



CHAPTER II

BACKGROUND & LITERATURE REVIEWS

2.1 Biomass

Biomass is a term for all organic material that can convert to renewable energy. As biomass is created from solar energy, water, and carbon dioxide, its utilization does not result in the increase in net carbon dioxide. In this respect, biomass is said to be “carbon neutral”.

Plant biomass is the world’s most abundant source energy and can serve as a direct nourishment as well as feedstock for chemical products. The plant biomass resources are present in three main groups [Vessia et al., 2005] as follow.

1. Cereals, grains, sugar crops and other starches.
2. Lignoellulosic materials like grasses, trees and different types of waste products and residuals from crops, wood processing, and municipal solid waste.
3. Oil-seed crops (e.g. rapeseed, soybean and sunflower).

Among these groups of biomass, lignoellulosic biomass is the most abundant in every country, especially in agricultural countries, making it interesting feedstock for alternative fuel production.

2.2 Important constituents of lignocellulosic biomass.

The proper utilization of plant biomass as feedstock for fuel production depends on the chemical compositions and the physical properties of the biomass. Different biomass contains varying amounts of cellulose, hemicellulose and lignin [Albrecht., 2006].

2.2.1 Cellulose

Cellulose (40-60% of the dry biomass) is an organic compound with the formula $(C_6H_{10}O_5)_n$, a polysaccharide consisting of a linear chain of several hundred to over ten thousand linked D-glucose units. The orientation of the linkages and additional hydrogen bonding make the polymer rigid and difficult to break. However, it can be broken down chemically into its glucose units by hydrolysis at high temperature or by acids or enzyme catalyzed processes.

2.2.2 Hemicelluloses

Hemicellulose (20-40%) is complex polysaccharides which consist of shorter chains - around 200 sugar units. Hemicellulose is derived from several sugars mainly xylose (five-carbon), and also arabinose (five-carbon), galactose, glucose and mannose (all six-carbon). It also contains smaller amounts of non sugars such as acetyl groups. Furthermore, hemicellulose is a branched polymer and it has amorphous structure with little strength. It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulase enzymes.

2.2.3 Lignins

Lignin (10-25%) is a cross-linked macromolecule that is relatively hydrophobic and aromatic in nature. Lignin is present in all lignocellulosic biomass, especially woody species whose content adds up to 27-33% for softwoods and 22% for hardwoods, respectively. It fills the spaces in the cell wall between cellulose, hemicellulose, and pectin components. Lignin is degradable by only few organisms, into several higher value products such as organic acids, phenols and vanillin. Valuable fuel additives may be produced via chemical processes.

2.3 Cassava waste

Cassava is a main raw material for use in many industrial especially production of cassava flour. The industry of cassava flour in Thailand is growing and about millions ton of fresh cassava was used for the production of flour [Srisoth et al., 2000] yearly. However, the production of flour results in solid waste which, which accounts for about 10-15% of fresh cassava root.

Cassava waste composes of starch 60%, cellulose 16%, hemicellulose 5% and lignin 19% [Pimpisit et al., 2008], is used as animal feed because it high contain of protein and nutrient [Srinorakutara et al.,2006]. However due to it high moisture content (60-70%), drying process is required. After drying, it is low value product used for animal feed, however the starch remained in the cassava waste (up to 50-60%, dry basis) could be suitable for the production of biofuel via BTL process.

2.4 Biomass to liquid fuel processes.

Biomass can be converted to various forms of energy by numerous technical processes, depending upon the raw material characteristics and the type of energy desired. The biomass derived energy, so called biofuel, can be divided into five main groups [Vessia et al., 2005]:

- Biodiesel (mainly RME and FAME)
- Alcohols (ethanol/methanol)
- Synthetic fuel (BTL-biomass to liquid)
- Biogas

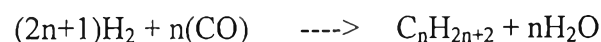
The biogas, biodiesel and ethanol have limited use compared with synthetic fuel. The use of biogas requires change in engine systems, while that of biodiesel and ethanol require blending with other fuel to improve their properties before they can be suitable for a standard engine. On the other hand, synthetic fuel has components that are similar to those of the current fossil-derived petrol and diesel fuels, thus they can be used with any standard engines. For this reason, the synthetic fuel has recently gained increased interest. The production of synthetic or biomass to liquid fuel can be achieved by several processes as follows:

- **Fast pyrolysis**

Fast pyrolysis is thermal decomposition of biomass that occurs in the absence of oxygen. It is also the first step in combustion and gasification processes where it is followed by total or partial oxidation of the primary products. Fast pyrolysis is operated in moderate temperature and short vapor residence time. The interest in pyrolysis is mostly due to the higher energy efficiency and the logistical advantages of the product. However, poor volatility, high viscosity, coking, and corrosiveness are among the most challenging problems that have so far limited its applications [Chernik., 2004].

- **Fischer-Tropsch**

The Fischer-Tropsch reaction converts a mixture of hydrogen and carbon monoxide derived from biomass to liquid hydrocarbons in various forms as shown by the following reaction. Generally the catalysts used in the reaction are based on iron and cobalt.



Typical operating pressures for Fischer–Tropsch synthesis are 15–40 bar, while two temperature modes can be distinguished: high temperature Fischer–Tropsch

(300–350°C) and low temperature Fischer–Tropsch (200–260°C). At lower temperature, the chain growth probability is higher, resulting in less gaseous products and more liquid products, such as diesel fuel. The Fischer–Tropsch fuels have less sulfur, nitrogen oxide, carbon monoxide and particulate matter emissions than petroleum fuels so this process produces high value, clean-burning fuels and it can be used in conventional engines with no modification. However, the process has high capital cost and high operating and maintenance costs that are problematic to use as commercial fuel [Dry et al., 2002].

