DEOXYGENATION OF SUGAR TO PETROCHEMICALS

THADA PHOTIVIHOK

THOMAS HENRY HARRIES

WATANA KANGWANWATANA

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Students Mr. Thada Photivihok ID: 50050557

Mr. Thomas Henry Harries ID: 50050561

Mr. Watana Kangwanwatana ID: 50050563

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Advisor Assoc. Prof. Dr. Tawan Sooknoi

ABSTRACT

Deoxygenation of sugar over some acid catalysts to petrochemical products including HMF is done in the reaction using sulfuric acid, zeolite Y, zeolite beta and amberlite 200C. The reaction is carried out by dissolving sugar with water. Then the acid catalyst is added and the reaction mixture is heated up at 110°C for 1, 2, 3,4,5,6 and 7 hours in a closed batch system. As the contact time increased, the condensation/polymerization of protonated HMF can be seen as a dark brown precipitate. The reaction is then cooled and butyl acetate is added as an extracting solvent. The product from the reaction can be identified and determined by gas chromatography (GC). Alternatively, gas chromatography with mass spectroscopy (GC-MS) is used to identify and determine the amount of product for deoxygenation of sugar with acid catalysts. It can be found that 0.25M H_2SO_4 gave a higher HMF yield of approximately 0.27mg/g as compared to that in 0.5M H_2SO_4 that gave HMF yield of approximately 0.13mg/g. This is in reaction with 0.25M H_2SO_4 had a slower condensation/polymerization rate. $CrCl_3$ was added to the reaction to increase the isomeriztion rate of glucose to fructose. The yield of HMF obtained is increased to approximately 2.96mg/g. Zeolite Y and Beta was found to have no conversion of sugar because the sucrose could not diffuse to the pore of Zeolites and be hydrolyzed to glucose and fructose. Amberlite 200C gave the highest HMF yield of 3.53mg/g in this experiment. This is because protonated HMF had a weaker adsorption on Amberlite 200C than that of glucose and fructose. Therefore, side reaction of HMF and by-products are reduced.

Keywords : Deoxygenation of sugar , isomerization, HMF , condensation/polymerization , hydrolysis of sucrose , homogeneous catalyst , heterogeneous catalyst , biomass , table sugar

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Mr. Thada Photivihok
Mr. Thomas Henry Harries
Mr. Watana Kangwanwatana

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CHAPTER 1

INTRODUCTION

1.1 STATEMENT AND SIGNIFICANCE OF THE PROBLEMS

Oil is a liquid fossil fuel that is formed from the remains of marine microorganisms deposited on the sea floor. After millions of years the deposits end up in rock and sediment where oil is trapped in small spaces. It can be extracted by large drilling platforms. Oil is the most widely used fossil fuel. Crude oil consists of many different organic compounds which are transformed to products in a refining process. The wide-scale use of fossil fuels, coal at first and petroleum later, to fire steam engines, enabled the Industrial Revolution. At the same time, gas lights using natural gas or coal gas were coming into wide use. The invention of the internal combustion engine and its use in automobiles and trucks greatly increased the demand for gasoline and diesel oil, both made from fossil fuels. To this invention, oil consumption per year by country indicates a tremendous affects to the world non-renewable resources.

By the year of 2006, Thailand was ranked #8 for the highest oil consumption 928,600 bbl/day in contrast with 156,731.9 bbl/day of the average oil consumption by country. Hence, sooner or later fossil fuels will run out eventually. In addition to solving the problems, scientists and researchers are inclined to develop new source of energy.[1]

Biomass can be an alternative source of energy. The components of interest in biomass are the mono- , di- of polysaccharides. Suitable six-carbon monosaccharide includes fructose, glucose, galactose, mannose and their derivatives. Where glucose is the most economic and preferred monosaccharide even though it is a little bit less reactive than fructose. The polysaccharides and disaccharides are converted into their monosaccharide component(s) and dehydrated to make the 5-HMF structure. [2] HMF can be convert to 2, 5-dimethylfuran (DMF), which is a liquid biofuel that in certain ways is superior to ethanol. Oxidation of HMF also gives 2, 5-furandicarboxylic acid, which has been proposed as a replacement terephthalic acid for the production of plastics.[2]

Table sugar is chosen to be studied due to its structure can easily be dehydrated to petrochemical products. Table sugar is exclusively referred to sucrose. Sucrose is a disaccharide which can be hydrolyzed with the aid of acid catalyst to be monosaccharide including glucose and fructose. Dehydration of glucose and fructose leads to formation of furan compounds such as furfural and HMF, which are essential intermediates for production of many petrochemicals and liquid alkanes[3]

1.2 GOAL AND OBJECTIVES

1.2.1 To obtain petrochemical products from deoxygenation of sugar over homogeneous catalyst such as H_2SO_4, H_2SO_4 with $CrCl_3$ and heterogeneous catalyst such as Zeolite Beta, Zeolite Y and Amberlite 200C.

1.2.2 To understand the effect of reaction time, type and concentration of acid catalysts for conversion of sugar to petrochemical products.

1.3 SCOPE OF THE STUDY

1.3.1 Preparation of acid catalyst

1.3.1.1 Preparation of 0.5M H_2SO_4, 0.25M H_2SO_4

1.3.1.2 Preparation of 0.25M H_2SO_4 with $CrCl_3$

1.3.1.3 Preparation of 5mmol proton and 2mmol proton Amberlite 200C

1.3.1.4 Preparation of Zeolite Beta and Zeolite Y

1.3.2 Reaction testing

1.3.2.1Study on the deoxygenation of sugar over 0.5M H_2SO_4, 0.25M H_2SO_4, 0.25M $H2SO_4$ with $CrCl_3$, 5mmol proton of Amberlite 200C, 2mmol proton of Amberlite 200C, Zeolite Beta and Zeolite Y for 1,2,3,4,5,6 and 7 hours.

1.3.3 Analysis of products

1.3.3.1Determine the product obtained from deoxygenation of sugar by gas chromatography (GC) and gas chromatography with mass spectroscopy (GC-MS)

1.4 EXPECTED RESULT

Providing the modest deoxygenation of HMF (Hydroxymethylfurfural) and its derivatives

Chapter 2

Theory and literature review

2.1 Biomass

For years people have worried about the decreasing amount of fossil fuels on the planet. These fuels, when they are gone, cannot be replaced. As a result several different alternatives have been approached. One of these, which are proving very encouraging, is Biomass Alternative Energy. Biomass energy is renewable source of energy that is found in plants. Plants take energy from the sun in the process of photosynthesis and use it to produce and grow biomass. Biomass is a known product or material that is found in most living things. It can be animal material, bacteria, or plant materials. The oldest example that we have of biomass energy today is wood, which we can burn to produce heat and to create steam which therefore, produces energy. To obtain a large amount of biomass energy, these plants such as wood are burned in internal combustion engines or broilers and this releases the energy that the plant holds. Animal wastes can also be used to produce gases that will serve as biomass energy. The waste will be treated and then burned in order to create electricity. Landfill sites function in the same manner, with the methane gases being used as the biomass. The gases emitted from landfill sites will be treated and burned in order to produce electricity. In some cases, crops themselves are used as biomass, with crops being grown specifically for the purpose of energy production. These crops are known as energy crops, and are used to produce oil. In crops such as oilseed rape, approximately 32% of the plant seed contains oil. These seeds are treated and are then used as biomass energy in order to fuel products and engines. Biomass energy is created when the biomass is collected and burned slowly to create steam. Generators then use the steam to turn it into heat and energy. It's believed that this is a very clean type of natural gas as it requires the plants to absorb the carbon dioxide from the environment before it can be used as a viable energy source. However, there is only so much carbon dioxide that a plant can absorb before it is full. With things such as deforestation, the source of this energy is rapidly being depleted and so, people must first become educated about how effective they are at providing us with the clean energy that is needed in our world[4]. Biomass is made up mainly of the elements carbon and hydrogen; we use technology to free the energy bound up in these chemical compounds.There are several ways of capturing the stored chemical energy in biomass:

-Direct Combustion is the burning of material by direct heat and is the simplest biomass technology and may be very economical if the biomass source is nearby.

-Pyrolysis is the thermal degradation of biomass by heat in the absence of oxygen. Biomass is heated to a temperature between 800 and 1400 degrees Fahrenheit, but no oxygen is introduced to support combustion resulting in the creation of gas, fuel oil and charcoal.

-Anaerobic Digestion converts organic matter to a mixture of methane, the major component of natural gas, and carbon dioxide. Biomass such as water waste (sewage), manure, or food processing waste, is mixed with water and fed into a digester tank without air.

-Gasification biomass can be used to produce methane through heating or anaerobic digestion. Syngas, a mixture of carbon monoxide and hydrogen, can be derived from biomass.

-Alcohol Fermentation fuel alcohol is produced by converting starch to sugar, fermenting the sugar to alcohol, then separating the alcohol water mixture by distillation. Feedstock such as wheat, barley, potatoes, and waste paper, sawdust, and straw containing sugar, starch, or cellulose can be converted to alcohol by fermentation with yeast.

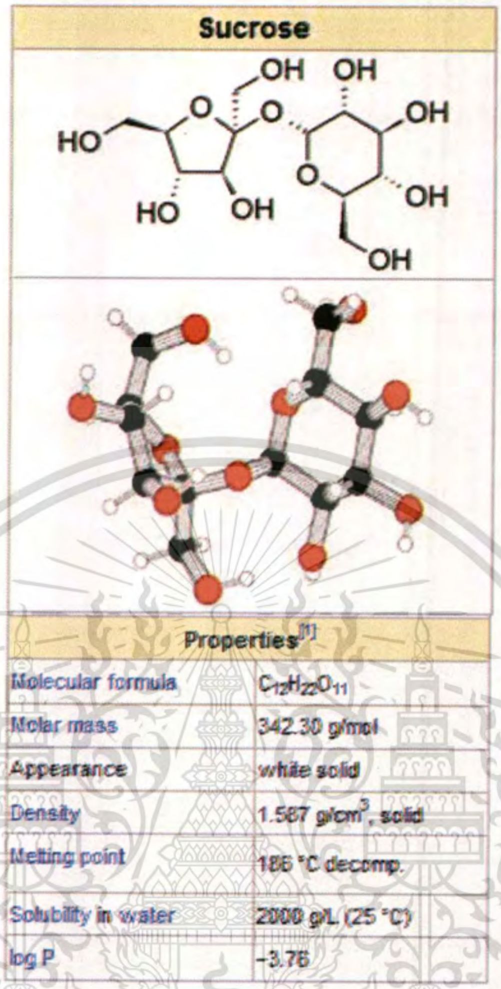
-Landfill Gas is generated by the decay (anaerobic digestion) of buried garbage in landfills. When the organic waste decomposes, it generates gas consisting of approximately 50% methane, the major component of natural gas.

-Congeneration is the simultaneous production of more than one form of energy using a single fuel and facility. Biomass cogeneration has more potential growth than biomass generation alone because cogeneration produces both heat and electricity.[5]

2.2 Table Sugar

2.2.1 Sucrose

Table sugar (sucrose) is one of the biomass which comes from plant sources. Two important sugar crops predominate: sugarcane (Saccharum spp.) and sugar beets (Beta vulgaris), in which sugar can account for 12% to 20% of the plants dry weight. Sucrose is obtained by extraction of these crops with hot water, concentration of the extract gives syrups, from which solid sucrose can be crystallized. Sucrose, a white, odorless, crystalline powder with a sweet taste, it is best known for its role in human nutrition. The molecule is a disaccharide derived from glucose and fructose with the molecular formula $C_{12}H_{22}O_{11}$. Sucrose is a molecule with five stereocenters and many sites that are reactive or can be reactive. The molecule exists as a single isomer. Hydrolysis breaks the glycosidic bond, converting sucrose into glucose and fructose. Hydrolysis is, however, so slow that solutions of sucrose can sit for years with negligible change. If the enzyme sucrase is added, however, the reaction will proceed rapidly. Hydrolysis can also be accelerated with acids, such as cream of tartar or lemon juice, both weak acids. Similarly gastric acidity converts sucrose to glucose and fructose during digestion.[6]



