THE SYNTHESIS OF FUNCTIONALIZED-SILICA/CARBON CATALYSTS FROM RICE HUSK FOR THE CONVERSION OF HEXOSE SUGAR INTO METHYL LEVULINATE AND 5-HYDROXYMETHYLFURFURAL

SYED MUHAMMAD AL-AMSYAR
BIN SYED ABD KADIR

UNIVERSITI SAINS MALAYSIA
2018

THE SYNTHESIS OF FUNCTIONALIZED-SILICA/CARBON CATALYSTS FROM RICE HUSK FOR THE CONVERSION OF HEXOSE SUGAR INTO METHYL LEVULINATE AND 5-HYDROXYMETHYLFURFURAL

by

SYED MUHAMMAD AL-AMSYAR
BIN SYED ABD KADIR

Thesis submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy

February 2018

ACKNOWLEDGEMENT

My greatest gratitude to my supervisor, Prof. Dr. Farook Adam, for his thoughtful advices, encouraging words, and continuous supervision. Deeply thanks to Dr. Anwar Iqbal, for his helpful guidance, comments, and helpful suggestions.

I would also like to express my appreciation to all professors and lecturers especially in School of Chemical Sciences for sharing their knowledge and expertise with me in order to complete this project. Not forgotten to all lab members. It has been such a pleasure to knowing you all.

I am truly thankful with the Skim Latihan Akademik IPTA (SLAI) awarded by Ministry of Higher Education and Universiti Malaysia Kelantan (UMK) for my PhD study. Also, a research grant from Universiti Sains Malaysia RUI grant 1001/PKIMIA/811269.

Last but not least, I would like to thank my parents, family members and beloved wife for their full support and encouragement during this project was executed.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

LIST OF ABBREVIATIONS

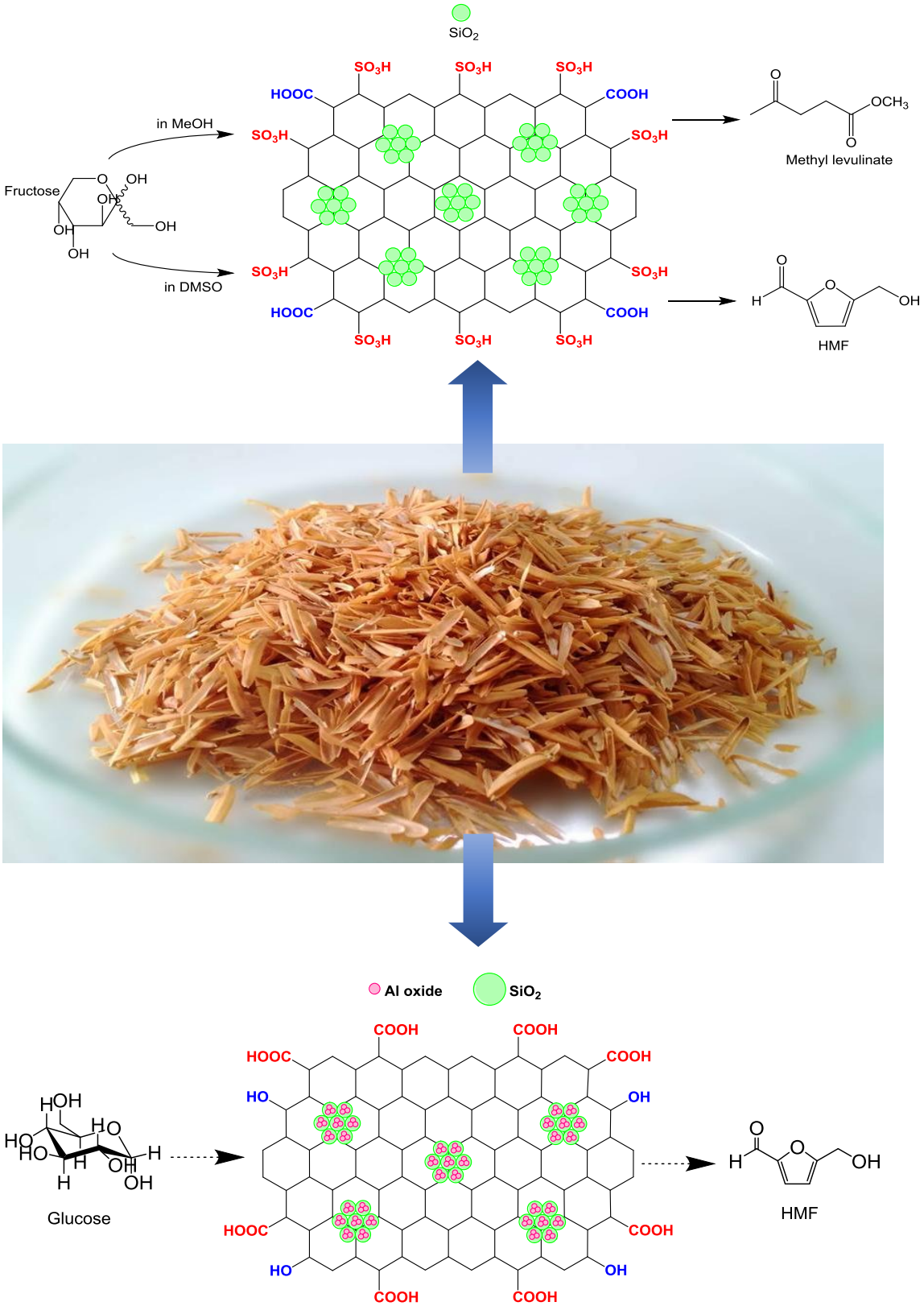
HMF	5-hydroxymethylfurfural
ML	Methyl levulinate
MML	5-methoxymethylfurfural
RH	Rice husk
RHA	Rice husk ash
MeOH	Methanol
FAME	Fatty acid methyl ester
MCM-41	Mobile Crystalline Materials-41
SBA-15	Santa Barbara Amorphous-15
LA	Levulinic acid
ALs	Alkyl levulinates
NMR	Nuclear magnetic resonance
DMSO	Dimethyl sulfoxide
VOP	Vanadyl phosphate
TON	Turn-over number
XRD	X-ray diffraction
NH_3-TPD	Ammonia-Temperature programming desorption

HPLC	High Performance Liquid Chromatography
GC	Gas chromatography
MS	Mass spectrometer
SEM	Scanning Electron Microscope
EDX	Energy Dispersive X-ray
XPS	X-ray Photoelectron Spectroscopy
ATR	Attenuated Total Reflection
FTIR	Fourier Transform Infra-Red
TGA	Thermogravimetric Analysis
DMF	Dimethylformamide
NMP	N-methylpyrrolidone
THF	Tetrahydrofuran
d-DMSO	Deuterated dimethyl sulfoxide
BET	Brunauer–Emmett–Teller
BJH	Barrett-Joyner-Halenda
S_{BET}	Surface area from BET method
V_{total}	Total pore volume
ICDD	International Centre for Diffraction Data

LIST OF SYMBOLS

-COOH	Carboxyl group
$-SO_3H$	Sulphonic group
-OH	Hydroxyl group
$SiO_2 + C-SO_3H$	Physical mixture of silica and sulfonated carbon
RH*	Silica-removed rice husk
M	Molar
Å	Angstrom
2θ	Bragg angle
°C	Celsius degree

GRAPHICAL ABSTRACT



SINTESIS PEMANGKIN SILIKA/KARBON YANG DIFUNGSIKAN DARIPADA SEKAM PADI UNTUK PENUKARAN GULA HEKSOSA KEPADA METIL LEVULINAT DAN 5-HIDROKSIMETILFURFURAL

