

การเตรียมสาร 5 ไฮดรอกซีเมทิลเฟอฟูรานด้วยการไฮโดรเทอร์มัล ทรีตเมนต์ของกากกะลาปาล์ม



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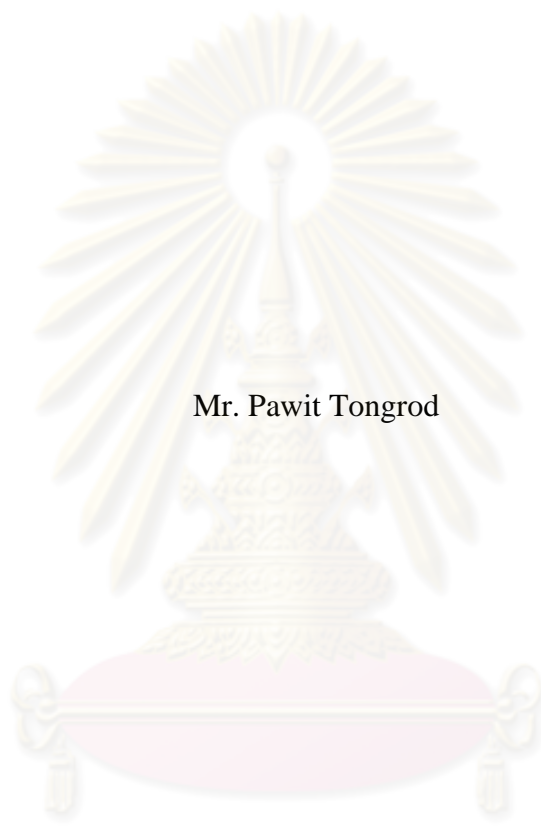
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ปีการศึกษา 2553

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREPARATION OF 5-HMF BY HYDROTHERMAL TREATMENT  
OF PALM KERNEL SHELL RESIDUES



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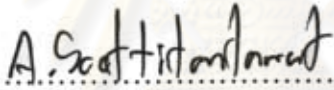
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By   Mr. Pawit Tongrod  
Field of Study                                 Chemical Engineering  
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ภวิศ ธงรอด : การเตรียมสาร 5 ไฮดรอกซีเมทิลเฟอฟูรานด้วยการไฮโดรเทอร์มัล ทรีตเมนต์ของกากกะลาปาล์ม. (PREPARATION OF 5-HMF BY HYDROTHERMAL TREATMENT OF PALM KERNEL SHELL RESIDUES) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร. ธวัชชัย ชรินพาณิชกุล, 102 หน้า.

กระบวนการไฮโดรเทอร์มัล ทรีตเมนต์ของชีวมวลนับเป็นเทคโนโลยีสะอาดที่สามารถสังเคราะห์ผลิตภัณฑ์ได้ในร้อยละสูงวิธีหนึ่ง และจากสภาพการณ์ปัจจุบันเป็นที่เชื่อกันว่าโลกจะเผชิญกับปัญหาด้านการขาดแคลนพลังงานในอนาคต ซึ่งเป็นปัญหาใหญ่ที่ต้องเร่งหาวิธีในการแก้ไข ดังนั้นในงานวิจัยนี้จึงมีวัตถุประสงค์ที่จะสังเคราะห์สาร 5 ไฮดรอกซีเมทิลเฟอฟูรานจากกากกะลาปาล์ม ซึ่งสารเคมีดังกล่าวสามารถจะนำมาใช้เป็นหนึ่งในพลังงานทดแทนได้

งานวิจัยนี้จึงนับว่าเป็นความท้าทายประการหนึ่งในการที่จะเตรียมสาร 5 ไฮดรอกซีเมทิลเฟอฟูรานจากชีวมวล โดยการใช้กากกะลาปาล์มภายใต้สภาวะการทดลองต่างๆ ประกอบด้วย อุณหภูมิที่ใช้ในการทำปฏิกิริยาในช่วง 200 ถึง 300 องศาเซลเซียส อัตราการให้ความร้อนตั้งแต่ 5 ถึง 10 องศาเซลเซียสต่ออนาที ความเข้มข้นของสารตั้งต้นที่ใช้ที่ 10 และ 20 ของร้อยละ โดยน้ำหนัก และปริมาณลิกนินที่มีต่อผลได้ของสาร 5 ไฮดรอกซีเมทิลเฟอฟูราน ซึ่งพบว่าการเกิดขึ้นของสารดังกล่าวจะขึ้นกับสภาวะที่ใช้ในการทดลองข้างต้นทั้งสิ้นแม้ว่าผลได้จะมีค่าค่อนข้างต่ำ นอกจากนี้จะตรวจสอบถึงผลของการเติมตัวเร่งปฏิกิริยาหลายชนิด ได้แก่ บิวทานอล ไคเมทิลซัลโฟนิกแอซิดและกรดฟอสฟอริกที่มีผลต่อการเพิ่มผลได้ของสาร 5 ไฮดรอกซีเมทิลเฟอฟูราน โดยพบว่า บิวทานอลและไคเมทิลซัลโฟนิกแอซิดเป็นตัวเร่งปฏิกิริยาที่ดีในการเพิ่มผลได้ของสาร 5 ไฮดรอกซีเมทิลเฟอฟูรานเมื่อเปรียบเทียบกับกรดทดลองในสภาวะปกติ นอกจากนี้ยังพบว่าสารประกอบที่เกิดขึ้นจากกระบวนการไฮโดรเทอร์มัล ทรีตเมนต์ของกากกะลาปาล์มยังประกอบไปด้วย สารไดไฮดรอกซีแอซิโตน กรดฟอร์มิก กรดแอซิดิก อะเซตทาลดีไฮด์และเฟอฟูราน

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PAWIT TONGROD: PREPARATION OF 5-HMF BY  
 HYDROTHERMAL TREATMENT OF PALM KERNEL SHELL  
 RESIDUES. ADVISOR: ASSOC. PROF. TAWATCHAI  
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Hydrothermal treatment of biomass is one of the most promising technologies for converting biomass into a higher value-added form. It is well recognized that palm oil production is one of the major industries in Thailand, which generates many palm kernel shell residues. This work focuses on utilizing hydrothermal treatment of cellulose in palm kernel shell residues for 5-hydroxymethyl-furfural (5-HMF) production. Because the palm kernel shell residues contain cellulose approximately 60 wt%, it would possibly provide a high yield of sugar and furfural products. Palm kernel shells residues were treated by alkali solutions before adding into a batch-type tubular reactor. A series of systematic experiments were performed in a reaction temperature range of 200 to 300 °C, heating rate ranging from 5 to 10 °C/min, concentration of palm kernel shell residues (feedstock) at 10 and 20 wt%, effect of lignin content. It was found that the 5-HMF yield was obviously dependent on the reaction temperature, heating rate, concentration of feedstock and lignin content. Furthermore, the effect of concentration of 2-butanol, phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) and dimethyl sulphoxide (DMSO) were also investigated. Experimental results have shown that 2-butanol and DMSO were good selective solvents for the production of 5-HMF in the hydrothermal treatment process. It could be firmly believed that the liquid product obtained from the hydrothermal treatment consisted of 1,3-dihydroxyacetone dimer, formic acid, acetaldehyde, 5-hydroxymethylfurfural (5-HMF), acetic acid and furfural.

Department : Chemical Engineering

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Field of Study : Chemical Engineering

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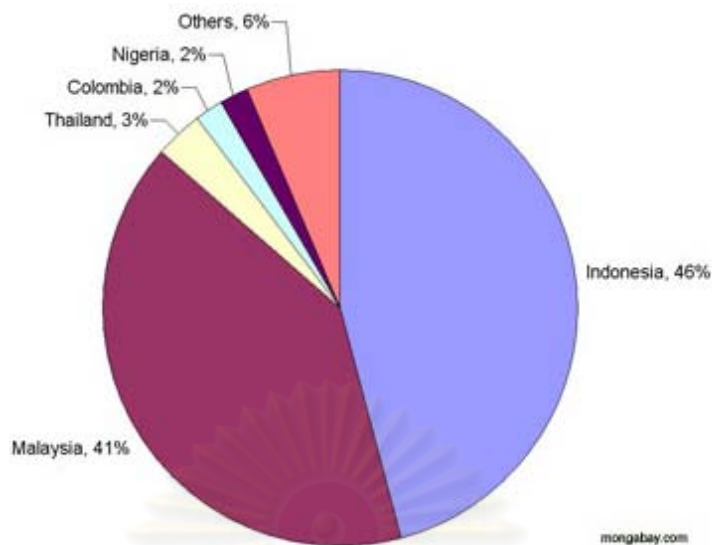
# CHAPTER I

## INTRODUCTION

### 1.1 Background

In recent years, an increasing of energy consumption led to rapidly deplete energy sources. The nonrenewable sources of energy available in the nature are coal and petroleum. The combustion of these hydrocarbons is not only a common source of energy, but common byproducts of the combustion process also produced carbon dioxide, carbon monoxide and nitrogen. For example, carbon dioxide is one of the greenhouse gases generated with a large amount each year, it was considered as one of the major effects of the global warming. For this reason, the global temperature continuously increases. Thus, the exploration of the substituting energy sources is the urgent issues to fulfill this recruitment. To reduce the demand of fossil fuels, many researchers have paid their attention to other sources of clean energy such as solar, wind, tides, geothermal heat and biomass. It should be note that biomass was a good candidate which has been employing a lot attention. Biomass is a biological material including biodegradable wastes that can be burnt as fuel. It excludes organic materials such as fossil fuels which have been transformed by geological processes into substances. Many researchers also showed its viability for large scale production of biomass. Moreover, biomass energy generation will cause lower green house effect due to the recycling process of the plant rotation [1]. There are various biomass materials available in Thailand. Especially, agricultural waste such as cob, husk, bagasse, sawdust, coconut shell and palm kernel shell which are abundant and inexpensive. Some of them could be used as promising sources of renewable energy.

Many countries in the world including Thailand are the producers of palm oil. Figure 1.1 shows the market share of palm oil production in 2008. Particularly, Thailand is the third palm oil production in the world. It could be supposed that the production of palm oil can be successfully mainstreamed in Thailand in the future.



**Figure 1.1** Palm oil exporting market shares

Taking into account that palm oil production is a large industry in the south of Thailand, generating annually 386,930 tons of empty fruit bunches, 165,830 tons of palm press fibers and 110,550 tons of palm kernel shells [2].

**Table 1.1** Chemical components of palm oil [3]

Types of biomass residues	Chemical compositions (%)			
	Cellulose	Hemicellulose	Lignin	Ash
Empty fruit bunch	38.3	35.3	22.1	1.6
Palm kernel shells	20.8	22.7	50.7	1.0
Palm tree trunks	34.5	31.8	25.7	4.3
Fronds	30.4	40.4	21.7	5.8
Mesocarp fibers	33.9	26.1	27.7	3.5

Table 1.1 shows the chemical composition of palm oil biomass residues in Malaysia. In addition, the compositions of palm oil biomass residues dependent on the species of palm oil, landscape and atmospheric conditions. The components of palm

oil biomass residues that could be used for hydrothermal process are empty fruit bunch, mesocarp fibers, palm kernel shells, palm tree trunks and fronds. The main components of palm oil biomass were cellulose and hemicelluloses that consisted in empty fruit bunch, palm tree trunks, fronds and mesocarp fibers. Expectable only for palm kernel shells which lignin is the most abundant constituent.



**Figure 1.2** Palm tree trucks - Mesocarp fibers - Fronds

It could be supposed that the main agricultural wastes from the palm oil industries, such as empty fruit bunch, mesocarp fibers, palm kernel shells, palm tree trunks and fronds can be employed for the generation of renewable energy [4]. The chemical compositions of these wastes mainly consist of cellulose, hemicellulose, lignin and ash.



**Figure 1.3** Empty fruit bunch - Palm kernel shells

Cellulose is a valuable renewable resource which store in biomass, and also glucose and its oligomers which can be obtained by the hydrolysis of cellulose are expected to be valuable chemicals, food and feedstock [5]. Several technologies have been developed for the hydrolysis and pretreatment of cellulose for the production of

fuel ethanol, including hydrothermal treatment, acid treatment, steam explosion and enzymatic hydrolysis [6-8]. Besides to these approaches, subcritical and supercritical water treatments have also been investigated and have shown some particular advantages, such as high reaction rate, no catalyst requirement and no product inhibition [9].

The transformations of cellulose hydrolysis in subcritical and supercritical water have been investigated and reported. When cellulose aqueous is hydrothermally treated at high temperature, cellulose chains are hydrolyzed, leading to the conversion of the cellulose into water-soluble oligosaccharides, including cellobiose, cellotriose, cellotetraose and cellopentaose. Thereafter, the original cellulose is converted further into glucose, fructose and fragmentation products, such as 1,6-anhydroglucose, erythrose and 5-hydroxymethylfurfural (5-HMF) [10].

One promising chemical transformation of biomass is 5-hydroxymethylfurfural (5-HMF), which is suitable for alternative polymers and for liquid bio-fuels. 5-HMF is a versatile chemical platform that can be used to integrate a wide range of chemicals derived from petroleum such as 2,5-furandicarboxylic acid (FDA) and 2,5-dimethylfuran (DMF). In addition, FDA has been proposed as a replacement both of polyethylene terephthalate and polybutelene terephthalate for the production of biodegradable plastic [11-12]. Especially, DMF has been proposed as a replacement of ethanol for the production of liquid bio-fuel [13-14]. However, it should be noted that there is no clear evidence of reported results of preparation of 5-HMF from palm kernel shell residues via hydrothermal treatment process. Therefore, the objective of this study is to investigate the preparation of 5-HMF from palm kernel shell residues using subcritical water treatment as well as to find out an optimal conditions to obtain a high yield of 5-HMF products in this process.

## **1.2 Objectives**

The object of this research is to examine condition for preparing 5-HMF from palm kernel shell residues in subcritical water and to find out an optimal condition for increasing high yield of 5-HMF products.

### 1.3 Scope of research

1. Palm kernel shell residues (feedstock) will be dried in the conventional oven at 80 °C for 10 minutes in order to remove the volatile matter.

2. Dried palm kernel shell residues will be used as a biomass feed stock under hydrothermal treatment conditions.

3. Cellulose will be extracted from the palm kernel shell residues by alkali treatment.

4. The experimental conditions for hydrothermal treatment process of palm kernel shell residues will be focused by variation of following parameters.

-Effect of reaction temperature in a range of 200-300 °C.

-Effect of heating rate ranging from 5-10 °C/min.

-Effect of concentration of palm kernel shell residues in a range of 10–20 wt%.

-Effect of lignin content in feedstock.

-Effect of extracting solvent and homogeneous catalyst consisted of 2-butanol, dimethyl sulfoxide (DMSO) and phosphoric acid (H<sub>3</sub>PO<sub>4</sub>).

### 1.4 Expected benefits

1. To obtain the guideline for preparing 5-HMF from palm kernel shell residues under subcritical water and to find out an optimal condition for gaining high yield of 5-HMF products.

2. To gain additional experimental data to support biomass technology in Thailand for the future renewable energy sources.

3. To discover the production of 5-HMF from palm kernel shell residues as real biomass material.

## CHAPTER II

### LITERATURE REVIEW

#### 2.1 The hydrothermal treatment of cellulose with non-catalytic conversion under subcritical and supercritical water.

**Zhang, Keitz, and Valentas (2007)** studied the effect of heating times in the range of 30 to 60 min. The hydrothermal liquefaction was performed by used batch pressure vessels reactor. In the chemical point of view, the heating rate can possibly affect yields and the composition of the resultant liquid products. It could be indicated that the mode of heat transfer becomes uncontrolled variable in kinetic studies and can seriously impact scale-up. To ensure this hypothesis, they designed a batch pressure vessel coupling with an induction heating system allowing the reduction of heat up times by about two orders of magnitude to several seconds, compared to tens of minutes with standard pressure reactors. This system was used to study the direct liquefaction of corn stove and aspen wood with a pretreatment. They observed that the heating rate have no significantly effect on the composition of liquid products. However, the liquid yields are dependent on the heating rate. In addition, the cooling rate does not obviously show effects on the composition and liquid yields of liquid products. The results confirm that the heating rate, as governed by the mode of heat transfer, is an important factor that needs to be considered during scale-up [15].

**Kruse and Dinjus (2007)** investigated the degradation of glycerol, a model substance for carbohydrates and biomass on hot compressed water (HCW) at the reaction temperature above 200 °C. This reaction shows a strong dependence on the properties of HCW. They found that water accelerates biomass de-polymerization by hydrolysis. The glycosidic bond of cellulose and hemicellulose were hydrolyzed very fast in HCW. Then, they are split in sugar units and the whole biomass structure breaks down. This improves a further attack by water molecules. Subcritical water conditions supports water eliminations from carbohydrates and alcohols because of the high ionic product increasing the reaction rate of this usually acid-catalyzed



reaction. Moreover, other reaction like aldol condensation is enhanced by the special properties of subcritical water [16].

**Eiji et al (2008)** proposed on the effect of heating rate on the liquefaction of a microcrystalline cellulose particle by using a batch type reactor with a temperature controller. The Experiments were carried out over the temperature range of 443–553 K with the heating rate ranged from 0.0167 to 0.167 K/s. The resulting concentration profiles of cellulose, oligosaccharides, monosaccharides and pyrolyzed products were analyzed using a theoretical model which considered temperature variation during the reaction. The calculated results showed a reasonable fit to the experimental data. The predicted cellulose concentration profiles over a wide range of heating rate indicated that the liquefaction of cellulose was affected when the heating rate is below 1 K/s. It was concluded that the consideration of the heating process necessary in the modeling of liquefaction when using slow heating [17].

## **2.2 The behavioral decomposition of pure 5-hydroxymethylfurfural (5-HMF) under subcritical and supercritical water.**

**Chuntanapum et al (2008)** studied the decomposition behavior of 5-HMF in both subcritical and supercritical water in the temperature range from 175-450 °C. The decomposition of 5-HMF had Arrhenius characteristics, which can be described by a first-order serial reaction. The 5-HMF clearly resisted decomposition at low temperatures of up to 250 °C. But the decomposition began at higher temperatures from 300 to 450 °C and complete decomposition at 450 °C. Moreover, they found that the reaction of pure 5-HMF in water did not produced any tar or char [18].

## **2.3 The hydrothermal treatment of D-fructose, D-glucose and xylose with catalytic conversion under subcritical and supercritical water for 5-HMF production.**

**Chen, Kuster, and Van Der Wiele (1991)** studied a new procedure for the preparation of 5-HMF from D-fructose. The reaction was performed in a continuous tubular reactor. 1,2:4,5-di-o-isopropylidene-B-D-fructopyranose (DIpF) was used as a reactant dissolved in ethylene glycol dimethyl ether (EGDE) containing some water

and sulfuric acid as a catalyst. They found that 5-HMF yields amounted to more than 70 mol% without the problem of plugging from insoluble solid. These results were obtained for several combinations of temperature, concentrations of both acid and water [19].

**Bicker et al (2005)** investigated the dehydration of D-fructose in various kind of solvent including Acetone/water, Methanol, Acetic acid and water in subcritical and supercritical water condition by using continuous high pressure reactor. They concluded that acetone molecule, which is very similar to dimethyl sulphoxide (DMSO) might be the reason for the high 5-HMF selectivity. Because of a fructose/DMSO associated, which the furanoid form of fructose would promote that is why the highest 5-HMF selectivity was obtained in that solvent and favor the formation of 5-HMF [20].

**Watanabe et al (2005)** discovered the use of titanium dioxide ( $\text{TiO}_2$ ) and zirconium oxide ( $\text{ZrO}_2$ ) as catalysts in hot compressed water (HCW). The  $\text{TiO}_2$  showed both basic, acidic and catalyst properties. The selectivity of D-glucose to 5-HMF was more than 90 %; however the yields were only 20% [21].

**Asghari and Yoshida (2006)** used D-fructose as substrate with zirconium phosphates ( $\text{Zr}(\text{HPO}_4)_2 \cdot n\text{H}_2\text{O}$ ) under subcritical water. They found that 5-HMF yields up to 50 mol% with the highest 5-HMF selectivity were not more than 61 %. In addition, they observed the liquid by products were furaldehyde and humins. The rehydration products were not found [22].

**Leshkov et al (2007)** demonstrated a batch process for dehydration of D-fructose to 5-HMF using a two-phase reactor system. The process for preparation of 5-HMF consist of stimulated countercurrent extraction and evaporation steps. In the process system, they used water, DMSO and poly-1-vinyl-2-pyrrolidinone (PVP) for the aqueous phase with the use of hydrochloric acid (HCl), sulphuric acid ( $\text{H}_2\text{SO}_4$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ) or acidic ion-exchange resin which acts as catalysts, combined with the organic extracting phase, the mixture of methyl isobutyl ketone (MIBK) and 2-butanol. The selective dehydration of fructose to 5-HMF dependent on

the fructose concentrations, with 80% 5-HMF selectivity at 90% conversion of fructose. In addition, 5-HMF was separated from the aqueous and extracting phase by the extractor [23].

**Chheda et al (2007)** studied the preparation of 5-HMF and furfural by dehydration of D-glucose, fructose and xylose. The reaction was performed in a biphasic reactor system; consist of an organic extracting phase, the mixture of MIBK and 2-butanol, combined with a reactive aqueous phase modified with DMSO. They concluded that, the process parameters that influence the selectivity and yields of 5-HMF and furfural were the concentration of sugar, nature of extracting solvent and the concentration of DMSO in aqueous phase. Moreover, it was concluded that the high conversion of feedstock could be led to the good selectivity of 5-HMF and furfural [24].

**Bao et al (2008)** investigated the dehydration of D-fructose in the presence of the Bronsted acidic ionic liquid, 3-allyl-1-(4-sulfobutyl) imidazolium trifluoromethanesulfonate, with its Lewis acid derivative, 3-allyl-1-(4-sulfurylchloride butyl) imidazolium trifluoromethanesulfonate as catalysts to obtain 5-HMF products. They concluded that this reaction could be smoothly carried out in the presence of both Bronsted and Lewis acidic ionic. As a results of their experiments, the ionic liquid was an importance catalyst and easy to use for the preparation of 5-HMF. The yields of 5-HMF were found to be dependent on the acidity type of the ionic liquids, the concentration, reaction temperature and time [25].

**Amarasekara, Williams, and Ebede (2008)** proposed a mechanism by using NMR spectra technique for the dehydration of D-fructose to 5-HMF in DMSO at 150 °C, which the solvent acts as catalyst. They showed the mechanism of the dehydration of the two furanose forms of D-fructose to 5-HMF by way of the elimination of three water molecules. Particularly, this experiment was the first specification of DMSO in the dehydration of D-fructose [26].

**Takeuchi et al (2008)** reported on the catalytic effect of  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{SO}_4$  and HCl as catalysts in the direct conversion of D-glucose to 5-HMF in water. They concluded that the weakest acid,  $\text{H}_3\text{PO}_4$ , was the best catalyst for the conversion of

glucose into 5-HMF, yields of up to 40%, and the strongest acid, HCl, was the best catalyst for the conversion of 5-HMF to levulinic acid [27].

#### **2.4 The hydrothermal treatment of cellulose and biomass with catalytic conversion under subcritical and supercritical water for 5-HMF production.**

**Sinag et al (2009)** studied hydrothermal treatments on cellulose and sawdust. They used potassium carbonate ( $K_2CO_3$ ), zeolite (HZSM-5), nickel (Ni) on silicon dioxide ( $SiO_2$ ) as catalyst with a ratio 0.5 % (w/w). They found the highest amounts of 5-HMF in case of cellulose and sawdust at 225 °C. The concentration of 5-HMF were 183.4 mg/g and 122 mg/g from cellulose and sawdust respectively. An increase in temperature led to a decrease in 5-HMF content of the aqueous phases obtained by hydrothermal conversion of both feed stocks. Degradation of 5-HMF to acids, aldehydes and phenols was enhanced by the temperature increase. Subsequently, they concluded that the use of catalysts have no significantly effect on the composition of 5-HMF liquid products [28].

**Su et al (2009)** found a new catalytic system using an ionic liquid that could be converted cellulose to 5-HMF in one step under mild conditions. They used copper (II) chloride ( $CuCl_2$ ) and chromium (II) chloride ( $CrCl_2$ ) as catalyst with a ratio ranged from 0-1. A balanced metal chloride composition, such as  $CuCl_2$  and  $CrCl_2$  at ( $X_{CuCl_2}$ ) = 0.17, offers the highest yields of 5-HMF [29].

**Zhao, Lu, and Wang (2009)** used a supercritical water technology as a pre-treatment and hydrolysis method for ethanol production from microcrystalline cellulose. The batch reactor was conducted under the desirable reaction temperature and reaction time. They found that a complete decomposition of hydrolysis products occurred at higher temperatures and longer reaction times. They achieved yields of 5-HMF only about 4.4 % [9].

Though there would be many literatures related to biomass conversion, it should be noted that preparation of 5-HMF from palm kernel shell residues has not been thoroughly examined and understood. Effect of treatment condition on the conversion and yield of 5-HMF converted from dried palm kernel shell residues would be experimentally investigated using various analytical methods.



ศูนย์วิจัยทรัพยากร  
จุฬาลงกรณ์มหาวิทยาลัย

## CHAPTER III

### FUNDAMENTAL KNOWLEDGE

#### 3.1 Biomass

Biomass is a biological organic material from living which is commonly planted to produce energy or heat. The heat can be used directly, for heating, cooking, and industrial processes, or indirectly, to produce electricity. Biomass consists of carbon, hydrogen and oxygen based. Nitrogen and small quantities of other atoms, including alkali, alkaline earth and heavy metals can be found. Metals and magnesium are often found in the functional molecules of porphyrins and chlorophyll. Moreover, this renewable energy source may also include biodegradable wastes that can be used as an energy source. Biomass is presumably our oldest source of energy after the sun. Since people have burnt wood to heat their homes and cook their food for thousands of years ago. Particularly, biomass differs from organic materials such as fossil fuels, which have been transformed by geological processes into substances such as coal and petroleum. Environmentally, biomass is used as a replacement of fossil fuel, even though when they are burnt, the same amount of carbon dioxide (CO<sub>2</sub>) is released into the atmosphere but when they are used for the energy production, it could be noted that a net amount of greenhouse gases are decreased because of the offset of methane (CH<sub>4</sub> is a much stronger greenhouse gas than CO<sub>2</sub>) that would have otherwise entered the atmosphere. Thereby, biomass has some advantages over fossil fuels. Moreover, since they contain little amount of sulfur and nitrogen, that is why they cannot cause the acid rain. By the way, they can remove carbon dioxide, one of the greenhouse gases from the atmosphere when they have photosynthesized.

According to the photosynthesis process as shown in equation 3.1, the sun always gives plants the energy and then plants would convert water and carbon dioxide into oxygen and sugars. Eventually, the whole organic matter contains stored in their leaves, stems and roots.

