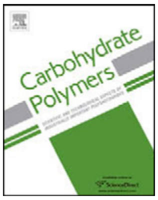
Carbohydrate Polymers 87 (2012) 939–942

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Short communication

Improvement of microwave-assisted hydrolysis of cassava pulp and tapioca flour by addition of activated carbon

Euis Hermiati[a,b,*], Jun-ichi Azuma[c], Shuntaro Tsubaki[c,d,1], Djumali Mangunwidjaja[b], Titi C. Sunarti[b], Ono Suparno[b], Bambang Prasetya[e,1]

[a] R&D Unit for Biomaterials, Indonesian Institute of Sciences (LIPI), Jl. Raya Bogor Km 46, Cibinong, Bogor 16911, Indonesia
[b] Department of Agroindustrial Technology, Faculty of Agricultural Engineering and Technology, Bogor Agricultural University, Kampus IPB Darmaga, PO Box 220, Bogor 16002, Indonesia
[c] Division of Environmental Technology and Science, Graduate School of Agriculture, Kyoto University, Sakyo-ku, Kyoto 606-8502, Japan
[d] Oceanography Section, Science Research Center, Kochi University, Akebono-cho 2-5-1, Kochi-shi, Kochi 780-8520, Japan
[e] Research Center for Biotechnology, Indonesian Institute of Sciences (LIPI), Jl. Raya Bogor Km 46, Cibinong, Bogor 16911, Indonesia

ARTICLE INFO

Article history:
Received 20 July 2011
Accepted 12 August 2011
Available online 19 August 2011

Keywords:
Microwave-assisted hydrolysis
Cassava pulp
Tapioca
Activated carbon

ABSTRACT

The superior effects of addition of activated carbon were evidenced for microwave assisted hydrolysis of starches in cassava pulp and tapioca flour under hydrothermal conditions varying irradiation temperature (160–230 °C at 5 min), duration of heating time (5–18 min at 210 °C) and amount of activated carbon at 0.5–2.0:1:20 of activated carbon:solid:liquid ratio. The presence of 1.0 g/g in microwave-assisted hydrolysis gave much improved glucose yields (44.49% for cassava pulp and 71.93% for tapioca flour) at lower heating temperature (220 °C and 200 °C, each for 5 min) with suppressed formation of secondary decomposed compounds than those without addition of activated carbon (32.41% in cassava pulp at 230 °C and 55.11% in tapioca flour at 240 °C, each for 5 min). The highest glucose yield from cassava pulp (52.27%) was obtained after heating at 210 °C for 15 min.

1. Introduction

Tapioca flour is one of the important products of cassava used for sizing textiles, adhesive, glucose syrup, vitamin C and food ingredients. Cassava pulp as a by-product of tapioca industry has been reported to contain 62–68% of starch and 13–27% of fiber (Kunhi, Ghildyal, Losane, & Natrajan, 1981; Sriroth, Chollakup, Chotineeranat, & Piyachomkwan, 2000). As starch is the main component in the cassava pulp, the important conversion step is focused on hydrolysis into glucose which can be further converted to different kinds of useful chemicals including ethanol.

Hydrolysis of starch in cassava pulp has been investigated by using several methods; acid hydrolysis (Ahmed, Ghildyal, Kunhi, & Losane, 1982; Srikanta, Jaleel, Ghildyal, & Losane, 1987), enzymatic hydrolysis (Chotineeranat, Pradistsuwana, Siritheerasas, & Tantratian, 2004; Jaleel, Srikanta, Ghildyal, & Losane, 1988; Kongkiattikajorn & Yoonan, 2004; Rattanachomsri, Tanapongpipat, Eurwilaichitr, & Champreda, 2009), and combination of hydrothermal and enzymatic hydrolysis (Kosugi et al., 2009).

Microwave assisted hydrolysis has been appreciated as a rapid and convenient method for conversion of biomass into useful chemicals (Tsubaki, Iida, Sakamoto, & Azuma, 2008; Yoshida, Tsubaki, Teramoto, & Azuma, 2010). Addition of activated carbon can further improve microwave heating effects by promoting hot spots (Zhang et al., 2007). Saccharification rate of corn starch can be improved at lower temperature without hazardous catalyst such as sulfuric acid (Matsumoto, Tsubaki, Sakamoto, & Azuma, 2011). Additionally, activated carbons are also attractive for adsorption of secondary degraded compounds such as 5-hydroxymethyl furfural (HMF) which will inhibit the fermentation of glucose into ethanol.

