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Clean to Clean: Using Paper Waste to Produce Fermentable Sugar for Bioethanol Production

Ali Arasteh Nodeh*, Sina Aghili

Department of Chemical Engineering, Quchan Branch, Islamic Azad University, Quchan, Iran

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Abstract

In this paper, using paper waste for producing fermentable sugar in bioethanol process and effect of three variables of acid concentration, acid type, and process time on sugar extracted from dilute acid hydrolysis of paper wastes has been investigated. Paper waste was hydrolyzed by Sulfuric and hydrochloric acids with 2, 3, 4, and 6 wt% within the intervals of 4, 6, 8, 12, 16, 20, and 40 min at 121.5 °C in autoclave and glucose concentration was determined by Lane-Eynon method. Response Surface Method (RSM) was applied to interoperated the result. The curves indicated that the greatest concentration of extracted sugar has been obtained at the highest acid concentration and longest hydrolysis time. Further, sulfuric acid has extracted greater amounts of sugar than hydrochloric acid.

Keywords: paper wastes, renewable energy, fermentable sugar, RSM, hydrolysis

1 Introduction

With the industrial development of the world in the past century, the global demand for energy resources especially fossil fuels increased dramatically. Alongside this elevation of demand for fossils fuels, the world has been witnessing ever-increasing environmental hazards especially production of greenhouse gases and global warming. Therefore, the necessity of using renewable energy resources capable of substituting fossil fuels has become evident to everyone more than ever (Le man et al. 2010)].

Bioethanol is one of the cleanest sources of renewable energy to replace petrol, as one of the modern and up-to-date forms of energy with high oxygen content. Universal production of bioethanol shows a growing trend in the past few decades. Over this time, extensive attention was dedicated to research on converting lignocellulose compounds into bioethanol (Rehman et al. 2014). Lignocellulose compounds including agricultural waste, forest waste, solid urban wastes, and papers waste are abundantly available in many countries with different meteorological conditions. Plant biomass is mainly composed of three compounds; cellulose, hemicellulose, and lignin (Arastehnodeh and Mohammadi sani 2015).

The overall process of converting cellulosic materials into bioethanol consists of four stages: pretreatment, hydrolysis, fermentation, and separation as well as purification. The pretreatment of the diluted acid has been successfully developed for pretreatment of lignocellulose compounds (Tiwari et al. 2015).

The effect of acid concentration and pretreatment time on the concentration of sugar extracted from straw oilseeds by sulfuric acid was investigated and observed that with the increase in the concentration of the acid as well as process time, the level of sugar extracted from the oilseeds increases (Mathew et al. 2011).

Similar works can be observed in the studies by: Del campo et al in hydrolysis of diluted acid of different types of wastes produced by food industry factories (2006), Juan et al in hydrolysis of diluted acid of Olive tree pruning waste (Juan et al. 2013), Avci et al on hydrolysis of corn straw diluted acid using phosphoric acid (Avci et al. 2012), and Arasteh et al using hydrolysis of diluted acid of walnut green skin by sulfuric acid (Arasteh et al 2012).

Ruiz et al studied diluted acid hydrolysis of sunflower stalks using sulfuric acid and examined the factors influencing it. They used response surface method for analyzing the results. They found that in every 100 g of raw materials, at most 33 g of glucose and xylose was obtained under optimal conditions. The optimal conditions were determined to be 167°C and 10.3% of sulfuric acid (Ruiz et al 2013).

Solid urban wastes is one of important environment pollution material consist of glass, paper and polymer material. Currently, paper is manufactured by agricultural and wood wastes that mainly composed of carbohydrate polymers (cellulose and hemicellulose) with different levels of lignin. The carbohydrate section of the cell is mainly composed of polysaccharide of cellulose (Stenius 2000; Wise 1946). Therefore, paper wastes are one of the suitable raw materials for production of fermentable sugar in bioethanol process. In this research, suitable conditions for chemical hydrolysis of paper wastes have been examined by Response Surface Methodology (RSM).

Corresponding author: Ali Arasteh Nodeh, Department of chemical engineering, Quchan branch, Islamic Azad University, Quchan, Iran. E-mail: aliarastehnodeh@yahoo.com.

2 Materials and methods

2.1 Design of experiment

Due to the problem of finding an accurate mechanism for hydrolysis reactions to predict the concentration of glucose in different conditions, Response surface methodology was used to obtain an optimal response model (Bezerra et al. 2008). According to Olywia et al (Olayiwola et al. 2011), second-order polynomial models (Eq. 1) are good assumptions for modeling in RSM.

$$y_n = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i<j} \sum \beta_{ij} x_i x_j + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \varepsilon \quad (1)$$

where xi represents the acid concentration, pretreatment time, and y represent glucose concentration (Eq. 2).

$$G = \beta_0 + \beta_1 c + \beta_2 t + \beta_3 c^2 + \beta_4 t^2 + \beta_5 ct \quad (2)$$

2.2 Preparation of the raw materials

Paper waste (PW) was gathered randomly from solid urban waste. It was washed by distillated water, air dried, milled using vibratory disc mill (Retsch RS 100) to particle size smaller than 50 micrometers and stored in sealed plastic bags at room temperature .

