Journal of Renewable Energy, Electrical, and Computer Engineering
Vol. 2, No. 1, March 2022, 1-6
e-ISSN: 2776-0049
DOI: https://doi.org/10.29103/jreece.v2i1.6382
Research Original Article

Hydrolysis of coffee pulp as raw material for bioethanol production: sulfuric acid variations

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Received: January 20, 2022 **Revision: February 18, 2022** **Accepted: March 15, 2022**

Abstract
Indonesia has enormous biomass resources due to its land territory is mostly surrounded by forests and agricultural area. One of the main agricultural commodities is Gayo Arabica coffee. Coffee agro-residue such as coffee-pulp contains glucose, organic matter, protein, nitrogen and high minerals. Therefore, coffee pulp can be a potential raw material for bioethanol production. In order to develop an effective technology for bioethanol production from coffee-pulp, it is necessary to investigate in early the way of glucose can be effectively prepared. In this preliminary investigation, glucose products ware prepared using two methods, i.e. method-I under several main-stages including extraction, delignification, and hydrolysis. While, under method-II, the sample was directly hydrolyzed at 100 °C for 4 h. Under both methods, hydrolysis process to get glucose was performed by adding sulfuric acid (H_2SO_4) at various concentrations (8 wt.%, 10 wt.% and 12 wt.%). Based on analysis results, the highest glucose level, i.e. 17 % was obtained from method-II by adding 8 wt.% sulfuric acid. The less the amount of sulfuric acid added, the higher the glucose level produced. No difference in pH was found from both methods. The color of glucose produced under method-I is clearer compared to those prepared under method-II.
Keywords: Coffee waste; bioethanol; glucose and sulfuric acid

Introduction
Concerns about environmental issues as well as the need for energy and chemical resources have increased researchers in using sustainable resources derived from biomass (Mirnezami et al., 2020; Nawaz et al., 2022). Bio-fuel production from lignocellulosic biomass has received global attention and can reduce greenhouse gas emissions and can minimize the use of fossil energy through the use of renewable energy (Halder et al., 2019).

Lignocellulosic biomass is one of the most abundant, sustainable and renewable resources that can be converted into bio-chemicals, bio-polymers and biofuels (Culaba et al., 2021). Biofuel production, one of which is bioethanol, is currently very dependent on starch and sugar (Wang et al., 2020). In this context, bioethanol produced from lignocellulosic biomass does not compete with food crops, is cheap and easy to obtain compared to conventional agricultural raw materials. Lignocellulose mainly consists of carbohydrate polymers (cellulose and hemicellulose), aromatic polymers (lignin) and other substances such as lipids, minerals, fibers and a number of other bioactive compounds and phytochemical compounds (Sarsaiya et al., 2019; Tu & Hallett, 2019).

Lignocellulosic materials such as agricultural waste are renewable resources that are waste for sugar production through the conversion of hydrolyzate biotechnology to produce food, liquid fuels and chemicals. (Ab Rasid et al., 2021; Hoang et al., 2021). Furthermore, the saccharification process is carried out in a medium catalyzed by acids or enzymes. Acid catalyzed hydrolysis is divided into two processes, namely the low temperature concentrated acid process or the high temperature dilute acid process, depending on the operational conditions and the nature of the raw materials (Harsono et al., 2015).

One of the plantation wastes that is abundant and has high economic value is coffee waste. The biggest coffee producing countries are Brazil (3,776 tons/year), Vietnam (1,900 tons/year), Colombia (830 tons/year), Indonesia (565 tons/year), and Ethiopia (470 tons/year)(Duarte et al., 2020). Indonesia is the fourth largest producing country in the world, one of which is Central Aceh Regency, where the majority of the population lives in the coffee farming sector

(Setiawan et al., 2019, 2020). When the harvest season arrives, the farmers dispose of the coffee husks they produce into the environment and not use them. As Chen explained, arabica coffee rind produces glucose (Chen & Jhou, 2020) and contains high organic matter, reducing sugar, protein, nitrogen, and minerals (Hoseini et al., 2021). So that a further study is needed regarding the utilization and processing of Arabica coffee coolies waste into bioethanol raw materials.
In many countries, including Indonesia, bioethanol has been used as a fuel blending material (S. Aiman., 2014). Therefore, the bioethanol industry continues to grow. In the period from 2013 to 2014, six large-scale bioethanol industries from lignocellulosic biomass have been established, with production capacities between 30 to 110 million liters per year, with raw materials for municipal waste, wheat straw, corn waste, or various other agricultural wastes (Aiman, 2016). In the Table 1, the development of bioethanol research from time to time are described with various sources of biomass.

