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นายธรรศ บุญญกาญจน์

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COMBINED HYDROTHERMAL CARBON-BASED AND LEWIS ACID CATALYSTS FOR CONVERSION OF CELLULOSE

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ธรรศ บุญญกาญจน์ : การแปรสภาพของเซลลูโลสโดยการใช้ตัวเร่งปฏิกิริยาไฮโดรเทอมอลคาร์บอนร่วมกับกรดลิวอิส (COMBINED HYDROTHERMAL CARBON-BASED AND LEWIS ACID CATALYSTS FOR CONVERSION OF CELLULOSE) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ศ. ดร.อาทิวรรณ โชติพฤกษ์, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: ศ. ดร.บรรเจิด จงสมจิตร, 94 หน้า.

ในปัจจุบันการผลิต 5-ไฮดรอกซีเมทิลเฟอร์ฟิวรัลและกรดเลวูลินิกได้รับความสนใจเป็นอย่างมาก เนื่องจากสารดังกล่าวเป็นสารตั้งต้นที่ใช้ในการผลิตพลังงานเชื้อเพลิงและสารอื่นๆที่มีมูลค่า ดังนั้นการศึกษานี้มีวัตถุประสงค์เพื่อเพิ่มประสิทธิในการผลิต 5-ไฮดรอกซีเมทิลเฟอร์ฟิวรัลและกรดเลวูนิลิกจากเซลลูโลสโดยการใช้ตัวเร่งปฏิกิริยาไฮโดรเทอมอลคาร์บอนแบบกรดร่วมกับกรดลิวอิส จากการศึกษากรดลิวอิส ได้แก่ แมงกานีสคลอไรด์ ไอเอิร์นคลอไรด์ โคบอลต์คลอไรด์ แคดเมียมคลอไรด์ และ โครเมียมคลอไรด์ ซึ่งพบว่าโครเมียมคลอไรด์ ให้ร้อยละผลได้ของ 5-ไฮดรอกซีเมทิลเฟอร์ฟิวรัลและกรดเลวูลินิก มากสุด เมื่อทำการผสมโครเมียมคลอไรด์ร่วมกับตัวเร่งปฏิกิริยาไฮโดรเทอมอลคาร์บอนแบบกรด สามารถเพิ่มการผลิต 5-ไฮดรอกซีเมทิลเฟอร์ฟิวรัลและกรดเลวูนิลิก ได้มากกว่าการใช้โครเมียมคลอไรด์เพียงอย่างเดียวสองเท่า โดยการศึกษาผลของอุณหภูมิ (160 - 220 องศาเซลเซียส) เวลา (0 - 60 นาที) ความเข้มข้นของโครเมียมคลอไรด์ (0 - 0.020 โมลาร์) และปริมาณตัวเร่งปฏิกิริยาไฮโดเทอมอลคาร์บอนแบบกรด (0 - 40 % โดยมวล) พบว่า สภาวะที่ผลิต 5-ไฮดรอกซีเมทิลเฟอร์ฟิวรัลและกรดเลวูลินิกได้สูงสุด คือ อุณหภูมิ 200 องศาเซลเซียส เวลา 5 นาที ปริมาณตัวเร่งปฏิกิริยาไฮโดเทอมอลคาร์บอนแบบกรด 5% โดยมวล และความเข้มข้นของโครเมียมคลอไรด์ที่เหมาะสมในการผลิต 5-ไฮดรอกซีเมทิลเฟอร์ฟิวรัลและกรดเลวูลินิก คือ 0.005 และ 0.015 โมลาร์ ตามลำดับ ที่สภาวะดังกล่าวนี้ให้ร้อยละผลได้ของผลิต 5-ไฮดรอกซีเมทิลเฟอร์ฟิวรัลและกรดเลวูลินิกถึง 6.8 และ40 โดยมวล นอกจากนี้ยังทำการศึกษาการผลิต 5-ไฮดรอกซีเมทิลเฟอร์ฟิวรัลในระบบสองเฟส (เฟสสกัดระหว่างเมทธิลไอโซบิวทิลคีโตน กับ 2-บิวทานอล และเฟสทำปฏิกิริยาระหว่างสารละลายกับโครเมียมคลอไรด์กับสารละลายอะซิโตน) พบว่าสามารถเพิ่มร้อยละผลได้ของผลิต 5-ไฮดรอกซีเมทิลเฟอร์ฟิวรัลถึง 17.7 โดยมวล

ภาควิชา วิศวกรรมเคมี ลายมือชื่อนิสิต ....
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TAT BOONYAKARN: COMBINED HYDROTHERMAL CARBON-BASED AND LEWIS ACID CATALYSTS FOR CONVERSION OF CELLULOSE. ADVISOR: PROF. ARTIWAN SHOTIPRUK, Ph.D., CO-ADVISOR: PROF.BUNJERD JONGSOMJIT, Ph.D., 94 pp.

The production of 5-hydroxymethylfurfural (HMF) and levulinic acid (LA) from cellulose is gaining considerable interests as these compounds are suitable starting materials for the preparation for valuable compounds. This study proposes a novel catalysis system, the combination of hydrothermal carbon based acid catalyst (HTCG-Sul) and Lewis acid, for the synergistic one-pot conversion of cellulose to HMF and LA. The $CrCl_3$ (Chromium chloride) Lewis acid, when used alone was a suitable catalyst for cellulose conversion, giving highest HMF and LA yields compared with other metal chloride catalysts. When $CrCl_3$ was combined with HTCG-Sul, the results showed that approximately 2 times higher of HMF (6.8 wt. % vs. 3.9 wt. %) and LA (22.9 wt. % vs. 11.2 wt. %), yields were obtained. Using combination of HTCG-Sul and $CrCl_3$ as catalyst, the effect of operating conditions: including reaction temperature (160^{o}C - 220^{o}C), reaction time (0 - 60 min), $CrCl_3$ concentration (0 - 0.02 molar) and HTCG-Sul dosage (0 – 40 wt. %) on cellulose conversion was studied first in a single phase reaction system. At the condition HTCG-Sul dosage of 5 wt. %, temperature of 200^{o}C, reaction time of 5 min and $CrCl_3$ concentration of 0.005 molar), the highest HMF yield of 6.8 wt. % operating conditions of the highest LA yield was found however at a different condition: HTCG-Sul dosage 5 wt. %, 200^{o}C for 5 min and 0.015 molar $CrCl_3$ concentration, which gave 40 wt. % LA yield. Furthermore, a biphasic system using methyl isobutyl ketone (MIBK)/2-butanol (7:3) as an extractive phase, water as a reactive phase, and acetone as a co-solvent and the combination of HTCG-Sul and $CrCl_3$ as catalyst was employed to improve the stability and the yield of HMF (17.7 wt. %).

Department:	Chemical Engineering	Student's Signature	....
Field of Study:	Chemical Engineering	Advisor's Signature	....
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CHAPTER I
INTRODUCTION

1.1 Motivation

Throughout the 20th century, the fuel cost has been rising enormously owing to the increases of the world population and of energy demand for industry and transportation. As a result, research on development of technologies for the processing and utilization of nonpetroleum feedstock for alternative fuel production has now gain popularity worldwide. Biomass or lignocellulosic biomass, mainly consist of cellulose hemicellulose and lignin, is generally the most abundant organic substance derived from agricultural residues and industrial food wastes. In order to convert biomass into valuable chemicals and liquid alkanes, a number of cascaded reactions such as hydrolysis, dehydration, aldol condensation and hydrogenation are required.

By hydrolysis, biomass is decomposed to simple sugars, which are dehydrated to 5-(hydroxymethyl) furfural (HMF) and furfural by dehydration. HMF and furfural are transformed to liquid alkanes by series of aldol condensation, hydrogenation, and dehydration reactions. HMF is produced is much considerable amount compared with fufural, and is the main raw material for the production of alkanes of various carbon numbers, it is therefore considered an important intermediate for liquid fuel production. Moreover HMF can be rehydrated by acid catalyst to levulinic acid (LA) which is considered a valuable compound for uses as, plasticizer, coating, fuel additive and antifreeze, in processing of resin, textile, and animal feed. Unfortunately, the HMF and LA production from biomass is inefficient when a mineral acid catalyst (or a Brønsted acid catalyst) alone, such as sulfuric acid, hydrochloric acid, carbon-based acid and so forth, is used. The poor conversion is linked to the need to isomerize glucose to fructose prior to subsequent dehydration. This isomerization reaction is usually stimulated by enzyme, Lewis acid, and Brønsted base.

The improvement of HMF and LA yields has been reported by using bi-functional catalysts consisting of two functional groups; (1) the Brønsted acid functional group of the catalyst promotes hydrolysis, dehydration or rehydration and

(2) functional group, which may be enzyme (Yan et al., 2009), Lewis acid (Choudhary et al., 2013), or Brønsted base (Liu et al., 2014), promotes isomerization of glucose to fructose.

In biomass to liquid fuel and valuable chemicals, combined Brønsted acid and Lewis acid catalysts that have been frequently used are metal salts such as salts of Cr(III), Al(III), Zn(II), Sn(IV) and so forth. It has been shown that in case of Cr(III) catalysts, the hydrolyzed Cr(III) complex $[Cr(H_2O)_5OH]^{2+}$ probably acts as a Lewis acid site to promote isomerization of glucose to fructose, while the intrinsic Brønsted acidity generated by $CrCl_3$, the proton resulted from hydrolyzed Cr(III), drives the dehydration (Choudhary et al., 2013). Despite the fact that metal salts seem to promote isomerization by the action metal complex and drive sufficient hydrolysis, dehydration, and rehydration reactions by intrinsic Brønsted acidity, without external addition of Brønsted acid, all Lewis acid catalysts give poor selectivity to HMF and LA, since Lewis acids generally simultaneously promote humin formation especially from sugars.

Recently, combination of Lewis acid and Brønsted acids such as mineral acids and organic acid externally added have been employed to promote the production of HMF and LA. By using combination of $CrCl_3$ and CO_2 compared with H_2SO_4 and HCl, Jing et al. (2016) reported that yield of LA compared $CrCl_3$ alone with combination of CO_2, H_2SO_4, and HCl in particular was increased approximately 5 times, 6 times and 8 times, respectively because the increase in selectivity to LA caused by the adding of external Brønsted acid. The relatively low HMF yield could be due to the fact it has been converted to LA in presence of acid catalyst. When it is desirable, the selectivity of HMF could generally be achieved by application a biphasic system, or a two-phase system, which allows the HMF from the reactive aqueous phase to be extracted into the organic phase and aqueous phase (i.e. methyl isobutyl ketone (MIBK), butanol, tetrahydrofuran (THF), acetone and so forth) (Choudhary et al., 2013), therefore the rehydration of HMF in reactive phase to LA would be avoided. From previous reports, applying a biphasic system with glucose conversion in the presence of combined $CrCl_3$ and HCl catalysts, LA yield was decreased from approximately 40 mol % to 5 mol %, while the HMF yield was increased from roughly 10 mol % to 59 mol % (Choudhary et al., 2013).

Despite the improved overall yields of HMF and LA by the system of combined mineral acid and Lewis acid, this system is highly corrosive and is not environmental friendly. Prepared from low cost carbon materials such biomass, sugar and so forth which are abundant in agriculture based country including Thailand, hydrothermal carbon acid (HTCG-Sul), classified as Brønsted acid catalyst, can potentially be used in combination with a Lewis acid for enhanced production of HMF and LA. The process is expected to be more environmental friendly, and the HTCG-Sul catalyst is recyclable and and is less corrosive to the equipment.

In this work, use of combined HTCG-Sul and Lewis acid as catalyst was investigated for the production of HMF and LA from cellulose. One-phase system was first employed, in which studies were conducted to make suitable selection of Lewis acids. In cellulose conversion in the presence of combined with HTCG-Sul and the selected Lewis acid, the effects of reaction temperature and time, Lewis acid concentration and HTCG-Sul dosage were determined on the HMF and LA production. In addition, various biphasic systems, using various organic phase, or in conjunction with co-solvent or added salt, were evaluated to improve the HMF yield. The effect of phase composition and mixing time on the HMF and LA yields were determined and the results were compared with those obtained with the one phase system.

1.2 Objectives

To investigate the possibility of combining a hydrothermal carbon acid catalyst and Lewis acid for HMF and LA production from cellulose both in both one-phase and two-phase systems.

1.3 Working scope

One-phase system

Selection of suitable Lewis acids ($FeCl_2$, $FeCl_3$, $CoCl_2$, $MnCl_2$, $CdCl_2$, and $CrCl_3$)

With the selected Lewis acid, study the effects of temperature (160, 180, 200 and 220 ^{o}C) and time (0, 10, 20, 40, 60 min) on the production of HMF and LA from cellulose

With the selected Lewis acid and the selected reaction temperature and time, study the effects of concentration of (0, 0.005, 0.010, 0.015 and 0.020 molar) on the production of HMF and LA from cellulose

Study the effect mass of hydrothermal carbon acid catalyst (0, 5, 10, 20 and 30, and 40 wt. %) at selected temperature, time and concentration of $CrCl_3$ the production of HMF and LA from cellulose.

Compare the activity of combination with using $CrCl_3$ in selected condition confirmed synergy effect on the production of HMF and LA from cellulose.

Compare the activity with another Lewis in selected condition Confirmed activity of suitable Lewis acid on the production of HMF and LA from cellulose.

Biphasic system

At selected temperature, concentration of suitable Lewis acid and mass of hydrothermal carbon acid catalyst based on one-phase system, in a biphasic system, study the effects of phase composition (MIBK/2-butanol/acetone/water) and reaction time (5, 10, 15, 30, 60 and 90 min) on HMF and LA yields from cellulose conversion.

1.4 Expected benefits

The possibility of using combined hydrothermal carbon acid catalyst (as a heterogonous Extrinsic Brønsted acid) and Lewis acid catalyst was evaluated for the production of high value biomass derived compounds, such as HMF and LA. The suitable process conditions would also be suggested.

CHAPTER II

BACKGROUND & LITERATURE REVIEWS

2.1 Biomass

Biomass is organic substance originated from creature, or recently living organisms such as wood, corn, coffee, poplar, bamboo and so forth. Biomass can be used as a sustainable source of energy and it most often refers to plants, not used for food or feed and specifically called lignocellulosic biomass such as grasses, trees and different types of waste products and residuals from crops, wood, and waste mainly composed of cellulose, hemicellulose, and lignin. As an alternative energy, biomass can either be used directly through combustion to produce heat, or indirectly after converting it to various forms of biofuel. Conversion of biomass to biofuel can be achieved by different methods which are broadly categorized into thermal, chemical, and biochemical methods. For example, valuable chemicals such as 5-(Hydroxymethyl) furfural (HMF) and levulinic acid (LA) which can be used as biofuel or precursors for various applications are obtained by thermal and chemical methods (sequences reactions such as hydrolysis, dehydration and rehydration in hydrothermal conditions).

- Cellulose

Cellulose is an organic compound, consisting of linear chain of several hundreds to plentifully linked D-glucose units with glycosidic bonds. Cellulose is high a crystalline compound compared with the other starches. Whereas starch undergoes a crystalline to amorphous transition when heated beyond 60–70 °C in water (such as in cooking), cellulose requires a temperature of 320 °C and pressure of 25 MPa to become amorphous in water (Deguchi & Horikoshi). The decomposition of cellulose into glucose can be achieved via hydrolysis at high temperature or via mineral acids or enzyme catalyzed processes.

- Hemicellulose

A hemicellulose refers to any of several heteropolymers (matrix polysaccharides), such as arabinoxylans, present along with cellulose in almost all plant cell walls (Scheller & Ulvskov 2010). In contrast to cellulose which contains only anhydrous glucose, hemicelluloses including xylan, glucuronoxylan, arabinoxylan, glucomannan, and xyloglucan contain many different sugar monomers. Besides glucose, sugar monomers in hemicellulose can include, for instance, xylose, mannose, galactose, rhamnose, and arabinose.

- Lignin

Lignin is a class of complex cross-linked organic phenolic polymers that form important structural materials in the support tissues of vascular plants and some algae

(Martone et al., 2009). Because of its rigidity, lignin is particularly important in the formation of cell walls, especially in wood and bark. Lignin is degradable by only few organisms, and by that, turns into several valuable products such as organic acids, phenols and vanillin. Valuable fuel additives may be produced via chemical processes.

2.2 Valuable chemicals from biomass

2.2.1 5-(Hydroxymethyl) furfural (HMF)

HMF is an organic compound derived from dehydration of sugars. It acts as an intermediate for important chemicals (Figure 2.1). For example, liquid alkanes, having properties similar to petroleum fuels, are produced from HMF through aldol condensation, hydrogenation and subsequently dehydration. 5-ethoxymethylfurfural derived from HMF via etherification is considered to be a promising liquid fuel. Moreover, HMF can be converted to 2,5-dimethylfuran (DMF), a liquid that potentially has greater energy degree than bio-ethanol. In addition, reduction and oxidation of HMF can produce 2,5-bis (hydroxymethyl) furan and 2,5-furandicarboxylic acid (FDCA), which have been proposed as replacements for terephthalic acid for the synthesis of polyester (van Putten et al., 2013). Furthermore, HMF can be rehydrated to levulinic acid (LA) used as a precursor for pharmaceuticals, plasticizers, and various other additives.

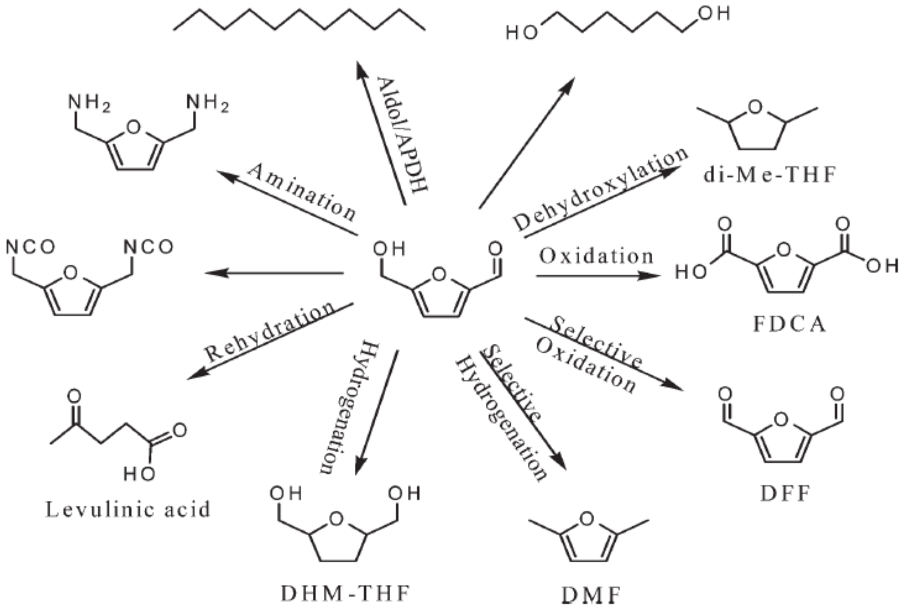


Figure 2.1 Reaction pathways for conversion of HMF into its derivatives (Zhou and Zhang, 2016)

2.2.2 Levulinic acid (LA)

LA, an organic compound derived from rehydration of HMF, is a solvent for aromatic constituents of crude mineral oil, and a valuable and versatile chemical with several industrial utilizations such as in the production of resin, plasticizer, textile, animal feed, coating, and as antifreeze (Figure 2.2). In hydrogenation, LA can be converted to valeric-γ-lactone, valuable solvent, and moreover, be transformed to 1,4 pentandiol dehydrated to 1,3-pentadine or piperylene, a crucial source of synthetic rubber. Esters of LA, such as the butyl, hexyl and cyclohexyl esters have been used as plasticizers. Other esters such as methyl isopropyl, isoamyl and 2-pentanol esters of LA have been used as solvents for synthetic glass and resins. Pseudo esters have been used as paint removers, solvents and lacquers. LA can be condensed with phenol to diphenolic, which is useful in the preparation of the modified phenol formaldehyde resins, polyether resins and as monocarboxylic acid chain stopper in alkyd resin. In addition, diphenolic acid can be an alternative of bis-phenol A, the primary raw material for the production of epoxy resin. LA also has potential application as an adhesive, for example, heat-setting resin was synthesized from a fusion of levulinic acid and amine (Ghorpade and Hanna, 1997).

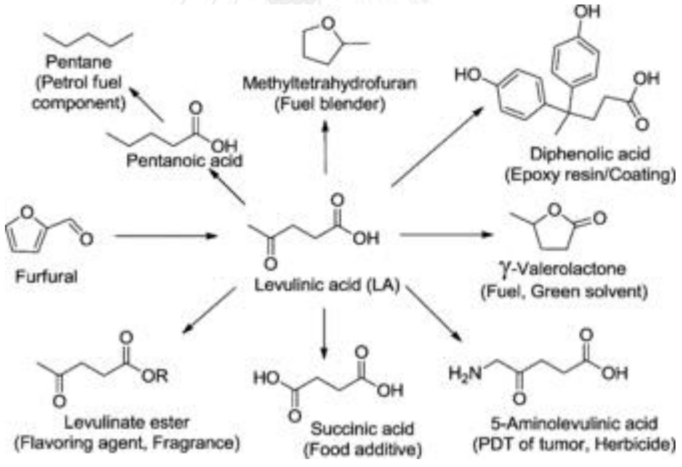


Figure 2.2 Reaction pathways for the conversion of LA into its derivative (Dwivedi et al., 2015)

2.3 Biomass conversion to valuable chemicals (HMF and LA)

Generally, the process of the synthesis of HMF and LA from biomass can be achieved by cascades of reactions as shown in Figure 2.3. In the first reaction, cellulose is hydrolyzed to produce glucose. Subsequently, glucose can be directly dehydrated to HMF or isomerizes to fructose, which can also be dehydrated to HMF. Finally, HMF rehydrates to LA. HMF and LA can be produced from various substrates such as sugar, cellulose, hemicellulose and biomass. Thus, conversion of biomass to HMF and LA can be categorized to 3 major parts. The first is the decomposition of biomass to monomer sugars, the second is the production of HMF from monomer sugars, and the third is the production of LA from HMF. Hydrolysis of cellulose, dehydration of fructose, and rehydration of HMF are generally promoted by Brønsted acids. Isomerization of glucose is generally promoted by Brønsted bases or Lewis acids.

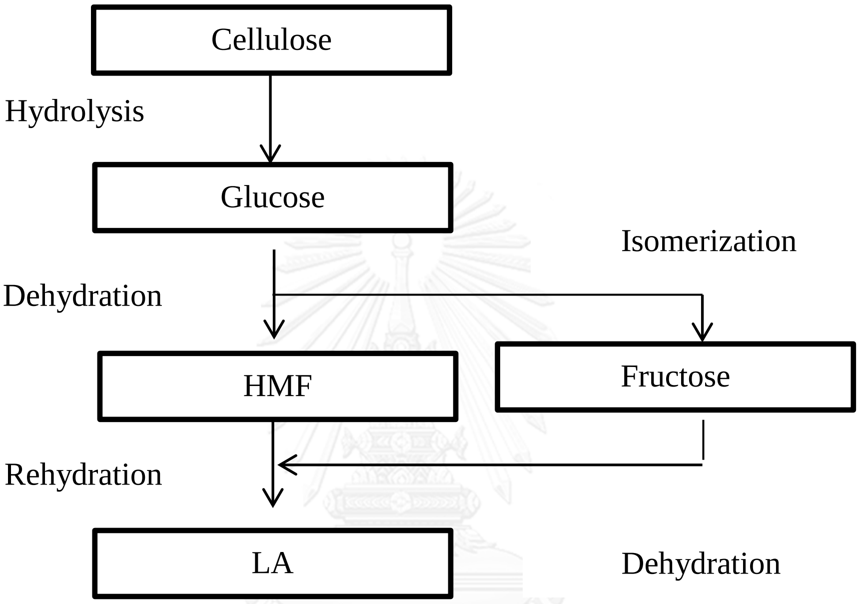


Figure 2.3 Reaction pathways for the conversion of cellulose to HMF and LA

2.4 Cascaded reactions in biomass conversion

2.4.1 Hydrolysis of cellulose

The hydrolysis of cellulose to monomeric sugars (Figure 2.4) is the first step in a bio-refinery. This reaction can be catalyzed by both enzymes such as cellulase or by chemical catalysts such as soluble mineral acids and solid acids.