Hydrolysis experiments were performed in screw-capped laboratory bottles (Pyrex bottles) as batch reactor placed in an autoclave with a temperature controller. The reactor was loaded with dried PW and sulfuric acid solution. The process variables were acid concentration (2, 3, 4, and 6 wt %) and reaction time (4, 6, 8, 12, 16, 20, and 40 min). Once the temperature of autoclave reached to the designed point (121.5^{oC}), pretreatment time was started. At the end of each experiment the bottle was removed from the autoclave and putted in a cool water bath, PH value reached 7 by Sodium hydroxide (NaOH). Solid residue was separated from solution by filtration, washed with distilled water and final solution reached to 1000 ml. A 200 ml sample of solution was analyzed. Based on factorial Design 28 experiments were run (Table 1).

2.3 Qualitative investigation of the extracted compounds

Before measuring the level of the extracted sugar, a random sample of the hydrolyzed solutions was chosen and the following experiments were done in two random samples to determine the quality and nature of its constituents.

- Molisch's test: after doing this experiment on the samples and having found that the answer was positive (formation of a purple ring across the sample), it was concluded that the solutions possessed sugar carbohydrate (Foulger 1931).
- Fehling's test: after doing this experiment on the samples and formation of brick-red deposits, presence of reducing sugar in the solution was confirmed. This sugar might be either a monosaccharide such as glucose or disaccharide such as lactose (Albrecht 2013; Fehling 1849).
- Barfoed's test: after doing this experiment on the samples and formation of red deposits, it was concluded that the reducing sugar was a monosaccharide (Barfoed 1873; Bowen et al 1957; Welker 1915,).
- Resorcinol's test: after doing this experiment on the samples and formation of red deposits following 15 min, presence of glucose sugar or fructose sugar in the samples was confirmed (Abramoff and Robert 1966; Chawla 2003; Katoch 2011; Seliwanoff 1887).
- Orcinol's test: after doing this experiment on the samples and formation of green deposits following 2 min, presence of six-carbon sugar such as glucose in the samples was confirmed (Baldwin and Bell 1955; Fernell and King1953).

By performing the abovementioned qualitative tests, it was found that the samples contained glucose.

2.4 Measurement of the extracted sugar of the solutions

In measurement of sugar using Lane-Eynon method, the sugar solution should be completely clear and filtered whereby the suspended solids are removed from the solution before titration and measurement of the level of the solution's sugar.

21.9 g zinc acetate and 3 ml acetate acid was added in a 100 ml volumetric flask then the volume was made up with water to prepare Carrez solution. 5 g of sample was transferred to a 200 ml volumetric flask and was diluted to 150 ml. 5 ml of Carrez solution and 5 ml of 10.6% aqueous solution of Potassium Ferro cyanide was added to flask and made up to 200 ml with water. After mixing, it was placed in a fixed position for 5 min in order to become bi-phased. It was then filtered resulting in a clear sugar solution. The Burette was then filled with 50 cc of the cleared sugar solution for doing Lane-Eynon experiment

A total of 5 cc of Fehling A solution (by dissolving 34.639 g of copper sulfate ($CuSO_4.5H_2O$) in 500 cc of distilled water), 5 cc of Fehling B solution (by dissolving 173 g of sodium potassium tartrate[2] and 50 g of NaOH in 500 cc distilled water) , and 10 ml water were poured into a 250ml flask. The flask was heated to boiling. 3 drops of methylene blue was added. 15 cc of the sugar solution was added into flask from the burette. Thereafter, while flask heating continues, the titration was continued until the blue color in the solution inside the flask was disappeared to a brick-red end point. The titration value was used in Lane-Eynon Table to determinate the sugar concentrations [14, 15].

3 Results and Discussion

3.*1 Glucose concentration*

Table 1 shows extracted glucose concentration in experiments condition.

3.2 The second-order polynomial models

Equations 3 and 4 represent the second-order polynomial models obtained from the analysis of variance table for different responses of dilute acid hydrolysis with sulfuric acid and hydrochloric acid, respectively.

$G=35.47999773+32.31218613\ c+4.89269778\ t-2.047762987\ c^2+0.046414418\ t^2+0.137236808\ ct$ (3)

$G=4.221405805+50.18288032\ c+5.813047117\ t-4.46549026\ c^2-0.052034296\ t^2-0.104095313\ ct$ (4)

[2] Rochelle salt

3.3- Study of the accuracy and validity of the models

The obtained models have a good accuracy to predict the result (figures 1- R^2 for both model are near 1).

