HYDROLYSIS OF CARBOHYDRATES IN CASSAVA PULP AND TAPIOCA FLOUR UNDER MICROWAVE IRRADIATION

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Received September 16, 2011; Accepted November 9, 2011

ABSTRACT

Cassava pulp and tapioca flour are potential sources of glucose. In this work, validity of microwave irradiation for hydrolysis of carbohydrates, especially starch, present in cassava pulp and tapioca flour was estimated as a non-enzymatic saccharification technique. Suspension of cassava pulp or tapioca flour in distilled water (1g/20 mL) was subjected to microwave irradiation at temperatures of 140-240 °C with pre-heating time of 4 min and heating time of 5 min. Solubilization rate of cassava pulp increased with increasing temperature of microwave heating treatment and reached maximum (92.54%) at 220 °C, while that of tapioca flour reached almost 100% at 140 °C. Production of malto-oligomers from starch in cassava pulp and tapioca flour was clearly observed at 220 °C. The highest glucose yields from cassava pulp and tapioca flour in this experiment were 28.59 and 58.76% dry matter, respectively. Variation of pre-heating time at 230 °C did not give significant effects on glucose yield from cassava pulp. However, glucose yield from tapioca flour decreased due to increase of pre-heating time. Microwave irradiation is a promising method of hydrolysis for cassava pulp and tapioca flour due to the fast process.

Keywords: *cassava pulp, microwave, hydrolysis, carbohydrate, glucose*

INTRODUCTION

Tapioca is starch extracted from cassava. It contains around 95% of starch and can be used in food, textile, chemical and pharmaceutical industry. Production of tapioca from cassava produces solid as well as liquid wastes. The solid waste consists of cassava peel and cassava pulp (some literature mention it as cassava bagasse). Processing 250-300 tons of cassava produces 1.16 tons of cassava peel and 280 tons of cassava pulp having around 85% moisture content [1]. Cassava pulp contains starch and fiber in significant amount, 68% and 27%, respectively [2]. This carbohydrate could be converted into different kinds of chemicals or products. The utilization of cassava pulp would be beneficial since the material is abundantly and continuously available in many big tapioca industries and could help solving the problem of waste disposal of tapioca industry.

Hydrolysis of starch in cassava pulp is mostly conducted using enzymatic [3-9] or acid process [4,10-12]. However, the hydrolysis could also be accomplished by other processes, such as hydrothermal [13-14] or hydrothermal combined with enzymatic process [15]. Production of brownish yellow hydrolysate from acidic process becomes a problem, although it can be overcome by using adsorption materials, such as bentonite and kaolin [10]. Enzymatic hydrolysis did not produce this yellowish color, however it is considered less economical than acidic hydrolysis due to longer time and higher cost of process [4]. Enzymatic hydrolysis with ultra-filtration resulted in more economic enzymatic process, since this system could increase the rate of reducing sugar production 20% higher than it was without ultra-filtration [5].

Microwave heating has been widely used in organic and inorganic synthesis due to its fast reaction rate and its product yield and quality. There are some reports regarding the use of microwave heating in the degradation of starch from different kinds of starches, such as wheat, rice, potato, and corn starches, in water or in dilute acid solutions. Most of studies reported the use 2,450 MHz microwave oven. Concentration of starch suspension varies from 1% up to 50%, but mostly 10% of starch suspension [16-17]. Studies were conducted either on lower starch suspension (1–8%)

