



Microwave-assisted Acid Hydrolysis of Starch Polymer in Cassava Pulp in The Presence of Activated Carbon

E. Hermiati^{a,b,*}, D. Mangunwidjaja^b, T.C. Sunarti^b, O. Suparno^b, B. Prasetya^c

^aR&D Unit for Biomaterials, Indonesian Institute of Sciences, Cibinong, Bogor, Indonesia

^bDept. of Agroindustrial Technology, Faculty of Agricultural Technology, Bogor Agricultural University, Bogor, Indonesia

^cIndonesian Institute of Sciences, Jakarta, Indonesia

Abstract

Cassava pulp contains significant amount of starch which can be hydrolyzed to glucose, and further converted to different kinds of chemicals, such as lactic acid, fumaric acid, and ethanol. Microwave irradiation is an alternative method for starch hydrolysis, and the addition of activated carbon has been reported could increase glucose yield at lower temperature in water medium. This research was to study the effects of two types of activated carbon on the acid hydrolysis of cassava pulp under microwave irradiation. The experiment was conducted at two microwave power level (30% and 50%), each with heating duration of 5, 7.5 and 10 min in 0.5% sulfuric acid medium. The addition of activated carbon with superior adsorption capacity in cassava pulp suspension resulted in lower glucose yield than the one without the addition of activated carbon at both power levels. On the other hand, the addition of activated carbon with inferior adsorption capacity resulted in much higher glucose yield than the one without the addition of activated carbon at microwave power 30% and slightly lower glucose yield at microwave power 50%. However, activated carbon with higher adsorption capacity was superior to the other one in suppressing the formation of colored secondary degradation materials. The highest glucose yield (91.52%) was obtained in the hydrolysates from the treatment at microwave power 50% for 10 min without the addition of activated carbon.

© 2012 Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](https://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: Microwave-assisted hydrolysis; starch; cassava pulp; acid; activated carbon.

1. Introduction

Cassava pulp is a by product of tapioca industry that contains significant amount of carbohydrates. It contains 61.80-63.00% of starch and 12.80-14.50% of fiber [1]. As starch is the main component in the cassava pulp, its conversion to glucose becomes the main and important conversion step. Glucose can be

* Corresponding author: tel.: +62-21-87914511; fax: +62-21-87914510
E-mail address: euis.hermiati@lipi.go.id

further converted to different kinds of chemicals, such as citric acid, fumaric acid, lactic acid, and ethanol. Efforts to hydrolyze starch in cassava pulp have been completed by other researchers using several methods, such as acid hydrolysis [2-5], enzymatic hydrolysis [4,6-11], hydrothermal process [12-13], or combination of hydrothermal and enzymatic hydrolysis [14].

Microwave-assisted hydrolysis of cassava pulp is a promising method, since it took only several minutes, while the other conventional processes took very much longer time, 90 min for acid hydrolysis and 48-72 h for enzymatic hydrolysis. In our previous experiment on hydrolysis of cassava pulp in water medium by using microwave irradiation it was found that the addition of activated carbon greatly increased the yield of glucose from 32.41% to 52.27% [15]. This result was higher than that produced from acid hydrolysis (36.40-41.34%) [5], but still lower than that resulted from enzymatic hydrolysis ($\pm 70\%$) [11], or combinations of hydrothermal and enzymatic hydrolysis ($\pm 75\%$) [14]. Activated carbon was reported can act as hot spots in some microwave-assisted reactions [16]. Other reports mentioned that activated carbon could increase saccharification rate of corn starch at lower temperature [17-18]. Even though several types of activated carbons used, there was still little information on the effects of different kinds of activated carbon on the hydrolysis of starch or starchy materials. Besides that, there was not any report on the effects of activated carbon addition on microwave-assisted hydrolysis in acid medium. Therefore, in this experiment two types of activated carbon were used to study the relationship between properties of activated carbon and properties of cassava pulp hydrolysates produced from the microwave-assisted acid hydrolysis.

2. Experiment

2.1. Materials

Cassava pulp was collected from a small-scale tapioca industry (home industry) located in Bogor, Indonesia. The material was dried at 60 °C for 30 h, then, it was ground and sieved to pass through 20 mesh sieve. The material was stored in plastic bags and the bags were put in a sealed plastic container. Activated carbon 1 (Y-8/20 AW, previously Y-10S AW) was granular type, purchased from Ajinomoto Fine Techno Co., Inc., Japan. Activated carbon 2 was also in granular form, purchased from local market in Bogor, Indonesia. The solvent and other reagents used were analytical grades.