ABSTRAK

Mutakhir ini, komposit silika/karbon telah mendapat perhatian dalam pemangkinan heterogen disebabkan oleh sifat-sifat hibridnya yang unik. Namun, kesukaran dalam merekabentuk kaedah sintetik hijau tetap mencabar. Dalam kajian ini, pemangkin heterogen silika/karbon dengan komposisi yang pelbagai disediakan secara terus daripada sekam padi dengan memvariasikan suhu pengkarbonan (250, 300, 350, 400, dan 450 °C). Komposit yang disediakan ini telah difungsikan secara berasingan dengan asid sulfonik dan aluminium oksida lalu menghasilkan pemangkin-pemangkin berikut: silika/karbon tersulfonat (SO_3H-SiO_2/C-250, SO_3H-SiO_2/C-300, SO_3H-SiO_2/C-350, SO_3H-SiO_2/C-400, SO_3H-SiO_2/C-450) dan aluminium oksida yang disokong silika/karbon (Al-SiO_2/C-350, Al-SiO_2/C-400, dan Al-SiO_2/C-450). Untuk pemangkin SO_3H-SiO_2/C, data daripada XRD mengesahkan komposit ini adalah amorfus. Suhu pengkarbonan yang lebih tinggi menunjukkan peningkatan keliangan (saiz liang meningkat daripada 40 kepada 53 Å), jumlah isipadu liang (meningkat daripada 0.031 kepada 0.288 cm^3/g), dan luas permukaan (meningkat daripada 39 kepada 260 m^2/g). Analisis EDX menunjukkan nisbah berat silikon-kepada-karbon meningkat daripada 0.114 kepada 1.12 dengan peningkatan suhu pengkarbonan. Walaubagaimanapun, nisbah berat sulfur-kepada-karbon menurun

daripada 0.040 kepada 0.0055. Untuk pemangkin Al-SiO_2/C, data XPS membuktikan kehadiran aluminium di dalam bentuk Al_2O_3 (1.03 wt%). Data XRD mengesahkan pemangkin ini adalah amorfus. Analisis jerapan-nyahjerapan nitrogen menunjukkan tiada impak besar terhadap sifat tekstural selepas cantuman Al_2O_3, dengan luas permukaan hanya menurun daripada 179 kepada 141 m^2/g. Jumlah isipadu liang mengecil daripada 0.155 kepada 0.124 cm^3/g, dan lebar liang meningkat daripada 44 kepada 48 Å. Pemangkin SO_3H-SiO_2/C digunakan sebagai pemangkin asid Brønsted heterogen untuk penukaran fruktosa kepada metil levulinat (ML) dan 5-hidroksimetilfurfural (HMF). Hasil ML sebanyak 90% dapat diperoleh pada suhu 165 °C selama 7 jam dengan menggunakan pelarut metanol. Hasil ML menurun di dalam eksperimen pengitaran semula didorong oleh pengendapan karbon berterusan, yang akhirnya menyebabkan penyahaktifan mangkin. Komposit ini juga mampu menukarkan fruktosa kepada 56 – 74% hasil HMF di dalam pelarut dimetil sulfoksida (DMSO) pada suhu 130 °C selama 5 jam. Untuk pemangkin Al-SiO_2/C, ianya digunakan sebagai mangkin asid heterogen Lewis-Brønsted dwifungsian untuk menukarkan glukosa kepada HMF. Penggunaan pemangkin ini menghasilkan 52% HMF pada suhu 170 °C selama 5 jam dengan menggunakan pelarut N-metilpirrolidon (NMP). Pemangkin ini dibuktikan stabil tanpa penurun hasil yang ketara selepas beberapa eksperimen pengitaran semula.

THE SYNTHESIS OF FUNCTIONALIZED-SILICA/CARBON CATALYSTS FROM RICE HUSK FOR THE CONVERSION OF HEXOSE SUGAR INTO METHYL LEVULINATE AND 5-HYDROXYMETHYLFURFURAL

ABSTRACT

Recently, silica/carbon composite material has received much attention in heterogeneous catalysis due to its unique hybrid properties. However, the difficulties in designing green synthetic methods remain challenging. In this study, varied proportion of silica/carbon heterogeneous catalyst was prepared directly from rice husk by varying the carbonization temperatures (250, 300, 350, 400, and 450 °C). The prepared composites were functionalized separately with sulfonic acid and aluminium oxide giving the following catalysts: sulfonated-silica/carbon (SO_3H-SiO_2/C-250, SO_3H-SiO_2/C-300, SO_3H-SiO_2/C-350, SO_3H-SiO_2/C-400, SO_3H-SiO_2/C-450) and silica/carbon-supported aluminium oxide (Al-SiO_2/C-350, Al-SiO_2/C-400, and Al-SiO_2/C-450). For the SO_3H-SiO_2/C catalysts, the XRD data confirms these composites were amorphous. Higher carbonization temperature showed an increase in porosity (pore size increased from 40 to 53 Å), total pore volume (increased from 0.031 to 0.288 cm^3/g), and surface area (increased from 39 to 260 m^2/g) of the composites. EDX analysis showed the silicon-to-carbon weight ratios of the composite increased from 0.114to 1.12 with increase in carbonization temperature. However, the sulfur-to-carbon weight ratio showed a decrease from 0.040 to 0.0055. In the case of Al-SiO_2/C catalyst, XPS data showed the presence of aluminium in the form of Al_2O_3 (1.03 wt%).

The XRD data confirms this catalyst was amorphous. N_2 adsorption-desorption analysis shows no major impact on textural properties after Al_2O_3 grafting, as the surface area just decreased from 179 to 141 m^2/g. The total pore volume decreased from 0.155 to 0.124 cm^3/g, and the pore width increased from 44 to 48 Å. The SO_3H-SiO_2/C catalysts were used as heterogeneous Brønsted acid catalyst in the conversion of fructose into methyl levulinate (ML) and 5-hydroxymethylfurfural (HMF). A product yield of 90% of ML was obtained at 165 °C in 7 hours in methanol solvent. The yield decreased in the recycling experiments due to continued carbonaceous deposition resulting in deactivation. These composites were also able to convert fructose to HMF in 56 – 74% yield in dimethyl sulfoxide (DMSO) solvent at 130 °C in 5 hours. For the Al-SiO_2/C composite, it was used as a bifunctional heterogeneous Lewis-Brønsted acid catalyst to convert glucose into HMF. The use of the catalyst resulted in 52% yield of HMF at 170 °C in 5 hours in *N*-methylpyrrolidone (NMP) solvent. This catalyst was stable without significant loss of yield after several recycling experiments.

CHAPTER 1

INTRODUCTION AND LITERATURE REVIEW

1.1 Heterogeneous Catalysis

Heterogeneous catalyst is the form of catalysis where catalyst and reactant are in different physical phases. In most cases, the catalysts are solid and the reactants are in liquid or gaseous form (Rothenberg, 2008). Homogeneous catalysts are when the catalyst and reactant are in the same physical phase. Homogeneous catalysis offers high activity and selectivity due to the high degree of interaction. The limitation of pore diffusion is eliminated in homogeneous catalysis. However, the difficulty in separation and recovery of the catalysts are the main drawback of the homogeneous catalysts.

The development of heterogeneous catalyst is desirable because it possesses important properties, especially recyclability, facile preparation and separation. In addition, it can be separated by using simple filtration. These advantages meet the requirement for green chemical principles and processes (Anastas & Warner, 1998) The Twelve Principles of Green Chemistry are:

a) **Prevention**

   It is better to prevent waste than to treat or clean up waste after it has been created.

b) **Atom Economy**

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

c) **Less Hazardous Chemical Syntheses**

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

d) **Designing Safer Chemicals**

Chemical products should be designed to affect their desired function while minimizing their toxicity.

e) **Safer Solvents and Auxiliaries**

The use of auxiliary substances (e.g. solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

f) **Design for Energy Efficiency**

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

g) **Use of Renewable Feedstocks**

A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

h) **Reduce Derivatives**

Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

i) **Catalysis**

Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

j) **Design for Degradation**

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

k) **Real-time analysis for Pollution Prevention**

Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

l) **Inherently Safer Chemistry for Accident Prevention**

Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

In this work, the author will utilize renewable feedstock (e.g. sugars) as a substrate to produce fine chemicals (e.g. hydroxymethylfurfural and alkyl levulinate) by using heterogeneous catalyst from agricultural waste as a catalyst precursor. The

current trend in research is mainly directed towards the development of high-performance heterogeneous catalysts for environmental-friendly chemical processes (Kaneda, et al., 2006). Therefore, this work will at least fulfill two out of twelve Principles of Green Chemistry (g and i).

1.2 Heterogeneous Catalyst Precursor from Biological Waste

Large-scale productions of biological waste especially in Malaysia, despite causing disposal problems, provide various opportunities in catalysis. For instance, waste materials can be used as active materials and precursor for catalyst synthesis (Balakrishnan, et al., 2011). In general, there are two major sources of waste in Malaysia; shells and rice husk.

