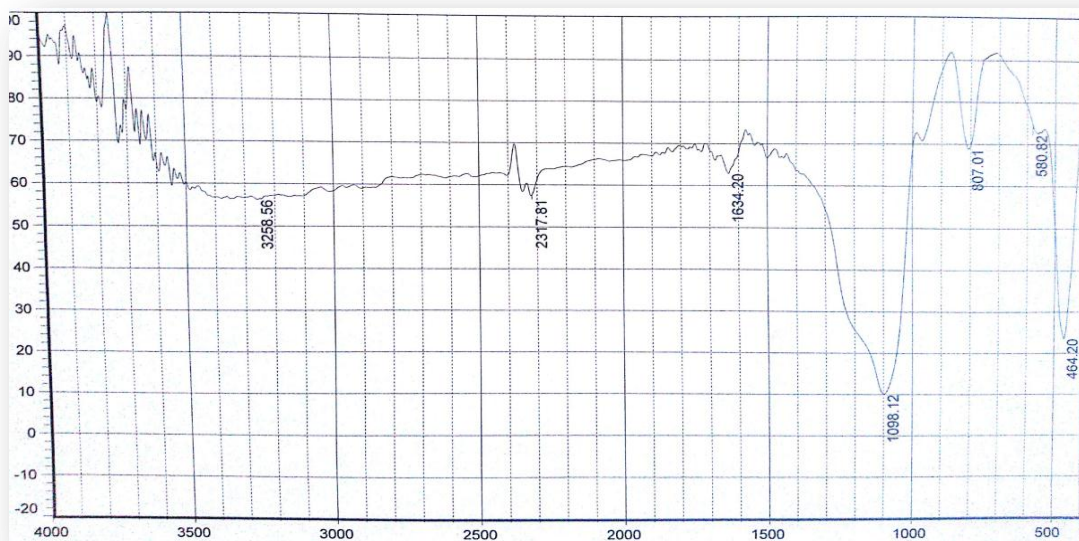
The FT-IR spectrum of AS is shown in Figure (3.1). As can be seen from the figure, the band in the range of 3500-3450 cm^{-1} is corresponding to SiO-H and HO-H hydrogen bonded of adsorbed water. The band at 1628 cm^{-1} is due to bending vibration of water molecules adsorbed in the surface of the material. The bands at 1000 to 670 cm^{-1} are due to asymmetric and symmetric stretching and bending vibrations of Si-O(Si), Si-O(Al), Si-O-Si and Si-O-Al (Kenneth *et al.,* 1995).
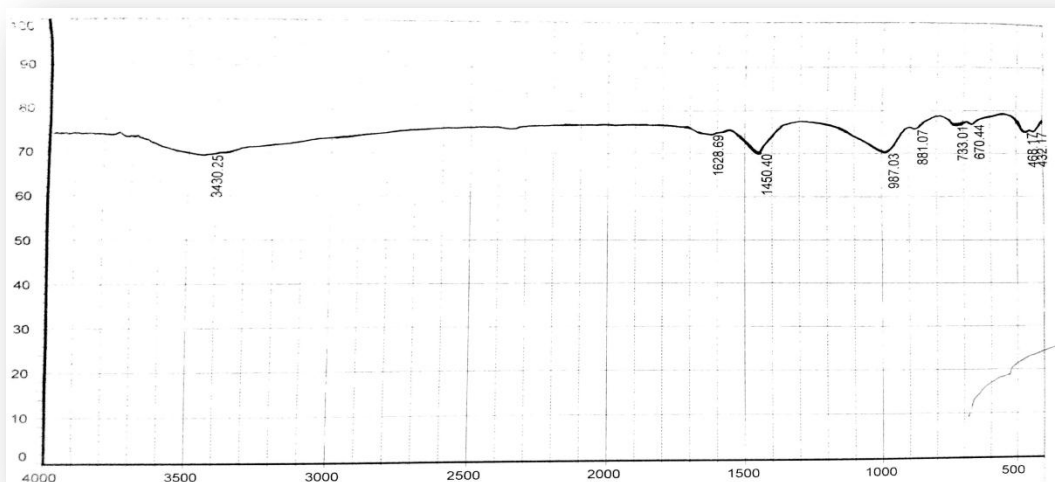
Figure 3.1: The FT-IR spectrum for AS sample