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[18] or on higher concentrations, 10–30% [19], 33–50% [20], and 33% [21]. Some studies reported the temperatures used [16,22-23]. Some other studies reported the degree of power used only, in the term of power percentage or wattage [17,20-21, 24]. The longest time use for starch treatment or degradation using microwave heating that has been reported was 10 min. Most processes could be completely finished in less than 10 min. Treatment or degradation of starch using microwave heating can use water or dilute acid, such as hydrochloric acid or sulfuric acid as medium. Hydrolysis of starch could be enhanced by addition of inorganic salts containing Cl or SO_4 ions with Cl ion gave better results [17]. However, this process needs further treatment to remove the salts from the hydrolysates. Saccharification of some starches was also improved by the addition of activated carbon [22-23]. All studies on microwave-assisted hydrolysis and saccharification were using pure starch, and there was no study that reported the use of starch that is still bound tightly in carbohydrate matrices, such as the starch in cassava pulp. This study reported the characteristics of carbohydrates, especially starch in cassava pulp and tapioca flour, and the effects of microwave irradiation on degradation and hydrolysis of carbohydrates, especially starch, present in cassava pulp and tapioca flour, which represent the bound and free starch, respectively.

EXPERIMENTAL SECTION

Materials

Cassava pulp was collected from a small-scale tapioca industry located in Bogor, Indonesia. The material was heated at 60 °C for 30 h, and then it was ground and sieved to pass through 20 mesh sieve. Tapioca flour was purchased from local market in Jakarta. These raw materials were stored in plastic bags and were put in a sealed plastic container. The solvent and other reagents used were analytical grades.

Procedure

Analysis of Raw Materials

Proximate analysis (moisture, ash, fat, crude protein) of cassava pulp was conducted as follows. Moisture content was determined gravimetrically by drying at 105 °C up to constant weight, ash content was determined by heating at 600 °C for 3 h, fat content was determined by Soxhlet extraction, and crude protein was determined by Kjeldahl method. Moisture content of tapioca flour and cassava pulp were also determined using MA 35 moisture tester (Sartorius Mechatronics, Sartorius AG, Goettingen, Germany) at 105 °C. Crude fiber of cassava pulp and tapioca flour were determined according to Indonesian National Standard (SNI) 01-2891-1992 point 11. Starch and amylose contents of the raw materials were determined using Total Starch kit (Megazyme Ltd., Ireland) following AOAC Official Method 996.11 and Amylose/Amylopectin kit (Megazyme Ltd., Ireland), respectively. Relative composition of carbohydrates of cassava pulp and tapioca flour were determined by analysis of their neutral sugar composition by high-performance anion exchnage chromatography (HPAEC) on a Dionex DX-500 system (Sunnyvale, CA, USA) with detector (ED-40) using 1.0 mM NaOH as a mobile phase, after complete hydrolysis with 72% (w/w) sulfuric acid 3% (w/v) at 120 °C for 1 h.

Morphological properties of cassava pulp and tapioca flour were analyzed using VE-8800 Low Voltage Scanning Electron Microscope (Keyence, Co., Osaka, Japan), while crystal pattern of the materials were analyzed using Ultima IV X-Ray Diffractometer (Rigaku Company, Tokyo, Japan).

Starch Hydrolysis Using Microwave Irradiation

Microwave used in this study was MycroSYNTH Lab Station (2,450 MHz) microwave oven (Milestone Inc., Shelton, CT, USA). It is a multimode microwave oven, equipped with a thermocouple thermometer to monitor the real time temperature inside the reactor. Heating temperature and time were controlled by changing the microwave input through PID algorithm on a PC unit (easyWAVE 3 software, Milestone, Inc., Shelton, CT, USA). Suspension of the material sample in distilled water (1g/20 mL) was put in a 100 mL teflon tube and mixed with a stirrer bar to homogenize the suspension. The sample was then subjected to hydrolysis at temperature of 140–240 °C with pre-heating time (the time to increase the temperature from ambient to desired temperature) of 4 min and heating time (the time at desired temperature) of 5 min. After microwave irradiation, the sample was cooled immediately in an ice bath to room temperature. Further, microwave irradiation was also conducted at 230 °C for cassava pulp and at 240 °C for tapioca flour, each with pre-heating time of 2–6 min and heating time of 5 min.