Sucrose

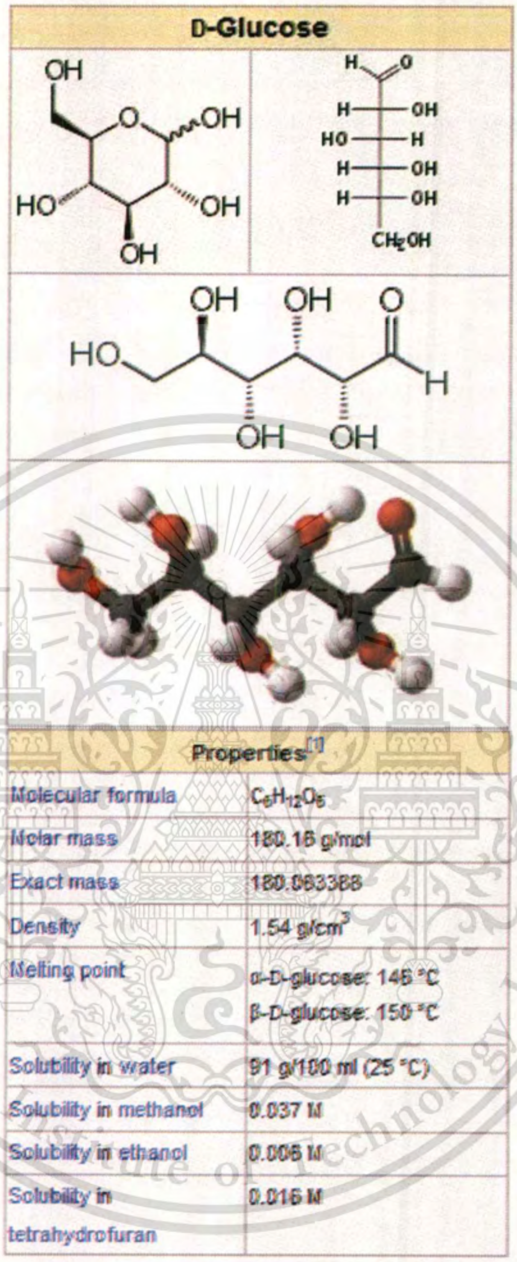
Properties[1]

Molecular formula	$C_{12}H_{22}O_{11}$
Molar mass	342.30 g/mol
Appearance	white solid
Density	1.587 g/cm^3, solid
Melting point	186 °C decomp.
Solubility in water	2000 g/L (25 °C)
log P	-3.76

Figure 2.1 Properties of sucrose

2.2.2 Glucose

Glucose ($C_6H_{12}O_6$), a simple sugar (monosaccharide), is an important carbohydrate in biology. Cells use it as a source of energy and a metabolic intermediate. Glucose is one of the main products of photosynthesis and starts cellular respiration. Starch and cellulose are polymers derived from the dehydration of glucose. Glucose is derived from hexanal, a chain of six carbon atoms terminating with an aldehyde group. The other five carbon atoms each bear alcohol groups. Glucose is called an aldohexose. In solution, glucose mainly exists as the six-membered ring containing a hemiacetal group, which arises from the reaction of the hydroxy group at C-5 and the aldehyde at C-1. Containing five carbon atoms and one oxygen atom, this ring is a derivative of pyran. This cyclic form of glucose is called a glucopyranose, of which two isomers exist.[7]



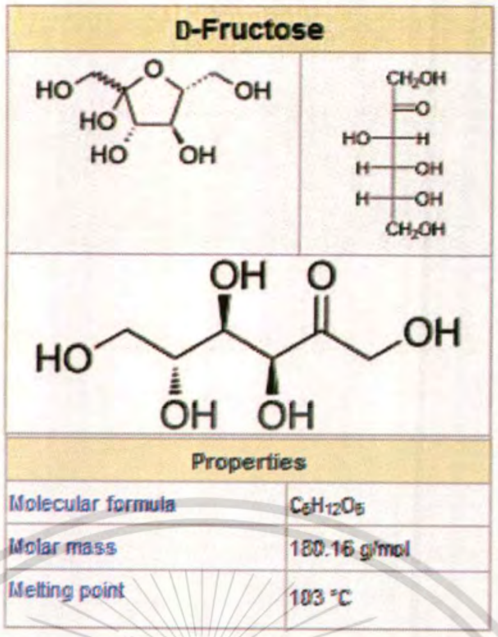
D-Glucose

Properties[1]	
Molecular formula	$C_6H_{12}O_6$
Molar mass	180.16 g/mol
Exact mass	180.063388
Density	1.54 g/cm^3
Melting point	α-D-glucose: 146 °C β-D-glucose: 150 °C
Solubility in water	91 g/100 ml (25 °C)
Solubility in methanol	0.037 M
Solubility in ethanol	0.006 M
Solubility in tetrahydrofuran	0.016 M

Figure 2.2 Properties of D-Glucose

2.2.3 Fructose

Fructose, or fruit sugar, is a simple monosaccharide found in many foods. It is one of the three important dietary monosaccharide along with glucose and galactose. Fructose is a white solid that dissolves in water – it is the most water-soluble of all the sugars.[4] Honey, tree fruits, berries, melons, and some root vegetables contain significant amounts of molecular fructose, usually in combination with glucose, stored in the form of sucrose. Fructose is a component of sucrose. Sucrose is a disaccharide derived from the condensation of glucose and fructose. Fructose is derived from the digestion of table sugar (sucrose). It is an isomer of glucose, i.e. both have the same molecular formula ($C_6H_{12}O_6$), but they differ structurally. Crystalline fructose adopts a cyclic six-membered structure owing to the stability of its hemiketal and internal hydrogen-bonding.Fructose readily dehydrates to give hydroxymethylfurfural (HMF). This process may in future be part of a low-cost, carbon neutral system to produce replacements for petrol and diesel from plantations. Fructose has a greater effect on freezing point depression than disaccharides or oligosaccharides, which may protect the integrity of cell walls of fruit by reducing ice crystal formation. However, this characteristic may be undesirable in soft-serve or hard-frozen dairy desserts. Fructose is a 6-carbon polyhydroxyketone. [8]



D-Fructose

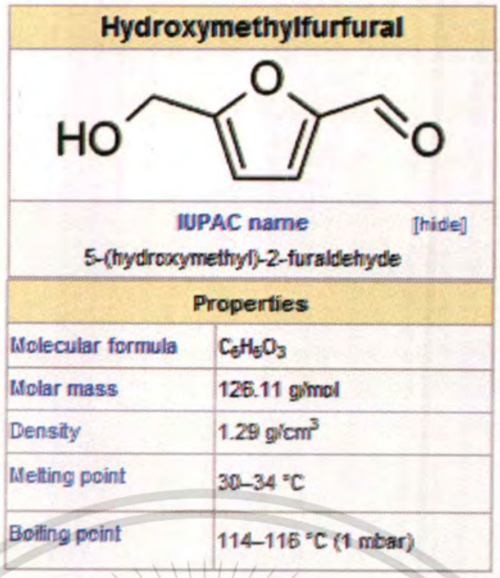
Properties

Molecular formula	$C_6H_{12}O_6$
Molar mass	180.16 g/mol
Melting point	103 °C

Figure2.3 Properties of D-Fructose

2.3 Product HMF

Hydroxymethylfurfural (HMF), also 5-(Hydroxymethyl) furfural, is the interested product which can be obtained from dehydration of table sugar. It is colourless solid and highly water-soluble. The molecule is a derivative of furan, containing both aldehyde and alcohol functional groups. Related to the production of furfural, HMF can be produced from sugars. It arises via the dehydration of fructose, a technology that is evolving through new extraction methods. In this new method, fructose is treated with aqueous hydrochloric acid and the HMF (very water-soluble) is continuously extracted into methyl isobutyl ketone as an organic phase at 180 °C. The aqueous phase is modified with DMSO and PVP, which minimizes the formation of side product. The organic phase is modified with 2-butanol in order to improve the yield of HMF in the organic phase. In an optimized system for fructose (but not raw biomass), conversion is 77%, with half the HMF ending up in the organic phase. Removing the (high boiling) solvents remain an issue. HMF can be converted to 2, 5-dimethylfuran (DMF), which is a liquid biofuel that in certain ways is superior to ethanol.[1] Oxidation of HMF also gives 2, 5-furandicarboxylic acid, which has been proposed as a replacement terephthalic acid for the production of plastics. 5-Hydroxymethyl-2-furfural (5HMF) has been found to bind specifically with intracellular sickle hemoglobin (HbS). Preliminary in vivo studies using transgenic sickle mice showed that orally administered 5HMF inhibits the formation of sickled cells in the blood. HMF is practically not present in fresh food, but it is naturally created in sugar-containing food during heat-treatments like drying or cooking. Along with many other flavor- and colour-related substances, HMF is formed in the Maillard reaction as well as during caramelization. In these foods it is also slowly created during storage. Acid conditions favour generation of HMF. HMF can be found in low amounts in honey, fruit-juices and UHT-milk. Here as well as in vinegars, jams, alcoholic products or biscuits HMF can be used as an indicator for excess heat-treatment. The codex alimentarius standard requires that honey has to have less than 40 mg/kg HMF, tropical honeys must be below 80 mg/kg, to guarantee that the honey has not undergone heating during processing. Fresh honey only has low amounts of HMF – less than 15 mg/kg, depending on pH-value and temperature and age. Higher quantities of HMF are found naturally in coffee and dried fruit. Several types of roasted coffee contained between 300 – 2900 mg/kg HMF. Dried plums were found to contain up to 2200 mg/kg HMF. In dark beer 13.3 mg/kg were found, bakery-products contained between 4.1 – 151 mg/kg HMF. HMF can form in high-fructose corn syrup (HFCS), levels around 20 mg/kg HMF were found, increasing during storage or heating. This is a problem for American beekeepers because they use HFCS as a source of sugar when there are not enough nectar sources to feed honeybees, and HMF is toxic to them. Adding bases such as soda ash or potash to neutralize the HFCS slows down the formation of HMF. Depending on production-technology and storage, levels in food vary considerably. To evaluate the contribution of a food to HMF intake, its consumption-pattern has to be considered. Coffee is the food that has a very high relevance in terms of levels of HMF and quantities consumed. HMF is a natural component in heated food but usually present in low concentrations. The daily intake of HMF may underlie high variations due to individual consumption-patterns. It has been estimated that in a western diet, in the order of magnitude of 5 – 10 mg of HMF are ingested per day from food. In former times, HMF was used in food for flavoring purposes, but in Europe this practice now is suspended. HMF is also found in cigarette smoke. A major metabolite in humans is 5-hydroxymethyl-2-furoic acid (HMFA), which is excreted in urine. HMF can also be metabolized to 5-sulfoxymethylfurfural (SMF), which is highly reactive and can form adducts with DNA or proteins. In vitro tests and studies on rats suggest potential toxicity and carcinogenicity of HMF. In humans, no correlation of intakes of HMF and disease could be demonstrated yet.[2]



Hydroxymethylfurfural

IUPAC name [hide]

5-(hydroxymethyl)-2-furaldehyde

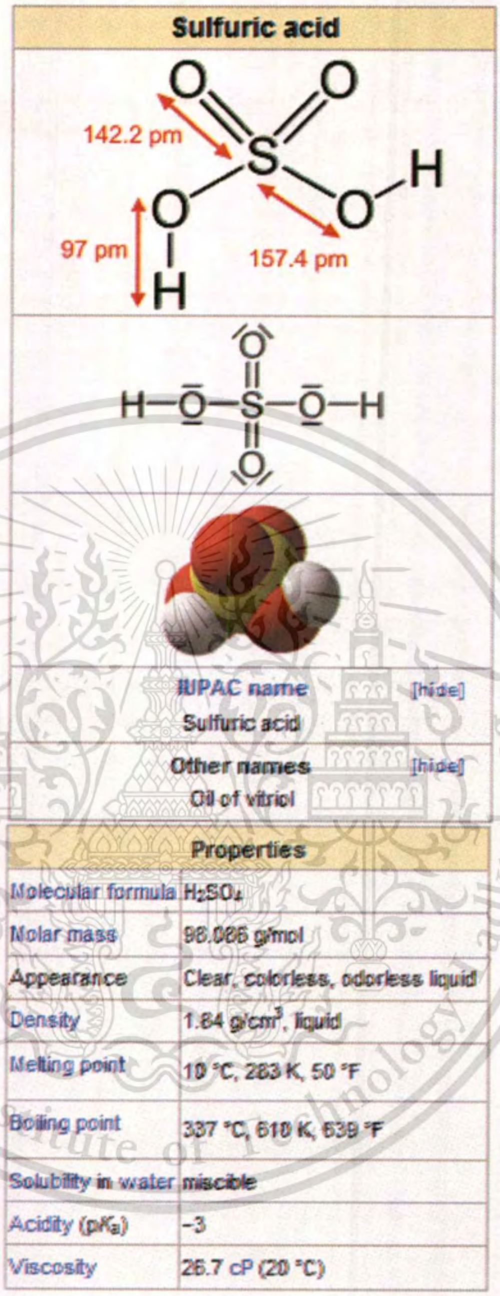
Properties	
Molecular formula	$C_6H_6O_3$
Molar mass	126.11 g/mol
Density	1.29 g/cm^3
Melting point	30–34 °C
Boiling point	114–116 °C (1 mbar)

Figure2.4 Properties of Hydroxymethylfurfural (HMF)

