OPTIMIZATION OF BIOMASS CONVERSION TO 5-HYDROXYMETHYLFURFURAL BY CATALYTIC HOT COMPRESSED WATER AND IONIC LIQUID PROCESSES

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Dedicate to my Beloved Parents

My siblings…

For all their endless love, prays and patience

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ABSTRACT

A versatile compound to replace petroleum-based compound for generating fuel and fine chemicals, 5-Hydroxymethylfurfural (HMF), was derived from biomass in this study. Catalytic hot compressed water (HCW) and ionic liquid processeswere investigated for HMF production from glucose.Anatase titanium dioxide (a-TiO_2) and ytterbium (III) triflate ($Yb(OTf)_3$) was employed as catalyst for HCW and ionic liquid, respectively. 1-butyl 3-methyl imidazolium chloride ([BMIM]Cl) was used as solvent in ionic liquid process. Complete glucose conversion was achieved at 100 % by using ionic liquid process while the highest glucose conversion for HCW process wasgained at 87.7 %. Yield for HMF was up to 56.5 % and 8.7 % by using ionic liquid and HCW, respectively. The process parameters for both processes were optimized by using STATISTICA 7. Interaction among the process variables and its effects such as reaction temperature, time and catalyst loading were investigated using central composite design (CCD) and response surface methodology (RSM) approach. It was revealed temperature has significant effect for converting glucose to HMF in both processes.The study found that by applying optimum condition, 2.7 % HMF yield was gained at 146^oC within 5 min with 1078 mg of a-TiO_2 for HCW process. On contrary, ionic liquid process gave 52.8 % HMF yield at 106^oC with 39.7 mg of Yb(OTf3)in 165 min. This study proved that CCD and RSM approach was applicable for HCW and ionic liquid processes in order to optimize the process condition.

ABSTRAK

Satu sebatian yang serba boleh untuk menggantikan sebatian berasaskan petroleum untuk menjana bahan api dan bahan kimia, 5-Hydroxymethylfurfural (HMF), telah diperolehi dari biojisim dalam kajian ini. Air termampat panas bermangkin (HCW) dan prose cecair ionic telah disiasat untuk pengeluaran HMF dari glukosa. Anatase titanium dioksida (a-TiO_2) dan ytterbium triflate ($Yb(OTF)_3$), masing-masing telah digunakan sebagai pemangkin untuk proses HCW dan proses cecairionik. 1-butil 3-metil imidazoliumklorida ([BMIM]Cl) telah digunakan sebagai pelarut di dalam proses cecairionik. Penukaran glukosa yang lengkap telah dicapai iaitu pada 100% dengan menggunakan cecair ionik manakala penukaran tertinggi glukosa bagi proses HCW hanya dicapai pada 87.7%. Hasil HMF tertinggi dicapai sehingga 56.5% dan 8.7% untuk proses cecair ionic dan proses HCW, masing-masing. Pembolehubah proses untuk kedua-dua proses telah dioptimumkan dengan menggunakan STATISTICA 7. Interaksi dan kesan pemboleh ubah seperti suhu tindakbalas, masa dan beban pemangkin disiasat menggunakan pendekatan reka bentuk komposit pusat (CCD) dan kaedah respon permukaan(RSM). Ia didedahkan bahwa suhu mempunyai kesan penting untuk menukarkan glukosa untuk HMF dalam kedua-dua proses. Kajian mendapati bahawa dengan keadaan optimumyang telah digunakan diperolehi hasil HMF sebanyak 2.7% pada 146^{o}C dalam masa 5 minit dengan 1078 mg a-TiO_2 untuk proses HCW. Sebaliknya, proses cecair ionic menunjukkan hasil HMF sebanyak 52.8% pada 106^{o}C dengan 39.7 mg $Yb(OTf_3)$ selama 165 minit. Kajian ini membuktikan bahawa pendekatan CCD dan RSM terpakai untuk proses HCW dan proses cecair ionic untuk mengoptimumkan keadaan process.

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LIST OF ABBREVIATIONS

Y_i	-	the predicted response
X_i	-	the uncoded of the independent variables
X_j	-	the uncoded of the independent variables
β_0	-	the intercept coefficient
β_j	-	the linear terms
β_{jj}	-	the squared terms
β_{ij}	-	the interaction terms
$C_{initialglucose}$	-	concentration of glucose before reaction
$C_{glucoseremained}$	-	concentration of glucose after reaction
N_{HMF}	-	number of carbon atoms of HMF
C_{HMF}	-	concentration of HMF
$N_{glucose}$	-	number of carbon atoms of glucose

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The dependence on chemical-based petroleum is moving slightly towards renewable bio sources. Soaring petroleum price has accelerated the urgency to dig out alternative renewable source, while the biomass abundance has become an attractive option because of its sustainability. Renewable biomass materials grow in forest, plantation and field. This propelled the exploitation of biomass using new technologies and methods (Saka and Ueno, 1999).

Biomass has attracted researchers to explore more about its use and the benefit due to the limitation of fossil fuel as a major source for fuel and fine chemicals. Biomass has emerged as a new power to replace petroleum source as energy resources. The most abundantly available biomass materials are forests; waste products from agricultural crops, energy plants, biodegradable wastes, landfills and others. These biomass materials can be efficiently converted to different form of energy based fuel such as transportation fuel, electricity, and cooking oil. Also, for chemical feedstock such as glycerin, 5-hydroxymethylfurfural (HMF), levoglucosan, phenol, levulinic acid, etc.