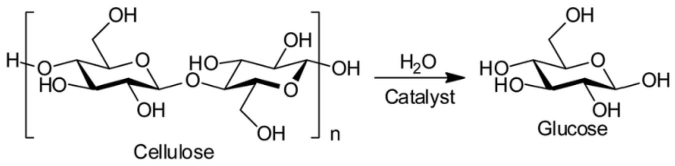


Figure 2.4 Hydrolysis of cellulose (Luterbacher et al., 2014)

2.4.2 Isomerization and dehydration

Glucose and fructose isomerization is a base catalyzed reaction, also known as the Lobry-de Bruyn-van Ekenstein transformation (Figure 2.5 and 2.6).

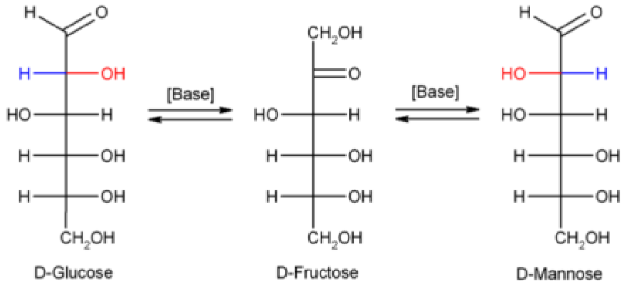


Figure 2.5 Epimerization of hexose.(MARTIN, 1955)

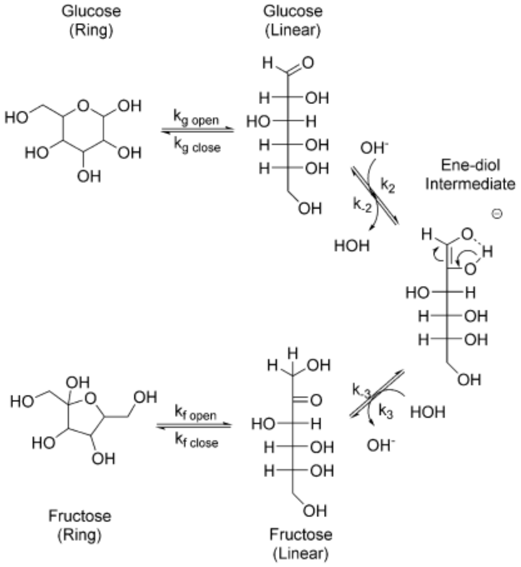


Figure 2.6 Reaction of mechanism for the Base-Catalyzed Isomerization of Glucose to Fructose (Liu et al., 2014).

Glucose isomerization to fructose can generally be catalyzed either Brønsted bases (i.e. alkaline bases and amine) or by Lewis bases. However, monosaccharide is unstable under strong alkaline conditions and degraded into more than 50 different byproducts. It has been widely reported that fructose yields are typically low by using Brønsted bases (<10%) and that high selectivity to fructose can only be obtained at low glucose conversion. On the other hand, amines provide additional advantages as they cannot form cation−ketose complexes, and present a much broader range of pKa values than inorganic bases. They offer significantly more flexibility to optimize the selectivity to fructose, even at high glucose conversion (Liu et al., 2014). The pathways for amine catalyzed glucose isomerization are shown in Figure 2.7.

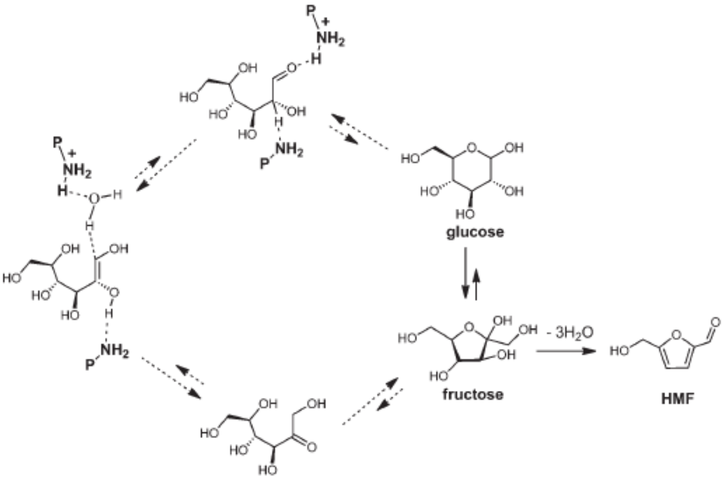


Figure 2.7 Reaction pathways for glucose dehydration in amine system (Cao et al., 2015)

Enzymes (i.e. glucose isomerase) are also potential catalysts for the isomerization of glucose to fructose because of their high selectivity under mild reaction conditions (Yan et al., 2009). Converted directly from glucose, very high yields of HMF (up to ~90 mol%) can be achieved through a proper multistep novel reactor design and separation scheme. Nevertheless, the need to perform multiple and separate processing steps, raise some concerns on the application of a large scale enzymatic process.

Alternative to the above mentioned catalysts, another interesting type of catalyst is that of Lewis acids, particularly metal oxides and metal salts. The former has both Lewis acidic and basic properties, and the latter has both Lewis acidic and brønsted-acidic properties. Both metal oxides and metal salts are efficient catalysts for biomass conversion. Although the activity in biomass conversion of metal salts is higher than that of metal oxides, metal salts are more difficult to separate from product solution. Choudhary et al. (2013) explained that the ion complex ($M_x(OH)_y^{(3x-y)+}$) resulted from the hydrolysis of a metal salt in the presence of water (Equation 1) promote isomerization more efficiently than xM^{3+}, and that hydrolysis, dehydration, and rehydration are promoted by intrinsic Brønsted acidity (yH^+).

$$xM^{3+} + yH_2O \rightleftharpoons M_x(OH)_y^{(3x-y)+} + yH^+ \qquad (1)$$

When Lewis acid catalyst is used for HMF production for biomass in particular, Lewis and Brønsted acidity will be present in the system as a result of hydrolysis, Therefore it can be used alone, or together as another Brønsted acid catalyst to enhance the fructose dehydration. Figure 2.8 shows the the mechanism of glucose isomerization to fructose and further fructose dehydration to HMF, by the action of Lewis acidity and Brønsted acidity, respectively.

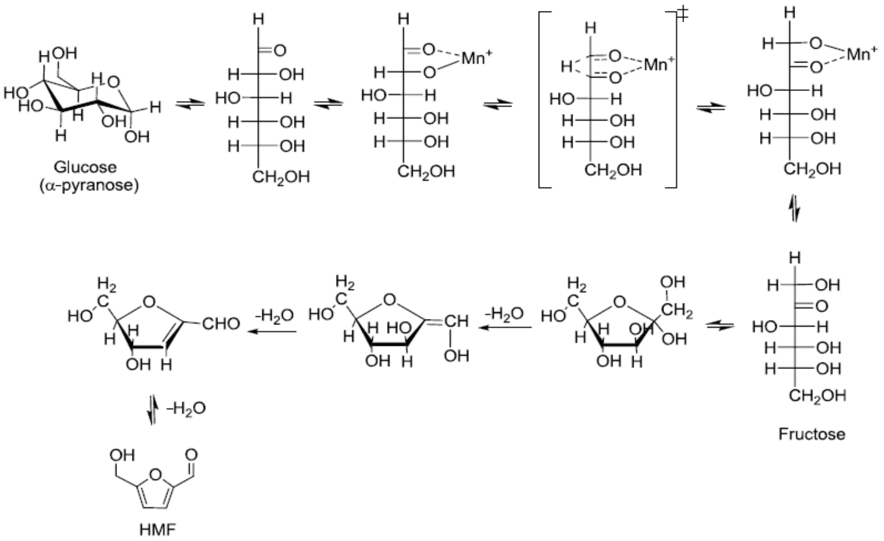


Figure 2.8 Reaction scheme for the conversion of glucose to HMF catalyzed by the combination of a Lewis and a Brønsted acid (Pagan-Torres et al., 2012).

2.4.3 Rehydration

HMF is converted to LA by rehydration reaction. HMF is easily rehydrated with Brønsted acid catalyst (Figure 2.9).

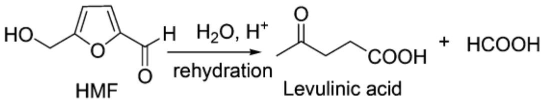


Figure 2.9 Reaction scheme for the conversion of HMF to LA catalyzed by the Brønsted acid

2.5 Process of one-phase system for LA production and biphasic system for HMF production

2.5.1 One phase system for LA production

One phase system is composed of only a reactive phase such as water, organic or mixed medium without salting effect. Some organic and mixed-organic medium, such as acetone, DMSO, Acetone-DMSO, water-acetone, water-acetone-DMSO and so forth, have been shown to improve the selectivity of HMF, nevertheless HMF is easily rehydrated to LA. Therefore, to maximize the LA production, is one-phase system, especially in hot compress water is preferred.

2.5.2 Biphasic system for HMF production

Improvement of HMF yield can be achieved by inhibiting the rehydration of HMF using a biphasic system. A biphasic system is composed of reactive phase (generally an aqueous phase or a mixed medium) and an extractive phase, or an organic phase. HMF is extracted from the aqueous phase to the organic phase in order to avoid both rehydration and side reactions. An organic phase can be 1-butanol, 2-butanol, methyl isobutyl ketone (MIBK), acetone, tetrahydrofuran (THF) and so forth. Salt, such as NaCl, KCl and other inorganic salts, may be introduced to extract HMF. Salt in solution impacts the interaction between solute or solvent and water molecules. As a consequence, the extraction of HMF into the organic is enhanced in a biphasic system modified with inorganic salt.

2.6 Biomass conversion to valuable chemicals (HMF and LA) with Brønsted acidic and basic catalysts

2.6.1 Graphene oxide (GO)

Grapehene oxide is an acid catalyst prepared from oxidation and exfoliation of graphite. The basal plane of graphene oxide, is heavily oxygenated, and is highly populated with hydroxyl (-OH) and epoxide (C-O-C) function groups, while the edge consists of carbonyl (C=O) and carboxylic acid (-COOH) groups like Brønsted acid.

2.6.1.1 Reviews on use of GO in biomass conversion

Wang et al., 2013 studied dehydration of sugar to HMF and then etherification of HMF to 5-ethoxymethylfurfural (EMF) (Figure 2.10) over graphene oxide (GO). Small yields of only 3 and 1 percent of EMF and HMF, respectively (Table 2.1), were produced from glucose. Their results suggested that only the fructose unit in sucrose can be converted into HMF and EMF, and that GO, classified as a Brønsted acid, could not be used as the catalyst for the isomerization of glucose to fructose.

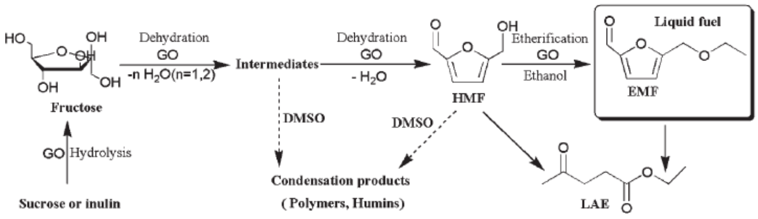


Figure 2.10 The conversion of carbohydrates to EMF catalyzed by GO.

Table 2.1 Production of EMF from various carbohydrates over GO under different conditions (Wang et al., 2013)

Entry	substrate	T(^{o}C)	Cat loading (mg)	Substrate conversion (%)	HMF yield (%)	EMF yield (%)
1[b]	Fructose	100	20	95	9	18
2	Fructose	100	20	98	31	23
3	Fructose	130	20	100	14	64
4	Fructose	130	20	100	9	71
5	Fructose	150	20	100	3	62
6	Fructose	130	20	100	6	67
7	Sucrose	130	20	100	4	34
8	Inulin	130	20	100	7	66
9	Glucose	130	20	99	1	3

[a] Reaction conditions: 0.5 mmol carbohydrate based on the monosaccharide with a specific amount of GO mixed in 0.7 mL ethanol and 0.3 mL DMSO reacted for 24 h. b 0.5 mmol fructose with GO mixed in 1 mL ethanol and reacted at 100 °C for 24 h

2.6.2 Carbon based acid catalyst

Carbon based acid catalyst is a type of Brønsted solid acid catalyst, having (C-COOH) similar to carboxylic group. Carbon based catalyst can be prepared by a 2 step method of (1) carbonization of carbon sources such as glucose or other biomass and (2) functionalization of hydrothermal carbon with acid site. Alternatively, one step process could also be acid promoted simultaneously carbonization and functionalization with carbon in one-pot system.

Carbonization

Carbonization process is conversion of organic chemicals to carbon. It might be done by pyrolysis, incomplete combustion and hydrothermal of carbon sources. For hydrothermal carbonization, the process occurs in water at lower operating temperatures (150-250 °C) than conventional pyrolysis process, which requires higher operating temperatures (400-800 °C). Mechanism of hydrothermal carbonization follows initially the pathways of cellulose conversion (Figure 2.11). Cellulose depolymerizes to glucose, which then converts to HMF. HMF is then polymerized and aromatized to form hydrothermal carbon (HTC). At high temperature (above 200^{o}C) (Matthiesen et al., 2014) , complex carbohydrate such as cellulose is directly carbonized both by melting process as well as by hydrothermal carbonization to HTC. The characteristic structure of HTC is aromatic ring and oxygen functional group, which is suitable for further functionalization (i.e. via sulfonation to obtain HTC (C-SO_3H)) to increase the acidity of the carbon, and thus improve catalytic activity.

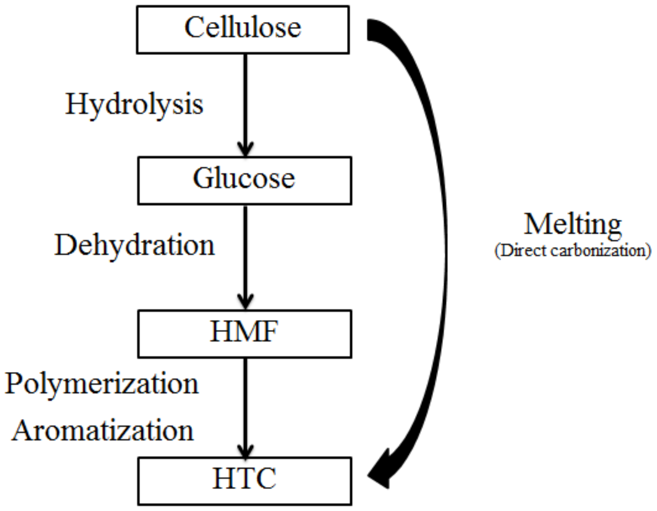


Figure 2.11 Pathways of cellulose to hydrothermal carbon catalyst (Matthiesen et al., 2014)

Functionalization of carbon catalyst

Sulfonation is a commonly used term for functionalization with a sulfonated group (-SO_3H) to increasing acidity of a carbon structure (Figure 2.12). In sulfonation of aromatic structure, direct sulfonation can be carried out in which sulfur trioxide (SO_3) or concentrated sulfuric acid (fuming) are directly reacted with the active species on the aromatic rings of HTCs and form C-SO_3H bonds. Alternatively, sulfonation may also be carried out via reductive alkylation/arylation, in which sulfonic acid containing aryl radical are attached on the surface of carbon materials such as ordered mesoporous carbon, nanotubes, graphite, and graphene (Figure 2.13).

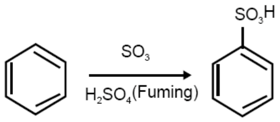


Figure 2.12 Mechanism of functionalization in aromatic structure by sulfonation (Emrani and Shahbazi, 2012)

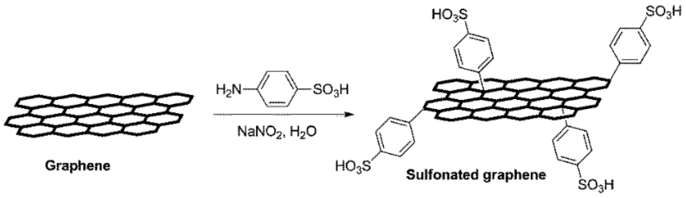


Figure 2.13 Procedure of graphene and reductive alkylation/arylation (Oger et al., 2016)

2.6.2.1 Review of carbon based acid catalyst for biomass conversion

Daengprasert et al. (2011) studied the production of hydroxymethylfurfural (HMF) and furfural from cassava waste, composed of cellulose and hemicellulose, in DMSO/Acetone using a sulfonated carbon-based catalyst or Brønsted acid (-SO_3H). Sulfonated carbon-based catalyst was found to promote hydrolysis of cellulose and hemicellulose and dehydration of fructose and xylose (Figure 2.14). Sulfonated carbon-based catalyst promoted hydrolysis of cellulose (Figure 2.15) and was found from the results that glucose and HMF yields were higher than those without catalyst. The overall glucose yields (Figure 2.15) from hydrolysis with catalyst was approximately 3 times higher than that without catalyst. For glucose dehydration (Figure 2.16), yield of HMF with catalyst was similar to without catalyst, implying that such catalyst can promote hydrolysis but cannot promote glucose dehydration.

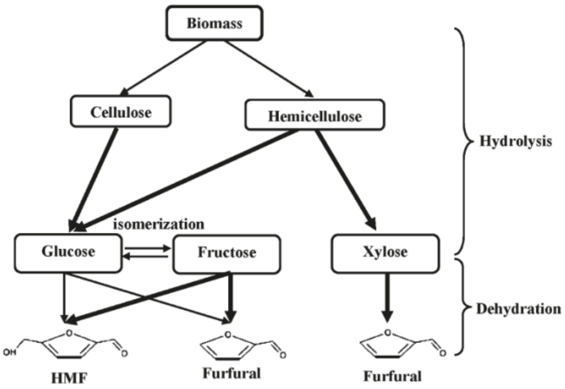


Figure 2.14 Pathway of HMF and furfural production from biomass (➔Stress line mean to Sulfonated carbon-based promote reaction). (Daengprasert et al., 2011)

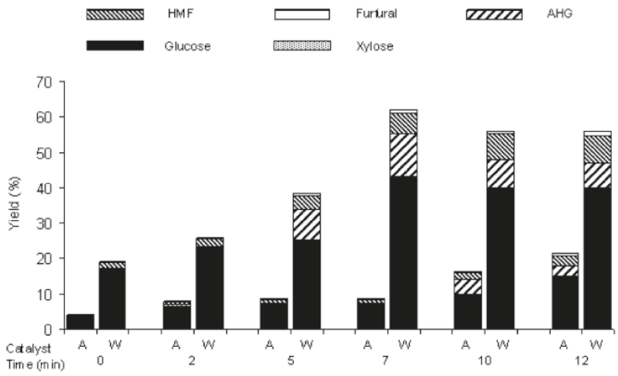


Figure 2.15 Conversion and yield of liquid products at 230 ^{o}C, 10/90 acetone/DMSO (70/30% w/w) to water as medium, with and without catalyst and range of time from 0 to 12 min from the reaction of cellulose.(Daengprasert et al., 2011)

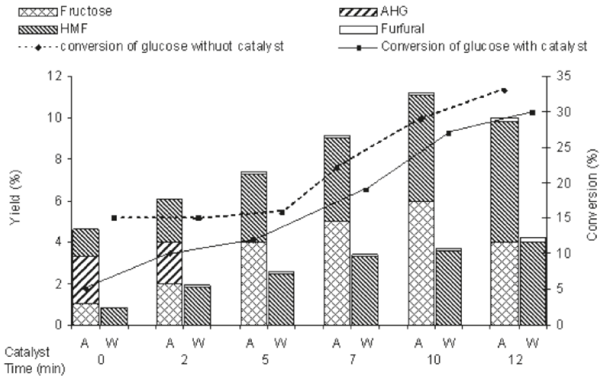


Figure 2.16 Conversion and yield of liquid products at 230^{o}C, 10/90 acetone/DMSO (70/30% w/w) to water as medium, with and without catalyst and range of time from 0 to 12 min from the reaction of glucose.(Daengprasert et al., 2011)

2.6.3 Cation and anion-exchange resins

Ion exchange resins are insoluble chemicals loosely holding ions able to exchange ion with other ions in solution. They are generally synthesized from styrene and different levels of the cross-linking agent divinyl benzene controlling the porosity of the particles. Ion exchange resins have been classified based on the charge on the exchangeable ion (cation or anion) and the ionic strength (strong or weak). For cation exchange resin, strong cation exchange resins contain sulfonic group and weak cation exchange resin contain carboxylic acid group. For anion exchange resin, Strong anion exchange resin contain quaternary ammonium groups such as trialkyl ammonium chloride or hydroxide (Type I), and dialkyl 2-hydroxyethyl ammonium chloride or hydroxide (Type II) and weak anion exchange resin contain ammonium chloride or hydroxide.

2.6.3.1 Review of cation and anion-exchange resins for biomass conversion

Perez et al., (2014) developed a method of sequential conversion of sucrose to HMF catalyzed by cation-exchange and anion-exchange resins that consist of separately individual four steps (Figure 2.17): (step 1) hydrolysis of sucrose , (step 2) first dehydration of fructose, (step 3) isomerization of glucose-to-fructose and (step 4) second dehydration of isomerized glucose. Hydrolysis and dehydration steps were in the presence of an acid (Amberlite IR-120 (H^+)) containing sulfonic acid while isomerization proceeded over base catalyst (Amberlite IRA-400 (OH^-)) or Type I (trialkylbenzyl Ammonium). Extraction of HMF after (step 2) first dehydration of fructose gave 29% yield and after (step 4) second dehydration of isomerized glucose gave 21 % yield. Total yield is 50 % on completion of all reaction steps. They combined of all the processes and acidic and basic in order to achieve the synthesis of 5-HMF starting from sucrose in one-pot synthesis but no HMF was detected (combination failure-Amberlite IR-120 (H^+) and Amberlite IRA-400 reacted to neutralization by acid-base reaction). From Perez et al, (2014), Combination between Amberlite IR-120 (H^+) and Amberlite IRA-400 are shown efficiently HMF production in tedious step but they are failure combination in one-pot system. Recently improvement combination for biomass conversion in one-pot system are such as combination of Lewis acid-base or Brønsted acid and Lewis acid in next section.