2.4 Acid Catalysts

2.4.1 Sulfuric Acid

Dehydration of sugar to HMF can be performed in sulfuric acid, a homogeneous catalyst. Sulfuric acid is a strong mineral acid with the molecular formula H_2SO_4. Sulfuric acid is soluble in water at all concentrations. Sulfuric acid has many applications, and is a basic substance in the chemical industry. Principal uses include lead-acid batteries for cars and other vehicles, ore processing, fertilizer manufacturing, and oil refining. For concentrated sulfuric acid, when heated, the pure 100% acid loses sulfur trioxide gas, SO_3, until a constant-boiling solution, or azeotrope, containing about 98.5% H2SO4 is formed at 337°C. Concentrated sulfuric acid is a weak acid and a poor electrolyte because relatively little of it is dissociated into ions at room temperature. When cold it does not react readily with such common metals as iron or copper. When hot it is an oxidizing agent, the sulfur in it being reduced; sulfur dioxide gas may be released. Hot concentrated sulfuric acid reacts with most metals and with several nonmetals, e.g., sulfur and carbon. Because the concentrated acid has a fairly high boiling point, it can be used to release more volatile acids from their salts, e.g., when sodium chloride (NaCl), or common salt, is heated with concentrated sulfuric acid, hydrogen chloride gas, HCl, is evolved. Concentrated sulfuric acid has a very strong affinity for water. It is sometimes used as a drying agent and can be used to dehydrate many compounds, e.g., carbohydrates. It reacts with the sugar sucrose, $C_{12}H_{22}O_{11}$, removing eleven molecules of water, H2O, from each molecule of sucrose and leaving a brittle spongy black mass of carbon and diluted sulfuric acid. The acid reacts similarly with skin, cellulose, and other plant and animal matter. When the concentrated acid mixes with water, large amounts of heat are released; enough heat can be released at once to boil the water and spatter the acid. To dilute the acid, the acid should be added slowly to cold water with constant stirring to limit the buildup of heat. Sulfuric acid reacts with water to form hydrates with distinct properties. For diluted sulfuric acid, it is a strong acid and a good electrolyte; it is highly ionized, much of the heat released in dilution coming from hydration of the hydrogen ions . The dilute acid has most of the properties of common strong acids. It turns blue litmus red. It reacts with many metals, releasing hydrogen gas, H_2, and forming the sulfate of the metal. It reacts with most hydroxides and oxides, with some carbonates and sulfides, and with some salts. Since it is dibasic, it forms both normal sulfates and acid sulfates, also called bisulfates or hydrogen sulfates. Sulfuric acid is stable under ordinary conditions of use and storage. Concentrated solutions react violently with water, spattering and liberating heat. Toxic fumes of oxides are released when heated to decomposition. It will react with water or steam to produce toxic and corrosive fumes. It reacts with carbonates to generate carbon dioxide gas, and with cyanides and sulfides to form poisonous hydrogen cyanide and hydrogen sulfide respectively. It is incompatible with water, potassium chlorate, potassium perchlorate, potassium permanganate, sodium, lithium, bases, organic material, halogens, metal acetylides, oxides and hydrides, metals, strong oxidizing and reducing agents and many other reactive substances. It needs to avoid conditions of heat, moisture, and incompatibles. When released into the soil, this material may leach into groundwater. When released into the air, this material may be removed from the atmosphere to a moderate extent by wet deposition. When released into the air, this material may be removed from the atmosphere to a moderate extent by dry deposition.[9]



Sulfuric acid

IUPAC name [hide]

Sulfuric acid

Other names [hide]

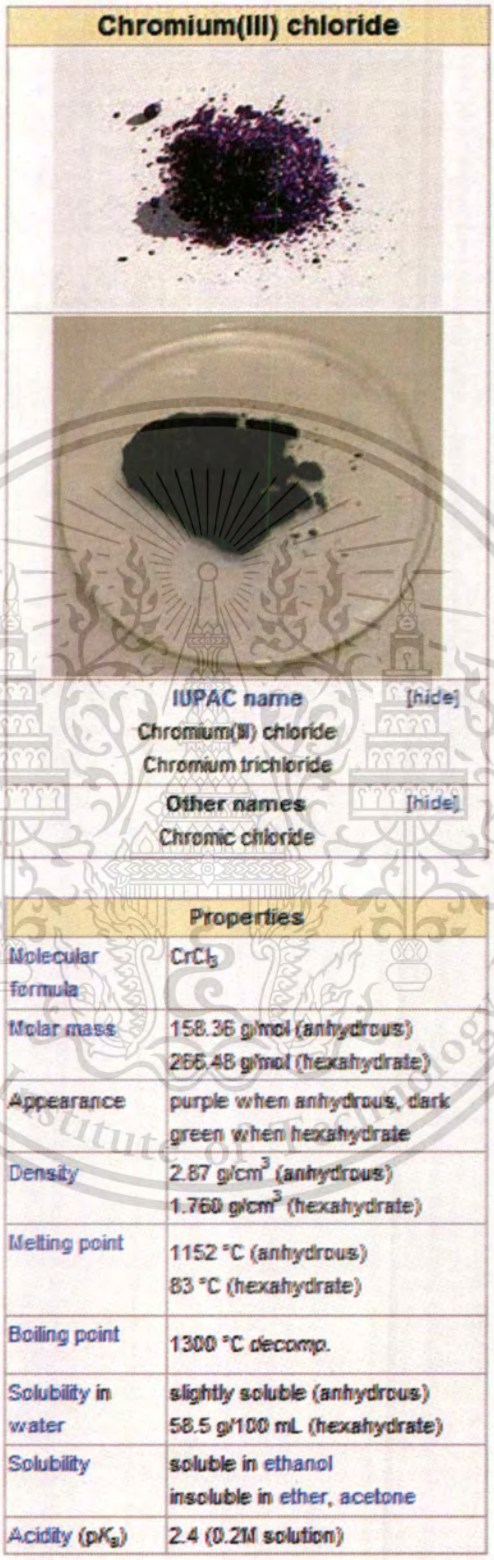
Oil of vitriol

Properties	
Molecular formula	H_2SO_4
Molar mass	98.086 g/mol
Appearance	Clear, colorless, odorless liquid
Density	1.84 g/cm^3, liquid
Melting point	10 °C, 283 K, 50 °F
Boiling point	337 °C, 610 K, 639 °F
Solubility in water	miscible
Acidity (pK_a)	−3
Viscosity	26.7 cP (20 °C)

Figure2.5 Properties of Sulfuric acid (H_2SO_4)

2.4.2 Chromium (III) chloride

Chromium (III) chloride can be added to the reaction using sulfuric acid to enhance the isomerization rate. Chromium (III) chloride (also called chromic chloride) is a violet colored solid with the formula $CrCl_3$. The most common form of $CrCl_3$ sold commercially is a dark green hexahydrate with the formula $[CrCl_2\ (H_2O)_4]Cl._2H_2O$. Two other hydrates are known, pale green $[CrCl(H_2O)_5]Cl_2.H_2O$ and violet $[Cr(H_2O)_6]Cl_3$. This unusual feature of chromium(III) chlorides, having a series of $[CrCl_{3n}(H_2O)n]_z^+$, each of which is isolable, is also found with other chromium(III) compounds. Anhydrous chromium (III) chloride adopts the YCl_3 structure, with Cr_3^+ occupying two thirds of the octahedral interstices in every other layer of a pseudo-cubic close packed lattice of Cl^- ions. The absence of cations in alternate layers leads to weak bonding between adjacent layers. For this reason, crystals of $CrCl_3$ cleave easily along the planes between layers, which results in the flaky appearance of samples of chromium (III) chloride. $CrCl_3$ is a Lewis acid, classified as "hard" according to the Hard-Soft Acid-Base theory. It forms a variety of adducts of the type $[CrCl_3L_3]_z$, where L is a Lewis base. Like most chromium (III) compounds, $CrCl_3$ is chemically inert but its neighboring redox state chromium (II) is reactive. Thus, $CrCl_3$ and its complexes generally react only sluggishly in the absence of a reducing agent capable of reducing Cr_3^+ to Cr_2^+. With the presence of some chromium (II), however, solid $CrCl_3$ dissolves rapidly in water. Similarly, ligand substitution reactions of solutions of $[CrCl_2\ (H_2O)_4]^+$ are accelerated by chromium(II) catalysts. Although trivalent chromium is far less poisonous than hexavalent, chromium salts are generally considered toxic.[10]



Chromium(III) chloride

IUPAC name [hide]

Chromium(III) chloride

Chromium trichloride

Other names [hide]

Chromic chloride

Properties	
Molecular formula	$CrCl_3$
Molar mass	158.36 g/mol (anhydrous) 266.48 g/mol (hexahydrate)
Appearance	purple when anhydrous, dark green when hexahydrate
Density	2.87 g/cm^3 (anhydrous) 1.760 g/cm^3 (hexahydrate)
Melting point	1152 °C (anhydrous) 83 °C (hexahydrate)
Boiling point	1300 °C decomp.
Solubility in water	slightly soluble (anhydrous) 58.5 g/100 mL (hexahydrate)
Solubility	soluble in ethanol insoluble in ether, acetone
Acidity (pK_a)	2.4 (0.2M solution)

Figure 2.6 Properties of Chromium (III) Chloride

2.4.3 Zeolite Y

Some heterogeneous catalysts are then introduced for the dehydration of sugar to HMF. Firstly, Zeolite Y was introduced. Zeolite Y exhibits the FAU (faujasite) structure. It has a 3-dimensional pore structure with pores running perpendicular to each other in the x, y, and z planes similar to LTA, and is made of secondary building units 4, 6, and 6-6. The pore diameter is large at 7.4Å since the aperture is defined by a 12 member oxygen ring, and leads into a larger cavity of diameter 12Å. The cavity is surrounded by ten sodalite cages (truncated octahedra) connected on their hexagonal faces. The unit cell is cubic (a = 24.7Å) with Fd-3m symmetry. Zeolite Y has a void volume fraction of 0.48, with a Si/Al ratio of 2.43. It thermally decomposes at 793°C. Zeolite Y is synthesized in a gelling process. Sources of alumina (sodium aluminate) and silica (sodium silicate) are mixed in alkaline (NaOH) aqueous solution to give a gel. The gel is then usually heated to 70-300°C to crystallize the zeolite. The zeolite is present in Na^+ form and must be converted to acid form. To prevent disintegration of the structure from acid attack, it is first converted to the NH_4^+ form before being converted to acidic form. If a hydrogenation metal such as platinum is needed, it is deposited via impregnation or ion exchange. The most important use of zeolite Y is as a cracking catalyst. It is used in acidic form in petroleum refinery catalytic cracking units to increase the yield of gasoline and diesel fuel from crude oil feedstock by cracking heavy paraffins into gasoline grade napthas. Zeolite Y has superseded zeolite X in this use because it is both more active and more stable at high temperatures due to the higher Si/Al ratio. It is also used in the hydrocracking units as a platinum/palladium support to increase aromatic content of reformulated refinery products. Zeolite-Y is a man-made crystalline mineral that is most often found in industry; used for filtering, processing and absorbing chemicals in industrial manufacturing processes.[11]

2.4.4 Zeolite Beta

Secondly, Zeolite Beta was introduced. It is a molecular sieve zeolite with Si/Al ratious from 10 to 100 or higher, with different surface characteristics. In contrast to the "low" and "intermediate" silica zeolites, representing heterogeneous hydrophilic surfaces within a porous crystal, the surface of the high silica zeolites is more homogeneous with an organophilic-hydrophobic selectivity. They adsorb stronger the less polar organic molecules and only weakly interact with water and other polar molecules.

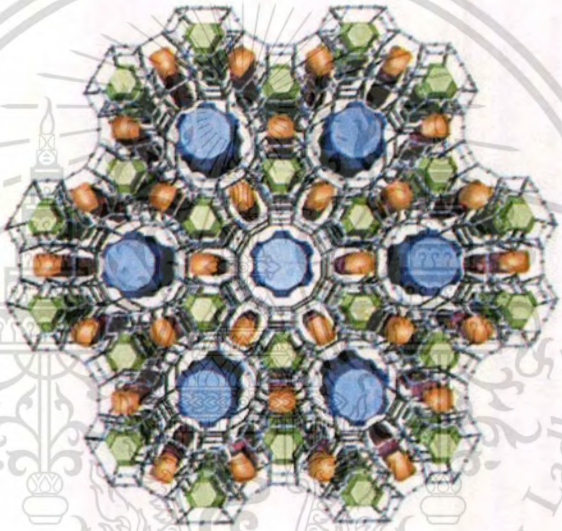


Figure 2.7 Tiling representation of the structure of the zeolite L (LTL). Blue tiles are channels in the structure running along direction of the crystallographic c axis.