Table 1. Bioethanol research development (Hajar et al., 2017).

No.	Bacteria Name	Raw material	(Sugar) (g/L)	Fermentation conditions	Ethanol (b)(g/L)	(ethanol)	Ref.
1.	*S. cerevisiae RL-11*	coffee plant	195.0	30˚C, 200 rpm, 48 h	11.7	0.49	(S.I. Mussato, E.M.S. Machado, L.M. Carneiro, 2012)
2.	*S. cerevisiae MTCC 173*	Sorghum	200.0	30˚C, 120 rpm,96 h	68.0	0.94	(C. Sathesh-Prabu, 2011)
3.	*S. thin CBS 6054*	giant reed	33.4	30˚C, 150 rpm, 96 h	8.2	0.17	(D. Scordia, S.L, Cosentino, J. W. Lee, 2012)
4.	*S. cerevisiae KL17*	Galactose and glucose	500.0	30˚C, 200 rpm, 28 h	96.9	3.46	(J.H. Kim, J. Ryu, I. Y. Huh, 2014)
5.	*S. pombe CHFY0201*	cassava starch	95.0	32˚C, 120 rpm, 66 h	72.1	1.16	(G.W. Choi, H.J.Um, M, Kim, 2010)
6	*S. cerevisiae CHY1011*	cassava starch	195.0	32˚C, 120 rpm, 66 h	89.1	135	(G.W. Choi, H.J. Um, Y. Kim, 2010)
7.	*S. cerevisiae ZU-10*	Corncob	99.0	30˚C, 180 rpm, 72 h	41.2	0.57	(J. Zhao, L, 2010)

[a] Sugar Concentration
[b] Ethanol Concentration
[c] Ethanol Productivity

The ethanol production process depends on the type of feedstock used. In general, there are three main steps in the production of ethanol, obtaining a solution containing fermentable sugars, converting the sugar into ethanol by fermentation and separating and purifying the ethanol. Raw materials are usually pretreated to reduce their size and facilitate subsequent processing. Then, hemicellulose and cellulose will be hydrolyzed into fermentable sugars. Yeast is given the responsibility of fermenting this sugar into ethanol. Separation technology is used to separate ethanol from water before it can be used as fuel (Hajar et al., 2017).
This study aims to develop an effective way for glucose preparation as initial stage of investigation for bioethanol production from Arabica coffee pulp. The glucose ware prepared using two methods, i.e. method-I under several main-stages including extraction, delignification, and hydrolysis. The second method was a direct-hydrolysis process of coffee-pulp at 100 °C for 4 h. The effect of sulfuric acid concentrations on the glucose level, pH and color were analyzed to find out the best method for glucose preparation.

Materials & Methods

The raw material used in this research was coffee pulp sourced from coffee a plantation in Aceh Tengah District, Aceh. The term of coffee pulp refers to the outer skin of coffee cherry peeled off during the process. The coffee pulp sample was initially cleaned-up and dried in an oven at 100 °C for 3 h. Hydrolysis of dried coffee pulp was carried out by varying the concentration of sulfuric acid, *i.e.* 8, 10 and 12 wt.% H_2SO_4 with a hydrolysis time of four hours at a temperature of 100 °C. In this investigation, there were two methods have been used to produce glucose, *i.e.* method-I by using several stages including extraction, delignification, and hydrolysis. The second method is direct hydrolysis method where 100 g dried coffee-pulp was hydrolyzed at 100 °C for 4 h. The procedures are detailed in Figure 1. For hydrolysis, H_2SO_4 was used by diluting to concentrations of 8, 10 and 12 %. Delignification process was carried out by using 65 vol.% HNO_3 (nitric acid), $NaNO_2$, Na_2SO_3. 15% NaOCl solution, 50% H_2O_2 solution and distilled water.

