Dilute Acid Hydrolysis of Walnut Green Skin for Fermentable Sugar Production

Ali Arastehnodeh

Abstract—The Influence of the main pretreatment variables on fermentable sugar generation from walnut green skin is studied by using design of experiment based on dilute acid hydrolysis. Levels for pretreatment temperature (124), process time (5, 10, 15 minute), solid content (5, 10, 15%) and concentration of sulfuric acid (3, 5, 7%) were selected according to previous results. Glucose and pentose composition, as well as furfural and acetic acid were analyzed by HPLC and modeled by a quadratic equation. Mathematical model was validated by independent experiment. Optimization based on mathematical model show that maximum Glucose concentration was obtained in 15 minutes residence time, 5% acid concentration and 5% solid content.

Keywords— walnut green skin, fermentable sugar, hydrolysis, pretreatment, bioethanol.

I. INTRODUCTION

Walnut is one of the most important nuts that culture widely around the entire world. In the year 2007, total production of this nut was forecast at a record of 1700000 tons. China (503000 tons), USA (209000 tons), Turkey (184000 tons) and Iran (170000 tons) are its important producers. Walnut consists of 3 main parts, meat, woody skin and green skin.

Green skin consists of cellulose, hemicelluloses and lignin. Cellulose is a linear, crystalline homo polymer with a repeating unit of Glucose strung together beta-glucosidic linkages. The structure is rigid and harsh treatment is required to break it down (Kevin, 2006). In contrast to cellulose, which is a polymer of only Glucose, hemicellulose is a hetero-polymer of D-xylose, D-glucose, D-galactose, D-mannose and L-arabinose (Shama, 1988). The carbohydrate polymers in the green skin need to be converted to simple sugars before fermentation through a process called hydrolysis.

It is important to determine the glucose concentration because this sugar is the main carbon source for most microorganisms (Aguilar et al., 2002). Before concentrated acid hydrolys was used to produce fermentable sugar by walnut green skin. (Arasteh nodeh 2012, 2013). This work deals with the acid hydrolysis of Walnut green skin with dilute sulfuric acid. A Taqushi method equation was used to evaluate the effect of acid concentration, process time, solid content on the pretreatment. In this study, a simple method was used. Furthermore, since concentrate of sulfuric acid was low (about 3 to 7%) and process time was short (about 5 to 15 minute) a combined Taqushi method was used. three variables should be studied in 3 levels then L-9 matrix of Taqushi could be deign. But at least fifteen parameters should be determined and fifteen run must be done. The two L-9 Matrix in revers level was combined and run.Special Picture (with “Float over text” unchecked).

II. PROCEDURE FOR EXPERIMENT

A. Raw Material

Walnut green skin (WGS) was gathered in September of 2009 from Spidan village from North Khorasan in Iran. It was washed by distilled 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. For the determination of the chemical composition of the WGS, preparation of the test specimens was carried out according to TAPPI T 257 om (1985) standard. Extracted materials, lignin and ash contents were determined according to TAPPI standards T 204 om (1988), T 222 om (1988), T 211 om (1988) standards, respectively. The hemicellulose and cellulose contents were determined according to Wise’s chlorite and K.rschner-Hoffner nitric acid methods. The resulted composition of WGS is shown in Table 1.

B. Dilute Acid Hydrolysis

All Dried WGS was treated with 3, 5, 7 wt% sulfuric acid in shaker autoclave in hot water jacket with an electric heater and temperature controller at 124°C for 5, 10, 15 hours. Solid to liquid ratio of 5%, 10%, 15% was applied. Once the temperature of reaction mixture reached to designed point, pretreatment time was started. At the end of each run the bottle was removed from autoclave and put in a cool water bath., sodium hydroxide (NaOH) was used until its PH reached around 7.0 and then solids were separated by filtering, washed with distilled water and final solution reached to 1000 ml. A
200 ml sample of solution was used to analyze by HPLC.

C. Analytical Methods

The composition of the hydrolyzate from acid hydrolysis (Glucose, Xylose, Mannose, Arabinose, Galactose, Furfural and Acetic acid) was determined by high performance liquid chromatography (HPLC). An HPLC model JASCO was used. Glucose, Xylose, Galactose, Mannose and Arabinose were analyzed by Bio-Rad column Aminex HPX-87P and detected by RI detector at 40oC and Acetic acid and Furfural analyze by Bio-Rad column Aminex HPX-87H and detected by UV detector at 210nm. To unify the response all results was divided on raw material content (gr WGS) and results were shown as percentage of gr product/gr raw material (e.g. 2 % gr glucose/gr raw material).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Percent dry weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cellulose</td>
<td>21.5</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>13.25</td>
</tr>
<tr>
<td>Extractive M</td>
<td>18.25</td>
</tr>
<tr>
<td>Lignin</td>
<td>26.07</td>
</tr>
<tr>
<td>Ash</td>
<td>20.93</td>
</tr>
</tbody>
</table>

III. RESULT AND DISCUSSION

Result was showed in figure 1,2,3 delicated that mass content has no big efficient on sugar production but has a big one on fufural and acetic acid production. Acid concentration increase sugar production and fufural but decrease acid acetic. Time, also, has this effect on production. Best condition for dilute hydrolysis can estimate at 2 minute residence time, 2% acid concentration and 3 % mass content.

IV. CONCLUSION

This work confirm that walnut green skin can be considered as a suitable feed stock for sugar generation as a first step toward fuel ethanol production. dilute acid hydrolysis helps us to reach the fermentable sugar in normal conditions. This process could be model by a three variable. These three variables were acid concentration, solid content and process time. Model allows adjusting these variables to reaches optimum condition for maximum glucose concentrations. This conditions base on model was acid concentration 2%, solid content 3%, temperature 124oC and process time 3 minute.
Figure 2 Average effect of Acid concentration on hydrolyzed product

Figure 3 Average effect of time on hydrolyzed product
REFERENCES


Ali ArastehNodeh (M’39) was born in 1974 in Mashhad- Iran. Field of study is Bio Energy. Research for Islamic Azad University – Quchan Branch