The FT-IR spectrum of Rice Husk Sulfonic (ASO_3H) catalyst is shown in Figure (3.2). The strong bands in the range of 3500-3258 cm^{-1} are assigned

to HO-H stretching vibration of adsorbed water on the silica surface as well as the hydroxyl stretching vibration of hydrogen bonded internal silanol groups (Kenneth *et al.,* 1995). The band centered at 2317 cm^{-1} is due to stretching vibration of S-H bond. The band around 1634 cm^{-1} is attributed to bending vibration of H-OH bond. The spectrum also shows bands at 1098 and 807 cm^{-1} due to the asymmetric and symmetric stretching bands of siloxane bands Si-O-Si, respectively. The weak bands at about 1380 and 1200 cm^{-1} (appear as shoulders) could be assigned to asymmetric and symmetric stretching vibrations of -SO$_2$- species. The band at about 970 cm^{-1} is attributed to Si-OH stretching vibration. The spectrum of ASO$_3$H also shows bending vibration bands of Si-O-Si bonds at 581 and 464 cm^{-1} (Kenneth *et al.,* 1995).

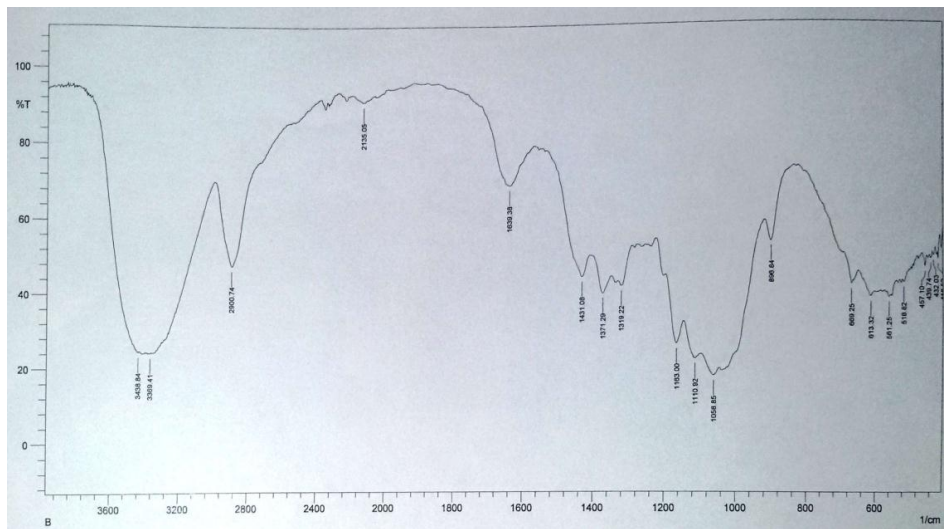
Figure (3.2): The FT-IR spectrum for ASO$_3$H sample

The FT-IR spectrum of cellulose is shown in Figure (3.3). The strong band in the range between 3600-3200 cm^{-1} regions is assigned to hydrogen bonded –OH group. The sharp band at 2900 cm^{-1} is due to stretching

vibration of C-H bond (saturated system). The band centered at 1635 cm^{-1} is assigned to bending vibration of –OH group and could also be due to adsorbed water. The spectrum also shows band at 1163 cm^{-1} attributable to the C-O stretching vibration. Interestingly, the absence of carbonyl band at 1731 cm^{-1}, which is observed in untreated RH sample Figure (3.4), is strong evidence for the complete removal of hemicellulose in purified cellulose sample (*Kenneth et al.,* 1995).