As raw material, Gayo Arabica coffee pulp was initially cleaned and dried in the oven at 100 °C for 3 h. The dried coffee pulp was then ground and sieved to ≤ 80 mesh size. A 100 grams of coffee pulp powder was placed into a glass beaker, mixed with 3.5% HNO_3 solution and 3 mg of $NaNO_2$, then heated on a hot plate at 100 °C for 2 h. Resulting substrate was filtered and washed until the filtrate was neutral. The next step is delignification process by adding 250 ml of 2 vol.% NaOH and 2 vol.% Na_2SO_3 solution and heated at 50 °C for 1 hour. After that, the extract was filtered and

washed. Next, the bleaching process was carried out by adding 85 ml of 75 vol.% NaOCl solution and heated at boiling temperature for 30 minutes, then filtered and washed until the pH of the filtrate was neutral. The second bleaching process was performed with 10 vol.% H_2O_2 solution and dried in an oven for 1 hour at 60 °C. The results obtained in the form of cellulose. The extracted cellulose was put into an Erlenmeyer flask as much as 5 grams and added with 100 ml of distilled water and 100 ml of H_2SO4 (at concentration of 8%, 10%, 12%). Then the solution was hydrolyzed at 100 °C for 4 hours.

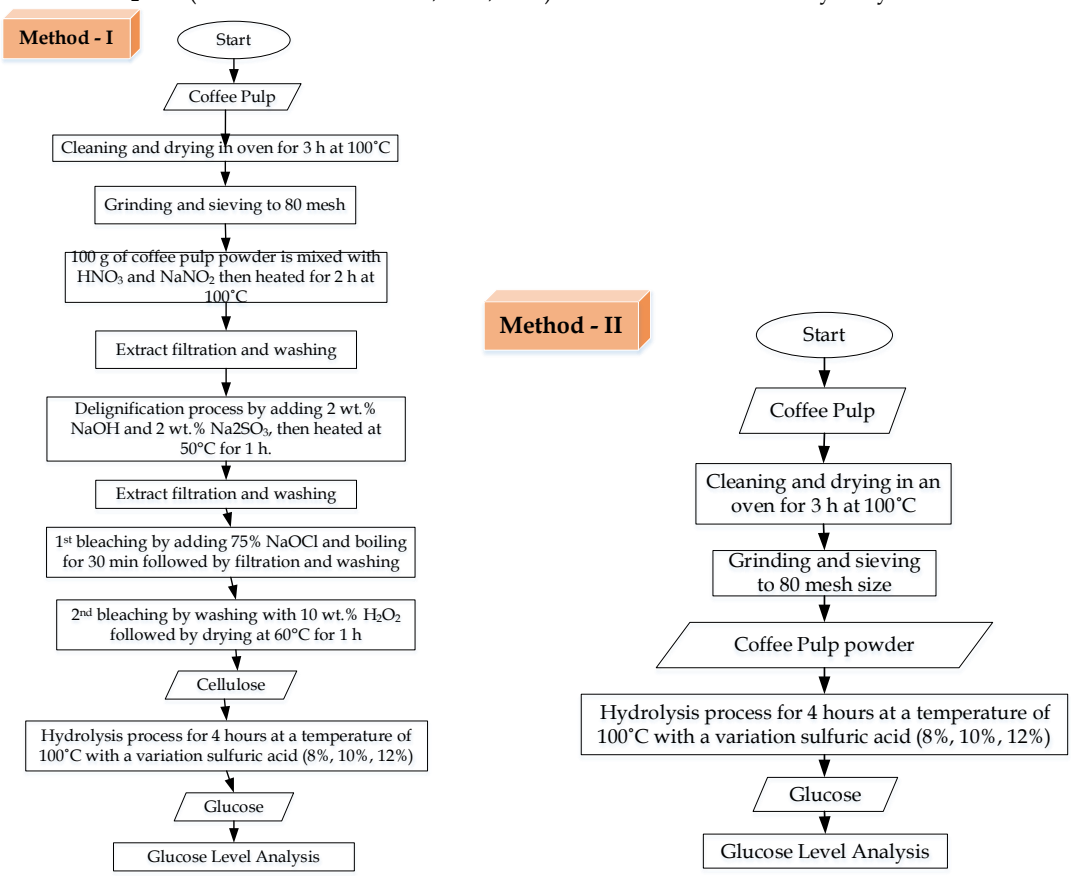

Figure 1. Methods for extracting glucose from Gayo Arabica coffee pulp

Sample Analysis

In this investigation, the pH level of glucose products was measured using a Mediatech digital pH meter. Glucose concentration was measured by using Brix Refractometer with measuring range 0-32%, resolution 0.2%, working temperature 10-30 °C.

