SOLID ACID CATALYST PREPARED VIA ONE STEP HYDROTHERMAL CARBONIZATION FOR PRODUCTION OF 5-HYDROXYMETHYLFURFURAL IN BIPHASIC SYSTEM

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A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2018
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ตัวเร่งปฏิกิริยาของแข็งแบบกรดที่เตรียมโดยการไฮโดรเทอร์มอลคาร์บอไนเซชันแบบขั้นตอนเดียว
เพื่อการผลิต 5-ไฮดรอกซีเมทิลเฟอฟิวรอลในระบบสองวัฏภาค

น.ส.พรวิมล เสียบบำรุง

Thesis Title   SOLID ACID CATALYST PREPARED VIA ONE
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                      SYSTEM
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พรวิมล เสียบบำรุง : ตัวเร่งปฏิกิริยาของแข็งแบบกรดที่เตรียมโดยการไฮโดรเทอร์มอลคาร์บอไนเซชันแบบขั้นตอนเดียวเพื่อการผลิต 5-ไฮดรอกซีเมทิลเฟอฟิวรอลในระบบสองวัฏภาค. (SOLID ACID CATALYST PREPARED VIA ONE STEP HYDROTHERMAL CARBONIZATION FOR PRODUCTION OF 5-HYDROXYMETHYLFURFURAL IN BIPHASIC SYSTEM) อ.ที่ปรึกษาหลัก : ศ. ดร.อาทิวรรณ โชติพฤกษ์

5-ไฮดรอกซีเมทิลเฟอฟลูรอลเป็นหนึ่งสารตั้งต้นสำคัญสำหรับการผลิตสารเคมีที่มีมูลค่าสูง ผลิตจากสารชีวมวล มีแนวโน้มการค้นคว้าและงานวิจัยเพิ่มสูงขึ้นในปัจจุบัน ในงานวิจัยนี้การผลิต 5-ไฮดรอกซีเมทิลเฟอฟลูรอลจากปฏิกิริยาดีไฮเดรชั่นโดยตรงจากกลูโคลได้ถูกพิจารณาพร้อมกับการใช้ตัวเร่งปฏิกิริยาชนิดต่างๆ ที่เตรียมโดยวิธีการปรับปรุงวิธีการไฮโดรเทอมอลคาร์บอไนเซชันแบบขั้นตอนเดียว ตัวเร่งปฏิกิริยาชนิดกรดสองชนิดถูกติดหมู่ฟังก์ชั่นด้วยกรดไฮดรอกซีเอทิลซัลฟูริก และไฮโดรคลอริกมีชื่อว่า C-SO₃H และ C-HCl นอกจากนี้ตัวเร่งปฏิกิริยาทั้งสองชนิดยังถูกสังเคราะห์โดยการเติมกรดอะคริลิกลายเป็นตัวเร่งปฏิกิริยา C-SO₃H-A และ C-HCl-A การวิเคราะห์ลักษณะทางกายภาพของตัวเร่งปฏิกิริยาและการทดสอบกับปฏิกิริยาดีไฮเดรชั่นของกลูโคลถูกอธิบายด้วยเช่นกัน จากตัวเร่งปฏิกิริยาทั้งสี่พบว่า C-SO₃H ให้ผลการผลิต 5-ไฮดรอกซีเมทิลเฟอฟลูรอลสูงที่สุด ถึงแม้ว่าการเติมกรดอะคริลิกลงในตัวเร่งปฏิกิริยาจะทำให้เกิดการเพิ่มพื้นที่ผิวและค่าความเป็นกรด แต่ก็ไม่ส่งผลที่มีนัยสำคัญต่อการผลิต 5-ไฮดรอกซีเมทิลเฟอฟลูรอลเมื่อเปรียบเทียบกับตัวเร่งปฏิกิริยาที่ไม่ได้เติมกรดอะคริลิก ค่าการผลิต 5-ไฮดรอกซีเมทิลเฟอฟลูรอลสูงสุดอยู่ที่ 51.61 % ได้มาจากสภาวะอัตราส่วนน้ำต่อแกมม่าวาเลอโรแลคโทน 4:6 โดยปริมาตร ปริมาณตัวเร่งปฏิกิริยาที่ใช้ 0.5 % โดยน้ำหนักของกลูโคสที่อุณหภูมิ 180 องศาเซลเซียสเป็นเวลา 45 นาที ณ ที่สภาวะเดียวกัน ตัวเร่งปฏิกิริยาถูกทดสอบการนำกลับมาใช้ใหม่ พบบ่าสามารถนำกลับมาใช้ใหม่ได้อย่างน้อย 5 ครั้ง

สาขาวิชา	วิศวกรรมเคมี	ลายมือชื่อนิสิต ....
ปีการศึกษา	2561	ลายมือชื่อ อ.ที่ปรึกษาหลัก ....

5970393321 : MAJOR CHEMICAL ENGINEERING
KEYWOR
D:

Phornwimol Siabbamrung : SOLID ACID CATALYST PREPARED VIA ONE STEP HYDROTHERMAL CARBONIZATION FOR PRODUCTION OF 5-HYDROXYMETHYLFURFURAL IN BIPHASIC SYSTEM. Advisor: Prof. Artiwan Shotipruk, Ph.D.

As one of the most important precursor for various high-value chemicals, 5-hydroxymethylfurfural (HMF) is a biomass-derived compound that has gained increasing chemical research and industrial interests in recent years. In this study, production of HMF from direct dehydration of glucose was investigated with various types of catalysts prepared by a modified one-step HTC method. Two type of acids were employed for the functionalization of the catalyst, namely, 2-Hydroxyethylsulfonic acid ($C_2H_6O_4S$) and Hydrochloric acid (HCl), making C-SO$_3$H and C-HCl catalysts. Moreover, both of them were synthesized by adding acrylic acid to the C-SO$_3$H-A and C-HCl-A catalysts. Their physicochemical characteristics and catalytic activities on glucose dehydration were also examined. Of the four types of catalysts, C-SO$_3$ catalyst gave the highest HMF yield. Despite an increase in surface areas and total acidity, the catalysts with acrylic acid addition have decreased thermal stability based on TGA results and did not have significantly different effect HMF yield compared to those without acrylic acid. The highest HMF yield of 51.61% yield was obtained with 4:6 of water/GVL ratio, C-SO$_3$H catalyst loading 0.5 wt% of glucose at 180 °C for 45 min. At this condition, the catalyst was also found to be recyclable on glucose dehydration up to at least five uses.

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Field of Study:	Chemical Engineering	Student's Signature ....
Academic Year:	2018	Advisor's Signature ....

ACKNOWLEDGEMENTS

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CHAPTER I
INTRODUCTION

1.1 Motivation

Being a key platform chemical for the production of high valuable chemicals, 5-hydroxymethylfurfural (HMF) is one of the most important product derived from biomass, which has gained significant research interest, as evidenced by the increasing number of research papers (Mika et al., 2018) in recent years. It can be chemically converted to platform compounds, for example, dimethylfuran (DMF), levulinic acid (LA), and 5-ethoxymethyl furfural (EMF) (Gyngazova et al., 2017; Karwa et al., 2016; Kumari et al., 2018), which can be used as a precursor of biofuel, polymers, solvents and pharmaceuticals. Normally, HMF can be produced from cellulose which is the main component of biomass. However, the production of HMF gave low production yield because the complex structure of lignin blocks the accessibility and reactivity of cellulose. As a result, the pretreatment process was required to destroy the structure of lignin which can improve the HMF production (Kumar et al., 2009). Research attempts have been put forth to improve HMF yield by investigating the mechanism of conversion of monosaccharide such as fructose and glucose to HMF. Starting from fructose, outstanding HMF production of 98-99% is resulted. This is because the fructose structure is favorable for the conversion to HMF (Hu et al., 2016; Qu et al., 2012). However, since the content of fructose in non-edible biomass is low, compared with glucose, the cost of fructose is relatively high.

Glucose is a potential substrate for HMF production because of its availability, and thus lower cost compared with fructose (Sasaki et al., 2000). The conversion of glucose to HMF can be carried out via one of the two routes. In the first, a combination of Lewis acid and BrØnsted acid catalysts is used. The former catalyzes the isomerization of glucose to fructose, while the latter catalyze dehydration of fructose to produce HMF. The process can take place either in a monophasic system (Lu et al., 2016; Yang et al.,

2015) or a biphasic system (Chen et al., 2016; Gallo et al., 2013; Xu et al., 2016). This process is sometimes known as a one-pot reaction because isomerization and dehydration take place simultaneously. The Lewis acids commonly used to catalyze glucose isomerization include metal (III) chloride (e.g., $CrCl_2$, $SnCl_4$, $AlCl_3$, and $FeCl_3$) (Pagán-Torres et al., 2012; Wrigstedt et al., 2016), while the BrØnsted acids for the dehydration of fructose to HMF for example, include HCl, H_2SO_4, sulfonated carbon, and Amberlyst (Gallo et al., 2013; Xin et al., 2017). However, one disadvantage of this route is the requirements for Lewis acids and BrØnsted acids, and the determination of suitable ratio (L: B ratio), which is a controlling factor affecting the production of HMF and the byproducts. Another disadvantage would in the use hazardous chemicals such as metal chlorides (Yu et al., 2017).

In the second route, glucose is directly converted to HMF without generating fructose. This reaction route only requires use of a strong BrØnsted acid catalyst (e.g., HCl and H_2SO_4) (Robyt, 1998). This process as a catalyst which can be achieved either in monophasic system or a biphasic system. In a monophasic system, for example, water (Daorattanachai et al., 2012; De Souza et al., 2012), organic solvents (e.g., DMSO, THF and GVL) (Gallo et al., 2013; Qi, L. et al., 2014) or ionic liquid (e.g., liquid salts) (Binder & Raines, 2009), or combination of these have been used. The HMF yield obtained are generally because HMF can be easily converted to LA in an acidic system, since it is difficult to control the side reaction in such system (Qi, L. et al., 2014). The HMF production can also be carried out employing a biphasic system, using of a mixture of immiscible solvents (e.g., MIBK, DMSO and n-butanol) with water (Daengprasert et al., 2011). Alternatively, a biphasic system may be resulted from a mixture of miscible solvents (e.g., THF, SPB and GVL) and water (Gallo et al., 2013), with addition of salts. In biphasic systems, HMF production is improved as the solvents phase acts as an extractive phase, into which HMF is extracted, immediately after it is produced in the reactive phase (aqueous phase). The extraction of HMF into the organic solvent results

in the reduction of side reactions and the increase in HMF production by promoting the forward reaction in the aqueous phase (Saha & Abu-Omar, 2014).

The production of HMF from the direct dehydration of glucose is advantageous in that, typically, the strong BrØnsted acid catalysts has low - cost and the catalyst preparation is simple are Qi and co- workers reported the use of H_2SO_4 as a homogeneous catalyst for HMF production from glucose in water/GVL (Qi, L. et al., 2014). Moreover, use of homogeneous catalyst HCl was also showed in another study to give an outstanding HMF production in water/ GVL/ NaCl (Li et al. , 2017). Nevertheless, a high separation cost of homogeneous catalyst due to the dissolution of the catalyst and in the product and the corrosion of the reactor are among the major concerns. As a consequence, a great deal of research effort has been put into the development of heterogeneous catalysts to replace homogeneous catalysts. For example, Dowex (e.g., 50wx8-100) (Qi et al., 2008), Amberlyst (e.g., 15 and 30) (Gallo et al., 2013; Yue et al., 2014) and Sulfonated carbon (Daengprasert et al., 2011), are among the strong BrØnsted acid solid catalysts, shown to possess high acidity, that have been used in direct dehydration of glucose to HMF. Of the heterogeneous catalysts, sulfonated carbon is widely used in many reactions due to its high acidity, low production cost and environmental friendliness.

The preparation of carbon acid catalyst is generally divided into two steps. The first step involves the preparation of carbon support by carbonization or pyrolysis, which are the processes that require high temperature (<400 °C) and long reaction time (~15 h). Hydrothermal carbonization (HTC) was later developed, in which carbonaceous materials are carbonized in compressed water at much lower temperature (150-250 °C). Because wet biomass can be used as a raw material in this process without prior drying and the requirement of mild preparation conditions, HTC has become an interesting alternative for the synthesis of catalyst carbon support. The second step of the carbon-based catalyst preparation is acid functionalization of the carbon support by heating the support in presence of relatively large acid for several hours (~15 h). Major problems

with the two‑step method of the catalyst preparation are long preparation time and the need for the elimination of residual acid, which also generate large amount of wastewater. In addition, leaching of acid after use has often been found as another major problem with this preparation (Wataniyakul et al., 2018).

Alternatively, a one‑step method for the preparation of sulfonated HTC catalyst has been proposed (Qi et al., 2014), whereby carbonization and acid functionalization simultaneously take place. The catalyst prepared by this process has been shown to maintain outstanding catalytic activity, even after at least 5 uses. In later study, Nata and co‑workers (2015) proposed to improve the catalyst performance by adding acrylic acid into the carbonization/sulfonation system of the one‑step process. Their results suggested that the addition of acrylic acid generated new surfaces on the catalyst, thus increased the surface area, which led to improved product yield (Nata et al., 2015).

In biomass conversion, reactions (i.e., hydrolysis, dehydration, and etc.) are generally carried out under hydrothermal/solvothermal conditions, effective heating is a very important feature in the reaction system for this purpose. Microwave (MW) assisted heating has recently been widely investigated. The key advantage of MW assisted reaction is that MW supply direct heating at molecular level, which leads to signification reduction in reaction time. Moreover, it has been reported in previous research that MW irradiation was able to improve product yield and reduce side reactions (Saha & Abu‑Omar, 2014). In dehydration of carbohydrate, Wrigstedt et al. (2016) reported that high HMF yield was achieved in a short time (~min rather hr.) with MW assisted reaction. For catalyst preparation by in a MW reactor, Guiotoku et al. (2009) conducted HTC using MW assisted heating. The result showed that the C H N and O contents in the resulted hydrothermally carbonized carbon were similar to those prepared in a conventional reactor, while the carbonization time was much shorter with a MW reactor.

In this study, MW assisted heating was employed both in the catalyst preparation and the dehydration of glucose to HMF. The preparation of various sulfonated BrØnsted acids carbon- based catalysts were prepared by a one-step HTC synthesis method described by Nata et al. (2015). The effect of acrylic acid addition on the catalyst performance was also investigated. Furthermore, the effect of various reaction conditions was determined on the production of HMF from the direct dehydration of glucose in Water/ GVL/ NaCl system. Moreover, the reusability of catalyst was evaluated.

1.2 Objectives

1.2.1 To synthesize BrØnsted acid catalysts and evaluate their performance on HMF production from the direct conversion of glucose, in a biphasic system of water/GVL/NaCl

1.2.2 To determine the effects of various reaction conditions, including types of BrØnsted acids, reaction temperature, reaction time and the amount of catalyst on HMF yield, and to find the suitable reaction condition

1.2.3 To evaluate the reusability of the catalyst at a selected condition

1.3 Working Scopes

1.3.1 Four types of carbon-based solid acid catalysts (C-SO$_3$H, C-SO$_3$H-A, C-HCl and C-HCl-A) were synthesized from glucose via a modified one-step HTC and functionalization under microwave irradiation, with BrØnsted acids (HCl, C$_2$H$_6$O$_4$S), with and without the addition of acrylic acid. The catalysts were compared The activity of the catalysts on the direct dehydration for glucose was compared base on HMF production under a specified condition (0.3 g glucose, catalyst loading 1 wt% of glucose, NaCl 20 wt% of glucose and 10 ml of water/GVL (2:8 v/v) using microwave irradiation at 150 °C for 30 minute).

1.3.2 With the selected catalyst, determine the effects of temperature (120˚C, 140˚C, 160˚C and 180˚C), time (10, 20, 30, 40, 50 and 60 min) and amount of catalyst (0.05, 0.1, 0.5 and 1 wt% of glucose) base on HMF production. The suitable reaction condition was then proposed.