2.5. The alkane production from biomass.

Recently, Huber et al. (2005) proposed a novel low cost process to produce C₇-C₁₅ alkanes from sugar-based compound. This process consists of 4 steps, including hydrolysis, dehydration, aldol condensation and hydrogenation, as shown in figure 2.1 and figure 2.2. In the first step, biomass is changed into glucose molecules via hydrolysis. This process is typically carried out at high temperatures in the presence of acid catalysts. Subsequently glucose isomerizes into fructose. Both glucose and fructose undergo dehydration by loss of three water molecules to form furan compounds such as HMF and furfural. Dehydration reactions are typically carried out in the presence of solid or mineral acid catalysts at high temperatures. Subsequently, via aldol condensation, larger organic molecules can be produced by the C–C coupling between two smaller compounds containing carbonyl groups (HMF and furfural). However, without an α -H atom, HMF and furfural cannot undergo self-condensation. Nevertheless, HMF and furfural have aldehyde group that can react with molecules that can form carbanion species, such as acetone and dihydroxyacetone. These aldol condensation reactions of HMF and furfural are shown in Figure.2.1 and Figure. 2.2, respectively. Figure.2.1 indicates that acetone react with HMF to form C₉, which then react with a second HMF molecule to form a C₁₅ molecule, while Figure 2.2 indicates that acetone reacts with furfural to form C₈, which then react with a second furfural molecule to form a C₁₃ molecule. The subsequent hydrogenation of C=C and C=O bonds of the product resulted from aldol-condensation process saturates the molecules and produces large water-soluble organic compounds. Finally, these molecules are then converted into alkanes by operating in dehydration/hydrogenation reaction in the presence of bifunctional catalysts containing acid and metal sites in four phase reactor.

From the pathway of alkane production from biomass described, it was demonstrated that HMF and furfural are important intermediates for the production liquid alkanes, and therefore the production of HMF and furfural from biomass is the most primary step for the production of future alternative liquid fuel.

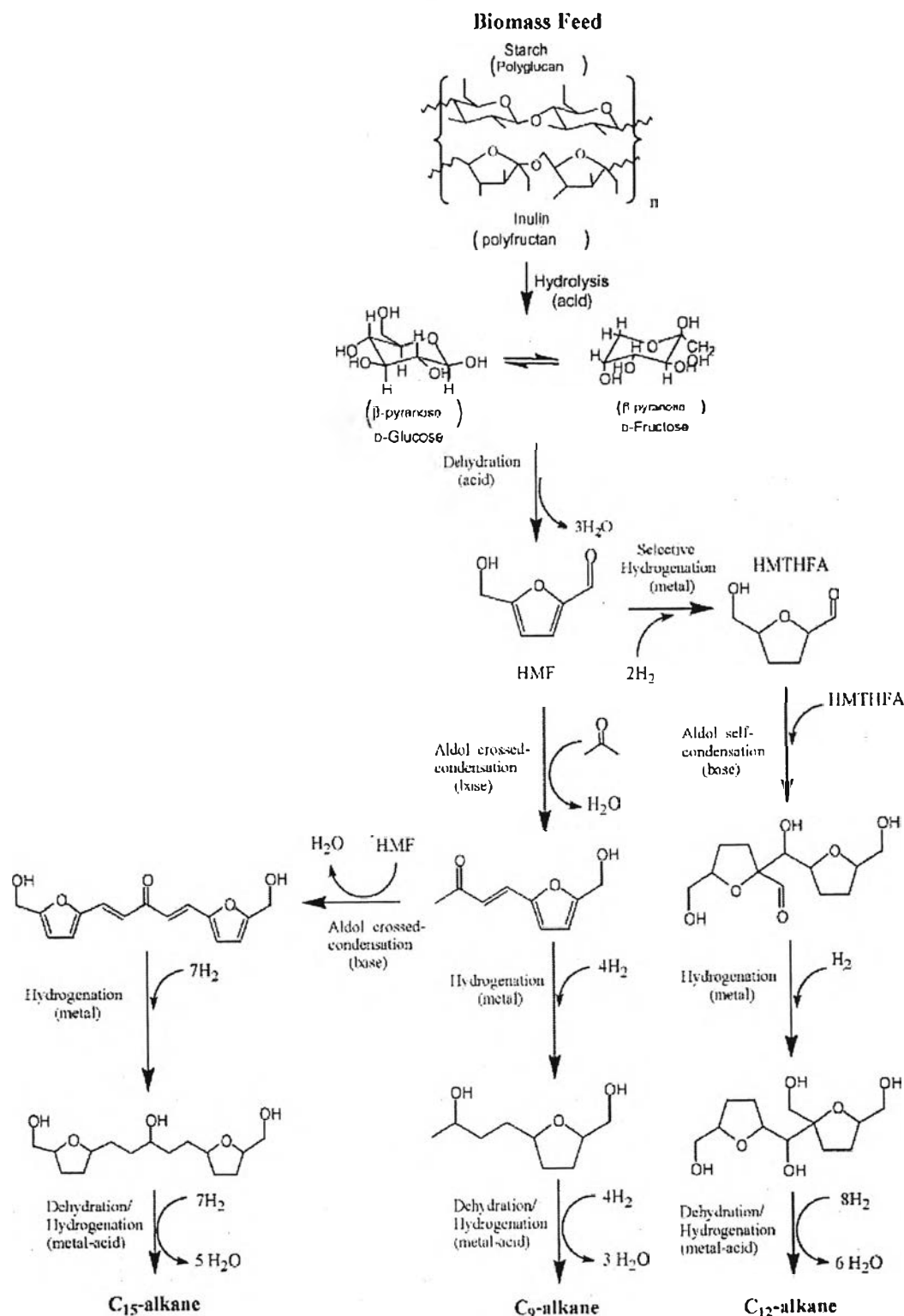


Figure 2.1 Reaction pathways for the conversion of biomass-derived glucose into liquid alkanes.