Determination of Solubilized Fraction

Microwave treated cassava pulp were centrifuged at 10 °C, 5,000 g for 15 min. The residues were separated from the supernatant, washed three times using 30 mL of water and centrifuged at 10 °C, 5,000 g for 15 min after each washing. The sample was then freeze dried. Percentage of solubilized fraction was calculated by the following equation:

Solubilized fraction (%) = (Weight of raw material – weight of residue) x 100 / (Weight of raw material)

Table 1. Carbohydrates in cassava pulp and tapioca flour

Compounds (%)	Cassava Pulp	Tapioca Flour
Starch	79.45	96.06
Amylose	21.36	20.47
Crude Fiber	4.84	0.13
Relative neutral sugar composition		
Glucose	94.04	93.72
Galactose	2.86	---
Xylose	2.07	6.28
Rhamnose	0.72	---
Arabinose	0.49	---
Mannose	0.05	---

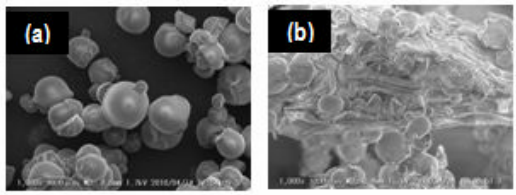

Fig 1. LV SEM images of tapioca flour (a) and cassava pulp (b)

Analysis of Solubilized Fraction

The solubilized fraction was analyzed for its oligomer distribution using HPLC with 7.5 x 200 mm MCI GEL CK04SS column, Shodex SE-51 refractive index detector, Jasco PU-980 pump, Jasco CO-965 column oven, and Jasco DG-980-50 degasser. Water was used as a solvent at 0.3 mL/min elution rate. The calculation was accomplished by Jasco Chrom NAV data station. Glucose content was determined using Glucose CII test kit (Wako Junyaku, Co., Osaka), pH value was using pH meter, and the formation of brown compound was determined by measuring absorbance at 490 nm [25-26]. Total sugar of cassava pulp supernatant was also determined by the phenol sulphuric acid method [27].

Analysis of Residues

Residues of cassava pulp was analyzed for their neutral sugar composition by high-performance anion exchange chromatography (HPAEC) as described above after complete hydrolysis with 72% (w/w) sulfuric acid 3% (w/w) at 120 °C for 1 h. Residues of cassava pulp was also analyzed for their morphological properties by LV SEM (Keyence VE-8800).

RESULT AND DISCUSSION

Compositional Analysis of Raw Materials

Proximate analysis of cassava pulp showed that it mostly contained carbohydrates (94.67% of dry matter), and had low ash and fat contents, which were 0.37 and 0.17% of dry matter, respectively. The pulp also contained crude protein at the amount of 4.79% of dry matter. These results were close to those reported previously [2], which mentioned that carbohydrate content of cassava pulp was around 95%. However, as shown in Table 1, the percentage of starch in the cassava pulp (79.45%) was much higher, while the crude fiber content (4.84%) was much lower than those in other reports [2,8,28], which were 60-70%, and 10-27%, respectively. These differences might be caused by different sources of cassava pulp. Our cassava pulp was collected from a small-scale tapioca industry in Bogor, West Java Province, where the peels of cassava were removed before the starch was extracted using simple equipment. Thus, there were less fibers and more starch left in our cassava pulp, due to the removal of peels and less efficient starch extraction. On the contrary, their cassava pulp might be from a big tapioca industry, where the peels were not removed before the starch extraction process using more sophisticated equipment, so that there were more fibers and less starch remained in cassava pulp. Results of starch and crude fiber analysis of cassava pulp from a big tapioca industry in Lampung Province, Indonesia (data not shown) confirmed this suggested reason. Besides that, results of a survey of tapioca industry in Lampung Province also reported that there were differences of tapioca flour yield between small scale tapioca industry and big tapioca industry [29]: Tapioca flour yield in small scale tapioca industry was around 22%, while that in big company was around 25%. This might also result in less starch and more fiber in cassava pulp from big tapioca industry.