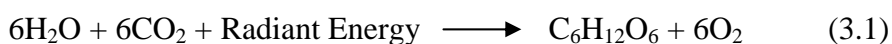
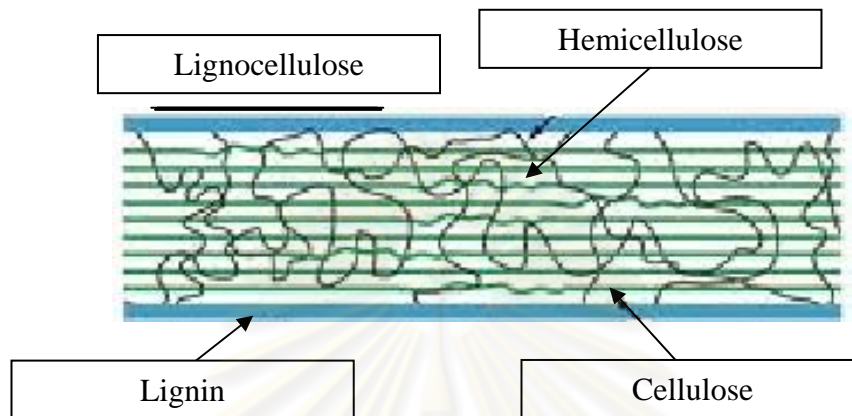


Figure 3.1 shows the physical structure of the whole plants, these sugars found in cellulose, hemicellulose and lignin, they are starting point for the major fractions in all of the terrestrial plants. For this reason, biomass is a renewable energy source because its supplies are not limited.



**Figure 3.1** The essential element of plants

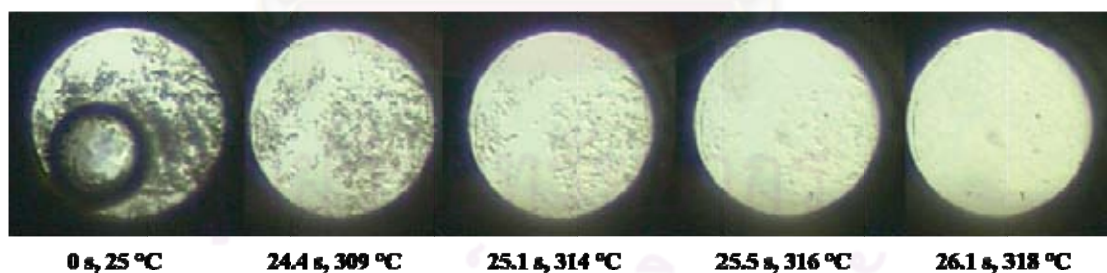
From the industrial point of view, biomass can be grown from many kinds of plants such as miscanthus, switchgrass, hemp, corn, poplar, willow, sorghum, sugarcane eucalyptus and oil palm. This particular plant is not only used to the end products, but it also affects the processing of the raw material. Even though fossil fuels have their origin in ancient biomass, they are not considered biomass as the generally accepted definition because they contain carbon that has been "out" of the carbon cycle for a very long time. Their combustion therefore disturbs the carbon dioxide content in the atmosphere.

The non-combustion processes convert raw biomass into a variety of gaseous, liquid, or solid fuels that can be used directly in a power plant for energy generation. The carbohydrates in biomass, which are comprised of oxygen, carbon, and hydrogen, can be broken down into a variety of chemicals which are used as fuels. This conversion can be done in two ways. Firstly, for thermo-chemical process, when plant matter is heated, it breaks down into various gases, liquids, and solids. These products can be used for further processed and refined into useful fuels such as methane and alcohol. Biomass gasifies capture methane which are released from the plants and burn it in a gas turbine to produce electricity. Another approach is to take these fuels

and run them through fuel cells, converting the hydrogen-rich fuels into electricity and water, with few or no emissions. Secondary, for biochemical process, bacteria, yeasts, and enzymes also break down carbohydrates. Fermentation, the process used to change biomass liquids into alcohol, a combustible fuel which is mixed with gasoline to make gasohol. Also, when bacteria break down biomass, methane and carbon dioxide are produced. This methane can be captured, in sewage treatment plants and landfills, for example, and burned for heat and power. Thirdly, for chemical process, biomass oils, like soybean and canola oil, can be chemically converted into a liquid fuel by transesterification process such as diesel fuel and gasoline additives. Cooking oil from restaurants, for example, has been used as a source to make "biodiesel" for trucks. In addition, a better way to produce biodiesel is to use algae as a source of oils.

### 3.2 Cellulose

Major component in the rigid cell walls in plants is cellulose. Cellulose is an organic compound with the formula  $(C_6H_{10}O_5)_n$ . The chains of cellulose are linear polysaccharide polymer of 2,000-26,000 glucose monosaccharide units. Cellulose requires a temperature about 320 °C and pressure of 25 MPa to become amorphous in water as shown in figure 3.2.1.

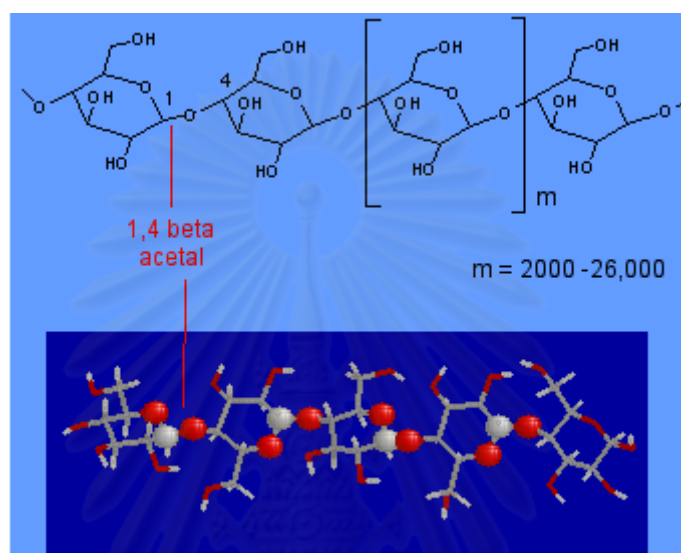


**Figure 3.2.1** Visual observation of cellulose complete dissolution in water for fasting heating rate: heating rate = 11.1 °C/s [30]

Moreover, cellulose is a straight chain polymer: unlike starch, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. The structure of cellulose consists of long polymer chains of glucose units connected by a beta acetal linkage. The small portion of cellulose chain is shown in figure 3.2.2. All



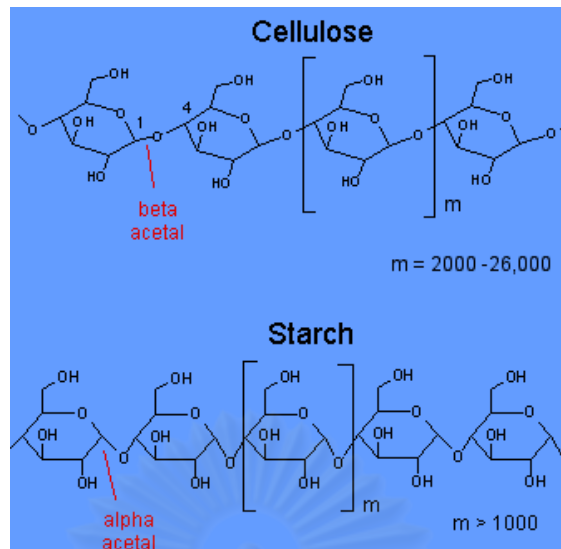
of the monomer units are beta-D-glucose, and all the beta acetal links connect C#1 to C#4 of the next glucose. Carbon#1 is called the anomeric carbon and is the center of an acetal functional group. A carbon that has two ether oxygens attached is an acetal. The Beta position is defined as the ether oxygen being on the same side of the ring as the C#6.



**Figure 3.2.2** The chemical structure of cellulose connected by a beta acetal linkage

[31]

The beta acetal linkage is the monomer unit in cellulose that is mostly a linear chain. On the other hand, starch is the monomer linkage of alpha acetal, as a result of the starch-amylose actually forms a spiral much like a coiled spring which makes it different from starch as shown in figure 3.2.3. Moreover, cellulose is higher crystalline than starch. Whereas starch could be transformed from a crystalline to amorphous when heated beyond 60-70 °C in water.



**Figure 3.2.3** The different of chemical structure of cellulose and starch [31]

Difference in acetal linkages results in a major difference in digestibility in humans. Humans are unable to digest cellulose because the appropriate enzymes to breakdown the beta acetal linkages are lacking (More on enzyme digestion in a later chapter.). Indigestible cellulose is the fiber which aids in the smooth working of the intestinal tract. Animals such as cows, horses, sheep, goats, and termites have symbiotic bacteria in the intestinal tract. These symbiotic bacteria possess the necessary enzymes to digest cellulose in the GI tract. They have the required enzymes for the breakdown or hydrolysis of the cellulose; the animals do not, not even termites and have the correct enzymes. No vertebrate can digest cellulose directly.

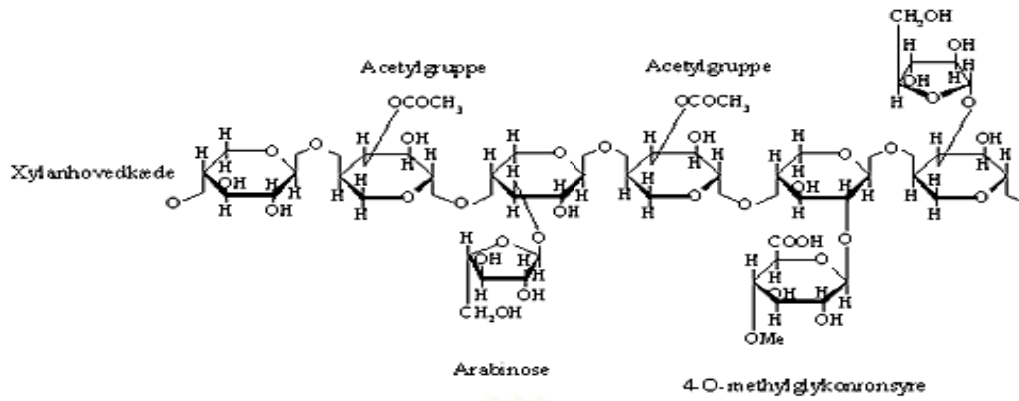
It is well understood that cellulose is derived from D-glucose units, which condense through  $\beta$  (1 $\rightarrow$ 4)-glycosidic bonds. This linkage motif contrasts with that for  $\alpha$  (1 $\rightarrow$ 4)-glycosidic bonds present in starch, glycogen, and other carbohydrates. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen molecules on the same or on a neighbor chain, holding the chains firmly together side-by-side and forming *microfibrils* with high tensile strength. This strength is important in cell walls, where the microfibrils are meshed into a carbohydrate *matrix*, conferring rigidity to plant cells. Cellulose can be broken down into its glucose units by treating it with concentrated acids at high temperature. Many properties of cellulose depend on its degree of polymerization or chain length, the

number of glucose units that make up one polymer molecule. Cellulose from wood pulp has typical chain lengths between 300 and 1700 units; cotton and other plant fibers as well as bacterial celluloses have chain lengths ranging from 800 to 10,000 units. Molecules with very small chain length resulting from the breakdown of cellulose are known as cellodextrins; in contrast to long-chain cellulose, cellodextrins are typically soluble in water and organic solvents. Plant-derived cellulose is usually contaminated with hemicellulose, lignin, pectin and other substances, while microbial cellulose is quite pure, has much higher water content, and consists of long chains.

For industrial use, cellulose is mainly obtained from wood pulp and cotton. It is mainly used to produce paperboard and paper; to a smaller extent it is converted into a wide variety of derivative products such as cellophane and rayon. Converting cellulose from energy crops into bio-fuels such as cellulosic ethanol is under investigation as an alternative fuel source.

### **3.3 Hemicellulose**

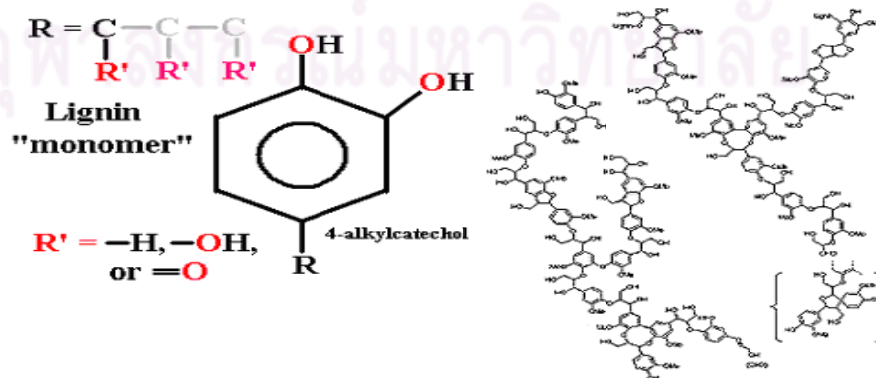
Hemicellulose is some of several hetero-polymers such as arabinoxylans, accompany along with cellulose in almost all of the plant cell walls. Besides glucose, sugar monomers in hemicellulose consist of xylose, mannose, galactose, rhamnose, and arabinose as shown in figure 3.3. In contrast, cellulose contains only anhydrous glucose. Moreover, xylose is always the sugar monomer present in the largest amount. They consists of shorter chains about 500-3,000 sugar units as objected to 2,000-26,000 glucose molecules per polymer as seen in cellulose. In addition, hemicellulose is a branched structure, while cellulose is unbranched. The structure of hemicellulose has a random, amorphous with little strength while cellulose is crystalline, strong, and resistant to hydrolysis.



**Figure 3.3** The chemical structure of hemicelluloses [32]

### 3.4 Lignin

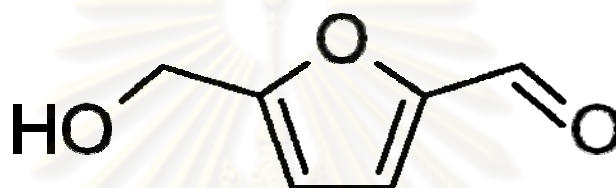
Lignin is a complex aromatic polymer that forms 15–30% of hardwoods, softwoods, and grasses but is often found in the secondary cell walls of sclerenchyma, xylem vessels, and tracheids, mostly between the cells and in the cell walls [33]. It makes plants rigid and crunchy. It functions to regulate the transport of liquid in the living plant by reinforcing cell walls and keeping them from collapsing and enables trees to grow taller and compete for sunshine. Besides cellulose, lignin is one of the most common organic substances on the Earth. Chemically, lignin is a polymer of phenyl-propane, that is, a benzene ring based monomers attached with ether and carbon-to-carbon linkages [34]. In their natural form, they have molecular weights that may reach to 15,000 or more. The process of removing them from the plant changes their form and chemical structure, which makes them hard to study.



**Figure 3.4** The chemical structure of lignin

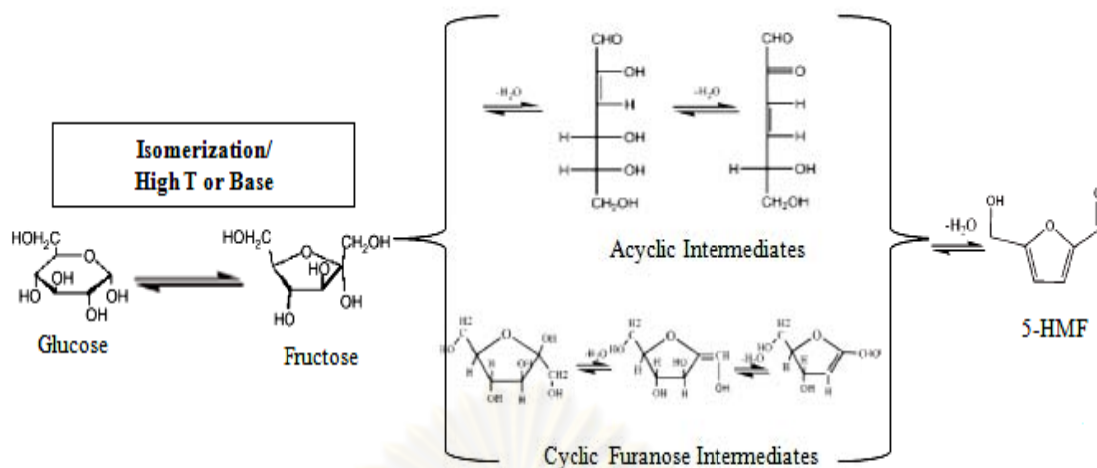
### 3.5 5-Hydroxymethylfurfural (5-HMF)

5-Hydroxymethylfurfural (5-HMF), also 5-(Hydroxymethyl) furfural, is an organic compound derived from dehydration of sugars with a formula ( $C_6H_6O_3$ ) as shown in figure 3.5.1 [35]. This yellow solid is highly water-soluble. The molecule is a derivative of furan, containing both aldehyde and alcohol functional groups. 5-HMF has been identified in a wide variety of heat-processed foods including milk, fruit juices and honey. In particular, 5-HMF, which is derived from cellulose without use of fermentation, is a potential "carbon-neutral" feedstock for fuels and chemicals.



**Figure 3.5.1** Molecular structure of 5-hydroxymethylfurfural (5-HMF)

Related to the production of furfural, 5-HMF can be produced from sugars. It was produced via the dehydration of fructose and glucose, a technology that is evolving through new extraction methods [23]. In this new method, fructose is treated with aqueous hydrochloric acid and then 5-HMF is continuously extracted into methyl isobutyl ketone (MIBK) as an organic phase at 180 °C. The aqueous phase is modified with dimethyl sulphoxide (DMSO) and polyvinylpyrrolidone (PVP), which can minimize the formation of side product such as levulinic and formic acid. The organic phase is modified with 2-butanol also as to improve the yield of 5-HMF in the organic phase by lowering the water concentration. So far, they found with a half amount of 5-HMF ending up in the organic. Furthermore, the method to remove the high boiling solvents would remain an interesting issue.



**Figure 3.5.2** The mechanism of chemical process to form 5-HMF [21, 24]

Figure 3.5.2 displays the synthesis of 5-HMF by means of elimination of three molecules of water called triple dehydration process from the hexose substrate. Researchers at Pacific Northwest National Laboratory (PNNL) reported a process by using chromium chloride as catalyst to directly convert both fructose and glucose into 5-HMF, leaving very little residual impurities [36-37]. In April 2009, a single-step process for converting cellulose directly into 5-HMF was outlined by researchers from the same laboratory [29]. The chromium chloride was used as catalyst to improve the conversion of glucose into fructose.

5-HMF can be converted into 2,5-dimethylfuran (DMF), which is a liquid bio-fuel that in certain ways is superior to ethanol. In addition, the oxidation of 5-HMF also gives 2,5-furandicarboxylic acid (FDA), which has been proposed as a replacement both of polyethylene terephthalate and polybutylene terephthalate for the production of biodegradable plastics. Moreover, 5-HMF has been found to bind specifically with intracellular sickle hemoglobin (HbS). Preliminary in vivo studies using transgenic sickle mice showed that orally administered 5-HMF inhibits the formation of sickled cells in the blood [38].

### 3.6 Hydrothermal treatment process

Hydrothermal treatment technology employs the combination of heat and water as a media to convert unutilized resources in various shapes and characteristics into uniform product. The treatment begins by loading the raw material into a reactor, and then injecting hot-compressed water or saturated steam of about 200 °C and 2 MPa into the reactor. Mixing process is conducted by a stirrer in the reactor while holding the temperature and pressure. After finishing the holding period and discharge of the steam, liquid and solid product can be obtained, and both of them will be separated by filter of the filtration system.



## CHAPTER IV

### EXPERIMENTAL PROCEDURE

#### 4.1 Preliminary analysis of chemical component of palm kernel shell residues

First of all, palm kernel shell residues were analyzed by American Society for Testing and Materials (ASTM) and Elemental Analyzer (CHNS/O Analyzer; Perkin Elmer, PE2400 Series II) to obtain the information of proximate and ultimate analysis, respectively. The chemical composition of palm kernel shell residues was illustrated in Table 4.1.1 and Table 4.1.2.

**Table 4.1.1** Proximate analysis of palm kernel shell residues

Composition	Amount (wt %)
Fixed carbon content	30.90
Volatile matter content	58.59
Moisture content	8.56
Ash content	1.57



**Table 4.1.2** Ultimate analysis of palm kernel shell residues

Composition	Amount (wt %)
Carbon	49.06
Hydrogen	7.41
Nitrogen	0.63
Oxygen	42.79

Next step, the content of cellulose in feedstock was determined following the procedure recommended by the United States Department of Agriculture (USDA), this method is performed by preparing of acid-detergent fiber, which was mainly consisted of lignin, cellulose, and insoluble minerals. Lignin is oxidized with an excess of acetic acid-buffered potassium permanganate solution [39]. Deposited manganese and iron oxides are dissolved with an alcoholic solution of oxalic and hydrochloric acid leaving cellulose and insoluble minerals. Lignin is measured as the weight lost by these treatments; whereas, cellulose is determined as the weight loss upon ash. Table 4.1.3 and Table 4.1.4 illustrated the components of the palm kernel shell residues particles and other biomass residues (dry weight basis) which were determined by the USDA's method.

**Table 4.1.3** Chemical compositions of the palm kernel shell residues (dry weight basis) employed in this work

Types of biomass residues	Chemical compositions (%)			
	Cellulose	Hemicellulose	Lignin	Ash
Palm kernel shell residues	58	33	6	3

**Table 4.1.4** Chemical composition of other agricultural wastes residues  
(dry weight basis)

Types of biomass residues	Chemical compositions (%)			
	Cellulose	Hemicellulose	Lignin	Ash
Water hyacinth	9	72	17	2
Rubber wood	39	29	28	4

From the previous work the hydrothermal pretreatment of rubber wood residue could provide substantial amount of glucose. They have discovered the glucose could be generated from cellulose. Nonetheless, the large amount of lignin in both water hyacinth and rubber wood could hinder hydrolysis process of cellulose. Based on this preliminary result, the composition of lignin in palm kernel shell was significantly less than in both water hyacinth and rubber wood. Thus, it is reasonable to deduce high yield of glucose which converted to be 5-HMF.

#### 4.2 Feedstock



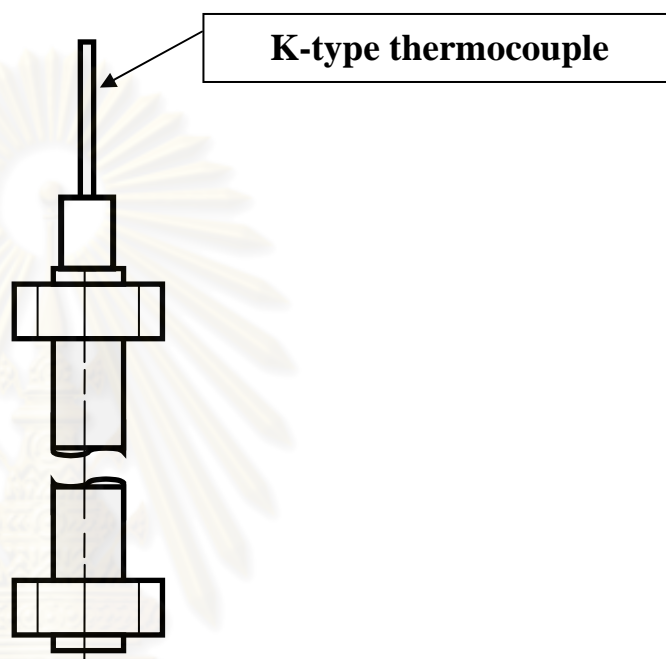
**Figure 4.2.1** Palm kernel shell residues

Palm kernel shell residues were initially ground and sieved to a powder with a particle size around 0.8 mm. Then, the ground residues were dried at 80 °C for 10 minutes to remove the volatile matter. Figure 4.2.1 shows the palm kernel shell residues before crushed by grinder.

### 4.3 Hydrothermal treatment

#### 4.3.1 Tubular reactor

Hydrothermal treatment of palm kernel shell residues conducted in a tubular reactor.



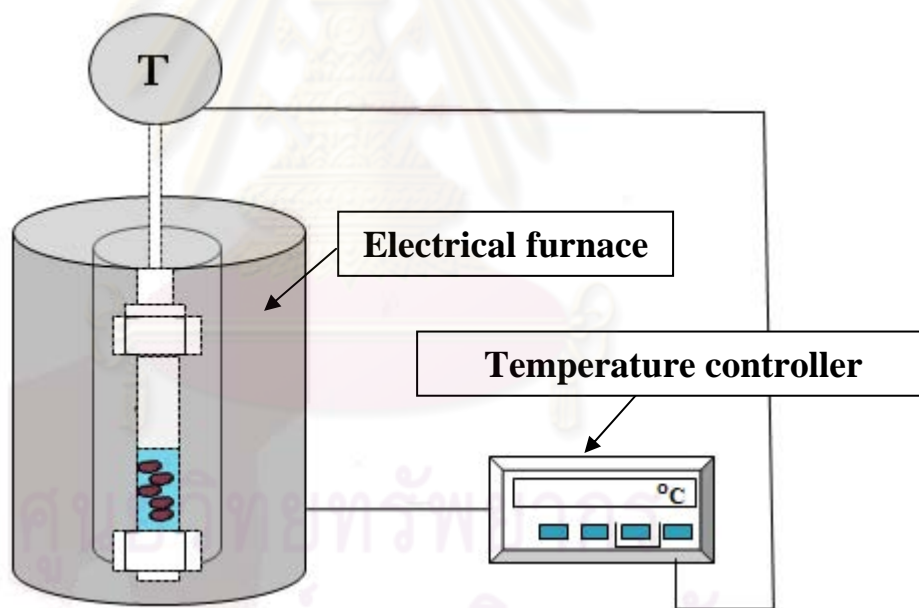
**Figure 4.3.1** Schematic diagram of a tubular reactor

Figure 4.3.1 shows the schematic of a tubular reactor. In addition, the physical properties of a tubular reactor were illustrated in Table 4.3.1.

**Table 4.3.1** The physical properties of a tubular reactor used in this work

Material	Stainless steel
Volume (ml)	24.70
Outside diameter (mm)	19.05
Wall thickness (mm)	1.65
Tolerant temperature (°C)	537
Tolerant pressure (atm)	177

For the proceeding, at first, cellulose was extracted from the palm kernel shell residues by the following steps. Briefly, the residues were pretreated by soaking into 1 w/v% sodium hydroxide (NaOH; Suksapan) solution at 80 °C for 2 h, followed by washing with adequate distilled water to remove the epidermis. The pretreated residues were treated further in a mixture of 1 w/v% NaOH solution and 1 w/v% sodium sulfide ( $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$ ; Panreac) with a volumetric ratio of 1:30 at 80 °C for 1.5 h to obtain cellulose fibers. The cellulose fibers were then bleached by a mixture of 0.7 v/v% sodium chlorite ( $\text{NaClO}_2$ ; Ajax Chemicals) aqueous solution and an acetate buffer at 80 °C for 1.5 h to remove the lignin residues [40]. The acetate buffer was prepared by dissolving 2.7 g of NaOH solid in a solution of 7.5 ml of glacial acetate acid ( $\text{CH}_3\text{COOH}$ ; QREC) in 100 ml of distilled water. The bleached fibers were washed repeatedly by distilled water and subsequently dried in oven at 90 °C for 10 minutes.



