A STUDY CONVERSION OF SUGARS TO BIOFUEL FROM LIGNOCELLULOSIC BIOMASS.

Nuttida Chanhom
Department of Electrical Industrial Technology
Suan Sunandha Rajabhat University, Bangkok, Thailand
E-Mail: nuttida.ch.@ssru.ac.th

ABSTRACT

Lignocellulosic biomass contains more than 60% of cellulose consisting of glucose that can be converted into synthetic fuel. Production of 5-Hydroxymethylfurfural (HMF) from raw lignocellulosic biomass is combination treatment of diluted acid/base-assisted pretreatment and catalytic conversion. The condition, using HCI as catalysts and carried out with dilute sulfuric acid concentrations between 1.0 to 5.0% w/w, and residence time between 33 to 40 min at stable temperature of 140 degree celsius. High glucose conversion to HMF yield of 61.3%, respectively. There were obtained at 3.3% w/w for 35 min. The activation energy for producing HMF was 76 kJ/mol in our system. The combinational treatment demonstrate an effective transformation of glucose into HMF with a high yield.

Keywords: Lignocellulosic, Glucose, 5-Hydroxymethyfurfural**,** Biofuel

INTRODUCTION

Synthetic fuel in the form of Dimethylfuran (DMF) has drawn attention lately due to the fact that it has high energy density (30 kJ cm^{-3}), high Research Octane Number (RON = 119) and low water solubility (2.3 g L^{-1}) [1]. This makes DMF more remarkable than ethanol as a blend fuel. The conversion of sugar such as fructose into DMF starts from removing oxygen atoms by acid-catalysed dehydration to produce an intermediate called 5-Hydroxymethylfural (HMF). Subsequently, HMF is extracted in the organic phase of the reactor and is subsequently converted into DMF by hydrogenolysis of C–O bonds over a copper based catalyst.

In each year, a large amount of raw materials containing sugar or starch has been converted into ethanol for fuelling vehicles through fermentation and distillation. As a result, the large scale production of ethanol would require the large land area for cultivating agricultural cash crops such as sugar cane, cassava and corn. Inevitably, the prices of the cash crops and also the food in the food industrial sectors would be partly driven by the fuel prices in energy markets. For these reasons, production of synthetic fuel from non-food crops and agriculture waste has become more attractive recently. Normally found in the cell wall of green plants, cellulose consists of glucose and fructose that can be converted into a range of polymers and synthetic fuels, especially DMF.

A key step of the conversion of lignocellulosic biomass into sugars belongs to the pretreatment step. The main goal of pretreatment is to separate the cellulose from the matrix polymers, and to make it more accessible for enzymatic hydrolysis. Lignocellulose consists of cellulose, hemicellulose, lignin, extractives, and several inorganic materials. Pretreatment of corn stover over a range of sulfuric acid concentrations of 0.22%, 0.49% and 0.98% w/w at 140, 160, 180 and 200° C. Up to 15% of the total potential sugar in the substrate could be released as glucose during pretreatment and between 15% and 90+% of the xylose remaining in the solid residue could be recovered in subsequent enzymatic hydrolysis, depending on the enzyme loading. Glucose yield was increased from as high as 56% of total maximum potential glucose plus xylose for just enzymatic digestion to 60%. Xylose yields was increased from as high as 34% of total potential sugars for pretreatment alone to between 35% and 37% when credit was taken for xylose released in digestion [2].

The conversion of fructose into DMF starts from removing oxygen atoms by acid-catalysed dehydration to produce an intermediate called 5-Hydroxymethylfural (HMF). Subsequently, HMF is extracted in the organic phase of the reactor and is subsequently converted into DMF by hydrogenolysis of C–O bonds over a copper based catalyst. It has been found that the conversion of fructose is more selective than that of glucose. With fructose, the selectivity is up to 84% [3]. This agrees well with the review done in which HMF can be synthesized by the dehydration of fructose and glucose with a variety of catalysts such as sulfuric acid, phosphoric acid, and hydrochloric acid even though the dehydration of glucose has been reported to have lower reaction rate and lower selectivity to HMF compared to these of fructose [4]. Also used acid catalysts (HCl and H_2SO_4) and found that the HMF selectivity could be increased by adding NaCl to create biphasic systems with solvents that were completely miscible with water, as well as to increase the upper critical solubility temperature of certain partially soluble solvents. The impact of solvent choice on HMF yield was also studied and it was found that Biphasic systems containing C4 solvents generated the highest HMF yields in which tetrahydrofuran demonstrated the best combination of high HMF selectivity of 83% [5].

The objective of this work is to study the conversion of glucose to HMF as an intermediate of producing DMF by an acid hydrolysis reaction. A range of acid concentration, and time and temperature of reaction will be investigated in order to obtain the highest yield of HMF which will be converted into DMF subsequently.

MATERIALS AND METHODS

The design of experiments

It has been reported in the work of that by using hydrochloric acid at 3.3% w/w, time of reaction of 15-30 mins and temperature at 170 °C [6], the reaction can yield the highest HMF content. However, with the limitation of equipment that can operate up to 140 °C, the temperature of dehydration reaction in this work is fixed at 140 °C and the time of reaction is extended to 40 mins. Consequently, only two parameters, acid concentration and time of reaction are studied. Since in this work both glucose and fructose used as raw materials are investigated. The design of experiment is therefore involved in this work to identify the most suitable condition for dehydration reaction producing the highest yield of HMF.