Cellulose is a polysaccharide consists of hundreds to over thousand of β-1,4 glycosidic bonds linked by D-glucose subunit. Hemicellulose has structures with complex carbohydrates such as hexoses, pentose and xylan. It is a sugar that consists of 6-carbon and 5-carbon. Glucose as sugar can be assumed as a representative of cellulose and hemicelluloses. Glucose has been used as raw materials by many researches to search for a new invention. Besides using as fuel, glucosecan be utilized for producing 5-hydroxymethylfurfural (HMF), 2-5 DMF, levoglucosan, 2-5 furan dicarboxylic acid and other chemicals. HMF is a derivative of furan that can be obtained from dehydration of sugars without fermentation. HMF is also an intermediate compound used to generate levulinic acid. Furfural and other anhydroglucose, such as levoglucosan also have the potential to be a building-block matter for chemical and resin. HMF is used for producing chemicals, fuel, fiber, and other useful things.

As mentioned in Energy Efficiency and Renewable Energy report, HMF is identified as a versatile intermediate matter between petroleum-based building blocks and biomass-based carbohydrate chemistry. HMF ease the conversion into 2,5-furandicarboxylic acid (FDCA), poly(ethylene terephthalate) (PET) and 2,5-dimethylfuran (DMF), etc. PET has the potential as replacement of terephthalic acid for polyester, while DMF has gained attraction for transportation fuel, which has 40 percent greater energy density than ethanol (Su *et al*., 2009).

Since the end of 19^{th} century, HMF has attracted the researcher's attention for generating chemical compound that they called "oxymethylfurfurol". Basically, HMF is produced from dehydration of hexoses. Polysaccharides and oligosaccharides are the variety of substrate that is mostly used. Antal*et al.* (1990) had proven that fructose is the appropriate substrate to engender HMF.

In addition, Asghari and Yoshida (2006) had synthesized HMF in water or organic solvent mixture by using acid-catalyzed dehydration process.In the beginning, the methods for syntheses of HMF were practiced by using oxalic acid and now critical water has been employed as the alternative methods(Watanabe *et al*., 2005a-b; and Asghari & Yoshida, 2006). Homogeneous or heterogeneous catalysts have been studied to improve the HMF yield such as heteropoly acid, zeolite, acidic acid, ZrP, H_2S0_4, TiO_2, and ZrO_2 (Shimizu *et al*., 2009; and Asghari and Yoshida, 2006; Watanabe *et al,* 2005a-b).

1.2 Problem Statement

Biomass is an attractive feedstock for energy and chemicals since it is renewable, zero carbon emission and has low sulphur character. This resource, especially cellulose is a potential raw material for future and many researches are working to utilize them efficiently. For examples, empty fruit bunches (EFB) comprise 18.1 wt% of lignin, 22.1 wt% of hemicelluloses and 59.7 wt% of cellulose (Misson *et al*., 2009). Cellulose can be converted into fuel and other chemicals using several methods. Breaking down the linkage of cellulose, hemicelluloses and lignin will provide a good substrate for producing chemical feedstock such as HMF, 2-5 dimethyl furfural, levoglucosan, etc. In this study, glucose is utilized as raw material to investigate as a sugar representative of cellulose.

A number of researches have been studied for generating HMF from fructose instead of using glucose as raw material. Whereas, fructose is an edible raw material and using it leads to food competition, which become disadvantages for human need. On the other hands, biomass consists of cellulose and hemicelluloses, which have sugar content within it. HCW and ionic liquid process are used to produce HMF with different catalyst and condition operation. Ionic liquid is identified as green solvent, which comprise of cations and anions that are weakly matched. The combination of cation and anion structure defined by physicochemical and thermodynamic properties of the ionic liquid (Simmons *et al*., 2010). Ionic liquid has the ability to disrupt the hydrogen bonding of the lignocellulosic complex compound (Olivier-Bourbigou *et al.*, 2010). Hot compressed water will be applied for the comparison of the process. Watanabe *et al*. (2005a) showed that by using base catalyst in hot compressed water promoted dehydration and condensation reaction.

However, the application of response surface methodology (RSM) with central composite design (CCD) approach has not been employed to assess the optimum condition for HCW and ionic liquid process. This study ascertained optimum condition for both processes using RSM with CCD approach and provide a maximum HMF yield.

1.3 Objectives of the Study

The objectives of study are given as below:

(i) To convert glucose into HMF by using catalytic process of HCW and ionic liquid process

(ii) To find an optimum condition for catalytic of HCW and ionic liquid process, hence generate a good yield of HMF.

(iii) To investigate potential of EFB as raw material for producing HMF at optimum condition.

1.4 Scope of the Study

The scopes of this study were:

(i) Characterization of biomass, which were glucose and EFB, by using FTIR and TGA were elucidated in Chapter 4.

(ii) Catalytic HCW and ionic liquid process to produce HMF. This study focused on temperature, reaction time and catalyst loading as process variables. Liquid products of HMF were identified and analyzed by FTIR and HPLC, while solid products using FTIR.

(iii) Utilization of response surface methodology (RSM) with central composite design (CCD) approach to obtain optimum condition for HCW and ionic liquid process. Results of optimization were presented in Chapter 4.

1.5 Significance of the Study

In this study, ionic liquid process produced higher HMF yield than HCW process. RSM and CCD approach provided acceptable modeling equations that are generated from optimum condition for both processes. Glucose and EFB were utilized as feedstock in optimum condition for both processes.