**Figure 4.3.2** Schematic diagram of experimental apparatus

A series of experiment of hydrothermal treatment of palm kernel shell residues were conducted in a batch-type tubular reactor system. The system consists of a tubular reactor with a vertical-tubular electrical furnace incorporated with a temperature controller as shown in figure 4.3.2.

At the beginning of experiment, the reactor was loaded with a designated amount of biomass and de-ionized water, and then heated to a designated temperature at a designated heating rate. The temperature and heating rate were varied from 200 to 300 °C and 5 to 10 °C/min, respectively. The volumetric ratio of space to the total volume is about 60 %. After the end of the hydrothermal treatment period, the reactor was immediately cooled down by quenching in water to stop the hydrothermal process.



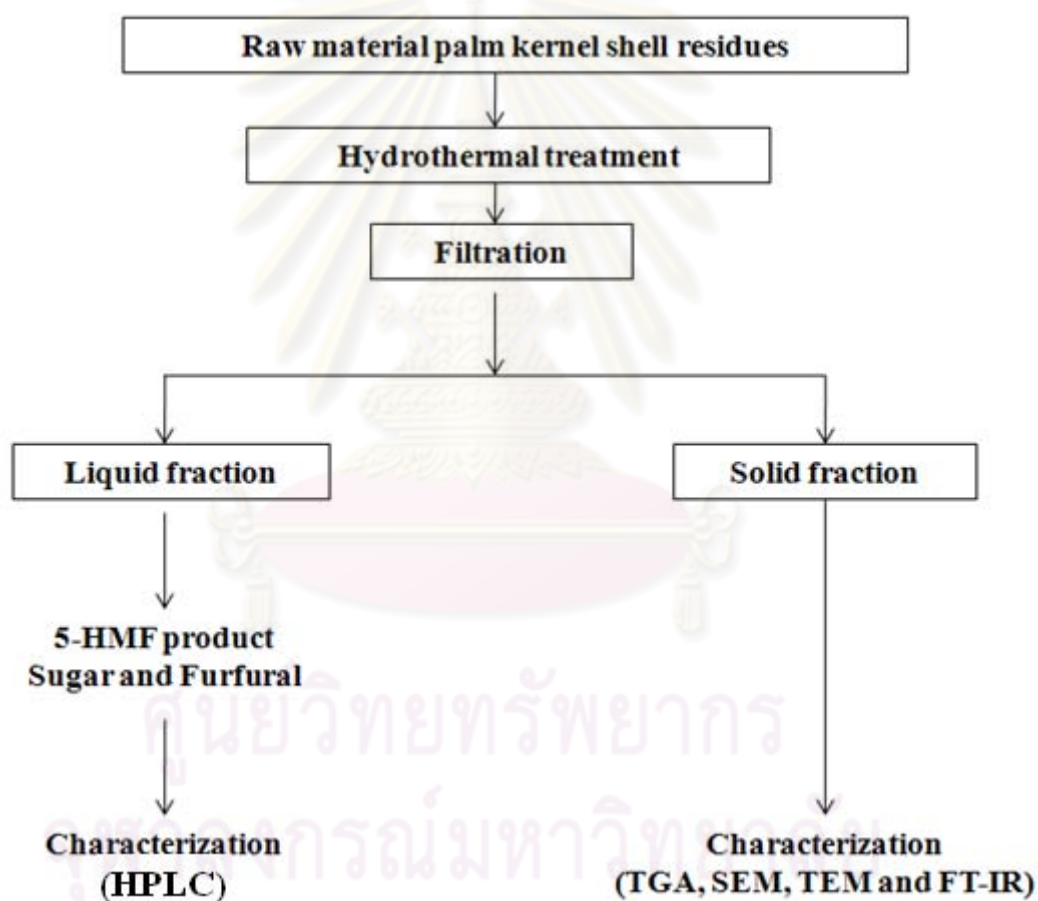
**Figure 4.3.3** Liquid-solid filtration systems



**Figure 4.3.4** High Performance Liquid Chromatography (HPLC)

Each sample contains both liquid and solid parts. Both of them were separated by the liquid-solid filtration systems as shown in figure 4.3.3. After that, the liquid part was taken for the determination of 5-HMF and other hydrolyzed products by

using High Performance Liquid Chromatography (HPLC; Varian, Prostar) analyzer equipped with a fluorescent detector and an Octadecyl Silane (ODS) C18 column as shown in figure 4.3.4. The amount of 5-HMF contained in the solid part was negligible because of 5-HMF is a highly water-soluble substance. For the solid part, they were taken for the investigation of the functional groups on the surface by Fourier Transform Infrared Spectrometer (FT-IR; Perkin Elmer, Spectrum One) in order to compare with the functional groups on the surface of palm kernel shell residues before reaction. Figure 4.3.5 illustrated a schematic of different steps in the hydrothermal treatment.



**Figure 4.3.5** Schematic diagram of different steps in the hydrothermal treatment

#### 4.4 Experimental condition

##### 4.4.1 The effect of reaction temperature in a range of 200 – 300 °C

At first, in this study, the effect of reaction temperature on a hydrothermal treatment of palm kernel shell residues has been investigated. By varies in a range of 200 – 300 °C to find out the optimal temperature of this process. Palm kernel shell residues were ground and sieved to a powder with a particle size around 0.8 mm. Table 4.4.1 illustrates the condition for studied on the effect of reaction temperature.

**Table 4.4.1** Reaction temperature conditions for the hydrothermal treatment.

Reaction temperature (°C)	220, 240, 260, 280 and 300
Palm kernel shell residues (g)	1
De-ionized water (g)	9

##### 4.4.2 The effect of heating rate in a range of 5-10 °C/min

By varies the heating rate of 5, 7.5 and 10 °C/min. The heating rate could be identified as the soaking time which was defined how long of the contact time between palm kernel shell residues subjected with the water vapor. Table 4.4.2 illustrates the heating rate condition.

**Table 4.4.2** Heating rate conditions for the hydrothermal treatment

Heating rate (°C/min)	5, 7.5 and 10
Reaction temperature (°C)	220, 240, 260, 280 and 300
Palm kernel shell residues (g)	1
De-ionized water (g)	9

#### 4.4.3 The effect of concentration of feedstock on the hydrothermal treatment

Palm kernel shell residues were varied concentration in ranging from 10 - 20 wt% for the hydrothermal treatment. When we know the optimal temperature and optimal heating rate for the hydrothermal treatment therefore they were used in this condition for studied the effect of concentration of feedstock on the hydrothermal treatment of palm kernel shell residues. Table 4.4.3 illustrates the concentration conditions.

**Table 4.4.3** Concentration conditions for the hydrothermal treatment.

Concentration of palm kernel shell residues (wt%)	10 and 20
De-ionizer water (g)	9 and 8
Reaction temperature (°C)	220, 240, 260, 280 and 300



#### 4.4.4 The effect of lignin content on the hydrothermal treatment

In this study, at first, the content of lignin in palm kernel shell residues were varied by varying the reaction time in the elimination of lignin step and then the content of lignin in treated palm kernel shell residues were determined by the USDA's method. Table 4.4.4 illustrates the effect of lignin content conditions.

**Table 4.4.4** Lignin content conditions for the hydrothermal treatment.

Lignin content in feedstock (wt%)	3.59, 5.78, 6.93 and 9.98
Palm kernel shell residues (g)	1
De-ionizer water (g)	9
Reaction temperature (°C)	280

#### 4.4.5 The effect of extracting solvent and homogeneous catalyst on the hydrothermal treatment

As shown in figure 4.4.5.1 and figure 4.4.5.2, we have found a good result in the previous work using  $\text{H}_3\text{PO}_4$  or DMSO as homogeneous catalysts and 2-butanol as extracting solvent. It could be noted that sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is too strong, and they are suffering from post treatment. In this study, the hydrothermal treatment was performed at the same concentration of feedstock with 10 wt%.

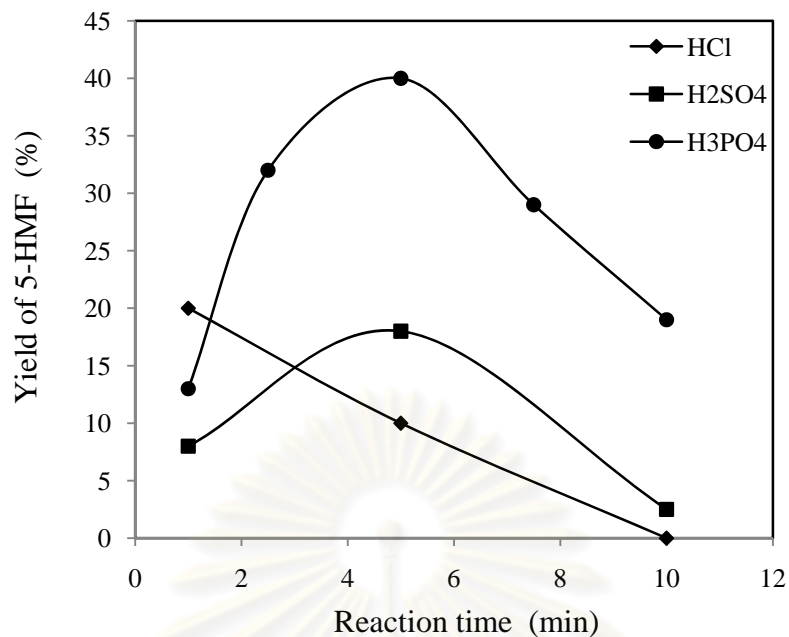
Table 4.4.5.1 illustrates the varying of concentration of 2-butanol for the hydrothermal treatment.

Table 4.4.5.2 illustrates the varying of concentration of DMSO for the hydrothermal treatment.

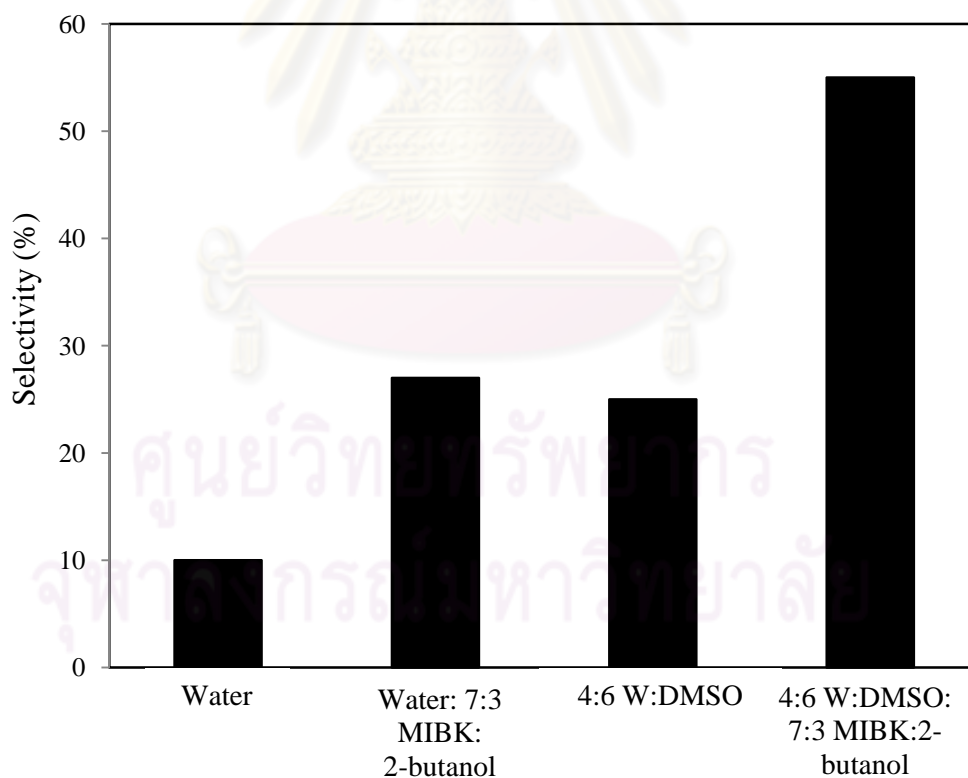
Table 4.4.5.3 illustrates the varying of concentration of  $\text{H}_3\text{PO}_4$  for the hydrothermal treatment.

Table 4.4.5.4 illustrates the adding of 2-butanol as extracting phase and DMSO as homogeneous catalyst conditions for the hydrothermal treatment.

Table 4.4.5.5 illustrates the adding of 2-butanol as extracting phase and  $\text{H}_3\text{PO}_4$  as homogeneous catalyst conditions for the hydrothermal treatment.



**Figure 4.4.5.1** Yields of 5-HMF from glucose by acid catalytic hydrothermal reaction under 250 °C [27]



**Figure 4.4.5.2** Effect on 5-HMF selectivity of adding an extracting organic solvent 7:3 (w/w) MIBK: 2-butanol and DMSO (60 wt%) to the aqueous phase for 10 wt% glucose dehydration at 170 °C using HCl as catalyst [24]

**Table 4.4.5.1** Adding of 2-butanol conditions for the hydrothermal treatment

Concentration of 2-butanol (v/v%)	20, 30, 40, 50 and 60
Palm kernel shell residues (g)	1
Reaction temperature (°C)	280

**Table 4.4.5.2** Adding of DMSO conditions for the hydrothermal treatment.

Concentration of DMSO (v/v%)	20, 40, and 60
Palm kernel shell residues (g)	1
Reaction Temperature (°C)	280

**Table 4.4.5.3** Adding of H<sub>3</sub>PO<sub>4</sub> conditions for the hydrothermal treatment.

Concentration of H <sub>3</sub> PO <sub>4</sub> (v/v%)	1, 3 and 5
Palm kernel shell residues (g)	1
Reaction Temperature (°C)	280

**Table 4.4.5.4** Adding of 2-butanol as extracting phase and DMSO as homogeneous catalyst conditions for the hydrothermal treatment.

Concentration of 2-butanol 99 v/v % (g)	4.5
Concentration of DMSO (v/v%)	20, 40, 60
Palm kernel shell residues (g)	1
Reaction Temperature (°C)	280

**Table 4.4.5.5** Adding of 2-butanol as extracting phase and H<sub>3</sub>PO<sub>4</sub> as homogeneous catalyst conditions for the hydrothermal treatment.

Concentration of 2-butanol 99 v/v% (g)	4.5
Concentration of H <sub>3</sub> PO <sub>4</sub> (v/v%)	1, 3 and 5
Palm kernel shell residues (g)	1
Reaction Temperature (°C)	280



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## CHAPTER V

### RESULTS AND DISCUSSIONS

#### Characterization of liquid products

##### 5.1 Calculation of conversion of glucose, yield of 5-HMF and selectivity of 5-HMF

Conversion of glucose ( $X_g$ ), yield of 5-HMF ( $Y_h$ ) and selectivity of 5-HMF ( $S_h$ ) in this study could be determined using equations 5.1.1, 5.1.2 and 5.1.3.

$$X_g (\%) = \frac{[G_o - G]}{G} \times 100 \quad (5.1.1)$$

whereas  $G_o$  is the concentration of glucose before reaction (mg/l) and  $G$  is the concentration of glucose after reaction (mg/l).

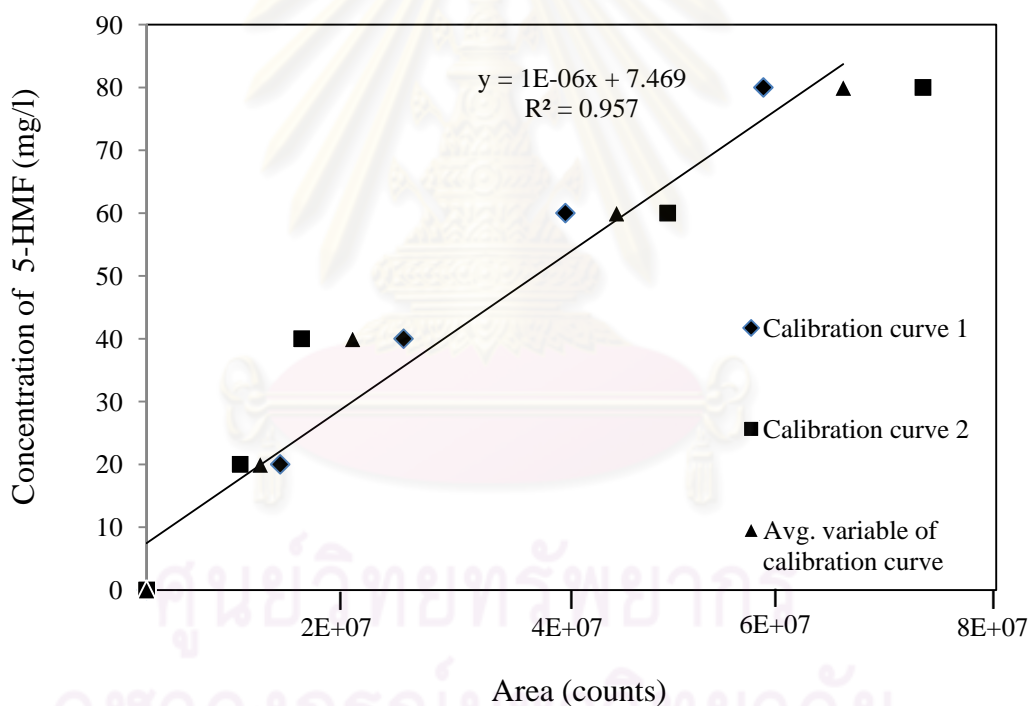
$$Y_h (\%) = \frac{[H - H_o]}{G_o} \times 100 \quad (5.1.2)$$

$H_o$  is the concentration of 5-HMF before reaction (mg/l) and  $H$  is the concentration of 5-HMF after reaction (mg/l).

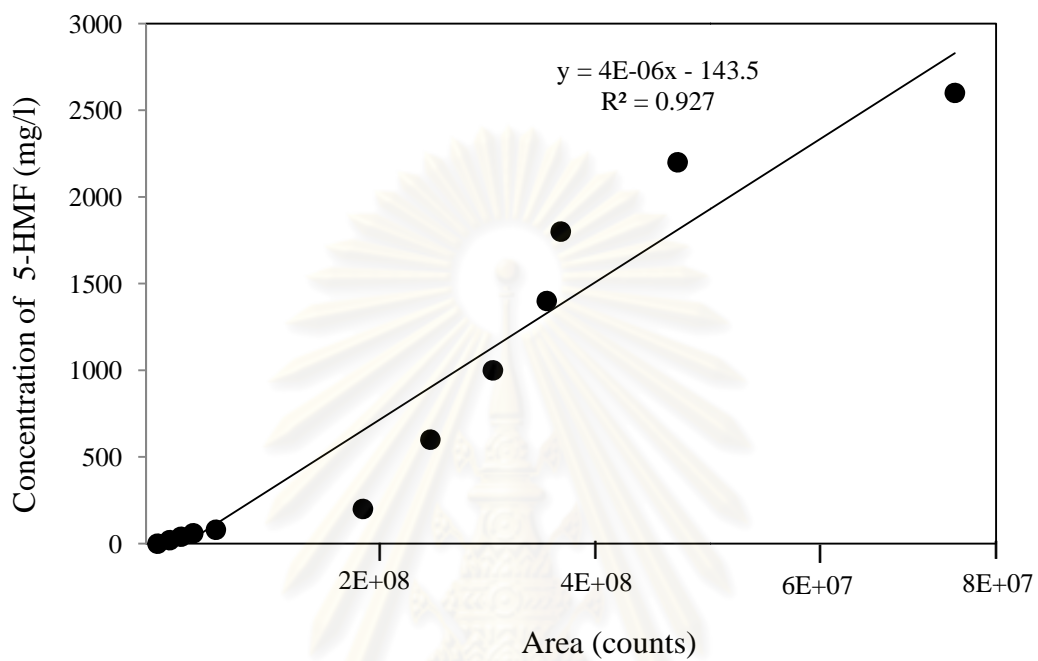
$$S_h (\%) = \left[ \frac{Y_h}{X_g} \right] \times 100 \quad (5.1.3)$$

## 5.2 Calibration curves of HPLC for determining glucose and 5-HMF for concentration in liquid product

First, calibration curves of glucose and 5-HMF were obtained by calibrating the HPLC (model) with standard samples (99%) of glucose and 5-HMF with various concentration. For a better precision, the calibration curves of 5-HMF are prepared in order to separated ranges as shown in figure 5.2.1 and 5.2.2, respectively. Meanwhile, the calibration curve of pure glucose illustrated in Figure 5.2.3 could be employed in a single chart because of its higher accuracy. The standard of variation ( $R^2$ ) of each calibration curve is acceptably higher than 92%. Based on, the calibration curve of pure glucose and 5-HMF illustrated in figures 5.2.1, 5.2.2 and 5.2.3.

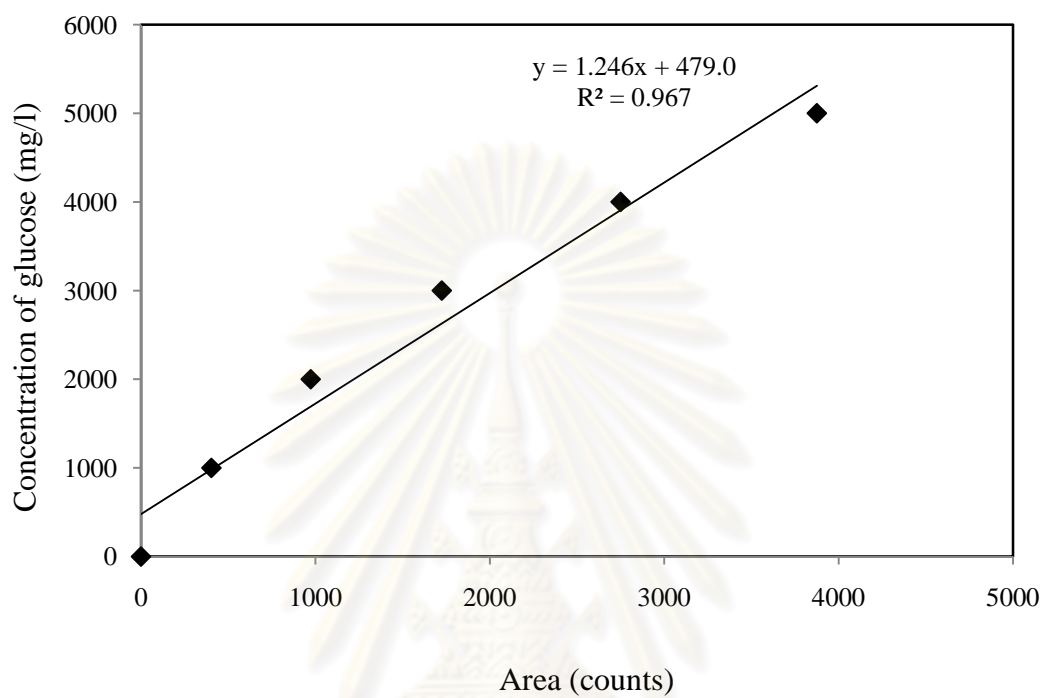


**Figure 5.2.1** The calibration curve of pure 5-HMF was used to calculate the concentration of 5-HMF in liquid product when area less than  $6.5E+7$  counts



**Figure 5.2.2** The calibration curve of pure 5-HMF was used to calculate the concentration of 5-HMF in liquid product when area greater than  $6.5E+7$  counts

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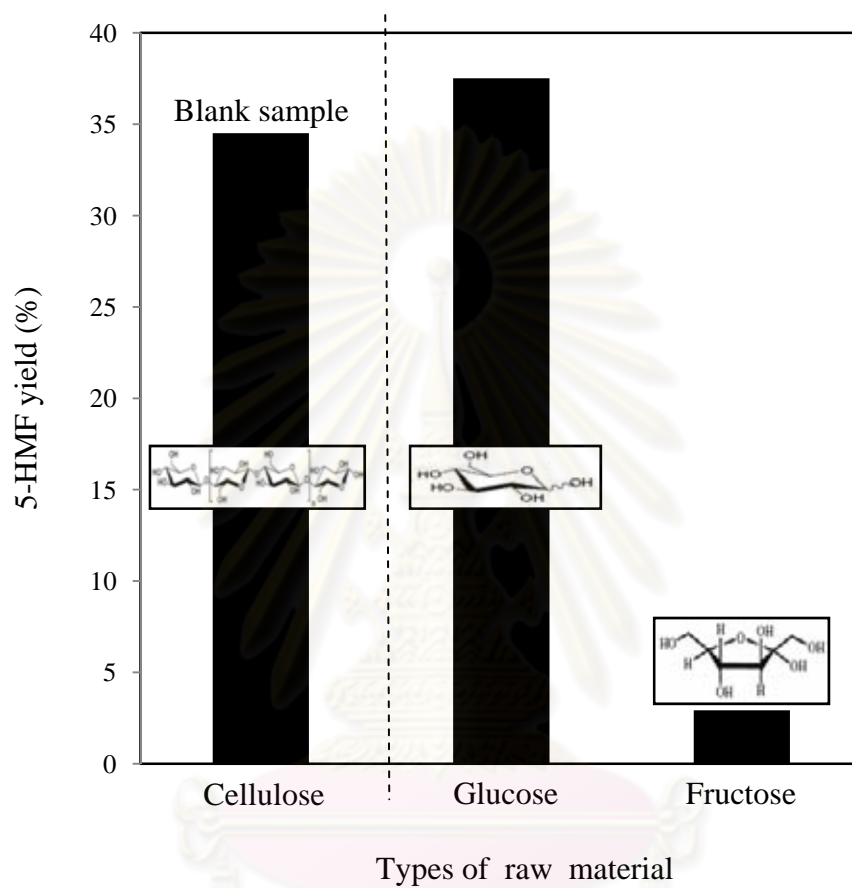
**Figure 5.2.3** The calibration curve of pure glucose was used to calculate the concentration of glucose in liquid product

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### 5.3 Direct conversion of various carbohydrates feedstock compound for 5-HMF production

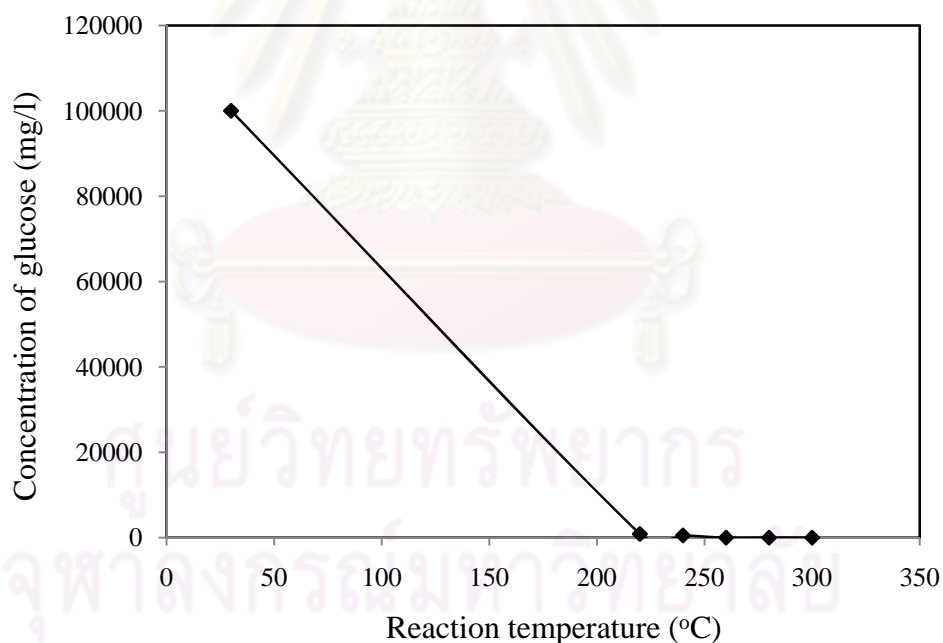
In this study, I would like to investigate the in situ of 5-HMF, “blank test”, which obtain from these preliminary tests. All experiments were performed under condition of 280 °C with 50 minutes, containing 10 wt% cellulose, glucose and fructose. Essentially, the usage of several sorts of raw material could lead to a variation of 5-HMF yield. Nonetheless, pure cellulose and pure fructose could not be employed as referable blank samples for our work because of both of them are not consistent in a proportion of molecules compare with biomass. Naturally, biomass is complicated molecules which are composes of cellulose, hemicellulose, lignin and ash for this reason the utility of pure cellulose is better alternative for “blank sample”. In addition, it is because the close proximity between simulate test and substantial test. With a tuning of processing parameters, it is found that the formation of 5-HMF could be generated from the dehydration process of cellulose, glucose and fructose with different yield as shown in figure 5.3. Furthermore, it could be confirmed that the majority of cellulose hydrolysis is glucose and fructose, leading to a possibility of their further degradation to form 5-HMF. Subsequently, it could be inferred that cellulose and glucose are viable substrates for 5-HMF production with a yield of 34 % and 37%, respectively.