Figure 3.3: The FT-IR spectrum of as-extracted purified Cellulose sample
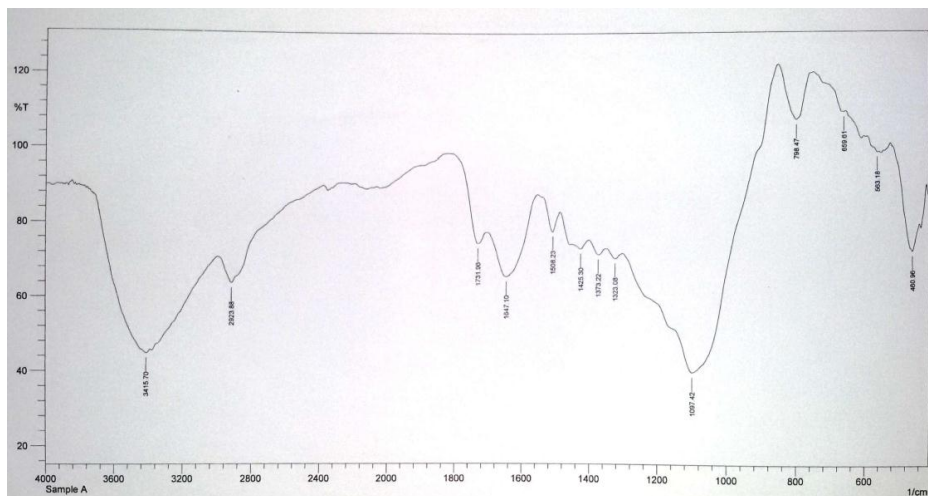
Figure 3.4: FT-IR The spectrum of untreated Rice husks sample

40

3.2.1 XRD of AS and ASO₃H

The XRD of the synthesized AS catalyst is depicted in Figure (3.5). The appearance of some sharp peaks at 2θ angle around $14°$ and $43°$ are due to some crystalline layer. A broad peak centered at 2θ angle around $25°$ confirming the amorphous sample. The chemical formula of AS is Sodalite zeolite is $Na_4AL_3Si_3O_{12}CL$.
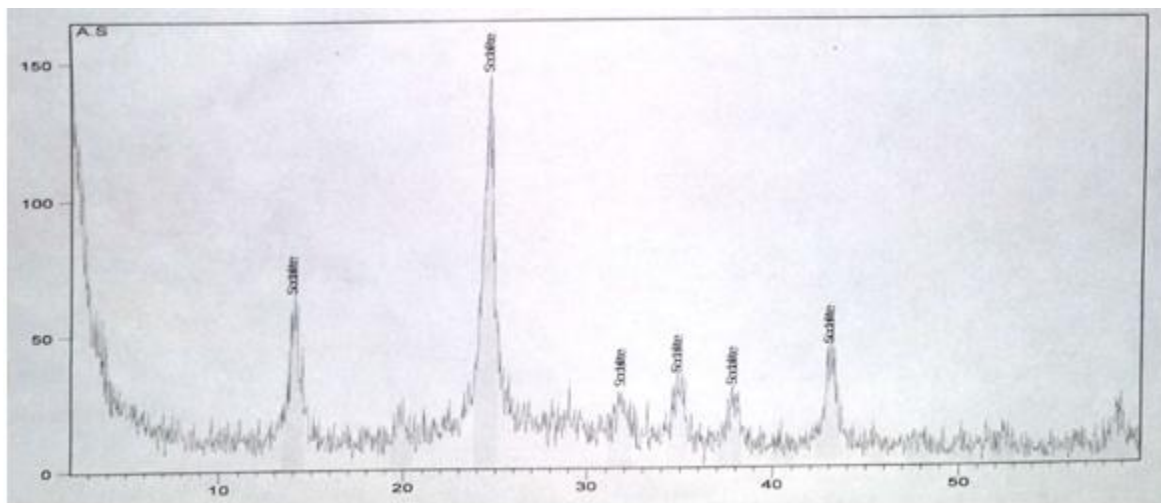
Figure 3.5: The X-ray diffraction pattern for ASO₃H catalyst

3.2.2 XRD of ASO₃H

The XRD pattern of ASO₃H catalyst is depicted in Figure (3.6). The obscurity sharp peak in the X-ray diffraction pattern of ASO₃H catalyst indicated the absence of any crystalline layer. A broad peak centered at 2θ angle around 22° confirming the amorphous nature of ASO₃H sample. This was observed by El Shafei *et al.,* [2000].
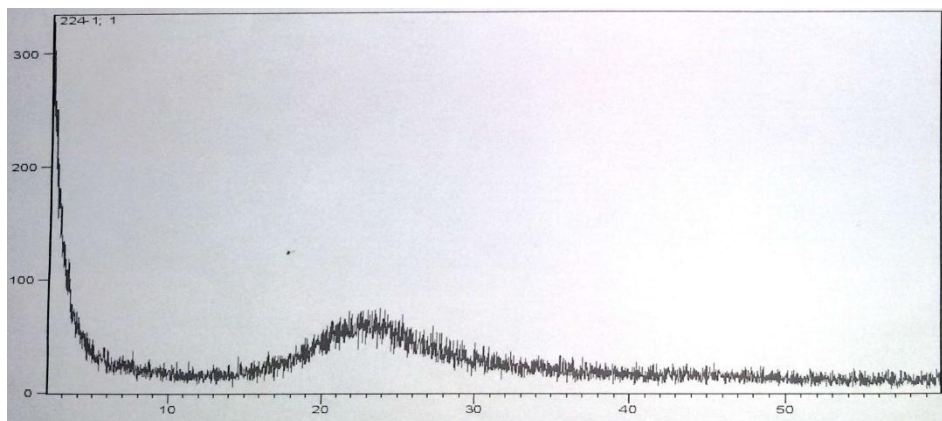
Figure 3.6: The X-ray diffraction pattern for ASO_3H catalyst