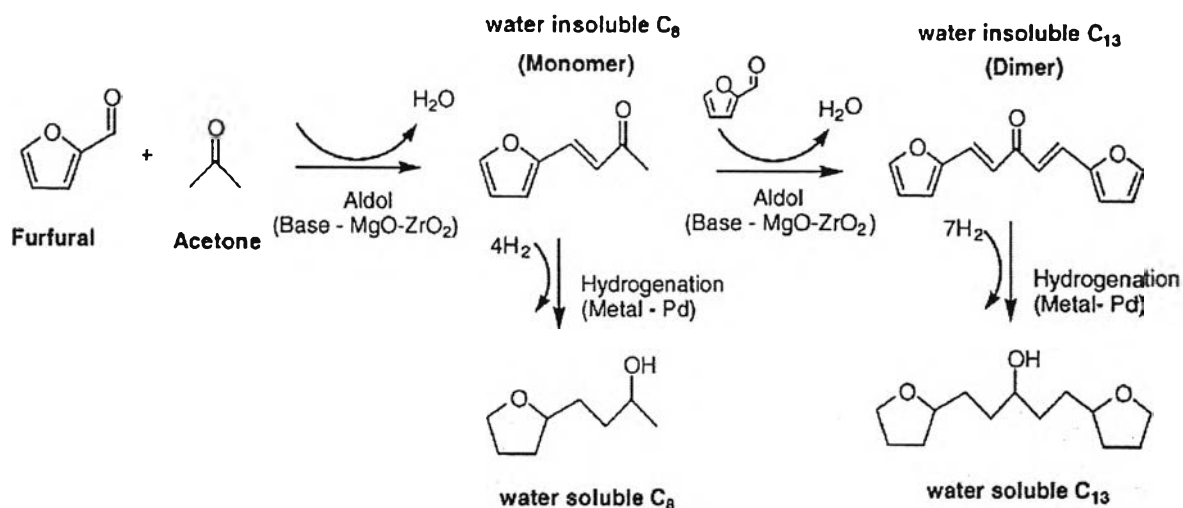


Figure 2.2 Reaction network for aldol-condensation of furfural (or HMF) and acetone, followed by hydrogenation of aldol-adducts.

2.6 HMF or 5-(Hydroxymethyl) furfural and its applications.

HMF is an organic compound derived from dehydration of sugars. The molecule is a derivative of furan containing both aldehyde and alcohol functional group. The synthesis of HMF is based on the triple dehydration of hexoses. Various substrates can be used: hexoses themselves, oligosaccharides and polysaccharides as well as biomass. The synthesis of HMF is very simple. But studies performed by a number of independent scientists demonstrated that the chemistry of the formation of HMF is very complex; it includes a series of side-reactions, which influence strongly on the efficiency of the process. The decomposition to levulinic acid and the polymerization to humic acids are the most important factors decreasing the yield of HMF [Lewkowski et al., 2001].

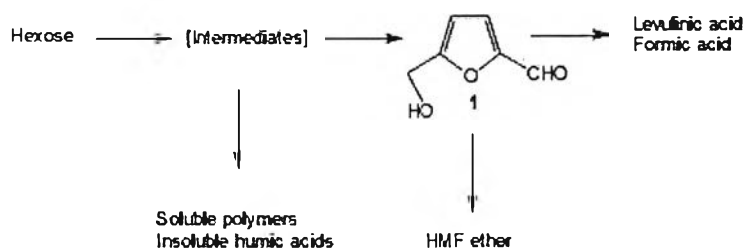


Figure 2.3 The synthesis of HMF from hexoses [Lewkowski et al., 2001].

HMF has several uses in chemical and food industries. It is used in the synthesis of dialdehydes, glycols, ethers, amino alcohols and acetals, and as a versatile

intermediate between biomass-based carbohydrate chemistry and petroleum-based industrial organic chemistry. HMF and its derivatives could potentially replace voluminously consumed petroleum-based building blocks [Bicker et al., 2003], which are currently used to make plastics and fine chemicals. Recently, Dumesic and co-workers introduced the idea of using HMF as a key intermediate to produce liquid alkanes from renewable biomass resources [Huber et al., 2005].

2.7 Furfural and its applications.

Furfural is an aromatic aldehyde, having the chemical formula $C_5H_4O_2$. In its pure state, it is a colorless oily liquid, but upon exposure to air it quickly becomes yellow. The production of furfural was prepared by hydrolysis of the pentosan polymers (e.g. xylan) to the pentoses (e.g. xylose) which is followed by catalytic dehydration to form furfural. Furfural dissolves readily in most polar organic solvents, but is only slightly soluble in either water or alkanes. Chemically, furfural participates in hydrogenation and other addition reactions more readily than many other aromatics. When heated above $250^\circ C$, furfural decomposes into furan and carbon monoxide, sometimes explosively. When heated in the presence of acids, furfural irreversibly solidifies into a hard thermosetting resin.

Furfural is an intermediate for chemical synthesis of a range of more specialized chemical products, starting mainly with furfural alcohol (FFA), which also has many derivatives. Furfural is important in a chemical industry dominated by hydrocarbons. Furfural is used largely in the resin production in which it is used as a binding agent in foundry technologies. The second main use is a selective solvent in petroleum production of lubricants [International Furan Chemicals, 2006].

2.8 Conversion of biomass to HMF and furfural.

Generally, the methods of the synthesis HMF and furfural from biomass consist of hydrolysis and dehydration process as shown in Figure 2.4. The first step, biomass decomposes to cellulose, hemicelluloses and lignin by hydrolysis process. Subsequently, cellulose hydrolyzes to glucose while hemicellulose hydrolyzes to glucose and xylose. Finally, glucose dehydrates to HMF and furfural while xylose dehydrates to only furfural. HMF and furfural can be produce from various substrates which want difference condition. Thus, conversion of biomass to HMF and furfural

can be devised to 2 parts. First part is the decomposition of biomass to monomer sugar and last part is the production of HMF and furfural from monomer sugar.