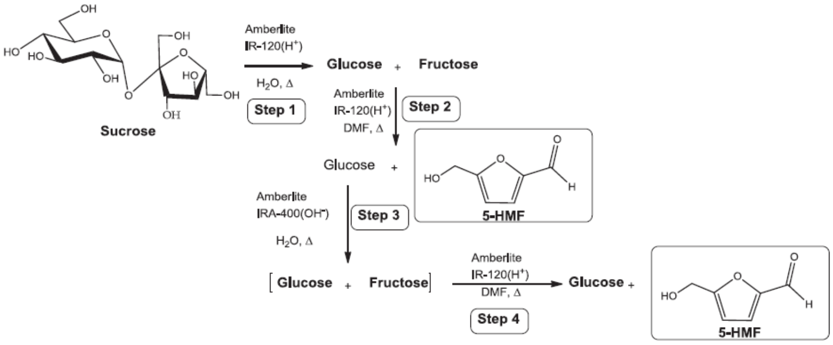


Figure 2.17 Preparation of 5-HMF from sucrose using cation- and anion-exchange resin catalysts. (Pérez-Maqueda et al., 2014)

2.7 Biomass conversion to valuable chemicals with Lewis acid

2.7.1 Metal oxides

Metal oxides are oxides of metals such as group II, III and transition metals. Metal (group II) oxides, such as CaO, MgO, SrO and so forth, are base catalysts normally use to promote isomerization of glucose. Transition metal oxides, such as TiO_2, ZrO_2, Cr_2O_3 and so forth, normally have acid and base properties, promoting hydrolysis, isomerization dehydration, and rehydration.

2.7.1.1 Reviews of use of metal oxides in biomass conversion

Qi et al., 2008 studied the dehydration of glucose and fructose in hot compressed water over TiO_2 and ZrO_2 catalysts. They proposed ZrO_2 is a preferred base catalyst promoting isomerization of glucose and TiO_2 is a preferred acid catalyst promoting dehydration of fructose (Figure 2.18). Both of TiO_2 and ZrO_2 act as Lewis acids as well as Lewis bases, meaning to combination of Lewis acid and base. Therefore, it is possible that both of these catalysts combined could not only promote the isomerization between glucose and fructose, but also improve the formation of 5-HMF form glucose and fructose. Moreover, they reported the synthesis of HMF promoted by TiO_2 and ZrO_2 as catalysts in hot compressed water under microwave irradiation as the heating source. The results show the improvement of product yield and conversion compared to traditional sand bath (SB) heating due to improved heating and cooling efficiency. For example, anatase-TiO_2 (Table 2.2) 27.4% yield of HMF and 73.1% conversion of fructose were obtained under microwave irradiation as compared to 12% yield of HMF and 35.3% conversion of fructose under conventional heating at 200 °C for 3 min.

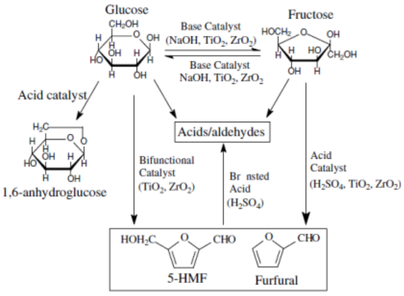


Figure 2.18 Main reaction pathways of glucose and fructose in hot pressed water by different catalysts.(Qi et al., 2008)

Table 2.2 Fructose conversion and products distribution by sand bath (SB) heating and microwave (MW) heating

Heating method	Reaction time (min)	Fructose conversion (%)	HMF (%)	Levunilic acid (%)	Lactic acid (%)	Formic acid (%)	Glucose (%)
SB	3	35.3	12.1	0.0	2.20	0.80	3.60
MW	3	73.1	27.4	0.70	7.00	1.80	5.30
SB	5	65.3	26.9	0.40	5.00	1.30	4.30
MW	5	84.1	33.5	1.00	8.80	2.00	5.30

Conditions: reaction temperature: 200 °C, 2 wt.% fructose aqueous solution, anatase TiO2 as catalyst, substrate to catalyst weight ratio (R) = 2.

Beside ZrO_2 acted as bi-functional catalyst, it improves catalytic activity of ZrO_2 by adding SO_4^{2-} during calcination of ZrO_2. In order insight the influence sulfates (SO_4^{2-}) to zirconia (ZrO_2) for one-pot conversion of glucose to HMF. Osatiashitani et al., 2014 studied effect of sulfates to activity of ZrO_2 in water medium at mild condition. They observed that low concentration of SO_4 (Figure 2.19a) coverage correlates with high fructose yields, indicating efficient isomerization of glucose at low SO_4, similar to that seen with pure ZrO_2. In contrast, high SO_4 (Figure 2.19) coverage (Brønsted acid site densities) suppressed glucose isomerization while enhanced dehydration of the fructose intermediate. Thus, the loss of basicity and Lewis acidity upon zirconia sulfation inhibits glucose to fructose isomerization but promotes the Brønsted acid catalyzed fructose to HMF. They concluded that if ZrO_2 saturated with sulfate, SO_4^{2-}/ZrO_2 property would be similar to Brønsted acid character that is least efficient for HMF formation. On the contrary, if catalyst was low sulfated, SO_4^{2-}/ZrO_2 property was mixed Lewis acid and base surface sites that effectively isomerize glucose to fructose but poorly fructose dehydration. Suitable content of SO_4 (0.3 ML) is key to successful generation of bi-functional catalyst with combination between optimum acid and base character (Figure 2.20).

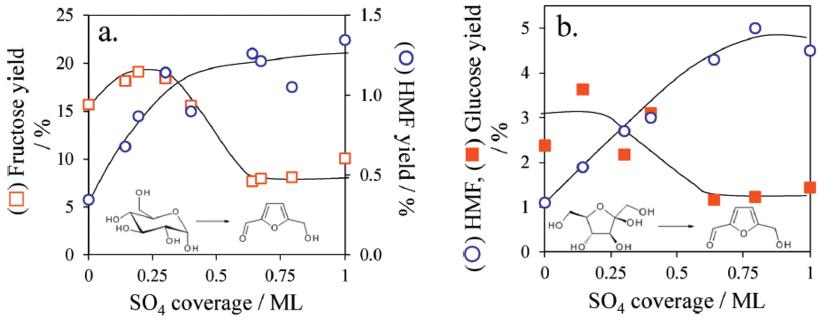


Figure 2.19 Yields of a) fructose and 5-HMF during SO_4/ZrO_2 catalysed glucose isomerization and dehydration and b) glucose and 5-HMF during SO_4/ZrO_2 catalyzed fructose isomerization after 6 h reaction at 100 °C

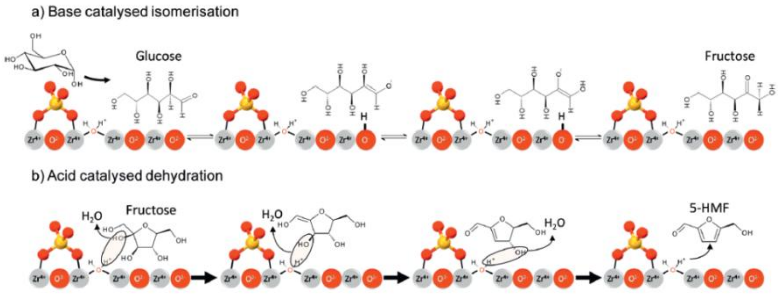


Figure 2.20 Bi-functional surface catalyzed mechanism for a isomerization of glucose to fructose over basic O^{2-} sites of monoclinic ZrO_2 (Lewis acidic Zr^{4+} may help stabilise the enolate intermediate) and b) dehydration of fructose to 5-HMF over Brønsted acid sites present in submonolayer SO_4/ZrO_2 catalysts.(Osatiashtiani et al., 2014)

2.7.2 Metal salts

Metal salts are salts of group I, II, III and transition metals. Similar to the effect of ionic liquid, salts of group I and II metals, such as NaCl, LiCl, $CaCl_2$, and so forth, improve the selectivity of HMF, the same by disrupting the hydrogen bond of cellulose and by extracting HMF into an organic phase of a biphasic system. Unlike the salts of group I and II which metals cannot directly promote reaction, due to the Lewis and intrinsic Brønsted acidity, salts of metal (group III, transition) such as $AlCl_3$, $CrCl_3$, $MnCl_2$, $CdCl_2$ and so forth, are efficient catalysts for biomass conversion. Cation of metal salt is impact to cellulose conversion (Peng et al., 2010) but anion of metal salt were found that property is similar such as HMF yield and PH using $CuCl_2$ similar to that using $CuSO_4$(Fachri et al., 2015).

2.7.2.1 Review of metal salt for biomass conversion

Peng et al, 2010 explored catalytic activities of various metal chlorides such as common metal chloride and transition metal chloride for the conversion of cellulose to LA in liquid water at high temperatures. They found that different types of metal chlorides effect to yields of LA at the same condition. For cellulose conversion, LA promoted by $CrCl_3$ (Figure 2.21) had the highest yield. However, LA yield promoted by $AlCl_3$ (Figure 2.22) was higher than those promoted by $CrCl_3$ for glucose conversion. They concluded that $AlCl_3$ is more efficient for promoting the isomerization of glucose to fructose, but $CrCl_3$ is more efficient than $AlCl_3$ for catalyzing hydrolysis of cellulose. Cellulose was easily depolymerized by $CrCl_3$ catalyst so that it was more effortlessly changed to abundant glucose, and then to LA. Yield of LA was dropped (Figure 2.23) due to the increasing temperature above 200^{o}C because LA is unstable above 230 °C, which would be dehydrated to unsaturated lactones. The optimal yield of LA was found to be 67 mol % promoted by CrCl. For Advantage of metal salt, they found that almost of chromium metal form convert to metal oxide in solid phase and only a small proportion of Cr^{3+} in liquid phase, thus easily separated from the reaction products.

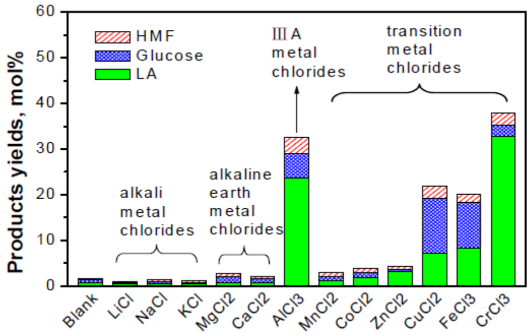


Figure 2.21 Catalytic effects of metal chlorides on the conversion of cellulose (Peng et al., 2010) Reaction conditions: 2 wt % cellulose, 0.01 M metal chlorides, temperature 180 °C, time 120 min

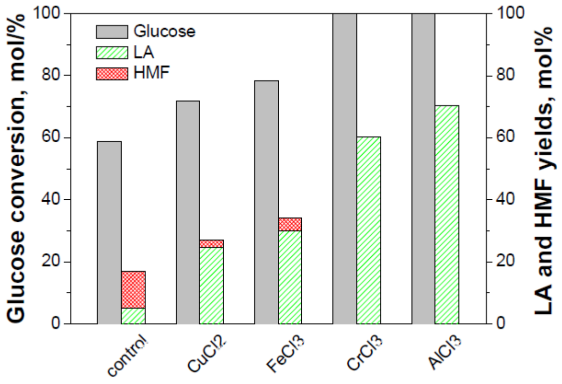


Figure 2.22 Catalytic effects of metal chlorides on the conversion of glucose (Peng et al., 2010) Reaction conditions: 2 wt % glucose, 0.01 M metal chlorides, temperature 180 °C, time 120 min

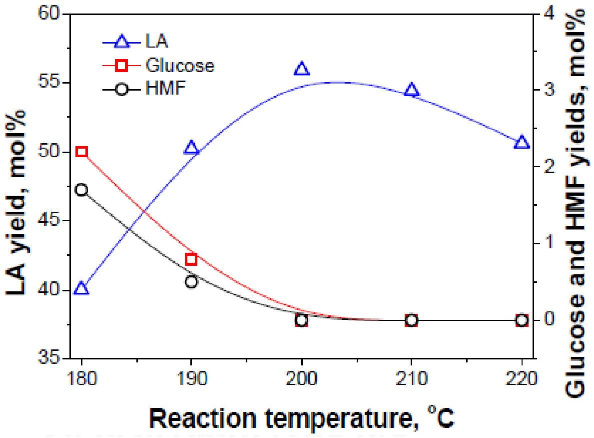


Figure 2.23 Catalytic effects of metal chlorides on the conversion of glucose (Peng et al., 2010) Reaction conditions: 2 wt % cellulose, 0.01 M chromium chloride, time 180 min

An insight to the interplay of Lewis and Brønsted acid in HMF and LA acid production from glucose and fructose in an aqueous Medium was given by the work of Choudhary et al (2013) indicated that the hydrolyzed Cr(III) complex $[Cr(H_2O)_5OH]^{2+}$ (Equation 2) is the most active Cr species in glucose isomerization and probably acts as a Lewis acid−Brønsted base bifunctional site. Equation 2 provides the rationalization as to how Lewis acid catalysts (various metal salts) used for isomerization of aldoses to ketoses drive Brønsted acid-catalyzed dehydration of ketoses to their corresponding furans. Intrinsic Brønsted acidity generated by $CrCl_3$ drives sufficient dehydration and rehydration reactions without external addition of Brønsted acid. However, $CrCl_3$ adversely affects both fructose conversion (Figure 2.24a and 2.24b) to HMF and HMF rehydration (Figure 2.25) to levulinic and formic acids. Negative effect of $CrCl_3$ in fructose conversion and HMF rehydration, due to undesired product promoted by $CrCl_3$, may be improved by adding extrinsic Brønsted acid (such as use of combined $CrCl_3$ and HCl), such as shown in Figure 2.24a and 2.24c.

$$[Cr(H_2O)_6]^{3+} + H_2O \leftrightarrow [Cr(H_2O)_5]OH^{2+} + H_3O^{3+} \qquad (2)$$

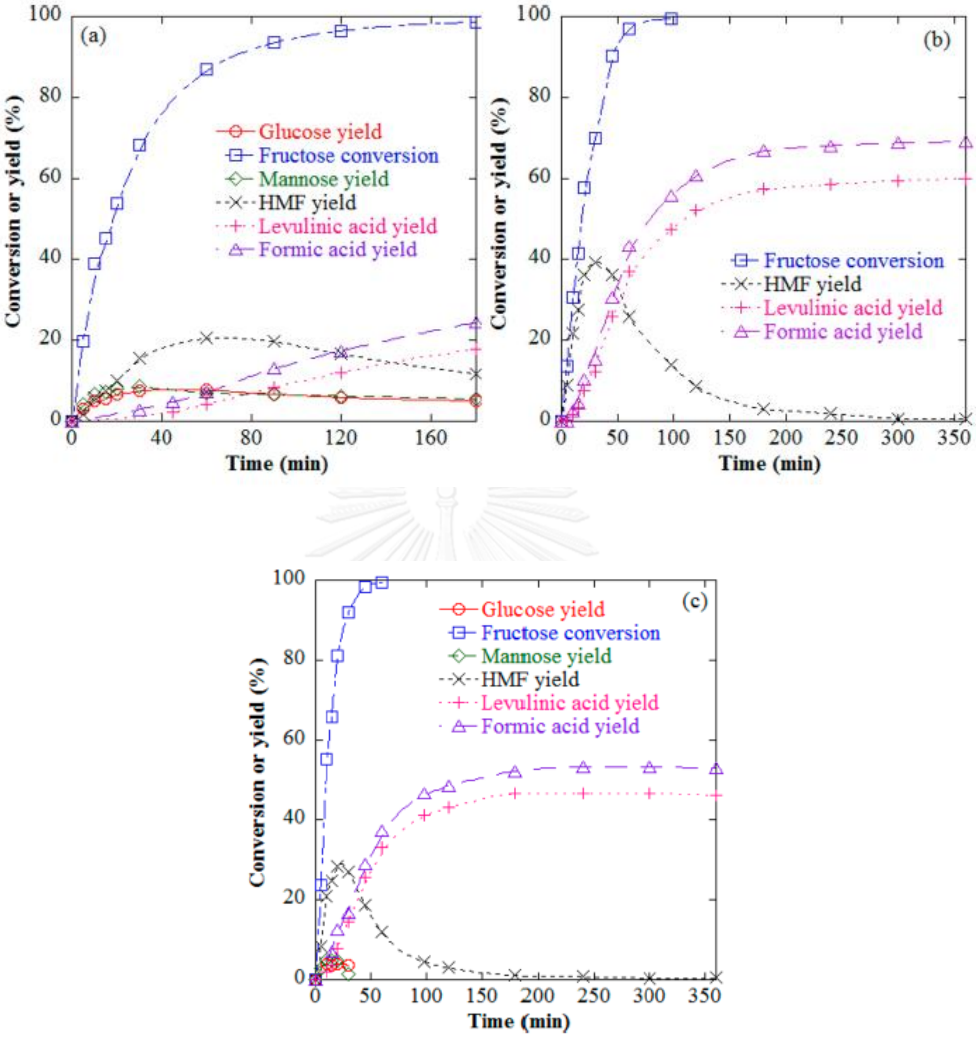


Figure 2.24 Fructose transformation to HMF and levulinic acid using (a) CrCl3 and (b) HCl (c) $CrCl_3$ with HCl as catalysts. Reaction conditions: initial reactant ~10 wt %, HCl (0.1 M, when used), Cr (when used)-to-fructose molar ratio of 3:100, and 413 K.(Choudhary et al., 2013)

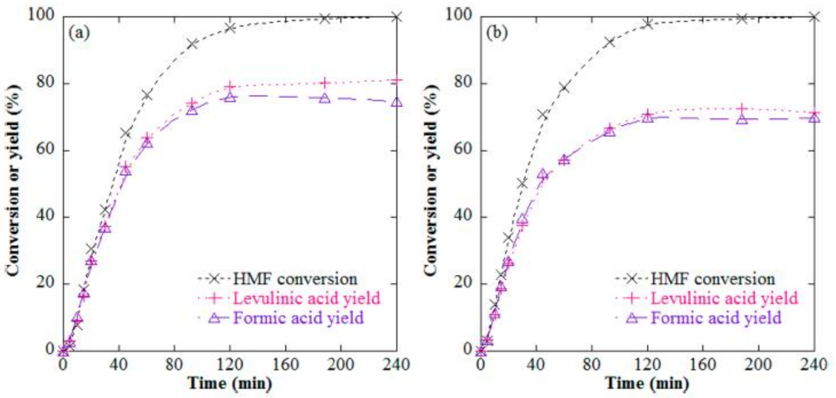


Figure 2.25 HMF transformation to levulinic and formic acids using (a) HCl and (b) HCl with CrCl3 (Cr-to-HMF molar ratio of 3:100). Reaction conditions: initial reactant ~1 wt %, HCl (0.1 M), and 413 K.(Choudhary et al., 2013)

Extrinsic Brønsted acids not only suppress side reaction generated by $CrCl_3$ and improve fructose dehydration and HMF rehydration, but extrinsic Brønsted acids also impede active Cr for glucose isomerization. For example, Rate of glucose consumption drops significantly in the presence of $CrCl_3$ with the addition of HCl (24% conversion in 10 min; see Figure 2.26b) compared to the case with $CrCl_3$ only (32% conversion in 10 min; see Figure 2.26a). That is, Brønsted acidity inhibits the Lewis acid-catalyzed isomerization of aldoses. Suitable composition of Lewis acid and Extrinsic Brønsted acid have synergistic effect on the synthesis of HMF and LA from various bio-based materials. The interplay between the acids indicates that, from a practical standpoint, optimizing the concentrations of Lewis and Brønsted acids in the cascade reactions to maximize the desired products yield is feasible and advisable. For example, high yields of glucose to LA in a single aqueous phase (46%) and to HMF in a biphasic system (59%) were achieved at a moderate reaction temperature (413 K) by combining $CrCl_3$ (Lewis acid) with HCl (Brønsted acid).

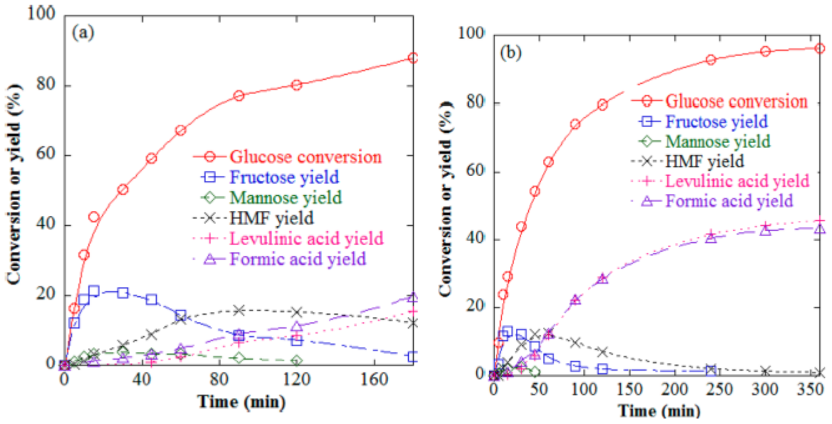


Figure 2.26 Glucose conversion using (a) $CrCl_3$, (b) CrCl3 and HCl as a catalyst in single aqueous phase (Choudhary et al., 2013)

In continuum to the work of Choudhary, Swift et al, 2015 studied kinetic model for the tandem conversion of glucose to 5- hydroxymethylfurfural (HMF) through fructose in aqueous $CrCl_3$–HCl solution, whose reaction networks are shown in Figure 2.27. The solid lines simulate the reactions related to the Brønsted acid chemistry.

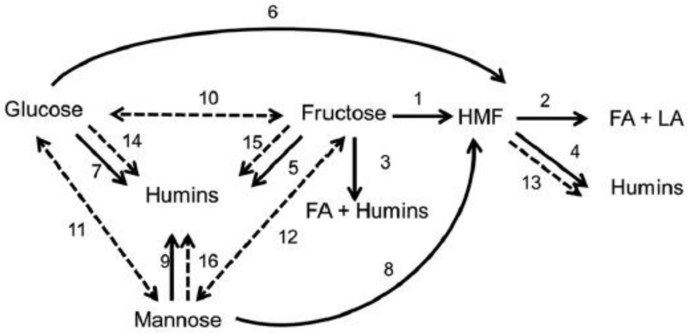


Figure 2.27 Reaction network for tandem reaction of glucose conversion to HMF by CrCl3 and HCl in aqueous phase (Swift et al., 2015)

Besides the effect of Brønsted acids on the rate of Lewis acid-catalyzed sugar isomerization, the authors found that Lewis acid catalysts also affect the rate of fructose dehydration and HMF degradation indirectly by promoting new paths leading to humins (Figure 2.28). Almost all humins were generated from either fructose (>50% from Lewis acid-catalyzed reactions) or glucose (25–40% from Lewis acid-catalyzed reactions).

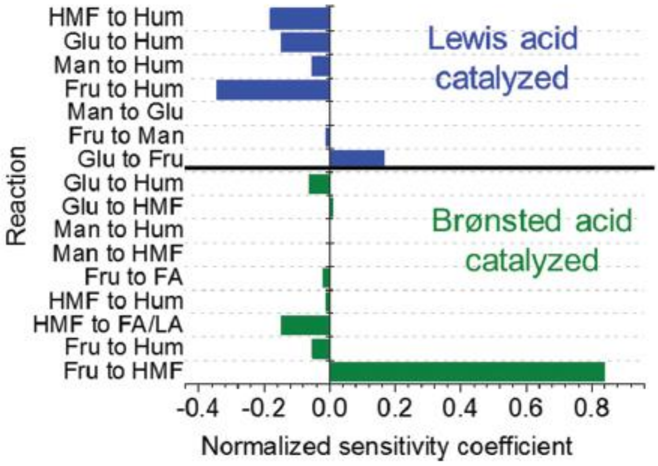


Figure 2.28 Normalized sensitivity coefficient of HMF selectivity after 5 h to rate constants of each reaction at 130 °C with 5 mM CrCl3. (Swift et al., 2015)

The additional HCl would be beneficial if the rate of fructose dehydration improved HMF selectivity is faster than rate at which glucose isomerization is retarded. Increasing concentration of HCl, the extrinsic Brønsted acid, (Figure 2.29a) decreased glucose isomerization, while on the other hand, increasing concentration of HCl could also increase HMF yield due to the increase fructose dehydration. From this study, the increase in HCl concentration from 0 to 0.01 molar (Figure 2.29b) increased HMF yield, but in 0.1 molar range of concentration, HCl decreased HMF yield. From this study, it was concluded that adjusting the HCl concentration should be the most influential factor on the HMF selectivity.