Tapioca flour contained starch up to around 96% accompanied with very low content of crude fiber (0.13%). This was close to that reported previously (95%) [30]. Amylose content of starch in tapioca flour (20.47%) was almost the same as that in cassava pulp (21.36%) (Table 1). These results were higher than that in another report [31], but lower than that reported by others [32-33]. However, the amylose content in our study was in the range of amylose content of cassava starch (16-24%) [34]. The difference in amylose content in cassava might be due to different cultivars or method of analysis of amylose. Carbohydrates in cassava pulp and tapioca flour are mainly consisted of glucan (Table 1). Cassava pulp was also composed of galactose, xylose, arabinose and mannose, while tapioca flour contained only glucose and xylose. The same types of carbohydrates in cassava pulp were also reported in Kosugi et al. [15].

Morphological and Physical Analysis of Raw Materials

Morphological analysis of tapioca flour showed that the flour contained starch granules typical of

cassava starch granules (size 10-23 μm) as shown in Fig. 1a, while that of cassava pulp showed that the cassava starch granules (size 10-16 μm) in it were attached to and trapped in a fibrous matrices (Fig. 1b). X-Ray diffractograms of cassava pulp and tapioca flour (Fig. 2) showed that the spectra of the two materials have strong peaks at 2θ at about 16°, 17°, 18°, and 23°. This type of spectrum was close to that of A-type spectrum, such as the spectrum of corn starch. The spectrum is almost the same as that of tapioca starch with strong peaks at 15°, 17°, 18° and 23° reported previously [35]. However, some studies reported that tapioca starch, which is extracted from the root of cassava, has two types of X-ray pattern, A and C [36] or C-type spectrum [31], but after heat-moisture treatment the C pattern was changed to A pattern [31,36]. Previously, it was thought that the drying process in the production of tapioca starch from cassava in the tapioca starch industry and in the preparation of cassava pulp in this study might promote to change the type of spectrum from the C pattern of the native starches to an A pattern in both tapioca flour and cassava pulp. However, the result of analysis of freeze-dried tapioca flour and cassava pulp using X-Ray Diffractometer revealed that X-Ray patterns of both samples were close to the pattern of A-type spectrum.

Effects of Microwave Irradiation on Carbohydrates in Cassava Pulp and Tapioca Flour

Solubilized Fraction

There was practically 100% soluble fraction formed after microwave treatment of tapioca flour at 140 °C, which was the lowest temperature in the experiment. This means that all the starch in tapioca flour was solubilized at and above that temperature. Solubilized fraction of cassava pulp increased with increasing temperature of microwave heating treatment and reached maximum (± 92%) at 210-220 °C, then decreased at temperatures above 220 °C (Fig. 3a). However, there was not any significant difference in