Results and Discussion

The results of the pH measurement and the color of glucose sample are shown in Table 2 for the process carried out by method-I and method-II. The pictures of glucose produced from both methods are displayed in Figure 2.

Table 2. The results of the analysis of pH and color changes of the glucose samples of coffee waste.

No	Variation of sulfuric acid concentration (%)	Method			
		Method I		Method II	
		pH	Color	pH	Color
1.	8				
2.	10	1	Clear	1	Brown
3.	12				

Based on pH measurement results, it was found that the methods I and II did not show a significant change in the pH value. This indicates that the addition of sulfuric acid did not affect the acidity of the glucose produced. Meanwhile, in term of glucose color, there was a significant difference. from method-I, a white color was produced, this is due to the process experienced in method I went through several stages and a new bleaching process occurred followed by a hydrolysis process for four hours, so that the resulting product was white. While in method II the resulting color tends to be brown, this is due to the direct hydrolysis process without going through the extraction and delignification process. As shown in Figures 2 and 3.

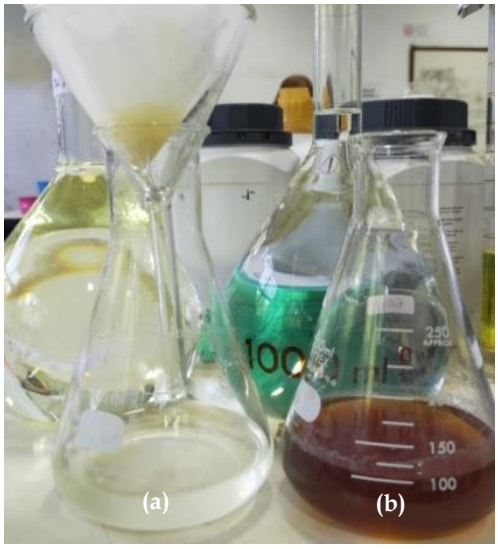

Figure 2. Glucose products after filtering process, (a) under method-I and (b) method-II

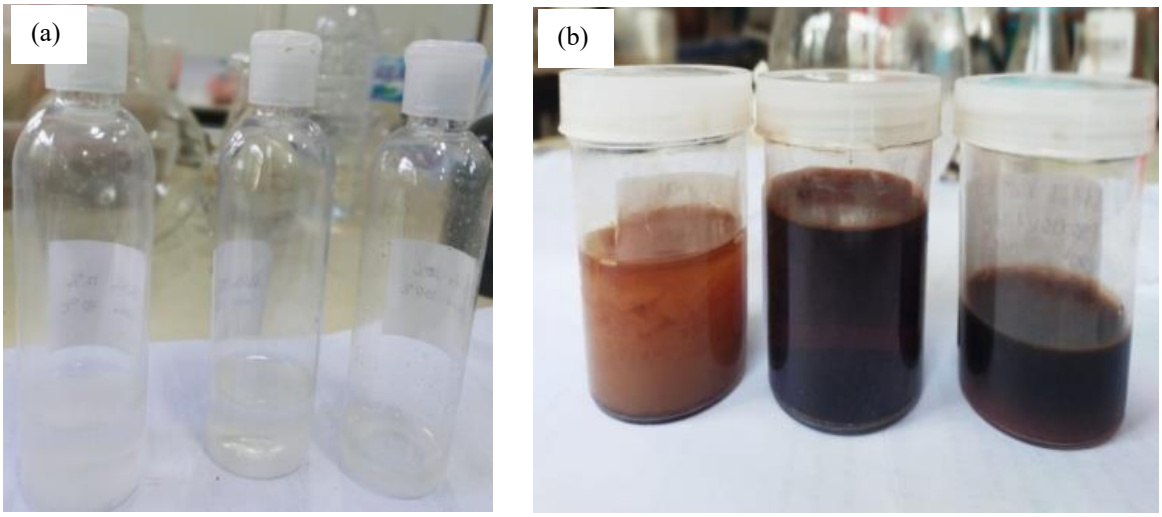

Figure 3. Glucose products (a) method I and (b) method II

From Figures 2 and 3 there is a difference in the color of the glucose produced, in method I it is white and method II is brown, the results of the study show that in method II the highest glucose product is obtained compared to the first method. Figure 4 shows the glucose levels resulting from the analysis using the Brix Refractometer.