1.3.3 At a selected suitable reaction condition, the reusability of catalyst up to 5 uses was evaluated.

1.4 Expected benefits

The possibility of using solid BrØnsted acid carbon-based catalyst was evaluated for direct dehydration in order to produce HMF, a high value chemical from biomass. The suitable process condition was determined and the reusability of the catalyst was evaluated

CHAPTER II
BACKGROUND & LITERATURE REVIEWS

2.1 Biomass

Biomass includes all the living matter on earth derived from growing plant such as crops, trees, algae or animals manure. It is also composing of carbon and appears to be one of the best renewable solutions for substitution of fossil resource in many applications. Biomass has always been a major source of energy which can be used in energy application for the production of heat, power, and transportation fuel (Saxena et al., 2009). Cellulose, hemicellulose, and lignin are found to be the major of biomass which can be converted biofuel in many methods such as thermal, chemical and biochemical. In part of production from biomass, a lot of valuable chemicals such as 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) was converted by series of hydrolysis, dehydration and rehydration reaction which can be used as biofuel or precursor for many applications.

2.1.1 Cellulose

Cellulose has general formula $C_6H_{12}O_6$ containing linear chains of (1,4)-D-glucopyranose unit as a glucose polymer. The degree of polymerization of the native cellulose depends on the source and can reach more than 5000 (Collard et al., 2014). Cellulose is crystalline glucose polymer and accounts for 30-40% of biomass. It can be converted to monomeric sugar such as glucose, fructose, and xylose by chemical or enzymatic hydrolysis and can produce liquid fuels and high valuable chemical.

2.1.2 Hemicellulose

Hemicellulose is various polymerized monosaccharides which is a mixture of glucose, mannose, galactose, xylose, arabinose, 4-O-methyl glucuronic acid, and galacturonic acid residues (Dinesh et al., 2006). Hemicellulose is generally fraction about 15-30 wt% of biomass and is an amorphous polymer consisting of C5 and C6 sugar. The ratio of C5 and C6 sugar depends on the type of biomass. Hemicellulose is more reactive and exhibits lower molecular weights than cellulose, is easier to remove from biomass, and is typically associated with the production of xylitol, furfural and furfural derivative (Alonso et al., 2013).

2.1.3 Lignin

Lignin is an amorphous polymer rich in aromatic monomers. The proportions of the monomer unit are various and depend on many factors and the source of biomass. Lignin accounts for 15-30 wt% of biomass and is composed of three main precursors which are 5 p-coumaryl, coniferyl, and sinapyl alcohol (Alonso et al., 2013). Lignin also has the potential to be converted into fuels and high-value chemicals, but the complexity of its structure and the non-uniformity of its composition makes it more difficult to process than the other fractions.

2.2 Valuable chemicals from biomass

2.2.1 5-Hydroxymethylfurfural (HMF)

The number of public papers about HMF production tends to increase (Figure 2.1) due to its abundant to use as a precursor for many high-value products which can be used as a precursor of biofuel, polymers, solvents, and pharmaceuticals. HMF is an organic compound produced from dehydration of monomeric sugar under acidic conditions. The molecule consists of a furan ring, containing both aldehyde and alcohol functional groups. HMF is not stable in aqueous acid and will continue to react forming to LA or other byproducts. A number of synthetic technologies have been developed such as the additions of ionic liquid, reactive distillation, and solid acid catalyst. Those

technologies can remove the HMF before it reacts further or to otherwise promote its formation and inhibit its decomposition. HMF can convert to various platform compound for the synthetic of products which can replace fossil resource-derived fuel and high-value chemicals. As shown in Fig. 2.2, the product derived from HMF can be produced by various reactions such as oxidation reaction was used to convert HMF to 2,5-furandicarboxylic acid (FDCA) which has been proposed as a replacement for terephthalic acid in the production of polyesters. Moreover, it can be converted to 2,5-dimethylfuran (DMF), a liquid that is a potential biofuel with a greater energy content than bioethanol. Rehydration reaction coverts HMF to LA used as a precursor for pharmaceuticals, plasticizers, and various other additives.
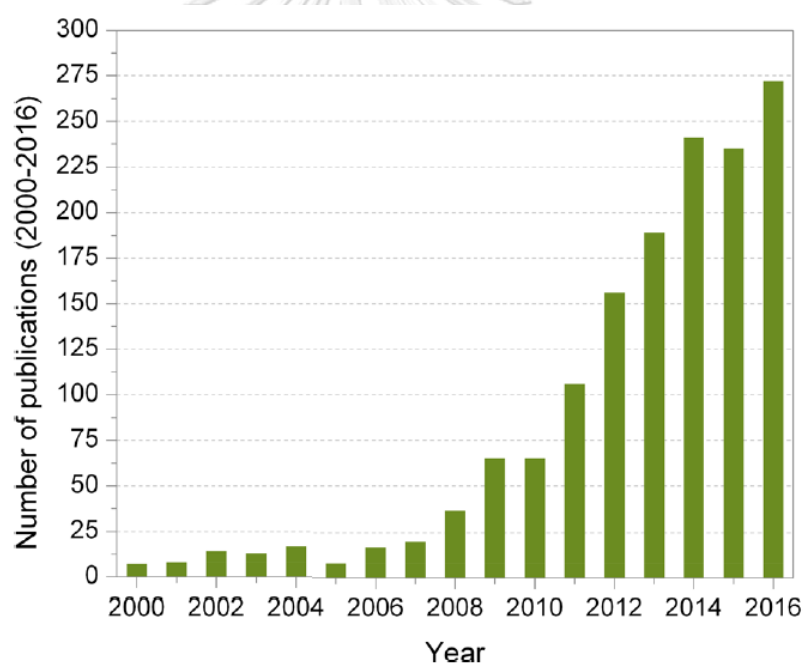
Figure 2.1 Number of publications on 5-HMF annually from January 2000 to

December 2016 (Mika et al., 2018)
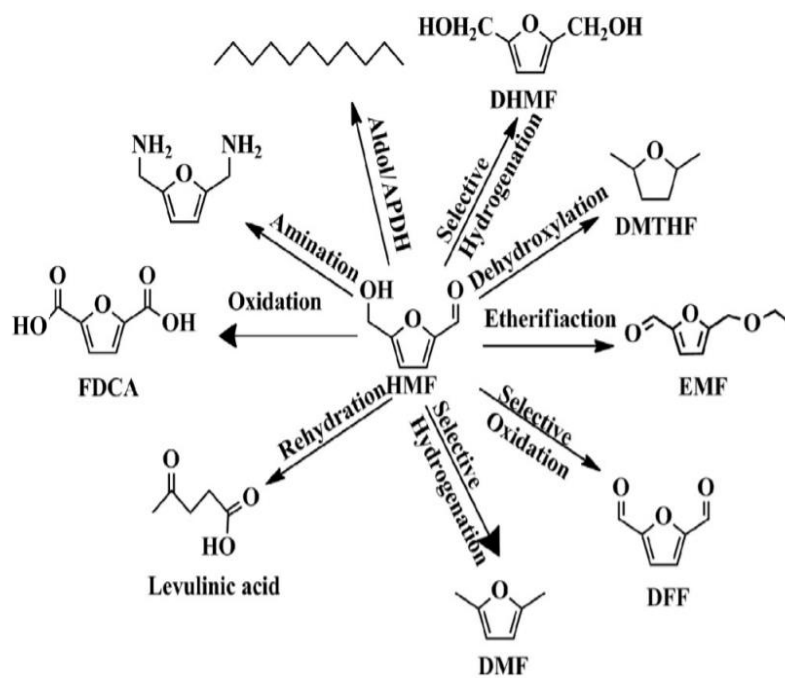
Figure 2.2 Catalytic conversion of HMF into various chemicals and liquid fuels.

(Xiao et al., 2014)

2.2.2 γ-valerolactone (GVL)

γ-valerolactone (GVL) is an organic compound which can be derived from biomass. GVL is cyclic of an ester with 4 carbon atoms and one oxygen atom in the
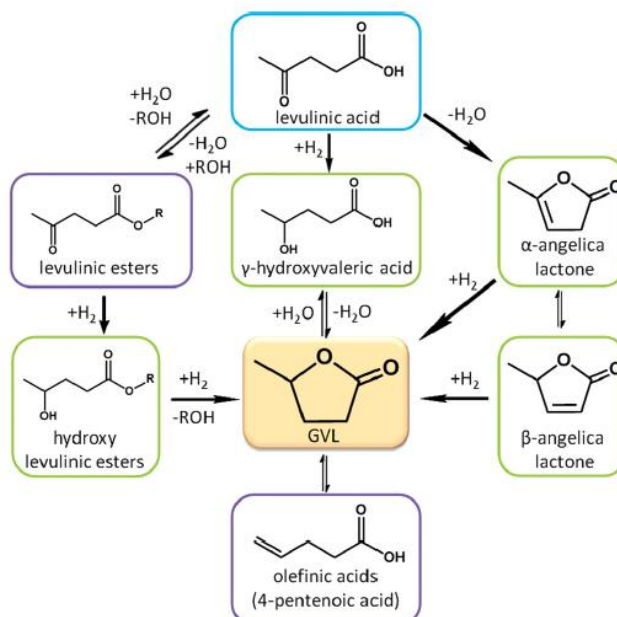
ring. The properties of GVL is suitable liquid solvent because it is miscible and does form an azeotrope with water, low vapor pressure and does not form hazardous peroxide under air. Owning to GVL properties, it can be considered as a sustainable liquid for production and energy. Moreover, GVL was claimed as a green solvent because it was renewable, non-toxic and biodegradable. As shown in Fig. 2.3, GVL can be produced from LA which is the product from HMF. The pathways to produce GVL was archived from many reactions such as produced from unstable γ-hydroxyvaleric acid which was hydrogenation from LA, hydrogenated from hydroxyl levulinic aster or β-angelica lactone. The application was popularly used as a solvent for production of HMF and LA which showed an outstanding production yield in the biphasic system. Moreover, it can blend with gasoline which was potential to compare with ethanol/gasoline (Alonso et al, 2013).

Figure 2.3 Reaction pathways to produce GVL

(Alonso et al., 2013)

2.2 HMF production pathway

The production of HMF from biomass can be achieved followed the cascade of reaction. It started with hydrolysis reaction of biomass promoted by BrØnsted acid as a catalyst which brakes the boning of cellulose to glucose. The conversion of glucose to HMF can be divided into two routes which can start with isomerization to fructose followed by dehydration to HMF. The isomerization uses BrØnsted base or Lewis acids to catalyst while the dehydration promoted by BrØnsted acids as a catalyst. The second route of glucose conversion is direct dehydration to HMF served by strong BrØnsted acids. Moreover, HMF can be converted to LA by rehydration catalyzed by BrØnsted acids as shown in Fig. 2.4. However, the production yield of HMF depended on the substrate as well as other factors such as types of catalyst, reaction medium, temperature and time.

```
Cellulose  --Hydrolysis-->  Glucose  --Isomerization-->  Fructose
             BrØnsted acids            BrØnsted bases
                                       or Lewis acids
```

Cellulose — **Hydrolysis** BrØnsted acids → Glucose — **Isomerization** BrØnsted bases or Lewis acids → Fructose

Glucose — **Dehydralysis** BrØnsted acids → 5-hydroxymethylfurfural (HMF)

Levulinic acid (LA) ← **Rehydration** BrØnsted acids — 5-hydroxymethylfurfural (HMF)
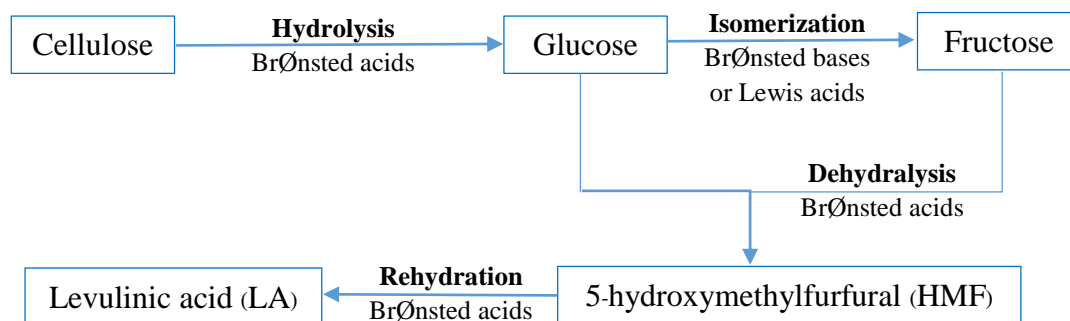
Figure 2.4 Pathways of biomass conversion to HMF

2.3.1 Using biomass as a substrate

There are many types of biomass substrate which can convert to HMF, for example, bread waste, corncob, corn stover, sugarcane bagasse, grass, vegetable waste and so on which can follow the reaction cascade to produce HMF. Each type of biomass showed the different production yield which caused by the cellulose composition inside biomass. As shown in Table 2.1. The cellulose percentage from corn stover, grass, and food west showed at 28-51 %, 45 %, and 25.6□26.8%, respectively. The cellulose percentage tended to relate with HMF yield, for examples, Yang and coworkers reported that the conversion of corn stover and grass for HMF production. The processes were achieved in water/THM/NaCl catalyzed by $AlCl_3 \cdot 6H_2O$ at 180 °C for 30 minutes. The results showed the HMF yield of 19 mol% from corn stover and 23 mol% from grass (Yang et al, 2012). Moreover, HMF production from bread waste reported by Yu and coworkers (Yu et al., 2017). A system of DMSO/water was used as a reaction medium served by $SnCl_4$ as a catalyst at 160 °C for 20 minutes. The results gave 21.4 mol% of HMF yield. As a previous study, the larger cellulose percentage tended to produce a large amount of HMF. However, the biomass conversion still showed low HMF production. The factor affected to biomass conversion need to consider for improving HMF production such as the mechanism of monosaccharide (glucose and fructose), reaction medium, catalyst, temperature and reaction time. Moreover, the pretreatment process was the one solution which was required for destroying lignin structure because

the complex structure of lignin affected on hydrolysis of cellulose. The pretreatment process can increase the accessibility and reactivity of cellulose for breaking to mono and di-saccharide (Raspolli Galletti and Anotonetti, 2011; Parveen Kumar et al, 2009).

Table 2.1 Composition of common biomass

Biomass	Cellulose	Hemicellulose	Lignin	reference
corn stover	28□51	28□31	11□14	(Demirbaş, 2010; Han, 1998)
corncob	41□52	32□36	6□15	(Han, 1998)
sugarcane bagasse	34□36	29□43	19□21	(Nassar, 1999)
food waste	25.6□26.8	22.1□30.4	42.9□52.3	(Demirbaş, 2010)
grass	45.0	31.4	12.0	(Jørgensen et al, 2007)
Hardwood	40-55	20-40	18-25	Raspolli Galletti and Anotonetti, 2011
Softwood	45-50	25-35	25-35	
Newspaper	40-55	25-40	15-30	

*wt% on dry biomass

2.3.2 Using fructose as a substrate

For improving HMF production, the studying mechanism of monosaccharide was required to find the affecting factor. Fructose, the component isomerized from glucose was a favor to study the mechanism for HMF production because the fructose structure is similar to HMF structure and it showed the lower activation energy (Ea = 29.4 kcal/mol) more than glucose (Ea = 35 kcal/mol) (Enslow et al, 2015). Moreover, the fructose conversion showed an outstanding for HMF production as shown in Table 2.2. The conversion of fructose to HMF with various solvents and catalyst gave the high percentage of HMF caused by the structure of fructose easily convert to HMF. For example, the using of H_2SO_4 as a catalyst in DMSO for fructose conversion gave the

HMF yield of 80% mol at 120 ° C for 2 h (Akien et al., 2012). Moreover, the results of the DMSO/water mixture showed the outstanding HMF yield with H_3PO_4 Si-OH used as a catalyst at 80 ° C for 6 h (Tsutsumi et al., 2014). The pathway of fructose conversion shown in Fig. 2.3, the cyclic of fructose start with D-fructofuranose form which was dehydrated at the C-2 position to tertiary carbenium cation form and turn to 3,4 DIOL. The dehydration of 3,4 DIOL converts to carbaldehyde-5 which ready to hydrate to HMF. However, the production of fructose required the hydrolysis of biomass followed by isomerization of glucose which caused the high substrate cost. The using another monosaccharide was the choice to improve the process in term of substrate cost and challenge the development of HMF production.