3.3 SEM_EDEX

SEM was used to study the effects of various treatments on the morphology of the samples AS and ASO_3 .

3.3.1 SEM_EDEX of AS

The SEM micrographs of the synthesized AS catalyst are shown in Figure (3.7). It seems that the catalyst has shown some rocky particles appeared on the surface . It is also indicated that the surface was highly rough and porous. The EDEX (figure 3.8) of AS was quietly homogeneous and the percentages of the elements were Aluminum 12%, silicon 21%, oxygen 45% and Chloride 2.9% .
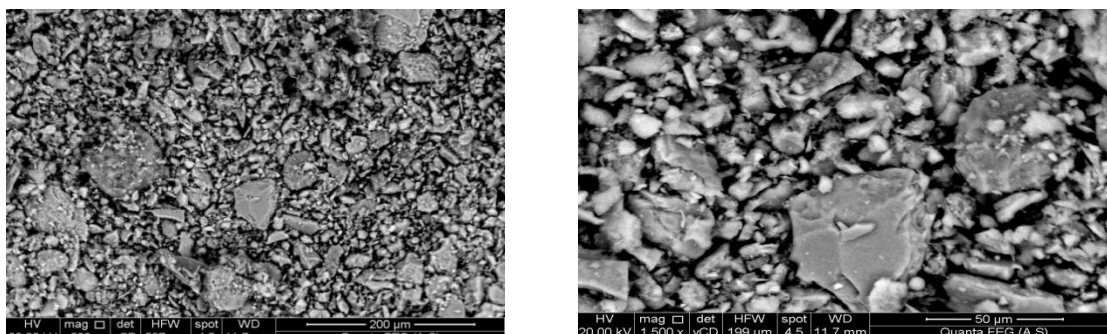
Figure 3.7: The SEM micrographs for AS sample

0.01. That means the catalysts AS and ASO_3H which were produced from RHA are very pure.

Table 3.1: XRF shows the element content in AS and ASO_3

Element	AS	ASO_3H
SiO_2	44.08	61.10
TiO_2	0.01	< 0.01
AL_2O_3	24.63	< 0.01
Fe_2O_3	0.06	< 0.01
MnO	0.01	< 0.01
MgO	0.09	< 0.01
CaO	0.023	< 0.01
Na_2O	17.12	< 0.01
K_2O	0.05	< 0.01
P_2O_5	0.01	< 0.01
CL	4.90	< 0.01
SO_3	0.01	< 0.01
LOI	8.30	38.55

3.5 Catalytic (ASO_3) reaction to hydrolyze cellulose

The catalyst ASO_3 was used to hydrolyze cellulose to glucose units and simultaneously dehydrate the produced glucose to 5-HMF. The reaction was conducted for 8 hours at 110 ℃ using DMF as a solvent. FT-IR spectroscopy was used to indicate the conversion of cellulose to 5-HMF, whereas, GC chromatography (Retention time = 1.94 min) was used to measure the percentage of the obtained furfural product.