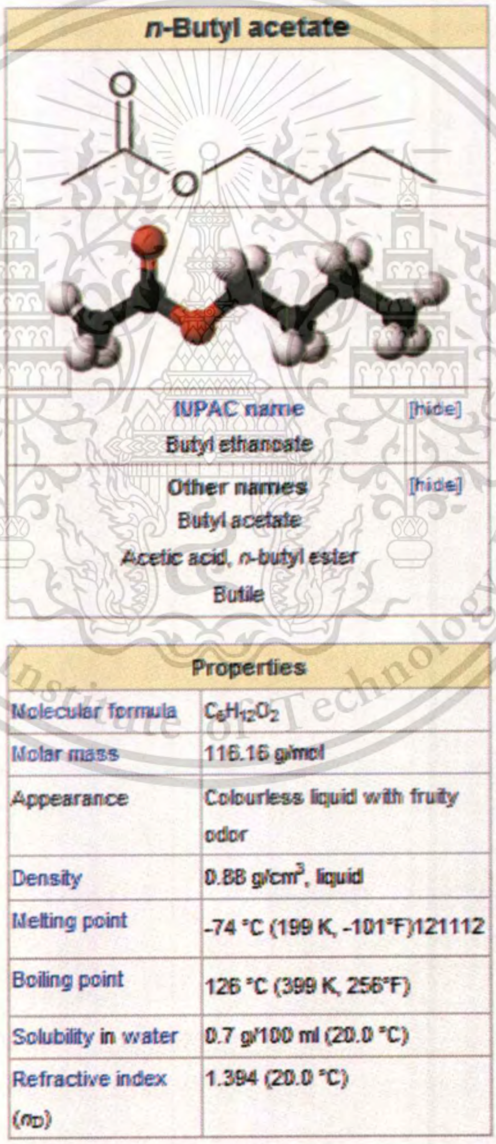
In addition to this novel surface selectivity, the high silica zeolite compositions still contain a small concentration of aluminum in the framework and the accompanying stoichiometric cation exchange sites. Thus, their cation exchange properties allow the introduction of acidic OH- groups via the well known zeolite ion exchange reactions, essential to the development of acid hydrocarbon catalysis properties.[12]The structure of zeolite beta was only recently determined because the structure is very complex and interest was not high until the material became important for some dewaxing opertions. Zeolite beta consists of an intergrowth of two distinct structures termed Polymorphs A and B. The polymorphs grow as two-dimensional sheets and the sheets randomly alternate between the two. Both polymorphs have a three dimensional network of 12-ring pores. The intergrowth of the polymorphs does not significantlyaffect the pores in two of the dimensions, but in the direction of the faulting, the pore becomes tortuous, but not blocked. The two hypothetical polymorphs are depicted here.[13]

2.4.5 Amberlite

Lastly, Amberlite 200C was introduced. It is the tradename of a range of ion-exchange resins. Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and thus acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. Each resin has a distinct number of mobile ion sites that set the maximum quantity of exchanges per unit of resin.[14]

2.5 Butyl Acetate

An extractant is needed to extract the product (HMF) from the reaction using the acid catalysts mentioned above. Acetate is the ester that an organic group replaces a hydrogen atom in -OH group of acetic acid through reaction (typically condensation) with alcohols. Condensation is the reaction in which two molecules having -OH groups are joined with eliminating a water molecule from their -OH groups. The term acetate is also for the salt that one or more of the hydrogen atoms of acetic acid are replaced by one or more cations of the base, resulting in a compound containing the negative organic ion of CH3COO$^-$. Organic acetates are good solvents for a broad range of resins as they are miscible with almost all common organic liquids. Due to their powerful solvency, high volatility and mild odor, acetates are widely used in the manufacture and in the processing of paints, coatings, adhesives, and printing industry. They have a very low solubility in water and used as extraction solvents for fine chemicals particularly for certain antibiotics. They are also used as components of aroma. They are used as chemical intermediate to manufacture pharmaceuticals, synthetic flavorings, cleaners, and other organic compounds.[15]



***n*-Butyl acetate**

IUPAC name [hide]
Butyl ethanoate

Other names [hide]
Butyl acetate
Acetic acid, *n*-butyl ester
Butile

Properties	
Molecular formula	$C_6H_{12}O_2$
Molar mass	116.16 g/mol
Appearance	Colourless liquid with fruity odor
Density	0.88 g/cm^3, liquid
Melting point	-74 °C (199 K, -101°F)121112
Boiling point	126 °C (399 K, 258°F)
Solubility in water	0.7 g/100 ml (20.0 °C)
Refractive index (n_D)	1.394 (20.0 °C)

Figure 2.8 Properties of n-butyl acetate[16]

2.5 LITERATURE REVIEW

2.5.1 Dehydration of Fructose to 5-Hydroxymethylfurfural in sub- and supercritical acetone

HMF is analyzed by HPLC. It is successfully obtained by dehydration of fructose over sulfuric acid. The solvent used is a composition of acetone with water. Four different effect are studied: (i) temperature, it was found that the highest yield of HMF obtained is at low temperature and high residence time, (ii) pressure, it was found that pressure had no significant changes to the yield of HMF, (iii) catalyst concentration, it was found that higher yield of HMF can be obtained as the acid concentration is increased and (iv) solvent composition, it was found that 0% of acetone give the highest yield of HMF.[17]

2.5.2 Selective Conversion of Fructose to 5-Hydroxymethylfurfural Catalyzed by Tungsten Salts at Low Temperature

HMF is analyzed by H NMR. It is successfully obtained by dehydration of fructose with an ionic liquid butylmethyl imidazolium chloride and metal chloride catalysts which are $CrCl_2$, CrC_{l3}, $PdCl_2$, $FeCl_2$, $CuCl_2$, $AlCl_3$, $RuCl_3$, WCl_4, WCl_6, $TiCl_4$ and $ZrCl_4$. The metal chloride is added to increase the conversion of fructose to HMF at low temperature. It was found that WCl_6 give the highest yield of HMF at 50°C.[18]

2.5.3 Syntheses of 5-Hydroxymethylfurfural and Levoglucose by Selective Dehydration of Glucose Using Solid Acid and Base Catalyst

HMF is analyzed by HPLC. It is successfully obtained by dehydration of glucose and fructose over acid catalyst. Three different chemicals were differed from this experiment: (i) the acid catalyst was Amberlyst-15, (ii) glucose is isomerized to fructose by hydrotalcite and (iii) glucose and fructose were dissolved in DMF.[19]

Chapter 3

Experimental Detail

3.1 Chemicals

1. Acetone (analytical grade) from CARLO ERBA
2. Air Zero (high purity) from TIG
3. Amberlite 200C (analytical grade) from Fluka
4. Butyl Acetate (analytical grade) from LAB-SCAN
5. Chromium (III) chloride (analytical grade) from LAB-SCAN
6. Distilled water
7. Helium gas (high purity) from TIG
8. Hydrogen gas (high purity) from TIG
9. Hydrochloric acid (analytical grade) assay 37% from LAB-SCAN
10. Paraffin Oil
11. Phenolphthalein
12. Potassium hydrogen phthalate (analytical grade)
13. Sodium hydroxide anhydrous pellets (analytical grade) from CARLO ERBA
14. Sugar
15. Sulfuric acid (assay 98%) from CARLO ERBA
16. Zeolite Beta (analytical grade) from TOSHO
17. Zeolite Y (analytical grade) from TOSHO

3.2 Apparatus and instruments

1. Beaker 50, 100, 250 and 500 ml
2. Buchner Flask
3. Burette 50 ml
4. Clamp
5. COD test tube
6. Dropper
7. Erlenmeyer Flask 250 ml
8. Filter paper: 5B 70mm
9. Furnace: Vecstar
10. Gas Chromatography: HEWLETT 5890 PACKARD Series II
11. Gas Chromatography-Mass Spectrometry
12. Glass Funnel
13. Litmus paper
14. Magnetic bar
15. Mass balance: Sartorius LP 1200S
16. Measuring Cylinder 10 ml
17. Micro Pipette: RAININ
18. Micro Syringe: HAMILTON
19. Oven
20. Pipette 5 and 10 ml
21. Stand
22. Spatula
23. Suction pump: BUCHI B-169
24. Test tube rack
25. Thermostat and hot plate stirrer: IKA RCT Basic
26. Volumetric Flask 100, 500ml
27. Vial

28. Watch glass

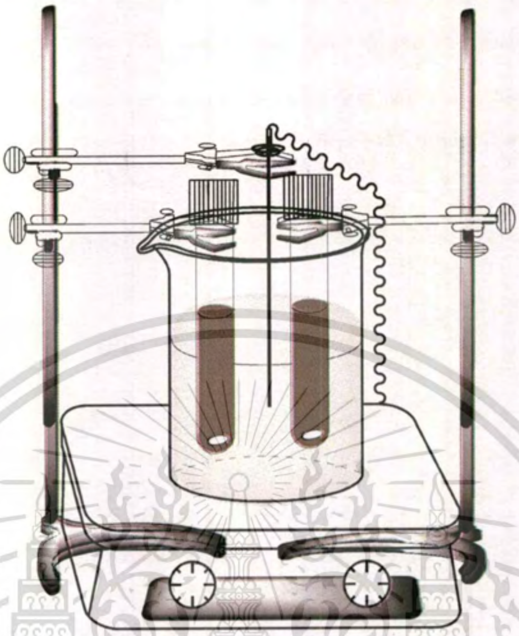


Figure3.1 demonstrating the close batch reaction system

3.3 Experimental Detail

3.3.1 Preparation of acid catalyst

3.3.1.1 Preparation of 0.5M H_2SO_4

0.5M H_2SO_4 was prepared by pipette 2.8ml of 98% assay H_2SO_4 solution into a 100ml volumetric flask (Appendix A). Then the volumetric flask is made-up with distilled water.

3.3.1.2 Preparation of 0.25M H_2SO_4

0.25M H_2SO_4 was prepared by pipette 1.4ml of 98% assay H_2SO_4 solution into a 100ml volumetric flask (Appendix A). Then the volumetric flask is made-up with distilled water.

3.3.1.3 Preparation of acidic Amberlite 200C

Commercially obtained acidic Amberlite resin, 50 grams was ion-exchanged by adding 500ml of 0.5M HCl solution. The mixture was then stirred with a magnetic bar at 600rpm and ambient temperature for 14 hours. The ion-exchanged resin is then filtrated with a Buchner flask, and rinsed with distilled water and then dried in an oven at 100°C for 5 hours. The dried resin was collected and the amount of proton per 1 gram of the resin was determined by back titration. In practice, 1 gram of acidic Amberlytst 200C was added with 10.8ml of 0.41M NaOH in 250ml Erlenmeyer flask. Phenolphthalein was added as an indicator, and then the mixture was titrated with 0.1M HCl until the purple color becomes colorless (Appendix A).

3.3.1.4 Preparation of Zeolite Beta and Zeolite Y

Zeolite Beta and Zeolite Y were calcined in a horizontal tube furnace under flow of air zero at 500°C with heating rate of 3°C per min and hold for 5 hours before testing.

3.3.2 Reaction testing of acid catalyst

3.3.2.1 Reaction testing of 0.5M H_2SO_4

The reaction mixture was prepared by adding 7 grams of sugar with 80.5 grams of 0.5M H_2SO_4 in a 250ml beaker. To ensure that the sugar is totally dissolved, the solution is then stirred with a magnetic bar 800rpm for 20minutes. 10ml of the mixture was pipetted into 7 COD test tubes and then sealed perfectly with a cap. The mixture was then heated at 110°C in a paraffin oil bath for 1, 2, 3, 4, 5, 6 and 7 hours. After reaction, the tubes were cooled in a refrigerator for 3 hours. After being cooled, 1ml of butyl acetate was pipette into each of the cooled COD test tube. The tubes were then shaken and left standing overnight for the mixture to separate into two layers. The top organic layer of the solution was later collected with a dropper into a vial. The extracted layer was then stored away from light at ambient temperature for future analysis.

3.3.2.2 Reaction testing of 0.25M H_2SO_4

For the reaction using 0.25M H_2SO_4, the above procedure (3.3.2.1) was repeated but 0.25M H_2SO_4 was used instead of 0.5M H_2SO_4.

3.3.2.3 Reaction testing of 0.25M H_2SO_4 with $CrCl_3$

For the reaction using 0.25M H_2SO_4 with $CrCl_3$, the above procedure (3.3.2.1) was repeated but 0.25M H_2SO_4 was used instead of 0.5M H_2SO_4 and 0.252 gram of $CrCl_3$ was added.

3.3.2.4 Reaction testing of Zeolite Beta

The reaction mixture was prepared by adding 1 gram of sugar, approximately 11.21 grams (Appendix C) of distilled water and 4.37 grams of Zeolite Beta (Appendix A). Then the reaction mixture was then applied into 7 COD test tubes. The mixture was then heated at 110°C while stirring with a magnetic bar at 700rpm for a completed reaction of the system for 1, 2, 3, 4, 5, 6 and 7 hours. After reaction, the tubes were then cooled in a refrigerator for 3 hours. After being cooled, 1ml of butyl acetate was pipetted into each of the cooled COD test tube. The tubes were then shaken and left standing overnight for the mixture to separate into two layers. The top layer of the solution was later collected with a dropper into a vial. The extracted layer was then stored away from light at ambient temperature for future analysis.

3.3.2.5 Reaction testing of Zeolite Y

For the reaction using Zeolite Y, the above procedure (3.3.2.4) was repeated but 1.3658 grams of Zeolite Y (Appendix A) was used instead of 4.37 grams of Zeolite Beta.