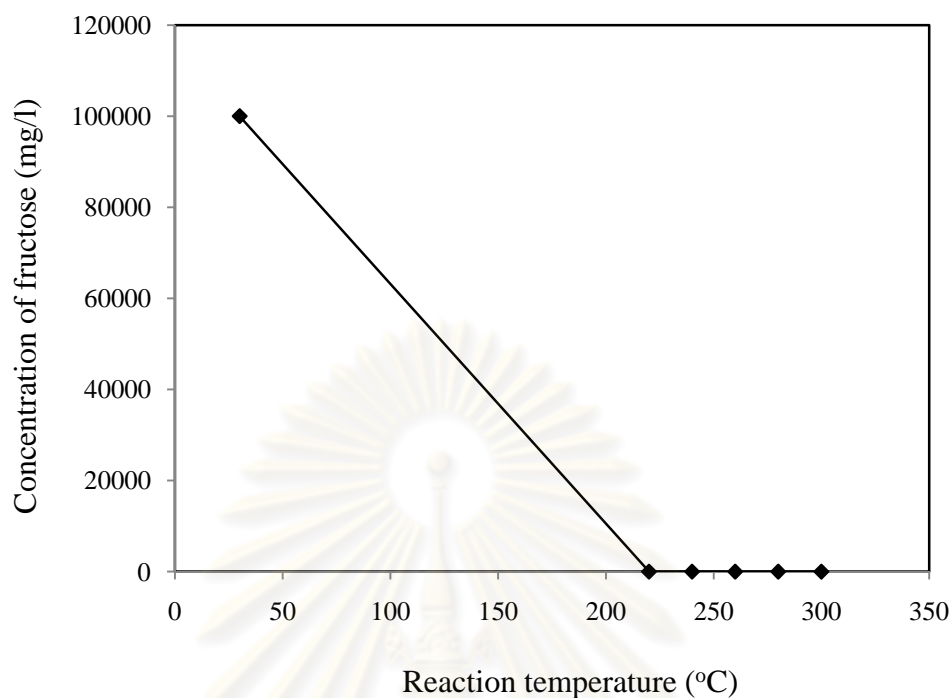
**Figure 5.3** Effect of various carbohydrates feedstock compound on 5-HMF yield from pure cellulose, pure glucose and pure fructose

#### 5.4 Thermal stability of reactants

Figure 5.4.1 and 5.4.2 display the thermal stability of glucose and fructose dissolved in water. Some previous works also show that glucose and fructose could undergo the dehydration process, leading to 5-HMF production. In this work, the thermal stability of each pure substance dissolved in water that examined in a temperature range of 220-300 °C. The initial concentration of glucose was rather high with a local maximum of 848 mg/l. After that, when the reaction temperature is greater than 220 °C the concentration of glucose decreased because of the degradation of molecule of glucose to form other substances such as 1,6-anhydroglucose, erythrose, glyceraldehyde, glycolaldehyde, di-hydroxyacetone and 5-HMF while the detectable concentration of fructose in the range of interested reaction temperature was not found [21].



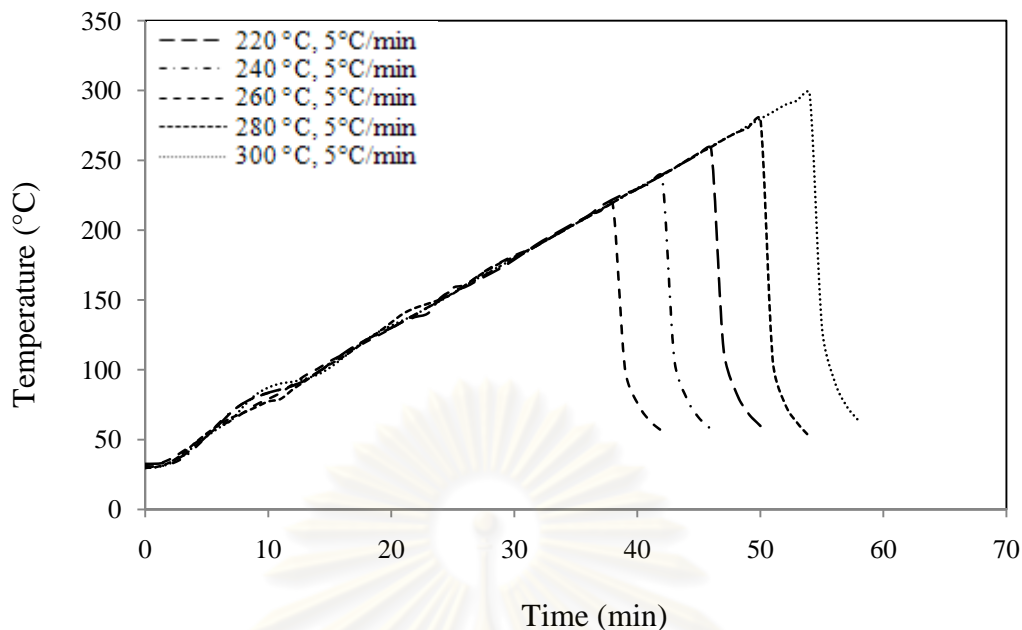
**Figure 5.4.1** Concentration curve of glucose



**Figure 5.4.2** Concentration curve of fructose

### 5.5 Effect of reaction temperature

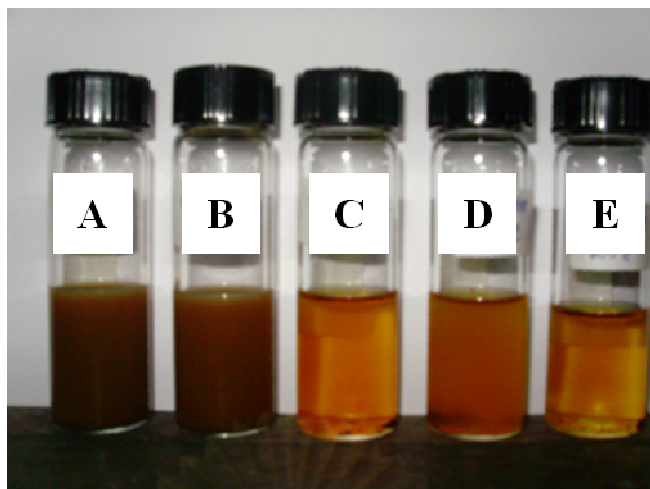
In this work, effect of each operating parameters on 5-HMF yield was examined experimentally. Among these parameters, reaction temperatures which are defined as a maximum temperature within the reactor, which could be achieved by a constant heating rate of 5 °C/min. Because of the reactor configuration, it is designed to heat up the reactor until the designated temperature is achieved and then the reactor will be immediately cooled down by quenching in water to stop the reaction in prior to sampling the product and residue from the reactor. Palm kernel shell residues were hydrothermally treated with the reaction temperature in a range of temperature 220 to 300 °C. Other operating parameters which are weight of palm kernel shell residues and weight ratio of de-ionized water to palm kernel shell residues were set constant at 9 g and 1 g, respectively. Figure 5.5.1 shows the temperature history inside tubular reactor at a constant heating rate of 5 °C/min.



**Figure 5.5.1** Temperature history regarding with different target temperature

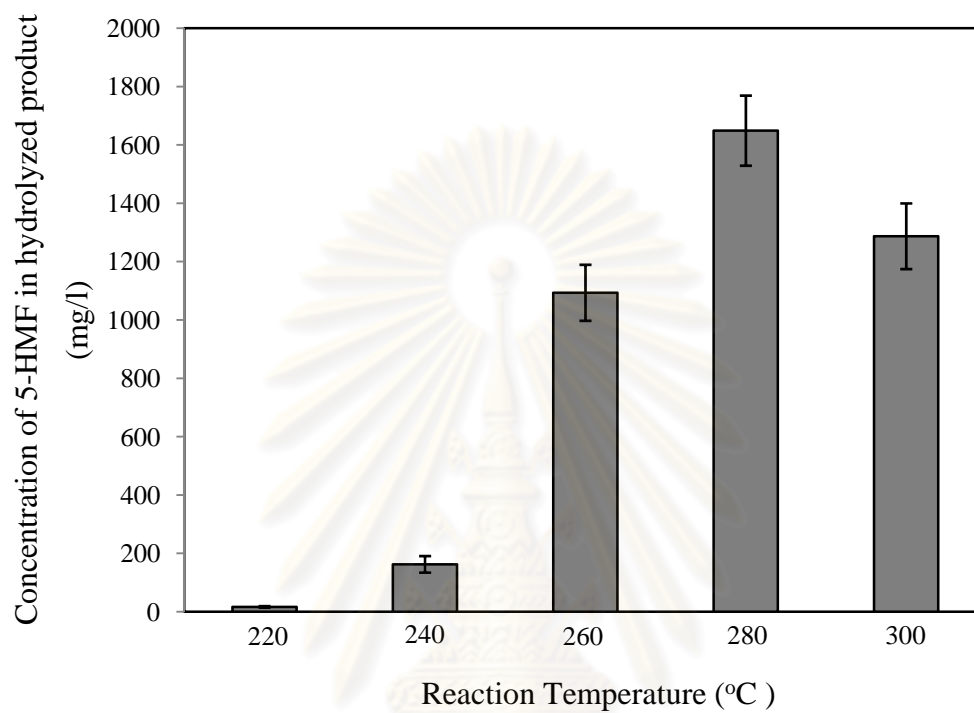
After hydrothermal treatment within the tubular reactor, liquid products with distinctively different appearance could be obtained. At least two experiments were conducted for confirming repeatability. In each experiment, solid and liquid sample were separated and then the liquid part analyzed for determining quantities of 5-HMF and other hydrolyzed products. Based on observation, the higher the reaction temperature was set the more transparent the appearance of the liquid products could be prepared as shown in figure 5.5.2.

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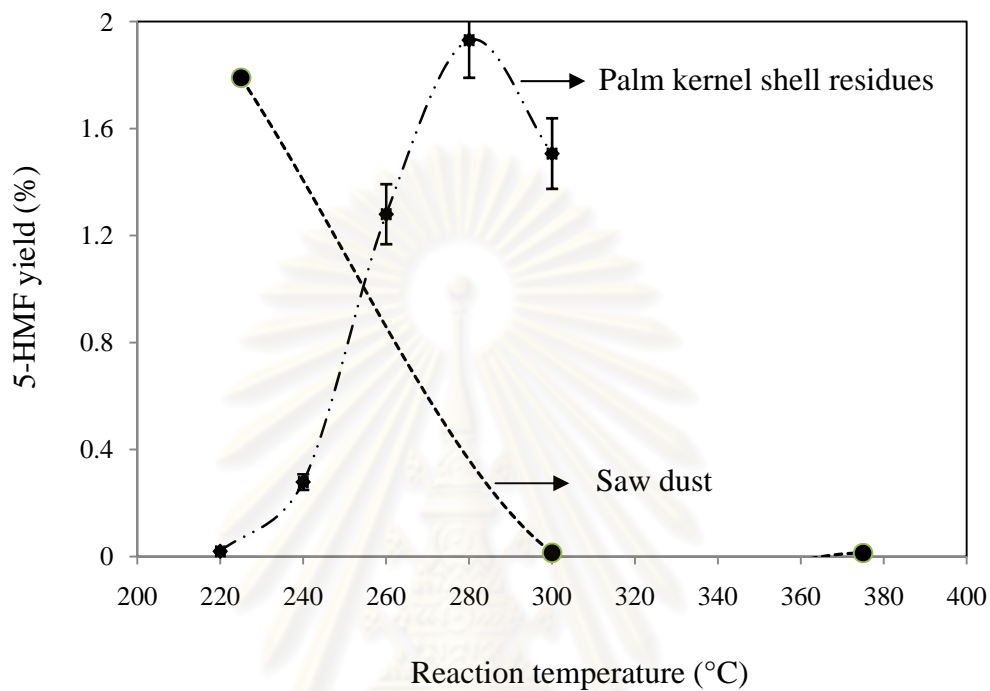
**Figure 5.5.2** Liquid samples after hydrothermal treatment at temperature of (A) 220, (B) 240, (C) 260, (D) 280, and (E) 300 °C

Figure 5.5.3 indicates the concentration of 5-HMF increases with the increased reaction temperature this result was attributed to the enhanced decomposition of raw material by increased temperature. The increase in the 5-HMF yield reaches a maximum of 1.9 % at the reaction temperature of 280°C. This observation is consistent with the result reported in previous studies on the decomposition of 5-HMF in the hydrothermal process. According to the synthesized of Chen et al (1991), yield of 5-HMF synthesized from fructose acetonides is dependent upon the synthesizing temperature. The side reactions preferably occur at an early stage, then the further increase in the reaction temperature would result in polymerization process caused by condensation of 5-HMF. As a result, the yield of 5-HMF would gradually decrease when the reaction temperature was increased from 180 to 240 °C [19]. In addition, Chuntanapum et al (2008) investigating the decomposition of pure 5-HMF by sub-critical water reported that 5-HMF would resist decomposition at low temperature and then the decomposition began at a temperature higher than 300 °C to 450 °C [18]. Sinag et al (2009) also reported the hydrothermal treatments of sawdust, that the highest amounts of 5-HMF could be achieved at 225 °C. As shown in figure 5.5.4, the excessive increase in the reaction temperature higher than 280 °C would lead to a decrease in 5-HMF content [28].



**Figure 5.5.3** The concentration of 5-HMF varied with different temperature in the range of 220 – 300 °C, average particle size 0.8 mm

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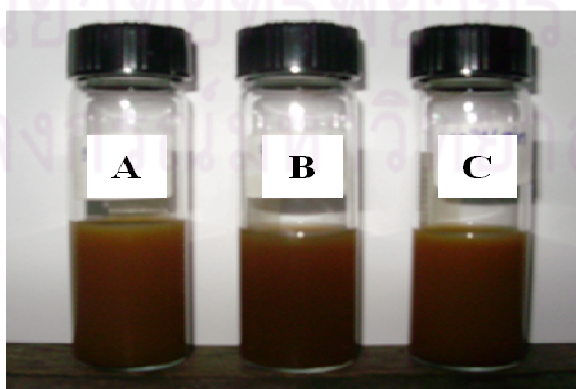
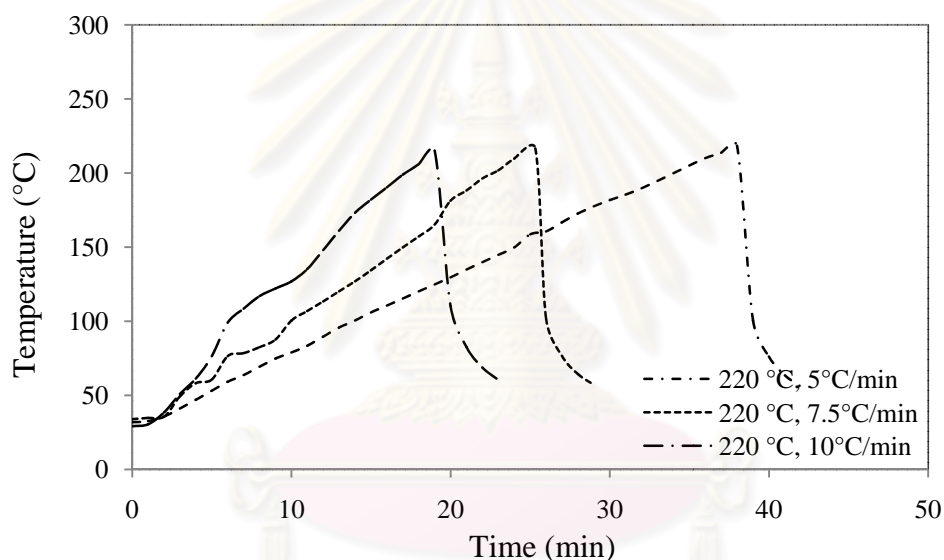
**Figure 5.5.4** Yield of 5-HMF varied with different reaction temperature compared between palm kernel shell residues (this work) and saw dust [28]

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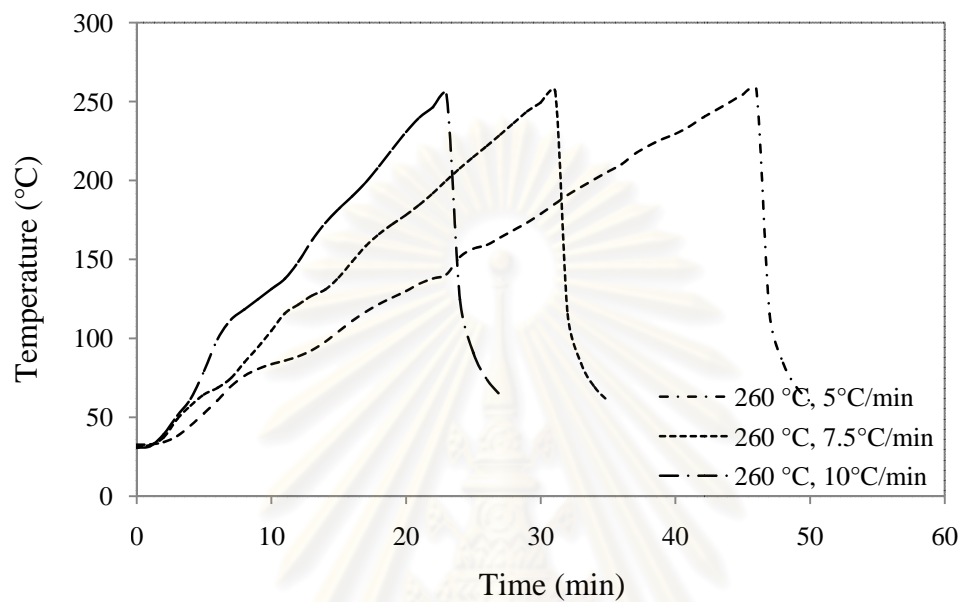


## 5.6 Effect of heating rate or soaking time

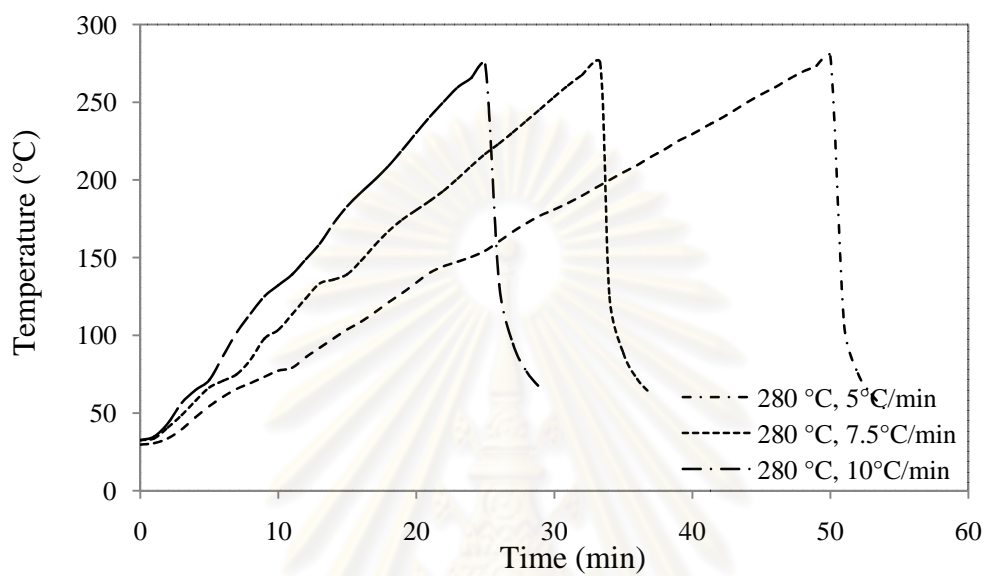
In this study, the effect of heating rate on 5-HMF yield was also investigated, dried palm kernel shell residues were hydrothermally treated under conditions of temperature from 220 to 300 °C with heating rate at 5, 7.5 and 10 °C/min. Figure 5.6.1 to 5.6.4 shows the temperature history inside the tubular reactor with various reaction temperature and heating rate, which is consistent with the appearance and physical properties of liquid products. In addition, heating rate is concerned with soaking time implying about the contact time between feedstock and water vapor for hydrothermal treatment process.



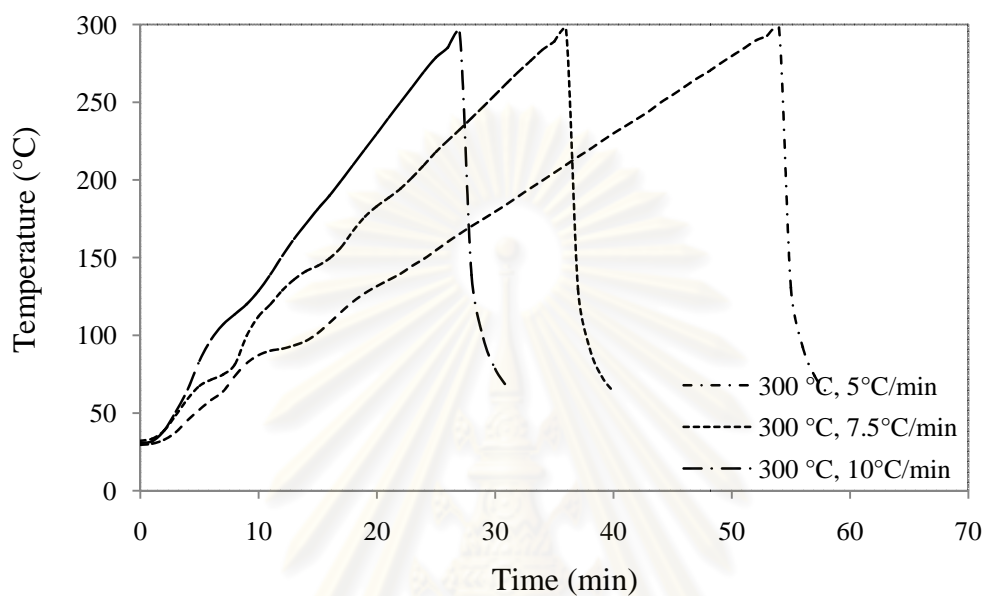
**Figure 5.6.1** Liquid samples after hydrothermal treatment at 220 °C with heating rate of (A) 5 °C/min, (B) 7.5 °C/min and (C) 10 °C/min



**Figure 5.6.2** Liquid samples after hydrothermal treatment at 260 °C with heating rate of (D) 5 °C/min, (E) 7.5°C/min and (F) 10 °C/min

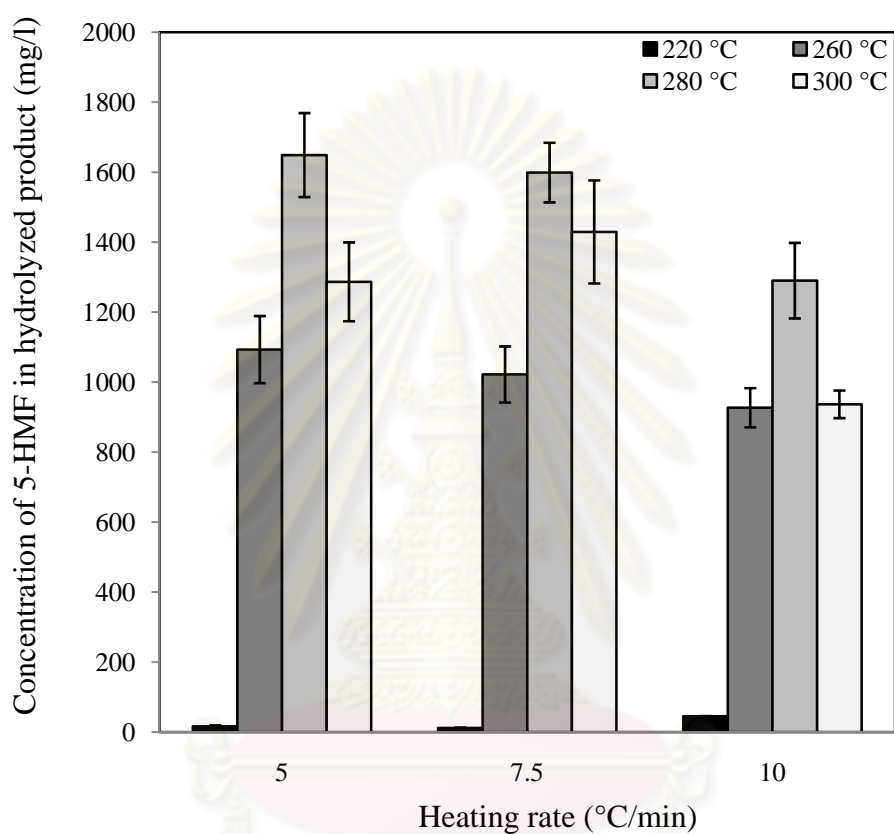


**Figure 5.6.3** Liquid samples after hydrothermal treatment at 280 °C with heating rate of (G) 5 °C/min, (H) 7.5 °C/min and (I) 10 °C/min

