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A Rapid Screening Approach to Factors Affecting Dilute Acid Hydrolysis of Hazelnut Shells

Sibel Uzuner [1,2+], Deniz Cekmecelioglu [1]

[1] Department of Food Engineering, Faculty of Engineering, Middle EastTechnicalUniversity,06800, Ankara, Turkey

[2]Department of Food Engineering, Faculty of Engineering and Architecture, AbantIzzetBaysalUniversity, 14280, Bolu, Turkey

Abstract. Hazelnut shell is a lignocellulosic waste obtained from hazelnut processing. It is a potential source of pentose and hexose sugars (xylose, glucose) which can be used as a raw material for production of food enzymes, biofuel, and chemicals (acetic acid, furfural, methanol). An increasing interest in lignocellulosic wastes seems to stay consistent as these materials are low cost, renewable and abundant. The objective of the present study was to determine the effect of dilute acid (H_2SO_4) concentration, temperature and time on production of reducing sugars.The conventional one factor at a time approach showed that the highest concentration of reducing sugar was 16.74 g/L at a temperature of 130 ℃, an acid concentration of 3%, and a reaction time of 37.5 min, which also revealed a saccharification yield of 64.4%. Thus, this study showed that dilute acid hydrolysis is a promising pretreatment for hazelnut shells.

Keywords: Lignocellulosic waste, reducing sugar, hazelnut shell, acid hydrolysis

1. Introduction

There is an increasing interest in utilization of lignocellulosic wastes for industrial purposes since these materials are inexpensive, renewable, and widely available in nature. Hazelnut shell is one of abundant lignocellulosic wastes found in Turkey. At present, two-thirds of the world production capacity of hazelnuts is provided by Turkey, being produced in the Black-Sea region of Turkey alone [1], andfollowed by Italy and the USA [2]. This gives an annual production of 250,000 tons of hazelnut shells. The hazelnut shells have 43.1% lignin, 27.5% hemicellulose, 24.7% cellulose, 3.4% alcohol-benzene extractives and 1.4% ash [3]. Today, its main utilization remains as a boiler fuel. Burning agricultural residues causes air pollution, and indirectly leads to soil erosion and a decrease in soil biological activity [3]. Therefore any possible usage of hazelnut shells will yield economic as well as environmental benefits. Also being a potent renewable source for production of value-added products such as ethanol, enzyme and other organic acids, it can compete with other lignocellulosic wastes.

Forefficient utilization of lignocellulosic wastes (herein hazelnut shells), it is necessary to develop an appropriate pretreatment process which eases the production of fermentable sugars. These sugar monomers can then be used as substrates for biotechnological and chemical processes stated above[4]. The hemicellulosic fraction of lignocellulosic materials is easily hydrolyzed by mild acid treatment due to its amorphous structure. The hydrolysis of different lignocellulosic materials using dilute acid has been studied by various researchers [5,6].Acid hydrolysis allows for the generation of a liquid phase rich in xylose and under harsh conditions it can produce higher levels of lignin derivatives that can inhibit the cell metabolism,compared to alkaline and organic pretreatments [7]. Thus, the amount of sugar released during

[+]Corresponding author. Tel.: + (90 312 210 5623); fax: +(90-312-2102767).
E-mail address: (suzuner@metu.edu.tr).

hydrolysis is dependent on the type of material and operating conditions including temperature, time and acid concentration [5]. In current literature,there are few studies on the acidic hydrolysis of hazelnut shells. To fulfill this gap, the present study aimed at determining the effect of dilute acid concentration, temperature, and time on hemicellulose sugars expressed as total reducing sugars.

2. Materials and Methods

2.1. Materials

Hazelnut shells were obtained from a local plant in Ordu, a province of Turkey. Before use, the shells were dried at 70 ℃ in an oven for 24 h and then ground into fine particles of 1 mm for easy reaction with the acid. The ground hazelnut shells were stored inside plastic bags and kept at room temperature until use.

2.2. Analytical analyses

The composition of ground hazelnut shells in terms of moisture, ash, cellulose, hemicellulose and lignin content was determined. For moisture content, samples were dried at 105 ℃ until constant weight was reached. For ash content, dried samples were burned in an oven for 24 h at 550 ℃ [8]. For hemicellulose and cellulose contents, holocellulose and alpha cellulose contents were first determined according to Browning[9].The difference between the holocellulose and cellulose contents was then considered as the hemicellulose content. Acid-insoluble lignin was calculated by the TAPPI standard method (T2220S-74) [10]. Total-reducing sugar of the hydrolyzate was estimated using DNS method [11]. A calibration curve for this method was prepared using analytical grade D-glucose solutions at 0.15-1 g/L.

2.3. Dilute sulfuric acid hydrolysis

The ground hazelnut shells were suspended in dilute sulfuric acid solutions (final concentration: 1, 3, 5% (w/w)) with a solid–liquid ratio of 1:20 (g dry weight per ml) and heated in an autoclave at 110, 120, 130°C with duration of 15, 37.5 and 60 min. After acid hydrolysis, the solid residue was separated by centrifugation (4307xg, 30 min) and then pH of the supernatant was adjusted to 5.0 using 10 M NaOH. The resulting supernatant was finally analyzed for reducing sugar content. The results are presented as averages of two replicates.

2.4. Statistical Analysis

The analysis of variance (ANOVA) was carried out to detect any significant differences between the means of reducing sugar measurements at $\alpha=0.05$ using MINITAB® 15.1 (Minitab Inc.).

3. Results and Discussion

3.1. Composition of raw material

The analytical tests showed that hazelnut shells used in this study contained 24.20% cellulose and 28.20 % hemicellulose, 34.64% lignin, 9.7% moisture and 1.13% ash. These results agreed well with a recent study reported by Demirbas [12].