In this study, we have investigated the use of activated carbon on microwave-assisted hydrolysis of cassava pulp and tapioca flour for establishment of practical application of this method as a biomass transformation.

2. Materials and methods

2.1. Materials

Cassava pulp was collected from a small-scale tapioca industry located in Bogor, Indonesia. Tapioca flour was purchased from a local market in Jakarta, Indonesia. Activated carbon Y-8/20 AW (previously Y-10S AW) was purchased from Ajinomoto Fine-Techno Co., Inc., Japan.

---

[*] Corresponding author. Tel.: +62 21 87914511; fax: +62 21 87914510.
E-mail addresses: euis.hermiati@lipi.go.id, e_hermiati@yahoo.com (E. Hermiati).
[1] Present address: Science Research Center, Oceanography Section, Kochi University, Akebono-cho 2-5-1, Kochi-shi, Kochi 780-8520, Japan.

0144-8617/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2011.08.033

Table 1
The effects of heating time and amount of activated carbon on glucose yield, pH, and formation of brown compound of cassava pulp hydrolysates after microwave heating at 210 °C.

Heating time (min)	Amount of activated carbon (g/g solid sample)	Glucose yield (%)	pH	Absorbance (490 nm)	HMF (mg/100 g)
5	1.0	19.60 ± 4.79	3.35 ± 0.04	0.247 ± 0.006	5.87 ± 0.83
8	1.0	42.69 ± 1.87	3.18 ± 0.03	0.291 ± 0.016	11.32 ± 1.59
10	1.0	47.97 ± 0.27	3.12 ± 0.02	0.374 ± 0.022	19.15 ± 1.22
12	0.5	50.32 ± 1.90	3.19 ± 0.04	0.783 ± 0.048	55.35 ± 0.07
12	1.0	50.85 ± 1.32	3.07 ± 0.02	0.421 ± 0.014	24.96 ± 2.76
12	1.5	50.86 ± 0.72	2.86 ± 0.01	0.264 ± 0.006	11.61 ± 0.88
12	2.0	31.12 ± 3.97	2.75 ± 0.02	0.135 ± 0.016	5.11 ± 0.44
15	1.0	52.27 ± 0.88	3.02 ± 0.02	0.510 ± 0.018	46.25 ± 2.13
18	1.0	49.15 ± 2.11	2.93 ± 0.02	0.645 ± 0.053	63.08 ± 0.71

Values are expressed as mean ± SD ($n = 3$), except for HMF ± SD ($n = 2$).

Starch contents of the raw materials were determined using Total Starch and Amylose/Amylopectin kits (Megazyme International Ireland Ltd., Wicklow, Ireland). Ash and nitrogen contents were determined according to AOAC 923.03 and AOAC 990.03, respectively. Lipid content was determined by extraction with chloroform: methanol (2:1, v/v) for 5 h at 50 °C. Monosaccharide composition was determined as described previously (Yoshida et al., 2010).

2.2. Hydrolysis using microwave irradiation

One gram of the sample was suspended in 20 mL water with and without activated carbon (0.5–2.0 g) in a 100 mL Teflon tube and subjected to hydrolysis using MicroSYNTH (2450 MHz) microwave oven (Milestone Inc., Shelton, CT, USA) at temperature range 180–240 °C for 5–18 min with pre-heating time of 4 min to reach the desired temperature in closed condition. After treatment, the sample was filtered through pre-weighed glass filter paper to separate solution from residues.

2.3. Analysis of soluble fraction

Oligomer distribution in the soluble fraction was analyzed by high performance liquid chromatography (HPLC) on a column of 7.5 mm × 200 mm MCI GEL CK04SS (Mitsubishi Chemical Industry Co., Ltd, Tokyo, Japan) and Shodex SE-51 refractive index detector (Showa Denko K. K., Tokyo, Japan). Water was used as an eluent at 0.3 mL/min of elution rate. Glucose content was determined by Glucose CII test kit (Wako Pure Chemical Industries, Ltd, Osaka, Japan) and estimated as starch based theoretical yield. The formation of brown compound was determined by measuring absorbance at 490 nm according to Warrand & Janssen (2007) and Whistler and Daniel (1985). HMF content was determined according to AOAC (980.23–1999).