2.2. Analysis of raw materials

Moisture content of cassava pulp was determined gravimetrically by drying in an oven at 105 °C until constant weight. Starch content of the raw material was as reported previously [15-19]. Adsorption capacity of the activated carbon was determined by analyzing the iodine and methylene blue adsorption according to Indonesian National Standard (SNI) 06-4253-1996. Surface area of activated carbon was calculated based on methylene blue adsorption as indicated in the SNI 06-4253-1996.

2.3. Cassava pulp hydrolysis using microwave irradiation

Suspension of cassava pulp in water (1 g/20 mL or 5%) was put in a 100 mL Teflon[®] tube and mixed with a stirrer bar to homogenize the suspension. Activated carbon (1 g) was added to samples with activated carbon treatment. The sample was then subjected to hydrolysis using SHARP R-360J(S) kitchen microwave oven, having frequency of 2,450 MHz, output power 1100 Watt. The irradiation was conducted at 30% and 50% power level for 5, 7.5 and 10 min. After microwave irradiation, the sample was cooled immediately in an ice bath to room temperature.

2.4. Analysis of soluble fraction

The soluble fraction was analyzed for its total soluble solid (TSS) using ATAGO Hand Refractometer N-20. Glucose content was determined by Glucose CII test kit (Wako Junyaku, Co., Osaka), and the glucose yield was estimated as starch based theoretical yield. The pH value was determined using pH meter, and the formation of brown compounds was determined by measuring absorbance at 490 nm [20-21], and hydroxymethyl furfural (HMF) content according to AOAC (980.23-1999).

3. Results and Discussion

3.1. Properties of raw materials

Results of analysis of cassava pulp revealed that moisture content of cassava pulp was 7.12%, while its starch content was 79.45%. Properties of the two activated carbons that used in this study were shown in Table 1. The physical appearance of the two activated carbons was almost similar. There was a little different of pH value of the two activated carbons, where activated carbon was more acidic than the other one. Adsorption properties of activated carbon 1 was very much superior to that of activated carbon 2, which was shown by higher value of iodine sorption, methylene blue sorption, and larger surface area for activated carbon 1.

Table 1. Properties of activated carbon

Properties	Activated Carbon	
	1	2
Shape	Granular	Granular
Size	10-20 mesh	6-20 mesh
pH	6.01	6.91
Adsorption properties		
- Iodine sorption (mg/g)	1213.15	1075.41
- Methylene blue sorption (mg/g)	264.53	18.11
- Surface area (m ² /g)	981.72	67.21

3.2. TSS in the hydrolysates produced from microwave-assisted acid hydrolysis of cassava pulp

There was an increase of total soluble solid due to the increase of irradiation time (Figure 1), except in the hydrolysates of cassava pulp produced from microwave irradiation at 50% power level with the addition of activated carbon 1. The extent of heating time caused the increase of solubilization of carbohydrates components in cassava pulp, thus, increased the total soluble solid in the hydrolysates. In the case of hydrolysates of cassava pulp heated at 50% microwave power level, some malto-oligomers produced might be adsorbed on the surface of activated carbon 1, due to its superior adsorption properties to the other activated carbon. At the lower power level (30%) the total soluble solid in the hydrolysates resulted from the addition of activated carbon 2 was slightly higher than those produced from the ones without activated carbon and with activated carbon 1, while at the higher power level (50%) it was similar with the one without activated carbon addition.