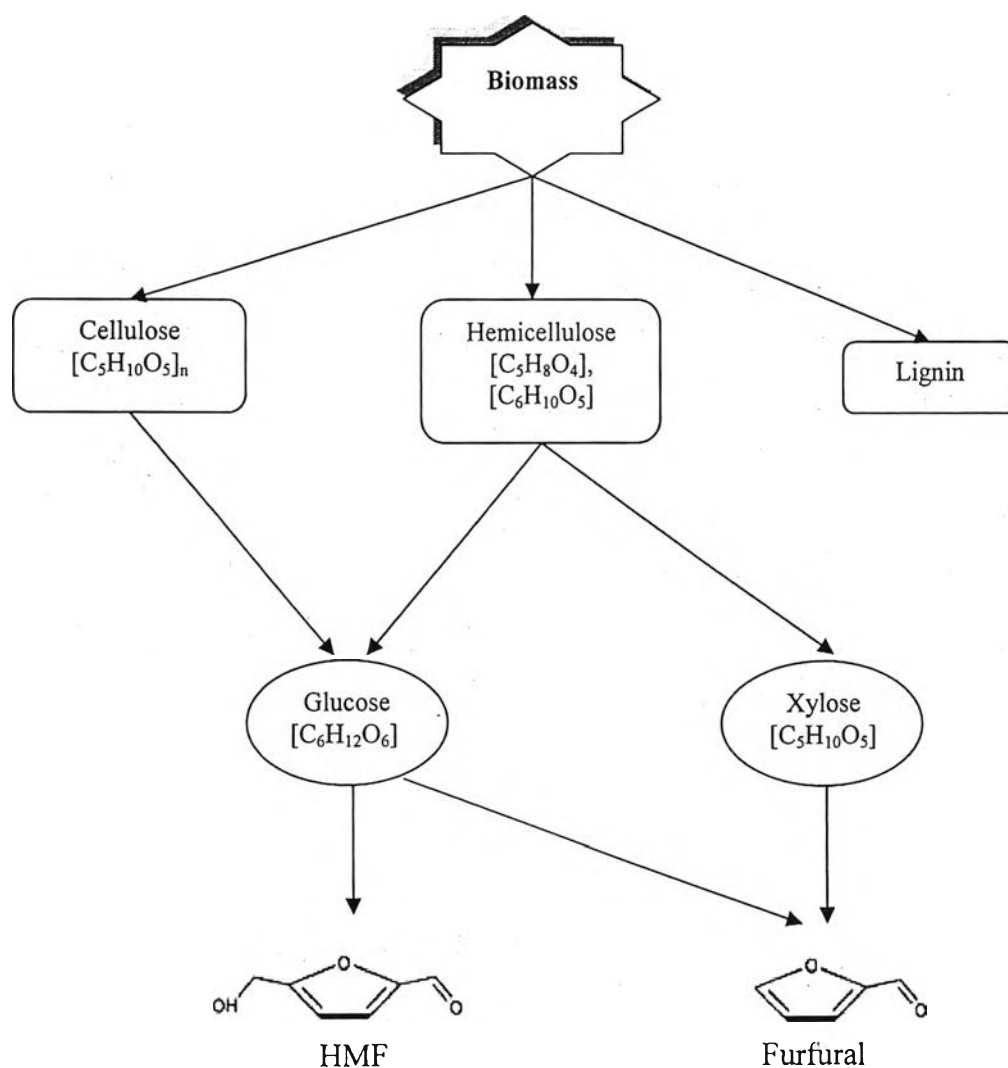


Figure 2.4 The pathways of Biomass to HMF and furfural.

2.8.1 Decomposition of biomass to monomer sugar

Generally, biomass decomposes to monomer sugar by hydrolysis which can be carried out as acid catalyst and/or enzymatic catalyzed process. However, these processes have many problem such as acid catalyst is corrosive and must be recovered the catalyst from product while enzymatic catalyzed process is long reaction time and to additional biomass. Thus, converting biomass to sugar in aqueous medium at high temperature, also known as hydrothermolysis, employing hot compress water (HCW) as a reaction medium is nowadays preferred because this process is environmentally

friendly, non toxic and short reaction time. Moreover, sugar can be dehydrated to HMF and furfural in this process.

2.8.1.1 Process in hot compress water

1. Hot compress water properties

HCW or water near and above its critical point ($T_c=647$ K; $P_c = 22.1$ MPa) offers the potential of high degree of conversion within short residence time, and it minimizes formation of toxic products. HCW serves as an excellent reaction medium due to the dielectric constant (ϵ) of water decrease at high temperature (Figure 2.5). The significant drops in the dielectric constant lead to a much increased solvent power. Furthermore, for process at near critical HCW, the ion product of water rises when the temperature is increased due to an increase in activity of hydronium ion and hydroxyl ion, and as a result, water itself acts as an acid and base catalyst. [Albrecht et al.,2006].

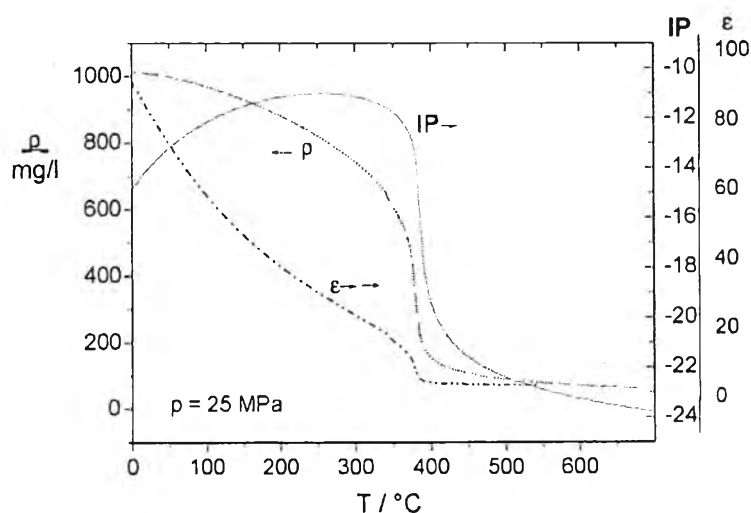


Figure 2.5 Selected properties of water at high temperature and high pressure [Kruse and Dinjus., 2007]

2. Hydrolysis mechanism in HCW

The mechanism of hydrolysis by HCW includes three steps. First, the water at high temperature and high pressure acts as an acid. Then, proton from acids adds to oxygen atom connecting the sugar unit and split C–O-linkage between the glycosidic oxygen. Lastly, acyclic carbonium ion in shape of a chair is form. Therefore, the water at high temperature and high pressure leads to an increase in the rate of hydrolysis and consequently to a high degree of decomposition.