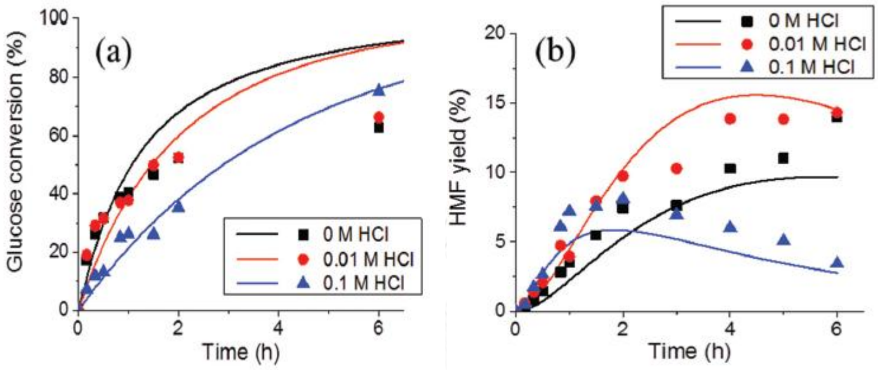


Figure 2.29 Normalized sensitivity coefficient of HMF selectivity after 5 h to rate constants of each reaction at 130 °C with 5 mM $CrCl_3$. (Swift et al., 2015)

Yao et al, studied HMF from sucrose in the presence of the Brønsted-Lewis acidic ionic liquids (ILs). Combination between Brønsted acid and Lewis acid IL 1-(3-sulfonic acid)-propyl-3-methylimidazole chlorochrominate [HO_3S-(CH2)3-mim]Cl-CrCl3 (molar fraction of CrCl3 x = 0.55) confirm that adding extrinsic Brønsted acid improves HMF yield (see entry 3 and entry 13 of Table 2.3). This combination resulted in good catalytic property and yield of product (78.7%). The type of acidity of ILs played a significant role in the efficiency of the reaction. The Brønsted-Lewis acidic sites of IL could selectively catalyze the protonation, dehydration, and deprotonation dehydrogenation in the reaction, and a synergetic effect of Brønsted and Lewis acid sites enhanced the catalytic performance of the IL.

Table 2.3 Effects of catalysts on the reaction results.(Yao et al., 2016)

Entry	Catalyst	H_0	Conversion (%)	Yield (%)
1	Blank	-	-	0
2	$[C_4mim]Cl$	-	95.0	14.6
3	$[C_4mim]Cl-CrCl_3$ (x=0.55)	-	92.9	37.1
4	30 wt% H_2SO_4	-1.53	96.5	46.6
5	$[HO_3S-(CH_2)_3-mim]Cl$	2.91	92.6	48.7
6	$[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$ (X= 0.33)	3.21	95.8	70.2
7	$[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$ (X= 0.55)	2.81	96.0	77.3
8	$[HO_3S-(CH_2)_3-mim]Cl-ZnCl_2$ (X= 0.60)	2.62	94.9	73.6
9	$[HO_3S-(CH_2)_3-mim]Cl-FeCl_3$ (X= 0.33)	2.84	94.9	60.7
10	$[HO_3S-(CH_2)_3-mim]Cl-FeCl_3$ (X= 0.55)	2.70	95.1	65.9
11	$[HO_3S-(CH_2)_3-mim]Cl-FeCl_3$ (X= 0.60)	2.64	95.1	66.1
12	$[HO_3S-(CH_2)_3-mim]Cl-CrCl_3$ (X= 0.33)	2.75	96.4	74.8
13	$[HO_3S-(CH_2)_3-mim]Cl-CrCl_3$ (X= 0.55)	2.56	97.7	78.7
14	$[HO_3S-(CH_2)_3-mim]Cl-CrCl_3$ (X= 0.60)	2.46	95.7	76.7

[a]Sucrose 2.0g, dimethyl sulfoxide 20 mL, catalyst 2.0g, T=200°C, t = 30min

Wang et al. (2012) studied the production of 5-hydroxymethylfurfural (HMF) from sucrose in the presence of the combination of metal chlorides and ammonium halides (acid salt) under mild conditions. Yield of HMF from sucrose was 87% obtained with a catalyst system combination of $CrCl_3$ and NH_4Br at 100°C for 1.0 h in

N,N-dimethylacetamide (DMAc) solvent (Table 2.4). It is confirmed that combination of chromium chlorides and ammonium halides is synergy effect.

Table 2.4 Dehydration of sucrose with different systems (Wang et al., 2012)

Entry	Catalyst	Promoter[b]	Yield[c] (%)
1	$CrCl_3$	No	66
2	$CrCl_3$	LiCl	64
3	$CrCl_3$	NaCl	67
4	$CrCl_3$	KCl	63
5	$CrCl_3$	LiBr	77
6	$CrCl_3$	NaBr	79
7	$CrCl_3$	KBr	77
8	$CrCl_3$	NH_4Cl	79
9	$CrCl_3$	NH_4Br	87
10	$CrCl_3$	NH_4I	73
11	$SnCl_4$	NH_4Br	66
12	$SnCl_4$	NH_4Br	48
13	$FeCl_3$	NH_4Br	42
14	No	NH_4Br	40

[a] Reaction conditions: 1.0 g sucrose, 9.5 mol % metal chloride, in 10 mL of DMAc, reaction time 1 h, temperature 100^{o}C.

[b] The concentration of the promoter was 0.16 M.

[c] The results were obtained by HPLC analysis.

Jing et al. (2016) studied cellulose conversion to formic acid and levulinic acid using a combination of $CrCl_3$ and CO_2 (carbonic acid). Carbonic acid can be used as a low-cost acid to replace mineral acids such as H_2SO_4, HCl, and H_3PO_4 and organic acids such as $C_6H_6O_3S$, $H_2C_2O_4$, and Cl_3CCOOH. There is a significant synergistic effect between in situ carbonic acid from CO_2 and $CrCl_3$ on the highly effective conversion of cellulose into formic acid (FA) and levunilic acid (LeA) simultaneously via hydrolyzing cellulose to glucose, isomerizing glucose to fructose, dehydrating fructose to HMF, and rehydrating HMF to FA and LeA in a one-pot way. High yields of FA (49%) and LeA (32%) could be obtained from cellulose at a moderate condition, which were comparable or even superior to other catalysis systems (Figure 2.30).

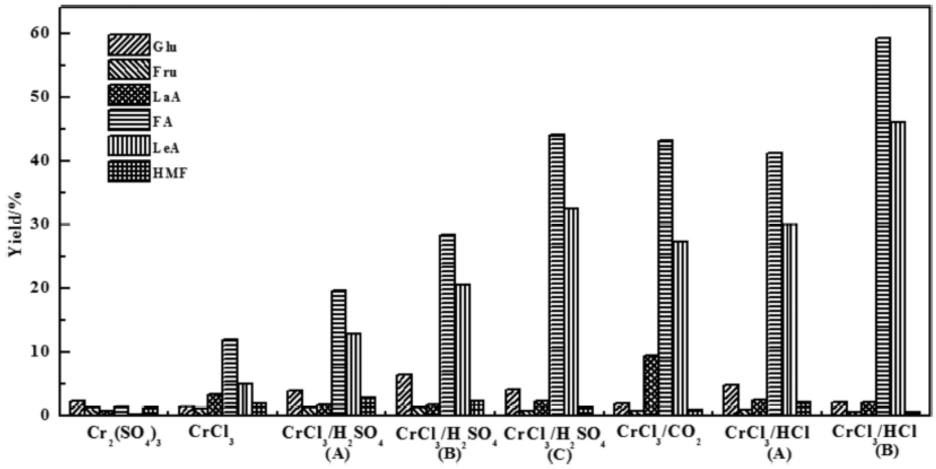


Figure 2.30 Yields of products from cellulose HTCs catalyzed by $CrSO_4$, $CrCl_3$, $CrCl_3/H_2SO_4$ (A), $CrCl_3/H_2SO_4$ (B), $CrCl_3/CO_2$, $CrCl_3$/HCl (A), and $CrCl_3$/HCl (B). Reaction conditions: initial reactant ~10%, Cr^{3+} to cellulose molar ratio of 2.7:100, H_2SO_4 (A): 0.05 mol/L, H_2SO_4 (B): 0.1 mol/L, H_2SO_4 (C): 0.25 mol/L, HCl (A): 0.1 mol/L, HCl (B): 0.25 mol/L, 4 MPa CO_2, 160°C, 90 min.(Jing et al., 2016)

Key of biomass conversion to HMF and LA is isomerization of glucose to fructose, which would be more easily dehydrated. However, Brønsted acid cannot promote isomerization. Other acid such as Lewis acids can efficiently isomerizes glucose, however hydrolysis, dehydration and rehydration promoted by Lewis acid is less efficient than by Brønsted acid. Brønsted base and Lewis base is also promote isomerization of glucose. Combination of Brønsted acid, Brønsted base, Lewis acid or Lewis base provide improvements on biomass conversion to HMF and LA Brønsted acid to Lewis acid is synergy effect. Brønsted acid such as mineral acids and organic acid is high corrosion and is not environment which replace by CO_2. In addition to CO_2, Hydrothermal carbon acid catalyst is considering environments and is not corrosive. Hydrothermal carbon catalyst prepared from carbon material such biomass, sugar and so forth. These materials are abundant in agriculture country. Besides valuable chemicals, these materials are converted to hydrothermal carbon acid catalyst for Brønsted acid improving efficient Lewis acid. Combination of hydrothermal carbon catalyst (Brønsted acid) and Lewis acid has not been reported. Combination of Hydrothermal carbon catalyst and Lewis $acid_3$ are investigated that confirmed synergy effect between heterogeneous and homogenous catalyst similar to literature review (Combination of homogenous catalyst)

CHAPTER III
MATERIALS AND METHODS

3.1 Materials and Chemicals

Cellulose powdered was purchased from HIMEDIA Company. Glucose, fructose, 5-(hydroxymethyl)furfural (HMF), levulinic acid (LA), concentrated sulfuric acid (98%), methyl isobutyl ketone (MIBK),2-butanol, acetone, sodium chloride (NaCl) and chromium chloride (hexahydrate) was purchased from Wako Pure Chemical Company (Osaka).

3.2 Preparation of hydrothermal carbon-based acid catalyst from glucose (HTCG-Sul)

To prepare carbon-based acid catalyst (HTCG-Sul), 2 steps of hydrothermal carbonization and acid functionalization were required. For hydrothermal carbonization, 30 g of glucose and 300 ml of deionized water were mixed in SUS-316 stainless steel closed batch reactor and heated at 220°C for 6 hours. After reaction, the black solid sample or hydrothermal carbon (HTCG) was washed by water, ethanol, and acetone and each step of washing with sonication for 1 hour. Hydrothermal Carbon (HTCG) was filtered and dried at 110°C overnight. The dried HTCG was then used for the second step of acid functionalization. For the acid functionalization, 10 grams of HTCG was functionalized with concentrated sulfuric acid at 150°C for 15 hours. The solids were washed repeatedly with hot distilled water until no acid ions were detected. The solid acid catalysts (HTCG-Sul) were dried at 110°C overnight and then ground to powder.

3.3 Cellulose conversion for HMF and LA production

The apparatus used for this work is shown in Figure 3.1, which consists of 8.8 ml SS 316 stainless steel reactor, a furnace heater, and a temperature controller. A furnace heater is composed of a preheating oven and a holding oven. For a typical run, cellulose (2 wt. %) will be charged into the reactor. The reactor was then heated from room temperature to desired temperature such as 160^{o}C, 180^{o}C, 200^{o}C and 220^{o}C by fixing temperature of the preheating oven (T_o) at 460oC. When the inside temperature of reactor (T_1) is reached to desired temperature, the reactor was then moved from the preheating oven to the holding oven setting temperature at desired temperature, to continue controlled inside temperature of reactor equivalent to desired temperature and starting measure reaction time. After completed reaction, reactor was quenched in a water bath and products in liquid phase were analyzed by HPLC

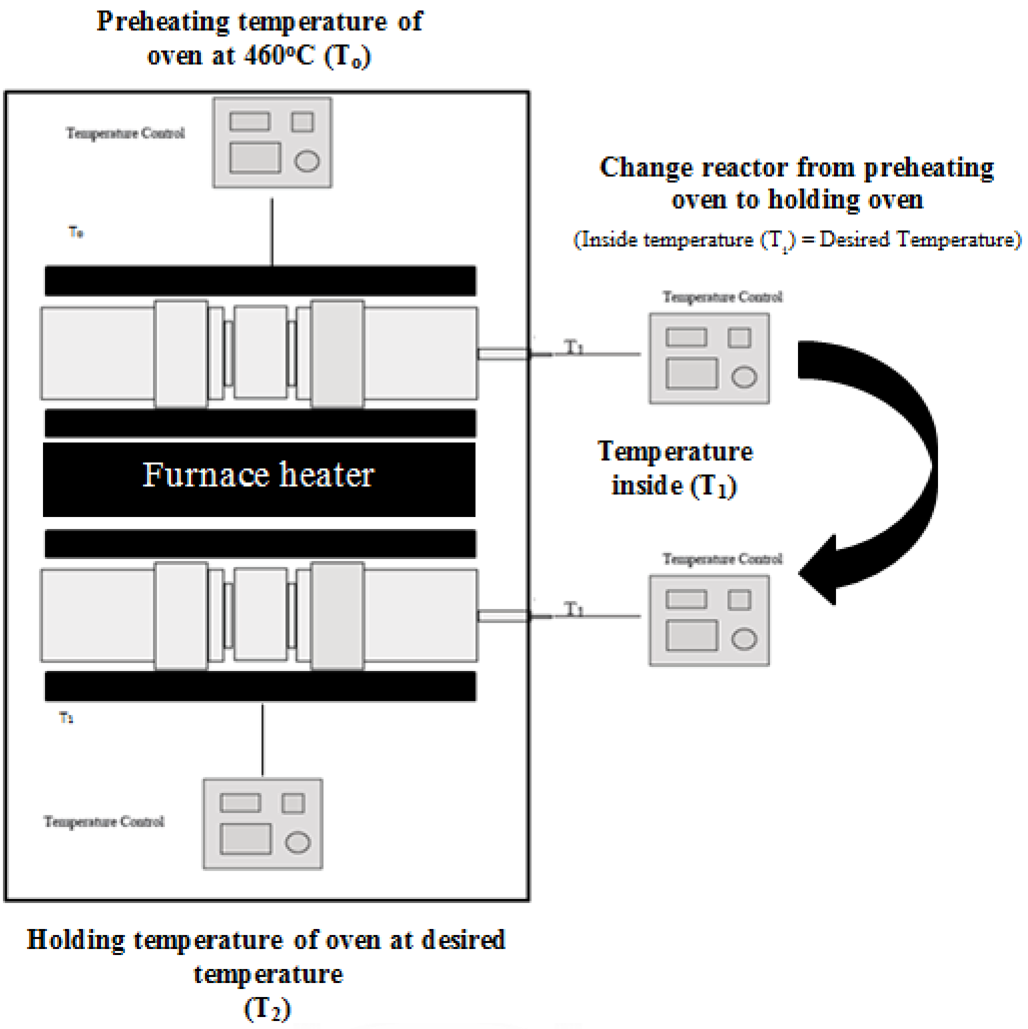


Figure 3.1 Experiment set

3.3.1 One phase system

For one phase system, 0.1 g of cellulose (2 wt. %) was mixed with 5 ml of varied concentration of suitable Lewis acid and varied mass of hydrothermal carbon acid catalyst in the stainless-steel reactor. The reaction was conducted as followed previous procedure. The effect of reaction parameters on product yield including temperature, time, concentration of Lewis acid and HTCG-Sul dosage were determined and summarized in Figure 3.2 and 3.3. We selected each reaction parameters based on HMF yield for applying to biphasic system improved HMF yield.

-Selection of Lewis acid

Cellulose (2 wt. %) was mixed with 0.005 molar of varied metal chloride catalyst ($FeCl_2$, $FeCl_3$, $CoCl_2$, $MnCl_2$, $CdCl_2$, and $CrCl_3$) in the stainless-steel reactor at 200°C for 5min.

-Evaluate biomass conversion with combination of suitable Lewis acid and HTCG-Sul

Cellulose (2 wt. %) was mixed with or 0.005 molar of suitable metal chloride catalyst and 5 wt. % of HTCG-Sul in stainless-steel reactor at 200°C for 5 min. HMF and LA yield compared with non-catalytic, only HTCG-Sul, only metal chloride and combination of metal chloride and HTCG-Sul.

-Determine effect parameters to HMF and LA

Cellulose (2wt. %) was mixed with combination suitable metal chloride catalyst varied concentration from 0 to 0.02 molar and HTCG-Sul dosage varied from 0 to 40%wt (mass of HTCG-Sul/mass of cellulose) in stainless-steel reactor varied temperature from 160°C to 220°C and time from 0 to 60 min.

3.3.2 Biphasic system

For biphasic system, cellulose 0.04 g (2 wt. %) mixing with 2 ml solution of suitable metal chloride with different of composition of MIBK, 2-Butanol, Acetone at selected condition from the previous studied (one phase system based on HMF yield) and reaction was conducted as followed previous procedure. and then we studied effect time in effect composition of biphasic system summarized in Figure 3.4. Products in organic and aqueous phase were analyzed by HPLC.

-Effect of composition

Cellulose (2 wt. %) mixing with 2 ml solution of Lewis acid with composition of extractive phase, mixing medium and salt at selected condition of one-phase system.

Type1: MIBK 1.4 ml, 2-butanol 0.6 ml (extractive/reactive 1:1)

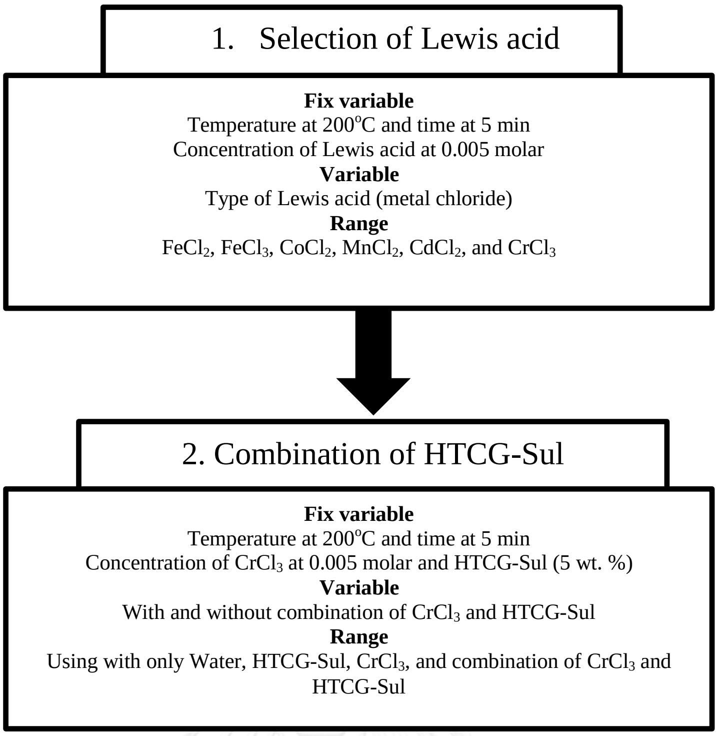
Type 2: MIBK 2.8 ml, 2-butanol 1.2 ml (extractive/reactive 1:1)

Type 3: MIBK 1.4ml, 2-butanol 0.6 ml, acetone 2ml (extractive/reactive /acetone 1:1:1)

Type 4: MIBK 1.4ml, 2-butanol 0.6ml, acetone 2 ml with salt (NaCl) 0.2g (10 wt. %) (extractive/reactive/acetone 1:1:1 with salt 10 wt. %)

-Effect of time

Cellulose (2 wt. %) mixing with 2 ml solution of Lewis acid with suitable composition of organic type followed selected condition of one phase system varied time from 5 to 90 min.