3.5.1 FT-IR of 5-HMF

The FT-IR spectrum of the catalytic reaction products is depicted in Figure (3.5). The broad band centered at 3397 cm^{-1} is attributed to hydrogen bonded HO-H of adsorbed water. The two bands at 2926 and 2849 cm^{-1} are assigned to asymmetric and symmetric stretching vibrations of CH_2 bond, respectively. The band at 1747 cm^{-1} is due to stretching vibration of carbonyl group. The bands at 1638-1452 cm^{-1} are attributable to asymmetric and symmetric stretching vibrations of C=C bond. The appearance of absorption bands at 1167-1041 cm^{-1} could be assigned to the C-O-C strong stretching vibrations for 5-HMF product. Similar spectrum was reported by Uppal *et al.,* (2011) in their finding of furfural (5-HMF) production from bagasse using different acids
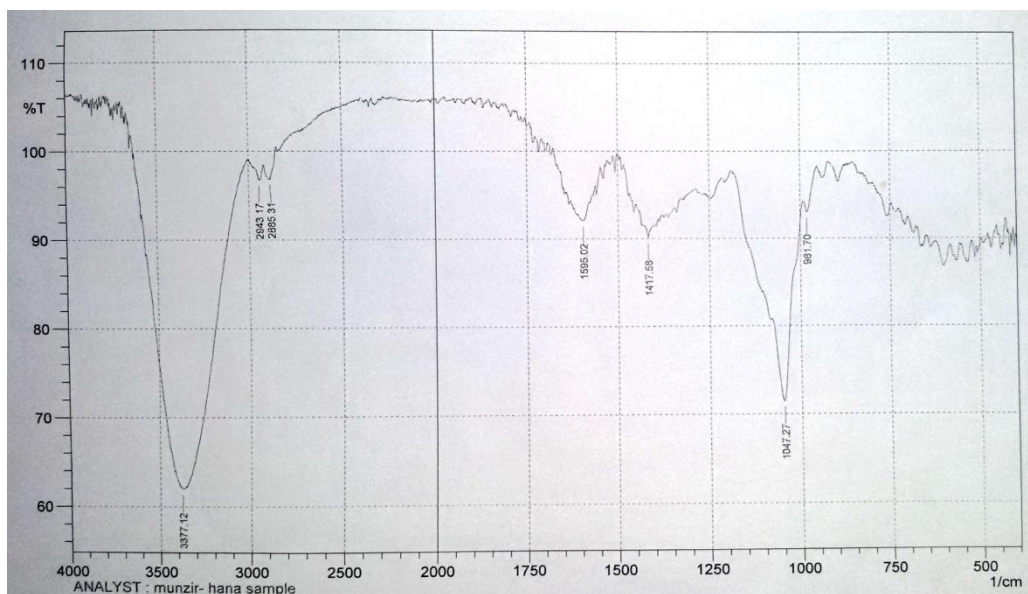
Figure 3.13: The FT-IR spectrum for catalytic reaction products

3.5.2 Solvent effect

The 5-HMF yield depends in general on the presence of stronger acidity of catalyzes the hydrolytic degradation of 5-HMF in aqueous media. Therefore, the pH level of the solvents plays an important role in the stability of 5-HMF. Aida *et al.,* [2007] studied the dehydration of D-glucose at 80Mpa in high-temperature water. Their results showed that water phase and high temperature and pressure are helpful to raise the yield of furan compounds. In another study, Ohara *et al.,* [2010] reported that the furanic is decreased in water as a solvent and when the temperature is raised up to 240°C the furanic undergoes further more dehydration to levulinic acid.

Organic solvents are always selected as non-aqueous media. Dimethyl-formamide (DMF), acetonitrile and polyethylene glycol and other organic solvents can improve the selectivity of sugar conversion reaction and these organic solvents with high boiling point can shorten reaction time and restrain the formation of humic matter (Juben *et al.,* 2007).

3.5.3 Mechanism of the reaction

Hexose isomerizes to 1, 2-enediol in solution; enol structure is considered to be the key for preparing 5-HMF. Then, 1,2-enediol transformed into 3-deoxy-hexose, further it dehydrates to 5-HMF. Besides 5-HMF, during the reaction process, it is also prone to aggregation, resulting in soluble polymer and insoluble materials, such as humic matter, levulinic acid, formic acid and other by-products (Jan *et al.*, 2008). The effect of Brønsted acid sites of modified silica, i.e. ASO_3H solid acid, was studied to hydrolyze cellulose to glucose and subsequently dehydrating the glucose to 5-HMF in one pot reaction. The reaction was conducted at 110℃ for 8 hours and the yield percentage of 5-HMF was registered to be only

5%. The low yield could be assigned to availability of only low acid sites in the catalyst surface. The EDX spectrum (Fig.3.11) of ASO₃H solid acid supports this assumption since there were no detectable levels of sulfur observed from EDX spectrum. The amorphous nature of the surface might play a great rule for embedding some acid site in the silicate structure. Low acid sites of RHA sulfonic acid was also reported by Hello *et al.,* 2014. However, more sensitive spectroscopic technique ca. XPS was used to indicated the introduction of sulfonic group. Despite the lower acidity and extremely low yield of products, the utilization of such wasteful material is considered good benefits. The modification in the preparation method could improve the acidity of the ASO₃H solid acid.