3. Variable affecting the rate of hydrolysis in HCW

Hydrolysis affecting of biomass to monomer sugar depend on several variable such as kind of biomass, temperature, pressure and time of reaction. Ando et al.(2000) studied decomposition behavior of plant biomass under 9.8 MPa in HCW. Bamboo, chinquapin, and Japan cedar was used as substrate. They found that the decomposition of soft wood such as Japan cedar is hard to compose more then hard wood because of cross-linked structure of soft wood. Furthermore, they reported that hemicelluloses started to decompose when the temperature of the HCW was 180 °C then cellulose started to decompose when the temperature was over 230 °C, while on the other hand, most lignin was extracted by HCW at low temperature. Moreover, Sasaki et al.,(1998) studied cellulose hydrolysis in subcritical and supercritical water to recover glucose, fructose and oligomers in the range of temperature from 290 to 400°C at 25 MPa. They found that hydrolysis product yield obtained form supercritical water were much higher than those in subcritical because of at high temperature region, the glucose or oligomer conversion rate was much slower than the hydrolysis rate of cellulose.

2.8.2 HMF and furfural production from monomer sugar

Pentose and hexose convert to HMF and furfural by dehydration. However, most of research studies the production of HMF and furfural from glucose because glucose can produce from cellulose that main component from biomass. The type of reaction medium and its influence on the efficiency of the dehydration is closely connected with temperature conditions. Cottier et al (1991) divided methods into 3 groups depending on the type of reaction medium

2.8.2.1 Processes in Hot Compress Water

1. The kinetics of HMF and Furfural synthesis via HCW.

The production pathways of HMF and furfural from glucose have been reported by a number of researches as shown in Figure 2.6. The main products of glucose decomposition are fructose, erythrose, glycolaldehyde, dihydroxyacetone, glyceraldehyde, 1,6-anhydroglucose, pyruvaldehyde, furfural and HMF. The reactions involve mainly three types of reactions, namely isomerization, aldol condensation and dehydration. Pathway [a], [b], [c] and [d] show the isomerization of glucose and fructose. The dehydration process is presented in pathway [e] and [n] from glucose and fructose to HMF. Pathway [f], [g] and [r] show the dehydration of glucose and

fructose to furfural. In addition, glucose react in dehydration process to 1,6 anhydroglucose (AHG) in pathway [o] then decomposition to acetic acid and formic acid in pathway [p]. Pathway [q], [s] and [t] were proposed by Kabyemela et al. (1999), in which glycolaldehyde and dihydroxyacetone can be formed by aldol condensation process of fructose and the intermediate compounds during isomerization. Furthermore, erythrose and glycolaldehyde were produced from glucose and fructose by aldol condensation in pathway [q], [s] and [t].