3.3.2.6 Reaction testing of Amberlite 200C (2mmol proton)

For the reaction using Amberlite 200C (2mmol proton), the above procedure (3.3.2.4) was repeated but 0.683 grams of Amberlite 200C (2mmol proton) was used instead of 4.37 grams of Zeolite Beta.

3.3.2.7 Reaction testing of 5mmol proton Amberlite 200C

For the reaction using 5mmol proton Amberlite 200C, the above procedure (3.3.2.6) was repeated but 1.65 grams of Amberlite 200C (5mmol proton) was used instead of 0.683 grams of Amberlite 200C (2mmol proton) as well as stirring rate at 1200rpm instead of 700rpm because Amberlite 200C (5mmol proton) was too heavy to be in suspension.

3.3.3 Analysis

0.5 μl of the extracted butyl acetate layer are taken by a micro syringe. Then the extracted layer was injected to the GC via heated injection port. The GC operating conditions are as following:

Column	DB-5.625
Diameter (mm)	0.25
Length (m)	30
Column head pressure (psi)	15
Linear velocity (cm/s)	30
Carrier gas	He
Injection temperature (^{O}C)	250
Detector temperature (^{O}C)	180
Oven	
• **Temperature (^{O}C)**	40
• **First hold time (min)**	5
• **Heating rate (^{O}C/min)**	10
• **Final Temperature (^{O}C)**	180
• **Second hold time (min)**	15
• **Total Time (min)**	34

The standard used for calculating the yield of all products was THF 0.5875%w (due to a similar molecular weight to HMF and its derivatives). 0.5170 grams of THF was added in a 50ml beaker. Then 1ml butyl acetate was pipetted to the beaker. The solution was then stirred with a magnetic bar at 500rpm and ambient temperature. 0.5µl of the solution was then taken by a micro syringe and then injected to the GC via heated injection port. The peak area of THF over butyl acetate from the GC was then integrated as a reference ratio. The yield of HMF was calculated using the integrated peak ratio of HMF over butyl acetate in the extracted layer divided by the reference peak ratio.

Chapter 4

Result and discussion

In this research, HMF and derivatives were synthesized by dehydration of table sugar using sulfuric acid, sulfuric acid with chromium chloride, Amberlite 200C, Zeolite Beta and Zeolite Y as catalysts. The results shown in this chapter are classified in two parts. In part one, the synthesis and characterization of HMF from dehydration reaction was explained. In part two, the reaction variables such as types of catalysts, reaction time and acid concentration that affect on HMF formation were discussed.

4.1 Product Distribution by GC-MS

Figure 4.1, shows the products from dehydration of using 0.5M H2SO4 as catalyst. From GC-MS the major product was found to be 5-Hydroxymethylfurfural (HMF) shown in Table 4.1. It shows that 0.084mg/g of HMF was produced after 2 hours. The minor products include Furfural, 4, 5-Dimethyl-2-formylfuran, 1-(2-Furyl)-2-Hydroxyethanone and 5- Acetoxymethyl-2-furaldehyde.

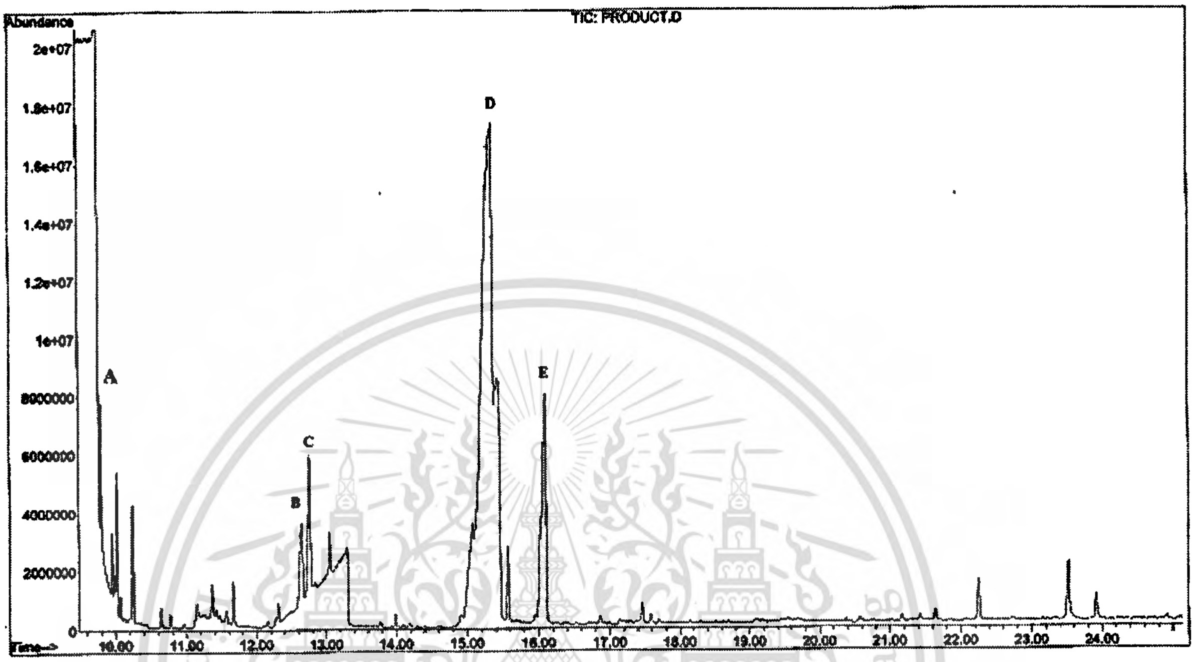
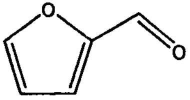
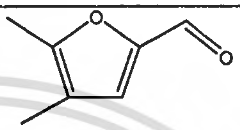
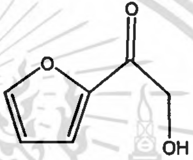
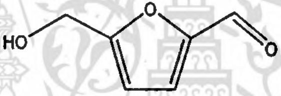
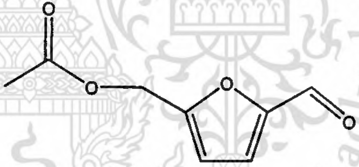


Figure 4.1 Product distributions by GC-MS

Table 4.1 Types of product, structure and retention time

Type Of Product	Retention Time (min)	Structure	Yield(mg/g)
(a)	9.81		0.166
(b)	12.65		0.059
(c)	12.78		0.101
(d)	15.25		0.373
(e)	16.09		0.175

(a) Furfural, (b) 4, 5-Dimethyl-2-formylfuran, (c) 1-(2-Furyl)-2-Hydroxyethanone,

(d) HMF, (e) 5- Acetoxymethyl-2-furaldehyde

To obtain the major product, sugar (sucrose) is broken down through hydrolysis process as shown in Fig4.2. Water (H_2O) molecule reacts with sucrose forming fructose and glucose. Under atmospheric pressure, this reaction cannot occur, therefore strong acid is applied to facilitate the hydrolysis. The acid is considered as a catalyst. Fructose obtained from hydrolysis can be directly converted to HMF through dehydration as shown in Figure 4.3. As the hydroxyl group (-OH) is a poor leaving group, having a Lewis acid catalyst often helps by protonating the hydroxyl group to give the better leaving group, $-OH_2+$. Fructose loses three molecules of water and forms HMF. Glucose obtained from hydrolysis cannot be directly converted to HMF but it can be isomerized to fructose, then the dehydration occurred as mentioned above. In addition, acid catalyst can be used to promote isomerization.

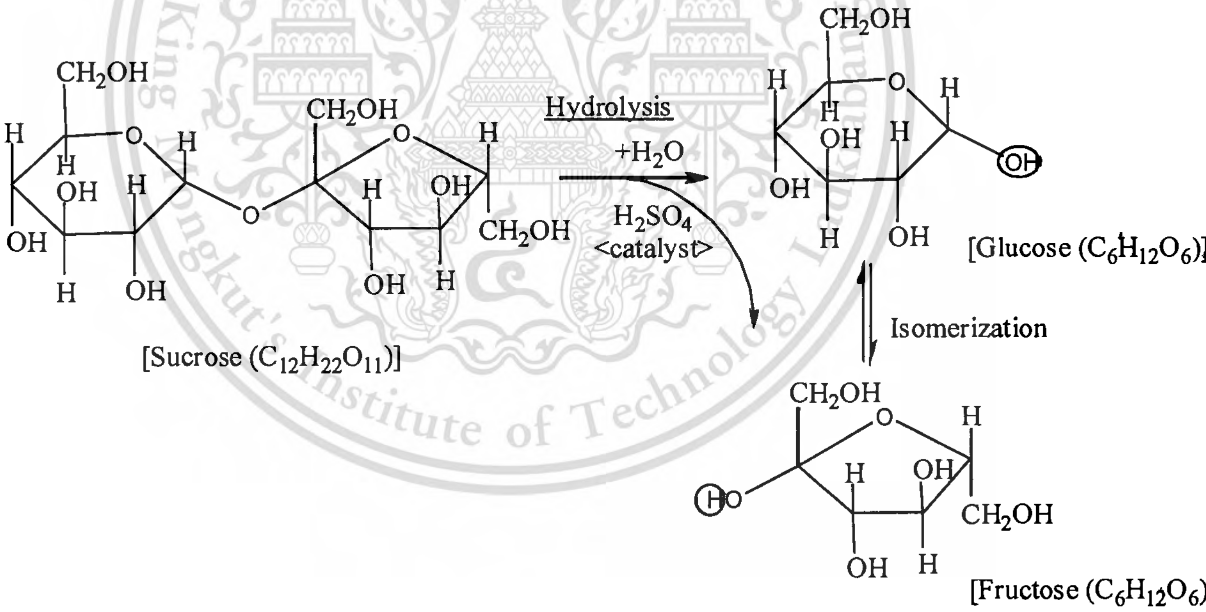


Figure 4.2 Hydrolysis of fructose and isomerization of glucose to fructose

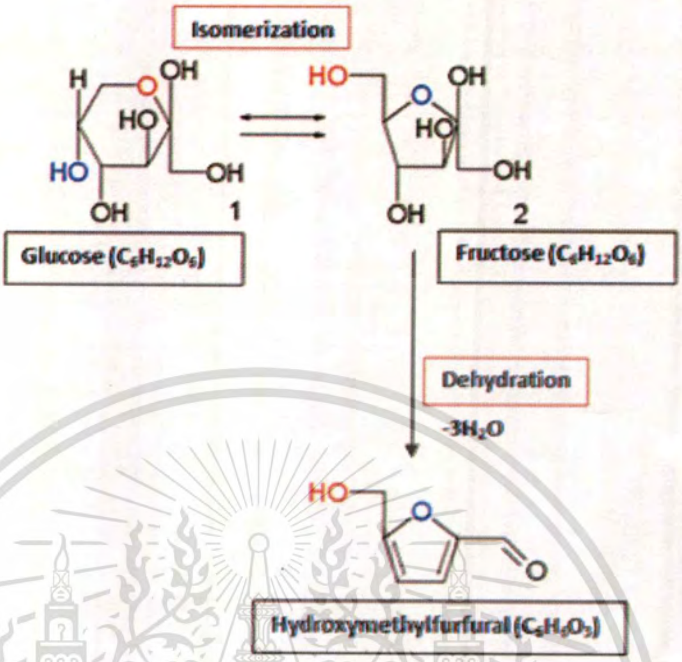


Figure 4.3 Dehydration of fructose to HMF

However, HMF is very reactive as it contains aldehyde and hydroxyl group. Therefore, self-condensation of HMF can be facilitated under acid solution to form high molecular weight oxygenated molecule as shown in Figure 4.4. More water is loss during this process. The high molecular weight oxygenated molecule can then be further cracked into products, such as Furfural, 4, 5-Dimethyl-2-formylfuran, 1-(2-Furyl)-2-Hydroxyethanone and 5- Acetoxymethyl-2-furaldehyde.