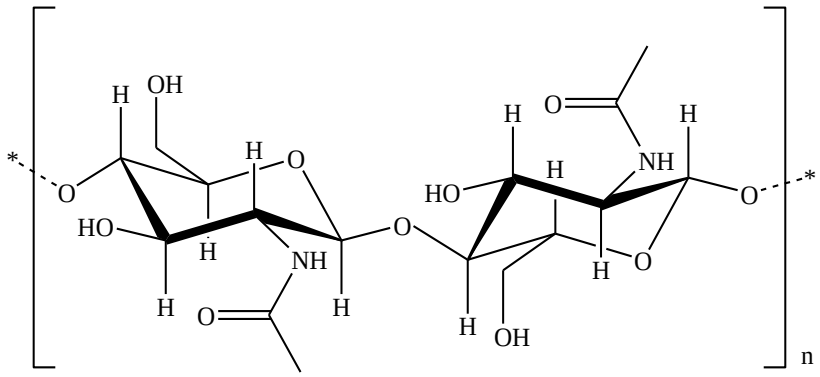
1.2.1 Waste from Shells

Shells mainly consists of $CaCO_3$ (Wei, et al., 2009). After thermal decomposition, CaO will be formed and release CO_2 gas. According to Tsai et al., (2008), despite consists of $CaCO_3$, it also has trace amounts of $MgCO_3$, $Ca_3(PO_4)_2$, and organic matters, as listed in Table 1.1. CaO has been used as a base catalyst in many catalytic reactions especially in transesterification to produce biodiesel. It has been reported that after calcination of powdered oyster shell above 700 °C, CaO act as a catalyst in esterification of soybean oil with more than 70% yield of high purity biodiesel (Nakatani, et al., 2009). Fly ash-supported CaO derived from egg shell has been used in transesterification of soybean oil to yield fuel grade biodiesel with higher fatty acid methyl ester (FAME) content (Chakraborty, et al., 2010).

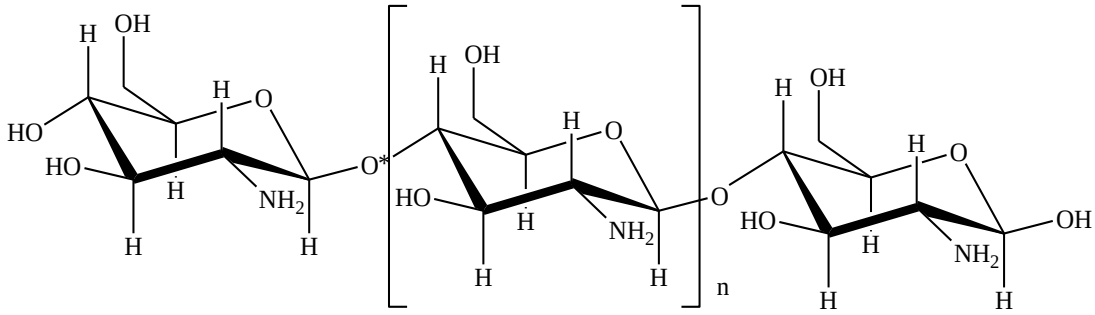
Table 1.1: Chemical compositions from egg shell.

Chemical compound	Weight percent (wt. %)
$CaCO_3$	94
$MgCO_3$	1
$Ca_3(PO_4)_2$	1
Organic matters	4

Waste mud crab (*Scylla serrata*) shell as CaO source have been employed to esterify palm oil (Boey, et al., 2009). Crab shells consist of chitin, second abundant biopolymer after cellulose, as shown in Figure 1.1(i). It is a long-chain polymer of an *N*-acetylglucosamine, one of the glucose derivatives. The annual production rate of chitin is enormous, and the number of literature regarding its application as catalyst support has been published is ever increasing (Macquarrie & Hardy, 2005). For instance, potassium fluoride (KF) loaded with incomplete carbonized shrimp shells has been demonstrated to become active catalyst in biodiesel production from rapeseed oil (Yang, et al., 2009). A conversion of 89.1% can be obtained after 3 hours reaction was carried out at 65 °C, 2.5 wt% catalyst, and 9:1 molar ratio of methanol/rapeseed oil. The authors claimed that the active site originated from the reaction of KF and incomplete carbonized shell. Figure 1.1(ii) illustrates the NH_2 groups in chitosan which could act as basic site for the base-catalyzed reactions.



(i)



(ii)

Figure 1.1: Chemical structure of (i) chitin and (ii) chitosan.

Thus, the utilization of shells as inorganic and organic components can be exploited, depending on the needs of the catalytic reaction. Shells from poultry industries can be used as a source of inorganic CaO for base-catalyzed reactions while crustacean's shells can be used as carbon-based materials for catalyst support.

1.2.2 Waste from Rice Milling Industry

In Malaysia, rice is the staple food. The paddy fields occupy vast area of land especially in the northern region (Kedah and Pulau Pinang). Therefore, the production of hefty amounts of rice husk is inevitable. Rice hull or rice husk (RH) which is produced from rice milling industry in Malaysia has been considered as one of the most abundant agricultural waste materials. Rice husk is the thin layer of material that

wraps the rice grain, protecting the grain as it grows and matures, as illustrated in Figure 1.2. The improper disposal of rice husk will create problems towards the environment.

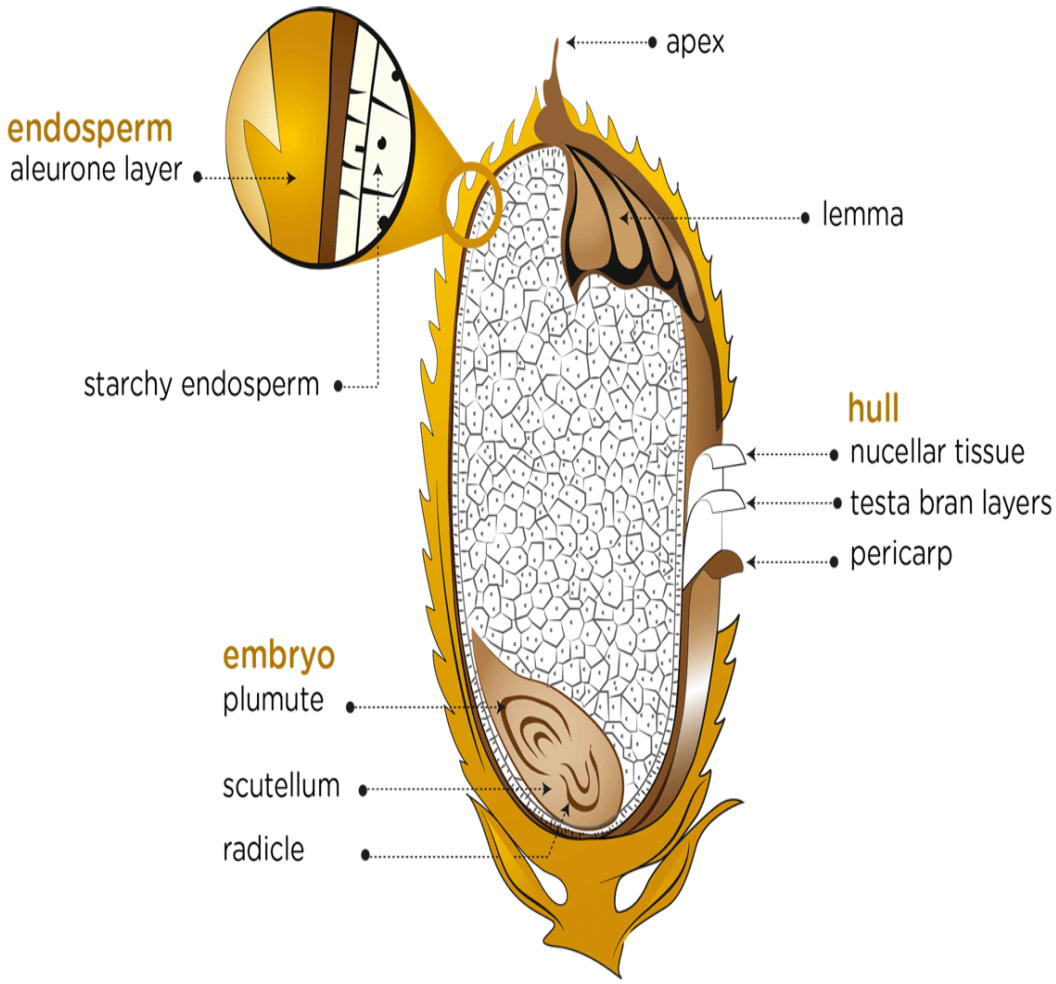


Figure 1.2: The anatomy of rice. Retrieved from http://www.bernas.com.my/index.php/rice-pedia/rice-anatomy.