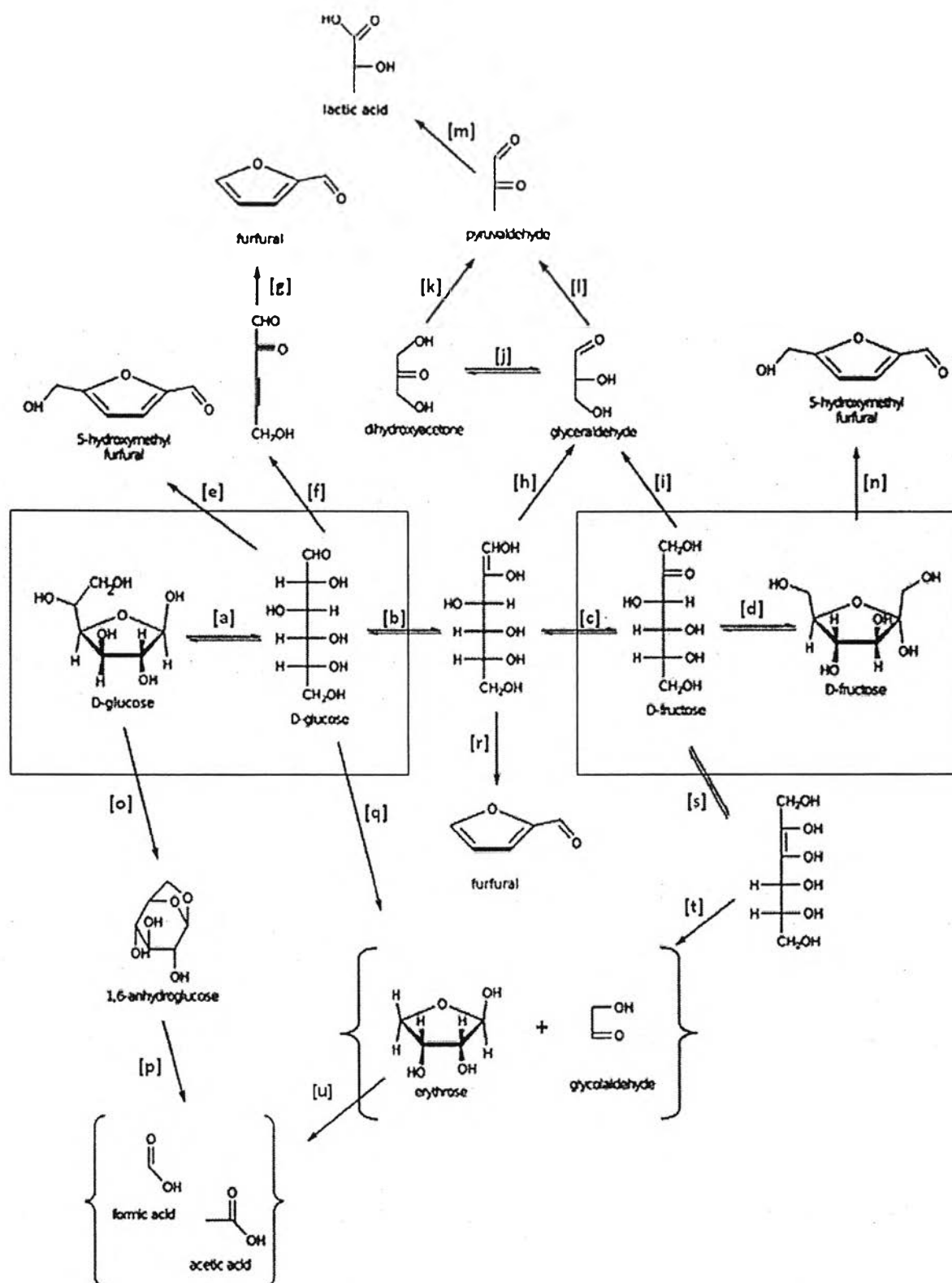


Figure 2.6 Pathway for degradation of D-glucose and D-fructose. References for individual reactions are given in brackets. [a], [b], [c] and [d] = Peterson et al. (2008), [e] = watanabe et al (2005) [r] = Aida et al.(2007), [f], [g] and [n] = Krishna et al. 1986, [h], [i], [m] and [o] = Antal et al. 1990, [j], [k], [l] = Bonn et al.1985, [p], [q], [s], [t] and [u] = Kabyemela et al. 1999.

Although HMF and furfural can be produced either from glucose, fructose and intermediate compounds during isomerization of glucose and fructose in HCW as shown in Figure 2.6, in several research works, the low yield of HMF and furfural in HCW was observed [Watanebe et al., 2008]. Previous research works suggested three possible reasons of this problem, which can be summarized as follow:

1. HMF can undergo further reactions in HCW to undesired products such as those shown in Figure 2.7. Aida et al (2007) indicated that under HCW process, HMF can be rehydrated to levulinic acid and formic acid, while 1,2,4 benzenetriol was produced by dehydration of HMF.

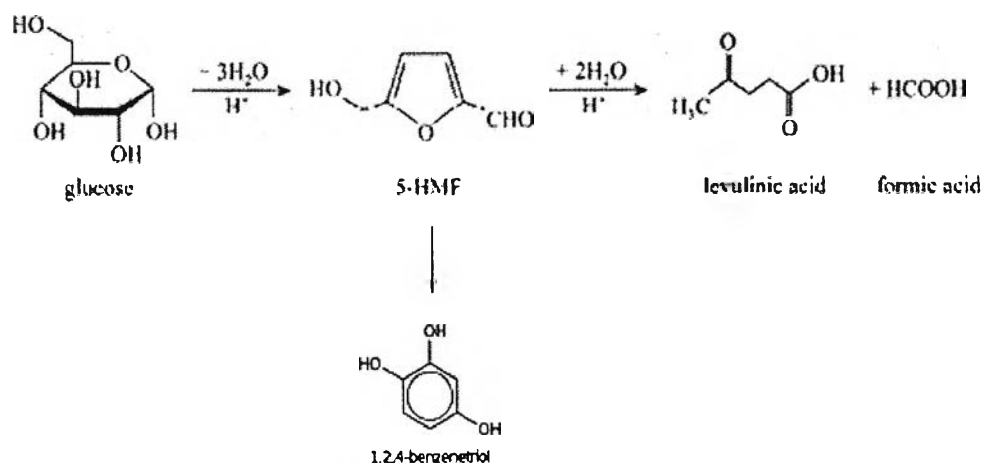


Figure 2.7 Decomposition pathways from 5-HMF [Aida et al.,2007].

2. In HCW process, furfural can decompose to other product as shown in Figure 2.8. Sinag et al. (2003), Dinjus et al.,(2004) and Kruse et al (2003) proposed that furfural under HCW process can convert to phenol and acids/aldehydes by dehydration and bond-breaking reaction, respectively.

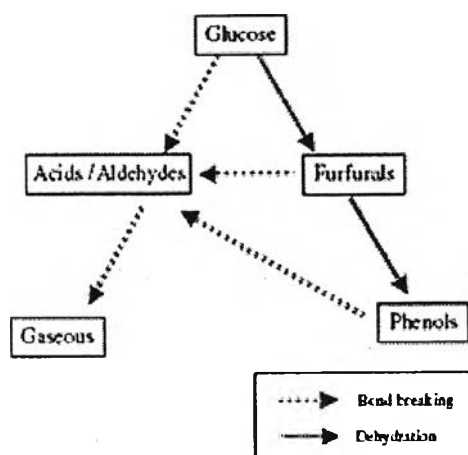


Figure 2.8 Simple reaction pathways of glucose reaction in HCW.

3. It is generally known that D-fructose exists in five different tautomeric forms. The two pyranoid and the two furanoid form are presented in Figure 2.9. However, only furanoid form of D-fructose can react to form HMF. Bicker et al. (2005) studied tautomeric forms of D-fructose in water and they found that the furanoid form is lower, whereas the pyranoid form is most preferred in water. Therefore in HCW process in which water was the only reaction medium, the furanoid form of D-fructose was suppressed, making the process unsuitable for HMF production.

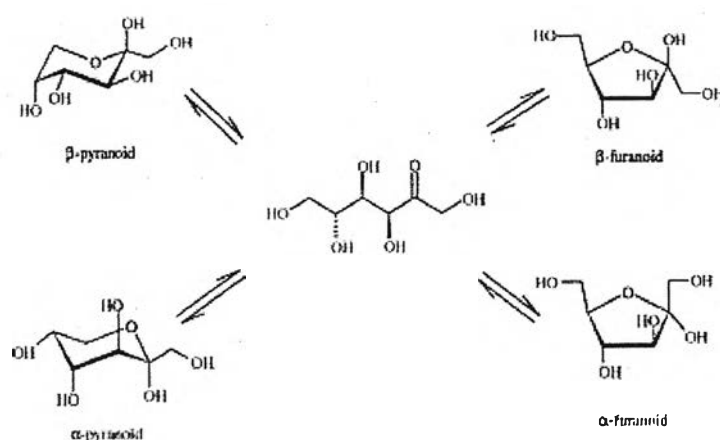


Figure 2.9 Tautomeric forms of D-fructose.