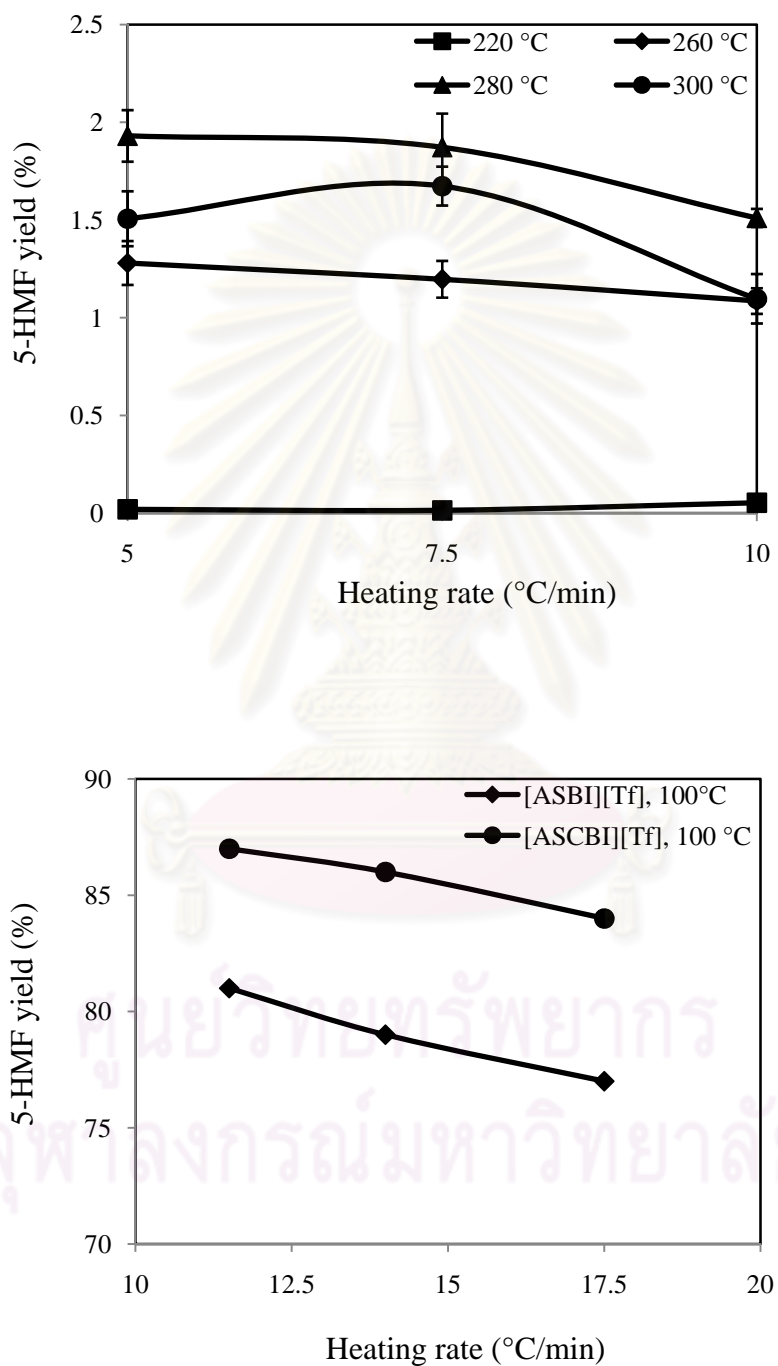


**Figure 5.6.4** Liquid samples after hydrothermal treatment at 300 °C with heating rate of (J) 5 °C/min, (K) 7.5 °C/min and (L) 10 °C/min

The dependence of 5-HMF concentration on the heating rate (soaking time) within the range of 5 to 10 °C/min at different temperature shows in figure 5.6.5. At the beginning with the lowest of the reaction temperatures of 220 °C, glucose is the main component in the liquid products, which was indicated in the previous study meanwhile 5-HMF will be converted from glucose therefore yield of 5-HMF can cause to the lowest concentration accordingly. Secondly, at the reaction temperatures of 260°C, the yield of 5-HMF became lower when the heating rate was increased. This result suggests that with a lower heating rate the palm kernel shell was subjected to water vapor with a longer contact time, resulting in a larger amount of cellulose converted to 5-HMF. Thirdly, a corresponding result was observed at the higher reaction temperature of 280 °C and above when the heating rate was increased from 5 to 7.5 °C/min. On the other hand, at the highest of heating rate, the contact time with water vapor was too short to allow the conversion of cellulose into 5-HMF sufficiently. This leads to a decrease in concentration of 5-HMF at all reaction temperature. This experimental result is accordance with the previous studied, Bao et al (2008), they synthesized of 5-HMF by the dehydration of fructose in the presence of the bronsted acidic and lewis acid derivative ionic liquid [25]. Figure 5.6.6 illustrates the yield of 5-HMF derived from two types of feedstock including palm kernel shell residues and fructose, respectively. This corresponding results show that yield of 5-HMF steadily decreases when the heating rate was increased.



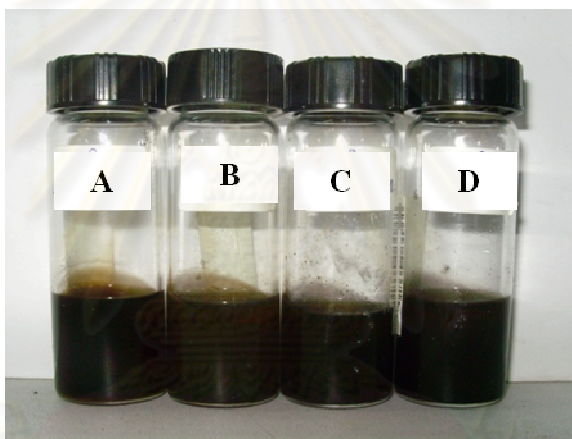
**Figure 5.6.5** Heating-rate dependence of 5-HMF concentration at difference reaction temperatures of 220-300 °C



**Figure 5.6.6** Yield of 5-HMF varied with heating rate compared between palm kernel shell residues (this work, upper) and fructose ([25], lower)

### 5.7 Effect of concentration of palm kernel shell residues

In this study, we focus on the effect of concentration of feedstock (palm kernel shell residues) on the hydrothermal treatment process with the target temperature at 220, 260, 280 and 300 °C. In each temperature, we employed the concentration of feedstock at 10 and 20 wt%, respectively. The appearances of liquid products from the hydrothermal treatment process were illustrated in figure 5.7.1 to 5.7.3. In contrast, it could be seen that these liquid samples is more turbidity than the liquid samples which obtained from the use of feedstock at 10 wt% because of the influence of the change in concentration of feedstock from 10 wt% to 20 wt%.

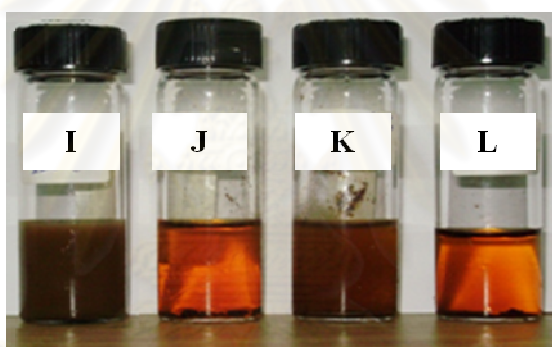


**Figure 5.7.1** Liquid samples after hydrothermal treatment with the concentration of feedstock at 20 wt % and 5 °C/min. (A) 220 °C, (B) 260 °C, (C) 280 °C and (D) 300 °C





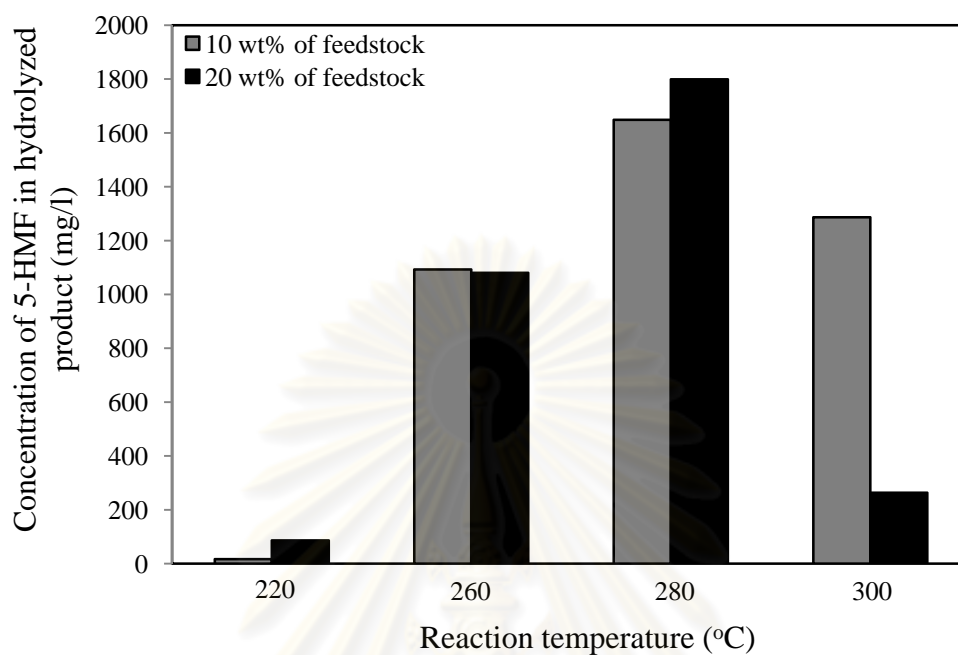
**Figure 5.7.2** Liquid samples after hydrothermal treatment with the concentration of feedstock at 20 wt % and 7.5 °C/min. (E) 220 °C, (F) 260 °C, (G) 280 °C and (H) 300 °C



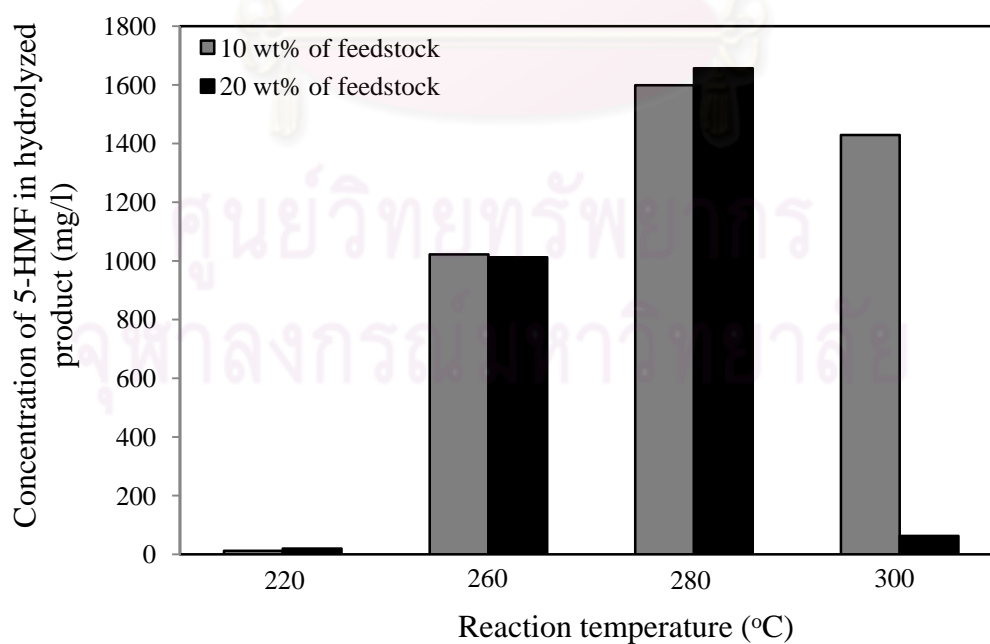
**Figure 5.7.3** Liquid samples after hydrothermal treatment with the concentration of feedstock at 20 wt % and 10 °C/min. (I) 220 °C, (J) 260 °C, (K) 280 °C and (L) 300 °C

Figure 5.7.4 to 5.7.6 shows the trend of 5-HMF concentration increased when the reaction temperature was increased up to 280 °C which was accompanied with the change in the initial concentration of feedstock from 10 to 20 wt%. In addition as shown in figure 5.7.7, when we changed the initial concentration of feedstock from 10 to 20 wt% at several of heating rate, it could be observed that the 5-HMF yield was apparently increased due to the fact that the larger surface area of feedstock could be caused the higher rate of reaction. This experimental result is consistent with the previous work, Chheda et al (2007), they studied the production of 5-HMF and furfural by dehydration of pure fructose [24]. It could be noted that the change in the

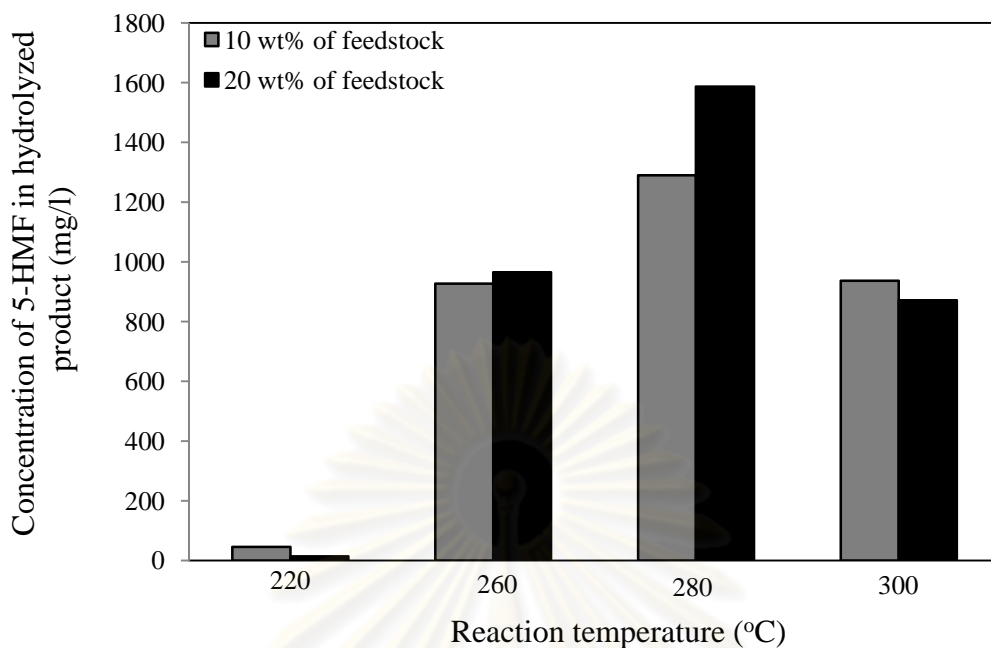
initial concentration of pure fructose from 10 to 30 wt% significantly increased in the concentration of 5-HMF in liquid product.



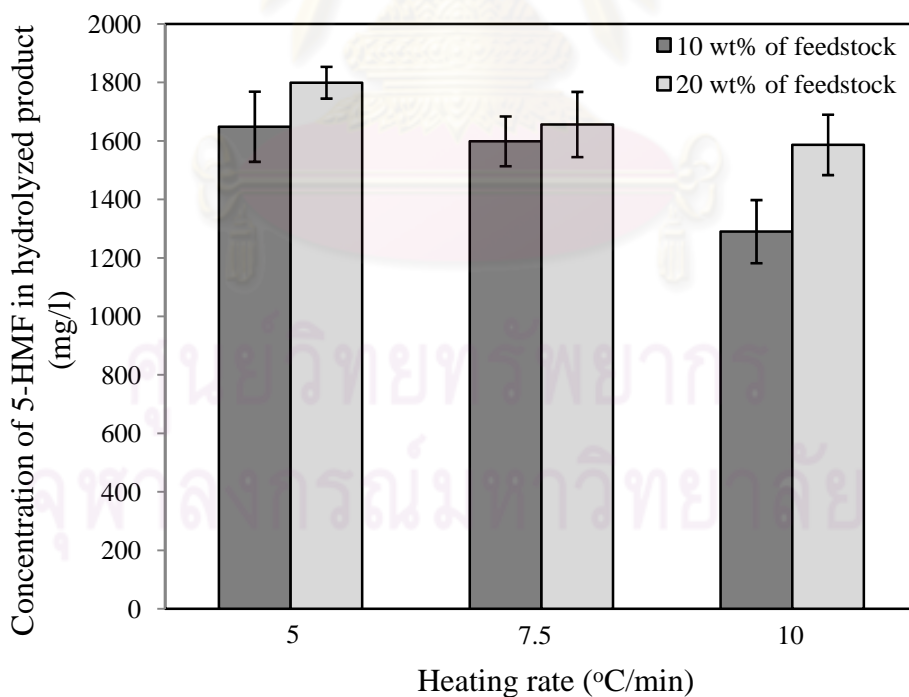
**Figure 5.7.4** Concentration changes of 5-HMF at heating rate of 5 °C/min with 10 and 20 wt% of feedstock concentration



**Figure 5.7.5** Concentration changes of 5-HMF at heating rate of 7.5 °C/min with 10 and 20 wt% of feedstock concentration



**Figure 5.7.6** Concentration changes of 5-HMF at heating rate of 10 °C/min with 10 and 20 wt% of feedstock concentration



**Figure 5.7.7** Concentration of 5-HMF varied with heating rate at the reaction temperature of 280 °C

### 5.8 Effect of lignin content of palm kernel shell residues

This study investigates the effect of lignin content of palm kernel shell residues on the hydrothermal treatment process.

**Table 5.8** The lignin content in several physical properties of feedstock

Chemical composition	wt %			
	Sample A	Sample B	Sample C	Sample D
Lignin	3.59	5.78	6.93	9.98

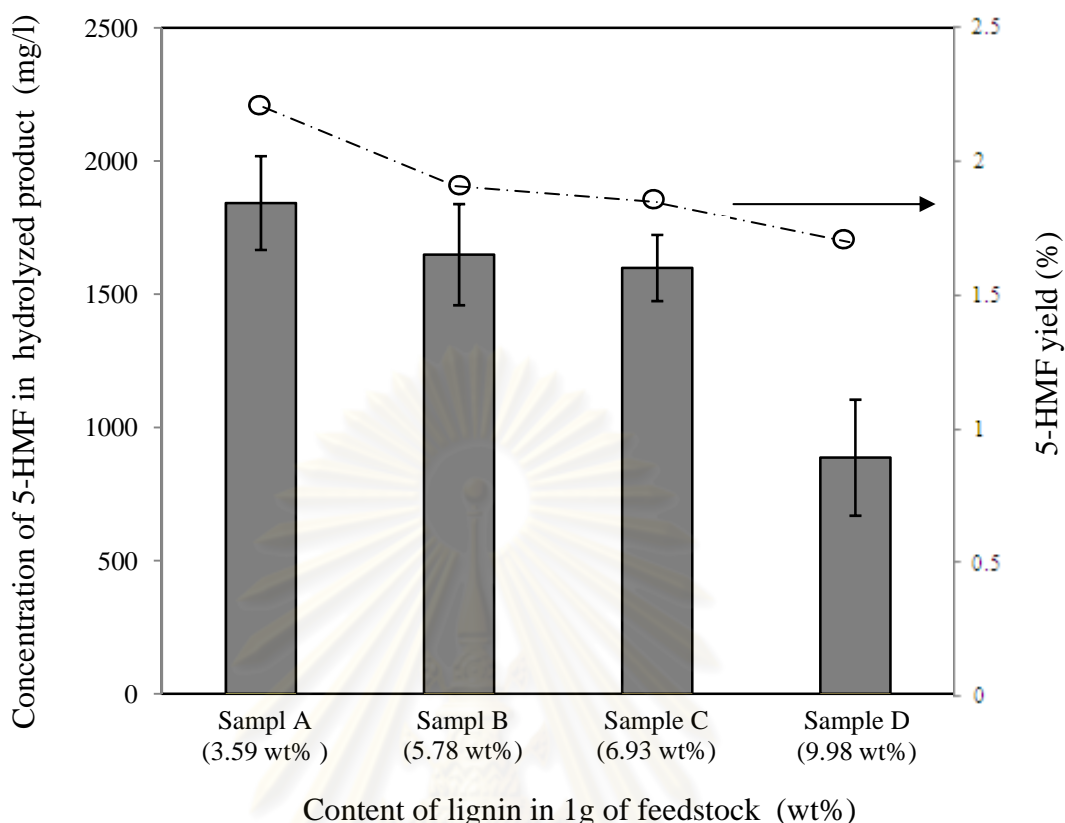
Sample A = Raw material residues treated with alkali solution for 3 hrs.

Sample B = Raw material residues treated with alkali solution for 1.5 hrs.

Sample C = Original raw material residues without alkali treatment and sift with size 800  $\mu\text{m}$ .

Sample D = Original raw material residues without alkali treatment and sift with size 250  $\mu\text{m}$ .

As shown in Table 5.8, it was not clear about how to control the lignin content in feedstock and how much its composition might be varied. A non-uniform lignin distribution should have to exist in palm kernel shell on account of variations in species of palm oil characteristics. Dried palm kernel shell residues were conducted in the hydrothermal treatment at different fiber lignin contents. The elimination of lignin contents from raw material were usually performed by alkali treatment method and determination the composition by USDA's method. Nonetheless, at least two times of experiment were significantly conducted for confirming repeatability.



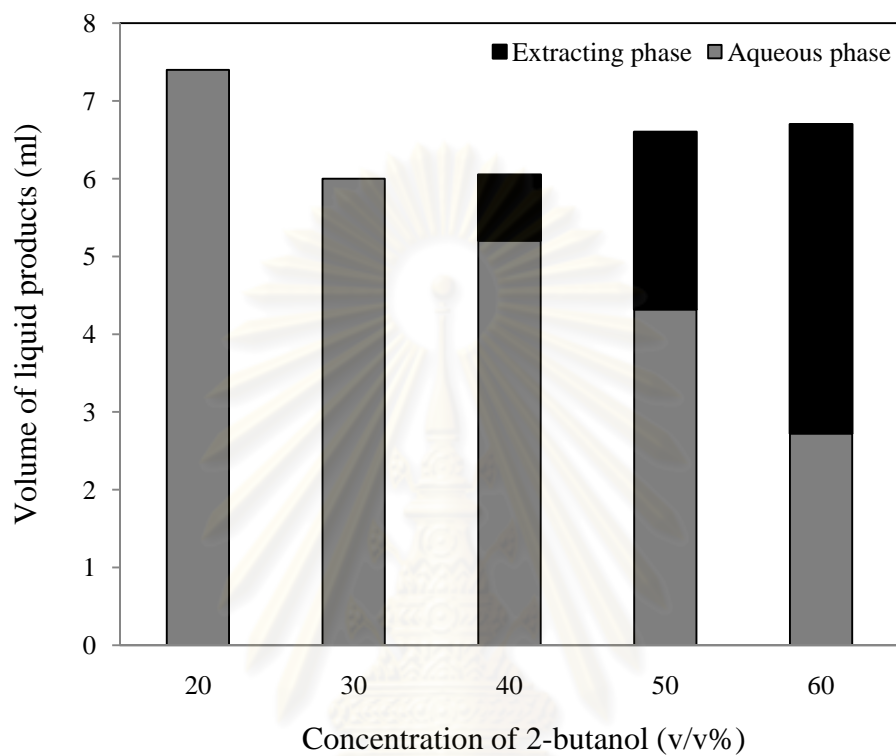
**Figure 5.8** Concentration and yield of 5-HMF varied with the lignin content under the reaction temperature and heating rate of 280 °C and 5 °C/min, respectively

As shown in figure 5.8, this experimental result indicated that the influence of lignin content led to decrease the concentration and yield of 5-HMF with an increase in lignin fraction. Furthermore, this study suggests that the amount of lignin content should be considered an important process parameter which affects the efficiency of hydrothermal treatment process. To the best of our knowledge, lignin is the major barrier to efficient extraction of cellulose fibers for pulp and paper production. Especially, for the bio-energy industry, lignin is a barrier to saccharification process and hydrolysis process for production of liquid bio-fuel [41-42]. In 2000, Demirba et al studied the effect of lignin content on the process of aqueous liquefaction, they concluded that when increasing in lignin content the oil yield decreased and the char yield increased [43].

### 5.9 Effect of 2-butanol as extracting solvent

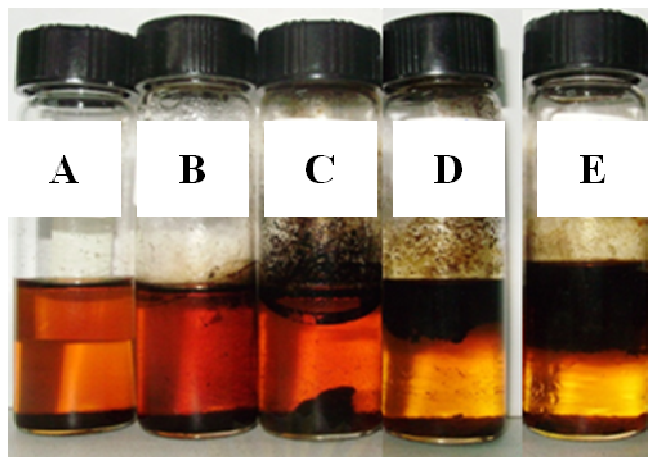
The aim of this study is to set up the viscous portion called “extracting phase or black portion” from 2-butanol as petroleum-derived product. Naturally, 5-HMF is water-soluble molecule. It could be converted into levulinic and formic acid by rehydration reaction. Moreover, when the temperature increase, the degradation of 5-HMF can be formed to acids, aldehydes and phenols [28]. According to the calculation of solubility of 5-HMF in water and 2-butanol, it could be noted that 5-HMF can more dissolve in 2-butanol than water. For this reason, the hydrothermal treatment of palm kernel shell residues should be expected with the presence of 2-butanol as extracting solvent in order to suppress the rehydration and degradation reaction.

Figure 5.9.1 shows the effects of adding 2-butanol at 20, 30, 40, 50 and 60 v/v% on the total volume of liquid product. It could be seen that an increasing in concentration of 2-butanol led to increase in the portion of extracting phase obtained from the hydrothermal treatment as shown in figure 5.9.2. After reaction, the liquid products consisted of portions of the aqueous and organic phase were separated and taken to determine the amount of 5-HMF using HPLC analysis.



