

CHAPTER I

INTRODUCTION



1.1 Rationale

Nowadays, the fuel price increases wildly due to the increase in world population and rising energy demand for industry and transportation. As a result, research on development of technologies for the processing and utilization of nonpetroleum feedstocks (e.g., gas, coal, and biomass) for alternative fuel production has now been the center of attention worldwide. Among various feedstocks, biomass is the most promising alternatives because of the current large world supply ($1.2\text{-}1.7 \times 10^{11}$ ton per years) of biomass from plant [vessia et al., 2005]. Lignocellulosic biomass, or biomass that contains cellulose, hemicelluloses and lignin as the main constituents, is basically the most abundant organic matter derived from agricultural residues and waste from food industries. As in one of the most important food industries in Thailand, for example the production of cassava flour solid which is accounted for about 10-15% of fresh cassava root. Cellulose, hemicellulose and lignin are the main constituents of cassava waste and make up the lignocellulosic structure.

To convert the lignocellulosic biomass into liquid fuels, various processes are currently used, including the formation of bio-oil by pyrolysis and the production of alkane by Fisher-Tropsch process. However, the uses of liquid fuels derived from these processes are limited due to the high cost of synthesis. In addition, the cost of property improvement remains relatively high.

Recently, Huber et al. (2005) and Juben et al. (2007) proposed a low cost process to produce liquid alkane from biomass, or so called biomass to liquid fuel, (BTL). The process consists of 4 steps, including hydrolysis, dehydration, aldol condensation and hydrogenation. The first process involves the conversion of biomass into glucose molecules through hydrolysis reaction. Subsequently, glucose isomerizes into fructose, and both glucose and fructose undergo dehydration to HMF and furfural. Subsequently, via aldol condensation and hydrogenation in the presence of acetone and hydrogen, HMF can be transformed to large water-soluble organic compounds. Finally, these molecules are then converted into alkanes through dehydration/hydrogenation reaction. In the BTL process, HMF and furfural are

considered the most important intermediates for the production of liquid fuel from biomass, not to mention its other uses in several chemical and petrochemical industries.

Generally, the production of HMF and furfural from biomass consist of 2 steps. First, biomass is hydrolyzed to monomer of sugar and which then dehydrates to HMF and furfural. In most of previous works, the hydrolysis from biomass to monomeric sugars has been carried out mostly in hot compressed water (HCW). The reason for HCW being the most widely used medium is that water at high temperature and high pressure acts as acid for hydrolysis. Moreover, process in HCW typically is environmental friendly, high conversion within short residence time could be achieved. In addition, the formation of toxic products is minimized. For the dehydration of monomeric sugars to HMF and furfural, HCW is till widely use. However, dehydration typical limitation for the process with water as reaction medium is that it is nonselective, leading to many by-products such as levulinic acid and formic acid. Furthermore, water suppresses furanoid form of D-fructose, which is the only form that can react to form HMF. These problems were resolved by using non-aqueous medium act as solvent [Roman-Leshkov et al., 2009]. Ionic liquids and organic solvent are advanced solvents in view of controllability of its properties and productivity. Among organic solvents, acetone and DMSO is of most interest as a solvent for such process because furanoid form of D-fructose is highly favored in these solvent. In addition, acetone and DMSO can react with fructose to form HMF readily. Moreover, HMF rehydration into many by-products was minimized in the reaction carried out in these solvents. Although under high pressure and temperature conditions, the dehydration of monomeric sugars to HMF and furfural can be conducted even in absence of catalyst, In the presence of catalyst, HMF and furfural product is increased. For instance, Chareonlimkun et al. (2010a,b) demonstrated that sulfate zirconia ($\text{SO}_4\text{-ZrO}_2$), TiO_2 , ZrO_2 and $\text{TiO}_2\text{-ZrO}_2$ promote the production of monomeric sugars to HMF and furfural in HCW process. Furthermore, Qi et al. (2008) studied the effect of sulfate zirconia ($\text{SO}_4\text{-ZrO}_2$) and ZrO_2 catalysts on the production of HMF and furfural from sugar in acetone/DMSO mixtures medium and the result indicated that low yield of HMF was obtained when ZrO_2 catalyst was used in this medium, while high production yield of HMF (72.8%) and high conversion of sugar (93.6%) could be achieved with use of sulfated zirconia catalyst. In addition, Chareonlimkun et al. (2010a,b) claimed that the catalyst preparation procedure, the

starting salt precursor and the calcinations temperature strongly affected in reaction of HMF and furfural production.

In this study low cost carbon based catalyst was employed for the production of HMF and furfural from cassava waste. The suitable composition of acetone/DMSO and water which is the most suitable medium for hydrolysis and dehydration processes were determined for the conversion of cassava waste both with and without catalyst. Moreover, the suitable temperature and reaction time for the production HMF and furfural from cassava waste were determined. In addition, through the reactions carried out with various reactants such as fructose, glucose, cellulose, and xylose, the process mechanisms of the reaction in the carbon based catalyst were examined. This type of catalyst could potentially provide a new alternative to economical acid catalyzed liquid fuel production from biomass

1.2 Objectives

1.2.1 To investigate the possibility of applying the carbon based catalyst to HMF and furfural production from biomass and compare its activity with that of commercial catalysts.

1.2.2 To determine the suitable conditions for the production of HMF and furfural from cassava waste.

1.2.3. To study the reaction pathway of HMF and furfural production using carbon based catalyst.

1.3 Working scope

1.3.1 Determine the suitable conditions for the production of HMF and furfural from cassava waste.

1.3.1.1 Determine the suitable composition of medium that consist of acetone/DMSO (70:30 w/w) and water whose weight ratios ranged from 100:0 (w/w) (i.e. pure acetone/DMSO (70:30 w/w)) to 0:100 (i.e. pure water) without and with carbon based catalyst at 250°C .

1.3.1.2 At suitable the composition of medium, determine the suitable temperature (230°C, 240°C, 250°C, 260°C and 270°C) for the production of HMF and furfural from cassava waste.

1.3.1.3 Determine the suitable time (0 min, 2 min , 5 min ,7 min ,10 min and 12 min) required for reaction at suitable the composition of medium and temperature from previous section.

1.3.1.4 At the optimum condition, determine the effect of dose of carbon based catalyst (0.05 g, 0.1 g and 0.15 g) for the production of HMF and furfural from cassava waste.

1.3.2. To understand the effect of the catalyst in the pathways of HMF and furfural production from biomass by examining the reactions of fructose, glucose, xylose, hemicelluloses and cellulose, carried out at suitable composition of medium. Fructose, glucose and xylose were reacted at 200°C while hemicelluloses and cellulose were reacted at 230°C. The reactions were carried out at various reaction times, with and without catalyst on rang of time (0 min, 2 min, 5 min, 7 min, 10 min and 12 min).

1.3.3 Compare the activity of the catalyst with commercial sulfate zirconia catalyst and H₂SO₄ catalyst at suitable condition.

1.3.4 Determine the effect of recycling of the catalyst on the production of HMF and furfural at suitable the composition of medium.

1.4 Expected benefits

1.4.1 This study investigates the possibility of HMF with and furfural production from biomass with carbon based catalyst as an alternative to other solid catalysts conventionally used.

1.4.2 The suitable conditions for the production of HMF and furfural from cassava waste with the new carbon based catalyst will be available.

1.4.3 The information regarding reaction pathway with the new carbon based catalyst can be used as guidelines for HMF and furfural production from other feedstock.