Table 1: Extracted glucose concentration (mg/100ml) in experiments condition

Acid concentration (%)	**Sulfuric acid**	**Hydrochloric acid**						
Time (min)	**2**	**3**	**4**	**6**	**2**	**3**	**4**	**4**
4	120	130	157	174	114	120	134	163
6	123	144	163	188	118	131	147	169
8	134	153	167	205	122	134	151	189
12	140	163	178	213	126	147	170	202
16	156	178	212	240	137	165	179	216
20	179	212	230	249	159	200	212	230
40	226	239	288	304	182	225	238	256

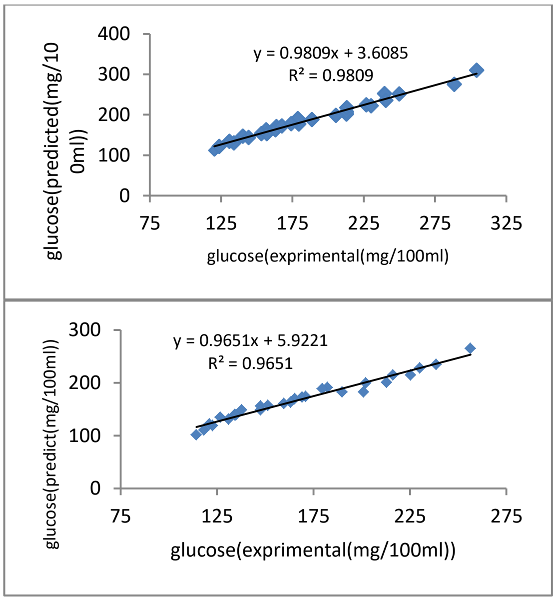

Figure 1. The proportion between experimental data and the model data (left) for hydrolysis by sulfuric acid (right) for hydrolysis by HCl.

To investigate the model validity, the results of the two other samples have been used randomly, followed by comparison of the model's response with the response of the experiments. The results are provided in Table 2. Based on the calculations, the extent of the model's error is lower than 5%, thus suggesting that the model is almost valid.

Table 1. Investigation of the models validity

Acid	**C (%)**	**Time (min)**		**Glucose (mg/100ml)**	**error**
H_2SO_4	2	6	predicted	120	2.9%
			experiment	123	
H_2SO_4	4	8	predicted	172	2.8%
			experiment	167	
HCl	2	6	predicted	110	6%
			experiment	118	
HCl	4	8	predicted	157	4%
			experiment	151	

It can be concluded from Figures 3 and 4 that: (a) sulfuric acid is more effective than hydrochloric acid. (b) The changes in the acid concentration influence the level of extracted sugar more than the changes in the

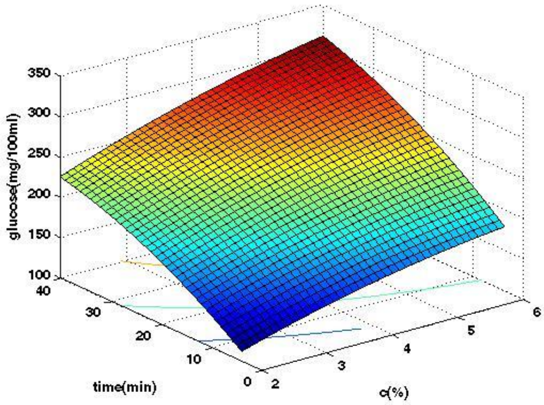

Figure 2. Surface response for glucose concentration in hydrolysis by sulfuric acid as a function of time ad acid concentration

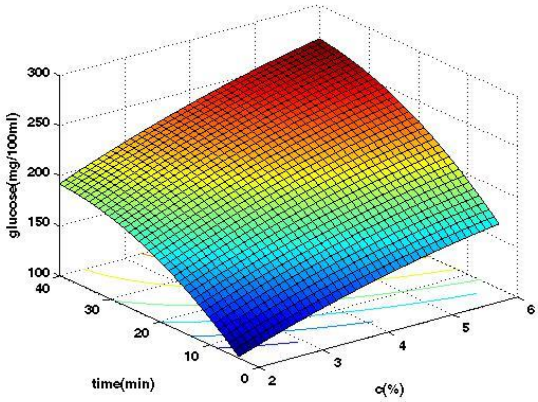

Figure 3. Surface response for glucose concentration in hydrolysis by HCl as a function of time ad acid concentration

4 Conclusion

Renewable fuels including bioethanol are able to decrease the demand for fossil fuels and bring about diminished by vehicles and production of greenhouse gases. In this research, it was demonstrated that wood and wooden wastes including paper can be used as a suitable raw material for production fermentable sugar as the first step towards production of fuel bioethanol. Glucose is the main product of pretreatment with diluted H_2SO_4 and HCl. This process was modeled using a quadratic equation obtained from the two variables of acid concentration and hydrolysis time. By studying the results obtained from the model, it was found that sulfuric acid extracts more sugar than HCl. Further, it was observed that the level of sugar increases with prolongation of hydrolysis time and increase of acid concentration.

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