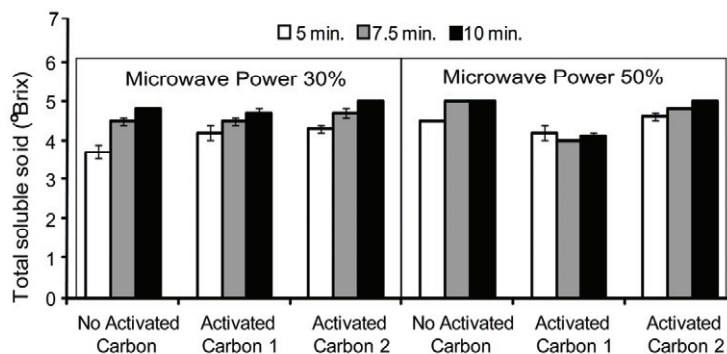


Fig. 1. Total soluble solid in cassava pulp hydrolysates produced from microwave-assisted acid hydrolysis of cassava pulp. Values in data points are mean \pm SD (n=3)

3.3. Glucose yield from microwave-assisted acid hydrolysis of cassava pulp

Results of microwave-assisted acid hydrolysis of cassava pulp at two microwave power levels with different heating times (Figure 2) showed that at the lower microwave power level (30%) glucose yield was very low after 5 and 7.5 min of irradiation. The glucose yield started to increase significantly after 10 min of irradiation, especially in the hydrolysates from the treatment with the addition of activated carbon 2.

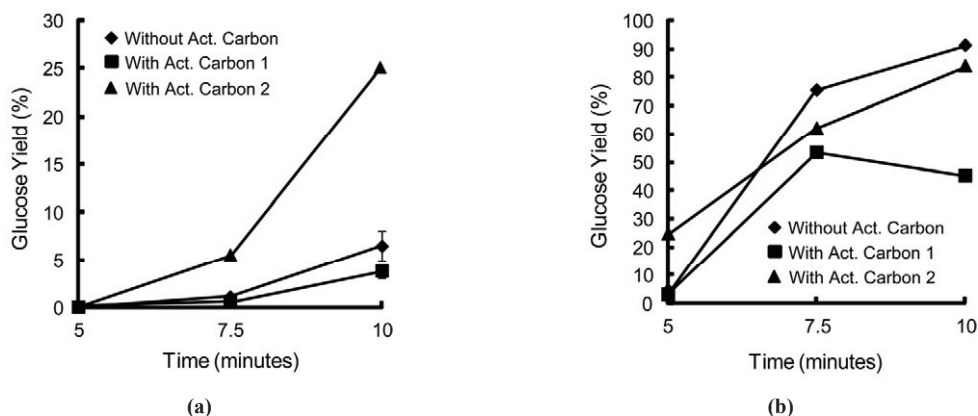


Fig. 2. Glucose yield from microwave-assisted acid hydrolysis of cassava pulp at microwave power level (a) 30% and (b) 50% with different heating times (\blacklozenge = without addition of activated carbon; \blacksquare = with addition of activated carbon 1; \blacktriangle = with addition of activated carbon 2). Values in data points are mean \pm SD (n=2)

At the higher microwave power level (50%) glucose yield obtained from hydrolysis with the addition of activated carbon 2 was higher than the ones without activated carbon and with activated carbon 1. However, at the longer duration of irradiation, glucose yield from hydrolysis without the addition of activated carbon surpassed the other two treatments, and reached maximum (91.52%) after 10 min of irradiation. The lower glucose yield in the hydrolysates obtained from the treatment with the addition of activated carbon might be caused by the adsorption of some malto-oligomers on the surface of activated carbon, especially on that of activated carbon 1, which had very much larger surface area than did

activated carbon 2. The highest glucose yield obtained in this experiment (91.52%) was higher than the yield of cassava pulp hydrolysis using acid hydrolysis (36.40–41.34%) [5], enzymatic hydrolysis (70%) [11], or combinations of hydrothermal and enzymatic hydrolysis (75%) [14]. Thus, microwave-assisted acid hydrolysis is a potential alternative method of hydrolysis of cassava pulp.

3.4. The pH value of hydrolysates produced from microwave-assisted acid hydrolysis of cassava pulp

There was not any significant effect of microwave power level, heating time and the addition of activated carbon on the pH values of the hydrolysates. The pH values of the hydrolysates ranged from 1.67 to 1.93 (Table 2). This phenomenon was different from previous reports, which mentioned that pH value decreased with increasing temperature, either in the hydrolysates with or without the addition of activated carbon [15, 19, 22].