1. Selection of Lewis acid

Fix variable
Temperature at 200°C and time at 5 min
Concentration of Lewis acid at 0.005 molar
Variable
Type of Lewis acid (metal chloride)
Range
$FeCl_2$, $FeCl_3$, $CoCl_2$, $MnCl_2$, $CdCl_2$, and $CrCl_3$

2. Combination of HTCG-Sul

Fix variable
Temperature at 200°C and time at 5 min
Concentration of $CrCl_3$ at 0.005 molar and HTCG-Sul (5 wt. %)
Variable
With and without combination of $CrCl_3$ and HTCG-Sul
Range
Using with only Water, HTCG-Sul, $CrCl_3$, and combination of $CrCl_3$ and HTCG-Sul

Figure 3.2 Procedure and condition of cellulose conversion in one phase system

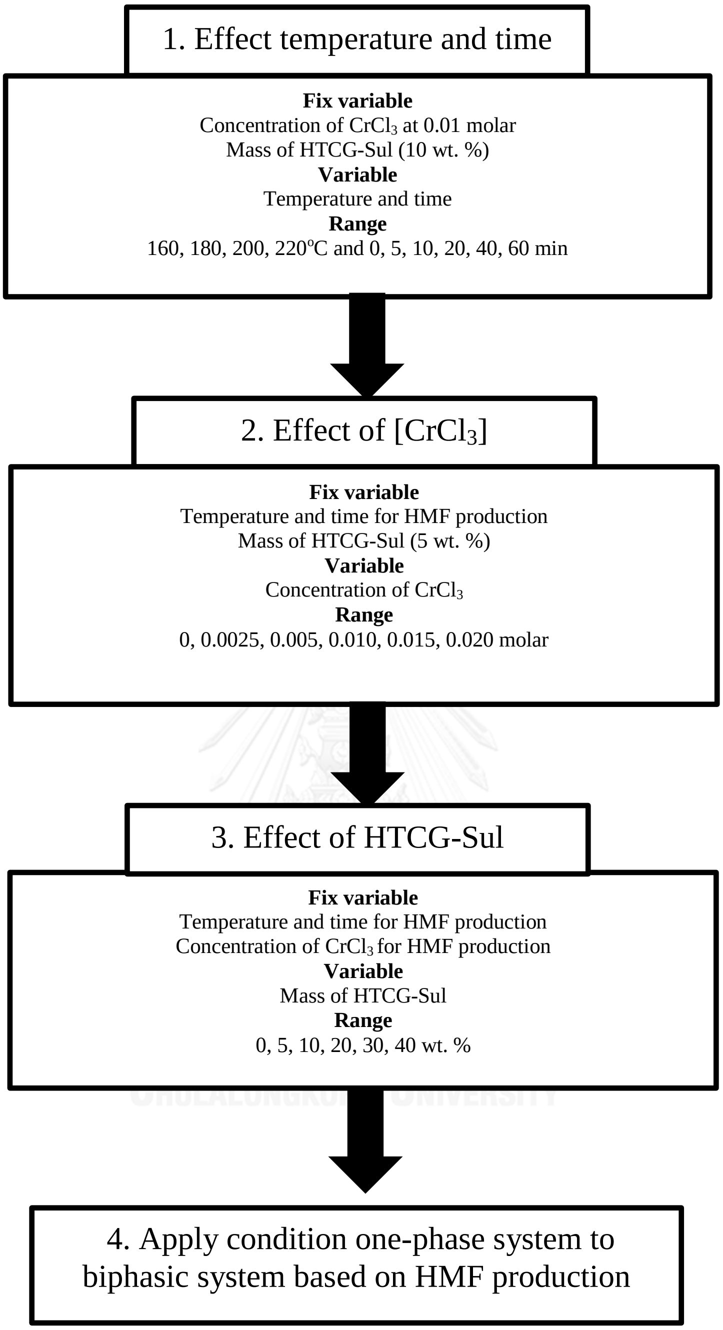


Figure 3.3 Procedure and effect of cellulose conversion in one phase system

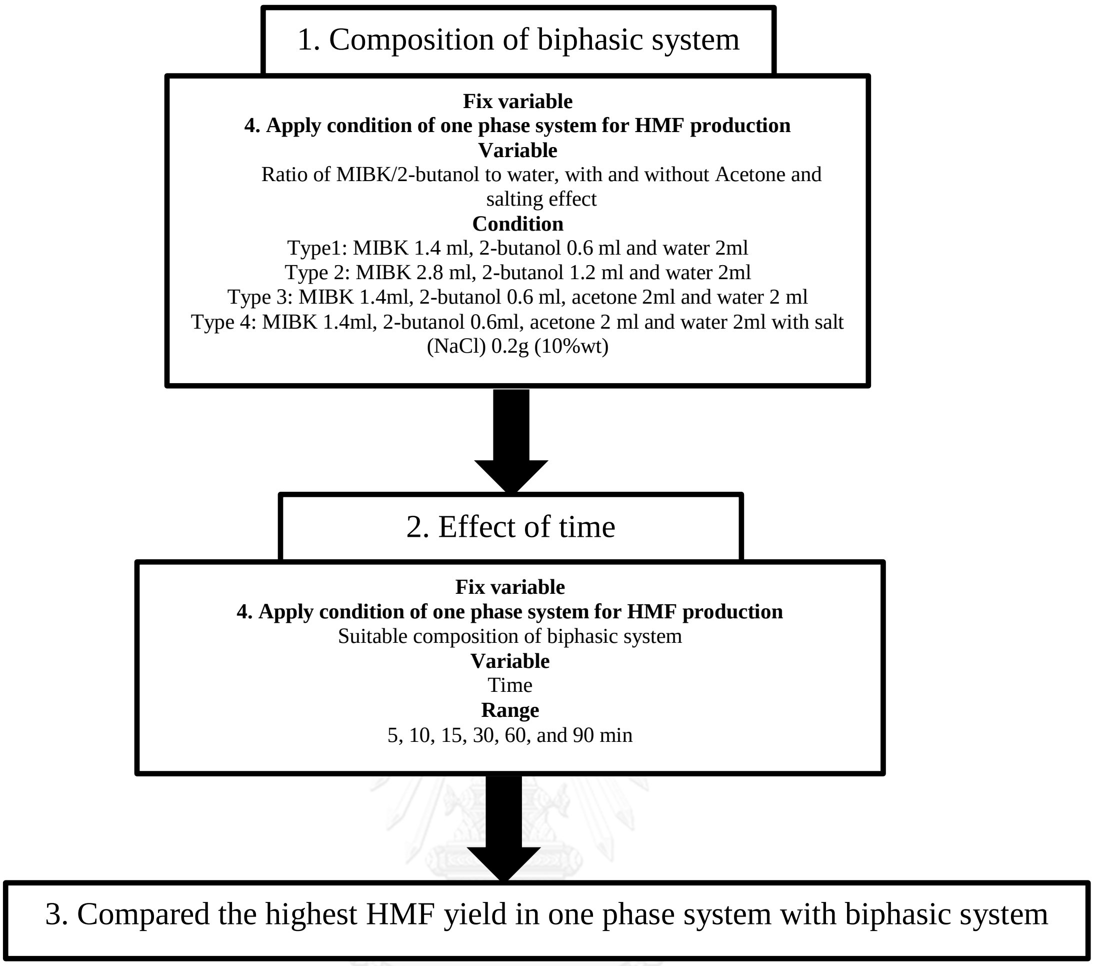


Figure 3.4 Procedure and condition of cellulose conversion in biphasic system

3.4 HPLC analysis

The quantification of glucose, HMF, and LA were conducted by using a high performance liquid chromatography (HPLC, JASCO AS-2055 plus, Japan) which consist of a Jasco RI-2031 plus detector, Jasco UV-970 detector, Jasco PU980 pump system, sugai U-620 column heater and a Jasco AS-2055 plus automated sampler injector equipped with a Shodex SUGAR SH1011 (8.0mmID*300mm) column at 60°C. The concentration of HMF and LA are analyzed based on UV absorbance at 220 nm and the concentration of glucose is analyzed based on RI. Perchoric acid (HClO4) was used as the eluent at a flow rate of 0.5 ml/min. Injection volume was 10 μl. The retention time for glucose, HMF and LA were 16.0, 39.4, and 23.3 min, respectively.

3.5 Statistical Analysis

Significant different results in one-phase and two-phase system were analyzed with a one-way analysis of variance (ANOVA test) using SPSS Version 16.0. Statistical differences among the means were evaluated using the LSD test at the $p \leq 0.05$ level to evaluate the significance of the analysis with 95 % confidence interval (Cl).

3.6 Characterization of HTCG-Sul

3.6.1 X-ray diffractometer (XRD)

The crystallinity analysis of HTCG-Sul was examined using automatic X-ray diffractometer (XRD; RINT 2100, Rigaku) performed using Miniflex Guidance software. Each sample was scanned in the range of 3^o-90^o.

3.6.2 Fourier transform infrared (FTIR)

Functional groups of samples were determined based on Fourier transform infrared (FTIR) spectra using Jasco FT-IR-4100 spectrometer (JASCO International Co., Japan). Prior to the measurement, the sample was ground into fine particles and mixed with KBr to prepare disks. Each sample was investigated in the wavenumber range of 4000-500 cm^{-1}.

3.6.3 Elemental analysis

The elemental (C, H, and N) analysis of HTCG-Sul samples was carried out using an elemental analyzer (J-Science Lab Micro Corder JM10), and the sulfur content was carried out using elemental analyzer (J-Science Lab Micro Corder JMSU10).

3.6.4 Brunauer-Emmet-Teller (BET)

The specific area, pore volume and pore size diameter of HTC-Sul were determined by N_2 physisorption technique using the Brunauer-Emmet-Teller (BET) method with a Belsorp-mini (BEL Japan, Tokyo, Japan); the samples were pre-treated to remove moisture at 150 °C for 3 h prior to the measurement.

CHAPTER IV

RESULTS AND DISCUSSION

The results of 5-Hydroxymethyl furfural (HMF) and Levulinic acid (LA) production from cellulose using combination of hydrothermal carbon-based acid catalyst (HTCG-Sul) and Lewis acid are reported in this chapter. In the first part of this study, the suitable Lewis acid was determined for HMF and LA production in one phase system without combination of HTCG-Sul. The suitable Lewis acid was then combined with HTCG-Sul for HMF and LA production in one phase system in order to improve product yields. The effects of temperature and time, Lewis acid concentration, and HTCG-Sul dosage were studied. In the second part of this study, to improve HMF yields, the combination of suitable Lewis acid and HTCG-Sul was evaluated on cellulose conversion in various biphasic systems to determine the effects of biphasic composition and mixing time on product yields. Detailed analysis of errors for all the results in this chapter can be found in appendix A.

4.1 Characterization of HTCG-Sul

For XRD pattern, HTCG-Sul was amorphous carbon structures. For FTIR analysis, HTCG-sul was found that the stretching vibration bands of O=S=O and –SO_3^{2-} at 1167 and 1027 cm^{-1}, respectively. For BET analysis, the surface area of HTCG-Sul was 7.394 m^2g^{-1} and pore volume of HTCG-Sul was 4.274 nm. For elemental analysis, HTCG-Sul was found to have the sulfur content of 0.709 mmol/g.

4.2 5-Hydroxymethyl furfural (HMF) and Levunilic acid (LA) production in one phase system

4.2.1 Selection of Lewis acid or metal chlorides

The effect of the type of metal chlorides, $FeCl_2$, $FeCl_3$, $CoCl_2$, $MnCl_2$, $CdCl_2$ and $CrCl_3$ on cellulose conversion to HMF and LA was determined at a fixed metal chloride concentration of 0.005 molar at 200°C, 5 min reaction time. The yields of the reaction products including glucose, HMF and LA are shown in Figure 4.1. The results suggested that $CrCl_3$ gave the highest yields of HMF and LA, which was found to be 3.9 % and 11.2 %, respectively, which were considerably higher than those using other metal chlorides (approximately 0 to 1 % yields of HMF and LA). Various types of metal chloride resulted in different yields of HMF and LA under identical conditions, and in the decreasing order: $CrCl_3$ > $FeCl_2$= $FeCl_3$ > $CoCl_2$ >$MnCl_2$ >$CdCl_2$.

Specifically from the results in Figure 4.1, one can see that when $CoCl_2$, $CdCl_2$, and $MnCl_2$ were used as catalysts, low glucose, HMF and LA yields were observed, while $CrCl_3$ gave the highest yields of all three products. It is also interesting to note that when Fe type catalysts were used, the yields of HMF and LA were relatively low, while that of glucose was relatively high. The reason of these findings has been explained in Peng et al, (2010), in which the importance of the acidity of metal chloride as well as the type of metal are described to be key attributes impacting cellulose conversion. Low acidity metal chlorides such as $CoCl_2$, $CdCl_2$ and $MnCl_2$ (~pH 7) lack catalytic activity for cellulose conversion to glucose, and as a result HMF and LA yields were also low. High acidity metal chlorides such as $FeCl_3$(~pH 2.5) was expected to have high catalytic activity to cellulose hydrolysis, however, the Fe type metal chlorides are not favorable for glucose isomerization, resulting in low HMF and LA yields. $CrCl_3$ (~pH 3.8) which is the most favorable in terms acidity that catalyzes hydrolysis, dehydration and rehydration, and metal type, capable of catalyzing isomerization, was therefore selected for subsequent experiment.

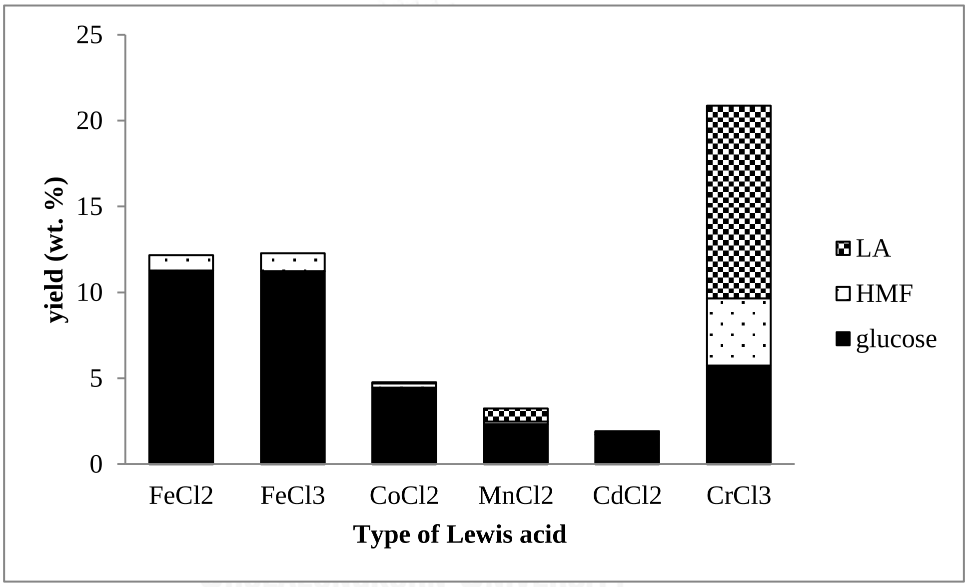


Figure 4.1 Catalytic of Lewis acid on the conversion of cellulose for HMF and LA production at 200°C and 5 min

4.2.2 Combination of carbon acid catalyst (HTCG-Sul) and Lewis acid

In this section, comparisons are made between the glucose, HMF and LA yields of cellulose conversion using $CrCl_3$ (at concentration of 0.005 M) and HTCG-Sul (at 5wt. %), and the combination of both. The yields of the products obtained after 5 min of the reaction at 200^oC are shown in Figure 4.2.

HTCG-Sul, a Brønsted acid catalyst, is expected to catalyze cellulose hydrolysis, however at the reaction conditions employed in this study, it gave no significant difference in glucose yield compared with the reaction without the catalyst. And since carbon-based catalyst are inefficient for further conversion of glucose to HMF (Daengprasert et al., 2011), the HMF and LA yields from the reaction catalyzed by HTCG-sul were also low (0.230 %, 0.037 %, respectively), and were not significantly different from those obtained without the catalyst (p-value=0.748 and

=0.978 for HMF and LA, respectively). On the contrary, significantly higher HMF and LA yields were observed using $CrCl_3$ alone. This is due to the presence of ion complex, $[Cr(H_2O)_5OH]^{2+}$, formed in presence of water, that catalyzes isomerization of glucose to fructose, and the presence of the intrinsic Brønsted acidity, that drives hydrolysis, fructose dehydration to HMF, and further HMF rehydration to LA. Nevertheless, Lewis acid sites are quite non-selectively active, and catalyze not only the aldose-to-ketose isomerization, but also catalyze the side reactions such as the generation of undesirable product, humin, from sugars (Swift et al, 2015). Further improvements in HMF and LA yields could be achieved, by adding a Brønsted acid catalyst, to help catalyze the production of HMF and LA before the side reactions took place by the action of the Lewis acid (Swift et al, 2015). The results in Figure 4.2 demonstrate that the addition of HTCG-sul as a Brønsted acid catalyst could significantly enhance the HMF and LA yields, from 3.9 wt. % and 11.2 wt. %, using $CrCl_3$ alone to 6.8 wt. % and 22.9 wt. %, respectively observed using $CrCl_3$ and combined.

From previously available data, the results can be suggested that combination of HTCG-Sul and $CrCl_3$ improve HMF and LA yields because the increase in selectivity to HMF and LA by the addition of external Brønsted acid (Choudhary et al., 2013).

Given the synergistic effect of $CrCl_3$ and HTCG-Sul catalysts, subsequent studies were conducted to determine the effects of reaction temperature, time, $CrCl_3$ concentration and HTCG-Sul dosage on cellulose conversion in such system.

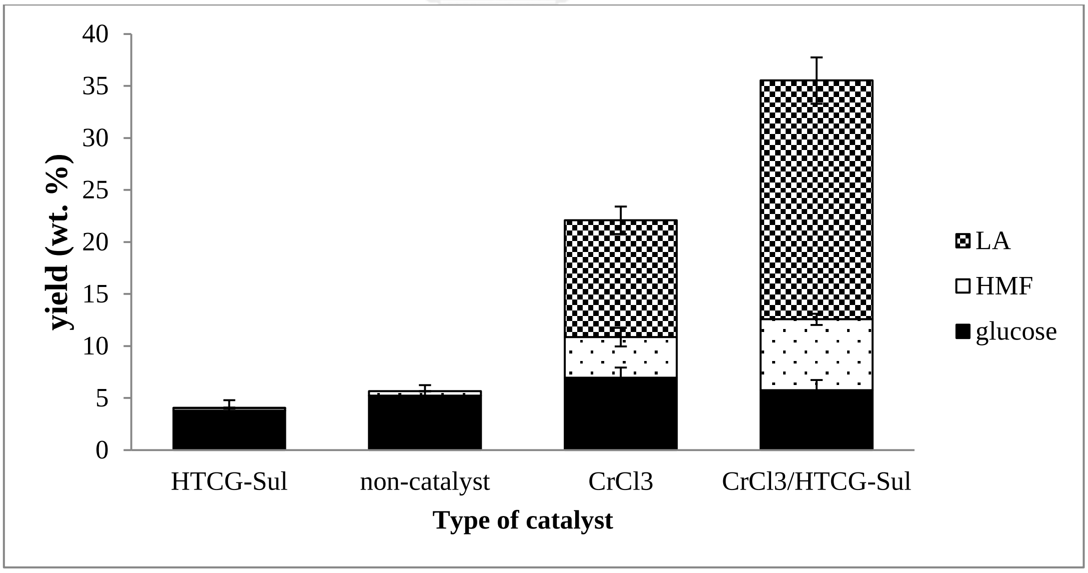


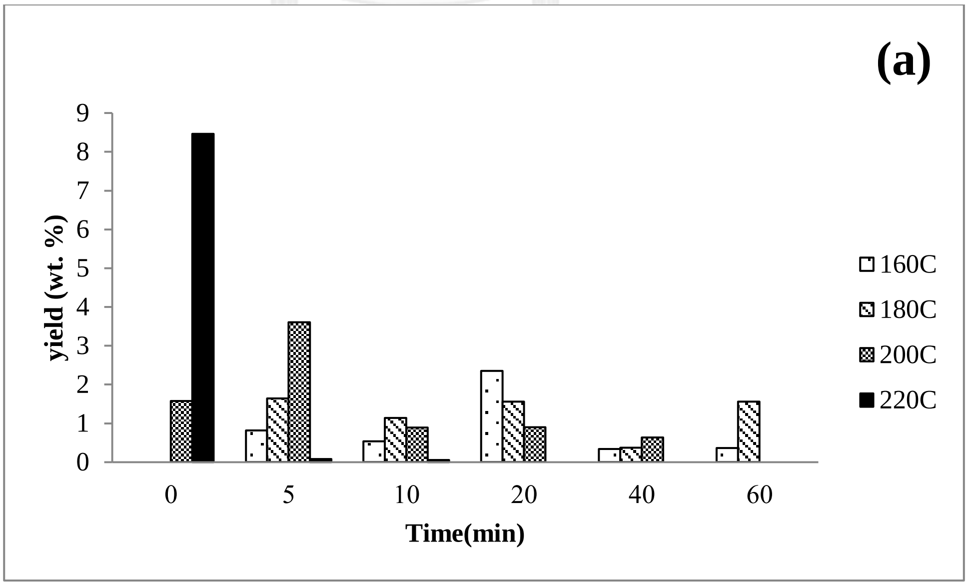
Figure 4.2 Catalytic of different catalyst on the conversion of cellulose for HMF and LA production at 200°C and 5 min

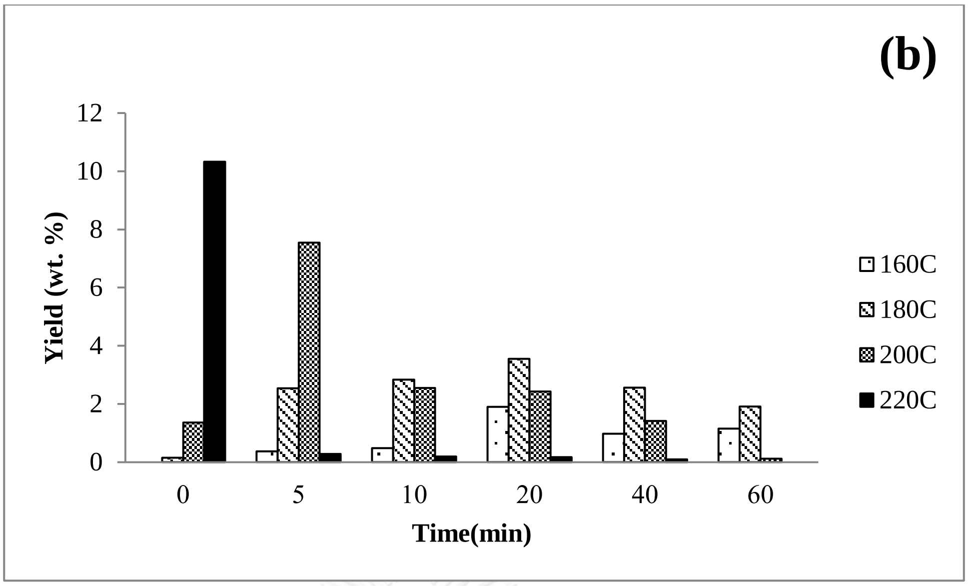
4.2.2.1 Effect of temperature and time

With the combined catalyst (at $CrCl_3$ concentration of 0.01 M and HTCG-Sul 10 wt. %), the effects of reaction temperature (160-220°C) and time (0-60 min.) on cellulose conversion were observed. The results in Figure 4.3a-c shows that at the reaction temperatures of 160 and 180^oC, the yields of glucose, HMF and LA were rather low for all reaction times (from 0 to 60 min). The higher overall yields of glucose, HMF and LA were observed at higher reaction temperatures (200 and 220^oC).

At the reaction temperature of 200^oC, glucose, HMF and LA yields increased as the reaction time increased from 0 to 5 min, and slightly decreased onwards. At the reaction temperature of 220^oC, glucose and HMF yields rapidly increased at reaction time of 0 min, and dropped abruptly onward. At lower temperatures, there might not be enough energy to exceed that of the activation energy, thus leading to lower conversions (both hydrolysis and isomerization). At higher reaction temperatures, the input energy might be higher than activation energy (Swift et al., 2015), resulting in the higher observed yields. Moreover, the increase in temperature might increase the number of $[Cr(H_2O)_5OH]^{2+}$ complexes that promoted isomerization and the H^+ molecules, promoting hydrolysis, dehydration, and rehydration (Choudhary et al., 2013).

Based on the results in Figure 4.3b and 4.3c, the reaction temperature at 200°C is favorable for HMF and LA production, while higher temperature at 220^oC might be more favorable for the production of LA. Considering the fact that unwanted side reactions (Peng et al, 2010) and carbonization of cellulose to hydrothermal carbon easily occur at high reaction temperature especially higher than 200^oC (Matthiesen et al., 2014), the reaction temperature of 200°C was chosen for subsequent experiments. At this temperature, the highest glucose and HMF yields of 4% and 8% were observed at the reaction time of 5 min, while the highest LA yield was observed at the reaction time of 10 min.