The Brønsted acid sites in ASO₃H believed to interact with glycosidic bonds of the polysaccharide units of cellulose and cleaved the C-O bond of the cyclic carbonium ion. According to literature, at 110℃ and pH 5 glucose was found to be reversibly transforms first to fructose (intermediate) and successively into 5-HMF through dehydration (Kuster *et al.,* 1977). This conversion is expected to occur by the cyclic pathway as illustrated Figure 3.14. The cyclic pathway was found to be more preferable in non-aqueous solvents like DMF (Qian *et al.,* 2011, Antal *et al.,* 1990 and Mednick *et al.,* 1962).
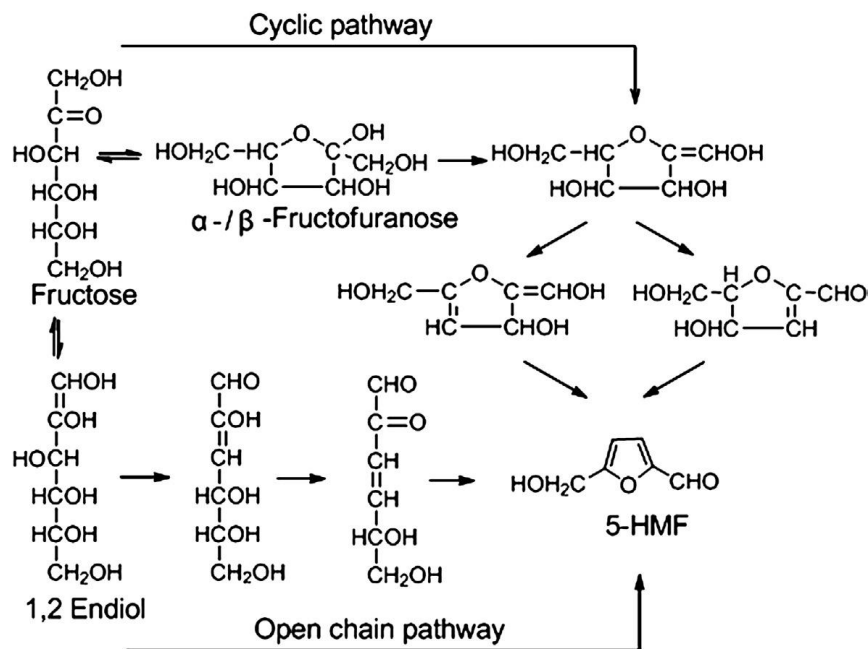
Figure 3.14: Cyclic and open chain pathway for the one-pot conversion of cellulose to 5-HMF (Kuster *et al.,* 1990)

3.6 Catalytic (AS) reaction to dehydration of xylose

The catalyst AS was used to dehydrate xylose to furfural. The reaction was conducted for 5 hours at 110 ℃ using water as a solvent. FT-IR spectroscopy was used to indicate the conversion of xylose to furfural, whereas, GC chromatography (Retention time = 1.9 min) was used to measure the percentage of the obtained furfural product.

3.6.1 Solvent effect

The dehydration of xylose is varying according to its solubility into different solvents. Xylose can be dissolved in several solvents, such as water, methanol and ethanol. It was mentioned that the xylose is completely soluble in water.