**Figure 5.9.1** Effect of concentration of 2-butanol on the total volume of liquid product

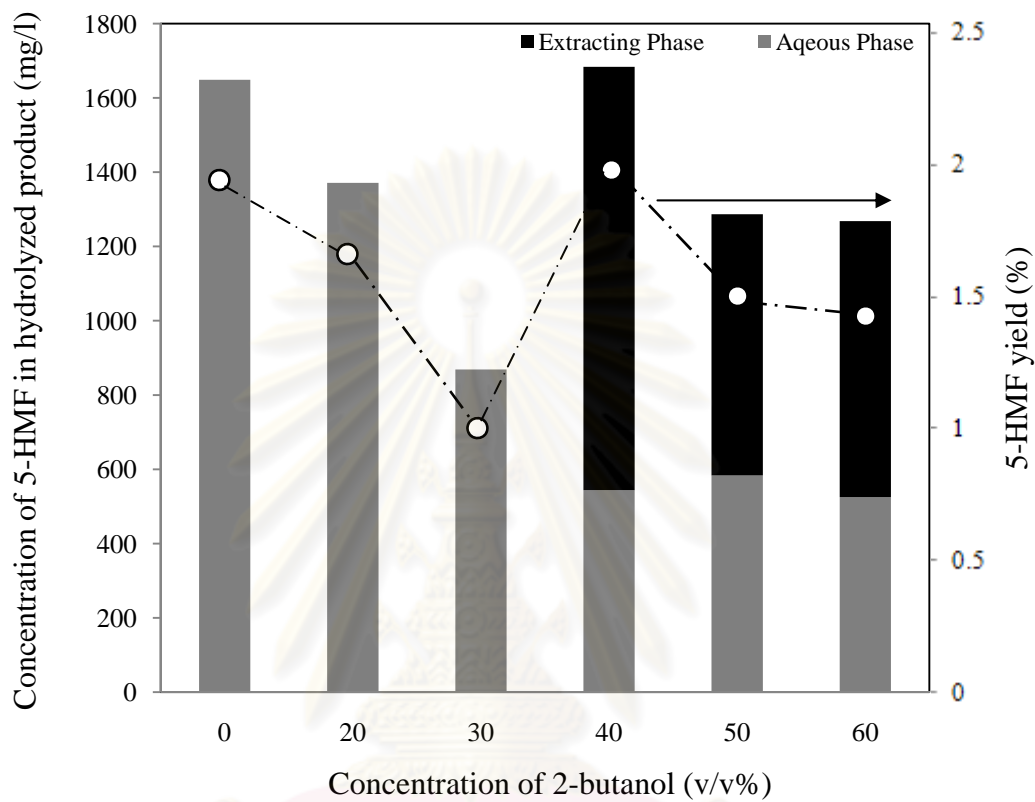
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**Figure 5.9.2** Liquid samples after hydrothermal treatment with the presence of 2-butanol under 280 °C and 5 °C/min. (A) 20 v/v%, (B) 30 v/v%, (C) 40 v/v% (D) 50 v/v% and (E) 60 v/v%

According to our experimental results, as shown in figure 5.9.3 and figure 5.9.4, the total concentration and yield of 5-HMF became higher with the increase in 2-butanol loading singlehandedly, in particular at 40 v/v% of 2-butanol, compared with non-added solvent condition. This is attributed to the extracting capability of 2-butanol which could suppress degradation reactions arising when 5-HMF came to contact with de-ionized water [24]. In addition, when 2-butanol was loaded more than 40 v/v%, it decreased in portion of water used for the conversion of cellulose to 5-HMF, yield of 5-HMF could be decreased accordingly. Moreover, it was reported that the yield of 5-HMF in the hydrothermal process of biomass could be promoted with the addition of 2-butanol in the presence of other species such as phosphoric acid ( $H_3PO_4$ ) and DMSO. According to Leshkov et al (2007), they suggested that 2-butanol is the best candidate as extracting solvent. It can generate high selectivity of 5-HMF from pure fructose [23]. For importance point, 2-butanol was obtained from petroleum-derived products unlike unsaturated solvents such as toluene or methyl isobutyl ketone (MIBK) which both of them are hazardous solvent that can cause cancer disease.



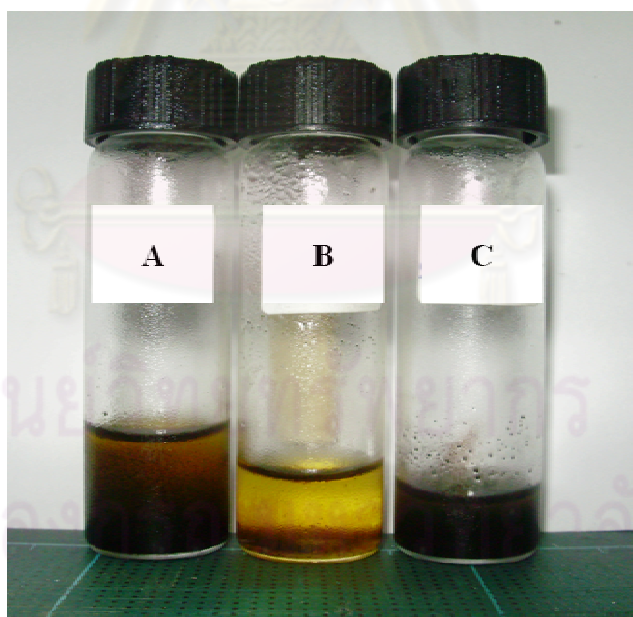


**Figure 5.9.3** Effect of 2-butanol loading on the concentration and yield of 5-HMF in liquid product under 280 °C and 5 °C/min

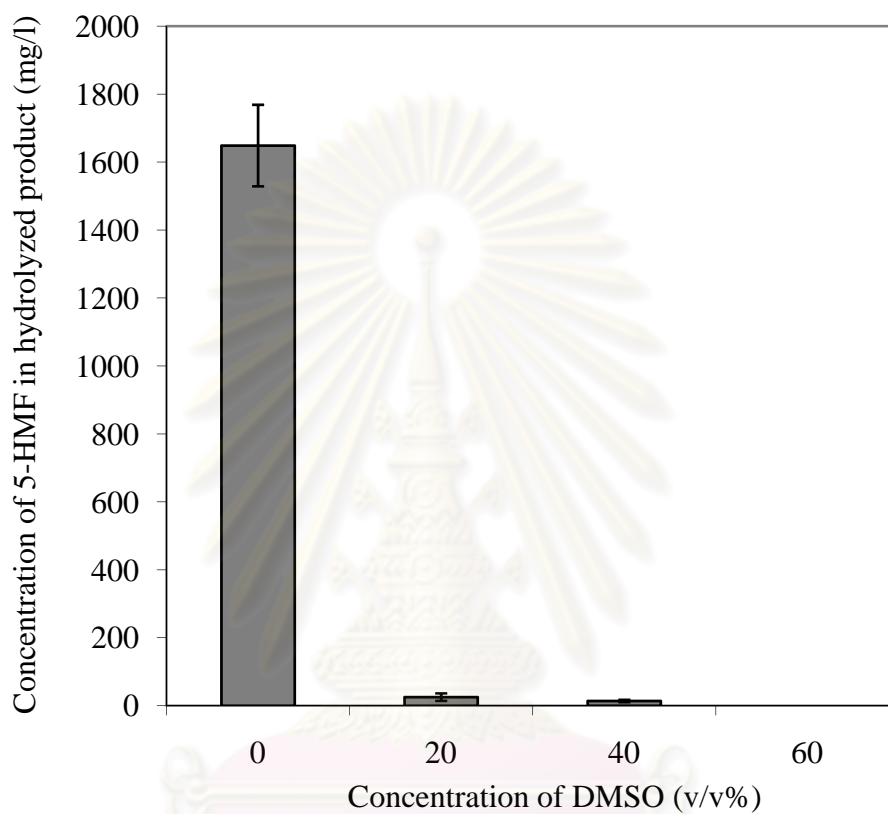
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### 5.10 Effect of dimethyl sulfoxide (DMSO) as homogeneous catalyst

This study was conducted using DMSO as homogeneous catalyst and palm kernel shell residues as the feedstock, with no presence of the extracting solvent. In this experimental result, as shown in figure 5.10.1 and figure 5.10.2, it could be noted that increasing the DMSO content could decrease the hydrolyzed power of de-ionized water, as indicated by increase in the dehydration rates, led to decrease volume of liquid product, when it was used with no presence of extracting solvent. According to Chheda et al (2007), they studied the effects of varying the DMSO level in the aqueous phase for improved selectivity of 5-HMF. They observed that when adding DMSO to a level of 50 wt% could moderately improved the selectivity of 5-HMF [24]. More than that, the previous works suggested that DMSO can suppress both the formation of condensation byproducts and the 5-HMF rehydration by lowering the overall water concentration [44-45].



**Figure 5.10.1** Liquid samples after hydrothermal treatment with the presence of DMSO under 280 °C and 5 °C/min (A) 20 v/v%, (B) 40 v/v% and (C) 60 v/v%



**Figure 5.10.2** Effect of DMSO loading on the concentration of 5-HMF in liquid product under 280 °C and 5 °C/min

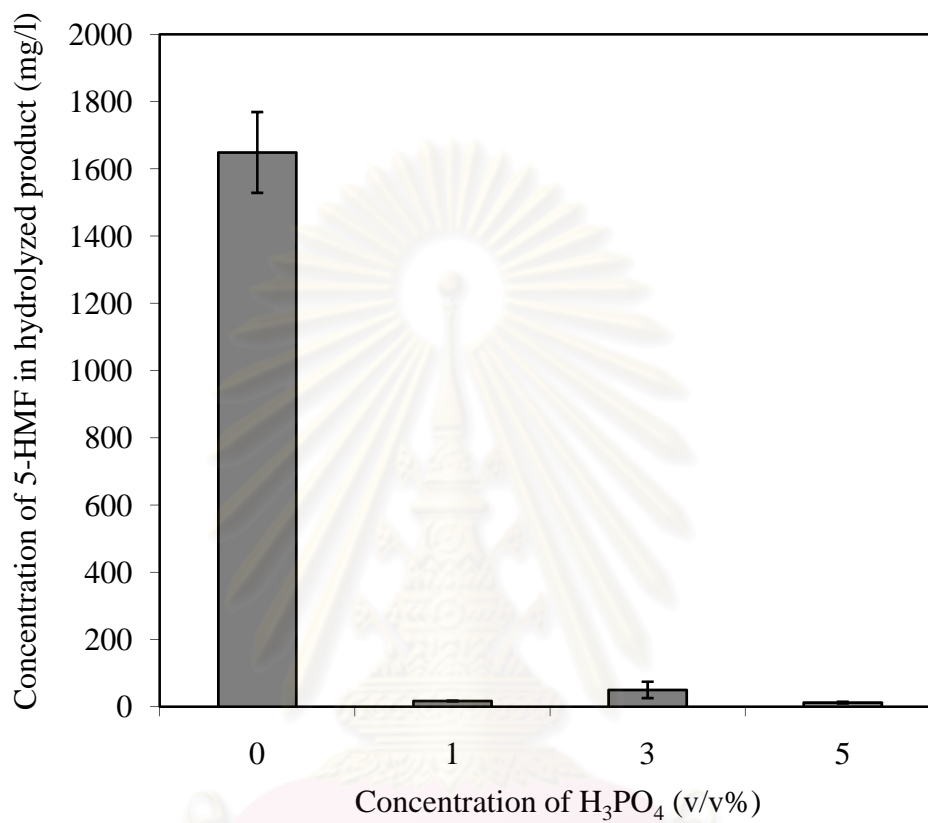
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### 5.11 Effect of $\text{H}_3\text{PO}_4$ as homogeneous catalyst or acid-catalyzed

This experiment was conducted using  $\text{H}_3\text{PO}_4$  as acid-catalyzed and palm kernel shell residues as the feedstock, with no presence of the extracting solvent. Figure 5.11.1 and figure 5.11.2 results the varied concentration of  $\text{H}_3\text{PO}_4$  affected on the concentration of 5-HMF in liquid products, it could be concluded that the concentration of 5-HMF decrease when the high content of  $\text{H}_3\text{PO}_4$  was loaded. It could be anticipated that with the high loading of  $\text{H}_3\text{PO}_4$  reached to increase the amount of condensation byproduct such as furfural obtained from HPLC's chromatograms. Our experimental result is dissimilar to the previous work, Chheda et al (2007), they conducted experiments to study the effect of less-corrosive mineral acids such as  $\text{H}_3\text{PO}_4$  and obtain in the high 5-HMF selectivity but the high selectivity achieved was accompanied by the need to use twenty times more acid compared to stronger acid [24].



**Figure 5.11.1** Liquid samples after hydrothermal treatment in the presence of  $\text{H}_3\text{PO}_4$  under 280 °C and 5 °C/min (A) 1 v/v%, (B) 3 v/v% and (C) 5 v/v%



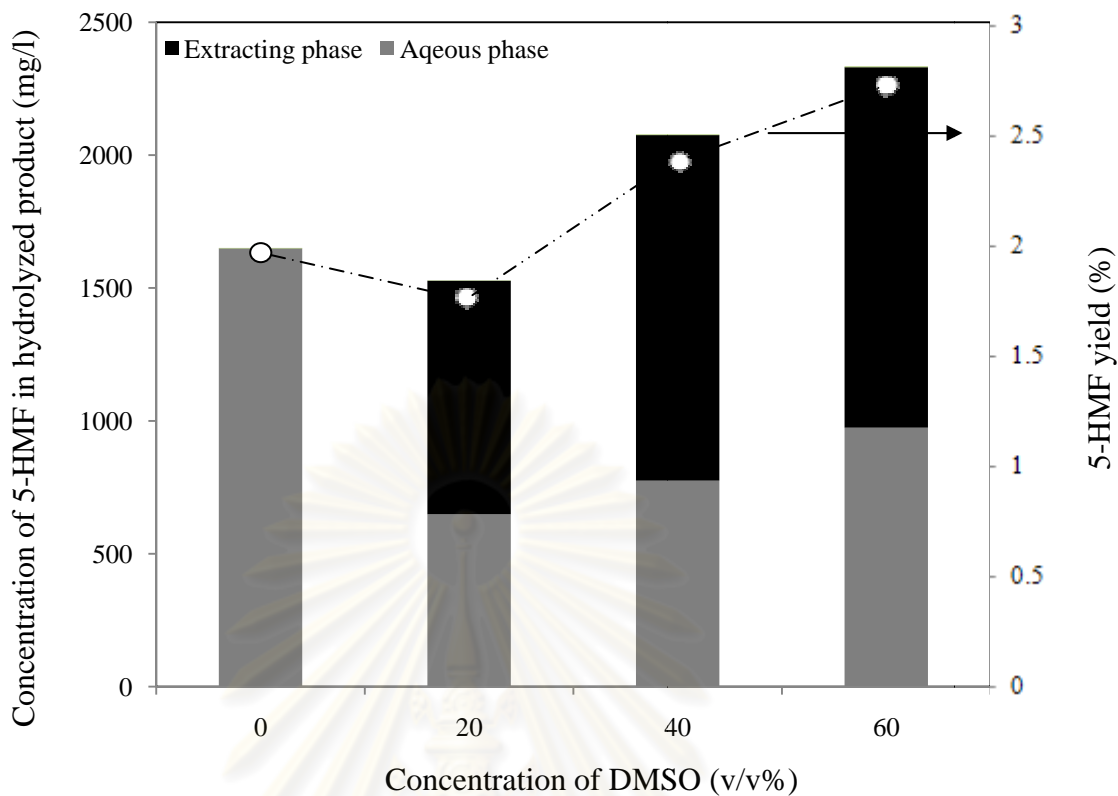
**Figure 5.11.2** Effect of H<sub>3</sub>PO<sub>4</sub> loading on the concentration of 5-HMF in liquid product under 280 °C and 5 °C/min

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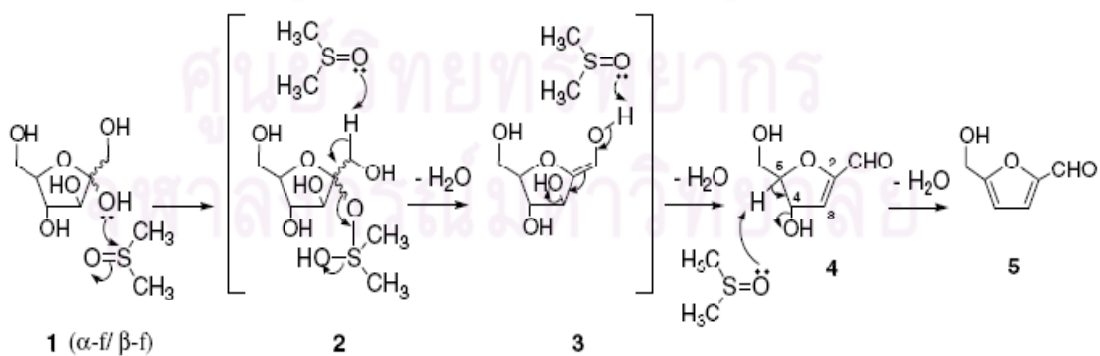
### 5.12 Effect of 2-butanol as extracting solvent in the presence of DMSO as homogeneous catalyst

In this studied, we investigated the production of 5-HMF by hydrothermal treatment of palm kernel shell residues using a batch-type tubular reactor system, consisted of reactive aqueous phase modified with DMSO, combined with an organic extracting phase applied with 2-butanol. As shown in figure 5.12.1, the overall concentration and yield of 5-HMF increased with the increase in DMSO loading, in particular at 40 and 60 v/v% of DMSO, the highest yield was found in this study, compared with previous experiment in this research.

This is suggested about the catalyzed capability of DMSO. Beside, DMSO not only can suppress the formation of condensation byproducts and the 5-HMF rehydration reaction, but it is also stabilized molecule for the furanose form at higher temperatures [46]. In 2008, Ananda et al investigated the mechanism of the dehydration of D-fructose to 5-HMF in DMSO without added acid by using NMR spectra method [26]. From the chemical point of view, they suggested a mechanism to explain the dehydration of the two furanose forms of D-fructose to 5-HMF as shown in figure 5.12.2. The liquid samples obtained from this hydrothermal treatment shows in figure 5.12.3 to 5.12.5.



**Figure 5.12.1** Effect of DMSO loading in the presence of 2-butanol as extracting solvent on concentration and yield of 5-HMF in liquid product under 280 °C and 5 °C/min



**Figure 5.12.2** A mechanism for the dehydration of D-fructose in form of furanose in DMSO; 1 ( $\alpha$ -f/ $\beta$ -f) to 5-HMF (5) [26]



**Figure 5.12.3** Liquid samples after hydrothermal treatment in the presence of 20 v/v% of DMSO and 2-butanol under 280 °C and 5 °C/min  
(A) aqueous phase and (B) extracting phase



**Figure 5.12.4** Liquid samples after hydrothermal treatment in the presence of 40 v/v% of DMSO and 2-butanol under 280 °C and 5 °C/min  
(C) aqueous phase and (D) extracting phase

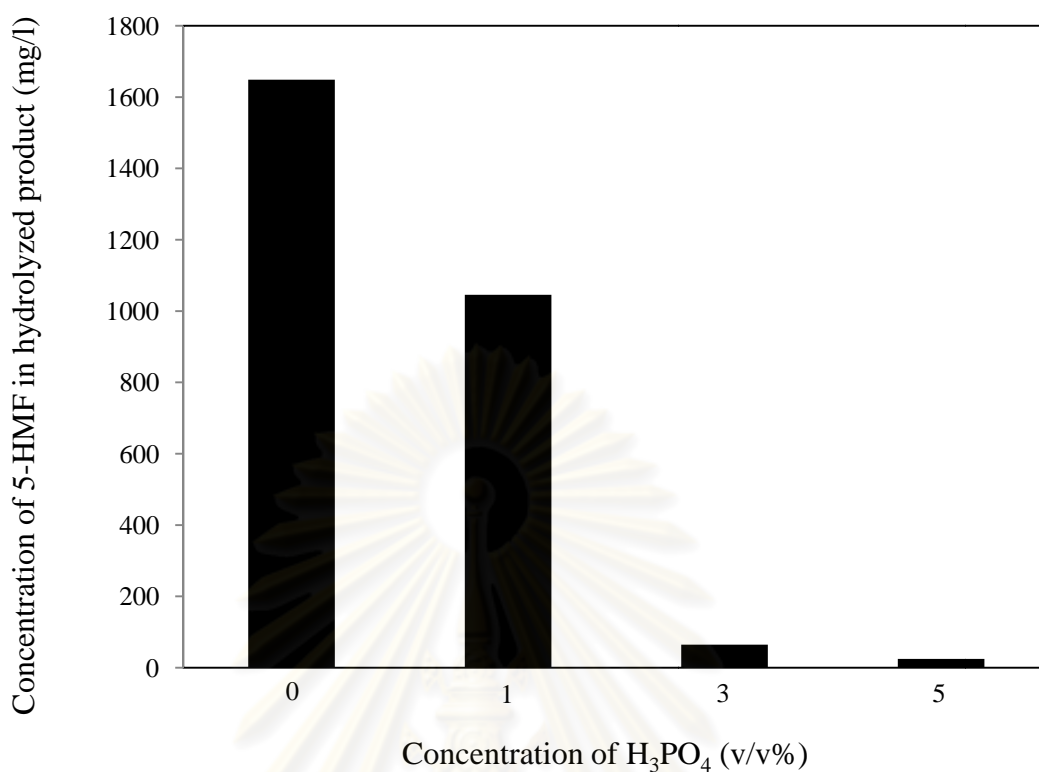


**Figure 5.12.5** Liquid samples after hydrothermal treatment in the presence of 60 v/v% of DMSO and 2-butanol under 280 °C and 5 °C/min  
(E) aqueous phase and (F) extracting phase

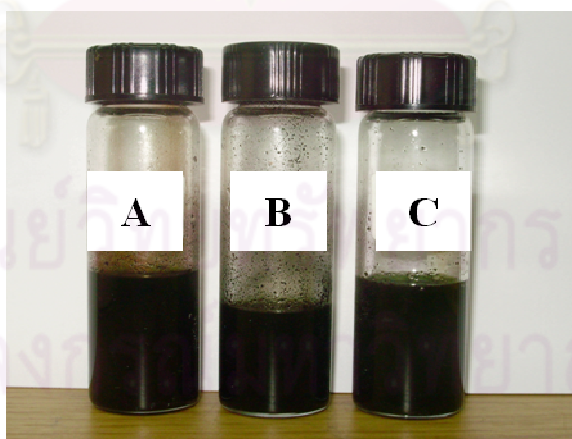


### 5.13 Effect of 2-butanol as extracting solvent in the presence of $H_3PO_4$ as homogeneous catalyst or acid-catalyzed

Similar to a previous study, we investigated the production of 5-HMF by hydrothermal treatment of palm kernel shell residues using a batch-type tubular reactor system, the system is comprised of reactive aqueous phase modified with  $H_3PO_4$ , combined with an organic extracting phase applied with 2-butanol. Figure 5.13.1 illustrates the effect of  $H_3PO_4$  content in the presence of 2-butanol as extracting solvent on the concentration of 5-HMF in liquid products, it could be concluded that the concentration of 5-HMF decrease when the high loading of  $H_3PO_4$  was carried out. In addition, the high loading of  $H_3PO_4$  led to increase the amount of condensation byproduct such as furfural obtained from HPLC's chromatograms. Unfortunately, this experiment could not discover the extracting phase owing to the effect of corrosive mineral acids such as  $H_3PO_4$  as shown in figure 5.13.2. Based on Kuster et al (1990) work, they demonstrated the use of acid-base mixtures for increasing the yield of 5-HMF, but they found the system containing furans, pyrroles, and pyridines which this experimental result is in accordance with our work [44].



**Figure 5.13.1** Effect of H<sub>3</sub>PO<sub>4</sub> loading in the presence of 2-butanol as extracting solvent on concentration of 5-HMF in liquid product under 280 °C and 5 °C/min



**Figure 5.13.2** Liquid samples after hydrothermal treatment in the presence of H<sub>3</sub>PO<sub>4</sub> and 2-butanol under 280 °C and 5 °C/min  
(A) 1 v/v%, (B) 3v/v% and (C) 5 v/v%

## CHAPTER VI

### CONCLUSIONS AND RECOMMENDATIONS

#### 6.1 Conclusions

Palm kernel shell residues could be converted to liquefied products including 5-HMF within a batch-type tubular reactor operated under subcritical water conditions. The process parameters which could affect the final yield of 5-HMF are reaction temperature, heating rate, concentration of feedstock, lignin content and concentration of extracting solvent and homogeneous catalysts. Moreover, the solid residues which were sampled before and after process we were investigated the change in physical structure and chemical component existing on surface as concluded in the previous content. Particularly, this research put the emphasis on the liquid product for preparing 5-HMF and find out for optimal conditions for increasing yield of 5-HMF in liquefied product alike.

The major conclusions of all experiments were summarized as follows;

- A remarkable yield of 5-HMF obtained under the reaction temperature ranging between 280-300 °C.
- An increase in heating rate decreased the yield of 5-HMF because a contact time between water vapor and cellulose was depleted.
- An increase in concentration of feedstock led to increase the yield of 5-HMF because the larger amount of palm kernel shell residues could increase the surface area of cellulose for hydrolysis process.
- The larger amount of lignin content in feedstock reduced the yield of 5-HMF because lignin is a striking barrier between cellulose and water vapor in the hydrolysis process.
- The addition of 2-butanol as extracting phase to the hydrothermal process of palm kernel shell residues could increase the total yield of 5-HMF with the

increase in the concentration of 2-butanol of which the optimum value was 40 v/v%.

- The addition of homogeneous catalysts could not increase the yield of 5-HMF, neither with DMSO nor  $\text{H}_3\text{PO}_4$ .
- The addition of 2-butanol as extracting solvent with the presence of DMSO as homogeneous catalyst could increase the total yield of 5-HMF to the highest value when compared with other results of this work.
- The addition of 2-butanol as extracting solvent with the presence of  $\text{H}_3\text{PO}_4$  as homogeneous catalyst could not increase the yield of 5-HMF because the extracting phase did not exist in this case.

## 6.2 Recommendations

- To study designed experiments using the smallest particles size of palm kernel shell residues before treated by alkali treatment.
- To study effect of common parameters such as reaction temperature, heating rate and lignin content on 5-HMF yield.
- To study separation process to extract 5-HMF and furfural from the extracting solvent and homogeneous catalyst. Meanwhile, simulation should be conducted for developing the understanding of this process.
- To study the hydrogenolysis reaction to convert 5-HMF into 2,5-dimethylfuran (DMF) which this molecule is the best candidate for replacement of ethanol for the production of liquid bio-fuel.