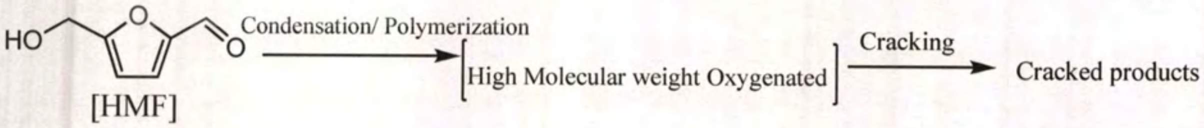


Figure 4.4 Condensation/polymerization of HMF and cracking

4.2 Deoxygenation of sugar to HMF

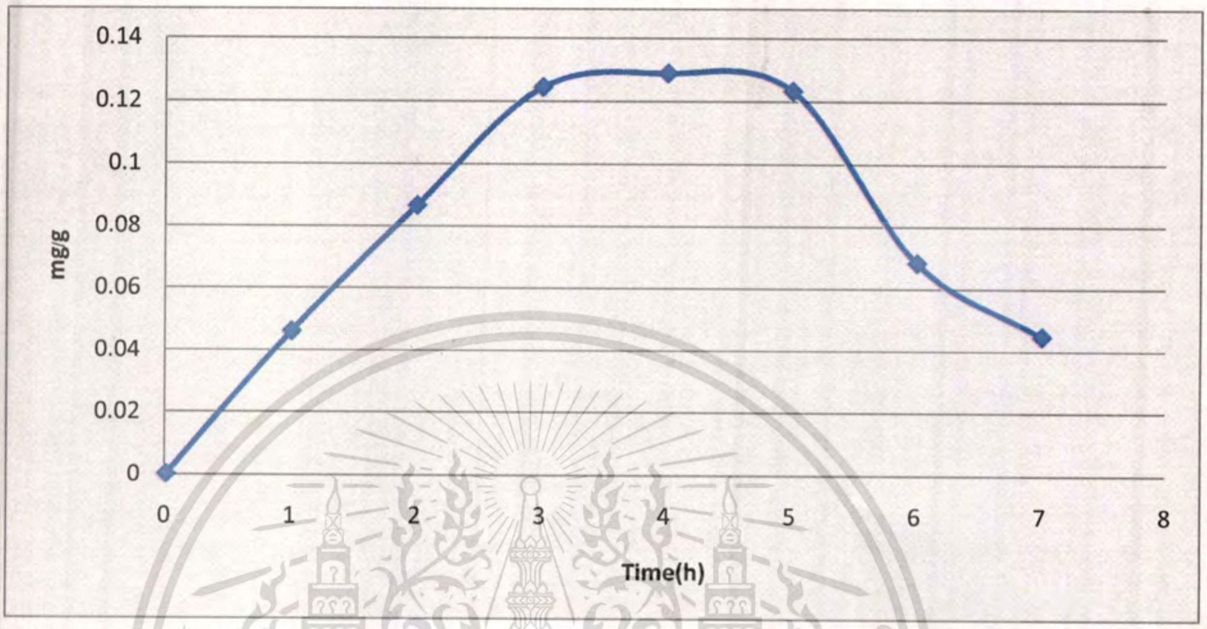
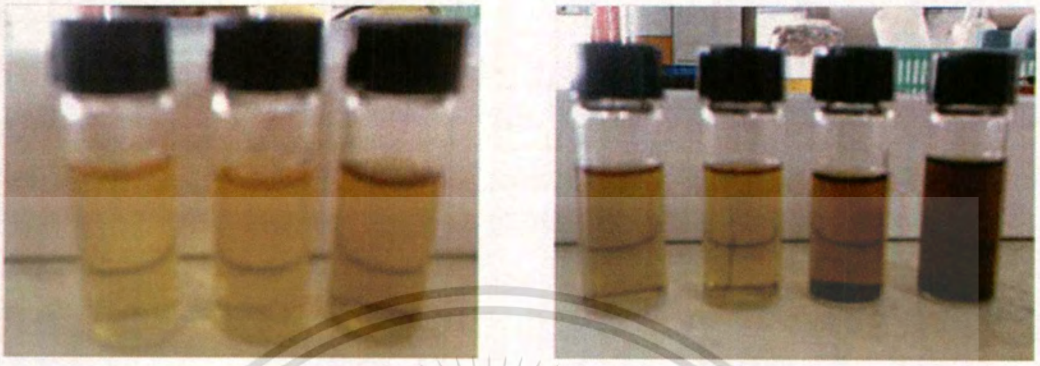


Figure 4.5 Yield of HMF from deoxygenation of sugar with 0.5M H_2SO_4

The reaction using sulfuric acid (0.5M) as catalyst shows that the dehydration rate of sugar to HMF steadily rose and reached its optimum after approximately four hours as shown in Figure 4.5. The highest yield obtained was approximately 0.13mg/g. It was shown that as the contact time was increased; the yield of HMF also increases. It was suggested that at the beginning, the polymerization rate was lower than HMF formation rate. However, after 5 hours the yield of HMF started to decrease. This is because the rate of polymerization was higher than the formation of HMF at this point. The polymerization precipitate can be seen in Figure 4.6. As contact time increase, the polymerization of HMF will occur and be seen as dark brown precipitate.

In addition, the high molecular weight oxygenated molecules can undergo cracking at 110°C into other products including Furfural, 4, 5-Dimethyl-2-formylfuran, 1-(2-Furyl)-2-Hydroxyethanone and 5- Acetoxymethyl-2-furaldehyde took place at high contact time. The cracked product is mainly Furfural. In consistence with this view, Figure 4.7 shows the increase in yield of furfural and other products as the contact time is increased.



[---------1hr---------2hr--------3hr---------]　[----4hr-------5hr------6hr-------7hr-----]

Figure 4.6 Product of 0.5M H_2SO_4 from1 hour (left) to 7 hours (right).

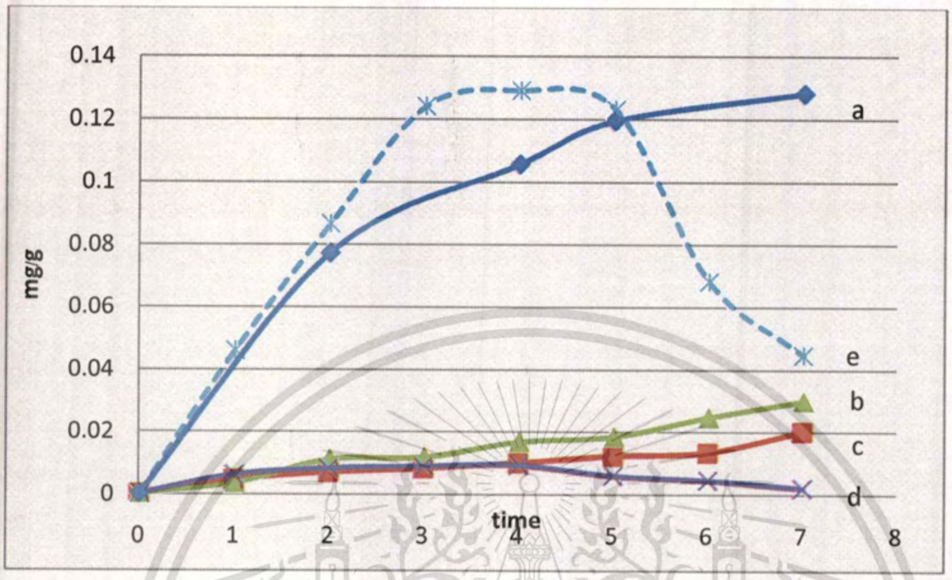


Figure 4.7 Other products from cracking (0.5M H_2SO_4)

(a) Furfural, (b) 1-(2-Furyl)-2-Hydroxyethanone, (c) 4, 5-Dimethyl-2-formylfuran,

(d) 2-Furancarboxaldehyde, (e) HMF

As discussed earlier the yield of HMF was decreased because the rate of polymerization was high. The rate of polymerization increased as the amount of proton is increased. Therefore, to reduce the polymerization rate, the sulfuric acid concentration was reduced to 0.25M and the result is shown in Figure4.8.

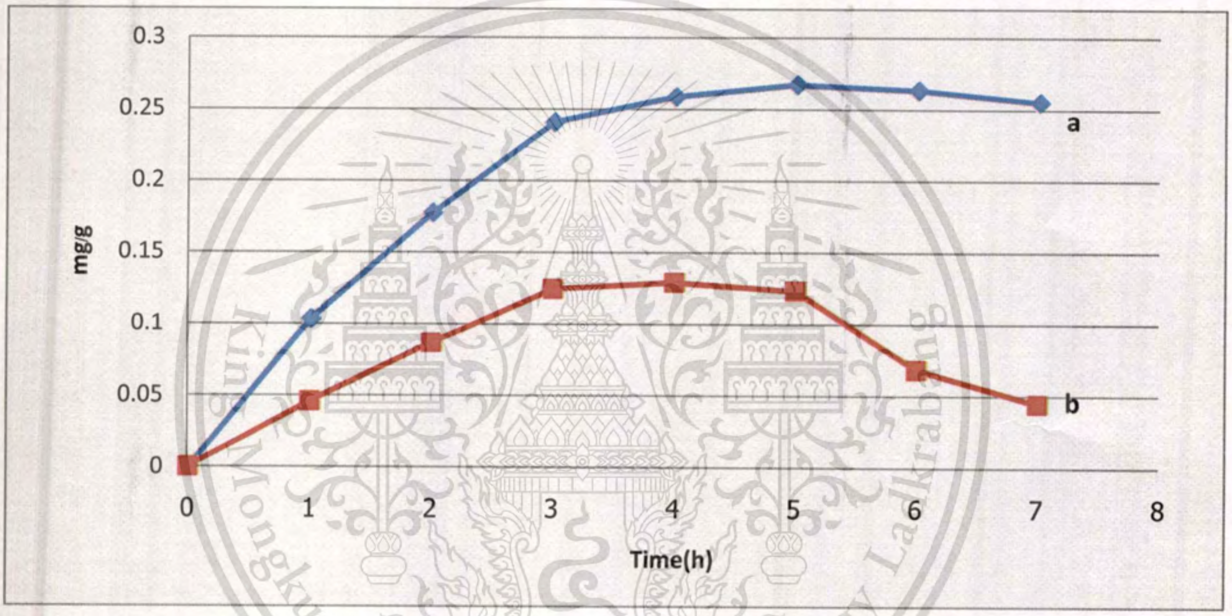


Figure 4.8 Comparison in yield of HMF from deoxygenation of sugar between concentrations with (a) 0.25M H_2SO_4, (b) 0.5M H_2SO_4

As expected, the yield of HMF increases as the contact time increases particularly for the reaction using 0.25M H_2SO_4 that gives a higher yield of HMF as compare to 0.5M H_2SO_4. The highest yield obtained for 0.25M H_2SO_4 was about 0.27mg/g while 0.5M H_2SO_4 gave only 0.13mg/g. It was suggested that as the amount of proton H^+ decreased, rate of HMF formation also decreased, therefore, rate of condensation/ polymerization of HMF was decreased. Hence, the reaction using 0.25M H_2SO_4 that contains less H^+, would have much slower rate of polymerization. Therefore, HMF can be retained in the reaction using 0.25M H_2SO_4, while HMF undergoes polymerization in the reaction using 0.5M H_2SO_4. However, after 4 hour the yield of HMF in 0.25M H_2SO_4 started to decrease, but in a rate much slower than that in the reaction using 0.5M H_2SO_4. This is because the rate of polymerization was not high enough as compared to the reaction using 0.5M H_2SO_4.

As discussed earlier, glucose had to be isomerized to fructose before it can be dehydrated to HMF. Therefore, chromium (III) chloride ($CrCl_3$) was added to enhance isomerization of glucose to fructose.

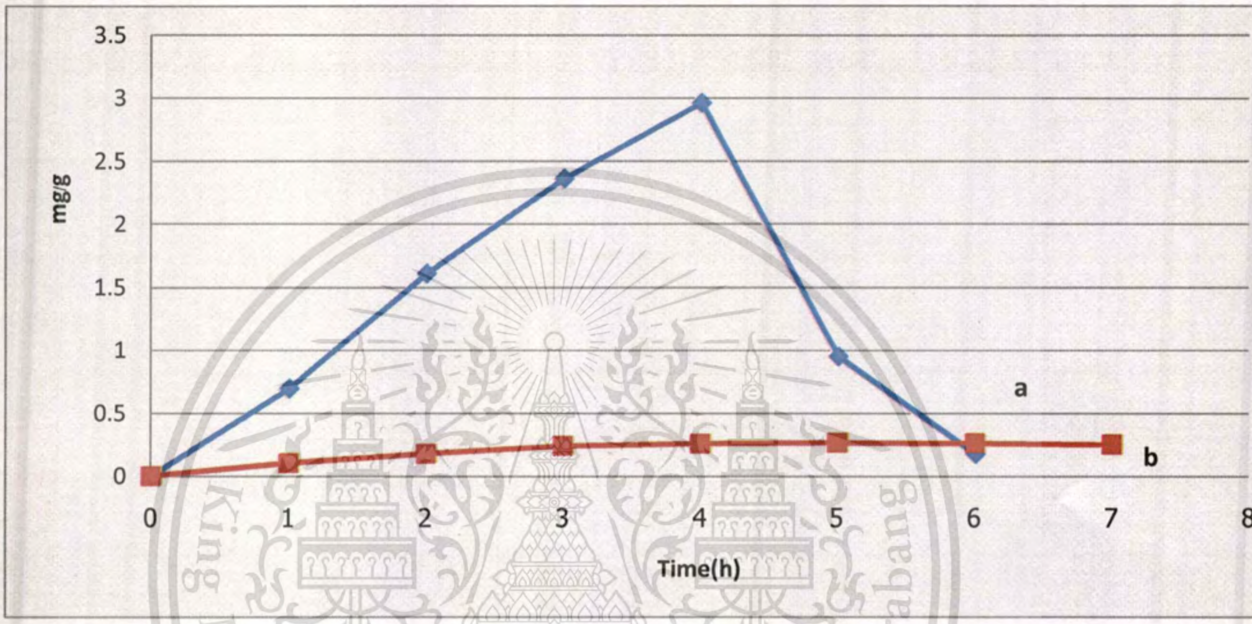


Figure 4.9 Comparison in yield of HMF from deoxygenation of sugar with

(a) 0.25M H_2SO_4 with $CrCl_3$, (b) 0.25M H_2SO_4 without $CrCl_3$

Figure4.9 shows that when $CrCl_3$ was added to the reaction using 0.25M H_2SO_4, a higher yield of HMF can be obtained, as compared to that 0.25M H_2SO_4.The optimum yield obtained for the reaction using 0.25M H_2SO_4 with $CrCl_3$ was approximately 2.96mg/g while approximately 0.25mg/g was obtained without $CrCl_3$. It was suggested that the rate of HMF formation with $CrCl_3$ was faster than the rate of HMF formation without $CrCl_3$. It is because $CrCl_3$ promote isomerization of glucose to fructose as shown in Figure 4.10