Table 2.2 Conversion of fructose to HMF

Fructose conc	Solvent	Catalyst	Temp (° C)	Time (min)	Yield (mol%)	reference
11 wt%	DMSO	0.5 M H_2SO_4	120	120	80	(Akien et al., 2012)
10.5 wt%	DMSO	2.6 wt% Amberlyst-15	120	60	83	(Sampath et al., 2013)
5 wt%	DMSO	1 mol% HCl	90	120	88	(Huang et al., 2014)
0.3 wt%	DMSO/water	31 wt% H_3PO_4 Si-OH	80	300	97	(Tsutsumi et al., 2014)
10 wt%	THF/water	HCl	160	60	76	(Guihua et al., 2015)
2 wt%	GVL/water	3.3 wt% amberlyst	130	9	71	(Gallo et al., 2013)
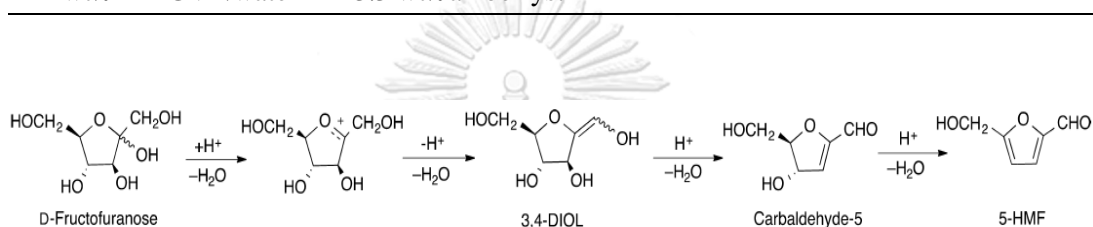
Figure 2.3 The cyclic pathway of Dehydration of fructose to HMF

(László et al., 2018)

2.3.3 Using glucose as a substrate

Glucose is the potential substrate to produce HMF. It showed a higher conversion from biomass when compared with fructose. Nevertheless, glucose showed the lower HMF production than fructose because of the structure evidenced from activation energy. The study of the effective factor from glucose was required such as reaction medium, types of catalysts, temperature and time for improving HMF yield. Normally, the glucose conversion to HMF can be divided into two groups followed by typed of the catalyst. The first is the combination of Lewis acids and BrØnsted acids which served the isomerization and dehydration at the same time. This process can call a one-pot reaction. The second way is the direct dehydration glucose to HMF bypassing generation of fructose which required only strong Br☐nsted acids as a catalyst.

2.4 Glucose conversion to HMF

2.4.1 Combination of Lewis acids and BrØnsted acids

The glucose conversion with the combined catalysts can generate the isomerization and dehydration at the same time. The isomerization was promoted by Lewis acids such as $CrCl_2$, $SnCl_4$, $AlCl_3$, and $FeCl_3$ (Pagán-Torres et al., 2012; Wrigstedt et al., 2016) to convert glucose to fructose followed by dehydration fructose to HMF served by Br□nsted acids such as HCl, H_2SO_4, Sulfonated carbon and Amberlyst (Gallo et al., 2013; Xin et al., 2017). As shown in Table 2.3, the conversion of glucose to HMF with the combination of catalyst gave the moderate HMF yield when compared with fructose (Table 2.2) because it affected from many factors such as the combining solvent, Lewis acid/BrØnsted acids ratio (L: B ratio), temperature and pressure. Nevertheless, some studies got the high yield around 86 mol% from glucose conversion with TiO_2-ZrO_2 and Amberlyst-70 used as a catalyst in THF/water at 175 °C for 3 h (Atanda et al., 2015), and 87 mol% in MeTHF/NMP/water when $ACl_3 \cdot H2O$ and HCl were served as a catalyst at 170 °C for 45 minutes (Atanda et al., 2016). As a result, it caused by other factors such as reaction medium, temperature and reaction time which can promote HMF production. However, the using of combined catalyst required many steps to prepare catalyst and it was dangerous in term of the type of Lewis acids. The metal chlorides affected to a human body (Yu et al., 2017). The using of combination catalyst need to concern the previous problems.

Table 2.3 Conversion of glucose to HMF using the combination of Lewis acids and BrØnsted acids

Glucose conc	Solvent	Catalyst		T (°C)	Time (min)	Yield (mol%)	reference
		Lewis â	Br□nsted â				
5 wt%	SPB/NaCl	AlCl₃	HCl	170	40	62	(Pagán-Torres et al., 2012)
5 wt%	SPB/NaCl	VCl₃	HCl	170	90	49	
5 wt%	GVL/water	Sn-□	Amberlyst-70	130	20	58	(Gallo et al., 2013)
5 wt%	THF/water	Sn-□	Amberlyst-70	130	30	63	
2 wt%	THF/water	TiO₂-ZrO₂	Amberlyst-70	175	180	86	(Atanda et al., 2015)
9 wt%	MeTHF/NMP/water	ACl₃·H₂O	HCl	170	45	87	(Atanda et al., 2016)

2.4.2 Using strong BrØnsted acids

The using strong Br□nsted acids as a catalyst is the second way for the conversion of glucose to HMF. These catalysts can directly convert glucose to HMF bypassing the generation of fructose (Robyt et al., 1998). As shown in Fig 2.4, the formation of carbocation at the C-2 position was opened-chain glucose which formed a tetrahydro-3,4-dihydroxy-5-(hydroxymethyl)–2–furan aldehyde intermediate when reacting with the hydroxyl group of glucose at C-5 position followed by removing water from intermediate to form HMF. Although the direct conversion of glucose can be achieved by strong Br□nsted acids. But, it showed the low HMF production, for examples, Daorattanachai and coworkers reported that the conversion of glucose in water gave 9 mol % of HMF yield catalyzed by H3PO4 (Daorattanachai et al., 2012). Some cases reported the result from other reaction media such as water mixed with the solvent such as the mixing of water/GVL promoted by H₂SO₄ as a catalyst gave 13% mol of HMF (Qi et al., 2014) as shown in Table 2.4. As a result, the low HMF

production caused from its structure which showed the high activation energy (Ea = 36.4 kcal/mol) from direct dehydration of glucose when compared with fructose dehydration (Ea = 29.4 kcal/mol). For improving

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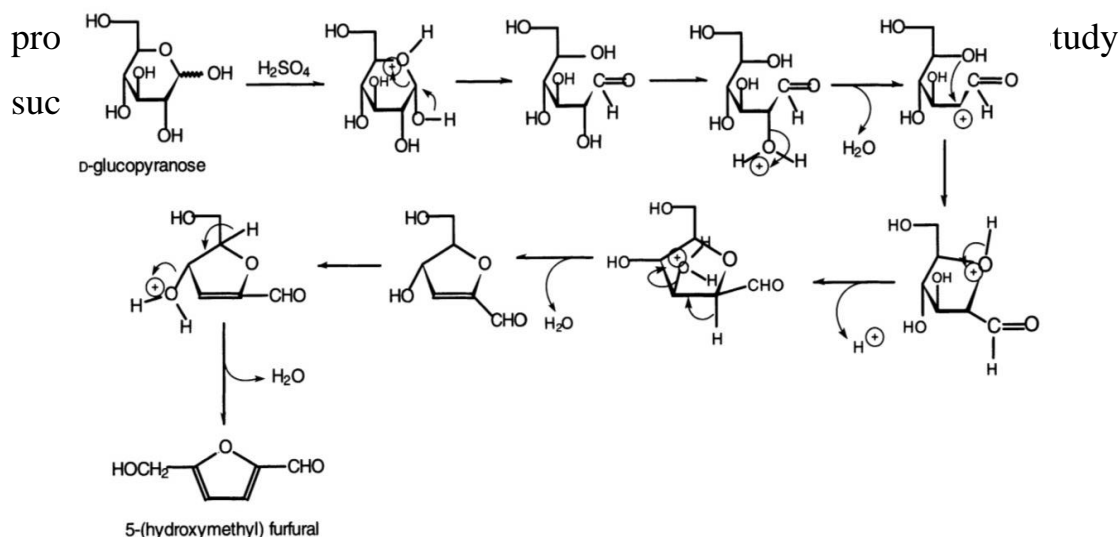
Figure 2.4 Reaction scheme for Brønsted acids catlazed dehydration of glucose to

HMF (Robyt et al, 1998)

Table 2.4. Conversion of glucose to HMF

Solvent	Glucose conc	Catalyst	T (°C)	Time (min)	Yield (mol%)	reference
water	9 wt%	0.1 M H_3PO_4	200	5	9	(Daorattanachai et al., 2012)
GVL/water	2 mM	7.5 mM H_2SO_4	130	60	13	(Qi et al., 2014)
THF/water	2 wt%	6.6 wt% Amberlyst-70	130	50	23	(Gallo et al, 2013)
GHL/water	2 wt%	6.6 wt% Amberlyst-70	130	30	26	
GVL/water	2 wt%	6.6 wt% Amberlyst-70	130	30	29	

2.5 Reaction medium for HMF production

As a problem of low HMF production from glucose, the reaction medium is one of factor affected to HMF production. As shown in Table 2.4, the using of solvent mixed

with water gave the different result yield. The percentage of yield showed 23, 26, 32 mol% of HMF from mixing of THF, GHL, and GVL with water, respectively. In addition, the reaction medium can group from phase system into two groups which are a monophasic and biphasic system.

2.5.1 Monophasic system

The phase consists of one solvent or two miscible solvents which will generate only one phase in system such as water, solvents (e.g. DMSO, MIBK, THF, Acetone, DMC, THL, GVL), miscible solvents (e.g. DMSO/water, THF/water, GVL/water, THL/water) and ionic liquid. The effect of solvent (e.g. DMSO, THF, MeCN, GVL, Acetone, and DMC) to HMF production at the same condition showed in Fig 2.4. All of the solvents are an organic solvent which can dissolve in water as a monophasic system. The results showed different HMF production. The highest HMF selectivity was presented with DMSO and the lowest of HMF selectivity was showed with DME. As a result, each solvent showed the different effect which can be considered for choosing the suitable solvent for HMF production. For Ionic liquid (IL), salts in liquid state showed an outstanding of HMF production such as 88 mol% of HMF yield was achieved in [BMIM][H2SO4] system served by SSBA as a catalyst at 120 °C for 90 min (Walia et al., 2014) and 85 mol% from [BMIM][Cl] promoted by CrCl3 reacted at 80 °C for 2.5 min (E. A. Khokhlova et al., 2013). However, ILs are expensive and required the high separation cost from the product which was not suitable to commercial scale.
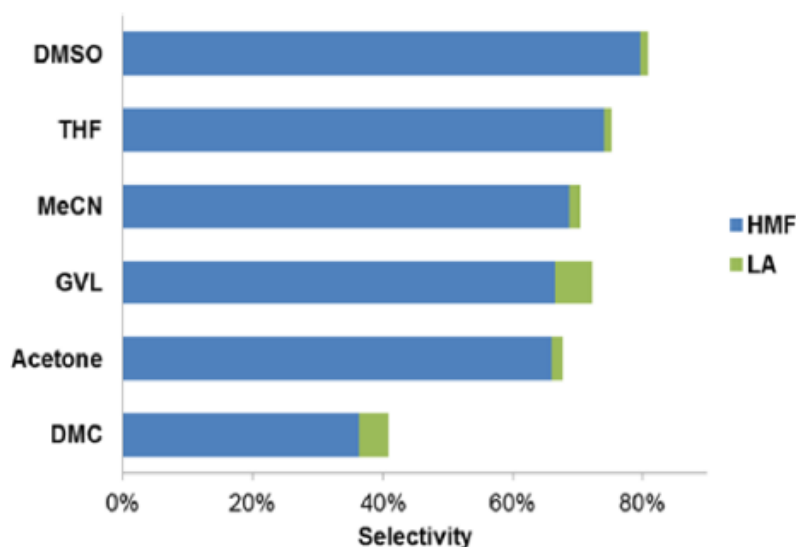
Figure 2.4 Complete conversion of fructose to HMF and LA by microwave heating of a mixture of 1.88 g (10.4 mmol) of fructose, 1.67 mL of 0.5 mol/L HCl, and 10 mL of solvent at 130 °C for10 min (Qi et al., 2014)

2.5.2 Biphasic system

The phase showed two liquid layers generated from two immiscible solvents or adding salt into a monophasic system. The upper layer will play as an extractive phase to extract product from a lower layer which acted as a reactive phase. For HMF production, the extraction product from reactive phase can improve product yield because the lack of product in the system will shift the reaction and the presence of HMF in solvent phase was not suitable to generate the side reaction. The performance of solvents depends on the partition coefficient (R) which referred the ratio HMF in the solvent phase to HMF in an aqueous phase. the higher R of solvents showed the effective extraction which can increase HMF yield. In term of adding salts, some cases tried to add salts for the separation phase by the effect of electrolyte celled salting-out effect (Saha et al, 2014). The molecular bonding between solvents is altered which decreased the solubility of an aqueous phase and a reactive phase. Saha and coworkers reported that the effect of adding salts to R-value presented in Fig. 2.5 (Saha et al., 2014). The addition of NaCl into each solvent for HMF production can increase R-value shown

in the black bar because of salting-out effect. In addition, the selectivity of HMF seems to depend on R values which can conclude that the HMF yield increased when R-value increased.
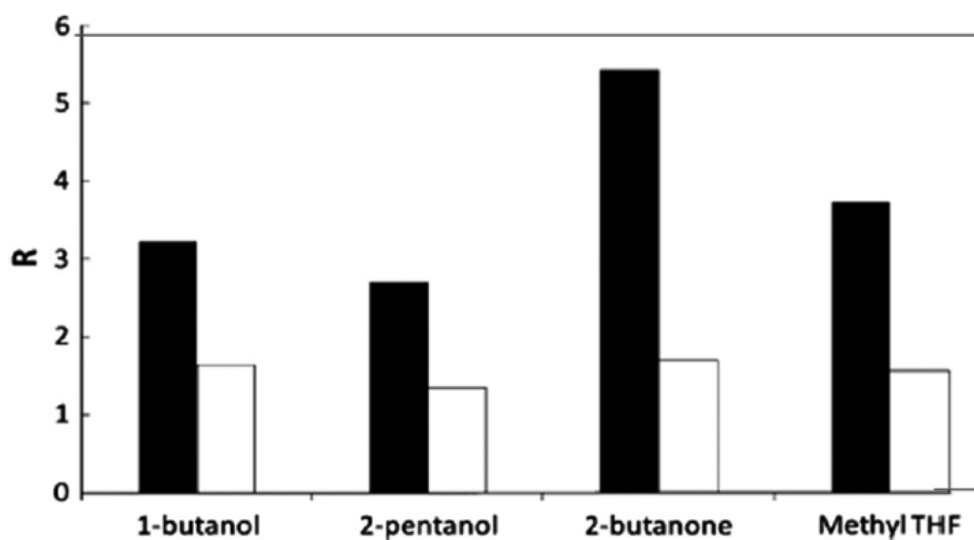
Figure 2.5 Effect of NaCl on the partition coefficient R of HMF extraction in representative biphasic systems. Black bars correspond to systems saturated with NaCl, while white bars represent systems without NaCl

Among the solvent used in a biphasic system, γ- Valerolactone (GVL) is the organic solvent derived from biomass. It was claimed as a green solvent due to non-toxic, biodegradable and renewable (Alonso et al., 2013). Moreover, it is popularly used for HMF production because of an outstanding HMF yield and high R-value when used GVL as a solvent in a biphasic system. As shown in Table 2.5, the comparison of each solvent used as a biphasic system for HMF production. the NaCl was added to the solution for generating of two-phase. The reaction occurred at 170 °C promoted by AlCl3 and HCl as a catalyst. As a result, GVL presented the high HMF selectivity (70 %) and HMF in the organic solvent layer (94%) (Gallo et al., 2013). Other research supported this result which reported by Li and coworkers (Li et al., 2017). They reported the glucose conversion used water/ GVL and various salts for investigating HMF production as shown in Table 2.5.

Table 2.5 Conversion of glucose to HMF in a biphasic system

Solvent	Time (min)	Glucose conversion (%)	HMF Selectivity (%)	HMF Yield (%)	% HMF in organic layer
GVL	40	88	70	61.6	94
GHL	40	88	65	57.2	92
GOL	40	89	65	57.8	92
GUL	40	92	54	49.7	83
THF	-	80	71	56.8	93
SBP	40	91	68	61.9	97

Reaction condition: 1.5 g of NaCl-saturated aqueous feed, 5 wt% glucose, 5 mM/L AlCl$_3$, 3.17 mmol/L HCl and 3 g of organic solvent at 170 °C (Gallo et al., 2013).