2. Variable affecting the rate of HMF and furfural formation in HCW

The maximum yield of HMF and furfural depends on the condition in HCW such as temperature and pressure, catalyst and the feedstock. The effects of the process variables are described as follow.

2.1. Effect of temperature and pressure

Temperature and pressure on the reactions in HCW are generally the main effects of HMF and furfural production. HMF and furfural slightly increase with increasing temperature and pressure. Nevertheless, the highest yields of HMF and furfural are usually obtained at the optimum condition before it decreased at higher temperatures and pressure. For instance, Asghari et al. (2006) investigated the reaction of D-fructose over a temperature range of 473 -593 K and found that the temperature had a strong influence on the reaction, from low to moderate temperature (473-533 K). However, at temperature higher than 533 K, the production yield decreases, because of the decomposition of HMF and furfural (Figure 2.7). Aida et al. (2007) studied the dehydration of D-glucose in high temperature water (up to 673 K)

at pressures up to 80 MPa using a flow reactor. They indicated that an increase in temperature (350 to 400 K) and pressure (40 MPa to 70 and 80 MPa) enhanced both dehydration reactions to 5-HMF and furfural and hydrolysis reactions of 5-HMF lead to the production of 1,2,4-benzenetriol (BTO). The enhanced hydrolysis of 5-HMF to BTO however led to lower yields of 5-HMF (below 10%). An increasing pressure and temperature on the dehydration and hydrolysis reactions may be due to the change of ion product (K_w) of HCW. Higher K_w values have been reported to enhance dehydration and hydration reactions by increasing the activity of the acid catalyst [Yoshida et al., 2006].

2.2. Effect of heating rate and reaction time

The effect of heating rate and reaction time on the reactions in HCW (473–773 K, 4–40 MPa) were studied by Watanabe et al. (2005b). They found that hydroglucose formation was increased and HMF production was suppressed when increasing the heating rate (from 4.2 to 15.8 K/s). The furfural yield was not affected by the increased heating rate. Furthermore, the conversion and gasification of glucose was enhanced with increasing heating rate. At 673 K, the dependence of reaction time on the glucose reaction was measured. HMF and furfural was slightly increased with increasing reaction time (30–45 s). After 45 sec, the yields of HMF and furfural gradually decreased with reaction time due to the decomposition of HMF to BTO, levulinic acid and formic acid and that of furfural to gas. This result was confirmed by the reaction pathways shown in Figure 2.7 and 2.8.

2.3. Effect of catalyst

Although under the high pressure and temperature conditions, the dehydration of fructose to HMF and furfural can be conducted even in absence of acid catalyst. However, in the presence of acids, the amount of conversion of fructose to HMF increases. As shown in Figure 2.10, an acid-induced elimination of 3 mol of water from saccharides occurs in the presence of acid catalyst.

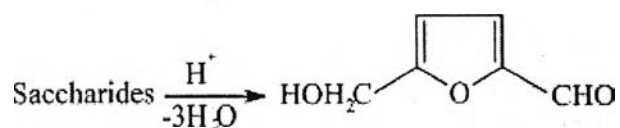


Figure 2.10 Dehydration of saccharides to 5-Hydroxymethyl Furfural (HMF)

Furthermore, many researchers also reported that acid catalyst could accelerate the production of HMF and levulinic acid under hydrothermal condition. Takeuchi et

al (2008) examined the effect of different homogeneous acid catalysts (H_2SO_4 , H_3PO_4 and HCl) on the production of HMF and levulinic acid. The H_2SO_4 and H_3PO_4 gave higher conversion of glucose to HMF than HCl , whereas HCl is more effective than H_2SO_4 and H_3PO_4 for further conversion of HMF into levulinic acid. Other than the type of the acid catalyst, Salak et al (2006) reported also the importance of the pH on the production of HMF and Furfural. In their work, of all acid catalyst (HCl , H_2SO_4 , citric acid, maleic acid, PTSA, oxalic acid) in the pH range of 1.5-5 used, phosphoric acid catalyst at pH 2 was found to give the highest yield of HMF. Compared with homogeneous catalysts however, heterogeneous acid catalysts offer higher selectivities towards HMF and furfural. Moreover, heterogeneous acid catalysts are easily separable from the reaction products, thus are recyclable. Watanebe et al (2005a) conducted an experiment on HMF production from fructose and glucose in HCW. They found that the process carried out using TiO_2 and ZrO_2 gave comparable HMF yield to those using homogeneous acid catalysts and they indicated that ZrO_2 promoted the isomerization reaction while TiO_2 promote both dehydration and isomerization reaction. Furthermore, Chareonlimkun et al (2010a) studied the effect of sulfate zirconia ($\text{SO}_4\text{-ZrO}_2$), TiO_2 and ZrO_2 and they found that $\text{SO}_4\text{-ZrO}_2$ promote the dehydration reaction as same as TiO_2 catalyst whereas ZrO_2 promoted the isomerization reaction. To improve the catalytic activity, Chareonlimkun et al (2010b) aimed to mixed-oxide $\text{TiO}_2\text{-ZrO}_2$ to enhance the HMF and furfural production. Compare with TiO_2 and ZrO_2 catalyst, they found that the $\text{TiO}_2\text{-ZrO}_2$ catalyst produced the highest HMF and furfural yields with less by product (e.g. glucose, fructose, xylose and xylose) selectivity. In addition, they claim that the catalyst preparation procedure, the starting salt precursor and the calcinations temperature strongly affected the acidity-basicity and the reactivity of catalyst in HMF and furfural production.