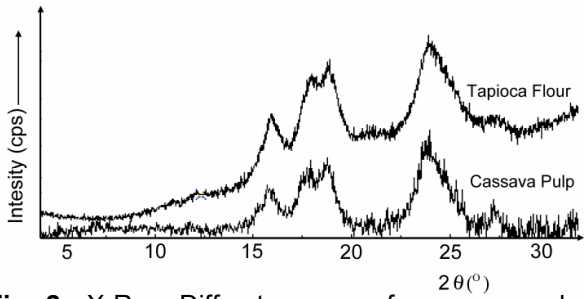

Fig 2. X-Ray Diffractograms of cassava pulp and tapioca flour

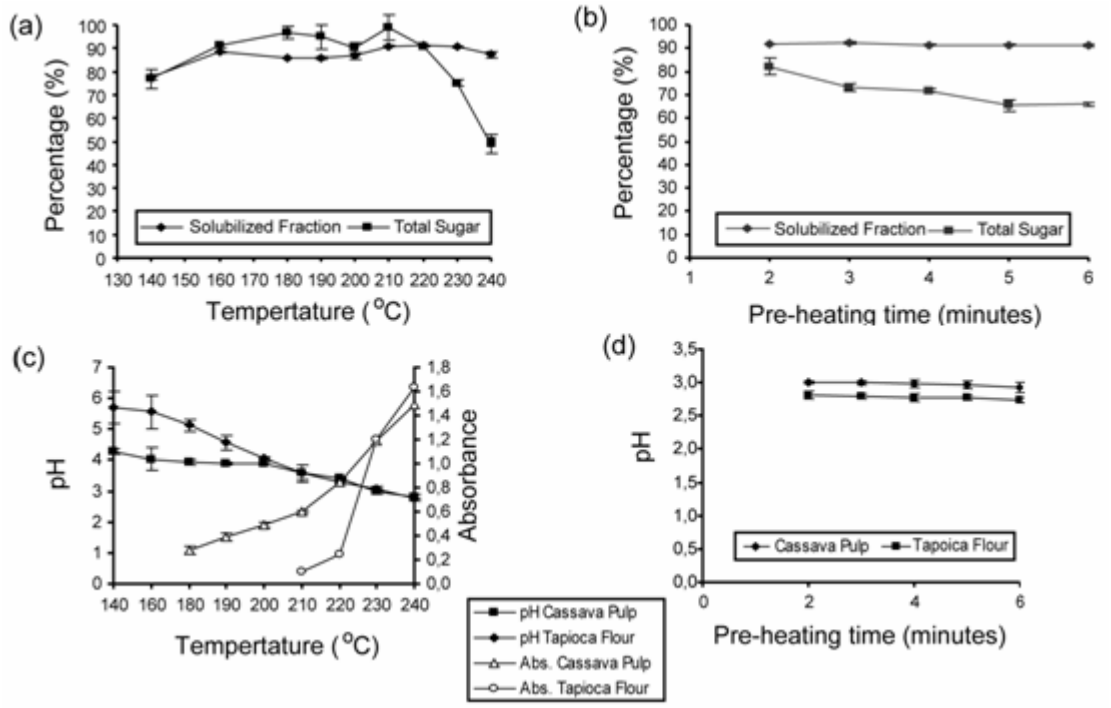

Fig 3. The effects of microwave irradiation on solubilization of cassava pulp. Solubilized fraction and total sugar at different heating temperatures, 4 min pre-heating (a), solubilized fraction and total sugar at different pre-heating times, heating temperature 230 °C (b), pH and absorbance at 490 nm of hydrolisates at different temperatures, 4 min pre-heating time (c), and pH and absorbance at 490 nm of hydrolysates at different pre-heating times at 230 °C (cassava pulp) and 240 °C (tapioca flour) (d)

Table 2. Glucose yields after microwave irradiation treatment of cassava pulp and tapioca flour

	Glucose Yield (% dry matter)[a]		Glucose Yield (% theoretical yield)[a]	
	Cassava Pulp	Tapioca Flour	Cassava Pulp	Tapioca Flour
Temperature (°C)				
210	0.93 ± 0.19	1.49 ± 0.71	1.06 ± 0.21	1.40 ± 0.66
220	3.84 ± 0.50	8.89 ± 3.41	4.35 ± 0.56	8.34 ± 3.19
230	28.59 ± 1.92	37.39 ± 4.43	32.41 ± 2.17	35.07 ± 4.16
240	22.43 ± 0.71	58.76 ± 2.68	25.44 ± 0.81	55.11 ± 2.51
Pre-heating (min)[b]				
2	23.76 ± 0.67	69.27 ± 4.17	26.95 ± 0.76	64.97 ± 3.91
3	24.50 ± 1.89	69.39 ± 2.58	27.78 ± 2.14	65.08 ± 2.42
4	25.35 ± 3.96	63.75 ± 7.65	28.74 ± 4.49	59.78 ± 7.17
5	26.76 ± 4.74	64.31 ± 1.78	30.35 ± 5.37	60.32 ± 1.67
6	27.41 ± 3.43	58.91 ± 0.75	31.08 ± 3.88	55.25 ± 0.71

[a]Values are expressed as mean ± SD (n=3).
[b]At heating temperature of 230 °C for cassava pulp and 240 °C for tapioca flour.