Table 2. The pH value of cassava pulp hydrolysates after microwave-assisted acid hydrolysis

Power (%)	Time (min)	Without Activated Carbon	With Activated Carbon 1	With Activated Carbon 2
30	5	1.79 ± 0.06	1.75 ± 0.02	1.70 ± 0.01
	7.5	1.86 ± 0.03	1.67 ± 0.04	1.64 ± 0.03
	10	1.86 ± 0.02	1.75 ± 0.04	1.67 ± 0.04
50	5	1.93 ± 0.03	1.73 ± 0.03	1.87 ± 0.01
	7.5	1.67 ± 0.03	1.77 ± 0.02	1.85 ± 0.01
	10	1.82 ± 0.01	1.84 ± 0.02	1.84 ± 0.01

Values are expressed as mean ± SD (n=3)

3.5. The formation of brown compounds in cassava pulp hydrolysates

Table 3. The absorbance value at 490 nm of cassava pulp hydrolysates after microwave-assisted acid hydrolysis

Power (%)	Time (min)	Without Activated Carbon	With Activated Carbon 1	With Activated Carbon 2
30	5	Hazy	Hazy	Hazy
	7.5	0.084 ± 0.008	Hazy	Hazy
	10	0.106 ± 0.006	Hazy	Hazy
50	5	0.065 ± 0.008	Hazy	Hazy
	7.5	0.051 ± 0.005	0.011 ± 0.001	0.031 ± 0.008
	10	0.210 ± 0.122	0.017 ± 0.001	0.205 ± 0.049

Values are expressed as mean ± SD (n=3)

Furfural compounds, that make the brown color of the hydrolysates, usually inhibit some fermentation processes, thus, the presence of the compounds was important to be analyzed. At the lower level (30%) of microwave irradiation power there was not any brown compound in the hydrolysates, which was shown by very low absorption values at 490 nm (Table 3) and undetected level of HMF (Table 4). Even, the absorption values at 490 nm of some hydrolysates cannot be analyzed because the solutions were not clear or hazy. There might be still large amount of high molecular weight compounds in the soluble fraction of the hydrolysates, which were resulted from starch degradation. At the higher level (50%) of microwave irradiation power the formation of brown compounds could be seen in the hydrolysates produced from

the treatment without the addition of activated carbon and that with the addition of activated carbon 2 for 10 min. The HMF content of both hydrolysates was almost the same (Table 4). Thus, activated carbon 2 was not a good adsorbent for HMF. This was in accordance with the lower surface area of activated carbon 2.

Table 4. HMF content (mg/100 g) of cassava pulp hydrolysates after microwave-assisted acid hydrolysis

Power (%)	Time (min)	Without Act. Carbon	With Activated Carbon 1	With Activated Carbon 2
30	5	ud	ud	ud
	7.5	ud	ud	ud
	10	ud	ud	ud
50	5	ud	ud	ud
	7.5	2.10 ± 1.13	ud	ud
	10	23.52 ± 5.51	ud	27.35 ± 1.40

Values are expressed as mean ± SD (n=3); ud = undetected

4. Conclusion

Adsorption properties of activated carbon affect glucose yield and the formation of brown compounds in the hydrolysates of cassava pulp. The addition of activated carbon with inferior adsorption properties in cassava pulp suspension slightly lowered glucose yield and did not decrease HMF content in the hydrolysates. The addition of activated carbon with superior adsorption properties in cassava pulp suspension greatly lowered glucose yield and suppressed the formation of brown compounds, such as HMF in the hydrolysates.

Acknowledgement

The authors gratefully acknowledge Ministry of Research and Technology of the Republic of Indonesia and Indonesian Institute of Sciences (LIPI) for supporting this research through the Incentive Research for Researchers and Engineers Program 2011. The authors thank Prof. Jun-ichi Azuma from Kyoto University, Japan for his help in providing activated carbon 1.