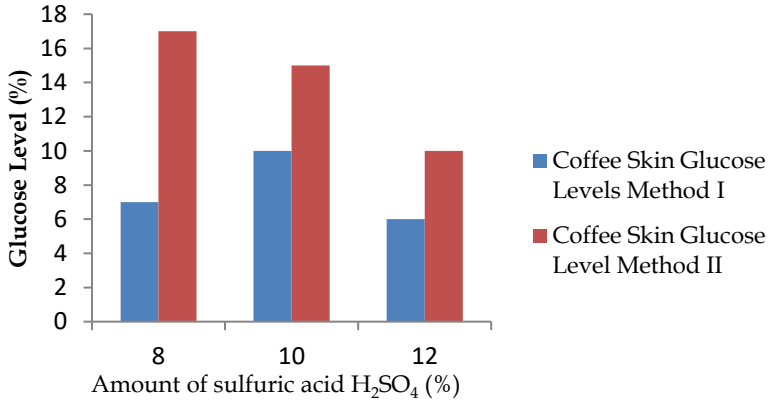

Figure 4. Glucose levels from coffee husk waste with variations in the amount of H_2SO_4

Figure 4 shows that the more sulfuric acid is added, the lower the glucose level produced is as in method II, but it is different from method I, the highest glucose level is at a concentration of 10% wt H_2SO_4 which is 10%. In method I the glucose obtained is lower than in method II, but the color of the glucose produced is white. This lower glucose level is

caused in the Extraction process there is a decrease in cellulose content caused by the reduced solubility of hemicellulose into NaOH solution, because most of the water has been used by NaOH to dissolve, so the water in the solution becomes small. This decrease in hemicellulose causes an increase in the content of cellulose and lignin in one lignocellulose bond. In the extraction process, the lignin compounds have not been degraded, only softening occurs, so that the hemicellulose which was originally bound by lignin becomes free and most of it can be dissolved into NaOH solution. Meanwhile, because lignin only softens, only a small part of it dissolves in NaOH or even nothing dissolves. In addition, the decreased cellulose content was due to the presence of a regular open structure of cellulose and the cellulose molecules were freely dispersed in the solvent (NaOH). With the structure of cellulose being freely dispersed in the solvent, it is expected that cellulose will be carried away by the solvent during the filtering process. Meanwhile, because lignin only softens, only a small part of it dissolves in NaOH or even nothing dissolves. In addition, the decreased cellulose content was due to the presence of a regular open structure of cellulose and the cellulose molecules were freely dispersed in the solvent (NaOH). With the structure of cellulose being freely dispersed in the solvent, it is expected that cellulose will be carried away by the solvent during the filtering process. Meanwhile, because lignin only softens, only a small part of it dissolves in NaOH or even nothing dissolves. In addition, the decreased cellulose content was due to the presence of a regular open structure of cellulose and the cellulose molecules were freely dispersed in the solvent (NaOH). With the structure of cellulose being freely dispersed in the solvent, it is expected that cellulose will be carried away by the solvent during the filtering process (Lestari et al., 2018). Unlike the case in method II which is directly related to the hydrolysis process by obtaining a higher amount of glucose and is brown in color.

Conclusions

Glucose produced from Gayo Arabica coffee pulp has been prepared at various sulfuric acid concentrations as initial stage in bioethanol production. Glucose content, pH and the color of glucose products were tested in order to decide the best method for bioethanol production. Based on the results of this investigation, the highest glucose level was obtained from method-II by adding 8 wt.% sulfuric acid. The less the amount of sulfuric acid added, the higher the glucose level produced. Under method-I, hydrolysis with 8 wt.% sulfuric acid produced glucose level as high as 10% only. No difference in pH was found from both methods. The color of glucose produced under method-I is clearer compared to those prepared under method-II.

Acknowledgments

The authors would like to thank Shafira Riskina and Siti Nurjannah for their help during sample preparation and authors also thanks to the Institute for Research and Community Services (LPPM), Universitas Malikussaleh for their support on this research.

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