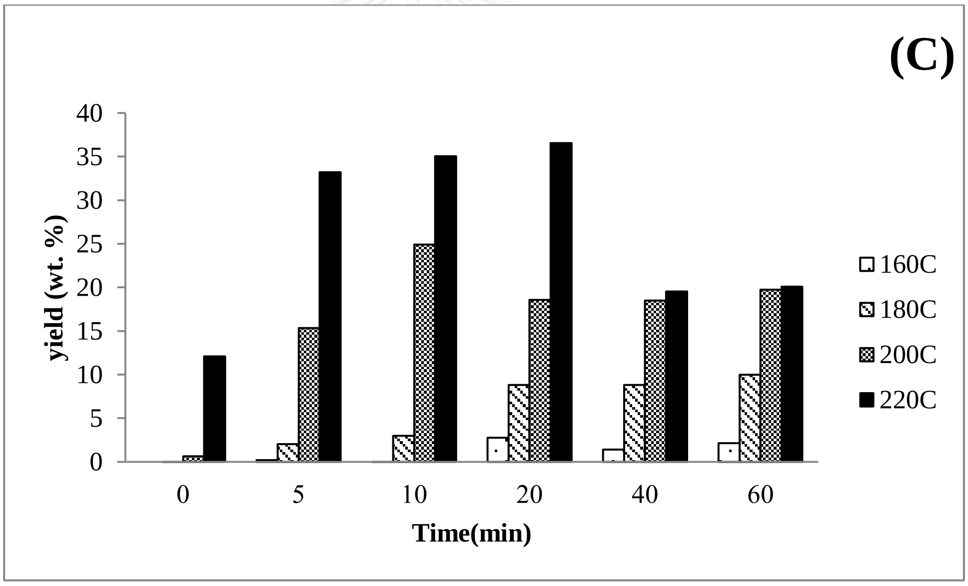


Figure 4.3 Conversion of cellulose for glucose (a), HMF (b) and LA (C) production at different temperature and time

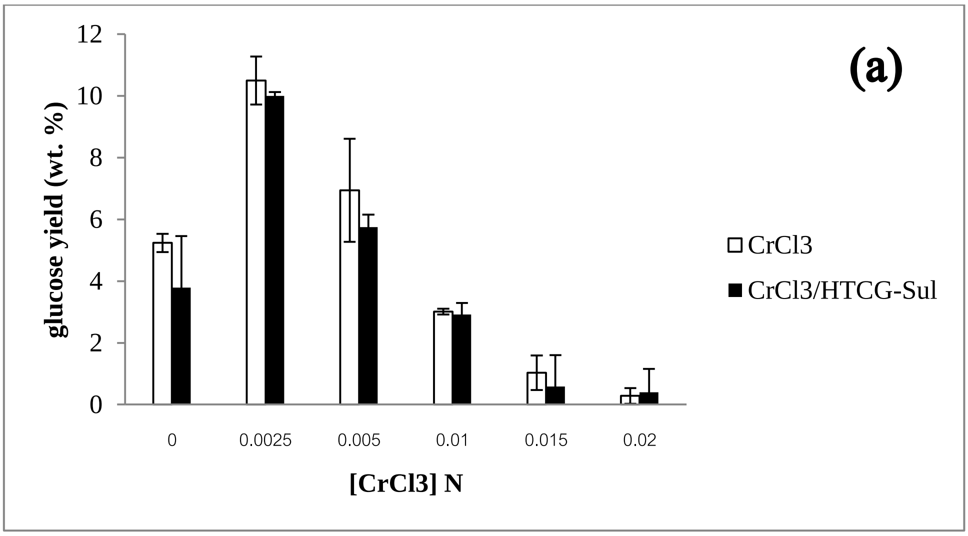
*Definition of reaction time in our experiment is “measuring time when desired temperature equal temperature inside reactor”. Before measuring time (before zero), system take time about 10 minute to preheating temperature of reactor until desired temperature equal temperature inside reactor and In this moment, cellulose convert to glucose, HMF and LA at 0 minute.

4.2.2.2 Effect of chromium chloride concentration

The effect of $CrCl_3$ concentration (0 to 0.02 molar) on cellulose conversion was studied at the reaction temperature of 200°C for 5 min and 5 wt. % HTCG-Sul. The results are shown in Figure 4.4a-c along with those of the reaction catalyzed with $CrCl_3$ alone. For the range of $CrCl_3$ concentration studies, it can be seen that glucose yields (Figure 4.4a) obtained in both cases were not significantly different (p-value >0.05). The highest glucose yield was approximately 10 wt. % and was found at the $CrCl_3$ concentration of 0.0025 M. As the $CrCl_3$ concentration increased from 0.005 to 0.02 M however, glucose yields decreased, probably because glucose can be more readily converted to HMF or LA at higher $CrCl_3$ concentration.

At $CrCl_3$ concentration of 0.0025 and 0.005 M, the HMF yields (Figure 4.4b) were higher when combined $CrCl_3$ with HTCG-Sul catalysts were used. . However, at higher $CrCl_3$ concentrations (0.01 to 0.02 M), the HMF yields were not significantly different (p-value >0.05). The highest HMF yield (6.8 wt. %) was observed in the system of combined catalyst at 0.005 M $CrCl_3$ concentration. Moreover, the results in Figure 4.4b also suggested that the HMF yields increased as $CrCl_3$ concentration increased from 0.0025 to 0.005 M but then decreased as the $CrCl_3$ concentration increased from 0.005 to 0.02 M. This result implied that at too high the $CrCl_3$ concentration, HMF might become unstable.

As for LA (Figure 4.4c), the LA yields obtained from the system of combined catalysts were higher than that of $CrCl_3$ alone, for the entire $CrCl_3$ concentration range studied (0.0025 to 0.020 M). In both cases, the LA yields increased with increasing $CrCl_3$ concentration. These results confirmed the synergy effect of the combination of $CrCl_3$ and HTCG-Sul. The presence of HTCG-Sul promoted not only hydrolysis, dehydration and rehydration but also suppressed side reaction caused by $CrCl_3$. Although the results suggested that the highest LA yield of 41 wt. % was observed in the combined system at 0.02 M $CrCl_3$, the yield obtained at $CrCl_3$ concentration of 0.015 molar was not significantly different (p-value> 0.05).



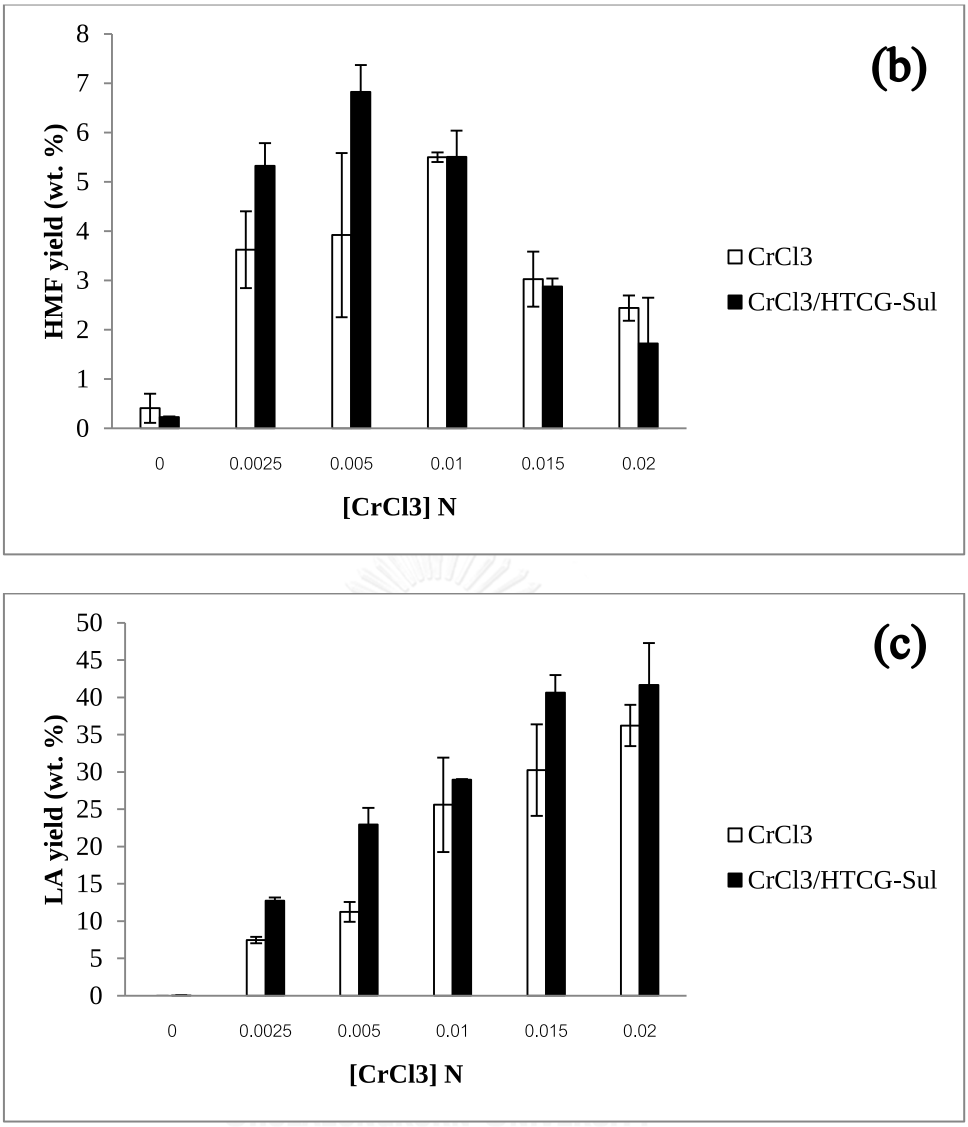


Figure 4.4 Catalytic of different concentration of chromium chloride on conversion of cellulose for glucose (a), HMF (b), LA (c) and LA production at 200°C and 5 min.

4.2.2.3 Effect of carbon based acid catalyst dosage (HTCG-Sul)

The effect of HTCG-Sul dosage (0 wt. % to 40 wt. %) on cellulose conversion was studied at 200^{o}C, 5 min in the system of combined catalysts at $CrCl_3$ concentration of 0.005 M. From Figure 4.5, increase in HTCG-Sul dosage from 0 to 5 wt. % resulted in significant increase in HMF and LA yields (p-value= 0.007 and =0.003, respectively). However, glucose yields were found not to be significantly different (p-value = 0.225). The highest HMF and LA yields of 6.8 and 23 wt. %, respectively, were observed at 5 wt. % HTCG-Sul dosage.

At higher HTCG-Sul dosage, overall LA yield decreased but overall glucose yield increased with increasing HTCG-Sul dosage from 10 wt. % to 40 wt. %. The decrease in overall LA yield and increase in overall glucose yield observed at higher HTCG-Sul dosage were possibly due to fact that the external Brønsted acid added to the system had driven the $CrCl_3$ hydrolysis backward, causing the shift of active form of chromium chloride (for glucose isomerization), $[Cr(H_2O)_5]OH^{2+}$ to the less active form, Cr^{3+} (Choudhary et al., 2013). This result therefore implied that excess amount of HTCG-Sul might have a negative effect on HMF and LA production.

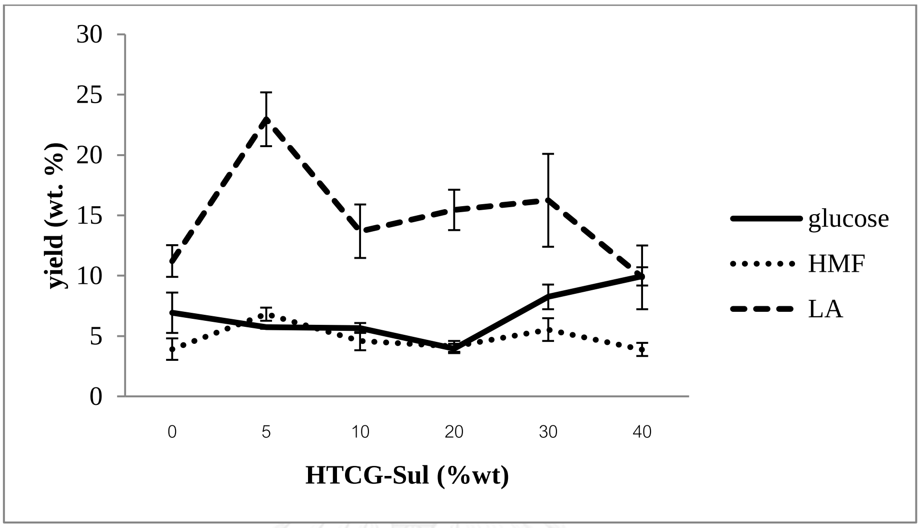


Figure 4.5 Catalytic of different dosage of carbon based acid catalyst on conversion of cellulose for HMF and LA production at 200°C and 5 min

4.3 Determine suitable condition for 5-Hydroxymethyl furfural (HMF) in biphasic system

Biphasic system, employed for improving the selectivity of HMF, is composed of an aqueous phase (or the reactive phase) and an organic phase (or an extractive phase) into which HMF from the aqueous is extracted, to avoid rehydration of HMF to LA or other side reactions. At a condition suggested by previous study to give relatively high HMF yield in a one phase system (200°C, 0.005 M $CrCl_3$ concentration, and 5 wt. % HTCG-Sul dosage), the effects of the ratio of the aqueous and organic (MIBK and 2-butanol at 7:3v/v) phase, and the use of acetone as a co-solvent, and the effect of salt addition, and the mixing time were determined on the HMF yield.

4.3.1 Effects of various biphasic systems

The product yields of cellulose conversion in various biphasic systems are shown in Figure 4.6. Increase in organic phase (MIBK and 2-butanol) to aqueous ratio from 1:1 v/v (type 1) to 2:1 v/v (type2) resulted in increase in HMF and LA yields.

The increase in HMF and LA yields by increasing higher ratio of organic to aqueous phase caused higher amount of HMF to be extracted from the aqueous phase, thus avoiding side reactions and enhancing the overall HMF yield. By adding acetone (Type3) into the system of type 1, HMF yield increased while the LA yield decreased.

This is because adding acetone which increase fructose conversion and improve selectivity to HMF (Bicker et al., 2003). The lowest HMF yield however was observed by adding 10% NaCl to the system consisting of MIBK, 2-butanol and acetone (type4). Surprisingly, LA was not detected in this biphasic system. The reason for low HMF yield and the absence of LA is still unclear and further investigation is needed to clearly explain the effect of salt addition. Nevertheless, the type 3 system with MIBK/2-butanol and acetone was selected for subsequent study to determine the effect of mixing time on cellulose conversion.

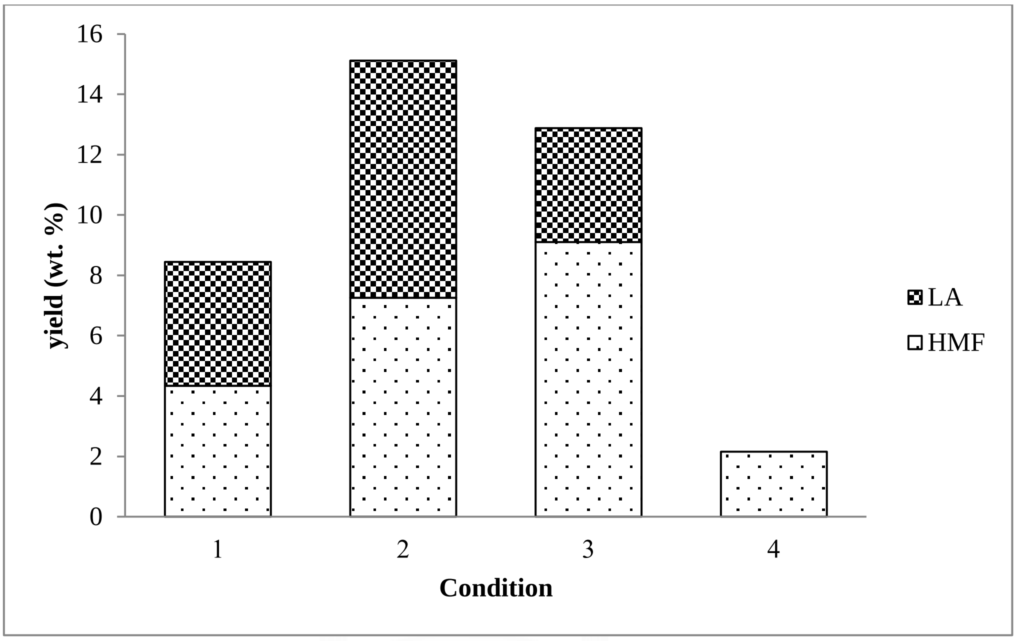


Figure 4.6 Catalytic of different biphasic composition on conversion of cellulose for HMF production at 200°C and 5 min

*1 mean to MIBK 1.4ml, 2-butanol 0.6ml and water 2ml

*2 mean to MIBK 2.8ml, 2-butanol 1.2 ml and water 2ml

*3 mean to MIBK 1.4ml, 2-butanol 0.6 ml, acetone 2ml and water 2 ml

*4 mean to MIBK 1.4ml, 2-butanol 0.6ml, acetone 2 ml and water 2ml with salt (NaCl) 0.2g (10wt. %)

4.3.2 Effect of mixing time

The effect of mixing time was studied between 5 to 90 minutes using biphasic system of type 3. The results shown in Figure 4.7 revealed that the HMF yield increased from 5 to 10 min, then slightly decreased onwards. The highest HMF yield was observed at the 10 min

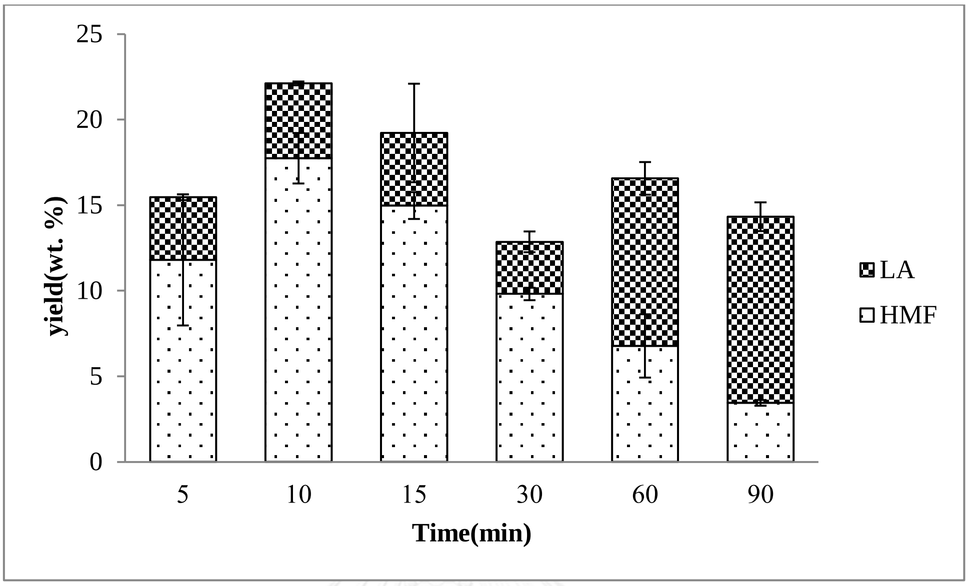


Figure 4.7 Catalytic of different time on conversion of cellulose for HMF production at 200°C in biphasic system (Type 3)

*Type 3 mean to MIBK 1.4ml, 2-butanol 0.6 ml, acetone 2ml and water 2 ml

4.3.2 Comparison of one-phase system with two-phase system (type 3)

The comparison of one-phase and two-phase system at their best conditions is shown in Figure 4.8., which demonstrated that the one-phase system gave significantly higher LA yield compared with the biphasic system (22.9 and 4.3 wt. %, p-value = 0.00). On the other hand, biphasic system gave significantly higher HMF yield compared to one-phase system (17.7 and 6.8 wt. %, p-value= 0.00). Moreover, HMF obtained from biphasic system was more stable since higher HMF yield was observed at the longer mixing time compared with the one-phase system (10 versus 5 min). It could therefore be concluded from these results that one-phase system was more favorable for LA production while the biphasic system was suitable for HMF production.

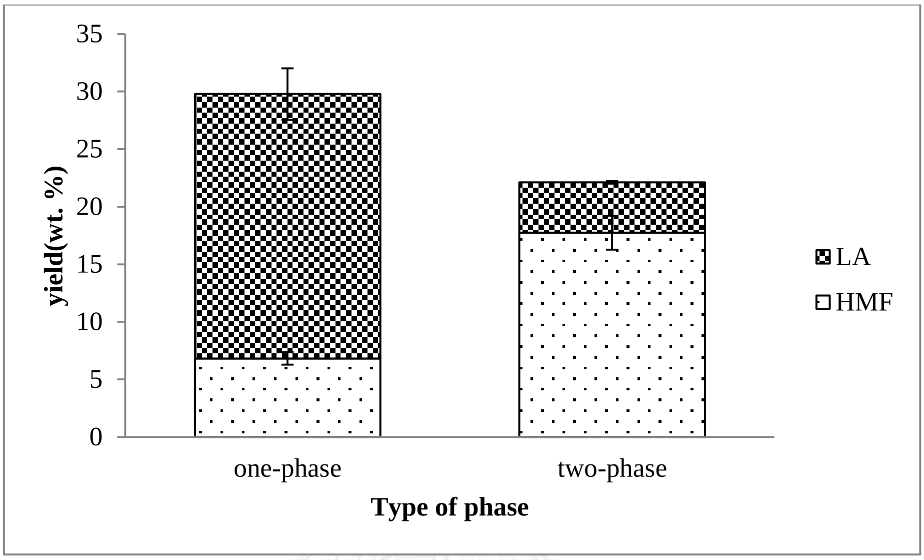


Figure 4.7 Catalytic of compared suitable yield of one phase (5min) with that of two phase system (10 min) on conversion of cellulose for HMF production at 200°C

*Condition of one phase system: $CrCl_3$ 0.005 N, HTCG-Sul 5 wt. % at 200^{o}C for 5min

*Condition of biphasic system (type 3): $CrCl_3$ 0.005 N, HTCG-Sul 5 wt. % at 200^{o}C for 10 min

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The study of cellulose conversion to HMF and LA in one-phase system using metal salts combined with hydrothermal catalyst acid (HTCG-Sul) was investigated in the first part of this work. The selection of suitable metal salts was firstly determined. Chromium chloride ($CrCl_3$) shows highest catalytic activity for cellulose conversion. It is therefore combined with HTCG-Sul in order to improve product yields. There is a significant synergy effect between in combination Brønsted acids from HTCG-Sul and $CrCl_3$ on the highly effective conversion of cellulose into HMF (6.8 wt. % with combination and 3.9 wt. % with $CrCl_3$) and LA (22.9 wt. % with combination and 11.2 wt. % with $CrCl_3$). From the results, it might be indicated that the combination of HTCG-Sul and $CrCl_3$ can improve hydrolysis of cellulose to glucose, isomerization of glucose to fructose, dehydrating fructose to HMF, and rehydrating HMF to LA in a one-pot synthesis. However, one-phase system using combination of HTCG-Sul and $CrCl_3$ as catalyst seems to more favorable for LA production since HMF is unstable in this system. At the best condition, HMF yield is found to be 6.8 wt. % at the condition of 0.005 molar of concentration $CrCl_3$ and 5 wt. % of HTCG-Sul dosage at 200^oC for 5 min. At the best condition, LA yield is found to be 40%wt at the condition of 0.015 molar of concentration $CrCl_3$ and 5 wt. % of HTCG-Sul dosage at 200^oC for 5 min

In the second part of this study, biphasic system improve yield of HMF by avoidance rehydration of HMF. MIBK/2-Butanol is efficient extract HMF from reactive phase to organic phase with adding acetone increasing selectivity to HMF and small LA yield was detected. By comparison of biphasic system with one-phase system, HMF yield production is improve from highest HMF yield of one-phase system (6.8 wt. %) to highest HMF yield of biphasic system (17 wt. %) with 0.005 molar of concentration $CrCl_3$ and 5 wt. % of HTCG-Sul dosage at 200^oC for 5min (one-phase system) and 10 min (two-phase system).