References

- [1] Kunhi A.A.M., Ghildyal N.P., Lonsane B.K., Ahmed S.Y., Natrajan C.P., *Starch/Stärke* 1981; **33**: 275-279.
- [2] Ahmed S.Y., Ghildyal N.P., Kunhi A.A.M., Lonsane B.K., *Starch/Stärke* 1982; **35**: 430-432.
- [3] Srikanta S., Jaleel S.A., Ghildyal N.P., Lonsane B.K., Karanth N.G., *Starch/Stärke* 1987; **39**: 234-237.
- [4] Woiciechowski A.L., Nitsche S., Pandey A., Soccol C.R., *Brazilian Arch. Biol. Technol.* 2002; **45**: 393-400.
- [5] Yoonan K., Kongkiattikajorn J., Rattanakanokchai K., *Ethanol production from acid hydrolysates of cassava pulps using fermentation by *Saccharomyces cerevisiae**; 2004. <http://www.lib.ku.ac.th/KUCONF/KC4305049.pdf> (accessed on 21 August 2009).
- [6] Jaleel S.A., Srikanta S., Ghildyal N.P., Lonsane B.K., *Starch/Stärke* 1988; **40**: 55-58.
- [7] Chotineeranat S., Pradistsuwana C., Siritheerasas P., Tantratian S., *J. Sci. Res. Chula. Univ.* 2004; **29**: 119-128.
- [8] Kongkiattikajorn J., Yoonan K., *Kasetsart J. (Nat. Sci.)* 2004; **38**: 29-35.

- [9] Srinorakutara T., Suesat C., Pitiyont B., Kitpreechavanit W., Cattithammanit S., Utilization of Waste from Cassava Starch Plant for Ethanol Production. *Proceedings of The Joint International Conference on "Sustainable Energy and Environment (SEE)"*, Hua Hin, Thailand 2004; 344-349.
- [10] Srinorakutara T., Kaewvimol L., Saengow L., *Approach of cassava waste pretreatments for fuel ethanol production in Thailand*; 2006. [http://www.energy-based.ncert.go.th/Article/Ts-3 approach of cassava waste pretreatments for fuel ethanol production in thailand.pdf](http://www.energy-based.ncert.go.th/Article/Ts-3%20approach%20of%20cassava%20waste%20pretreatments%20for%20fuel%20ethanol%20production%20in%20thailand.pdf) (accessed on 21 August 2009).
- [11] Rattanachomsri U., Tanapongpipat S., Eurwilaichitr L., Champreda V., *J. Biosci. Bioeng.* 2009; **107**: 488-493.
- [12] Yamaji K., Matsumura Y., Ishitani H., Yamada K., Wyman C.E., Tolan J.S., *Production of Low-Cost Bioethanol to be a Rival to Fossil Fuel*; 2006. www.nedo.go.jp/itd/teian/ann-mtg/fy18/project_grant/pdf/h/h-03y_e.pdf (accessed on 16 May 2008).
- [13] Yamaji K., Yamamoto H., Nagatomi Y., Evaluation of Ethanol Production from Cassava Pulp in Thailand with a Biomass Collection and Utilization Model, *Paper presented at COE Symposium on Advanced Electronics for Future Generations, The 21st Century COE in Electrical Engineering and Electronics for Active and Creative World*, The University of Tokyo, 15 January 2007.
- [14] Kosugi A., Kondo A., Ueda M., Murata Y., Vaithanomsat P., Thanapase W., et al., *Renew. Energy* 2009; **34**: 1354-1358.
- [15] Hermiati E., Azuma J., Tsubaki S., Mangunwidjaja D., Sunarti T.C., Suparno O., et al., *Carbohydr. Polym.* 2012; **87**: 939-942.
- [16] Zhang Z., Shan Y., Wang J., Ling H., Zang S., Gao W., et al., *J. Hazard. Mater.* 2007; **147**: 325-333.
- [17] Matsumoto A., Tsubaki S., Sakamoto M., Azuma J., Oligosaccharides adsorbed on activated charcoal powder escaped from hydrolysis by microwave heating in water, *Proceedings of Global Congress on Microwave Energy Applications*, Otsu, Japan, August 4-8, 2008; 785-788.
- [18] Matsumoto A., Tsubaki S., Sakamoto M., Azuma J., *Bioresour. Technol.* 2011; **102**: 3985-8.
- [19] Hermiati E., Azuma J., Mangunwidjaja D., Sunarti T.C., Suparno O., Prasetya B., *Indonesian J. Chem.* 2011; **11**: 238-245.
- [20] Warrand J., Janssen H.G., *Carbohydr. Polym.* 2007; **69**: 353-362.
- [21] Whistler R.L., Daniel J.R., Carbohydrates in Fennema O.R. (editor). *Food Chemistry*, New York: Marcel Dekker; 1986; 69-137.
- [22] Khan A.R., Johnson J.A., Robinson R.J., *Cereal Chem.* 1979; **56**: 303-304.