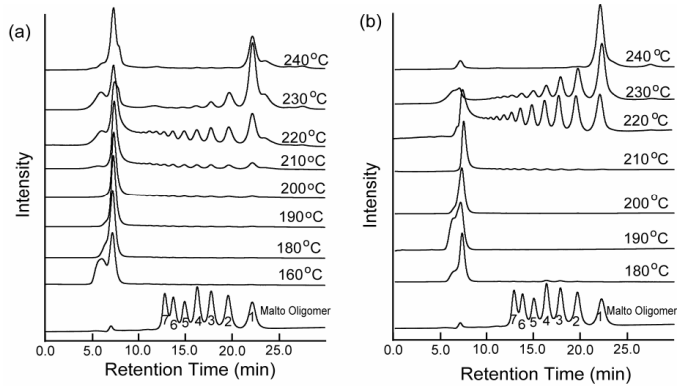

Fig 4. HPLC chromatograms of degradation products of starch in cassava pulp (a) and tapioca flour (b) after microwave treatment at different temperatures. Peaks 1, 2, 3, 4, 5, 6, 7 show glucose and malto-oligomers having degree of polymerization (DP) of 2-7

percentage of solubilized fraction due to different times of pre-heating treatment conducted at 230 °C. This suggested that heating temperature gave more significant effects than did pre-heating time at high temperature on the solubilization of chemical components of cassava pulp. The increase of percentage of solubilized fraction was mainly due to the increase of solubilized carbohydrates present in cassava pulp as shown in Fig. 3a.

Hydrolysis Products

Presence of malto-oligomers in hydrolysates of cassava pulp and tapioca flour after microwave irradiation is demonstrated in Fig. 4a and b. Cassava pulp and tapioca flour had a difference in production of oligomers by microwave treatment. Formation of small amount of oligomers in cassava pulp hydrolysate was started at 210 °C, while that in tapioca flour was at 220 °C. Formation of high amount of oligomers from starch in tapioca flour was observed after microwave treatment at 220–230 °C, while that from starch in cassava pulp was given at 220 °C. At 240 °C, almost all larger molecules in tapioca flour hydrolysate were converted to glucose, while in cassava pulp remaining of high molecular weight compounds was observed in the hydrolysate.

The yields of glucose from hydrolysis of tapioca flour and cassava pulp using microwave heating at different temperatures were presented in Table 2. Glucose yield from tapioca flour increased with increasing of heating temperatures and the highest yield of glucose from tapioca flour (58.76% of dry matter, 55.11% of theoretical yield) was found in hydrolysate after microwave treatment at 240 °C. However, glucose yield from cassava pulp increased up to heating temperature of 230 °C, reached maximum at this temperature (28.59% of dry matter, 32.41% of theoretical yield), and then decreased when it was heated at 240 °C. It was also interesting to note that the yield of glucose from cassava pulp was approximately half lower than that of from tapioca starch. The cause of this phenomena was not due to the ratios of amylose and amylopectin content of the two materials, since they were almost the same (20:80, amylose:amylopectin). Based on the present study, entanglement and or wrapping of starch with non-starchy material may be a major factor which disturbs its hydrolysis. In previous studies on hydrolysis of starch by microwave in the presence of activated carbon [22-23], survival of oligomers adsorbed on activated carbon against hydrolysis supports the present observation. Glucose yield from tapioca flour slightly decreased due to increase of pre-heating times and more remarkably by heating at 240 °C, while that from cassava pulp slightly increased with increase in pre-heating time at heating temperature of 230 °C. Maximum glucose yield obtained either from tapioca flour or from cassava pulp was higher than that (23.9%/starch) from wheat flour given under the condition of microwave heating temperature at 191-198 °C, and heating time of 20 min [19]. However,