5.2 Recommendation

Preparation of hydrothermal carbon based catalyst

Since Lewis acids promote biomass conversion, necessary for the preparation of hydrothermal carbon based catalyst, in preparing a hydrothermal carbon for the carbon based catalyst, it is possible that a Lewis acid or the combination of a Brønsted acid and a Lewis acid be employed to catalyze the process. By this, carbonization can take place more rapidly and at milder conditions. . The idea of using of combined Lewis acid and Brønsted acid catalysts, i.e., sulfuric acid, would be interesting to investigate, since the combined catalyst system not only catalyze the carbonization process, functionalization of the hydrothermal carbon may occurred, making it possible to synthesize the sulfonated hydrothermal carbon-based catalysts in one pot. Additional advantage of using the combination of sulfuric acid and Lewis acid could be envisaged. In such system, particularly at high temperature, Lewis acids (i.e. metal chloride such as $FeCl_2$ and $FeCl_3$) transform into metal oxides such as Fe_2O_3 which may be precipitated onto the hydrothermal sulfonated carbon based catalyst, making it possible to synthesize a heterogeneous bi-functionalized Lewis and Brønsted acid hydrothermal carbon based catalyst from biomass. Fe_2O_3 which has a magnetic property when deposited onto the catalyst, might assist the removability and recyclability of the catalyst as was suggested by a previous study by (Yang et al., 2015)

Biomass conversion (Single-phase system)

In this study, $CrCl_3$ was found to be the most suitable Lewis acids for biomass conversion of all the Lewis acids that were evaluated which includes $FeCl_2$, $FeCl_3$, $CdCl_2$, $CoCl_2$, $MnCl_2$ and $CrCl_3$. As an interesting alternative, $AlCl_3$ which have been proven to be more efficient than $CrCl_3$ on isomerization of glucose should possibly be investigated combination with sulfonated hydrothermal carbon based catalyst for biomass conversion.

Biomass conversion (Biphasic system for increasing HMF yield)

As seen in the previous results that the selectivity of HMF could be improved with use of a biphasic phase (MIBK/2-butanol/acetone) and saturated salt (via a salting out effect). The biphasic system is composed of a reactive phase (i.e., water-acetone) used for biomass reaction and an extractive phase (i.e., MIBK/2-butanol/acetone) used for extraction of HMF from reactive phase to avoid rehydration of HMF.

In the biphasic system, 2-butanol improves mass transfer of HMF from reactive phase to extractive phase. Acetone not only improves mass transfer of HMF, but it also increases the selectivity of HMF from fructose dehydration.

The salting out effect takes place as the salt saturated in reactive phase helps improve the selectivity of HMF by increasing the partition of HMF into the extractive phase.

It is interesting to note that salting out effect in the MIBK/2-butanol/acetone as shown by the results in the previous chapter, despite very high HMF selectivity, did not lead to high HMF yield. Rather, the yield was found to be the lowest of all the systems evaluated. As mentioned, acetone in the reactive phase promotes HMF formation via fructose dehydration. It is possible that, in the presence of salt in this system, that acetone also shifted to extractive phase, causing not enough acetone to remain in the reactive phase. It might also be possible that, in such system with salt, “acetone in extractive phase improves the transfer of HMF from reactive phase to extractive phase” or that “salt has an effect on the equilibrium of Lewis acid ($CrCl_3$) or on reactivity of Brønsted acids (sulfonated hydrothermal carbon based catalyst). Which of these possibilities play the big parts in the final results on the yield and the selectivity of HMF remained to be investigated. With this understanding of the phenomena occurring in the biphasic system such as that of MIBK, 2-butanol, acetone and with salt addition, further process optimization will be possible.

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APPENDIX

APPENDICE A

STATISTICAL DATA FOR ANALYSIS

A-1 Significant data of effect combination

Table A-1.1 significant of glucose yield in effect combination

Multiple Comparisons

Glucose
LSD

(I) Group	(J) Group	Mean Difference (I-J)	Std. Error	Sig.
HTCGSul	Withoutcatalytic	-1.45	1.14	.274
	CrCl3	-3.15	1.14	.051
	Combination of HTCGSul and CrCl3	-1.95	1.14	.163
Withoutcatalytic	HTCGSul	1.45	1.14	.274
	CrCl3	-1.70	1.14	.211
	Combination of HTCGSul and CrCl3	-.50	1.14	.681
CrCl3	HTCGSul	3.15	1.14	.051
	Withoutcatalytic	1.70	1.14	.211
	Combination of HTCGSul and CrCl3	1.19	1.14	.355
Combination of HTCGSul and CrCl3	HTCGSul	1.95	1.14	.163
	Withoutcatalytic	.50	1.14	.681
	CrCl3	-1.19	1.14	.355

Table A-1.2 significant of HMF yield in effect combination

Multiple Comparisons

HMF
LSD

(I) Group	(J) Group	Mean Difference (I-J)	Std. Error	Sig.
HTCGSul	Withoutcatalytic	-.178	.51	.748
	CrCl3	-3.68	.51	.002
	Combination of HTCGSul and CrCl3	-6.59	.51	.000
Withoutcatalytic	HTCGSul	.17	.51	.748
	CrCl3	-3.50	.51	.002
	Combination of HTCGSul and CrCl3	-6.41	.51	.000
CrCl3	HTCGSul	3.68	.51	.002
	Withoutcatalytic	3.50	.51	.002
	Combination of HTCGSul and CrCl3	-2.90	.51	.005
Combination of HTCGSul and CrCl3	HTCGSul	6.59	.51	.000
	Withoutcatalytic	6.41	.51	.000
	CrCl3	2.90	.51	.005

*. The mean difference is significant at the 0.05 level.

Table A-1.3 significant of LA yield in effect combination

Multiple Comparisons

LA
LSD

(I) Group	(J) Group	Mean Difference (I-J)	Std. Error	Sig.
HTCGSul	Withoutcatalytic	.03	1.29	.978
	CrCl3	-11.18	1.29	.001
	Combination of HTCGSul and CrCl3	-22.91	1.29	.000
Withoutcatalytic	HTCGSul	-.037	1.29	.978
	CrCl3	-11.22	1.29	.001
	Combination of HTCGSul and CrCl3	-22.95	1.29	.000
CrCl3	HTCGSul	11.18	1.29	.001
	Withoutcatalytic	11.22	1.29	.001
	Combination of HTCGSul and CrCl3	-11.73	1.29	.001
Combination of HTCGSul and CrCl3	HTCGSul	22.91	1.29	.000
	Withoutcatalytic	22.95406*	1.29	.000
	CrCl3	11.73391*	1.29	.001

*. The mean difference is significant at the 0.05 level.

A-2 Significant data of effect concentration of $CrCl_3$

Table A-2.1 significant of glucose yield in effect concentration of $CrCl_3$

Multiple Comparisons

CrCl3andcombination
LSD

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0 N CrCl3	0.0025 N CrCl3	-5.25	.76	.000
	0.005 N CrCl3	-1.70	.76	.045
	0.01 N CrCl3	2.22	.76	.013
	0.015 N CrCl3	4.20	.76	.000
	0.020 N CrCl3	4.95	.76	.000
	0 N Combination	1.45	.76	.080
	0.0025 N combination	-4.75	.76	.000
	0.005 N combination	-.50	.76	.517
	0.01 N combination	2.32	.76	.010
	0.015 N combination	4.65	.76	.000
	0.020 N combination	4.83	.76	.000

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.0025 N	0.0025 N CrCl3	5.25	.76	.000
	0.005 N CrCl3	3.55	.76	.001
	0.01 N CrCl3	7.48	.76	.000
	0.015 N CrCl3	9.46	.76	.000
	0.020 N CrCl3	10.21	.76	.000
	0 N Combination	6.71	.76	.000
	0.0025 N combination	.50	.76	.523
	0.005 N combination	4.75	.76	.000
	0.01 N combination	7.58	.76	.000
	0.015 N combination	9.90	.76	.000
	0.020 N combination	10.09	.76	.000
0.005 N CrCl3	0 N CrCl3	1.70	.76	.045
	0.0025 N CrCl3	-3.55	.76	.001
	0.01 N CrCl3	3.92	.76	.000
	0.015 N CrCl3	5.91	.76	.000
	0.020 N CrCl3	6.65	.76	.000
	0 N Combination	3.15	.76	.001
	0.0025 N combination	-3.05	.76	.002
	0.005 N combination	1.19	.76	.141
	0.01 N combination	4.02	.76	.000
	0.015 N combination	6.35	.76	.000
	0.020 N combination	6.54	.76	.000

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.01 N CrCl3	0 N CrCl3	-2.22	.76	.013
	0.0025 N CrCl3	-7.48	.76	.000
	0.005 N CrCl3	-3.92	.76	.000
	0.015 N CrCl3	1.98	.76	.023
	0.020 N CrCl3	2.73	.76	.004
	0 N Combination	-.77	.76	.329
	0.0025 N combination	-6.98	.76	.000
	0.005 N combination	-2.73	.76	.004
	0.01 N combination	.10	.76	.897
	0.015 N combination	2.42	.76	.008
	0.020 N combination	2.61	.76	.005
0.015 N CrCl3	0 N CrCl3	-4.20	.76	.000
	0.0025 N CrCl3	-9.46	.76	.000
	0.005 N CrCl3	-5.91	.76	.000
	0.01 N CrCl3	-1.98	.76	.023
	0.020 N CrCl3	.74	.76	.346
	0 N Combination	-2.75	.76	.003
	0.0025 N combination	-8.96	.76	.000
	0.005 N combination	-4.71	.76	.000
	0.01 N combination	-1.88	.76	.029
	0.015 N combination	.44	.76	.572
	0.020 N combination	.62	.76	.425

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.020 N CrCl3	0 N CrCl3	-4.95	.76	.000
	0.0025 N CrCl3	-10.21	.76	.000
	0.005 N CrCl3	-6.65	.76	.000
	0.01 N CrCl3	-2.73	.76	.004
	0.015 N CrCl3	-.74	.76	.346
	0 N Combination	-3.50	.76	.001
	0.0025 N combination	-9.71	.76	.000
	0.005 N combination	-5.46	.76	.000
	0.01 N combination	-2.63	.76	.005
	0.015 N combination	-.30	.76	.695
	0.020 N combination	-.11	.76	.879

Table A-2.2 significant of HMF yield in concentration of $CrCl_3$

Multiple Comparisons

CrCl3andcombination
LSD

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0 N CrCl3	0.0025 N CrCl3	-3.21	.57	.000
	0.005 N CrCl3	-3.50	.57	.000
	0.01 N CrCl3	-5.08	.57	.000
	0.015 N CrCl3	-2.61	.57	.001
	0.020 N CrCl3	-2.03	.57	.004
	0 N Combination	.178	.57	.761
	0.0025 N combination	-4.91	.57	.000
	0.005 N combination	-6.41	.57	.000
	0.01 N combination	-5.09	.57	.000
	0.015 N combination	-2.46	.57	.001
	0.020 N combination	-1.31	.57	.041

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.0025 N CrCl3	0 N CrCl3	3.21	.57	.000
	0.005 N CrCl3	-.29	.57	.616
	0.01 N CrCl3	-1.87	.57	.007
	0.015 N CrCl3	.59	.57	.321
	0.020 N CrCl3	1.18	.57	.062
	0 N Combination	3.39	.57	.000
	0.0025 N combination	-1.69	.57	.012
	0.005 N combination	-3.19	.57	.000
	0.01 N combination	-1.88	.57	.007
	0.015 N combination	.74	.57	.219
	0.020 N combination	1.89	.57	.006

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.005 N CrCl3	0 N CrCl3	3.50974*	.57543	.000
	0.0025 N CrCl3	.29616	.57543	.616
	0.01 N CrCl3	-1.57827*	.57543	.018
	0.015 N CrCl3	.89122	.57543	.147
	0.020 N CrCl3	1.47782*	.57543	.025
	0 N Combination	3.68865*	.57543	.000
	0.0025 N combination	-1.40215*	.57543	.031
	0.005 N combination	-2.90247*	.57543	.000
	0.01 N combination	-1.58969*	.57543	.017
	0.015 N combination	1.04209	.57543	.095
	0.020 N combination	2.19590*	.57543	.002

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.01 N CrCl3	0 N CrCl3	5.08	.57	.000
	0.0025 N CrCl3	1.87	.57	.007
	0.005 N CrCl3	1.57	.57	.018
	0.015 N CrCl3	2.46	.57	.001
	0.020 N CrCl3	3.05	.57	.000
	0 N Combination	5.26	.57	.000
	0.0025 N combination	.17	.57	.765
	0.005 N combination	-1.32	.57	.040
	0.01 N combination	-.011	.57	.984
	0.015 N combination	2.62	.57	.001
	0.020 N combination	3.77	.57	.000

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.015 N CrCl3	0 N CrCl3	2.61852*	.57543	.001
	0.0025 N CrCl3	-.59506	.57543	.321
	0.005 N CrCl3	-.89122	.57543	.147
	0.01 N CrCl3	-2.46949*	.57543	.001
	0.020 N CrCl3	.58659	.57543	.328
	0 N Combination	2.79742*	.57543	.000
	0.0025 N combination	-2.29337*	.57543	.002
	0.005 N combination	-3.79369*	.57543	.000
	0.01 N combination	-2.48091*	.57543	.001
	0.015 N combination	.15087	.57543	.798
	0.020 N combination	1.30468*	.57543	.043

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.020 N CrCl3	0 N CrCl3	2.03	.57543	.004
	0.0025 N CrCl3	-1.18	.57543	.062
	0.005 N CrCl3	-1.47	.57543	.025
	0.01 N CrCl3	-3.05	.57543	.000
	0.015 N CrCl3	-.58	.57543	.328
	0 N Combination	2.21	.57543	.002
	0.0025 N combination	-2.87	.57543	.000
	0.005 N combination	-4.38	.57543	.000
	0.01 N combination	-3.06	.57543	.000
	0.015 N combination	-.43	.57543	.464
	0.020 N combination	.71	.57543	.236

Table A-2.3 significant of LA yield in effect concentration of $CrCl_3$

Multiple Comparisons

CrCl3andcombination
LSD

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0 N CrCl3	0.0025 N CrCl3	-7.44	3.28	.043
	0.005 N CrCl3	-11.22	3.28	.005
	0.01 N CrCl3	-25.59	3.28	.000
	0.015 N CrCl3	-30.25	3.28	.000
	0.020 N CrCl3	-36.21	3.28	.000
	0 N Combination	-.037	3.28	.991
	0.0025 N combination	-12.71	3.28	.002
	0.005 N combination	-22.95	3.28	.000
	0.01 N combination	-28.95	3.28	.000
	0.015 N combination	-40.64	3.28	.000
	0.020 N combination	-41.64	3.28	.000

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.0025 N CrCl3	0 N CrCl3	7.44	3.28	.043
	0.005 N CrCl3	-3.77	3.28	.274
	0.01 N CrCl3	-18.14	3.28	.000
	0.015 N CrCl3	-22.81	3.28	.000
	0.020 N CrCl3	-28.76	3.28	.000
	0 N Combination	7.41	3.28	.044
	0.0025 N combination	-5.26	3.28	.135
	0.005 N combination	-15.50	3.28	.001
	0.01 N combination	-21.51	3.28	.000
	0.015 N combination	-33.19	3.28	.000
	0.020 N combination	-34.19	3.28	.000

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.005 N CrCl3	0 N CrCl3	11.22	3.28	.005
	0.0025 N CrCl3	3.77	3.28	.274
	0.01 N CrCl3	-14.37	3.28	.001
	0.015 N CrCl3	-19.03	3.28	.000
	0.020 N CrCl3	-24.99	3.28	.000
	0 N Combination	11.18	3.28	.005
	0.0025 N combination	-1.49	3.28	.658
	0.005 N combination	-11.73	3.28	.004
	0.01 N combination	-17.73	3.28	.000
	0.015 N combination	-29.42	3.28	.000
	0.020 N combination	-30.42	3.28	.000

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.01 N CrCl3	0 N CrCl3	25.59	3.28	.000
	0.0025 N CrCl3	18.14	3.28	.000
	0.005 N CrCl3	14.37	3.28	.001
	0.015 N CrCl3	-4.66	3.28	.181
	0.020 N CrCl3	-10.62	3.28	.007
	0 N Combination	25.55	3.28	.000
	0.0025 N combination	12.88	3.28	.002
	0.005 N combination	2.63	3.28	.438
	0.01 N combination	-3.36	3.28	.326
	0.015 N combination	-15.05	3.28	.001
	0.020 N combination	-16.05	3.28	.000

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.015 N CrCl3	0 N CrCl3	30.25	3.28	.000
	0.0025 N CrCl3	22.81	3.28	.000
	0.005 N CrCl3	19.03	3.28	.000
	0.01 N CrCl3	4.66	3.28	.181
	0.020 N CrCl3	-5.95	3.28	.095
	0 N Combination	30.22	3.28	.000
	0.0025 N combination	17.54	3.28	.000
	0.005 N combination	7.30	3.28	.046
	0.01 N combination	1.29	3.28	.700
	0.015 N combination	-10.38	3.28	.008
	0.020 N combination	-11.38	3.28	.005

(I) Concentration	(J) Concentration	Mean Difference (I-J)	Std. Error	Sig.
0.020 N CrCl3	0 N CrCl3	36.21	3.28	.000
	0.0025 N CrCl3	28.76	3.28	.000
	0.005 N CrCl3	24.99	3.28	.000
	0.01 N CrCl3	10.62	3.28	.007
	0.015 N CrCl3	5.95	3.28	.095
	0 N Combination	36.17	3.28	.000
	0.0025 N combination	23.50	3.28	.000
	0.005 N combination	13.26	3.28	.002
	0.01 N combination	7.25	3.28	.048
	0.015 N combination	-4.42	3.28	.203
	0.020 N combination	-5.42	3.28	.125

A-3 Significant data of effect mass of HTCG-Sul

Table A-3.1 significant of glucose yield in effect mass of HTCG-Sul

Multiple Comparisons

Glucose
LSD

(I) MassofHTCGSul	(J) MassofHTCGSul	Mean Difference (I-J)	Std. Error	Sig.
0 %wt	5 %wt	1.19	.88	.225
	10 %wt	1.27	.88	.200
	20 %wt	2.97	.88	.015
	30 %wt	-1.31	.88	.188
	40 %wt	-3.00	.88	.015
5 %wt	0 %wt	-1.19	.88	.225
	10 %wt	.077	.88	.933
	20 %wt	1.77	.88	.092
	30 %wt	-2.51	.88	.030
	40 %wt	-4.20	.88	.003
10 %wt	0 %wt	-1.27	.88	.200
	5 %wt	-.077	.88	.933
	20 %wt	1.69	.88	.104
	30 %wt	-2.59	.88	.026
	40 %wt	-4.28	.88	.003
20 %wt	0 %wt	-2.97	.88	.015
	5 %wt	-1.77	.88	.092
	10 %wt	-1.69	.88	.104
	30 %wt	-4.28	.88	.003
	40 %wt	-5.97	.88	.001

(I) MassofHTCGSul	(J) MassofHTCGSul	Mean Difference (I-J)	Std. Error	Sig.
30 %wt	0 %wt	1.31	.88	.188
	5 %wt	2.51	.88	.030
	10 %wt	2.59	.88	.026
	20 %wt	4.28	.88	.003
	40 %wt	-1.69	.88	.105
40 %wt	0 %wt	3.00	.88	.015
	5 %wt	4.20	.88	.003
	10 %wt	4.28	.88	.003
	20 %wt	5.97	.88	.001
	30 %wt	1.69	.88	.105

Table A-3.2 significant of HMF yield in effect mass of HTCG-Sul

Multiple Comparisons

HMF
LSD

(I) Massof HTCGSul	(J) Massof HTCGSul	Mean Difference (I-J)	Std. Error	Sig.
0 %wt	5 %wt	-2.90	.71	.007
	10 %wt	-.66	.71	.384
	20 %wt	-.23	.71	.753
	30 %wt	-1.61	.71	.064
	40 %wt	.022	.71	.976
5 %wt	0 %wt	2.90	.71	.007
	10 %wt	2.23	.71	.020
	20 %wt	2.66	.71	.010
	30 %wt	1.28	.71	.122
	40 %wt	2.92	.71	.006

(I) Massof HTCGSul	(J) MassofHTCGSul	Mean Difference (I-J)	Std. Error	Sig.
10 %wt	0 %wt	.66	.71	.384
	5 %wt	-2.23	.71	.020
	20 %wt	.43	.71	.565
	30 %wt	-.94	.71	.232
	40 %wt	.69	.71	.370
20 %wt	0 %wt	.23	.71	.753
	5 %wt	-2.66	.71	.010
	10 %wt	-.43	.71	.565
	30 %wt	-1.38	.71	.101
	40 %wt	.25	.71	.731
30 %wt	0 %wt	1.61	.71	.064
	5 %wt	-1.28	.71	.122
	10 %wt	.94	.71	.232
	20 %wt	1.38	.71	.101
	40 %wt	1.64	.71	.061
40 %wt	0 %wt	-.022	.71	.976
	5 %wt	-2.92	.71	.006
	10 %wt	-.69	.71	.370
	20 %wt	-.25	.71	.731
	30 %wt	-1.64	.71	.061

Table A-3.3 significant of LA yield in effect mass of HTCG-Sul

Multiple Comparisons

LA
LSD

(I) Massof HTCG Sul	(J) MassofHTCGSul	Mean Difference (I-J)	Std. Error	Sig.
0 %wt	5 %wt	-11.73	2.45	.003
	10 %wt	-2.45	2.45	.355
	20 %wt	-4.22	2.45	.136
	30 %wt	-5.01	2.45	.087
	40 %wt	1.35	2.45	.602
5 %wt	0 %wt	11.73	2.45	.003
	10 %wt	9.27	2.45	.009
	20 %wt	7.50	2.45	.022
	30 %wt	6.71	2.45	.034
	40 %wt	13.08	2.45	.002
10 %wt	0 %wt	2.45	2.45	.355
	5 %wt	-9.27	2.45	.009
	20 %wt	-1.76	2.45	.498
	30 %wt	-2.55	2.45	.337
	40 %wt	3.80	2.45	.172

(I) Massof HTCGSul	(J) MassofHTCGSul	Mean Difference (I-J)	Std. Error	Sig.
20 %wt	0 %wt	4.22	2.45	.136
	5 %wt	-7.50	2.45	.022
	10 %wt	1.76	2.45	.498
	30 %wt	-.79	2.45	.758
	40 %wt	5.57	2.45	.063
30 %wt	0 %wt	5.01	2.45	.087
	5 %wt	-6.71	2.45	.034
	10 %wt	2.55	2.45	.337
	20 %wt	.79	2.45	.758
	40 %wt	6.36	2.45	.041
40 %wt	0 %wt	-1.35	2.45	.602
	5 %wt	-13.08	2.45	.002
	10 %wt	-3.80	2.45	.172
	20 %wt	-5.57	2.45	.063
	30 %wt	-6.36	2.45	.041

A-4 Significant data of effect time in biphasic system and 5 min for one phase system

Table A-4.1 significant of HMF yield in biphasic system

Multiple Comparisons

HMF
LSD

(I) Time	(J) Time	Mean Difference (I-J)	Std. Error	Sig.
5 min	10 min	-5.94	1.74	.011
	20 min	-3.17	1.74	.111
	40 min	1.98	1.74	.292
	60 min	5.02	1.74	.024
	90 min	8.35	1.74	.002
	5 min one-phase system	4.98	1.74	.024
10 min	5 min	5.94	1.74	.011
	20 min	2.76	1.74	.157
	40 min	7.93	1.74	.003
	60 min	10.96	1.74	.000
	90 min	14.29	1.74	.000
	5 min one-phase system	10.92	1.74	.000
20 min	5 min	3.17	1.74	.111
	10 min	-2.76	1.74	.157
	40 min	5.16	1.74	.021
	60 min	8.19	1.74	.002
	90 min	11.53	1.74	.000
	5 min one-phase system	8.15	1.74	.002