Other researches supported the effect of a biphasic system when used water/GVL and salt as a reaction medium. Li and coworkers reported that the glucose conversion used water/GVL and various salts for investigating HMF production as shown in Table 2.6 (Li et al., 2017). The production of HMF and LA depended on types of salts. The high HMF yield of 58.97 and 59.06 molar% promoted by HCl as a catalyst were achieved with KCl and NaCl, respectively. As a result, the effect from both salts was not a significant difference. Thus, the NaCl was considered to use due to the low price and easy purchase.

Table 2.6 The performance of different acid and salts combination on the HMF yield

Entry	Catalyst	Salts	HMF yield (molar %)	LA yield (molar %)
1	0.2 M HCl	0.1 M Na$_2$SO$_4$	49.28	16.23
2	0.2 M HCl	0.2 M NaCl	58.97	21.36
3	0.2 M HCl	0.2 M KCl	59.06	16.16
4	0.2 M HCl	0.1 M K$_2$SO$_4$	32.48	14.60
5	0.2 M HCl	0.1 M NaNO$_3$	1.95	10.16
6	0.2 M HCl	0.1 M LiCl	45.40	14.78
7	0.2 M HCl	0.1 M MgSO$_4$	12.78	34.58
8	0.1 M H$_2$SO$_4$	0.2 M NaCl	48.56	17.56

9	0.1 M H_2SO_4	0.1 M Na_2SO_4	48.20	14.91
10	0.1 M H_2SO_4	0.1 M K_2SO_4	29.39	14.03
11	0.1 M H_2SO_4	0.2 M KCl	48.49	18.20
12	0.1 M H_2SO_4	0.1 M $NaNO_3$	3.20	32.17
13	0.1 M HNO_3	0.1 M Na_2SO_4	0.62	33.21
14	0.1 M HNO_3	0.1 M NaCl	2.20	17.01

Reaction condition: 1.5 g glucose, 10 mL H_2O, 40 ml GVL at 150 °C for 60 min

According to all of the literature review about reaction medium, the using of GVL/water/NaCl as a biphasic system tend to be used for the improvement of glucose conversion to HMF because this system showed an outstanding result. Moreover, each material was a good combination such as green solvent (e.g. GVL, water) and easy to purchase.

2.6 Solid Brønsted acids

Previously, the direct dehydration of glucose to HMF required strong Brønsted acids as catalyst supported from results of reaction medium which shown High HMF production when used HCl and H2SO4 in water/GVL/NaCl (Li et al., 2017). However, the using of strong Brønsted acids as a homogeneous catalyst need to concern the drawback. The mixing of strong solid with the crude product required insensitive energy to separation. Moreover, the strong acid was corrosive to the reactor which reduced the lifetime. To avoid the drawbacks, the replacement of homogeneous catalyst by heterogeneous catalyst has been interesting due to non-corrosiveness and easily to separation. However, there is many factors of the heterogeneous catalyst such as acidity, surface area, pore size and pore volume which played an important role in HMF production. For HMF production, the type of heterogeneous was favored such as commercial catalyst (Dowex 50wx8-100, Amberlyst-15,70) (Qi et al., 2008; Gallo et al., 2013) and carbon supported. Nowadays, many research is focusing to use the biomass materials and green process which are environmentally friendly. The development of

carbon supported was interested in heterogeneous filed. It can be prepared from biomass and used in many reactions such as esterification, hydrolysis, and dehydration.

2.6.1 Catalyst preparation

Carbon supported was called the catalyst used carbon source to prepared carbon support but the complete preparation of carbon acid catalyst was divided into two-step which is the preparing carbon supported and functionalization of carbon supported. Firstly, the carbon supported was prepared from carbon sources such as biomass (e.g., wood, corn cob, rice brane), cellulose and glucose. The pyrolysis and carbonization process was used to convert carbon source, but those process required high temperature. Thus, the hydrothermal carbonization (HTC) was developed for carbonizing carbon source as a carbon support because this process required low temperature ($T < 250$ °C). Moreover, this process has more advantages such as simple preparation, low operating cost and use water as a reaction medium. Secondly, the carbon supports were functionalized with a large amount of acid at a high temperature for a long time (~15 h). Nevertheless, both steps of synthesizing carbon acid catalyst should be concerned about the elimination of acid and the long operation time. Moreover, the problem of leaching acid was also papered when the catalysts were reused (Wataniyakul et al., 2018).

2.6.2 One-step Hydrothermal Carbonization (one-step HTC)

One-step HTC, in which carbonization and functionalization take place at the same time, is one process developed for synthesizing carbon acid catalyst. In addition, some studies claimed that the catalysts prepared by this method showed an outstanding recyclability and required a small amount of acid. For example, Qi and coworkers reported that the solid acid catalyst prepared by the one-step method for cellulose hydrolysis at 130 °C and 120 min which showed the reusability of catalyst at least 5 times as shown in Fig. 2.6 (Qi et al., 2014).
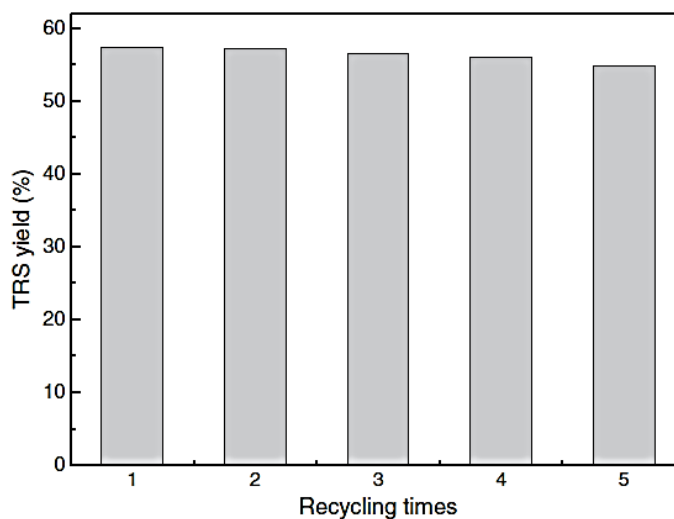
Figure 2.6 Recycle of the CM-SO$_3$H catalyst for cellulose hydrolysis in ionic liquid.

Reaction conditions: cellulose 0.05 g, [BMIM][Cl] 1 g, CM-SO$_3$H 0.05 g,

130 °C, 120 min.

For the one-step method, some studies tried to improve the performance of catalyst by adding acrylic acid which reported by Nata and workers (Nata et al, 2015). The catalyst was various as 4 type as shown in Fig. 2.7 which presented the glucose solution (C1), glucose solution with acrylic acid (C2), glucose solution with hydroxyethylsulfonic acid (C3-SO$_3$H) and glucose solution with hydroxyethylsulfonic acid and acrylic acid (C4-SO$_3$H). As a result, the catalyst with adding acrylic acid can generate the new surface noticed from the roughness of catalyst surface as shown in the result from FESEM (Fig.2.8b and 2.8d). The C3-SO$_3$H and C4-SO$_3$H were evaluated on hydrolysis starch as shown in Fig 2.9. A highest of total reducing sugar showed with C4-SO$_3$H referred to the addition of acrylic acid at 150°C for 6 hours. As a result, the addition of the acrylic acid can improve the performance of catalyst and increase the production yield. Moreover, the recovered of C3-SO$_3$H and C4-SO$_3$H were tested on hydrolysis of starch at 150°C for 3 hours. Before using next time, the both of catalyst was washed with 3000 ml of warm DI water and collected by centrifugation. Both catalysts showed at least 5 times for reusability of the catalyst.
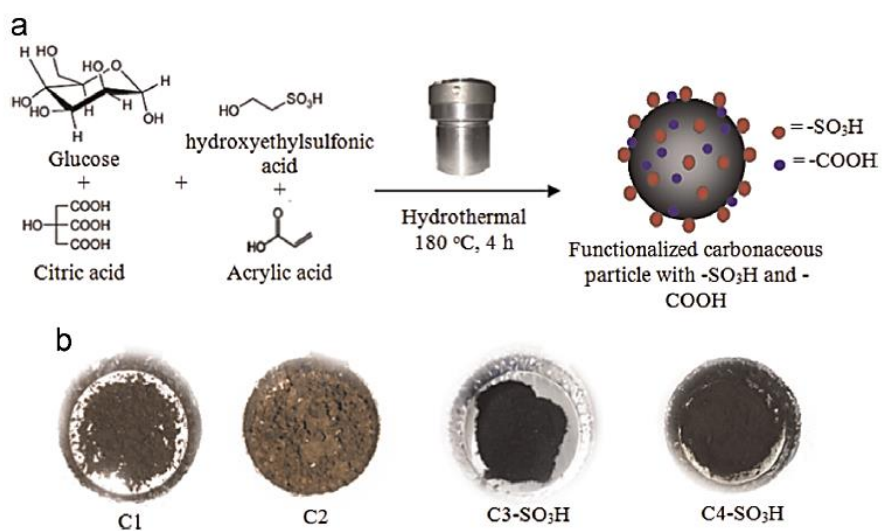
Figure 2.7 (a) Preparation of solid acid catalyst by one step hydrothermal carbonization and (b) product of carbonaceous materials for C1, C2, C3-SO$_3$H and C4-SO$_3$H
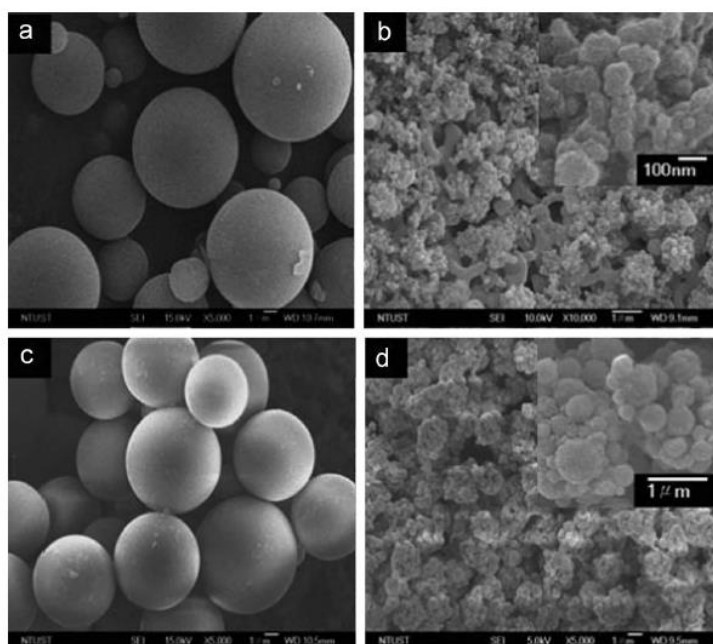
Figure 2.8 FESEM micrograph of carbonaceous particle produced by hydrothermal carbonization of (a) glucose solution (C1), (b) glucose solution with acrylic acid (C2), (c) glucose solution and sulfonic group (C3-SO_3H), and (d) glucose solution with sulfonic acid and acrylic acid (C4-SO_3H).
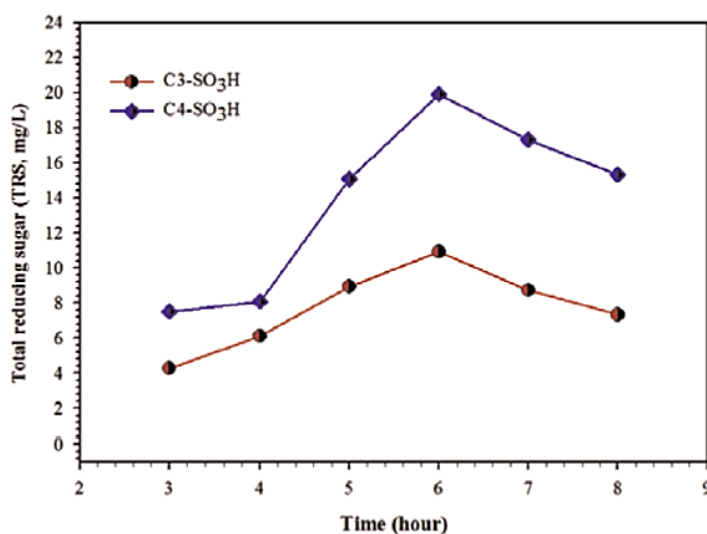
Figure 2.9 Total reducing sugar (TRS) for starch hydrolysis by C3-SO_3H and C4-SO_3H in the variation of reaction time. **Reaction condition**: 0.8 g starch, 0.4 g C3-SO_3H and 40 mL DI water at 150 °C. (Nata et al, 2015)

2.7 Microwave Reactor

In term of the reactor, the conventional heating is the general heating reactor such as salt bath, oil bath, aluminum heating block, and autoclave but those reactors were easy to lose heat caused the system opened to surrounding, and transferred by conduction affected the long reaction time which causes the high energy consumption. The development of microwave (MW) reactor for solving problems was interested in heating because it was direct heating into molecular which used the shorten reaction time from hour to minute. Moreover, some research claimed the MW assisted heating can improve production yield (Yu et al., 2017). However, the MW reactor required to use the absorbing materials such as polar solvents and some system needs to consider

the reaction temperature because the material at critical temperature will become microwave-transparent (Yu et al, 2017) which was the limitation of the reactor. MW reactor was used in many reactions such as HMF production and the preparation of carbon-supported.

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2.7.1 HMF production using MW reactor

The production of HMF in subcritical water using a microwave reactor showed a high yield of 47 mol% and 30 mol% from fructose and glucose, respectively (Möller et al., 2012). This process was uncatalyzed decomposition of fructose and glucose which achieved at 250 °C for 10 min. In addition, the HMF production from fructose was reached to 85 mol% when the using solvents and salt as a biphasic system showed in Table 2.7. As a result, the highest HMF yield was 85% showed with KBr and MeCN at 160 °C for 1 min. However, the fructose conversion in water/GVL/NaCl also showed an outstanding of 79 % HMF yield using the microwave heating. Thus, the combination of water/GVL/NaCl and MW reactor provide a good result of HMF production.

Table 2.7 The influence of alkali metal salts and organic solvents in the microwave-assisted aqueous biphasic fructose dehydration to HMF[a]

Entry	Salt[b]	Organic phase	Conversion (%)	Yield (%)
1[c]	KBr	MeCN	1	<1
2	NaBr	MeCN	>99	82
3	KBr	MeCN	>99	85
4	NaCl	MeCN	98	77
5	KCl	MeCN	97	78
6	NaI	MeCN	94	68
7	KI	MeCN	96	67
8	KF	MeCN	99	—
9	KBr	GVL[d]	>99	84
10	NaCl	GVL	96	79
11	KBr	THF	95	76
12	NaCl	THF	83	68
13	KBr	DMF	11	6
14	KBr	i-PrOH	n.d[e]	73
15	KBr	2-BuOH	79	61
16	KBr	MIBK/2-BuOH	98	74
17[f]	KBr	MeCN	96	79

[a] **Reaction conditions**: ~10 wt% fructose in (0.1 M HCl–salt) $_{(aq)}$–solvent 1:2 v/v, MW 160 °C, 1 min. [b] Saturated solution. [c] Without HCl. [d] GVL = □-valerolactone. [e] Fructose and i-PrOH peak overlapped (HPLC). [f] with 5 mol% $CrCl_3 \cdot 6H_2O$ (Wrigstedt et al., 2016)

2.7.2 Preparation carbon supported

Guiotoku et al. (2009) used the microwave in the HTC process for biomass conversion. They reported that the C, H, N and O percentage and atomic ratio from pine sawdust and cellulose presented with various temperature. However, the result was not significantly different when the reaction time was operated more than 60 minutes at 200 °C as shown in Table 2.8. Thus, the preparation of carbon-supported from biomass using MW assisted heating can reduce the reaction time when compared with convention reactor.