2.8.2.2 Processes in non-aqueous medium.

As already mentioned and schematically shown in Figure 2.9, fructose dehydration in pure water is generally nonselective, leading to many by-products besides HMF and furfural. Moreover, furanoid form of D-fructose is lower in process in pure water. These problems were resolved by employing non-aqueous medium [Richard et al, 1987; Roman-Leshkov et al., 2009]. Richard et al. (1987) demonstrated high yields of HMF and furfural could be obtained from fructose by using strong polar organic solvents. Dehydration of fructose in dimethylsulfoxide (DMSO) at 150 °C for 2 h. DMSO was found to give as high as 92% HMF yield. The reason for high yielding reaction in DMSO was due to the fact that furanoid forms of D-fructose are highly favored and highly stable in this solvent. This explanation was confirmed by the study of Lichtenthaler et al (1990) which demonstrated a fructose and DMSO associate in Figure 2.11, which conceivable dimethyl sulphoxide cis-diol hydrogen bonding in the β -f-tautomer of fructose. In addition, Ananda et al (2008) propose mechanism for the dehydration of D-fructose furanose form to HMF in DMSO (Figure 2.12).

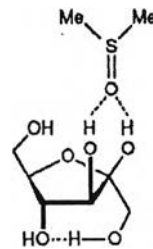


Figure 2.11 d-fructose/DMSO associate

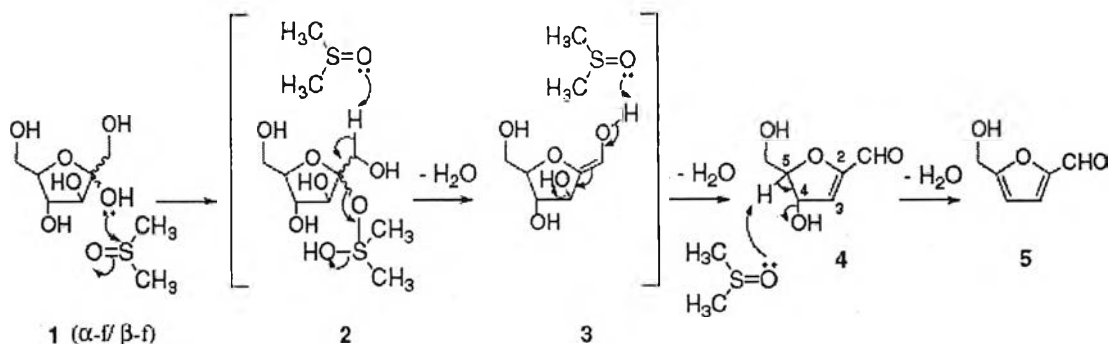


Figure 2.12 Proposed mechanism for the dehydration of D-fructose furanose forms 1 (a-f/b-f) to 5-hydroxymethylfurfural (5) in dimethyl sulfoxide at 150 °C.

Other than DMSO, ionic liquids have also been applied as solvents due to their unique properties such as very low vapor pressures, unusual modes of coordination and the tendency to form solvent cages and capability of acting both as solvent and catalyst. Several studies have investigated ionic-liquid-phase reactions, which are relevant as potential routes for the production of HMF and furfural. For example, Moreua et al (2003) have demonstrated that neutral ionic liquid such as 1-butyl 3-methyl imidazolium tetrafluoroborate ($\text{BMIM}^+\text{PF}_4^-$) can act as a suitable reaction medium for dehydration of fructose to HMF in the presence of the Amberlyst-15 catalyst. They found that as high as 92% HMF yield was achieved within 15-45 min at 90°C using 1-H-3-methylimidazolium chloride (HMIM^+Cl^-), acting both as solvent and catalyst [Moreau et al., 2006]. Moreover, when 1-ethyl-3-methylimidazolium chloride ($[\text{EMIM}]\text{Cl}$) was used as a solvent and metal chlorides ($\text{CuCl}_2, \text{CrCl}_2$) as catalyst, 96% yield of HMF could be produced at 80-120°C [Yu Su et al]. Although, Ionic liquids are advanced solvents in view of controllability of its properties and productivity, but many of these are too expensive to allow their use on a practical scale.

2.8.2.3 Processes in mixed medium.

Because of its similar to the DMSO molecule (Figure 2.13), acetone is considered another essential reaction medium that can promote conversion of fructose to the furan form [Qi et al., 2008]. Unfortunately, the solubility of fructose in pure acetone is almost negligible (0.5 g/L at 25 C) [Bicker et al.,2002] and thus, either water or another solvent is needed to allow improved conversion. Bicker et al. (2003) studied the dehydration of fructose to 5-HMF in sub-and supercritical acetone/water mixtures and obtained the results that both the 5-HMF selectivity and the fructose conversion increased with increasing acetone content and that the optimal selectivity to 5-HMF of 77% could be obtained with 99% fructose conversion using acetone/water in a 90:10 v/v ratio. Qi et al (2008) found that the use of a 70:30 (w/w) acetone/water reaction medium resulted in as high as 73.4% yield of 5-HMF and 94% conversion at 150 °C in the presence of a strong cation-exchange resin as the catalyst under microwave heating. This result confirms that the problems concerning the solubility of hexoses or pentose in organic solvents were resolved by the application of mixed-solvent (water-organic) systems. Unfortunately, although the use of water as a solvent does increase the solubility of fructose in the solvent, it also promotes side reactions such as luvelinic acid and formic acid. Hence, other types of solvents

instead of water are need. Qi et al (2008) found that the acetone/DMSO (70:30 w/w) mixture were shown to be effective for the dehydration fructose to 5-HMF selectivity in the presence of a strong acidic cation exchange resin catalyst (dowex 50wx 8-100) under microwave heating. The higher HMF yield of 89.8% (selectivity of 91.7%) was achieved compared with that obtained with the reaction with 70:30(w/w) acetone/water as solvent. Furthermore, they investigated the dehydration of fructose to 5-HMF in aqueous and acetone–DMSO mixture solvents in the presence of sulfated zirconia catalyst and found that high fructose conversion of 93.6% with 72.8% 5-HMF yield could be attained at 180 °C for 20 min reaction time in acetone–dimethylsulfoxide (DMSO) mixtures under microwave heating.

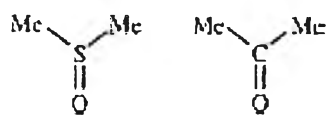


Figure 2.13 Structure analogy of DMSO and acetone.