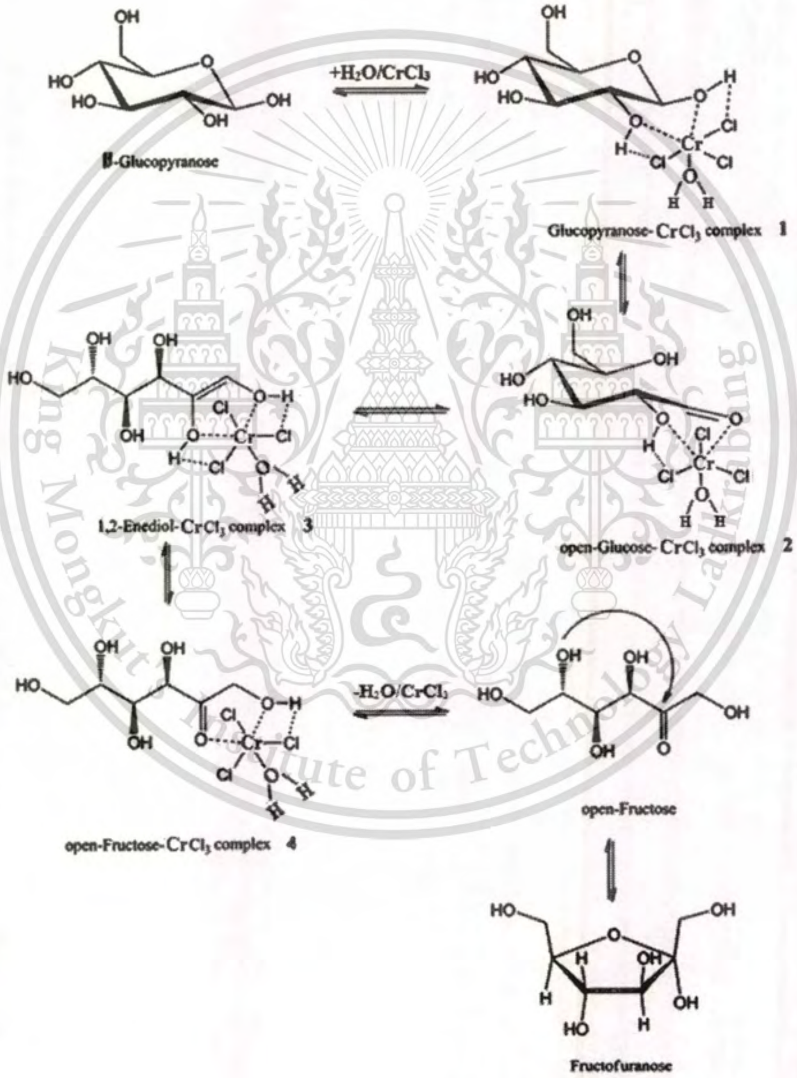


Figure 4.10 Isomerization of glucose to fructose using $CrCl_3$

In addition, in the presence of $CrCl_3$ acting as Lewis acid can also promote dehydration of fructose to HMF. This is demonstrated by Figure 4.11.

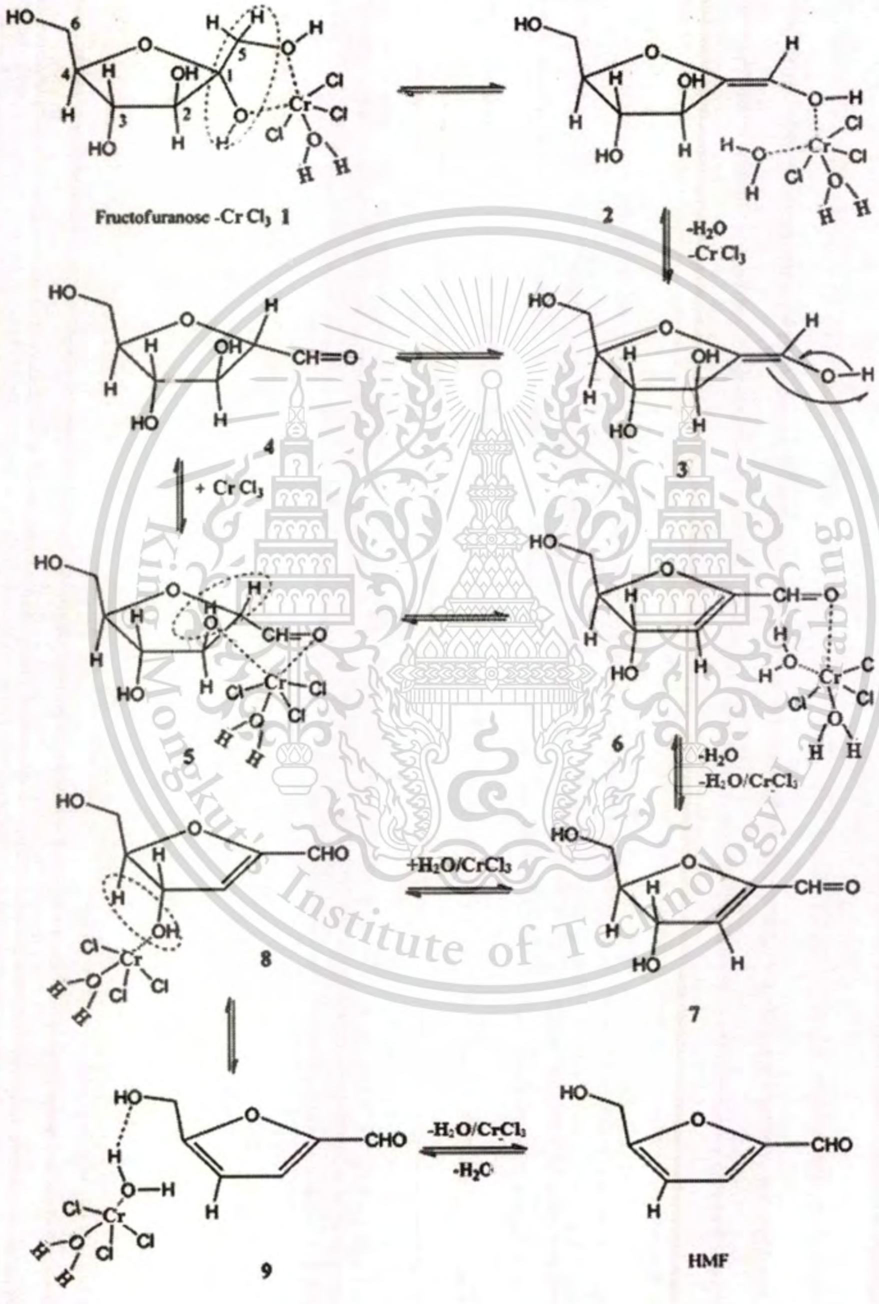


Figure 4.11Dehydration of fructose to HMF

After 4 hour, the yield of HMF of 0.25M H_2SO_4 with $CrCl_3$ decreased rapidly. It was suggested that since the rate of HMF formation was very fast, therefore, the rate of polymerization is also very fast, particularly with the presence of $CrCl_3$.

As discussed earlier, the reaction using H_2SO_4 shows that at high H^+ concentration will increase the high molecular weight oxygenated molecules. In addition, when $CrCl_3$ was added to the reaction using H_2SO_4, the yield of HMF formation was also increased. This is because the reaction takes place over homogeneous catalyst, therefore, condensation/ polymerization rate was increased when H^+ concentration has increased. Therefore, heterogeneous catalysts were tested to reduce the rate of condensation/ polymerization to high molecular weight oxygenated molecules. Different type of catalyst contains approximately 5mmol of proton per gram of sugar were tested, in comparable to the reaction using 0.25M H_2SO_4 (equivalence to 5mmol of proton).

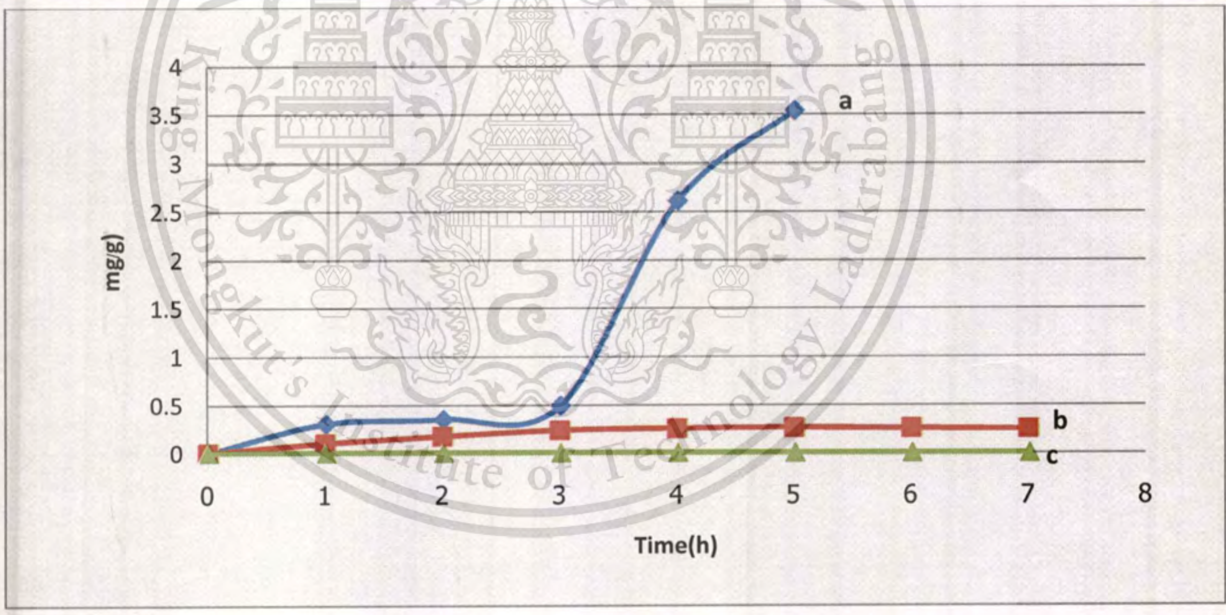


Figure4.12 Comparison in yield of HMF from deoxygenation of sugar with

(a) Amberlyst 200C, (b) 0.25M H_2SO_4 sulfuric, (c) Zeolite Beta and Y

Figure 4.12 show that Zeolite Y and Zeolite Beta had no conversion. It was suggested that the pore structure of both Zeolite Y and Beta were too small to occlude table sugar as shown by kinetic diameter in Figure 4.13. Sucrose, a disaccharide was unable to enter the active acid sites in the inner pore. Therefore, sucrose cannot be hydrolyzed to fructose and glucose and no HMF were obtained.