Table 2.8 Elemental analysis for pine sawdust and α-cellulose at different times of MAHC and α-cellulose charcoal

Time (min)	C (wt.%)	H (wt.%)	N (wt.%)	O^a (wt.%)	Atomic ratio	
					H/C	O/C
Pine sawdust						
0	45.45 ± 0.06	6.22 ± 0.09	0.02 ± 0.01	48.31 ± 0.16	1.16	0.79
60	60.01 ± 0.15	5.51 ± 0.00	0.02 ± 0.00	34.46 ± 0.16	1.10	0.43
120	64.74 ± 0.15	5.29 ± 0.18	0.04 ± 0.01	29.93 ± 0.35	0.98	0.35
240	63.54 ± 0.12	5.19 ± 0.10	0.71 ± 0.01	30.56 ± 0.20	0.98	0.36
α-cellulose						
0	40.5 ± 0.15	6.43 ± 0.02	0.09 ± 0.06	52.98 ± 0.11	1.90	0.97
60	63.11 ± 0.08	4.74 ± 0.007	0.26 ± 0.05	31.89 ± 0.13	0.90	0.38
120	63.63 ± 0.00	4.64 ± 0.03	0.06 ± 0.02	31.67 ± 0.06	0.87	0.37
240	63.75 ± 0.09	4.50 ± 0.04	0.46 ± 0.01	31.29 ± 0.10	0.85	0.37
α-cel charcoal	91.08 ± 0.12	1.33 ± 0.05	0	7.59 ± 0.08	0.17	0.06

[a] The oxygen content was determined by difference [100%□(C%+H%+N %)].

The finding of the ways for improving HMF production from glucose required to consider the effect factors such as reaction medium, reactor, and catalyst. According to literature review about reaction medium, the system of GVL/water/NaCl tends to give the good result of HMF production due to the properties of GVL and the increased extraction phase by adding salt. Moreover, the using microwave assisted heating tends to reduce the reaction time for catalyst preparation and have potential to improve HMF production for dehydration reaction.

CHAPTER III
MATERIALS AND METHODS

3.1 Materials and Chemicals

D‑Glucose, 2‑Hydroxyethylsulfonic acid ($C_2H_6O_4S$, 98%), Hydrochloric acid (HCl, 37%), Acrylic acid ($C_3H_4O_2$, 98%) and sodium hydroxide (NaOH), used for the synthesis of carbon catalyst, were purchased from Wako Pure Chemical company (Osaka, Japan. Chemicals used in dehydration reaction; γ-valerolactone (GVL, 98%), d-glucose and sodium chloride (NaCl), were purchased from Tokyo Chemical Industry (Tokyo, Japan), and Wako Pure Chemical company (Osaka, Japan). Standard chemicals used for HPLC analysis: d‑glucose, fructose, 5‑hydroxymethylfufural (HMF, 99%), levulinic acid (LA, 99%), Furfural (FFR, 99%) were purchased from Wako Pure Chemical company (Osaka, Japan).

3.2 Microwave reactor

The schematic of MARS6 microwave assisted reactor system (CEM Matthews NC Company, USA) used in this study is shown in Fig.3.1. The microwave reactor has two main parts: the body and the vessels. The turntable installation can house up to 12 vessels, one of which is temperature and pressure control vessel, which was connected with connector port for a pressure sensor and a fiber optic thermocouple. In operating the system, pairs of vessels (2,4,6 or 12) are generally used to ensure that the sample in each vessel, was uniformly irradiated. The operational limits of the systems are the ramp time (0-60 minutes), hold time (0-60 minutes), temperature (0-300 °C), pressure (0-800 psi), power (0-1800 watt) and stirring options (on or off).

MW Reactor

Load Disk

Screw

Nut, plug
Ferrule

Support
Module

Control Cover
P&T Control

Nut
Thermowell

Liner

Thermowell,
Sapphire

Sleeve
Composite

**Temperature and Pressure
Control Vessel**

Vessels

Display

Temperature and
Pressure

Connector Port

Door Seal

Turntable
installation

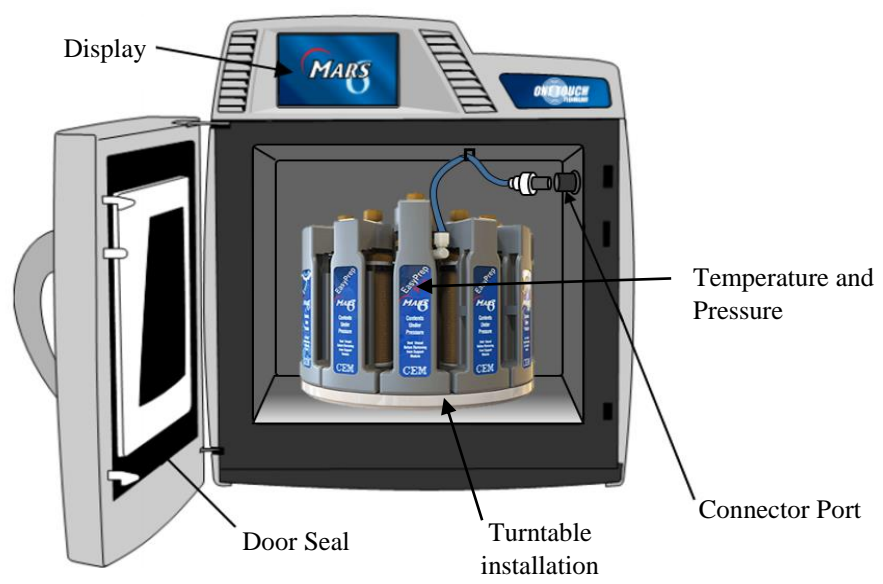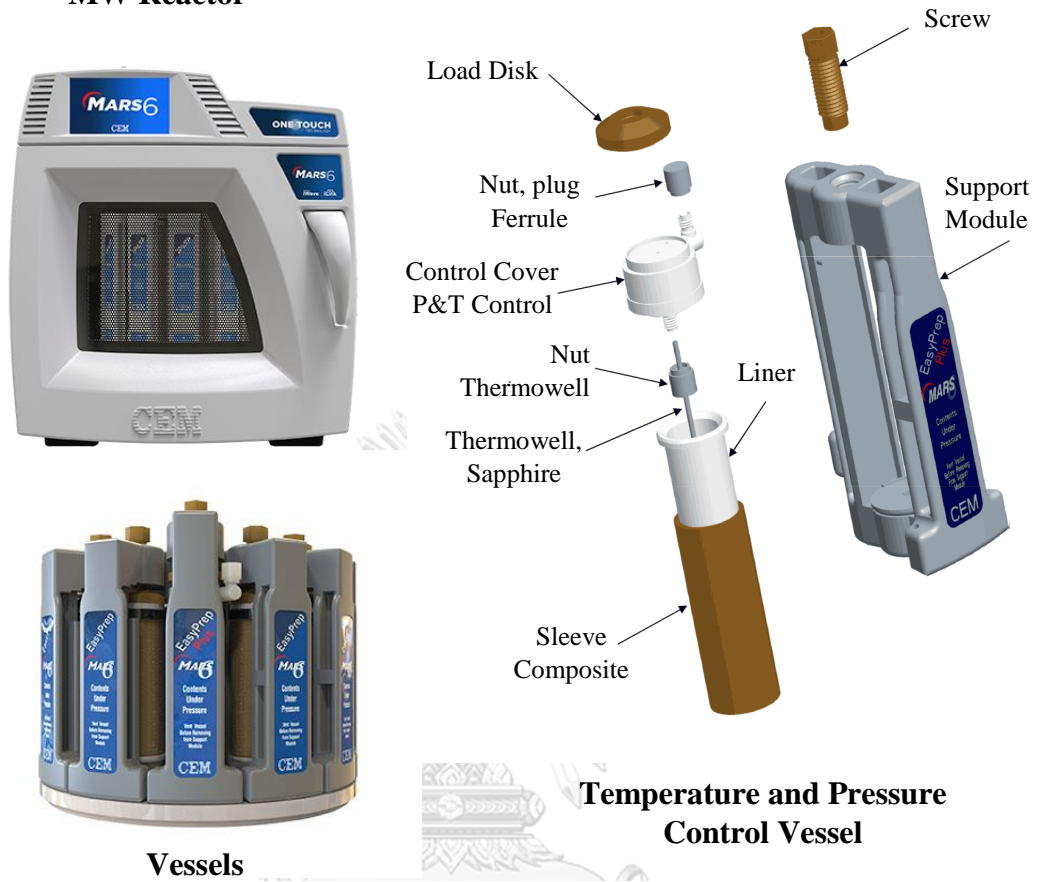Figure 3.1 Microwave Assisted Reactor system (MARS6)

(www.CEM.com)

3.3 Carbon acid catalyst preparation

Schematically shown in Fig. 3.2, solid acid catalyst was prepared by modified one-step hydrothermal carbonization, modified from the method described by Nata et al. (2015) by applying MW heating instead of conventional heating. First, glucose (10 g), acids (5 g) and deionized (DI) water (80 ml) were placed in 100 ml Teflon vessel and heated at 200℃ for 1 hour with ramp time 15 minutes by MARS6 reactor. Two types of functionalization acids were investigated: 2-Hydroxyethylsulfonic acid and Hydrochloric acid. Moreover, the effect of the addition of acrylic acid to the catalyst was studied. Without acrylic acid, the catalyst prepared with each acid. 2-Hydroxyethylsulfonic acid was named C-SO₃H, and that prepared hydrochloric acid was named C-HCl. The catalysts containing acrylic acid were prepared by adding to the 10% v/v of acrylic acid into the Teflon reactor vessel. The prepared, 2-Hydroxyethylsulfonic acid and Acrylic acid was called C-SO₃H-A, and the hydrochloric acid and acrylic acid was called C-HCl-A. After the reaction was completed, the resulting solid was recovered using a filter paper, and washed with hot DI water until the pH around 6-7. The resulting catalyst was dried in an oven at 110℃ overnight. The dried catalyst was sieved and kept in a desiccator unit use.
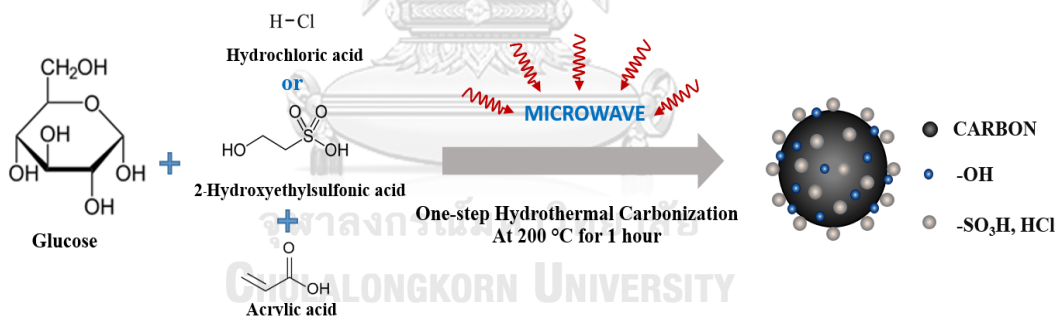
Figure 3.2 Solid acid catalyst was prepared by modified one-step hydrothermal carbonization, modified from the method described by Nata et al. (2015) by applying MW heating

3.4 Catalyst characterization

3.4.1 Total Acidity

The total acidity of the four types of catalysts were measured by determining the BrØnsted acid sites on the surface of the catalysts using a titration method. Firstly, the solution of sodium hydroxide (0.01 M, 20 ml) was mixed with the catalysts (0.04 g), under constant stirring at room temperature for 2 hours. After separation of the solid by filtration, the solution was titrated by hydrochloric acid (0.001M).

3.4.2 Elemental compositions

the elemental compositions (C, O, S and Cl) of the catalysts were analyzed by Scanning electron microscopy and Energy Dispersive X-ray (SEM-EDS, JSM-6380LV).

3.4.3 Surface area and surface morphologies

The Brunauer-Emmett-Teller (BET) method was used to analyze surface area of the catalysts using an automated chemisorption/physisorption surface area (BELSORP-minill-S, MicrotracBEL) at 77K and estimated using N_2 adsorption. The surface morphologies were characterized by a scanning electron microscope (SEM, JSM-6380LV).

3.4.4 Fourier transform infrared (FTIR)

The function groups on the catalysts were confirmed by using Fourier transform infrared (FT-IR, Nicolet 6700)

3.4.4 Thermal gravimetric analysis (TGA)

The thermal stability was investigated by using a thermal gravimetric analysis (TGA, Shimadzu DTG-60, Shimadzu, Japan) with a ramping rate of 10 ˚C/min and nitrogen flow rate of 50 ml/min.

3.5 Catalyst activity tested on dehydration reaction for HMF production

The activity of all catalysts was evaluated based on dehydration of glucose for HMF production. In a typical experiment, glucose, sodium chloride, water, GVL, carbon acid catalysts charged into 100 ml Teflon vessels. Microwave irradiation was applied to the reactor mixture using the MW reactor at the prescribed conditions with the ramp time 15 minutes, in which the reaction medium was heated from room temperature to the set temperature. After a specified period of hold time, the reaction was completed, the solution was cooled by a cooling system in microwave reactor. The catalyst was removed from the reaction medium by filtration, prior to the HPLC analysis of the reaction product.

3.5.1 Effect of temperature

The mixture of 0.3 g glucose, 10 ml of water/GVL (2:8 v/v) solution, NaCl 20 wt% of glucose and catalyst loading 0.1 wt% of glucose were loaded into a 100 ml Teflon vessel. The reaction was heated to the specified temperature of 120 °C, 150 °C, 180 °C or 210 ° C for 30 minutes in a microwave reactor. The reaction temperature resulted in the highest HMF yield was selected for the study on the effect of reaction time in the subsequent experiment.

3.5.2 Effect of reaction time

For the determination of the effect of reaction time, 0.3 g glucose, 10 ml of water/GVL (2:8 v/v) solution, NaCl 20 wt% of glucose and catalyst loading 0.1 wt% of glucose were loaded into a 100 ml Teflon vessels. The reaction mixture was heated with microwave, for a specified hold time of 0 to 60 minutes. The reaction time giving the highest HMF yield was selected for the subsequent study to determine the effect of catalyst loading.

3.5.3 Effect of catalyst loading

The effect of catalyst loading was investigated at the suitable condition selected based on the preceding experiments. Into the 100 ml Teflon vessel, 0.3 g glucose, 10 ml

of water/GVL (2:8 v/v) solution and NaCl 20 wt% of glucose were charged and heated under microwave irradiation. The effect of various catalyst loading (0.5, 1, 2.5 and 5 wt% of glucose) were determined. The most suitable loading was selected for the subsequent study to determine the effect of water/GVL ratio.

3.5.4 Effect of water/GVL ratio

The effect of the ratio of water/GVL ratio was determined. Various water/GVL ratios of 0:10, 2:8, 4:6, 6:4, 8:2 and 10:0 v/v were studied for the dehydration of .3 g glucose and NaCl 20 wt% of glucose at the selected suitable catalyst loading, temperature and time.

3.5.5 Reusability of catalyst

The suitable condition was selected to study the reusability of catalyst. After each run, the catalyst was filtered, washed by 50 ml Hexane, followed by 30 ml acetone and dried in an oven at 110 ˚C overnight, and then used in the subsequent run at an identical condition

3.6 Analytical methods

The concentration reaction products were analyzed using high performance liquid chromatograph (HPLC, JASCO International Co., Ltd., Japan). Shodex Sugar column (SH1011) was used to detect compounds at 60 °C with refractive index detector (Jasco, RI-2031 plus) and ultraviolet detector (Jasco, UV-970). The sample was filtered using a 0.45 µL syringe filter before the injection into the system. The injection volume of sample was set at 10 µL. The solution of $HClO_4$ (3 mM) was used as a mobile phase at a flow rate 0.5 ml/min. The quantities of HMF was detected using UV-970 detector at 220 nm. The retention time of HMF is 37.3 minute. The calibration curve was used for the quantification of product. The HMF yield was defined as follows:

$$\text{HMF yield (\%)} = \frac{\text{Moles of HMF product}}{\text{Moles of starting Glucose}} \times 100$$

3.7 Statistical Analysis

      The statistic calculation was studied for choosing the parameters. The proving of static calculation showed significant difference of data which can choose for investigating next step. Actually, there are many stat test but we have to choose the relating test of our data. In this study, the Fisher's Least Significant Difference (LSD) test was chose to calculation which used to compare the smallest significant difference between two different mean. However, LSD required the data from statistic calculation. The confidence interval was set at 90% ($\square = 0.1$).