## REFERENCES

- [1] Antal, M.J., Allen, S.G., Schulman, D., and Xu, X., 2000, Biomass gasification in supercritical water, Ind. Eng. Chem. Res., 39: 4044-4053.
- [2] Prasertsan, S., and Prasertsan, P., 1996, Biomass residues from palm oil mills in Thailand: An overview on quantity and potential usage, Biomass and Bioenergy, 11: 387–395.
- [3] Yong, T.L.K., Lee, K.T., Mohamed, A.R., and Bhatia, S., 2007, Potential of hydrogen from oil palm biomass as a source of renewable energy worldwide, Energy Policy, 35: 5692–5701.
- [4] Saka, S., 2005, Whole efficient utilization of oil palm to value-added products, Proceeding of JSPS-VCC Natural Resources & Energy Environment Seminar, Japan.
- [5] Sasaki, M., et al., 1998, Cellulose hydrolysis in subcritical and supercritical water, J. Supercrit. Fluids, 13: 261-268.
- [6] Saha, B.C., Iten, L.B., Cotta, M.A., and Wu, Y.V., 2005, Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol, Process Biochem., 40: 3693–3700.
- [7] Xu, F., Sun, R., Fowler, P., and Baird, M.S., 2005, Characteristics of degraded cellulose obtained from steam-exploded wheat straw, Carbohydr. Res., 340: 97–106.
- [8] Yu, B., and Qi, L., 2006, Research status of lignocellulosic materials for fuel ethanol, Ind. Eng. Chem. Res., 25: 244–249.
- [9] Zhao, Y., Lu, W.J., and Wang, H.T., 2009, Supercritical hydrolysis of cellulose for oligosaccharides production in combined technology, J. Chem. Eng., 150: 411–417.
- [10] Sasaki, M., Fang, Z., Fukushima, Y., Adschiri, T., and Arai, K., 2000, Dissolution and hydrolysis of cellulose in subcritical and supercritical water, Ind. Eng. Chem. Res., 39: 2883–2890.
- [11] Kunz, M., and Fuchs, A., 1993, Inulin and inulin-containing crops, p.149, Amsterdam: Elsevier Publishing Company.
- [12] Gandini, A. and Belgacem, M.N., 1997, Furans in polymer chemistry, Progress in Polymer Science, 22: 1203–1379.

- [13] Werpy, T.A., and Petersen, G., 2004, Top value added chemicals from biomass, Department of Energy (DOE), Golden, CO; DOE/GO-102004-1992, USA.
- [14] Huber, G.W., Chheda, J.N., Barrett, C.J., and Dumesic, J.A., 2005, Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates, Science, 308: 1446–1450.
- [15] Zhang, B., Keitz, M., and Valentas, M., 2007, Thermal effects on hydrothermal biomass liquefaction, Appl. Biochem. Biotechnol., DOI 10.1007/s12010-008-8131-5.
- [16] Kruse, A., and Dinjus, E., 2007, Hot compressed water as reaction medium and reactant Properties and synthesis reactions, J. Supercrit. Fluids, 39: 362–380.
- [17] Eiji, K., Susumu, T., Hidehiko, N., Chouji, F., and Takanari, O., 2008, Effect of heating rate on liquefaction of cellulose by hot compressed water, J. Chem. Eng., 137: 328–338
- [18] Chuntanapum, A., Yong, T.L.K., Miyake, S., and Matsumura, Y., 2008, Behavior of 5-HMF in subcritical and supercritical water, Ind. Eng. Chem. Res., 47: 2956-2962.
- [19] Chen, J.D., Kuster, B.F.M., and Van Der Wiele, K., 1991, Preparation of 5-hydroxymethylfurfural via fructose acetonides in ethylene glycol dimethyl ether, Biomass and Bioenergy, 1: 211-223.
- [20] Bicker, M., Kaiser, D., Ott, L., and Vogel, H., 2005, Dehydration of d-fructose to hydroxymethylfurfural in sub and supercritical fluids, J. Supercrit. Fluids, 36: 118–126.
- [21] Watanabe, M., Aizawa, Y., Iida, T., Nishimura, R., and Inomata, H., 2005, Catalytic glucose and fructose conversions with TiO<sub>2</sub> and ZrO<sub>2</sub> in water at 473 K: Relationship between reactivity and acid–base property determined by TPD measurement, Appl. Catal. A: Gen., 295: 150-156.
- [22] Asghari, F.S., and Yoshida, H., 2006, Dehydration of fructose to 5-hydroxymethylfurfural in sub-critical water over heterogeneous zirconium phosphate catalysts, Carbohydr. Res., 341: 2379–2387.
- [23] Leshkov, Y.R., Barrett, C.J., Liu, Z.Y., and Dumesic, J.A., 2007, Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates,

Nature, 447: 982-986.

- [24] Chheda, J.N., Leshkov, Y.R., and Dumesic, J.A., 2007, Production of 5-hydroxymethylfurfural and furfural by dehydration of biomass-derived mono- and poly-saccharides, Green Chem., 9: 342–350.
- [25] Bao, Q., Qiao, K., Tomida, D., and Yokoyama, C., 2008, Preparation of 5-hydroxymethylfurfural by dehydration of fructose in the presence of acidic ionic liquid, Catal. Commun., 9: 1383–1388.
- [26] Amarasekara, A.S., Williams, L.D., and Ebede, C.C., 2008, Mechanism of the dehydration of D-fructose to 5-hydroxymethylfurfural in dimethyl sulfoxide at 150 °C: an NMR study, Carbohydr. Res., 343: 3021–3024.
- [27] Takeuchi, Y., Jin, F., Tohji, K., and Enomoto, H., 2008, Acid catalytic hydrothermal conversion of carbohydrate biomass into useful substances, J. Mater. Sci., 43: 2472–2475.
- [28] Sinag, A., Gulbay, S., Uskan, B., and Gullu, M., 2009, Comparative studies of intermediates produced from hydrothermal treatments of sawdust and cellulose, J. Supercrit. Fluids, 50: 121–127.
- [29] Su, Y., Brown, H.M., Huang, X., Zhou, X.D., Amonette, J.E., and Zhang, Z.C., 2009, Single-step conversion of cellulose to 5-hydroxymethylfurfural (HMF), a versatile platform chemical, Appl. Catal. A: Gen., 361: 117–122.
- [30] Fang, Z., et al., 2008, Catalytic hydrothermal gasification of cellulose and glucose, Int. J. Hydrogen Energy, 2008, 33: 981-990.
- [31] Ophardt, C., Virtual Chembook, 2003.
- [32] Jorgensen, H., Lignocellulose – planternes "grundstof" [online], 2011, Available from: <http://www.life.ku.dk/> [2011, February 22].
- [33] Novaes, E., Kirst, M., Chiang, V., Sederoff, H.W., and Sederoff, R., 2010, Lignin and Biomass: A negative correlation for wood formation and lignin content in trees, Plant Physiology, 154: 555–561.
- [34] Miller, J.E., Evans, L.R., Littlewolf, A.E., and Trudell, D.E., 2002, Batch microreactor studies of lignin depolymerization by bases, Technical Library, 9616: 4.
- [35] Huber, G.W., Iborra, S., and Corma, A., 2006. Synthesis of transportation fuels from biomass: Chemistry, Catalysts, and Engineering, Chem. Rev., 106: 4044.

- [36] Pacific Northwest National Laboratory, 2007, Plastic that grows on trees, Press release.
- [37] Zhao, H., Holladay, J.E., Brown, H., and Zhang, Z.C., 2007, Metal chlorides in ionic liquid solvents convert sugars to 5-hydroxymethylfurfural, Science, 316: (5782) 1597–1600.
- [38] Abdulmalik, O., et al., 2005, 5-hydroxymethyl-2-furfural modifies intracellular sickle haemoglobin and inhibits sickling of red blood cells. British journal of haematology, 128: (4) 552–61.
- [39] United States Department of Agriculture, 1970, Forage Fiber Analyses (Apparatus, Reagents, Procedures, and Some Applications), Agriculture Handbook, 379: 1-20.
- [40] Li, R., Fei, J., Cai, Y., Li, Y., Feng, J., and Yao, Y., 2009, Cellulose whiskers extracted from mulberry: A novel biomass production, Carbohydr. Polym., 76: 94–99.
- [41] Li, L., et al., 2003, Combinatorial modification of multiple lignin traits in trees through multigene cotransformation, Proc. Natl. Acad. Sci., 100: 4939–4944.
- [42] Chen, F., and Dixon, R.A., 2007, Lignin modification improves fermentable sugar yields for bio-fuel production. Nat. Biotechnol., 25: 759–761.
- [43] Demirba, A., 2000, Effect of lignin content on aqueous liquefaction products of biomass, Energy Conversion and Management, 41: (15) 1601-1607.
- [44] Kuster, B. F. M., 1990, 5-Hydroxymethylfurfural (HMF). A review focussing on its manufacture, Starch, 42: (8) 314–321.
- [45] Van Dam, H. E., Kieboom, A. P. G., and Van Bekkum, H., 1986, The conversion of fructose and glucose in acidic media: Formation of hydroxymethylfurfural, Starch, 38: (3) 95-101.
- [46] Dias, A.S., Pillinger, M., and Valente, A.A., 2005, Dehydration of xylose into furfural over micro-mesoporous sulfonic acid catalysts, J. Catal., 229: 414-423.
- [47] Guo, J., and Lua, A.C., 2002, Characterization of adsorbent prepared from oil-palm shell by CO<sub>2</sub> activation for removal of gaseous pollutants, Materials Letters, 55: 334–339.



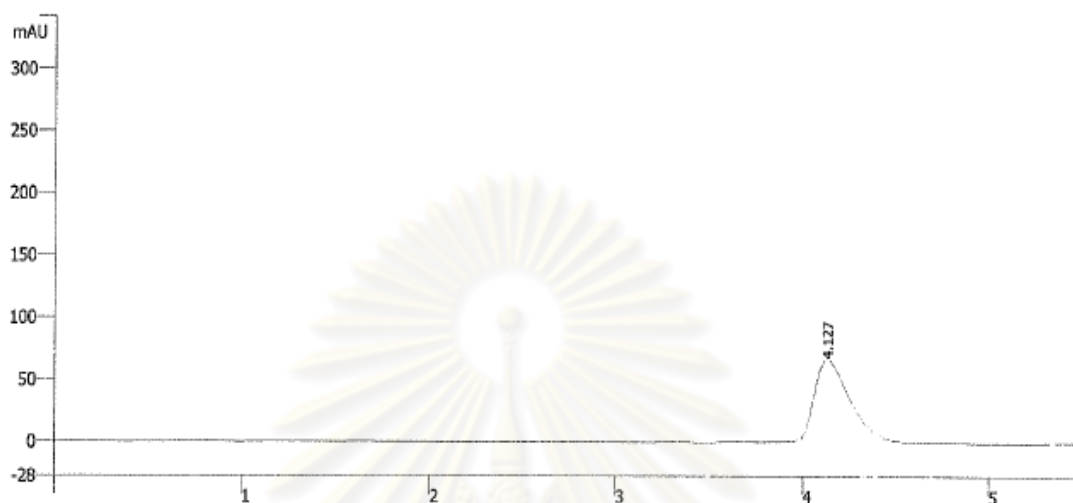


## **APPENDICES**

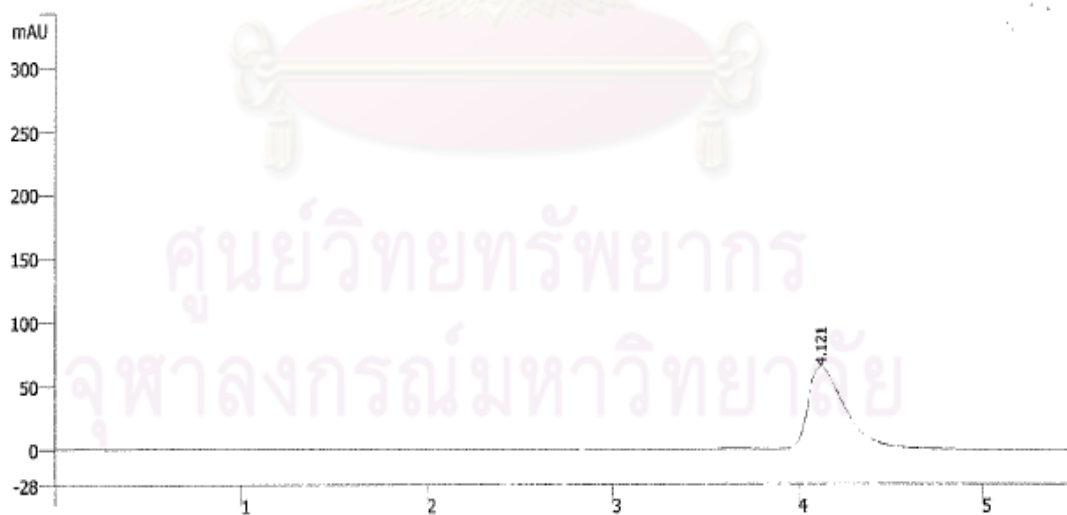
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## APPENDIX A

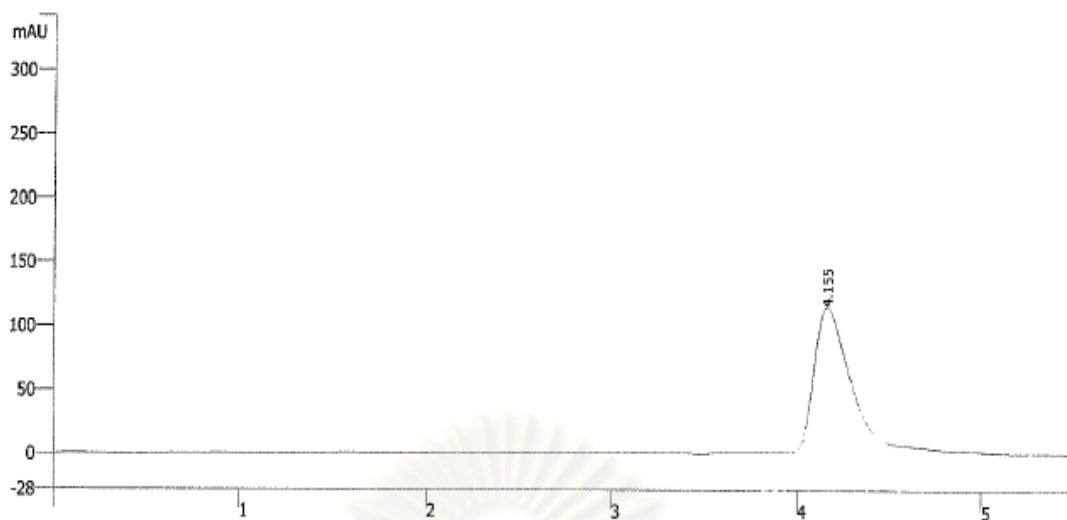
## HPLC chromatogram of 5-HMF solution



**Figure A1** HPLC chromatogram of 5-HMF solution at 20 ppm, 5 $\mu$ l,  
area 8,815,117 counts



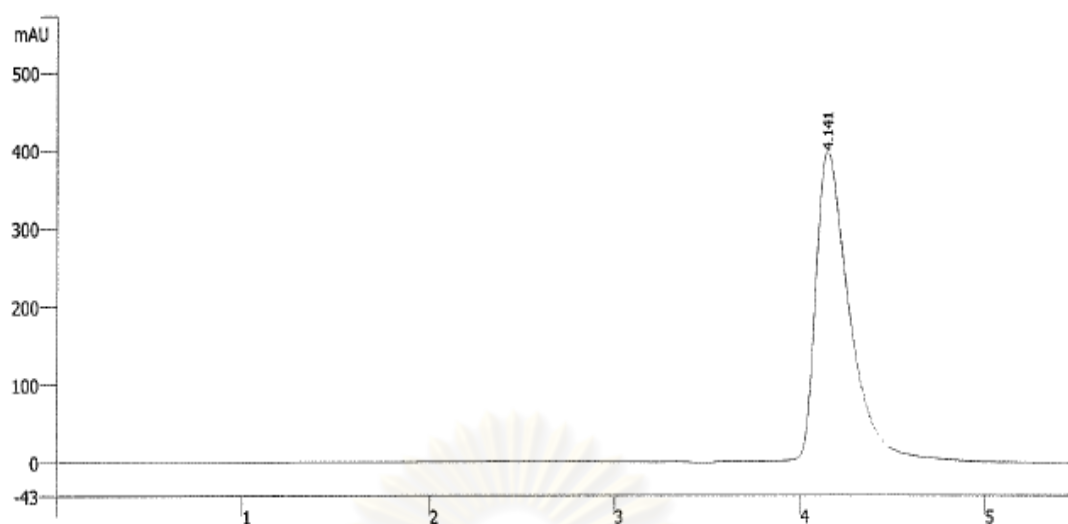
**Figure A2** HPLC chromatogram of 5-HMF solution at 20 ppm, 5 $\mu$ l,  
area 12,582,159 counts



**Figure A3** HPLC chromatogram of 5-HMF solution at 40 ppm, 5 $\mu$ l,  
area 14,599,178 counts



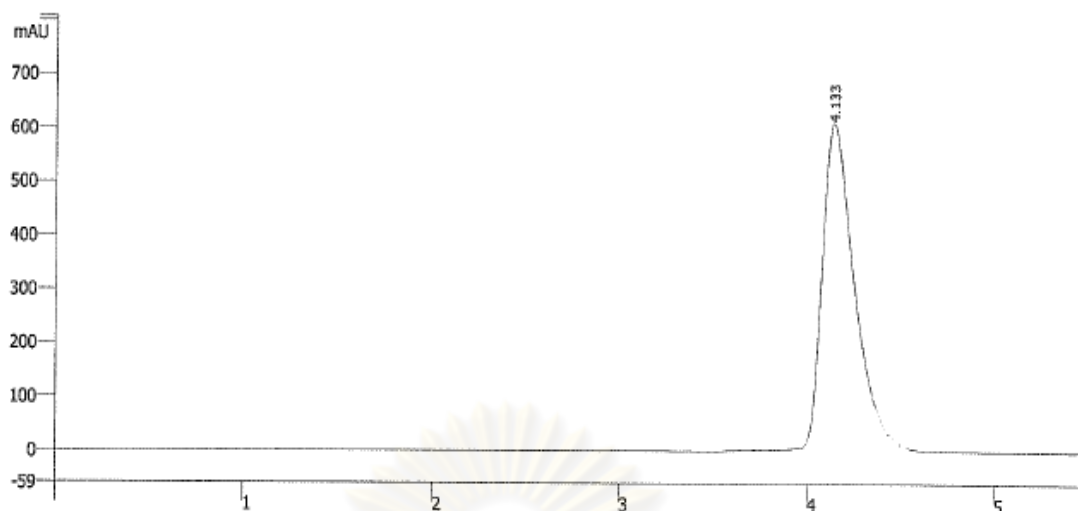
**Figure A4** HPLC chromatogram of 5-HMF solution at 40 ppm, 5 $\mu$ l,  
area 24,200,936 counts



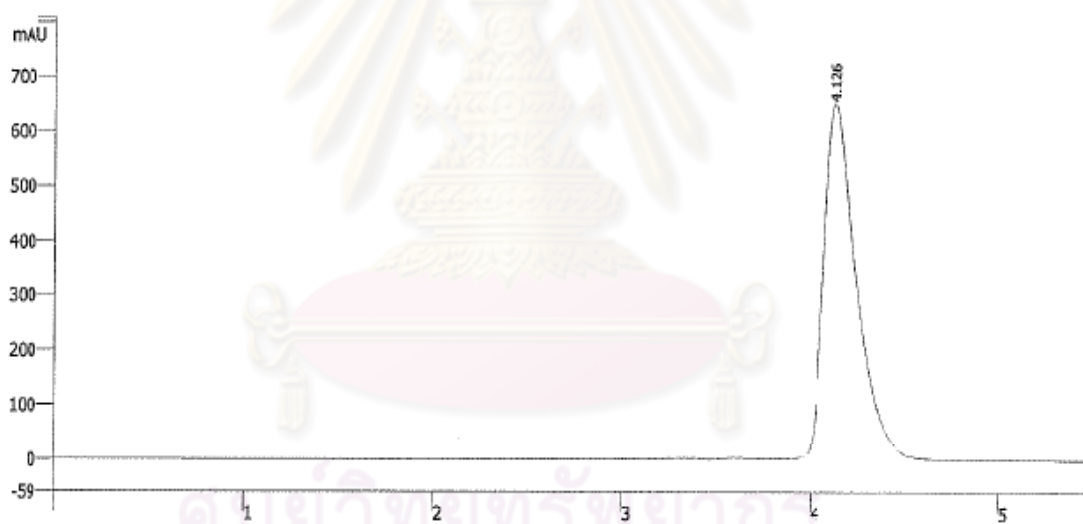
**Figure A5** HPLC chromatogram of 5-HMF solution at 60 ppm, 5 $\mu$ l,  
area 49,064,040 counts



**Figure A6** HPLC chromatogram of 5-HMF solution at 60 ppm, 5 $\mu$ l,  
area 39,436,527 counts



**Figure A7** HPLC chromatogram of 5-HMF solution at 80 ppm, 5 $\mu$ l,  
area 73,112,464 counts



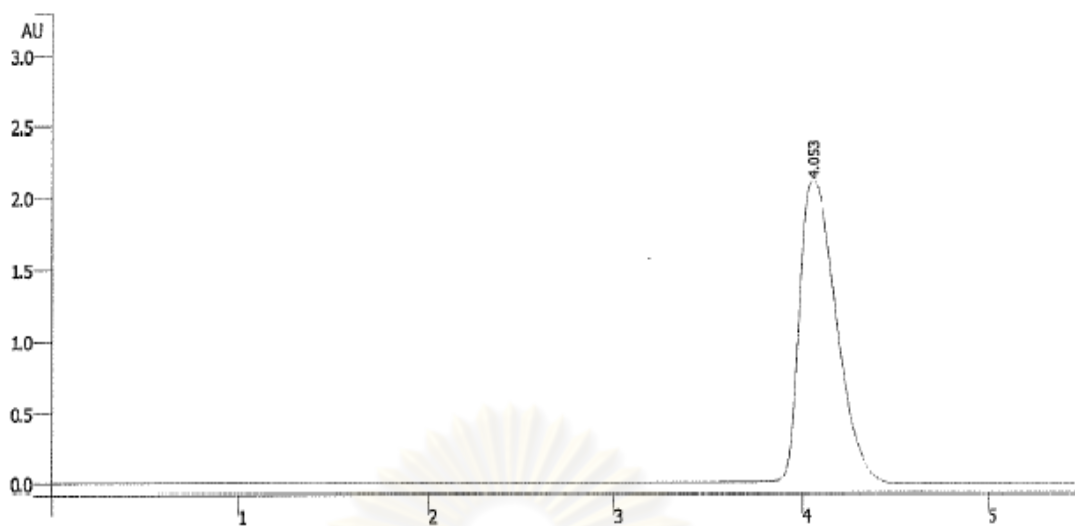
**Figure A8** HPLC chromatogram of 5-HMF solution at 80 ppm, 5 $\mu$ l,  
area 58,085,390 counts



**Figure A9** HPLC chromatogram of 5-HMF solution at 200 ppm, 5 $\mu$ l,  
area 191,403,792 counts



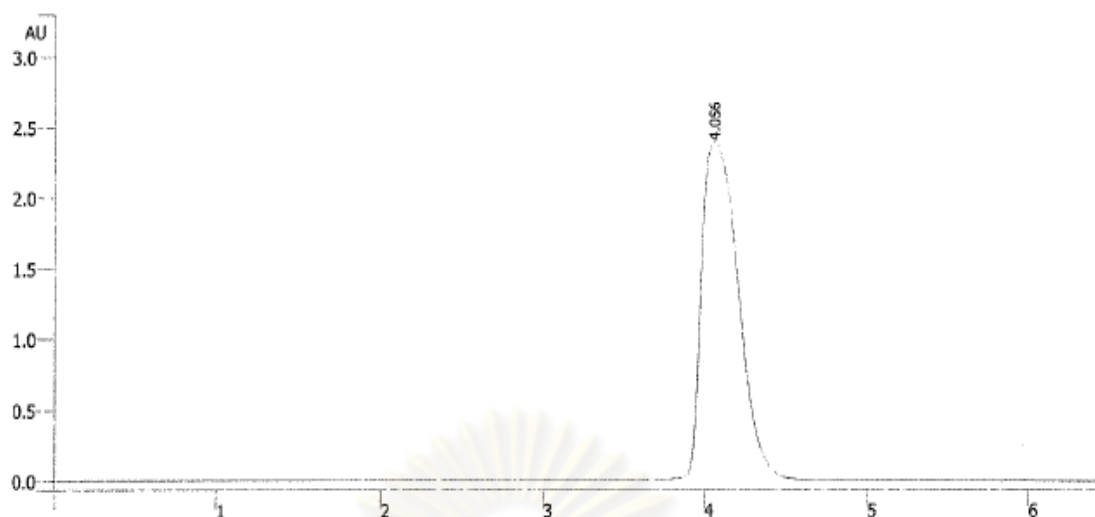
**Figure A10** HPLC chromatogram of 5-HMF solution at 200 ppm, 5 $\mu$ l,  
area 216,642,096 counts



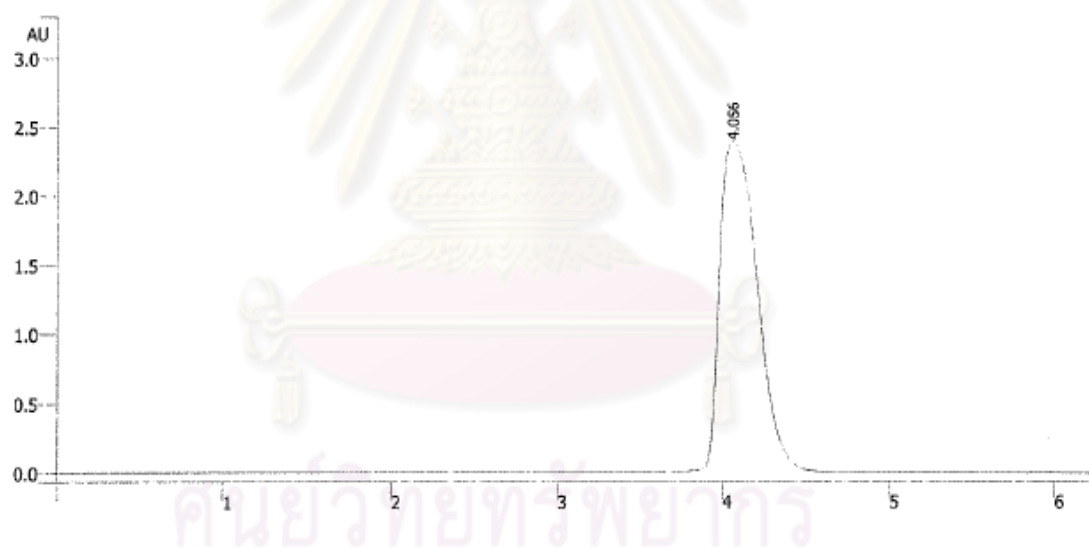
**Figure A11** HPLC chromatogram of 5-HMF solution at 600 ppm, 5 $\mu$ l,  
area 275,978,048 counts