The technique used to design the experiments is called Response Surface Methodology or RSM with steps as follows:

1. The experiments are planned and the samples are prepared in order to obtain sufficient data for making contour plots by considering a factor or 2 to 3 factors to define steps of studied factors.
2. The data from step 1 is used to create regression equations (SAS, SPSS).
3. The contour plot is created from the regression equations.
4. The model is investigated.
5. The model is verified and optimized by doing the independent run under each factor condition.

In this work Central Composite Designs or CCD is performed by using minitab version 14 in which the range of studied factors is shown in table 1. This results in 12 experiments per one set including the 4 experiments as the center point, 4 experiments of axial point and 4 experiments for factorial point. Since it has been reported in literature elsewhere that the most

suitable conditions are 3.3% w/w hydrochloric acid and time of reaction at 35 mins, the center point is this work is the same as stated. More details are available as follows:
Step 1: Specify the function of studied parameters which are acid concentration and time of reaction.

$$\mathrm{Glucose} = 66.011 - 0.706x_t - 0.447x_c - 6.723x_t^2 - 2.234x_c^2 - 0.4x_t x_c$$

Step 2: Identify the factors, steps of condition and symbols to obtain the optimum value.

Table 1. Condition and symbols to obtain the optimum value

Condition and symbol 5 levels of factors						
Factor	Level					Symbol
	-1.5	-1	0	+1	+1.5	
Concentration	2.7	3.0	3.3	3.5	3.8	x_c
Time	30	33	35	38	40	x_t

With the center point at 3.3% w/w and 35 mins, the model is recalculated for 4 experiments. Therefore, 12 experiments are contained in 1 set and the experiments are repeated 3 times, leading to 36 experiments totally.

RESULTS AND DISCUSSION

Using CCD technique to obtain the optimum condition of producing HMF from Glucose

From the results, the acid concentration of 3.3 % w/w and 35 mins of the time of reaction is the optimum condition obtaining highest yield of HMF. 4 experiments are focused with 3 repetitions for each experiment. It has been found that the conditions with high yield of HMF are conditions 9 -12 with % HMF of 60.4 %, 59.8 %, 60.5 % and 60.7 %, respectively. This can be compared with the simulation of CCD technique where condition 9 -12 can yield HMF 67.1 %, 66.8 %, 66.1 % and 66.3 %, accordingly as in Table 2.

Table 2. Results of **CCD condition of producing HMF from glucose**

Run	X_t	X_C	X_1	X_2	Glucose (%)
1	33	2.2	-1	-1	58.0
2	38	2.2	1	-1	57.3
3	33	4.2	-1	1	57.8
4	35	4.2	1	1	55.5
5	30	3.3	-1.5	0	51.8
6	40	3.3	1.5	0	49.8
7	35	1.0	0	-1.5	61.5
8	35	5.0	0	1.5	60.3
9	35	3.3	0	0	67.1
10	35	3.3	0	0	66.8
11	35	3.3	0	0	66.1
12	35	3.3	0	0	66.3

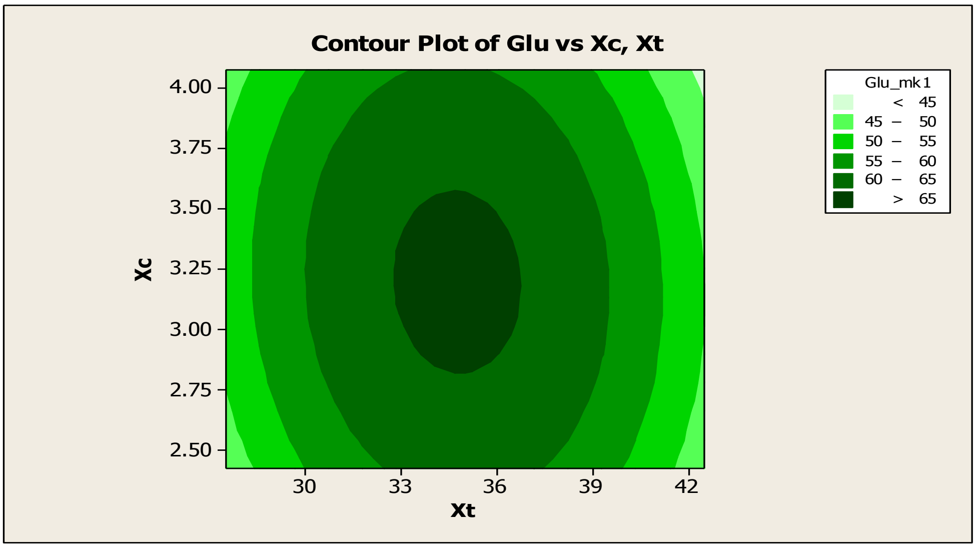

Fig.1. Picture of CCD optimum condition of producing HMF from glucose

CONCLUSION

There are 3 influential factors in converting glucose to 5-hydroxymethyfurfural (HMF) by dehydration, the acid concentration, the time of reaction and the temperature. From the results, at the acid concentration of 3.3 % w/w and the time of reaction at 35 mins, HMF can be yielded 61.3 % from glucose.

These agree well with the results obtained from CCD technique in the case that fructose can perform with higher yield of HMF than glucose. However, the yields of HMF attained from the experiments from both fructose and glucose are lower those of the simulation technique. It has been reported that the optimum condition is at the acid concentration of 3.0 % w/w, the temperature at 60 degrees Celsius and the time of reaction at 24 hours yielding HMF higher than 8 %. The optimum condition of this work can save a large amount of energy input through the shorter time of reaction at 140 degrees Celsius.

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