CHAPTER IV
RESULTS AND DISCUSSIONS

Normally, the preparation of carbon-based acid catalyst required two-steps which is carbonization of carbon source to produce carbon supported and functionalization of the carbon support with acid. This two-step method; however, has some drawbacks in that a large amount of acid and long reaction time are required. Moreover, the problem with acid leaching is often seen (Wataniyakul et al, 2018a). The one-step HTC catalyst was employed in which carbonization and acid functionalization took place simultaneously. The method was modified from that described in Nata et al. (2015) by applying MW heating instead of the conventional heating. In this chapter, the results on the characteristics of the synthesized sulfonated carbon-based HTC catalysts and the evaluation of the catalyst on dehydration of glucose to HMF are presented.

4.1 Catalyst characterization

The carbon catalysts prepared via modified one-step HTC method were functionalized with sulfuric acid and hydrochloric acid, with and without acrylic acid, as described in Chapter 3, making four types of catalysts: C-SO$_3$H, C-SO$_3$H-A, C-HCl and C-HCl-A. The elemental compositions, surface area, and total acidity of the catalysts shown in Table 4.1. From the elemental analyses, HTC was found to contain no S nor Cl. The percentages S in the C-SO$_3$H and C-SO$_3$H-A were 0.57 and 0.04, respectively, while the Cl percentages were 0.16 and 0.11 for C-HCl and C-HCl-A, respectively. These results confirmed functionalization of the catalysts with the acids. It is also noted that, with the addition of acrylic acid, the C/O ratio increased. For sulfuric acid functionalized catalysts, the increase in the carbon content from 77.89% in C-SO$_3$H to 85.76% in C-SO$_3$H-A and the decrease in the oxygen content from 21.54% to 14.20% were observed. Whereas for the chloric acid functionalized HTC, and the increase in the carbon content from 71.01% in C-HCl to 76.04% in C-HCl-A, and the corresponding decrease in the

oxygen from 28.83% to 23.85% were observed. The BET specific surface area of the catalysts were found to be relatively low (between 1.1-1.9 m^2/g), but lie in a typical range (1-2 m^2/g) for this type of carbon-based catalyst prepared via HTC (Mo et al, 2008; Kitano et al, 2009; Honglei Zhang et al, 2016). As for the total acidity of catalyst measured by titration method, the total acidity increased, as expected, when acrylic acid was added, i.e., from 2.125 mmol/g for C-SO$_3$H to 3.625 mmol/g for SO$_3$H-A, and from 2.906 mmol/g for C-HCl 3.469 mmol/g for C-HCl-A.

Table 4.1 Elemental analysis, surface area and total acidity

Type of Catalyst	Elemental compositions				Surface area (m^2/g)	Total acidity (mmol/g)
	C %	O %	S %	Cl %		
C-SO$_3$H	77.89	21.54	0.57	0.00	1.474	2.125
C-SO$_3$H-A	85.76	14.20	0.04	0.00	1.874	3.625
C-HCl	71.01	28.83	0.00	0.16	1.125	2.906
C-HCl-A	76.04	23.85	0.00	0.11	1.912	3.469

The FTIR spectra shown in Fig. 4.1 confirmed the presence of main functional groups on the catalysts. The aromatic component was found at the band 875-750 cm^{-1} referred to the aromatic C-H (Niki Baccile et al, 2013). The absorption bands of C=C approximately at 1600 cm^{-1} and the C=O vibrations band approximately at 1700 cm^{-1} (referred to carbonyl, quinone, ester or carboxyl groups) for all of catalysts were similar. Moreover, the appeared band of aliphatic C-H at approximately 3000-2815 cm^{-1}. In term of sulfonating carbon support, the appearance of adsorption band approximately at 1040 cm^{-1} indicated that symmetric O=S stretching vibrations was noticed for C-SO$_3$H and C-SO$_3$H-A, which can confirm the existence of sulfonic group (Nakhate et al., 2016).
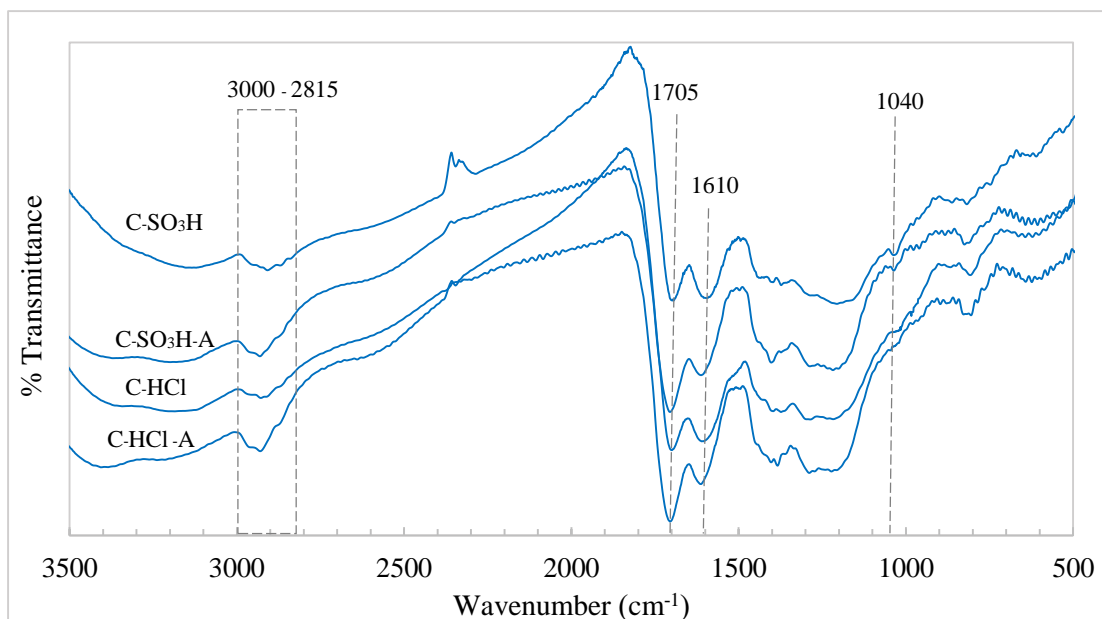
Figure 4.1 FTIR spectra of C-SO$_3$H, C-SO$_3$H-A, C-HCl and C-HCl-A

by one-step hydrothermal carbonization at 200 °C for 1 h.

The morphology of the catalysts seen under SEM is shown in Fig.4.2. Without acrylic acid, the catalysts prepared from carbon material by modified one-step HTC method displayed a spherical shape. The particle size of the catalyst functionalized by chloride group was around 3-4.5 μm, which was slightly bigger than the catalysts functionalized by sulfonic group (2-4 μm). For those with acrylic acid (Fig. 3.2b and Fig. 3.2d), there appeared to be new surfaces on the catalysts, as evidenced by the rough surfaces of the C-SO$_3$H-A and C-HCl-A catalysts. This was also reported in Nata et al. (2015), as an effect of acrylic acid addition during the two step HTC catalyst preparation. Moreover, in presence of acrylic acid, the dispersion of catalyst was noticeable, and the particle size appeared to decrease slightly.
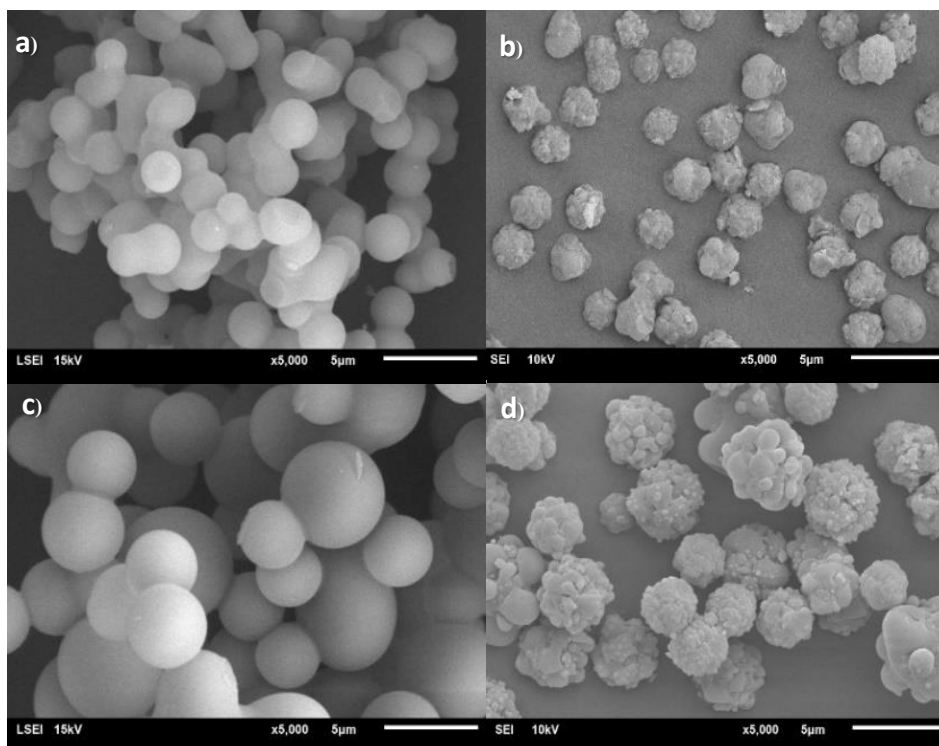
Figure 4.2 SEM of a) C- SO$_3$H, b) C- SO$_3$H -A, c) C-HCl and d) C-HCl-A
by one-step hydrothermal carbonization at 200 °C for 1 h.

The thermal stability of catalyst was determined by TGA analysis as shown in Fig.4.3. All of the catalysts displayed a good thermal stability up to the temperature around 300 °C. In C-SO$_3$H and C-HCl, there appeared to be three distinct weight losses, the first is the loss of free water from the catalyst surface noticed from the slight drop of the TGA graph around 100-200 °C. The second weight loss occurred at 300-400 °C, suggesting the loss of some functional groups on the catalysts. The last weight loss appeared at over 400 °C, which could be assigned to the loss of the main carbon structures. For C-SO$_3$H-A and C-HCl-A, only two distinct weight losses were observed. The first was a slight drop of graph around 100-200 °C, which again, was a result of free water loss. The second weight loss was evident at over 300 °C, which could be attributed to the loss of functional groups and the main carbon structures. In these cases, the weight loss of the main carbon structure was observed earlier. The reason for this was probably due to the fact that the addition of acrylic acid resulted in the certain degree of destruction of the carbon structures of the catalysts. At 600 °C, the lower

carbon residual in the catalyst with added acrylic acid suggested possible destruction of carbon structure by acrylic acid. This was also evident by the smaller particle size catalyst with acrylic acid seen from the SEM analysis (Fig. 4.2b and d). which also cause
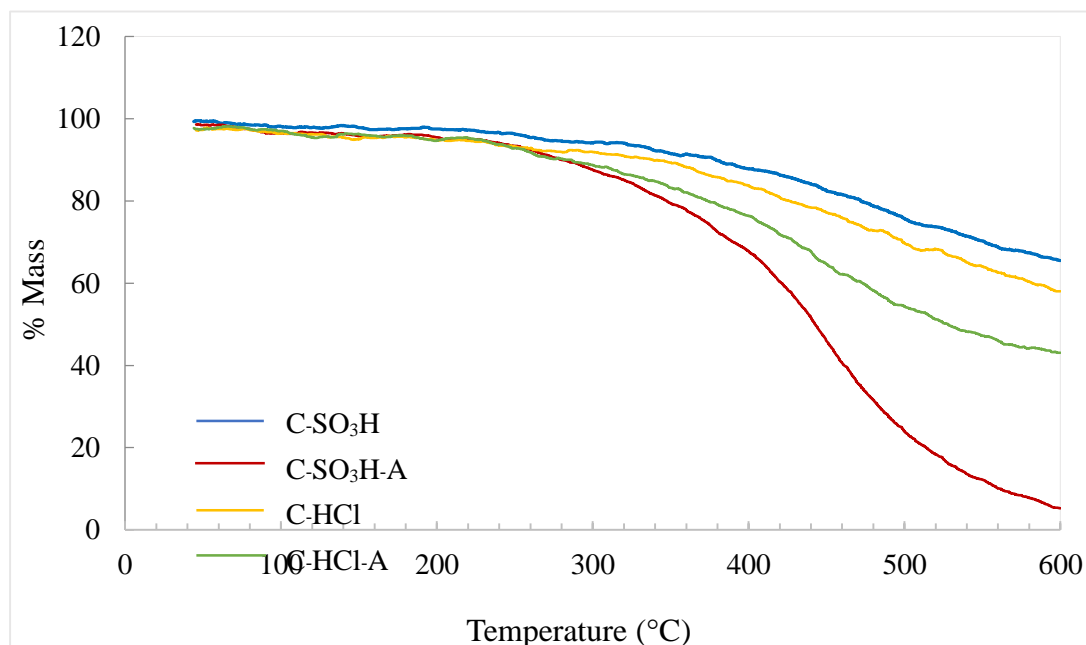
by the. As a result, thermal stability was decreased in the catalysts with the addition of acrylic acid

Figure 4.3 TGA analysis of catalyst for C-SO₃H, C-SO₃H-A, C-HCl and C-HCl-A

4.2 Catalyst evaluation on dehydration reaction for HMF production

All synthesized catalysts were tested toward the direct dehydration of glucose using microwave reactor. The effect of temperature on the reaction performance was studied based on HMF production using the constant reaction time of 30 minutes. As shown in Fig. 4.4, the results indicated that the HMF yield increased when the temperature increased. However, the benefit of catalyst presenting was not clearly noticed at 120 °C and 210 °C. At 150 °C and 180 °C, the presence of catalysts promoted the reaction. The highest HMF yield was observed from the reaction catalyzed by C-SO₃H at 180 °C. From the study, it can be revealed that the catalyst with the sulfonic