Basically, silicic acid and water are taken into the plant via the roots from the soil (Ma & Takahashi, 2002). Amorphous silica can be found on the rice's cell wall on the surface of leaves, stems and husks in form of silica-cuticle and silica-cellulose double layers (Currie & Perry, 2007; Ma, et al., 2006). In addition, small and large silica particles also exist in the intercellular layers, as shown in Figure 1.3.

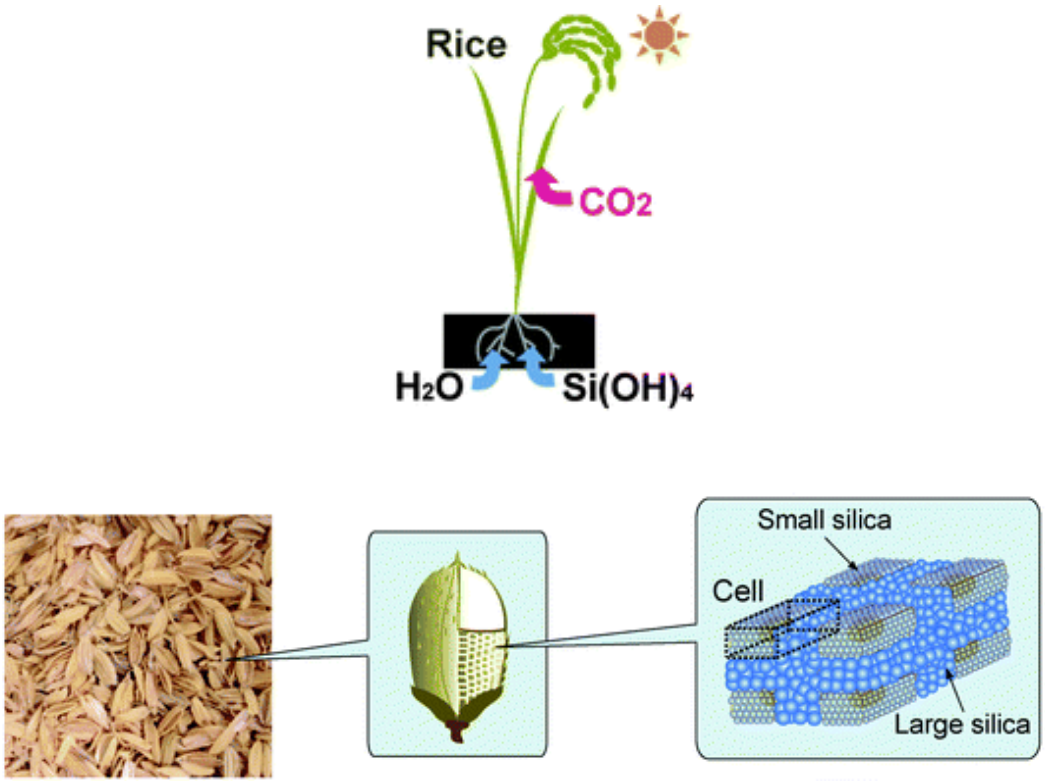


Figure 1.3: Formation of silica on the cell wall of rice husk (Tabata, et al., 2010).

1.3 Utilization of Rice Husk

Rice husk consist of 15 – 20% of silica (SiO_2) and its ash (RHA) contains about 95% SiO_2 depending on the temperature at which the RH is burnt. The RH also consists of cellulose, lignin, pentose, and other organic components. There are two common methods to obtain SiO_2 from rice husk; by calcination and solvent extraction. The latter is more environment-friendly (since open burning can cause health problems) and better purity of SiO_2 can be yielded. Under solvent extraction, the result of mixing rice husk in NaOH solution will produce silica in the form of sodium silicate and organic residues. By adding suitable amount of mineral acids into this solution, sodium silicate is converted into silica form.

Many examples of utilizing silica from rice husk as a catalyst precursor have been demonstrated. This catalyst framework has been demonstrated recently via grafting and sol-gel techniques. Furthermore, addition of surfactant will create pores in the solid structure. Such treatment can increase the surface area of the prepared catalyst. These catalysts showed good potential as heterogeneous catalysts such as in alkylation, benzylation, degradation of phenol, oxidation, and esterification (Adam, et al., 2012).

On the other hand, silica-removed rice husk (denoted as RH*) was produced too, mainly consists of cellulose, hemicelluloses, pentose, and lignin (James & Rao, 1986). This lignocellulosic biomass can be used as a substrate in conversion of sugars into fine useful chemical reagents (Alonso, et al., 2010). However, the fractionation is a difficult process and requires physical or chemical pretreatment for easier degradation of cellulose. Another alternative is to employ starch or shorter carbohydrates such as disaccharide or monosaccharide since complexity to isolate of sugars from lignocellulosic biomass could double the production cost.

Also, lignocellulosic components in rice husk can be transformed into carbon material by carbonization under air or N_2 atmosphere. Recently, silica in rice husk has been used as a natural template to synthesize hierarchical porous carbon, as depicted in Figure 1.4 (Tabata, et al., 2010). Whilst many researchers focusing on utilizing rice husk as a silica or carbon sources, the development of silica/carbon composite directly from rice husk are less reported. This composite have been widely used in transparent conductors (Watcharotone, et al., 2007), solar absorber (Mastai, et al., 2002), heterogeneous catalyst support (Wan, et al., 2009), and many more.

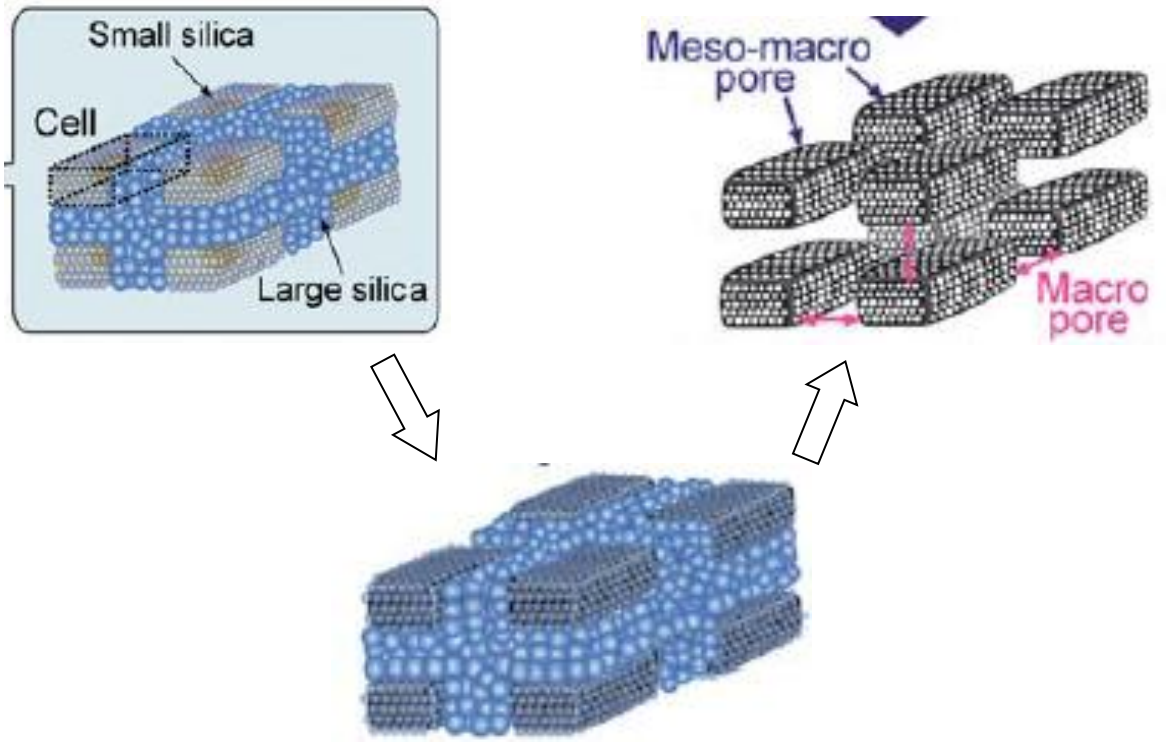


Figure 1.4: Fabrication of hierarchical porous carbon from rice husk (Tabata, et al., 2010).