The effect of the solvent on the hydrolysis of xylose over RS was shown in Fig. 3.15. The hydrolysis was studied over different solvents such as water,

methanol, ethanol, toluene and benzene. It was observed that the dehydration of xylose over these solvents was increased according to the following order:

Water < Methanol < Ethanol < Toluene < benzene

The increase in the solubility of xylose makes the dehydration easier. The other solvents have only one center able to form a hydrogen bond with xylose. While toluene does not form a hydrogen bond and it has a very low solubility for xylose.
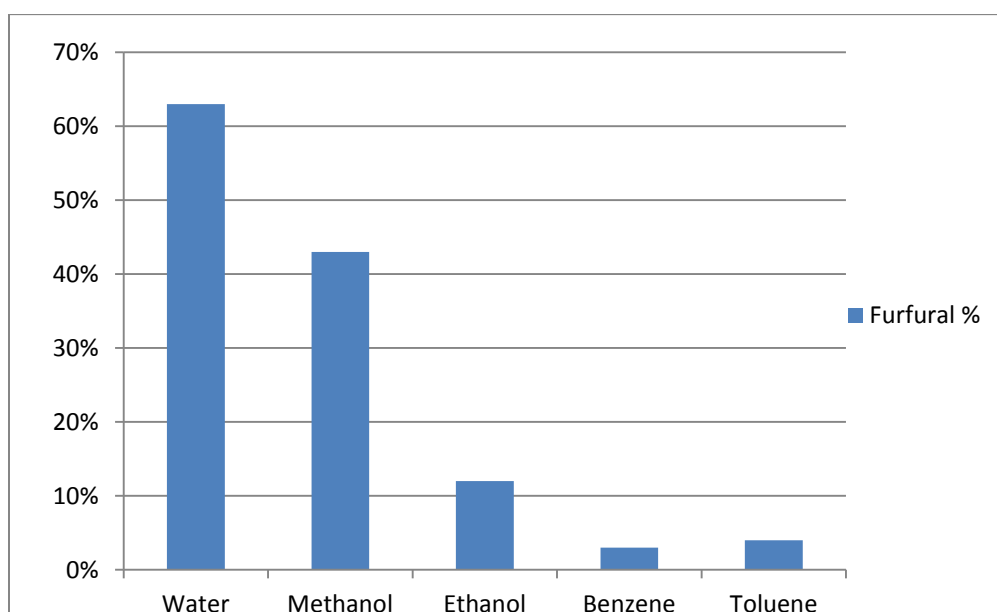
Figure 3.15: The effect of solvents

3.6.2 The effect of catalyst mass

The dehydration of xylose was carried out by varying the amount of RS (200, 300 and 500 mg) while keeping the other parameter fixed as, 5 h dehydration time at 110° C. The effect of the amount of catalyst on the dehydration of xylose is shown in Fig. 3.16. When the catalyst mass was increased from 200 to 300 mg, the xylose dehydration decreased from 63 to 31 %. Further increase of the catalyst mass had no significant effect. The reduction in the amount of the produced furfural was justified by two

theories, the first one suggested that the produced furfural was dehydrated when the acidity increased and converted to levulinic acid (Uppal *et al.*, 2011), the second one proposed that the furfural was absorbed by the catalyst (Kralj *et al.,* 2003).
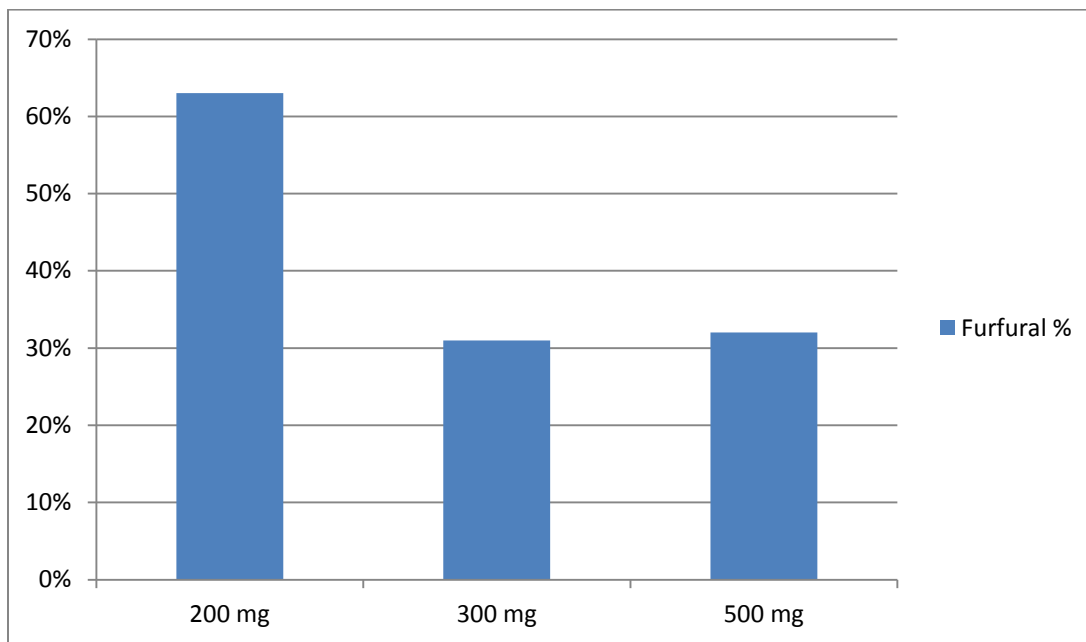
Figure 3.16: Effect of the amount of the catalyst