**Figure A12** HPLC chromatogram of 5-HMF solution at 600 ppm, 5 $\mu$ l,  
area 288,983,488 counts

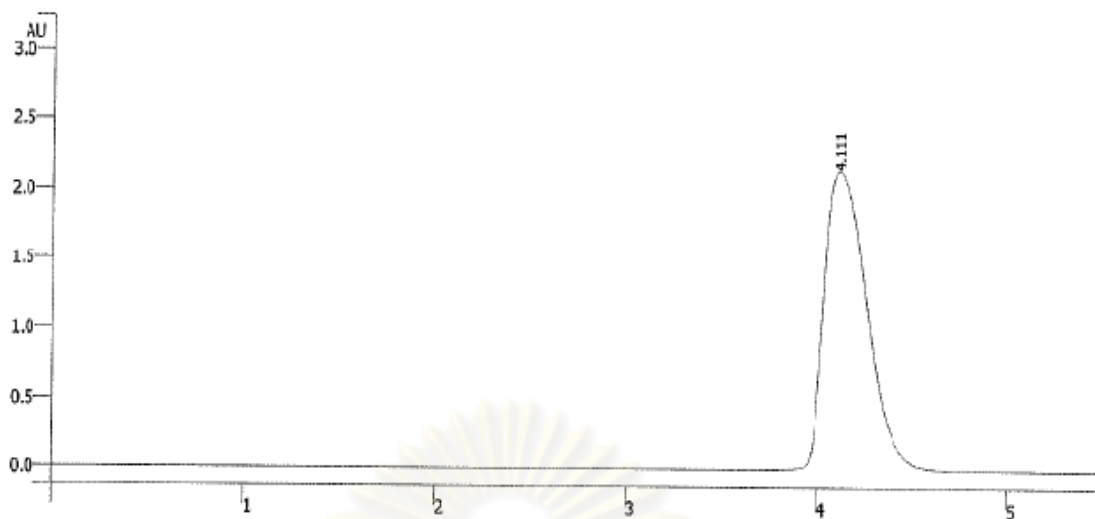


**Figure A13** HPLC chromatogram of 5-HMF solution at 1,000 ppm, 5 $\mu$ l,  
area 320,728,192 counts

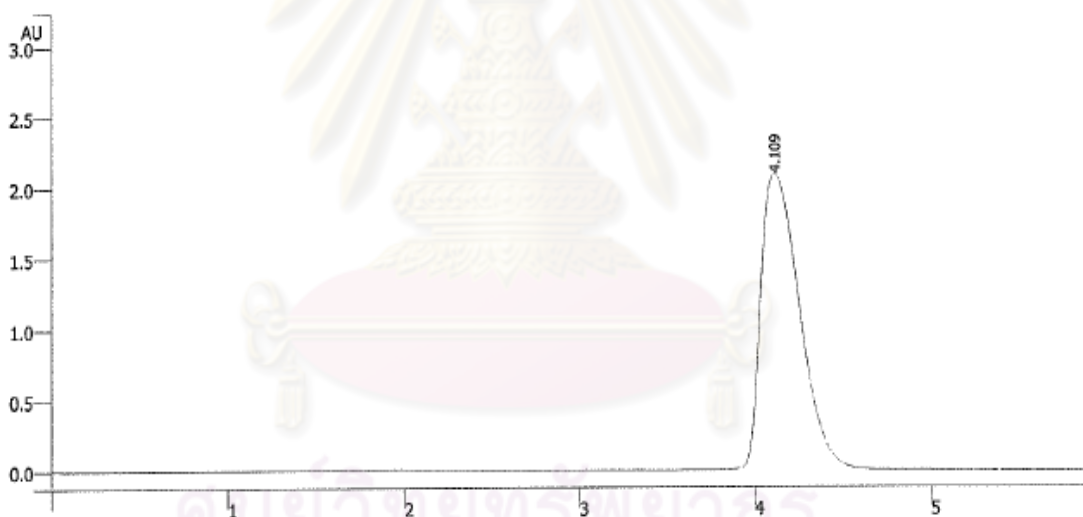


**Figure A14** HPLC chromatogram of 5-HMF solution at 1,000 ppm, 5 $\mu$ l,  
area 332,015,136 counts

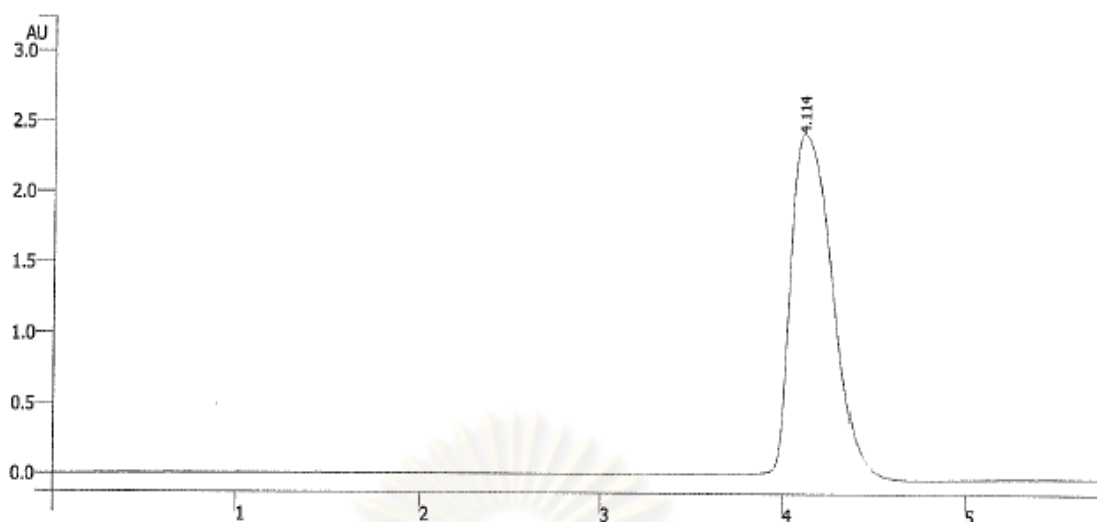




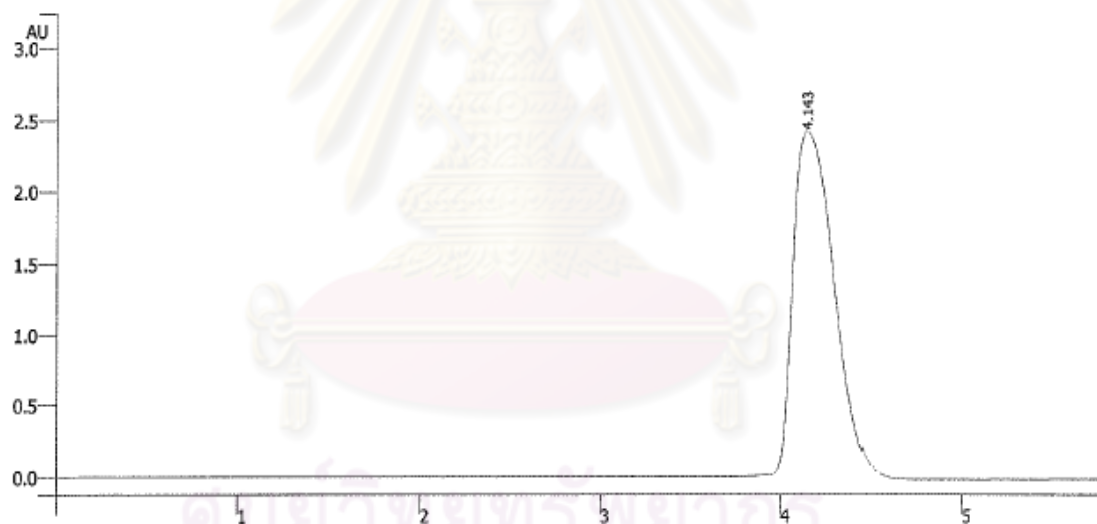
**Figure A15** HPLC chromatogram of 5-HMF solution at 1,400 ppm, 5 $\mu$ l,  
area 377,027,328 counts



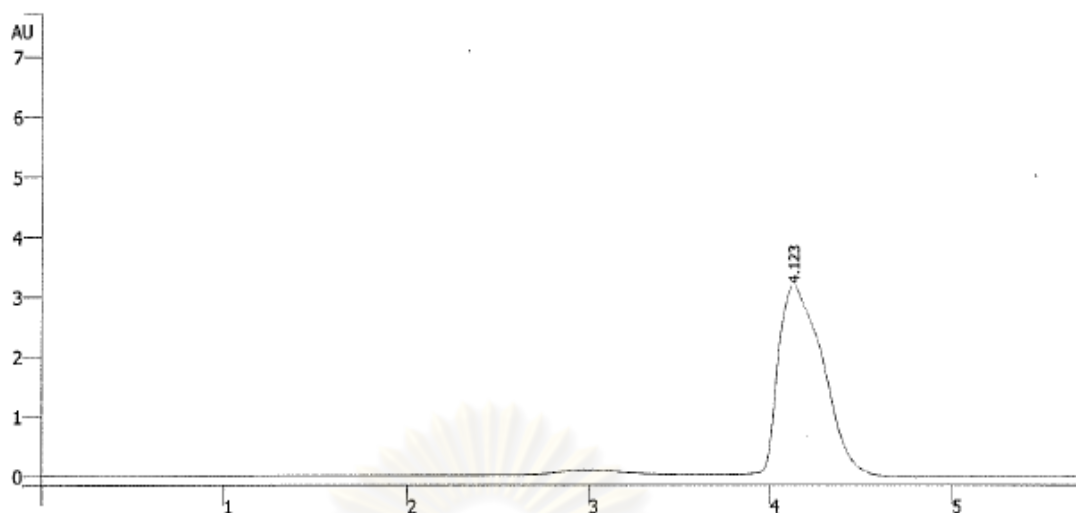
**Figure A16** HPLC chromatogram of 5-HMF solution at 1,400 ppm, 5 $\mu$ l,  
area 387,283,264 counts



**Figure A17** HPLC chromatogram of 5-HMF solution at 1,800 ppm, 5 $\mu$ l,  
area 390,223,744 counts



**Figure A18** HPLC chromatogram of 5-HMF solution at 1,800 ppm, 5 $\mu$ l,  
area 416,521,280 counts



**Figure A19** HPLC chromatogram of 5-HMF solution at 2,200 ppm, 5 $\mu$ l,  
area 537,328,488 counts



**Figure A20** HPLC chromatogram of 5-HMF solution at 2,200 ppm, 5 $\mu$ l,  
area 495,760,672 counts



**Figure A21** HPLC chromatogram of 5-HMF solution at 2,600 ppm, 5 $\mu$ l,  
area 761,128,448 counts



**Figure A22** HPLC chromatogram of 5-HMF solution at 2,600 ppm, 5 $\mu$ l,  
area 877,233,344 counts

## APPENDIX B

### USDA's method

#### Equipment:

1. Crucible
2. Shallow enamel pan
3. Suck dry
4. Oven
5. Cooling bath
6. Reflux set

#### Reagents:

1. *acid-detergent fiber* (1 L)

Sulfuric acid	49.04	g
Cetyl trimethylammonium bromide (CTAB)	20	g

Weigh sulfuric acid and make up to volume with distilled water at 20°C. Check normality by titration before addition of detergent. Then add CTAB and stir.

2. Decahydronaphthalene
3. Acetone
4. Hexane
5. *Saturated potassium permanganate* (1 L)

- Distilled water	1	L
- Potassium permanganate	50	g
- Silver sulfate	0.05	g

Dissolve potassium permanganate and silver sulfate in distilled water.

Keep out of direct sunlight.

6. *Lignin buffer solution*: (1 L)

- Ferric nitrate nanohydrate	6	g
- Silver nitrate	0.15	g
- Acetic acid	500	ml
- Potassium acetate	5	g

- Tertiary butyl alcohol                    400    ml
- Distilled water                            100    ml

Dissolve ferric nitrate nonahydrate and silver nitrate in distilled water. Combine with acetic acid and potassium acetate. Add tertiary butyl alcohol and mix.

7. **Combined permanganate solution** : (1 L)

Combine and mix *saturated potassium permanganate* and *lignin buffer* solution in the ratio of 2:1 by volume, before use. Unused mixed solution kept about a week in a refrigerator (purple).

8. **Demineralizing solution** (1 L)

- Oxalic acid dehydrate                    50    g
- Ethanol 95 %                                700   ml
- Hydrochloric acid                         50    ml
- Distilled water                              250   ml

Dissolve oxalic acid dehydrate in ethanol .Add concentrated hydrochloric acid and distilled water and mix.

9. **Ethanol 80 %**

- 95 % ethanol                                845   ml
- Distilled water                              155   ml

Step;

1. Dry sample at less than 65 °C. And grind through 20-30 mesh (1mm). Add *acid-detergent fiber* to 1 (g) samples in crucibles in a shallow enamel pan containing cold water 1 cm.

Acid-detergent fiber:

- 1) Weight 1 g air dry sample ground to pass 1 mm.
- 2) Add 100 ml acid detergent solution and 2 ml decahydronaphthalene. Heat to boiling in 5 to 10 minutes. Reflux 60 min.
- 3) Filter on a previous tare crucible and suck dry. Break up the filtered and wash twice with hot water (90-100 °C).

- 4) Repeat wash with acetone until remove no more color: break up all lumps.
  - 5) Optional wash with hexane. Suck dry the acid detergent fiber free of hexane. Dry overnight at 100 °C.
2. Add 25 ml of combined saturated potassium permanganate and Lignin buffer solution (*2:1 by volume*) to crucibles in the enamel pan containing cold water. Adjust level (2-3cm.) of water in pan. Stir contents to break lump and draw *permanganate solution* up on side of crucibles to wet all particles.
  3. Allow crucible to stand at 20-25 °C for 90-100 min. add more mixed *permanganate solution* if necessary. Purple color must be present at all time.
  4. Remove crucibles to filtering apparatus. Suck dry. Do not wash. Place in a clean enamel pan, and fill crucibles no more than half full with *Demineralizing solution*, maybe added directly to crucible. Care must be taken foaming.

After 5 min, suck dry on filter and refill half full with *Demineralizing solution*. Repeat after second interval of solution is very brown. Rinse side crucible with solution from a wash bottle with a fine stream. Treat until fiber is white (20-30 min).
  5. Fill and thoroughly wash crucible and contents with ethanol. Suck dry and repeat two times. Wash twice in similar manner with acetone. Suck dry.
  6. Dry at 100 °C overnight. And weigh. Calculate lignin content as loss weight from ADF.
  7. Ash at 500 °C for 3 hr, cool and weigh. Calculate residual ash as the difference between the weigh original tares of crucible. Calculate cellulose by weight loss upon ash.

## APPENDIX C

### CALCULATION OF PRESSURE CHANGE IN THE REACTOR UNDER SUBCRITICAL WATER CONDITION

Temperature – pressure table of water at subcritical water condition were exhibited in appendix C. The density of water under subcritical condition was calculated from amount of water added and volume of reactor by;

$$\rho_{T,P} = \frac{M}{V_{\text{reactor}}}$$

$\rho_{T,P}$  = density of water at each temperature ( $^{\circ}\text{C}$ ) and pressure (psia)

$M$  = amount of water added to reactor (g)

$V_{\text{reactor}}$  = volume of tubular reactor (ml)

In this work, the density of water was calculated from mentioned correlation, 0.364 g/ml, with 9 g of water added and 24.7 ml of reactor volume.



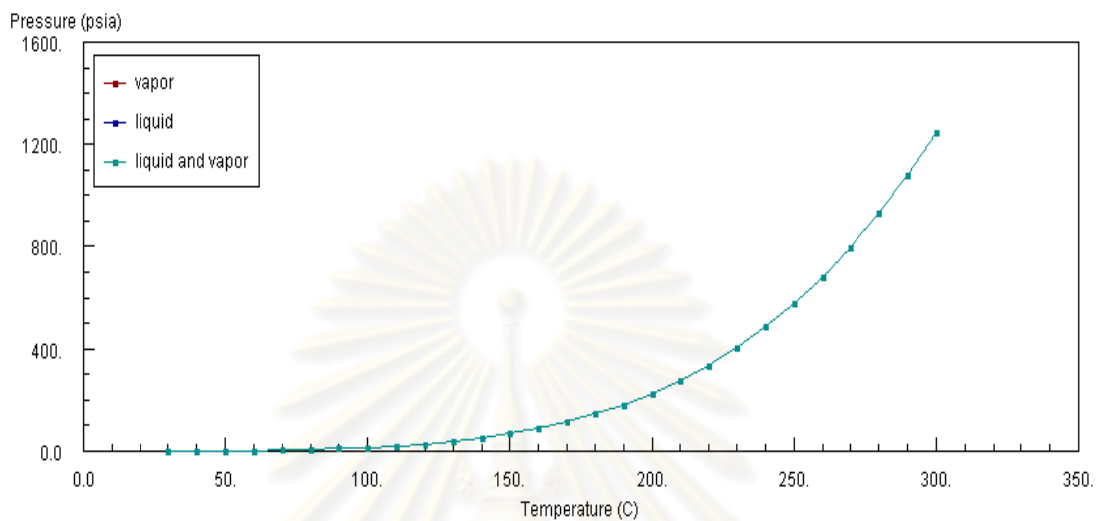
## APPENDIX D

**Table D1 Isochoric properties of pure water at D = 0.364 g/ml**

(NIST for thermo-physical properties of fluid systems calculation program:

<http://webbook.nist.gov/chemistry/fluid/>)

Temperature (°C)	Pressure (psia)	Internal Energy (kJ/mol)	Enthalpy (kJ/mol)	Entropy (J/mol*K)	Phase
30.00	0.615	2.267	2.267	7.876	liquid and vapor
40.00	1.071	3.021	3.022	10.32	liquid and vapor
50.00	1.791	3.777	3.777	12.699	liquid and vapor
60.00	2.893	4.533	4.534	15.005	liquid and vapor
70.00	4.525	5.292	5.294	17.250	liquid and vapor
80.00	6.876	6.054	6.056	19.437	liquid and vapor
90.00	10.179	6.819	6.822	21.573	liquid and vapor
100.00	14.709	7.588	7.593	23.663	liquid and vapor
110.00	20.795	8.362	8.369	25.710	liquid and vapor
120.00	28.815	9.142	9.152	27.720	liquid and vapor
130.00	39.201	9.930	9.943	29.697	liquid and vapor
140.00	52.437	10.725	10.743	31.645	liquid and vapor
150.00	69.062	11.529	11.553	33.569	liquid and vapor
160.00	89.667	12.344	12.374	35.470	liquid and vapor
170.00	114.90	13.169	13.209	37.355	liquid and vapor
180.00	145.45	14.007	14.057	39.225	liquid and vapor
190.00	182.06	14.859	14.922	41.084	liquid and vapor
200.00	225.52	15.726	15.803	42.935	liquid and vapor
210.00	276.68	16.608	16.704	44.781	liquid and vapor
220.00	336.43	17.508	17.625	46.625	liquid and vapor
230.00	405.68	18.427	18.567	48.470	liquid and vapor
240.00	485.43	19.366	19.534	50.318	liquid and vapor
250.00	576.70	20.327	20.526	52.172	liquid and vapor
260.00	680.55	21.311	21.546	54.035	liquid and vapor
270.00	798.14	22.320	22.595	55.909	liquid and vapor
280.00	930.65	23.355	23.676	57.799	liquid and vapor
290.00	1079.3	24.420	24.793	59.706	liquid and vapor
300.00	1245.6	25.517	25.947	61.637	liquid and vapor



**Figure D1** The correlation between temperature and pressure in the reactor

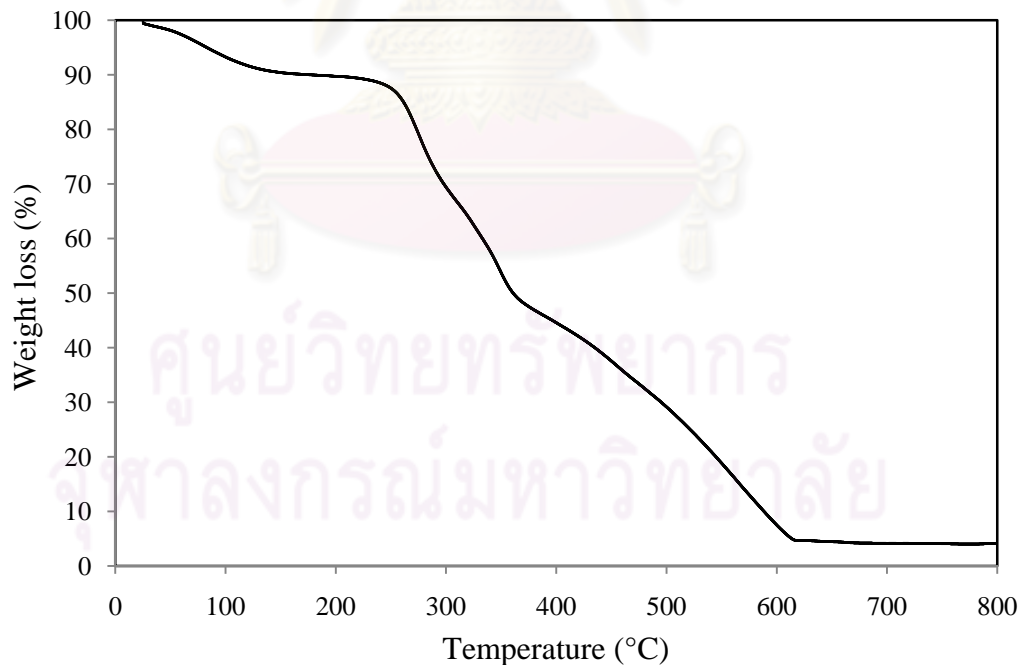
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## APPENDIX E

### Characterization of solid residues

#### The thermal behavior of raw material

Figure E1 shows the thermal behavior of raw palm kernel shell residues, which was analyzed by the Simultaneous Thermal Analyzer (STA; Netzsch, STA490C). It is clear that weight loss of palm kernel shell residues could be divided in to four steps, happened between 274 °C and 620 °C. Complete decomposition of palm kernel shell residues is observed above 620 °C. According to the thermo gram, it could be cleared that palm kernel shell residues structure decomposed in extensive temperature region because of the complicated structure comprised of glucose, hemicelluloses, lignin and ash.



**Figure E1** Thermo gravimetric (TG) analysis results of raw palm kernel shell residues

### Surface characteristic of solid residues

As shown in figure E2 , the scanning electron microscope (SEM-EDS; JEOL, JSM-5800LV) and transmission electron microscope (TEM; JEM-2100) illustrates the unprocessed and processed of palm kernel shell residues. For the unprocessed sample, the surface was dense and flat without any cracks. This would account for its poor or negligible BET surface area [47]. In contrast, for the processed one, it could be apparently seen that there were no lingo-cellulosic structures on the surface but many small cavities over the surface because of the surface were hydrolyzed by hot compressed water.





**Figure E2** SEM (A,B) and TEM (C,D) images of the surface sample

(A) and (C) raw palm kernel shell residues;  
(B) and (D) palm kernel shell residues after hydrothermal treatment process

### Identification of functional groups on surface of solid residues

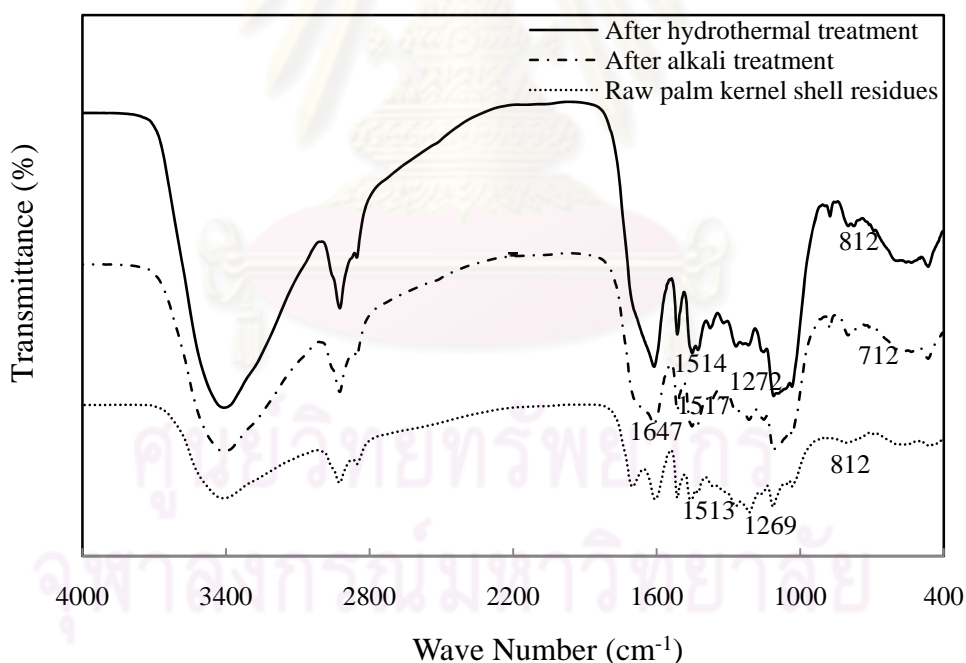
As shown in figure E3, the Fourier Transform Infrared spectra (FT-IR; Perkin Elmer, Spectrum One) of the raw palm kernel shell residues, the alkali pretreated of palm kernel shell residues and the palm kernel shell residues after hydrothermal treatment were displayed the following bands:

1647  $\text{cm}^{-1}$ : C=C stretching vibration in quinines;

1,513 – 1,517  $\text{cm}^{-1}$ : C=C stretching vibration in aromatic rings;

1,269 – 1,272  $\text{cm}^{-1}$ : C-O stretching vibration in ethers;

712 and 812  $\text{cm}^{-1}$ : C-H out-of-plane bending in benzene derivatives



**Figure E3** FT-IR spectra of the raw palm kernel shell residues, the alkali pretreated of palm kernel shell residues and the palm kernel shell residues after hydrothermal treatment

The major surface functional groups showed in the raw palm kernel shell residues were aromatic rings, the carbonyl groups such as ethers and benzene derivatives. After the alkali pretreatment, the surface displayed the functional groups of quinines, aromatic rings and benzene derivatives. For the palm kernel shell residues after hydrothermal treatment, the ketonic groups should be absent owing to their thermal degradation at high temperatures [47]. Anyway, the hydrothermal treated surfaces were composed of aromatic rings, ethers and benzene derivatives.



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## BIOGRAPHY

Mr. Pawit Tongrod was born in Bangkok, Thailand on 25 December 1986. He is the younger of the two children of Mr. Komol and Mrs. Pongtip Tongrod. He later moved to Nonthaburi province where he has lived until now with his family. He completed high school at Horwang School before accessing to Chulalongkorn University. At the University he completed a Bachelor of Science, majoring in Chemical Technology. After four years of study he gained admission to Graduate School of Chulalongkorn University. On 22-23 November 2010, he participated The 17<sup>th</sup> Regional Symposium on Chemical Engineering with the content of “Preparation of 5-hydroxymethylfurfural by hydrothermal treatment of palm kernel shell residues”. (CET 520), pp. 79. Eventually, in 2011, he graduated with the thesis entitled “Preparation of 5-HMF by hydrothermal treatment of palm kernel shell residues”.



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