group (C-SO₃H) catalyzed the dehydration reaction better than chloride group (-Cl). This observation presents some contradictions with the previous research, which reported the highest HMF yield with a chloride group in homogeneous phase (Li et al., 2017). As a result, it might result from functionalization of chloride group on the surface of the catalyst which was not suitable evidence from result of SEM-EDS. It showed the lower percentage of chloride when compared with sulfur (Table 4.1). So, the effect of sulfur group was dominated on dehydration more than chloride group. From this study, the addition of acrylic does not provide significant effect on HMF production although the high total acidity was found. From the elemental analysis (Table 4.2), C-SO₃H contains high percentage of sulfur, thus, the high sulfur on surface of catalyst can perform the highest HMF production.
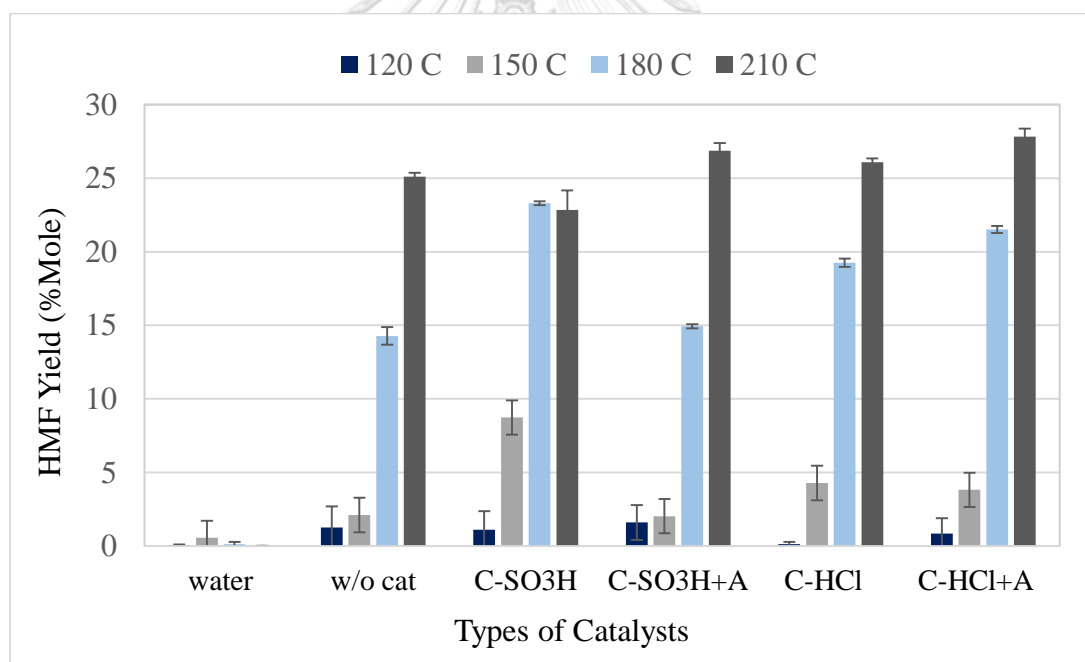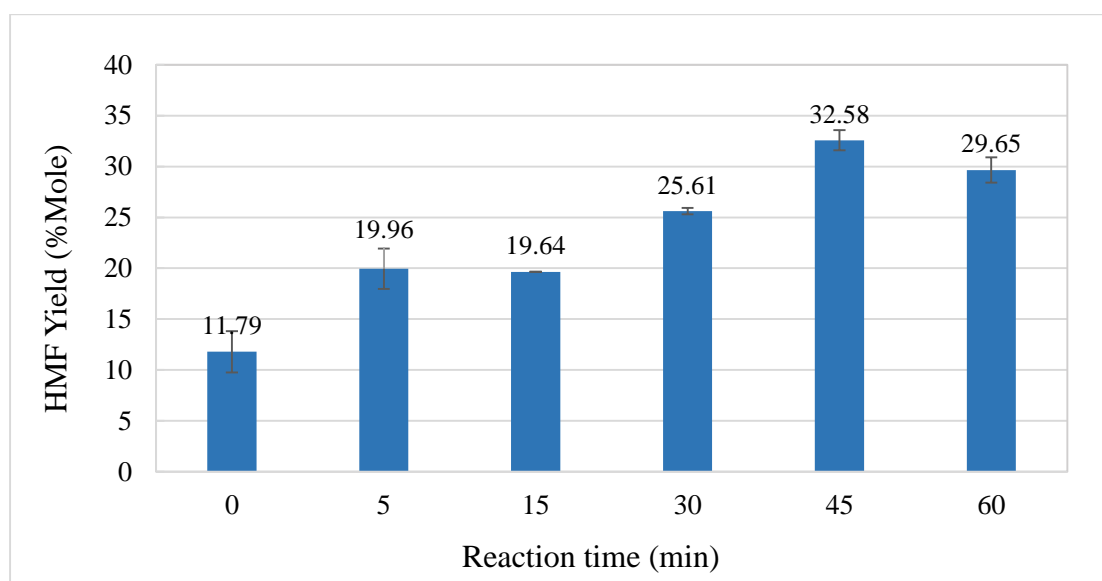

Figure 4.4 The catalytic effect for HMF production.

Reaction condition: 0.3 g glucose, catalyst loading 1 wt% of glucose, NaCl 20 wt% of glucose, water/GVL ratio 8:2 v/v, DI water 10 ml and 30 minutes of reaction time

From these observed results, C-SO₃H were chosen to study the effect of reaction time (using the reaction temperature of 180 °C). As shown in Fig.4.5, HMF yield tended

to significantly increase by increased the reaction time until 45 minutes. At 60 minute, the HMF yield was slightly dropped, but the result was not significantly different from 45 min. The dropped of HMF production could be caused from its further conversion to by-products as reported by Li and coworkers (2017). Thus, the condition of C-SO$_3$H at 180 °C for 45 minute were chosen for further studies.

Figure 4.5 The effect of Time for HMF production.

Reaction condition: 0.3 g glucose, catalyst loading 1 wt% of glucose, NaCl 20 wt% of glucose, water/GVL ratio 8:2 v/v at 180 °C for 45 minutes

Next, the effect of catalyst amount (based on percentage by weight of glucose) was studied. The amount of catalyst was varied with a double amount of catalyst: 0.5, 1, 2.5 and 5 % wt of glucose as shown in Fig. 4.6. It was found that the highest yield of 37.71% can be achieved when 0.5 %wt of catalyst was loaded. The increasing amount of catalyst tended to decrease the HMF yield because the high acidity in system can promote the side-reactions as evidenced from Qi et al. (2014). They studied the effect of H$_2$SO$_4$ loading on the dehydration of fructose to HMF in water/GVL system at 130 °C for 10 minutes by microwave and reported that the increasing of H$_2$SO$_4$ decrease the HMF production due to the further conversion of HMF to LA (Qi et al, 2014).
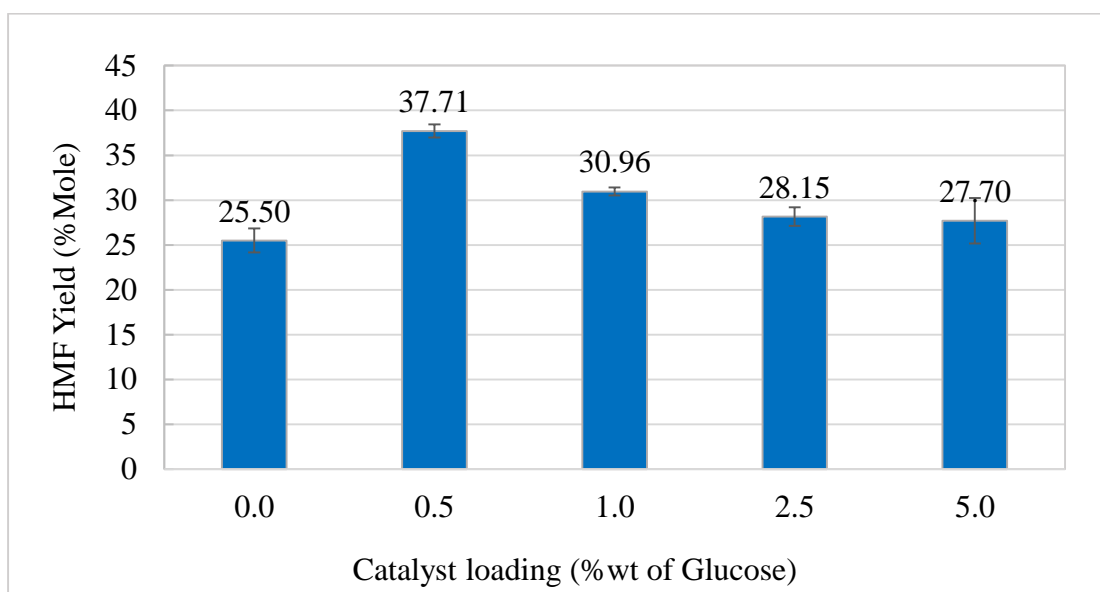
Figure 4.6 The effect of catalyst loading for HMF production.

Reaction condition: 0.3 g glucose, NaCl 20 %wt of glucose, water/GVL ratio 8:2 v/v at 180 °C for 45 minutes

As the next step, the effect of reaction medium on the reaction performance at 180 °C for 45 min was investigated. 10 ml of water, GVL and water/GVL (2:8 v/v) ratio were tested. As shown in Table 4.2, the combination of water/GVL/NaCl as biphasic system with C-SO$_3$H performed the highest HMF production (as high as 37.71% yield can be obtained). When considering the reaction medium, the conversion of glucose in water gave a very low HMF yield while the use of GVL can promote the conversion of glucose to HMF, but the product yield was not satisfying (23.50 %) because glucose partially dissolves in GVL. Thus, the addition of water to GVL was required. Moreover, the biphasic system was generated when NaCl was added into a water/GVL solution which showed the higher HMF production compared with monophasic system (water/GVL) because the GVL phase acted as an extractive phase for extraction the HMF from reactive phase (aqueous phase). Moreover, the leak of HMF in aqueous phase

can shift the reaction which caused the high production yield. The HMF yield of 30.262%
and 37.71% can be achieved from monophasic and biphasic system, respectively.

Table 4.2 Combination of Chemicals on HMF production

Reaction medium	Catalyst	HMF Yield (% Mole)
Water[a]		0.0789
Water[a]	C-SO$_3$H	25.98
GVL[b]		23.50
GVL[b]	C-SO$_3$H	14.55
Water/GVL[C]	C-SO$_3$H	30.26
Water/GVL/NaCl[C]		25.50
Water/GVL/NaCl[C]	C-SO$_3$H	37.71

*Conditions: 0.3 g glucose and catalyst loading 0.5 %wt of glucose at 180 °C for 45
minute. [a] DI water 10 ml. [b] GVL 10 ml. [C] NaCl 20 %wt of glucose and water/GVL ratio
8:2 v/v.

The effect of water/GVL ratio was further investigated since the price of GVL
is fairly high. The testing conditions were 0.3 g glucose, catalyst loading 0.5 %wt of
glucose and 10 ml of solution at 180 °C and 45 minute. The result (Fig. 4.7) demonstrated
that an increasing of GVL can increase the HMF production until the ration of
water/GVL was 8:2 %v/v where HMF yield trended to decline. It should be noted that,
during the experimentation, two phases were generated at 4:6 and 2:8 v/v of water/GVL
ratio. The increasing amount of water generated only one phase caused from the amount
of salt which was not enough for generating two phases. As a result, the effect of phase
formation was related to HMF yield which was grouped into monophasic and biphasic
system. For biphasic system, the water/GVL at 4:6 v/v gave higher HMF yield (51.65%)
than 2:8 v/v ratio (38.87%) which could be affected by the glucose concertation.

According to previous hypothesis about biphasic system, the reaction occurs in aqueous phase and the products are immediately extracted to solvent phase (Saha et al, 2014). By considering only aqueous phase, the glucose concentration at 6:4 v/v of GVL/water ratio was 0.42 M which was lower than ratio at 2:8 v/v (0.83 M), but the lower concentration gave the higher HMF production. This observation is in good agreement with Qi et al. (2014) who studied the effect of fructose concentration for HMF production in water/GVL system served by H_2SO_4 as a catalyst and reported that the use of 0.53 M fructose concentration gave higher HMF production than the use of 1.7 M fructose. For monophasic system (0:10, 2:8, 4:6 and 10:0 v/v of water/GVL ratio), the result showed the lower HMF production than biphasic system which could be caused by several factors such as the immediately conversion of HMF to LA in monophasic system (Qi et al, 2014) and partial dissolve of glucose in GVL evidenced from residual solid glucose after finished reaction. Thus, the highest HMF yield was presented at 51.65% with 4:6 %v/v of water/GVL ratio. The optimal conditions to gain the highest HMF were using 4:6 %v/v of water/GVL with catalyst loading 0.5 %wt of glucose at 180 °C for 45 minute.
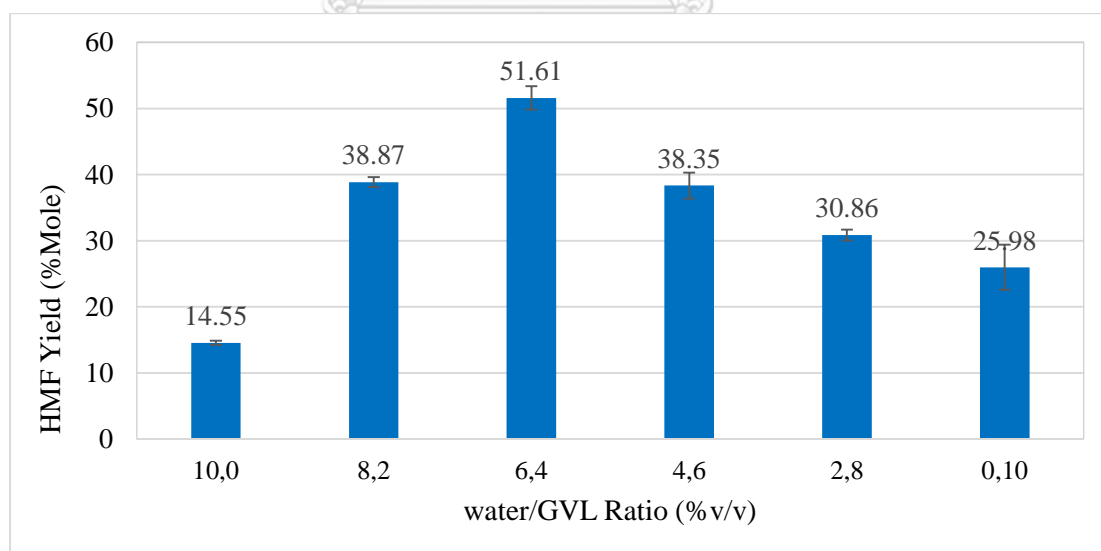
Figure 4.7 The effect of GVL/water ratio for HMF production.

Reaction condition: 0.3 g glucose, catalyst loading 0.5 %wt of glucose, 20 %wt NaCl at 180 °C for 45 minutes

4.3 Reusability of C-SO$_3$H catalyst

The reusability of catalyst was then tested. After finished the reaction, the catalysts were filtrated, and washed with 50 ml of hexane followed by 30 ml of acetone, and then dried in an oven at 110 °C for 12 h. The reusability of C-SO$_3$H on dehydration for production of HMF is presented in Fig. 4.8. It can be seen that the HMF yield did not significantly decrease after reused at least 5 times. SEM and SEM-EDS analysis of catalyst after 4 times reusability was also performed. As shown in Fig. 4.9, the surface area and size of catalyst was not changed.
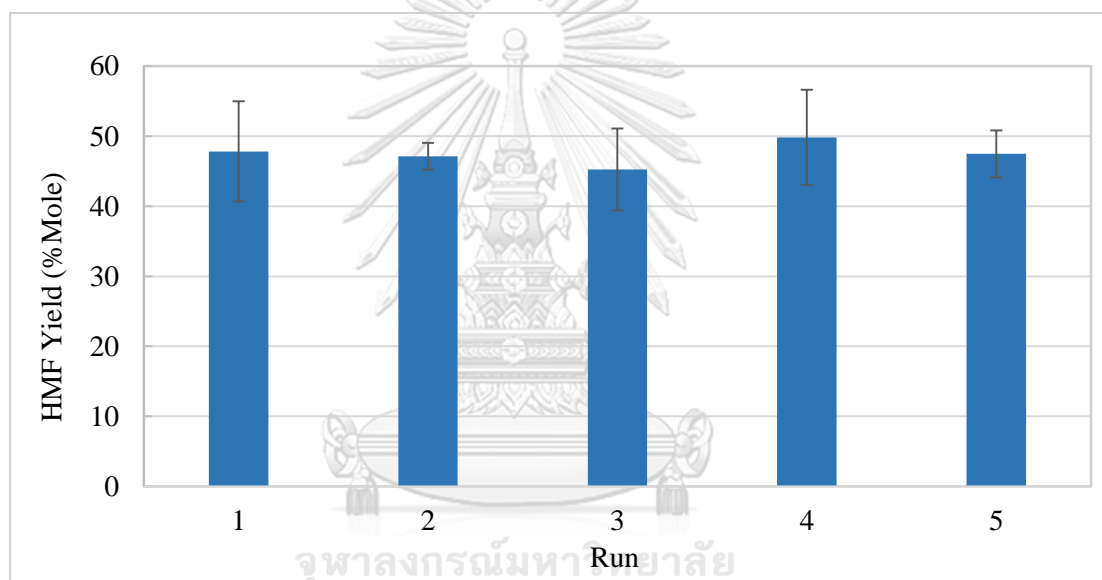
Figure 4.8 The reusability of C-SO$_3$H on dehydration for production of HMF

Reaction condition: 0.3 g glucose, catalyst loading 0.5 %wt of glucose, 20 %wt NaCl,

4:6 %v/v of water/GVL at 180 °C for 45 minutes

Fresh Catalyst   4 times Reusability
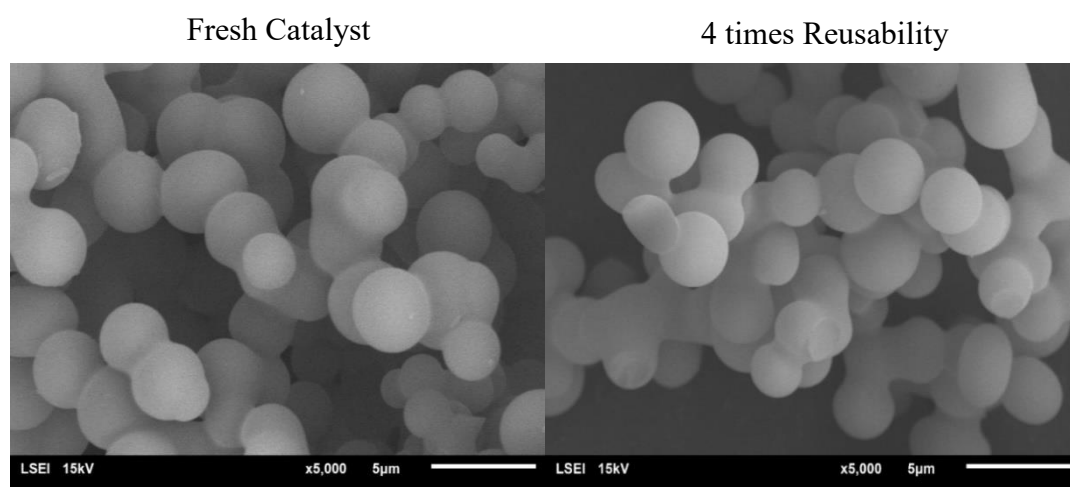
Figure 4. 9 SEM of C-SO₃H by one-step hydrothermal carbonization at 200 °C for 1 h.