3.2. Effective factors on production of reducing sugars

The effects of acid concentration, time, and temperature on hydrolysis of hazelnut shells were examined. To determine the temperature effect,three different temperatures (110, 120 and 130 ℃) were applied at 3% acid concentration for 37.5 min. As temperature increased, the reducing sugar concentration increased (Fig.1). For temperatures of 110–120 ℃, the reducing sugar contents were not significantly different ($P>0.05$), however the reducing sugar at 130 ℃ (16.74 g/L) was significantly higher than the level at 110 ℃ (9.67 g/L) ($P<0.05$). Therefore, the highest temperature level (130^{o}C) was chosen as the ideal temperature for subsequent trials.

Different acid (H_2SO_4) concentrations (1%, 3% and 5%) were then used at 130^{o}C for 37.5 min to assess the impact of acid concentration. The average results are shown in Fig. 2. As ANOVA results indicated that acid concentration had significant effect on reducing sugar concentration ($P<0.05$). Increasing the acid concentration from 1% to 3% increased the reducing sugar concentration from 12.56 g/L to 16.74 g/L whereas increasing the acid concentration from 3% to 5% decreased the reducing sugar concentration from 16.74 g/L to 15.18 g/L. Thus, the 3% acid concentration was chosen as the best level.

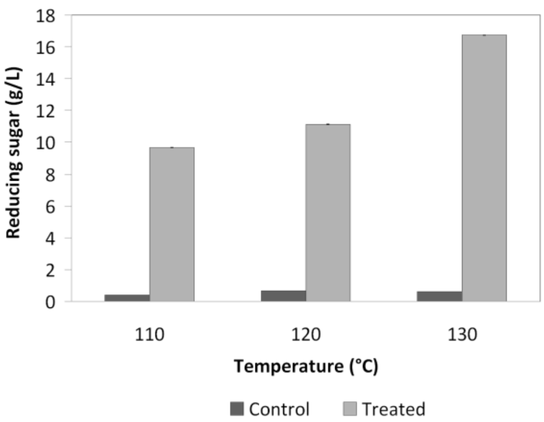

Fig. 1: Hydrolysis of hazelnut shell at various temperatures (3% acid, 37.5 min).

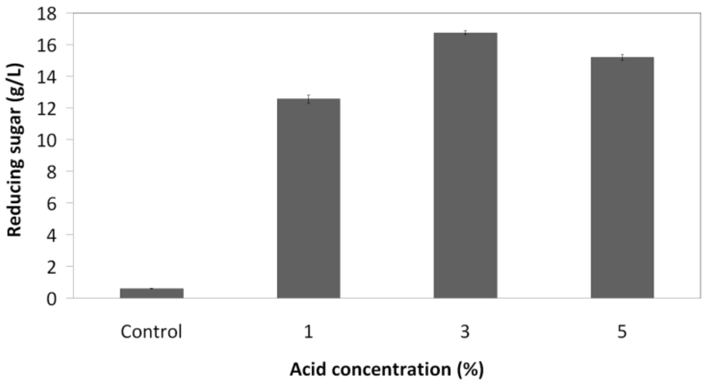

Fig. 2: Hydrolysis of hazelnut shell at various acid concentrations (130^{o}C, 37.5 min).

Finally, the time effect was examined using the aforementioned ideal temperature and acid concentration levels for periods of 15, 37.5 and 60 min. The results are shown in Fig. 3. It was clear that, the time had a limited impact, yielding a decrease in reducing sugar concentration after a 60 min hydrolysis. A period of 37.5min showed the highest reducing sugar concentration (16.74 g/L). Therefore, it was chosen as the best time among the tested levels for production of high fermentable sugars.

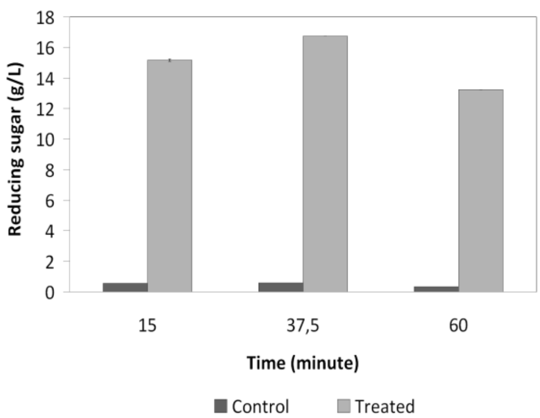

Fig. 3: Hydrolysis of hazelnut shells at various times (130^{o}C, 3% acid).

The results of this study indicated that a temperature of 130^{o}C, a period of 37.5 min and 3% acid concentration revealed the highest reducing sugar concentration (16.74 g/L), which was also equal to 64.4% yield. For comprehensive understanding of interactions between each factor and for complete optimization, further study is needed to maximize the sugar yields. Arslan and Saracoglu [13] studied the hydrolysis of hazelnut shells using 3-5% H_2SO_4 at 100-120^{0}C with the 1/7 solid to liquid ratio. They reported the highest reducing sugar concentration for conditions of 120^{0}C, 5% H_2SO_4 and 30 min.It was concluded that the overall sugar yield of this study was higher than that of Arslan and Saracoglu [13], Woiciechowski et al. (2002) [14], who used cassava bagasse and Akpinar et al. (2011)[15], who used cotton stalk.

4. Conclusion

This study showed that dilute-acid hydrolysis is a feasible process to produce sugars from hazelnut shell for further processing to different value added products. The conventional one factor at a time approach showed that the highest concentration of reducing sugar was obtained as 16.74 g/L, at 130 ℃, 3%, acid concentration and 37.5 min, which revealed a saccharification yield of 64.4%.

5. Acknowledgements

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