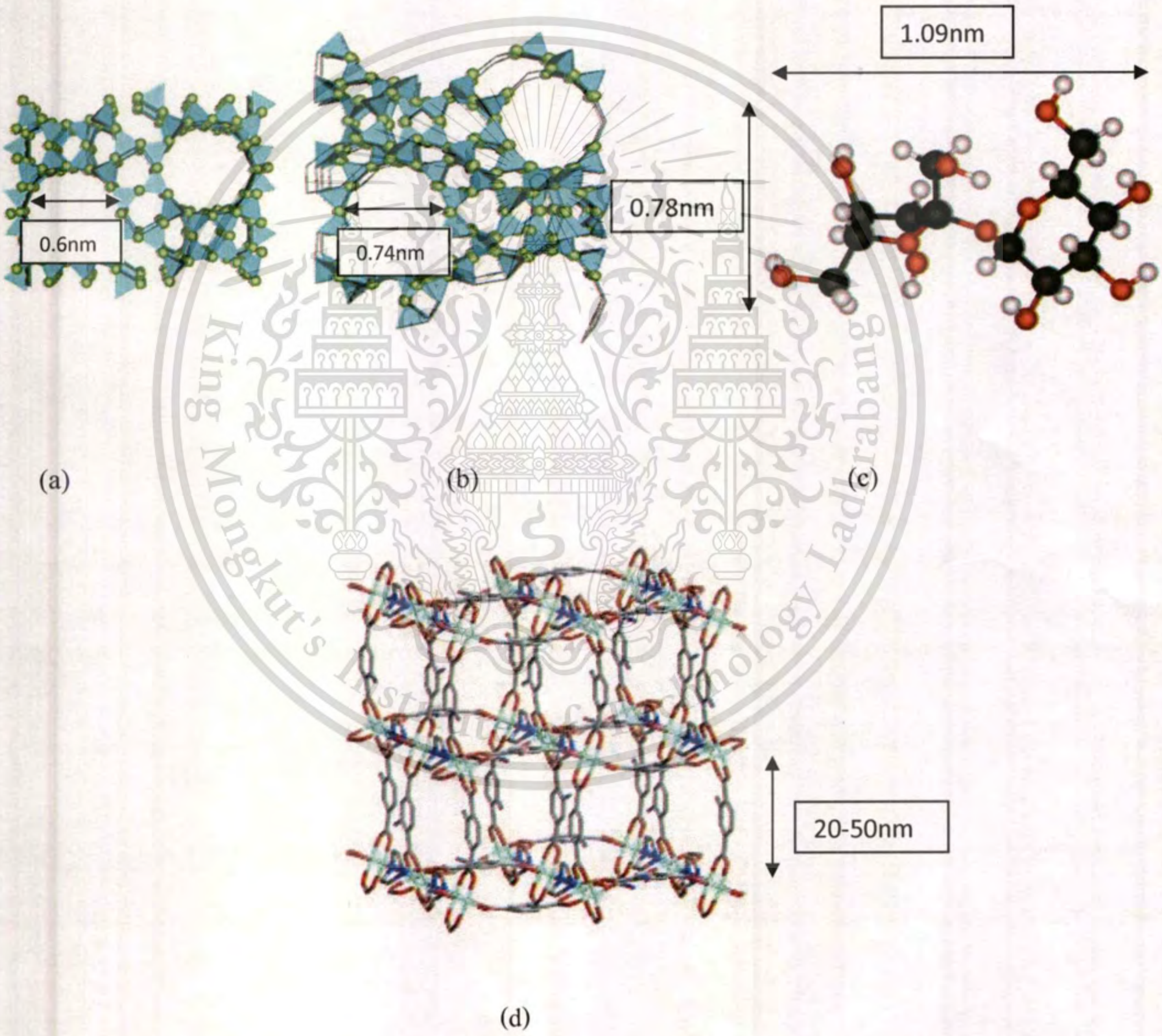


Figure 4.13 Structure of kinematic diameter (a) Zeolite Beta, (b) Zeolite Y, (c) Sucrose, (d) Amberlite 200C

As for Amberlite 200C, the formation of HMF slowly rose from 0 to 3hours. This shows that Amberlite 200C has a larger pore size than sucrose (Figure 4.13)in the range of mesopore, therefore, sucrose can be hydrolyzed to fructose and glucose. It was suggested that due to the heterogeneous phase of reaction, diffusion rate of table sugar to the active acid sites in the pore of Amberlite 200C was slow at the beginning. In consistence, as the hydrolysis rate of sucrose was also slow, the rate of HMF formation is also delayed. This is because sugar need to be hydrolyzed to glucose and fructose whereas glucose also need to be isomerized to fructose before HMF can be formed. The rate of HMF formation started to increase noticeably after three hours. It was suggested that as sugar was hydrolyzed to fructose and glucose which had smaller diameter, more fructose are formed over the active acid sites and can be dehydrated to HMF. The highest yield obtained was approximately 3.53 mg/g that is higher than that obtained from the reaction using 0.25 M H_2SO_4. It was suggested that polymerization rate of HMF in Amberlite was inhibited. This is because in homogeneous catalyst, the interaction of protonated HMF with proton was very strong. Therefore, at high contact time, protonated HMF can undergo self-condensation/ polymerization. However, in heterogeneous catalyst, the adsorption of HMF with proton was weaker than that of glucose and fructose. The colour was lighter and less brown precipitates were formed than the reaction using H_2SO_4.Therefore, the desorption of HMF was facilitated by the strong adsorption of glucose and fructose. With this, the rate of condensation/ polymerization of HMF was much slower as compare to that in homogeneous catalysis.

As discussed earlier, hydrolysis had to take place at the beginning to form fructose otherwise no HMF can be obtained. Therefore, to confirm the effect of acid on hydrolysis, the proton of Amberlite 200C was reduced to 2mmol. The result is shown in Figure 4.14

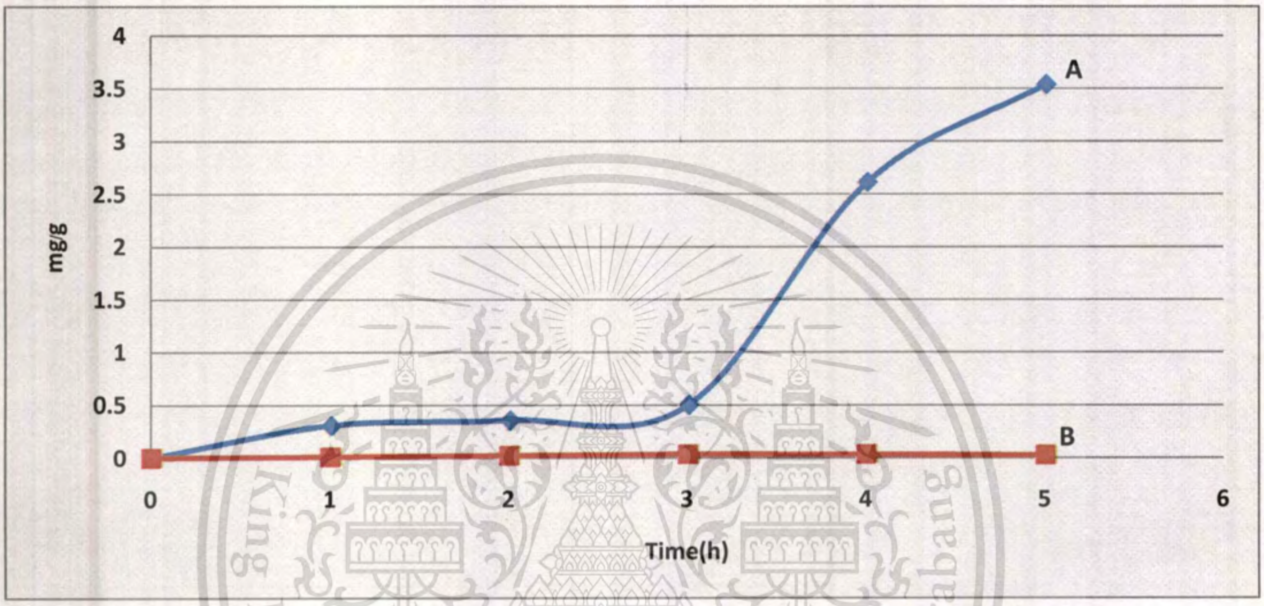


Figure 4.14 Comparison in yield of HMF from deoxygenation of sugar with

(a) 5mmol Amberlite 200C, (b) 2mmol Amberlite 200C

Experimental result showed that 2mmol of Amberlite 200C give a small amount of HMF. This is because the amount of H^+ was too low to facilitate the hydrolysis. Therefore, little amount of glucose and fructose were obtained from hydrolysis.

Chapter 5

Conclusion and Recommendations

5.1 Conclusion

HMF can be obtained by dehydration of table sugar with the reaction using H_2SO_4 as an acid catalyst. It was found that the reaction using 0.25 M of H_2SO_4 had suitable concentration that inhibits condensation/polymerization of HMF and reduces the yield of side products.

Yield of HMF can be increased by increasing the rate of isomerization from glucose to fructose. It was found that $CrCl_3$ also promotes dehydration of fructose to HMF. Therefore, higher yield of HMF can be obtained as compared to that in H_2SO_4 without $CrCl_3$. However, when HMF formation rate is high, the rate of condensation/polymerization is also high.

To reduce the condensation/polymerization rate, heterogeneous catalysts were introduced. In heterogeneous catalyst, sucrose needed to diffuse to the acid sites in the pore of catalyst to be hydrolyzed. However, for Zeolite Y and Beta, sucrose could not diffuse to the acid sites of the catalysts as the pore diameters of the catalysts were too small. Therefore, no HMF yield can be produced. As for Amberlite 200C, sucrose was able to diffuse to the acid sites and hydrolysis can occur. It was found that in Amberlite 200C, adsorption and desorption of feed (glucose and fructose) and product (HMF) plays an important role for the catalyst stability. The adsorption of protonated HMF was weaker than that of glucose and fructose, as the desorption of HMF was facilitated by the strong adsorption of glucose and fructose. With this, the formation of high molecular weight oxygenated molecule was reduced.

5.2 Recommendations

5.2.1 For heterogeneous catalyst, other catalysts should be tested such as $MeCl_x$/ionic liquid/SBA-15[20], Amberlyst-15[21],

5.2.2 In the reaction to increase the rate of isomerization, different catalyst should be tested other than $CrCl_3$ such as $RuCl_3$, WCl_4[18]

5.2.3 The amount of proton in heterogeneous catalyst should be varied. By increasing the amount of proton may increased the HMF formation rate.

5.2.4 The effect of temperature should be studied. The temperature should be lower to reduce the polymerization rate and the severity of the reaction condition.

5.2.5 The type of solvent that can dissolve sugar should be tested other than water such as DMSO.[22]

5.2.6 Different extractants should be tested other than butyl acetate such as MIBK[23], ethyl acetate, DIBK.

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APPENDIX A

PREPARATION OF ACID CATALYST

Preparation for 0.25M H_2SO_4

$C_1V_1=C_2V_2$; C_1= the concentration of H_2SO_4 (0.5M), V_1= volume needed to prepare (100ml)

C_2= concentration of 98% assay H_2SO_4 (18M), V_2= volume required to pipette (x=1.385)

Preparation for 0.5M H_2SO_4

$C_1V_1=C_2V_2$; C_1= the concentration of H_2SO_4 (0.5M), V_1= volume needed to prepare (100ml)

C_2= concentration of 98% assay H_2SO_4 (18M), V_2= volume required to pipette (x=2.77)

Preparation for Amberlite 200C

Ion-exchanging 50 grams of resin with 500ml of 0.5M HCL solution

$C_1V_1+C_2V_3=C_3V_3$; C_1V_1 = proton of the resin, C_2= concentration of KHP used

V_2= volume of KHP used (x=14, 14.6, 13.4; x-bar=14), C_3= concentration of NaOH (0.41M)

V_3= volume of NaOH (10.8ml)

Preparation of Zeolite Beta

Equation $U=H_nAl_nSi_{64-n}O_{128}$ n<7, Si/Al =13.5, n= 4.4

$U=H_{4.4}Al_{4.4}Si_{64-4.4}O_{128}$; H=1, Al=26.98, Si=28.09, O=16, U=3,845.27

Amount of proton= n/U, 4.4/3,845.27= 0.001144mol/g

Amount of gram use in the reaction 5mmol/1.144mmol= 4.37g

Preparation of Zeolite Y

Equation $U=H_nAl_nSi_{64-n}O_{128}$ n<7, Si/Al =3.5, n= 42.5

$U=H_{4.4}Al_{4.4}Si_{64-4.4}O_{128}$; H=1, Al=26.98, Si=28.09, O=16, U=11,532.605

Amount of proton= n/U, 42.5/11,532.605= 0.0036852mol/g

Amount of gram use in the reaction 5mmol/3.6852mmol= 1.3568g

APPENDIX B

HMF yield calculation

$$Reference\ peak\ ratio = \frac{Peak\ area\ of\ THF}{Peak\ area\ of\ butyl\ acetate}$$

$$Peak\ ratio\ of\ HMF = \frac{Peak\ area\ of\ THF}{Peak\ area\ of\ butyl\ acetate}$$

$$Yield\ of\ HMF = \left[\frac{Peak\ ratio\ of\ HMF}{Reference\ peak\ ratio}\right] * weight\ of\ THF$$

Weight of THF used= 0.517 gram

APPENDIX C

Gram of distilled water

Density of sulfuric acid =1.84g/cm^3 at 20°C

Density of distilled water = 1 g/cm^3 at 20°C

0.25M H_2SO_4 (Appendix A) was prepared by 1.385ml in 100ml volumetric flask.

Therefore, volume of distilled water = 100ml-1.385ml=98.615ml

Mass of H_2SO_4 = 1.84g/ml × 1.385ml = 2.5484g

Mass of distilled water = 1g/ml × 98.615ml = 98.615g

Total mass = 2.5484 + 98.615g = 101.1634g

Therefore, mass of water in 11.5g = $\frac{11.5g \times 98.615g}{101.1634g}$ = 11.21g