1.4 Silica/Carbon Composite in Heterogeneous Catalysis

Silica/carbon composite received much attention as heterogeneous catalyst in organic synthesis due to its hybrid organic-inorganic properties. The presence of silica provides durability and thermal stability to this hybrid structure while the carbon matrix could be used for further modification with other functional group (Liu, et al., 2006). For example, the preparation of mesoporous Sn-grafted carbon-silica catalysts for the conversion of sugars into lactic acid and its esters has been demonstrated (de Clippel et al., 2012). This catalyst with dual functionalities as Lewis and weak Brønsted acid sites from Sn and carbon fraction respectively have been proved to catalyze dihydroxyacetone into ethyl lactate efficiently compared to carbon-free Sn-MCM-41.

Functionalization of silica/carbon composite with sulfonic groups has been demonstrated recently (Valle-Vigón, et al., 2012). This mesostructure silica (SBA-15, KIT-6, and mesocellular silica) coated with sulfonic groups-attached carbon have been used in esterification of maleic anhydride, succinic acid and oleic acid with ethanol. This catalyst performed better than commercial acid catalyst such as Amberlyst-15 due to the high density of sulfonic groups and accessibilities of substrate into active site that located inside wide mesopores which allow high mass transfer rate.

Hydrolysis of cellulose into glucose by using sulfonated silica-carbon nanocomposites have been reported (Van de Vyver, et al., 2010). Sulfonic group that attaches on carbon act as strong Brønsted acid sites while silica act as a favourable adsorption site for β-1,4 glucan. As a result, catalyst with higher silica-carbon ratio showed the best catalytic conversion of cellulose. It has been suggested that hydrophilic character of silica facilitate substrate adsorption.

Another example of silica/carbon as catalyst support has been demonstrated (Wan, et al., 2009). In this study, heterogeneous Pd catalysts grafted on ordered mesostructure silica-carbon nanocomposite have been employed in the Heck coupling reaction and in the Ullmann coupling reaction in aqueous media without any phase-transfer catalysts. As a result, ~60% *trans*-stilbene in Heck coupling of chlorobenzene and styrene was produced and of 46% for biphenyl in Ullmann coupling of chlorobenzene was yielded. The factors such as hybrid pore surface constituted by continuous and interpenetrated silica and carbon components, large pore size, uniform dispersion of Pd, and relatively small metal particle size are responsible for high catalytic performance.

The preparation of catalyst from renewable biomaterials such as starch, glucose, maltose, cellulose, and chitosan as carbon precursor is gaining interest recently. Amorphous sulfonated-carbon-silica catalyst for the protection of aldehydes as 1,1-diacetates and for N-, O- and S-acylations has been reported (Gupta & Paul, 2011). It was found that composite derived from starch was the most active catalyst and can be reusable without significant loss of catalytic activity.

1.5 Sugars as Chemical Feedstock

In this era of diminishing petroleum reservoir, researchers around the world have made tremendous efforts to reduce the dependency on crude oil by shifting their focus to use biomass as a chemical feedstock (Huber, et al., 2005). For instance, biodiesel and bioethanol have been used as blending agents for gasoline and diesel. Among biomass products, terpenes have the highest energy content, followed by vegetable oils, lignin, and sugars (Corma et al., 2007). However, due to scarcity of terpenes to meet the requirements, an attention has been shifted towards vegetable oils although there are some issues regarding ethical and limited source.

Figure 1.5 represents the chemical structure of starch and triglycerides, as compared to cellulose. Starch is an α-glycosidic bond of glucose polysaccharide. Therefore, it is very easy to break this bond to produce glucose monomer. The first generation of bioethanol could be obtained facilely from this source.

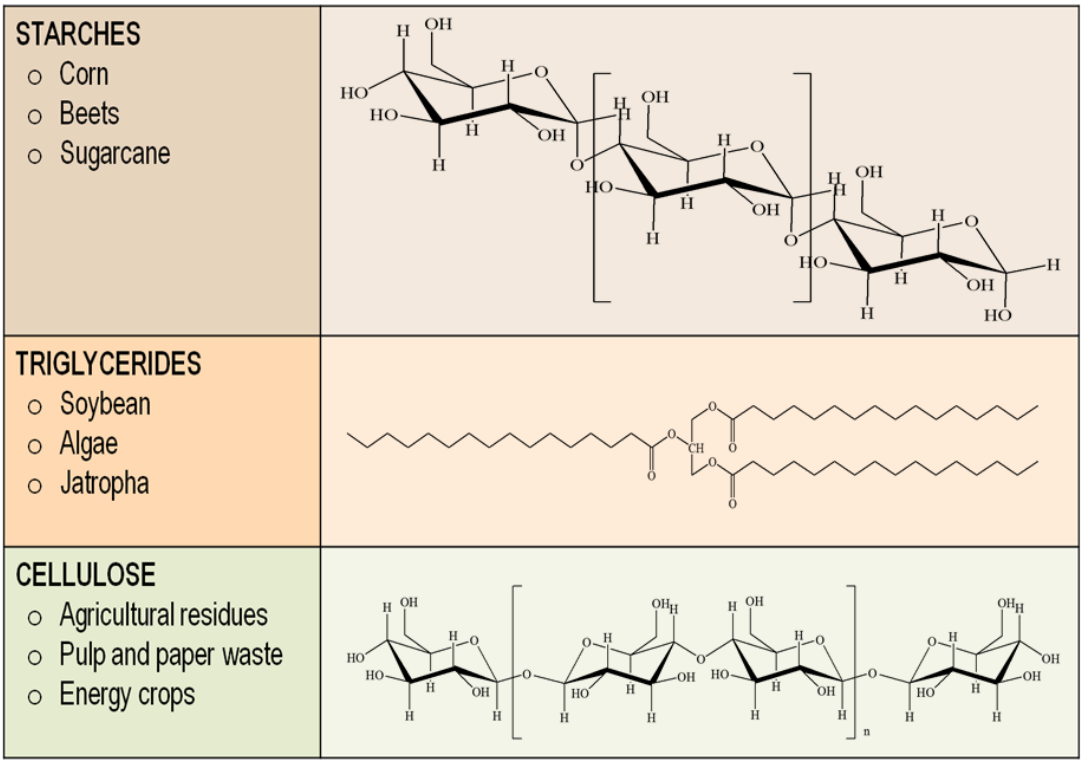


Figure 1.5: The biomass feedstock and their chemical structure (Alonso et al., 2010).

Triglycerides are comprised of fatty acid and glycerol, which could be derived from both animal and plant sources. Alas, triglycerides along with starch are not always present in the crops. Instead, lignocellulosic which contributes structural integrity to plants is always present in biomass fraction. It consists of cellulose, hemicelluloses, and lignin, as illustrated in Figure 1.6.

Cellulose is a crystalline glucose polymer connected by β-glycosidic bond. Thus, it is very difficult to break this type of bond, unless a strong acid/harsher condition is used (Lynd, et al., 1991).