3. Results and discussion

3.1. Chemical contents of raw materials

Cassava pulp contained higher ash (0.64%), lipid (1.78%) and protein (5.36%) than tapioca flour which contained 0.11% ash, 1.19% lipid and a trace amount of protein. Starch contents of cassava pulp and tapioca flour were 79.45% and 96.06%, respectively, with similar amylose contents (21.36% and 20.47%). The amount of starch in the cassava pulp used was higher than those reported in Sriroth et al. (2000) and Kunhi et al. (1981) amounting around 60–70%. The relative neutral monosaccharide composition of cassava pulp was mainly glucose (94.0%) followed by galactose (2.9%), xylose (2.1%), rhamnose (0.7%), arabinose (0.5%) and mannose (0.1%) indicating presence of cellulose and a slight amount of hemicellulose in cassava pulp in addition to starch.

3.2. Effects of temperature on hydrolysates of cassava pulp and tapioca flour

Microwave heating with activated carbon under hydrothermal condition was applied to an actual starchy biomass, cassava pulp, for the first time with use of tapioca flour as a reference (Table 1 and Fig. 1). The activated carbon which had the lowest oligosaccharide adsorption ability with the highest filtration property among activated carbons tested previously (Matsumoto et al., 2011) was selected as a sensitizer. Production of glucose from cassava pulp occurred above 210 °C without activated carbons and attained at 32.4% at 230 °C. Addition of activated carbon, however, lowered this temperature to 220 °C (Fig. 1). The maximum glucose yield improved to 52.3% at 210 °C for 15 min with 1.0 g/g activated carbon. In the case of tapioca flour, the glucose yield obtained without activated carbon (55.1% at 240 °C) was also greatly improved to 71.9% at 200 °C with 1.0 g/g activated carbon. The low hydrolyzability of the starch in cassava pulp probably ascribed to the tight wrapping or association with cell wall components.

The production of glucose was accompanied by production of malto-oligosaccharides at around 180–200 °C (Suppl. Fig. 1A and B). The higher production of oligosaccharides from cassava pulp was observed above 200 °C due to stability of starch as described above.

Degree of secondary decomposition was evaluated by pH, browning and HMF production (Fig. 1). Suppression of decrease in pH by addition of activated carbon is in accord with lower degree of secondary degradation. The development of brown colored materials monitored by measuring absorbance at 490 nm progressed remarkably above 220 °C in the case of tapioca flour without activated carbon. The absorption gradually increased in the case of cassava pulp. This is probably explained by amino-carbonyl reaction in addition to degradation of sugars due to protein in the cassava pulp. The addition of activated carbon significantly prevented the browning of the hydrolysate. The production of HMF from tapioca flour showed similar profile with absorbance at 490 nm. Previously, these fermentation inhibitors were removed by filtration through activated carbons after conversion into glucose. The present process offers hydrolysis of the substrate and removal of the secondary decomposed materials in one pot reaction in addition to the microwave sensitizing effects provided by the activated carbon.

3.3. Effects of heating time and activated carbon amount on hydrolysis of cassava pulp

The duration of heating time (5–18 min) was varied to explore the effective heating condition for production of glucose at constant heating temperature (210 °C). Elongation of heating time increased glucose yield up to 52.3% (Table 1). Since the production of glucose from starch occurs after liquefaction, the longer time was