Table 3. Relative composition of neutral sugar in native cassava pulp and cassava pulp residues after microwave irradiation treatment

	Arabinose	Rhamnose	Galactose	Glucose	Xylose	Mannose
Native	0.49 ± 0.11	0.72 ± 0.13	2.86 ± 0.39	94.04 ± 0.08	2.07 ± 0.99	0.05 ± 0.01
Temperature (°C)						
140	0.66 ± 0.23	2.73 ± 0.30	11.42 ± 0.40	76.29 ± 1.24	7.71 ± 1.68	1.20 ± 0.57
160	0.86 ± 0.07	1.39 ± 0.06	8.49 ± 0.54	76.49 ± 1.58	11.23 ± 0.89	1.20 ± 0.57
180	---	0.78 ± 0.02	2.50 ± 0.22	79.14 ± 2.94	15.58 ± 3.30	2.00 ± 0.59
190	---	0.12 ± 0.04	2.34 ± 0.02	82.39 ± 1.68	13.36 ± 2.95	1.80 ± 1.27
200	---	trace	2.10 ± 0.09	85.21 ± 3.68	11.34 ± 2.05	0.86 ± 1.10
210	---	---	2.25 ± 0.15	88.02 ± 1.10	8.23 ± 1.46	1.52 ± 0.50
220	---	---	1.57 ± 0.28	90.56 ± 0.94	7.16 ± 0.76	0.72 ± 0.10
230	---	---	2.06 ± 0.42	96.23 ± 0.15	1.72 ± 0.28	---
240	---	---	---	100.00 ± 0.00	---	---
Pre-heating (min)						
2	---	trace	0.77 ± 0.28	96.89 ± 0.26	2.19 ± 0.14	0.17 ± 0.16
3	---	---	0.71 ± 0.10	97.40 ± 0.38	1.80 ± 0.54	0.09 ± 0.06
4	---	---	trace	97.75 ± 0.39	2.00 ± 0.37	0.19 ± 0.12
5	---	---	---	97.63 ± 0.09	2.23 ± 0.03	0.16 ± 0.12
6	---	---	---	98.10 ± 0.81	1.75 ± 0.88	0.16 ± 0.08

Values are expressed as mean ± SD (n=2)

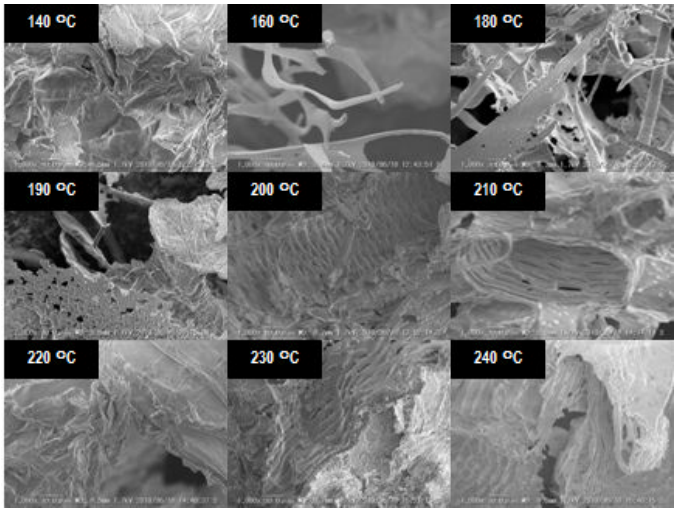

Fig 5. SEM images of cassava pulp residues after microwave heating at 140-230 °C

glucose yield from cassava pulp by the present microwave assisted hydrolysis was still lower than those produced from other methods, such as acid hydrolysis (36.40–41.34%) [12], enzymatic hydrolysis (± 70%) [9] or combinations of hydrothermal and enzymatic hydrolysis (± 75%) [15]. Nevertheless, these processes took very much longer time, 90 min for acid hydrolysis and 48–72 h for enzymatic hydrolysis, than did microwave assisted hydrolysis which only took several minutes.