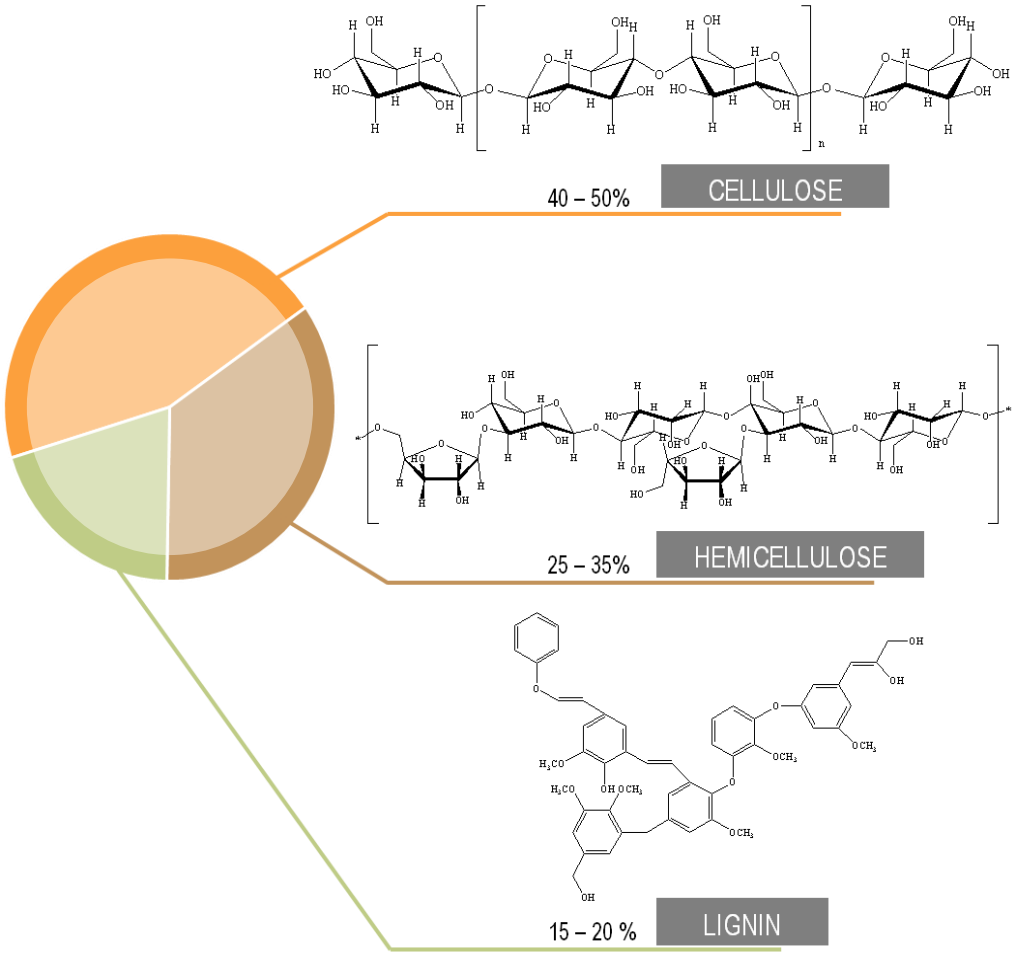


Figure 1.6: Lignocellulosic components in biomass (Alonso, et al., 2010).

However, this condition will favour the formation of HMF, LA, and humins. Hemicellulose is an amorphous polymer that is generally consisting of D-xylose, L-arabinose, D-galactose, D-glucose, and D-mannose, with xylose being the most abundant (Lynd, et al., 1991). Lignin is an amorphous polymer composed of methoxylated phenylpropane structures, such as coniferyl alcohol, sinapyl alcohol, and coumaryl alcohol (Huber, et al., 2006). Lignin which surrounds the hemicellulose and cellulose fractions provide plants with structural rigidity and a hydrophobicvascular system for the transportation of water and solutes (Vanholme, et al., 2008).

Naturally, 170 billion metric tons of biomass is produced per year mainly by photosynthesis while human only consume 3-4% for food and non-food purposes (Röper, 2002). Woody biomass has been identified as largest source of biomass materials despite the fact that essential, yet economical source of sugars could be obtained as compared to corn. Thus, this advancement makes sugars a readily available chemical feedstock for chemicals synthesis. Figure 1.7 demonstrates how biofuels could be derived from different feedstock.

The overabundance of oxygen in sugar's chemical structure could be troublesome especially in selectivity of desired products. In order to lower their oxygen contents, three ways to resolve this problem have been identified (Van Putten, et al., 2013). First method is to eliminate small, highly oxidized carbon molecules, such as CO_2, formaldehyde, and formic acid by means of fermentation to produce ethanol, butanol and CO_2. The second method is hydrogenolysis in which water is formed by removing oxygen from the molecule. The final option is removing water from hexoses. There are some important chemicals that can be derived from dehydration of hexoses in acidic media which have been identified as the basic non-petroleum chemicals; 5-hydroxymethylfurfural (HMF), levulinic acid (LA), and its esters (alkyl levulinates) (Werpy, et al., 2004)

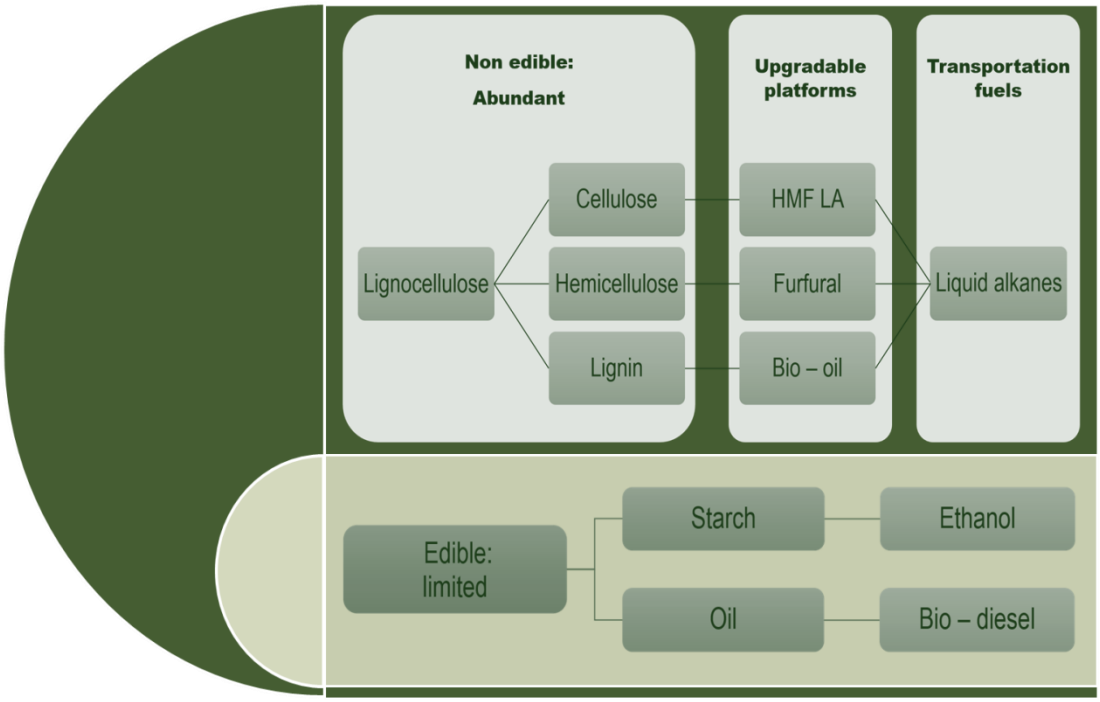


Figure 1.7: Feedstock from biomass and potential as chemical platform for biofuels.

HMF has been identified as a chemical intermediate in biofuel and fine chemicals (Chheda, et al., 2007). HMF stands out among the platform chemicals as it has retained all six carbon atoms. It can be obtained from dehydration of C6 sugars such as glucose and fructose with the presence of acid catalyst, in which the latter is a more reactive substrate (Antal, et al., 1990).The glucose enolyzes in a very low degree and the enolization is a determining step of the HMF formation from glucose. The intricacy to obtain high selectivity and isolated yields render HMF to become costly and thus restrict its potential as a key chemical platform, as illustrated in Figure 1.8.