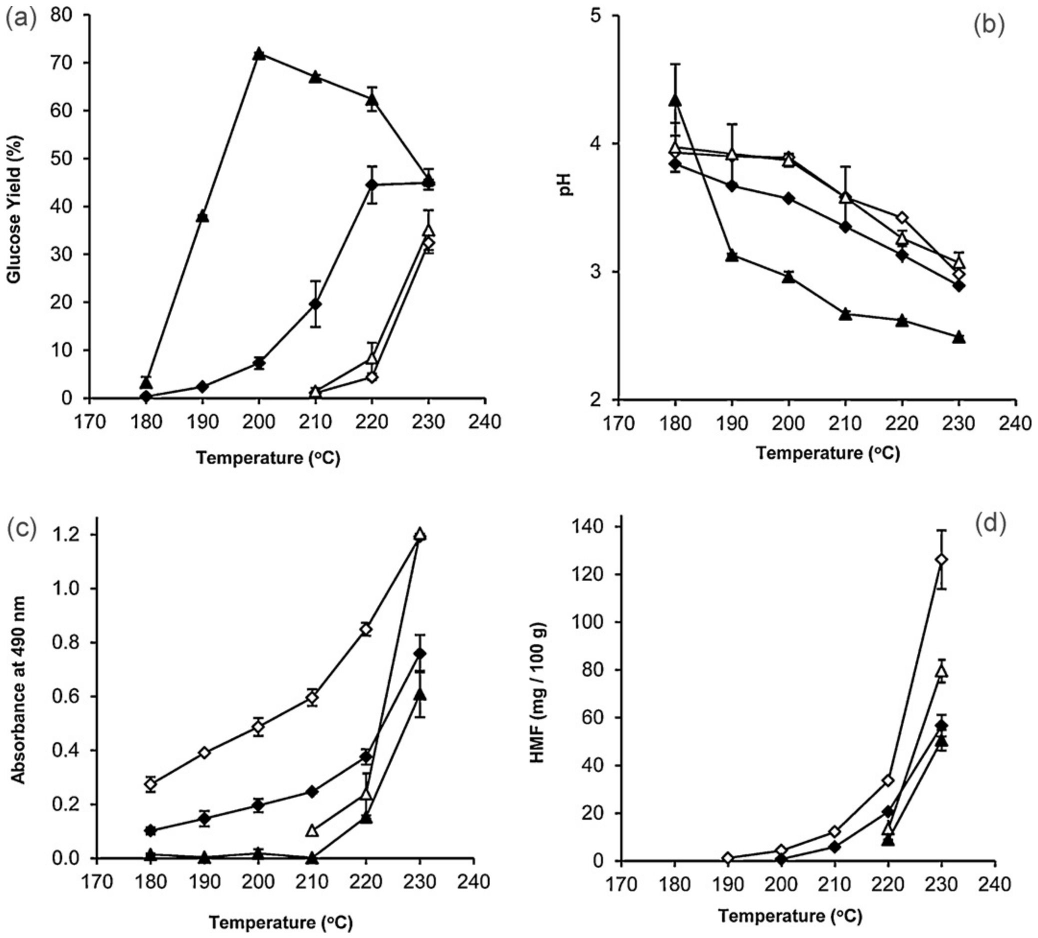


Fig. 1. The effects of heating temperature on glucose yield (a), pH (b), formation of brown compounds (c) and HMF content (d) of cassava pulp and tapioca flour hydrolysates (white diamond, cassava pulp; black diamond, cassava pulp with activated carbon; white triangle, tapioca flour; black triangle, tapioca flour with activated carbon). Values in data points are mean ± SD ($n = 3$), except for HMF ± SD ($n = 2$).

necessary (12–15 min) for conversion into glucose than that required for extraction of polysaccharide (5 min, Tsubaki et al., 2008). From the results of HPLC analysis more than 12 min of heating time was required for complete hydrolysis of malto-oligosaccharides into glucose, corresponding to the reaction behavior of glucose production (Suppl. Fig. 1C).

Subsequently, the effects of the amount of activated carbon (0.5–2.0 g of loading for each 1 g of solid sample) on glucose production were investigated. The results (Table 1 and Suppl. Fig. 1) clearly showed that use of 1.0 g/g of activated carbon at heating temperature of 210 °C and heating time of 12 min was enough to give lower absorption at 490 nm and HMF yield.

4. Conclusions

This study demonstrated that addition of activated carbon improved hydrolysis of starches in cassava pulp and tapioca flour with suppression of formation of the secondary decomposed materials. The addition of activated carbon up to 1.5 g/g of solid sample was effective for production of glucose. This method provides one pot reaction for hydrolysis of starch and removal of fermentation inhibitors simultaneously.