(I) Time	(J) Time	Mean Difference (I-J)	Std. Error	Sig.
40 min	5 min	-1.98	1.74	.292
	10 min	-7.93	1.74	.003
	20 min	-5.16	1.74	.021
	60 min	3.03	1.74	.126
	90 min	6.36	1.74	.008
	5 min one-phase system	2.99	1.74	.130
60 min	5 min	-5.02	1.74	.024
	10 min	-10.96	1.74	.000
	20 min	-8.19	1.74	.002
	40 min	-3.03	1.74	.126
	90 min	3.33	1.74	.098
	5 min one-phase system	-.039	1.74	.983
90 min	5 min	-8.35	1.74	.002
	10 min	-14.29	1.74	.000
	20 min	-11.53	1.74	.000
	40 min	-6.36	1.74	.008
	60 min	-3.33	1.74	.098
	5 min one-phase system	-3.37	1.74	.095
5 min one-phase system	5 min	-4.98	1.74	.024
	10 min	-10.92	1.74	.000
	20 min	-8.15	1.74	.002
	40 min	-2.99	1.74	.130
	60 min	.039	1.74	.983
	90 min	3.37	1.74	.095

Table A-4.2 significant of LA yield in biphasic system

Multiple Comparisons

LA
LSD

(I) Time	(J) Time	Mean Difference (I-J)	Std. Error	Sig.
5 min	10 min	-.70	1.47	.648
	20 min	-.57	1.47	.707
	40 min	.61	1.47	.689
	60 min	-6.12	1.47	.004
	90 min	-7.21	1.47	.002
	5 min one-phase system	-19.29	1.47	.000
10 min	5 min	.704	1.47	.648
	20 min	.12	1.47	.935
	40 min	1.32	1.47	.401
	60 min	-5.42	1.47	.008
	90 min	-6.51	1.47	.003
	5 min one-phase system	-18.59	1.47	.000
20 min	5 min	.57	1.47	.707
	10 min	-.12	1.47	.935
	40 min	1.19	1.47	.445
	60 min	-5.54	1.47	.007
	90 min	-6.63	1.47	.003
	5 min one-phase system	-18.71	1.47	.000

(I) Time	(J) Time	Mean Difference (I-J)	Std. Error	Sig.
40 min	5 min	-.61	1.47	.689
	10 min	-1.32	1.47	.401
	20 min	-1.19	1.47	.445
	60 min	-6.74	1.47	.003
	90 min	-7.83	1.47	.001
	5 min one-phase system	-19.91	1.47	.000
60 min	5 min	6.12	1.47	.004
	10 min	5.42	1.47	.008
	20 min	5.54	1.47	.007
	40 min	6.74	1.47	.003
	90 min	-1.09	1.47	.485
	5 min one-phase system	-13.16	1.47	.000
90 min	5 min	7.21	1.47	.002
	10 min	6.51	1.47	.003
	20 min	6.63	1.47	.003
	40 min	7.83	1.47	.001
	60 min	1.09	1.47	.485
	5 min one-phase system	-12.07	1.47	.000
5 min one-phase system	5 min	19.29	1.47	.000
	10 min	18.59	1.47	.000
	20 min	18.71	1.47	.000
	40 min	19.91	1.47	.000
	60 min	13.16	1.47	.000
	90 min	12.07	1.47	.000

APPENDICE B
EXPERIMENTAL DATA FOR ANALYSIS

B-1 Standard calibration curve for HPLC analysis of HMF

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

Peak area(UV detector at 220 nm)	Concentration of HMF (mg/ml)
1789276	0.05
3708422	0.2
9314567	0.5
14861719	0.8
19044361	1

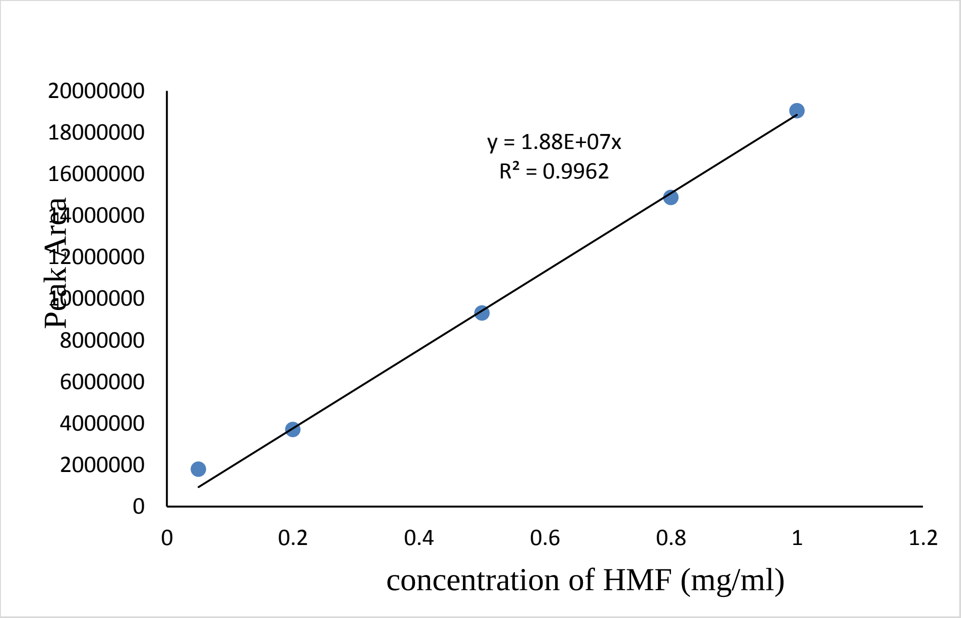

Figure B-4.1 Standard curve of HMF

Table B-2 Standard calibration curve for HPLC analysis of levulinic acid

Table B-2 Standard calibration curve for HPLC analysis of LA

Peak area (UV detector at 220 nm)	Concentration of levulinic acid (mg/ml)
1854	0.05
88289	0.5
319008	2
816871	5
1565800	10
2402527	15
3287849	20

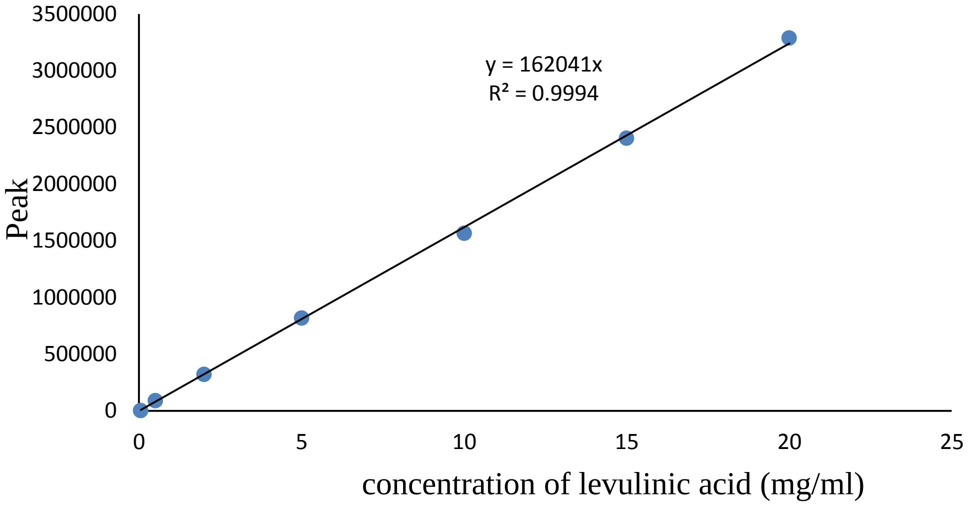

Figure B-4.2 Standard curve of HMF

Table B-3 Standard calibration curve for HPLC analysis of glucose

Table B-3 Standard calibration curve for HPLC analysis of glucose

Peak area (RI detector)	**Concentration of Glucose (mg/ml)**
1582540.48	5
3236042.57	10
4822728.05	15
6283278.35	20
8002229.99	25

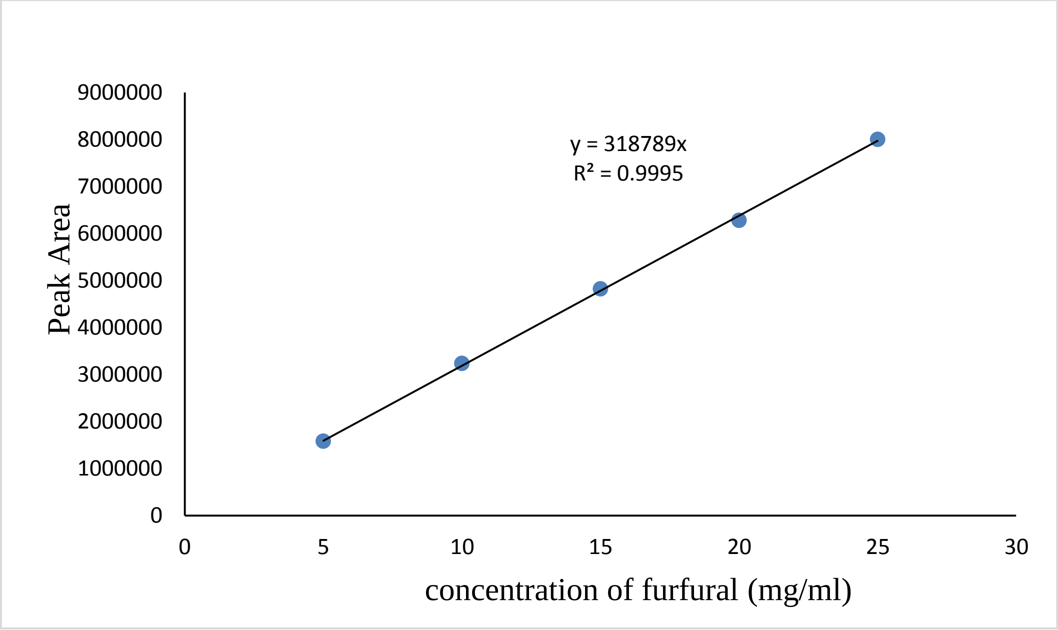

Figure B-4.3 Standard curve of glucose

APPENDICE C
EXPERIMENTAL DATA

C-1 Calculation of yield (wt. %) of glucose, LA, and HMF

$$\text{Product yield (\%)} = \frac{\text{gram of glucose, HMF or LA in product x 100}}{\text{gram of feedstock (Cellulose)}}$$

C-2 Experimental data of glucose, HMF, and LA from cellulose

Table C-2.1 Effect of type Lewis acid

Type of Lewis acid	glucose(wt. %)	HMF(wt. %)	LA (wt. %)
$FeCl_2$	11.27	0.89	0
$FeCl_3$	11.24	1.04	0
$CoCl_2$	4.45	0.25	0.07
$MnCl_2$	2.33	0.13	0.77
$CdCl_2$	1.72	0.10	0.10
$CrCl_3$	5.74	6.82	11.22

C-3 Effect of temperature and time

Table C-3.1 Effect of time at 160°C

time (min)	Glucose (wt. %)	HMF(%wt. %)	LA(wt. %)
0	0	0	0
5	0.81	0.37	0.19
10	0.53	0.47	0.01
20	2.35	1.89	2.77
40	0.33	0.97	1.43
60	0.36	1.15	2.16

Table C-3.2 Effect of time at 180°C

time (min)	Glucose (wt. %)	HMF(wt. %)	LA(wt. %)
0	0	0.15	0.01
5	1.64	2.54	2.03
10	1.13	2.83	2.99
20	1.55	3.55	8.81
40	0.36	2.55	8.81
60	1.56	1.91	9.98

Table C-3.3 Effect of time at 200°C

time (min)	Glucose (wt. %)	HMF(wt. %)	LA(wt. %)
0	1.56	1.35	0.63
5	3.60	7.54	15.37
10	0.88	2.55	24.94
20	0.89	2.42	18.59
40	0.63	1.41	18.52
60	0	0.11	19.77

Table C-3.4 Effect of time at 220^{o}C

time (min)	Glucose (wt. %)	HMF (wt. %)	LA (wt. %)
0	8.46	10.32	12.09
5	0.07	0.28	33.22
10	0.05	0.19	35.04
20	0	0.16	36.57
40	0	0.09	19.55
60	0	0	20.07

C-4 Effect of concentration $CrCl_3$

Table C-4.1 Effect of concentration $CrCl_3$ of without combination with two experiments

[$CrCl_3$]	Glucose (wt. %) EXP1	Glucose (wt.%) EXP2	HMF (wt.%) EXP1	HMF (wt.%) EXP2	LA (wt.%) EXP1	LA (wt.%) EXP2
0	5.02	5.44	0.40	0.40	0	0
0.0025	9.94	11.04	3.68	3.56	7.73	7.15
0.005	8.11	5.76	4.54	3.29	12.15	10.28
0.01	2.94	3.08	5.53	5.45	30.07	21.10
0.015	0.63	1.42	3.22	2.83	34.59	25.92
0.02	0.09	0.46	1.59	3.28	34.25	38.17

Table C-4.2 Effect of concentration $CrCl_3$ of without combination with mean and variance of two experiments

[$CrCl_3$] molar	Mean glucose	SD glucose	Mean HMF	SD HMF	Mean LA	SD LA
0	5.23	0.29	0.40	0.00	0	0
0.0025	10.49	0.77	3.62	0.08	7.44	0.41
0.005	6.94	1.66	3.91	0.88	11.22	1.32
0.01	3.01	0.09	5.49	0.05	25.59	6.33
0.015	1.02	0.55	3.02	0.279	30.25	6.13
0.02	0.28	0.25	2.44	1.19	36.21	2.76

Table C-4.3 Effect of concentration $CrCl_3$ of combination with two experiments

$[CrCl_3]$ molar	Glucose (wt.%) EXP1	Glucose (wt.%) EXP2	HMF (wt.%) EXP1	HMF (wt.%) EXP2	LA (wt.%) EXP1	LA (wt.%) EXP2
0	2.69	4.87	0.24	0.22	0.02	0.05
0.0025	10.41	9.57	5.65	4.99	12.38	13.03
0.005	5.83	5.65	7.21	6.43	24.53	21.37
0.01	3.14	2.67	5.88	5.13	28.91	29.00
0.015	0.56	0.60	2.76	2.99	42.29	38.98
0.02	0.73	0.06	2.37	1.06	37.66	45.62

Table C-4.4 Effect of concentration $CrCl_3$ of combination with mean and variance of two experiments

$[CrCl_3]$ molar	Mean glucose	SD glucose	Mean HMF	SD HMF	Mean LA	SD LA
0	3.78	1.54	0.23	0.01	0.03	0.024
0.0025	9.99	0.59	5.32	0.46	12.71	0.45
0.005	5.74	0.12	6.82	0.54	22.95	2.22
0.01	2.91	0.33	5.50	0.52	28.95	0.06
0.015	0.58	0.02	2.87	0.16	40.64	2.34
0.02	0.39	3.31	1.72	0.92	41.64	5.62

C-5 Effect of mass of HTCG-Sul

Table C-5.1 Effect of mass of HTCG-Sul of two experiments

HTCG-Sul (wt.%)	Glucose (wt.%) EXP1	Glucose (wt.%) EXP2	HMF (wt.%) EXP1	HMF (wt.%) EXP2	LA (wt.%) EXP1	LA (wt.%) EXP2
0	8.11	5.76	4.54	3.29	12.15	10.28
5	5.83	5.65	7.21	6.43	24.53	21.37
10	5.95	5.37	5.12	4.05	15.24	12.11
20	4.24	3.70	4.47	3.83	16.62	14.26
30	7.53	8.97	6.20	4.87	18.95	13.51
40	10.48	9.41	4.29	3.50	11.72	8.00

Table C-5.2 Effect of mass of HTCG-Sul with mean and variance of two experiments

HTCG-Sul (wt.%)	Mean glucose	SD glucose	Mean HMF	SD HMF	Mean LA	SD LA
0	6.94	1.66	3.91	0.88	11.22	1.32
5	5.74	0.12	6.82	0.54	22.95	2.22
10	5.66	0.41	4.58	0.75	13.67	2.21
20	3.97	0.38	4.15	0.45	15.44	1.66
30	8.25	1.01	5.53	0.941	16.23	3.84
40	9.94	0.75	3.89	0.55	9.86	2.63

C-6 Effect of composition of biphasic system

Table C-6.1 Effect of composition of biphasic system

Type of composition	Glucose (wt.%)	HMF (wt.%)	LA (wt.%)
1	0	7.25	7.85
2	0	4.33	4.10
3	0	9.09	3.77
4	0	2.15	0

C-7 Effect of time in biphasic system

Table C-7.1 Effect of time (min) in biphasic system (Type 3)

Time (min)	HMF (wt.%) EXP1	HMF (wt.%) EXP2	LA (wt.%) EXP1	LA (wt.%) EXP2
5	9.09	14.50	3.77	3.54
10	18.79	16.70	1.71	1.79
15	15.53	14.42	0.88	2.53
30	9.56	10.07	1.04	1.41
60	8.09	5.47	4.20	3.66
90	3.57	3.32	4.14	4.62

Table C-7.2 Effect of time (min) in biphasic system (Type 3) with mean and variance of two experiments

Time (min)	Mean HMF	SD HMF	Mean LA	SD LA
5	11.80	3.82	3.65	0.16
10	17.74	1.47	4.36	0.10
15	14.98	0.78	4.23	2.88
30	9.81	0.36	3.04	0.60
60	6.78	1.84	9.78	0.95
90	3.45	0.17	10.87	0.83

APPENDICE D

CONFERENCE PROCEEDINGS

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ECBA-17

Combining Hydrothermal Carbon-Based and Lewis Acid Catalysts for One-Pot Synthesis of 5- (Hydroxymethyl) furfural from Cellulose

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Abstract

Conversion of cellulosic biomass to fuels is a cascade process involving a number of reactions, including hydrolysis of cellulose to glucose, followed by dehydration of glucose to 5-hydroxymethylfurfural (HMF). Brønsted acids such as sulfuric acid, hydrochloric acid, graphene oxide or hydrothermal carbon-based catalysts are considered suitable for hydrolysis of cellulose and dehydration of fructose. However, the more difficult step seems to be the dehydration of hydrolyzed product, namely glucose to HMF due to the stable ring structure of glucose, compared with its isomerized form, namely fructose. As a result, the isomerization of glucose to fructose, which is a Lewis acid- catalyzed reaction, represents an important intermediate step between hydrolysis and dehydration in improving the conversion of cellulosic biomass to fuels or to other renewable chemicals. Therefore, the aim of this study is to combine Brønsted acid, particularly hydrothermal carbon-based acid catalyst, for hydrolysis of cellulose and dehydration of fructose with Lewis acid, chromium chloride ($CrCl_3$) for isomerization of glucose to fructose. The reaction catalyzed by the combination of hydrothermal carbon-based acid catalyst and $CrCl_3$ showed higher HMF yield than that catalyzed by $CrCl_3$ alone. The effects of various operating variables were investigated.

Peer-review under responsibility of the Scientific & Review committee of ECBA- 2017.

Keywords— 5-Hydroxymethylfurfural (HMF), Lewis Acid and Hydrothermal Carbon Based Acid Catalyst

Introduction

The process of converting cellulose into 5-hydroxymethylfurfural (HMF), an important intermediate of liquid fuels consists of 3 steps, including hydrolysis, isomerization and dehydration. The first step involves the conversion of cellulose into glucose molecules through hydrolysis reaction. Subsequently, glucose isomerizes into fructose, and both glucose and fructose undergo dehydration to HMF and furfural. In this process, the HMF yield is low using Brønsted acid such as hydrothermal carbon based acid, graphene oxide, hydrochloric acid and sulphuric acid catalyst due to difficulty in dehydrating glucose, but high yields of HMF could be obtained using fructose as starting material [1]. As a result, glucose isomerization to fructose followed by its subsequent dehydration to HMF in a one-pot synthesis has recently gained attention. Particularly, various metal salts have been found to be highly active for isomerization of glucose such as metal chloride of Cr, Al, Zn, Co and Mn. They have been applied to HMF synthesis from glucose in aqueous media-especially $CrCl_3$. $CrCl_3$ is very active for aldose-to-ketose isomerization. Thus, using $CrCl_3$ in the aldose (glucose) conversion to its respective furan exhibits a trade-off between accelerating the rate of aldose-to-ketose isomerization and so $CrCl_3$ has a drawback in giving off undesired products then. It should also be noted that the selectivity to HMF increases in fructose dehydration with increasing temperature, implying that the apparent activation energy associated with the HMF formation from fructose is higher compared with the side reactions. Thus, HMF selectivity can be improved by either lowering the solution pH (increasing Brønsted acid or increasing the reaction temperature) [2]. In this work, we investigate the Lewis acid ($CrCl_3$)-promoted cellulose conversion to HMF in aqueous media combined with a Brønsted acid (hydrothermal carbon-based catalyst) for improving selectivity of HMF.

Experimental

Catalytic activity test for cellulose conversion to HMF by hydrolysis, isomerization and dehydration

Catalytic activity was tested in an 8.8 ml SUS-316 stainless steel closed batch reactor. 0.1 g of cellulose and 5 ml of deionized water or 0.01 N $CrCl_3$ solution and HTCG-Sul 0.01 g were charged into the reactor, which was subsequently heated with an electric heater at 200°C for 5 min. After a specified reaction period, the reactor was cooled to room temperature. The amount of glucose and HMF in the liquid product was also analyzed by HPLC (high-performance liquid chromatography)

Result and Disscussion

Catalytic Activity Testing

The hydrothermal carbon-based acid catalyst (HTCG-Sul) and $CrCl_3$ was tested for hydrolysis, isomerization and dehydration. The results in Figure 1 showed that the yield of HMF was low using only water and HTCG-Sul because hydrolyzed glucose could not isomerize to fructose, thus difficult to dehydrate. However, higher yield of HMF was obtained using only CrCl3 because it can catalyze hydrolysis, isomerization and dehydration reactions. Moreover, using HTCG-Sul in combination with $CrCl_3$ showed the highest yield of HMF because HTCG-Sul not only promotes hydrolysis and dehydration, but could also improve selectivity in synergy with $CrCl_3$.

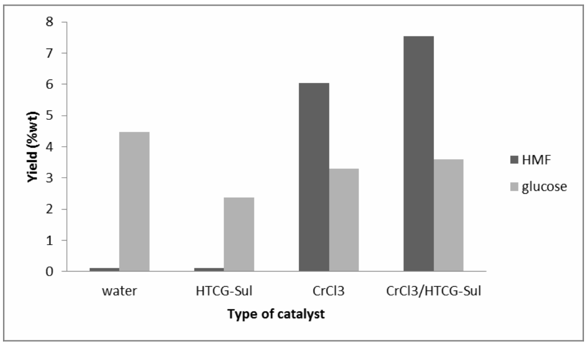

Figure 1: Yield of glucose, HMF obtained in the liquid product of cellulose hydrolysis, isomerization and dehydration promoted by various catalysts.

Conclusion

Using only HTCG-Sul is not suitable for efficient cellulose conversion to HMF because it cannot promote isomerization of glucose. Similarly, using only $CrCl_3$ could not provide highest yield of HMF. The combination of both could give higher yield of the target HMF.

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VITA

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