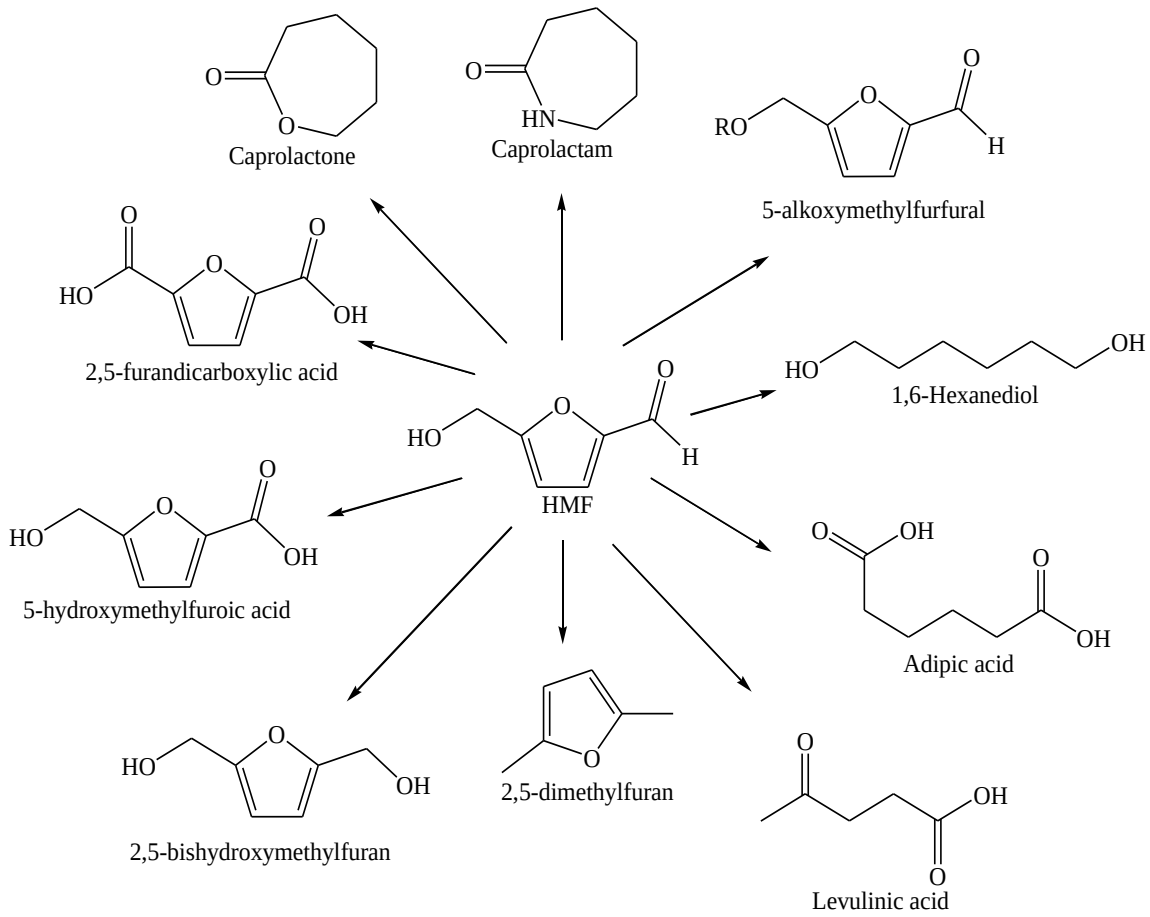


Figure 1.8: Various chemical intermediates from HMF (Van Putten, et al., 2013).

For instance, HMF can be used to produce δ-aminolevulinic acid, an herbicide with a target market of 200-300 lb per year. Remarkably, it also can produce diphenolic acid, a replacement for bisphenol A in polycarbonate production with a target market of 4 billion lb per year. Further rehydration of HMF will produce LA, a highly potential feedstock for herbicide, polymers and petrochemical production. Under alcoholic solvent, sugars can be converted to alkyl levulinates (ALs), commonly used in flavour and fragrance industries and recently has been identified as an additive for gasoline and diesel for transportation fuels (Fagan & Manzer, 2003).

1.6 Mechanism of HMF Formation

In general, the HMF formation from hexoses involves elimination of three molecules of water from the sugar molecule. However, the detail in mechanistic aspect on this conversion is far complicated. Several mechanisms have been proposed in the literature via acyclic and cyclic intermediates.

In acyclic pathways, the formation of a linear 1,2-enediol has been assumed as the rate-limiting step, as depicted in Figure 1.9 (Antal, et al., 1990; Kuster, 1990) which is widely accepted as the intermediate in the aldose-ketose isomerization by the so-called Lobry de Bruyn-Alberda van Ekenstein (LBAE) transformation followed by two consecutive β-dehydrations and a ring closure with a final water elimination to yield HMF (Speck, 1958)

In cyclic pathways, cyclic ketofuranose is a starting form before undergoes the dehydration of the hemiacetal at C2 to form a tertiary carbenium cation. It is followed by two consecutive β-dehydrations in the ring to form HMF. D_2O labeling study verifies this proposed mechanism that irreversible process is taking place after first dehydration as less incorporation of deuterium in HMF structure was observed (Akien, et al., 2012). Thus, it is unlikely for this reaction to proceed via acyclic pathway because it would require the deuterium incorporation during formation of intermediate 3-deoxyglucosone.2,5-anhydro-D-mannose 2,5-anhydro sugar, also refer as chitose, is produced from the first step of D-fructofuranose dehydration. However, since the formation of HMF from chitose was slower than fructose, it was unlikely to become an intermediate (Anet, 1964).

Other researcher was using 2,5-anhydro-L-idose as an intermediate to form HMF (Dekker, 1958). They found that 2,5-anhydro-L-idose reacts 200-300 times faster

than glucose. The formation of C1-aldehyde once undergo dehydration at C2 has been identified as a factor for subsequent dehydration step. ^{13}C NMR study reveals that fructose C-1 forms the carbonyl carbon and fructose C-6 forms the hydroxymethyl carbon of HMF (Zhang & Weitz, 2012). This result confirms plausible mechanism via acyclic and cyclic pathways.

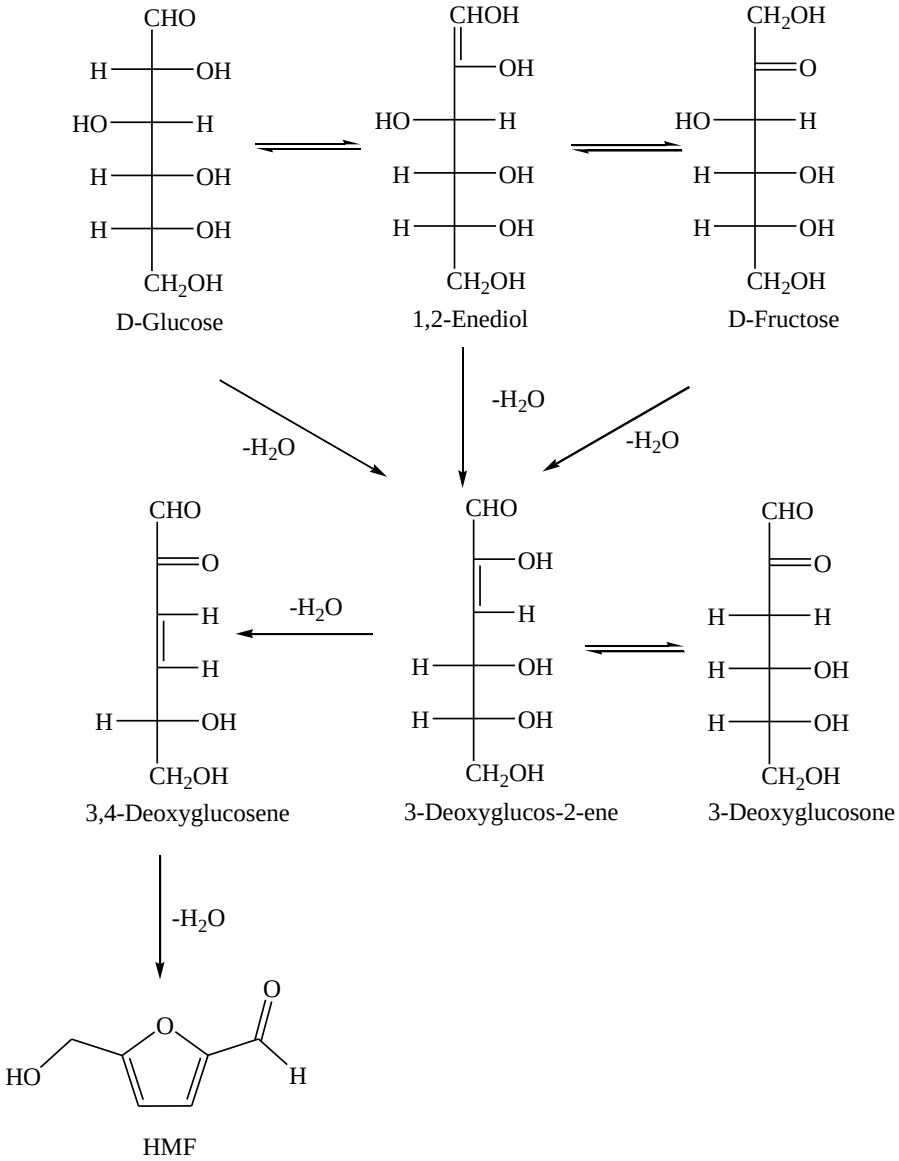


Figure 1.9: Acyclic pathway of HMF formation from hexoses.

The HMF formation could also be achieved by auto-catalysis, especially when using DMSO as a solvent and fructose as a substrate (Amarasekara, et al., 2008). In DMSO, where furanose form is dominant, the O atoms at C1 and C2 are coordinated with DMSO prior to dehydration step, as shown in Figure 1.10.