CHAPTER V
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The carbon acid catalyst prepared by modified one-step HTC was evaluated on dehydration for HMF production. In term of adding acrylic acid, the performance of catalyst was noticed with the new surface evidenced from the roughness on surface of catalyst, and the increase of total acidity. Moreover, the adding acrylic also affected on elemental compositions evidenced from increasing of carbon percentage and decreasing of oxygen percentage. However, this effect was not noticed with HMF production. The comparison between four types of catalyst showed the C-SO$_3$H showed the highest HMF production. In term of the optimal condition, the highest HMF yield was noticed with 4:6 % v/v of water/GVL, NaCl 20 wt% of glucose, catalyst loading 0.5 % wt of glucose at 180 °C for 45 minute when the C-SO$_3$H was used as a catalyst. Furthermore, the reuse of catalyst showed at least 5 time which can confirm the stability and reusability of catalyst.

5.2 Comparison of catalyst preparation method

The comparison between two steps method and one step method were showed in Table 5.1. As a result, the one step method used 1:0.5 wt % of carbon/acid ration which was lower than two step method (1:10 wt%) around 20 times. However, it showed the similar total acidity and an outstanding reusability of catalyst (5th times). In this study, the modified one step method using microwave was used to prepare the catalyst which also showed a good reusability and low amount of acid. Moreover, this method showed 1 hour of reaction times which was lower than the one-step method described by Nata et al. (2015).

Table 5.1 The comparison of each method for preparation of carbon acid catalyst

Method	Carbon/acid ratio (by weight)	Condition	Total acidity (mmol/g)	Reuse[*] (time)	reference
Two steps	1:10	Carbonization: 200 °C, 4 h Sulfonation: 150 °C, 15 h	7.944	1	(Wataniyakul et al, 2018)
Two steps	1:10	Carbonization: 400 °C, 1 h Sulfonation: 120 °C, 15 h	1.500	3	(Kitano et al., 2009)
One-steps HTC[a]	1:0.5	180 °C, 4 h	2.100	5	(Nata et al, 2015)
Modified one-step HTC[a]	1:0.5	200 °C, 1 h	2.125	5	This study

[*] The number of catalyst stability based on 5th times

5.3 Comparison of HMF production from different types of catalysts

The comparison of HMF yield from different types of catalyst showed in Table5.2. The conversion of glucose for HMF production using GVL as a solvent and Brønsted acid as a catalyst from other studies showed that the HMF production from Li et al. (2017) reported the highest HMF yield at 62. 45 % used system of water/GVL/NaCl as a biphasic system with homogeneous HCl as a catalyst. They also used H_2SO_4 as a homogeneous catalyst which gave the 55 % of HMF yield. However, the homogeneous catalyst has a drawback such as separation cost from product and corrosion of reactor. The development of heterogeneous catalyst for solving their problem has been interested. In terms of heterogeneous catalyst for HMF production, Gallo et al (2013) reported that 29% of HMF yield used Amberlyst-70 as a catalyst in water/GVL system. This study also used carbon acid catalyst for HMF production which gave 51.61 % yield with water/GVL/NaCl system. Although the result showed lower HMF production caused by the limitation of solid catalyst, it showed an outstanding of reusability at least 5 times.

Table 5.2 The glucose conversion for HMF production using GVL as a solvent

Glucose	Solvent	Catalyst	Temp (° C)	Time (min)	Yield (mol%)	Reuse (times)	Reference
0.36 g	Water/GVL[a]	7.4 mmol H_2SO_4	130	60	13.00	0	(Qi et al, 2014)
1.50 g	Water/GVL/ NaCl[b]	0.2 mmol HCl	140	60	62.45	0	(Li et al, 2017)
		0.1 mmol H_2SO_4	150	60	55.00	0	
1.50 g	water/GVL[a]	0.1g Amberlyst 70	130	30	29.00	N/A	(Gallo et al, 2013)
5 wt%	water/GVL/NaCl[b]	5 mmol/l $AlCl_3$	170	40	61.60	0	
0.3 g	water/GVL/NaCl[b]	3.17 mmol/l HCl 0.0015 g C-SO_3H	180	45	51.61	5	This study

[a]monophasic system, [b]biphasic system

5.4 Recommendations

5.4.1 Catalyst preparation

For catalyst preparation, a solid BrØnsted acid prepared by modified one- step hydrothermal carbonization (HTC) was synthesized at 200 ˚C for 1 h under microwave irradiation and evaluated on dehydration reaction for HMF production. For preparation condition, this study fixed at one condition which might be the best condition for the catalyst. We would like to recommend for finding the optimal condition of the catalyst which can study with the effect of temperature, reaction time, types of acids and amount of acid. However, one-step HTC required water in the system for carbonizing the carbon source to carbon supported. So, the types of strong acid should not be a concern the form after mixed with water. For example, the functionalization with the sulfonic group (-SO_3H) cannot be achieved with sulfuric acid (H_2SO_4) because the form after mixed with water is HSO_4^{-1} or SO_4^{-2} which cannot show sulfonic group after functionalization. Moreover, the synthesis under microwave irradiation should start at least 200 °C for 1 h because the lower this condition cannot generate the solid form of carbon. For HTC of the solid catalyst under microwave can study from Guiotoku et al. (2009). They

reported about the percentage of C H N O with different temperature and time form cellulose and pine sawdust.

5.4.2 Dehydration reaction for HMF production

In this study, the dehydration reaction was studied on the effect of temperature, reaction time and catalyst loading with C-SO3H as the catalyst. As a result, some parameters were fixed such as glucose concentration and amount of salt which noticed the effect on HMF production. For examples, fig 4.7 showed the effect of water/GVL ration combined with the effect of glucose concentration. The lower glucose concentration at 4:6 %v/v of water/GVL ratio showed the higher HMF production. However, that condition was not the highest HMF production. The effect of the parameter should be separate for finding the highest HMF production. In addition, the ratio at 4:6 %v/v of water/GVL showed the lower GVL ratio when compared with other studies. We recommend starting with this ratio to find the effect of each parameter on dehydration for HMF production.

APPENDIX A
STATISTICAL DATA FOR ANALYSIS

A.1 Statistic calculation

The statistic calculation was studied for choosing the parameters. The proving of static calculation showed significant difference of data which can choose for investigating next step. Actually, there are many stat test but we have to choose the relating test of our data. In this study, the Fisher's Least Significant Difference (LSD) test was chose to calculation which used to compare the smallest significant difference between two different mean. However, LSD required the data from statistic calculation. The confidence interval was set at 80% ($\alpha = 0.2$). The calculating was followed by hypothesis and formula as

Hypothesis $\quad\quad H_0: \mu_i = \mu_j$

$\quad\quad\quad\quad\quad\quad H_1: \mu_i \neq \mu_j$

LSD formula $\quad LSD = t_{\alpha/2, N-a} \sqrt{\dfrac{2MSE}{n}} \quad\quad$ if $n_i = n_j$

$$SSE = \sum_{i=1}^{a}\sum_{j=1}^{n}(y_{ij} - \bar{y}_i)^2 \quad\quad SST = \sum_{i=1}^{a} n_i(\bar{y}_i - \bar{y}_.)^2$$

$$SSE = SST - SSA \quad\quad MSE = \dfrac{SSE}{N-a}$$

$$If \quad I\bar{x}_i - \bar{x}_jI > LSD \; ; reject \; H_0$$

$$I\bar{x}_i - \bar{x}_jI \leq LSD \; ; accept \; H_0$$

Table A.1 Statistic data of each parameter

Parameter	Factor	Pair of factor (i,j)	$\left\|\bar{x}_i - \bar{x}_j\right\|$	LSD	note
Temperature at 180°C	(1) No catalyst	1,2	9.02	3.21	significant
	(2) C-SO₃H	1,3	0.66	3.21	
	(3) C-SO₃H-A	1,4	4.97	3.21	significant
	(4) C-HCl	1,5	7.24	3.21	significant
	(5) C-HCl-A	2,3	8.36	3.21	significant
		2,4	4.05	3.21	significant
		2,5	1.78	3.21	
		3,4	4.31	3.21	significant
		3,5	6.58	3.21	significant
		4,5	2.27	3.21	
Time	(1) 0 min	1,2	8.17	5.57	significant
	(2) 5 min	1,3	7.85	5.57	significant
	(3) 15 min	1,4	13.82	5.57	significant
	(4) 30 min	1,5	20.79	5.57	significant
	(5) 45 min	1,6	17.86	5.57	significant
	(6) 60 min	2,3	0.31	5.57	
		2,4	5.66	5.57	significant
		2,5	12.62	5.57	significant
		2,6	9.69	5.57	significant
		3,4	5.97	5.57	
		3,5	12.94	5.57	significant
		3,6	10.01	5.57	significant
		4,5	6.97	5.57	significant
		4,6	4.04	5.57	
		5,6	2.93	5.57	
Amount of Catalyst (% wt of glucose)	(1) 0	1,2	12.21	4.02	significant
	(2) 0.5	1,3	5.47	4.02	significant
	(3) 1	1,4	2.66	4.02	
	(4) 2.5	1,5	2.20	4.02	
	(5) 5	2,3	6.74	4.02	significant
		2,4	9.55	4.02	significant
		2,5	10.01	4.02	significant
		3,4	2.81	4.02	
		3,5	3.27	4.02	significant
		4,5	0.46	4.02	

APPENDIX B
EXPERIMENTAL DATA

B.1 Standard calibration curve for HPLC analysis of HMF

Table B.1 Standard calibration curve for HPLC analysis of HMF

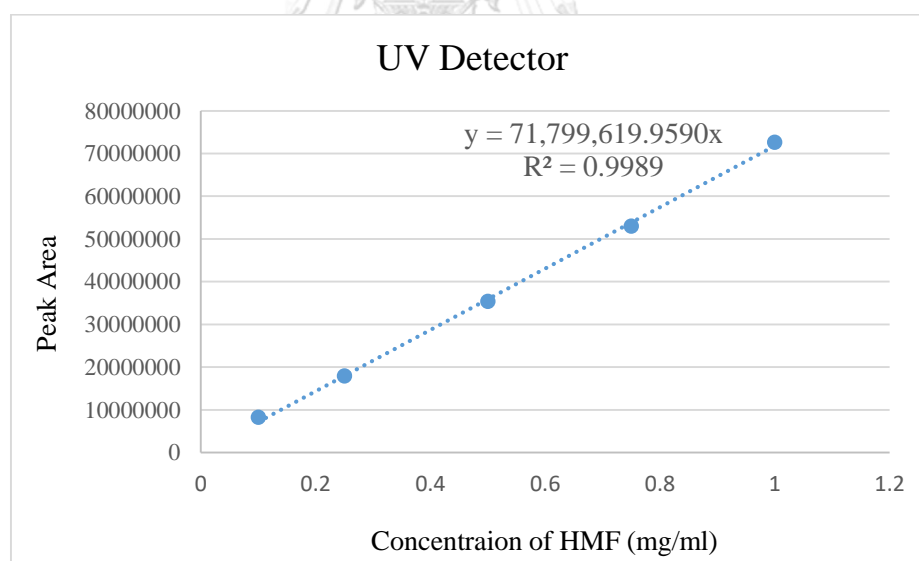| HMF concentration (mg/ml)	Peak area (UV detector at 220 nm)
0.1	8257524
0.25	17918142.19
0.5	35355648.58
0.75	52961306.83
1	72638191.27

Figure B.1 Standard curve of HMF

B.2 Calculation of HMF yield

$$\text{HMF yield }_{(\%)} = \frac{\text{Moles of HMF product}}{\text{Moles of starting Glucose}} \text{ x } 100$$

Table B.1 Effect of various catalyst and temperature

Temperature	Type of catalyst	HMF yield (% mol)		Average	SD
		1	2		
120 °C	water	0.008	0.077	0.042	0.049
	without catalyst	0.252	2.275	1.263	1.431
	C-SO₃H	0.216	2.002	1.109	1.263
	C-SO₃H+A	0.305	2.878	1.592	1.820
	C-HCl	0.019	0.229	0.124	0.148
	C-HCl+A	0.110	1.583	0.846	1.042
150 °C	water	0.286	0.813	0.550	0.373
	without catalyst	1.590	2.615	2.102	0.724
	C-SO₃H	9.760	7.698	8.729	1.459
	C-SO₃H+A	1.254	2.784	2.019	1.082
	C-HCl	4.036	4.518	4.277	0.341
	C-HCl+A	3.995	3.627	3.811	0.260
180 °C	water	0.225	0.020	0.122	0.145
	without catalyst	14.703	13.848	14.275	0.605
	C-SO₃H	23.381	23.206	23.294	0.124
	C-SO₃H+A	14.831	15.033	14.932	0.143
	C-HCl	19.442	19.047	19.245	0.279
	C-HCl+A	21.687	21.336	21.512	0.248
210 °C	water	0.002	0.002	0.002	0.001
	without catalyst	24.918	25.293	25.106	0.265
	C-SO₃H	23.776	21.911	22.844	1.319

C-SO₃H+A	26.512	27.236	26.874	0.512
C-HCl	25.909	26.277	26.093	0.260
C-HCl+A	27.451	28.213	27.832	0.538

Table B.2 Effect of reaction time

Reaction time (min)	HMF yield (% mol)		Average	SD
	1	2		
0	10.359	13.221	11.790	2.024
5	18.554	21.360	19.957	1.984
15	19.634	19.653	19.644	0.014
30	25.385	25.839	25.612	0.321
45	31.887	33.276	32.581	0.982
60	30.529	28.770	29.650	1.244

Table B.3 Effect of catalyst loading

catalyst loading (wt% of glucose)	HMF yield (% mol)		Average	SD
	1	2		
0	24.543	26.452	25.498	1.349
0.5	37.190	38.226	37.708	0.733
1	30.659	31.270	30.965	0.432
2.5	28.888	27.421	28.155	1.037
5	25.898	29.494	27.696	2.543

Table B.4 Effect of water/GVL ratio

water/GVL ratio	HMF yield (% mol)		Average	SD
	1	2		
0:10	28.405	23.560	25.983	3.425

2:8	31.455	30.266	30.860	0.841
4:6	36.958	39.733	38.346	1.962
6:4	50.354	52.870	51.612	1.779
8:2	38.340	39.408	38.874	0.755
10:0	14.332	14.765	14.549	0.306

Table B.5 Reusability of catalyst

Reuse (time)	HMF yield (% mol)		Average	SD
	1	2		
1	54.614	52.870	53.742	1.233
2	48.483	45.754	47.118	1.930
3	45.090	49.381	47.235	3.034
4	45.010	54.341	49.676	6.598
5	53.813	42.763	48.288	7.814

APPENDIX C
CONFERENCE PROCEEDINGS

The 24th PPC Symposium on Petroleum,

Petrochemicals, and Polymers

and

The 9th Research Symposium

on Petrochemical and Materials Technology

Co-organized by

The Petroleum and Petrochemical College

Center of Excellence on Petrochemical and Materials Technology

Chula Global Network

Chulalongkorn University

At

Mandarin Hotel Managed by Centre Point

Bangkok, Thailand

จุฬาลงกรณ์มหาวิทยาลัย
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