Acknowledgement

The authors thank Japan Society for the Promotion of Science and Ministry of Research and Technology of the Republic of Indonesia (Incentive Program for Researchers and Engineers 2010) for supporting this research.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carbpol.2011.08.033.

References

Ahmed, S. Y., Ghildyal, N. P., Kunhi, A. A. M., & Lonsane, B. K. (1982). Confectioner's syrup from tapioca processing waste. *Starch/Stärke*, *35*, 430–432.

Chotineeranat, S., Pradistsuwana, C., Siritheerasas, P., & Tantratian, S. (2004). Reducing sugar production from cassava pulp using enzymes and ultra-filtration. I. Enzymatic hydrolation. *Journal of Science Research Chulalongkorn University*, *29*, 119–128.

Jaleel, S. A., Srikanta, S., Ghildyal, N. P., & Lonsane, B. K. (1988). Simultaneous solid phase fermentation and saccharification of cassava fibrous residue for production of ethanol. *Starch/Stärke*, *40*, 55–58.

Kongkiattikajorn, J., & Yoonan, K. (2004). A study of optimal conditions for reducing sugars production from cassava peels by diluted acid and enzymes. *Kasetsart Journal (Natural Science)*, *38*, 29–35.

Kosugi, A., Kondo, A., Ueda, M., Murata, Y., Vaithanomsat, P., Thanapase, W., et al. (2009). Production of ethanol from cassava pulp via fermentation with a surface engineered yeast strain displaying glucoamylase. *Renewable Energy*, *34*, 1354–1358.

Kunhi, A. A. M., Ghildyal, N. P., Lonsane, B. K., Ahmed, S. Y., & Natrajan, C. P. (1981). Studies on production of alcohol from saccharified waste residue from cassava starch processing industries. *Starch/Stärke*, *33*, 275–279.

Matsumoto, A., Tsubaki, S., Sakamoto, M., & Azuma, J. (2011). A novel saccharification method of starch using microwave irradiation with addition of activated carbon. *Bioresource Technology*, *102*, 3985–3988.

Rattanachomsri, U., Tanapongpipat, S., Eurwilaichitr, L., & Champreda, V. (2009). Simultaneous non-thermal saccharification of cassava pulp by multi-enzyme activity and ethanol fermentation by *Candida tropicalis*. *Journal of Bioscience and Bioengineering*, *107*, 488–493.

Srikanta, S., Jaleel, S. A., Ghildyal, N. P., Lonsane, B. K., & Karanth, N. G. (1987). Novel technique for saccharification of cassava fibrous waste for alcohol production. *Starch/Stärke*, *39*, 234–237.

Sriroth, K., Chollakup, R., Chotineeranat, S., Piyachomkwan, K., & Oates, C. G. (2000). Processing of cassava waste for improved biomass utilization. *Bioresource Technology*, *71*, 63–69.

Tsubaki, S., Iida, H., Sakamoto, M., & Azuma, J. I. (2008). Microwave heating of tea residue yields polysaccharides, polyphenols, and plant biopolyester. *Journal of Agricultural and Food Chemistry*, *56*, 11293–11299.

Warrand, J., & Janssen, H. G. (2007). Controlled production of oligosaccharides from amylose by acid-hydrolysis under microwave treatment: comparison with conventional heating. *Carbohydrate Polymers*, *69*, 353– 362.

Yoshida, T., Tsubaki, S., Teramoto, Y., & Azuma, J. (2010). Optimization of microwave-assisted extraction of carbohydrates from industrial waste of corn starch production using response surface methodology. *Bioresource Technology*, *101*, 7820–7826.

Whistler, R. L., & Daniel, J. R. (1985). Carbohydrates. In O. R. Fennema (Ed.), *Food chemistry* (pp. 69–137). New York: Marcel Dekker.

Zhang, Z., Shan, Y., Wang, J., Ling, H., Zang, S., Gao, W., et al. (2007). Investigation on the rapid degradation of congo red catalyzed by activated carbon under microwave irradiation. *Journal of Hazardous Materials*, *147*, 325–333.