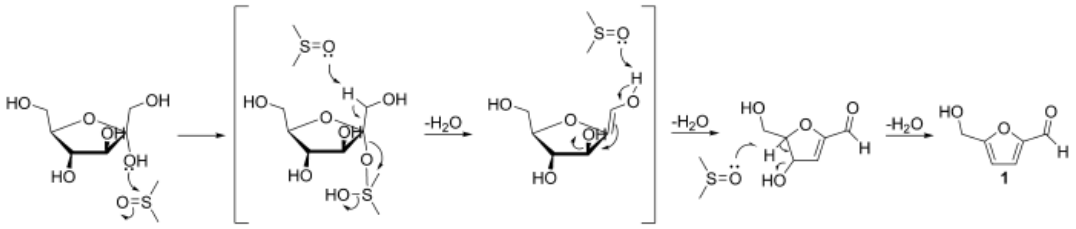


Figure 1.10: Plausible mechanism of fructose dehydration by DMSO as catalyst (Van Putten, et al., 2013).

Besides fructose, glucose could also be converted to HMF and is considered more attractive as the price is cheaper than fructose and could be obtained from lignocellulosic biomass. But, it reacts slower because isomerization of glucose into fructose is necessary before dehydration step to obtain HMF. In the absence of catalyst, glucose conversion in hot compressed water reported the formation of fructose along with HMF. In contrast, no glucose was detected when fructose was treated as a substrate (Watanabe, et al., 2005). This trend even noticeable when operate under higher pressures and temperatures (Aida, et al., 2007). Watanabe et al. (2005) claimed that by using α-TiO_2, this catalyst acts as bifunctional acid-base catalyst. Nevertheless, it enhanced glucose conversion (97% vs 40%) but not HMF yields (22%), as compared to without catalyst. Therefore, it suggests that α-TiO_2 behave as base catalyst that isomerizes glucose into fructose.

Yan et al. (2009) investigated sulphated ZrO_2 and ZrO_2-Al_2O_3 as heterogeneous catalyst in this conversion. By using fructose as a substrate, the yield of HMF was similar whether the catalyst was used or not. In comparison, when using glucose as starting material, 48% yield of HMF was obtained with the presence of sulphated ZrO_2-Al_2O_3 catalyst and only 4% of HMF without the presence of catalyst. This observation indicates that this catalyst acts as base catalyst that catalyzes glucose isomerization.

It can be concluded that fructose is more reactive to be converted into HMF compare to glucose as the latter requires base catalyst to promote isomerization. Thus, mechanism via cyclic pathway is more likely to take place, as demonstrated in Figure 1.11, since acyclic pathway, so far, does not provide sufficient evident why there is a large gap on catalytic activity and selectivity between glucose and fructose if 1,2-enediol is their common intermediate (Van Putten, et al., 2013).

Besides dehydration, this transformation also involves isomerization, fragmentation, and condensation to yield by-products such as levulinic acid, formic acid, 5-methyl-2-furaldehyde, α-angelica lactone, humins, and many more (Antal, et al., 1990). In fact, aqueous and non-aqueous dehydration processes led to about 37 products.

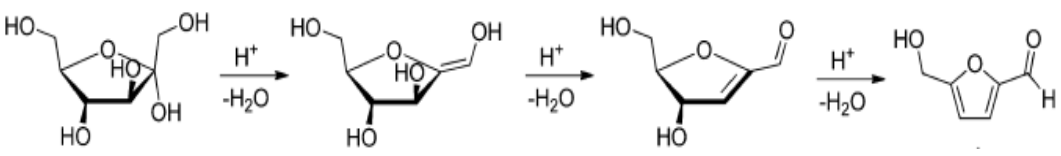


Figure 1.11: Cyclic pathway of HMF formation from fructose (Van Putten, et al., 2013).

1.6.1 HMF Formation from Dehydration of Hexoses by Heterogeneous Catalysts

More efficient and selective formation of HMF can be achieved from dehydration of aldohexose (fructose). Fructose can be obtained from acid hydrolysis of sucrose, inulin and isomerisation of glucose by using homogeneous and heterogeneous acid catalysts. Since heterogeneous acid catalysts is more interesting in term of environmental aspect, the author will be focusing on the use of heterogeneous catalysts.

1.6.1 (a) Aqueous Solvent

Niobic acid and niobium phosphate have been studied as Brønsted heterogeneous catalysts to dehydrate fructose into HMF in aqueous media (Carniti, et al., 2006). Operated at continuous reactor, temperature ranging from 90-110 °C, and pressure from 2-6 bar, niobium phosphate showed better catalytic activity than niobic acid due to effective acidity on the surface. HMF selectivity was higher under flow reactor compare to batch reactor as the fructose concentration increased. Later, they claimed that no side-product from rehydration such as levulinic acid and formic acid were detected. But, the formation of humin was traced.

Carlini et al. (2004) compared vanadyl phosphate (VOP) and substituted VOP with trivalent metals; M^{3+}-VOP (M = Fe^{3+}, Cr^{3+}, Ga^{3+}, Mn^{3+}, Al^{3+}) for this reaction. VOP itself gave turn-over frequency (TOF) ~200 mmol HMF/g_{cat}h. By substituting Fe^{3+} in the VOP framework, the TOF reached 376. Interestingly, even at higher fructose concentration (40 wt.%), the authors claimed neither insoluble polymeric by-products nor HMF rehydration compounds (levulinic acid and formic acid) were formed.

Qi et al. (2009) tested sulfated zirconia (ZrP) at different calcinations temperatures (500, 600, and 700 °C). They found that in aqueous media, the best calcinations temperature was 600 °C, to give 79.9% fructose conversion and 36% HMF. Asghari & Yoshida (2006) prepared amorphous and crystalline zirconia phosphate catalysts and tested in sub-critical water at 240 °C. As a result, 80% fructose was converted and 61% selectivity of HMF was achieved. They found that no correlation between physicochemical properties and catalytic performances.

Series of layered zirconium- and titanium-hydrogenphosphates in the α and γ structural arrangements, their corresponding α and γ-layered pyrophosphates as well as cubic pyrophosphates were prepared (Benvenuti, et al., 2000). Cubic zirconium pyrophosphate was the most active catalyst (TON = 8.9 mmol HMF/g_{cat}h) followed by γ-titanium phosphate (TON = 6.1 mmol HMF/g_{cat}h). As the reaction time was prolonged to increase fructose conversion, HMF selectivity dropped significantly. The problem was alleviated by applying continuous extraction with methyl isobutyl ketone (MIBK).

An example of mixed-oxides has been demonstrated by Stošić et al. (2012). The preparation of ceria-niobic via coprecipitation methods resulting amphoteric and possess redox centers on their surface. These properties are dependent on the ratio of ceria-to-niobic. The increase of niobic contents increased the catalytic activity as the acid amount of niobic was the highest compare to ceria and ceria-niobic mixed oxides.

Glucose shows to have much lower selectivity for HMF formation because of its more stable ring structure, which hinders its ability to form the acyclicenediol intermediate (Kuster, 1990). This mechanism requires glucose to isomerize to fructose prior to dehydration to HMF.

Zeolite-Y has been tested as heterogeneous catalyst in aqueous glucose solutions (Lourvanij & Rorrer, 1993). Although quantitative glucose conversion was achieved, only <10% of HMF yield was attained while the presence of levulinic acid, formic acid, and coke deposition were also detected.

Chareonlimkun et al. (2010) studied TiO_2, ZrO_2 and SO_4–ZrO_2 in hot compressed water at 473-673 K to catalyze HMF formation. TiO_2 (27% yield) and SO_4–ZrO_2 (22% yield) were identified as the most active catalyst to produce HMF while ZrO_2 was efficient in isomerization. The selection of salt precursor (nitrates and chlorides), sulfur-doping contents, and calcinations temperature (773, 873, and 973 K) of the catalysts were the important factors that influence catalytic activity. Nitrates-based precursor was inferior compared to chlorides-based precursor. The best calcinations temperature was 773 K in which different calcinations temperatures caused different portions of phase to form, as confirmed by XRD. This phase strongly affects acidity-basicity of the catalysts thus affect catalytic performances, as confirmed by NH_3-TPD and CO_2-TPD.

Heterogeneous Lewis acid catalyst niobic acid, $Nb_2O_5.nH_2O$, has been tested in glucose conversion into HMF in water (Nakajima, et al., 2011). NbO_4 tetrahedra, Lewis acid sites, on niobic acid surface immediately form NbO_4-H_2O adducts in the presence of water. 12.1% of HMF yield was yielded while $Na^+/Nb_2O_5.nH_2O$ without Brønsted acid sites showed similar yield (12.4%). This indicates the formation of HMF under this catalyst system was catalyzed by Lewis acid site alone, as depicted in Figure 1.12.

The formation of unknown products was detected but could not be identified by HPLC and GC-MS. Significant decrease of unknown products was observed when