Total sugar content in the solubilized fractions of microwave treated cassava pulp reached around 78% and increased steadily up to 210 °C (Fig. 3a). Above 210 °C, total sugar content decreased due to secondary degradation of depolymerized carbohydrates into lower molecular weight compounds, such as furfural, hydroxy methyl furfural, acetic acid, and so on. This can be seen in the great increase of absorbance value and great decrease of pH value (Fig. 3c) of cassava pulp supernatant that was given after microwave irradiation above 210 °C. Increase in pre-heating time at high temperature therefore decreased total sugar yield as shown in Fig. 3b. The formation of lower molecular weight compounds might affect further process, such as fermentation. Thus, the hydrolysates might need some treatment using adsorbent, such as bentonite or kaolin [10].

Brown compounds

The formation of brown compounds increased with increase of temperature, as shown by increase of absorbance value at 490 nm (Fig. 3c). The increase of absorbance value of starch hydrolysates due to increase of microwave heating temperature was also reported by Warrand and Janssen [25]. The absorbance value of cassava pulp hydrolysates was higher than that of tapioca flour started at lower temperature. This might due to the present of crude protein in cassava pulp, which supports browning reaction in the hydrolysate. There were also more types of polysaccharides containing galactose, rhamnose, arabinose and mannose, in cassava pulp which were degaraded more easily than xylan and glucan.

pH Value

The initial pH values of suspensions of cassava pulp and tapioca flour were 4.29 and 5.10 respectively. The pH of hydrolysates gradually decreased with increasing temperature of microwave heating. Hydrolysates of cassava pulp and tapioca flour reached

almost the same pH after heating at 210 °C (Fig. 3c). The decrease of pH was probably due to the formation of some acids, such as acetic acid during hydrolysis. The decrease of pH in hydrolysates of microwave-treated wheat flour in water medium due to increase of temperature was also reported previously [19]. There was not any significant difference due to differences of pre-heating time at high temperatures (Fig. 3d). Fig. 3d also shows that the pH of cassava pulp hydrolysate was slightly higher than that of tapioca flour hydrolysate after heating at high temperatures leading to weak acid-catalyzed reactions resulting in recalcitrance of cassava pulp.

Cassava Pulp Residues

Native cassava pulp was composed of different kinds of polysaccharides containing arabinose, rhamnose, galactose, glucose, xylose and mannose. Microwave heating solubilized some of those carbohydrates, thus the relative composition of the neutral sugars produced were also changed (Table 3). Based on this Table, it can also be inferred that the most resistant carbohydrate in cassava pulp was glucan (cellulose), and the other resistant carbohydrates were galactan and xylan. Either temperature or pre-heating time influenced the solubilization of the carbohydrates in cassava pulp. Gradual disappearance of some neutral sugars due to increase of heating temperature or pre-heating time meant occurrence of their decomposition into lower water-soluble components.

Results of SEM analysis of cassava residues (Fig. 5) showed that microwave heating remained fibrillated fibers as the residues. However, at higher heating temperature, there was not any sign of further fibrillation of the fibers. The cellulose fibers survived the hydrolysis were still in the form of fiber bundles up to temperature of 230 °C.

CONCLUSION

Microwave irradiation is a promising method of hydrolysis for cassava pulp as well as tapioca flour due to its rapid process. However, further studies are still needed in order to increase the glucose yield and to reduce the formation of lower molecular weight compounds that might influence further processing of the glucose produced.

ACKNOWLEDGEMENT

The authors would like to gratefully acknowledge Japan Society for the Promotion of Science (JSPS) for providing a fellowship to conduct this research at Kyoto University, Japan, and the Ministry of Research and Technology of the Republic of Indonesia for funding part of this research through Incentive Program for Researchers and Engineers 2010.

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