3.6.3 Mechanism of conversion to furfural

The effect of Brønsted and Lewis acid sites of modified silica sodalite Zeolites solid acid was studied to dehydrating the xylose to furfural in one pot reaction. The reaction was conducted at 110 ℃ for 5 hours and the yield percentage of furfural was registered to be 63%. The high yield could be assigned to availability of two acid sites in the catalyst surface. The EDX spectrum (Fig.3.8) of AS solid acid supports this assumption since there was two detectable levels AL and SiO_2 EDX spectrum also in the SEM spectrum (Fig.3.7) the amorphous nature of the surface might play a great rule for embedding some acid site in the catalyst structure. The Brønsted acid

sites is generated due to Si-O-AL bond that was shown in FT-IR spectrum (band 733-670 cm^{-1} (Fig.3.1)). Despite the lower acidity Lewis acid sites formed from siloxane bands Si-O-Si that spectrum shows bands at 987-881cm^{-1} (Fig.3.1). Utilizing such wasteful material is considered good benefits. Solid acid can catalyze Xylose dehydration selectively to furfural.

The Brønsted and Lewis acid sites in AS believed lowered the pH value. According to literature, at 110℃ and pH 5 pentose sugars are dehydrated to furfural (Kuster *et al.,* 1977). This conversion of pentose's sugars to furfural is similar in mechanism to hexose's sugars. It is expected to occur by the non-cyclic pathway as illustrated Figure 3.14 above. The non-cyclic pathway was found to be more preferable in aqueous solvents (Zhang *et al.,* 2013).

Summary

The furfural and HMF production via catalyzed dehydration shows greater benefits in the agricultural use of residual like Rice husk. Rice husks (RH) were used as a dual source for silica and cellulose. Amorphous silica was extracted from rice husks ash (RHA) and were treated with chlorosulfonic acid to produce silica sulfuric solid acid (ASO$_3$H) also aluminosilicate (AS) was obtained by mixing equal amount from sodium silicate and sodium aluminates. Whereas pure cellulose was extracted from RH through treatment with strong alkaline solution and subsequently bleaching with sodium hypochlorite solution. The purity of RHA, amorphous silica, extracted cellulose, ASO$_3$H and aluminosilicates were indicated by FT-IR, XRD, XRF and SEM-EDX spectroscopic techniques. A catalyzed hydrolysis reaction was performed for extracted cellulose and xylose over ASO$_3$H and AS Respectively. The hydrolysis of cellulose carried out for 8h at 110 °C in the presence of DMF as a solvent. Xylose dehydration carried out for 4h at 110 °C in different solvents such as water, methanol, ethanol, benzene and toluene. Low amount of 5-HMF of about 5% was detected after hydrolysis of cellulose and high amount of furfural about 63% from xylose dehydration using water as a solvent. The low percent of HMF was thought to be due to weak acidity of ASO$_3$H solid acid and the higher percent of furfural using water as a solvent was due to the good acidity of AS solid acid.

Suggestions for further works

According to the findings of this research silica sulphuric acid, sodalite, cellulose, HMF and furfural can be produced from rice husks at reasonable conditions. However; more studies are recommended to overcome or minimize the problems. These problems can be summarized as follow:

- ✓ Study the possibility for application of sodalite to dehydrate cellulose.
- ✓ Examine the possibility for application of silica sulphuric acid to dehydrate xylose.
- ✓ Investigate the possibility for raising the acidity of catalysts by introducing another metal in the catalysts.
- ✓ Deep investigation of the effect of temperature in the hydrolysis of cellulose.
- ✓ Inspect the effect of biphasic system to minimize the hydrolysis of HMF and furfural.

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