Review

Potential utilization of cassava pulp for ethanol production in Indonesia

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Cassava is one of the major crops produced in Indonesia. Cassava grows in all provinces in Indonesia. In the last decade, even though cassava plantation area is decreased, cassava production and its productivity in Indonesia have been on the increase steadily. The tendency of using cassava for ethanol production would affect supply of cassava for food. Cassava pulp, a by- product of tapioca industry is one of the potential biomass that can be used for ethanol production because it contains starch and fiber in significant amounts which could be further converted to ethanol. A large scale of tapioca plant having production capacity of 20 ton tapioca flour per day has a potency to produce 8.7 kL of ethanol per day. Conversion of cassava pulp to ethanol can be accomplished through different kinds of processes such as physical, chemical, biological process or combinations of those processes. The utilization of cassava pulp for ethanol production would be beneficial since the material is abundantly and continuously available in many big tapioca industries and could help in solving the problem of waste disposal of tapioca industry. However, comprehensive studies are still needed for establishment of bioethanol industry from cassava pulp.

Key words: Cassava, cassava pulp, utilization, starch, fiber, ethanol.

INTRODUCTION

Cassava (Manihot esculenta) is one of the important crops in the world. Global production of cassava reached 228.14 million tons in 2007 (Wuttiwai, 2009). Nigeria and Brazil were the two most leading cassava producers. Cassava is also one of the major crops in Southeast Asia, especially in Thailand and in Indonesia. According to Wuttiwai (2009), Thailand was so far the third largest cassava producers with a total production of 26 million tons. On the other hand, Indonesia produced around 20 million tons of cassava per year with total area of plantation around 1.2 million ha (Ministry of Agriculture of Republic of Indonesia, 2009). Recently, there is a

tendency to use more cassava for the production of bioethanol. According to Prihandana et al. (2007), cassava is among the crops that are projected for production of biofuels in Indonesia. Of the four crops (oil palm, sugarcane, jatropha, cassava), cassava is planned to give 29% of the total contribution of these crops in providing biofuels. Table 1 shows cassava production and strategic plan of bioethanol production from cassava in Indonesia. If the plan was really executed, there would have been no cassava for tapioca industry or for other food industries in 2010. In order to accomplish the need of cassava, much more land should be provided for cassava plantation, so that there is a sustainable supply of cassava for food and for energy.

One of the important products of cassava is tapioca flour. Tapioca production from cassava produces solid as well as, liquid wastes. The solid waste consists of

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Table 1. Cassava production and strategic plan of bioethanol production from cassava in Indonesia.

a)Ministry of Agriculture of Republic of Indonesia (2009, 2011); ^{b)}Prihandana et al. (2007).

Table 2. Plantation area, production and root productivity of cassava in Indonesia.

Source: Ministry of Agriculture of Republic of Indonesia (2009, 2011).

cassava peel and cassava pulp (some literature mention it as cassava bagasse). Processing 250 to 300 tons of cassava produces 1.16 ton of cassava peel and 280 tons of cassava pulp having around 85% moisture content (Pandey et al., 2000). Cassava pulp contains starch and fiber in significant amount. This by product of tapioca industry raises problems to the environment around the industry. It contaminates the air with smelly odour due to degradation of organic compounds to volatile matters by micro-organisms. It also contaminates rivers and wells of people living near the industry. Starch and cellulose contained in cassava pulp are potential sources of carbohydrates. These carbohydrates could be converted into different kinds of chemicals or products as well as for energy. The utilization of cassava pulp would be beneficial since the material is abundantly and continuously available in many big tapioca industries and could help in solving the problem of waste disposal of tapioca industry.

In this review, cassava production and utilization in Indonesia would be first summarized, followed by the characteristics of cassava pulp, and finally, its potential for energy would be discussed.

PRODUCTION AND UTILIZATION OF CASSAVA IN INDONESIA

Cassava grows in all provinces in Indonesia. In the last decade, even though cassava plantation area is decreased, cassava production and its productivity in Indonesia have been increased steadily (Table 2). Although, the crop grows in all provinces, there are ten major provinces that produce cassava as shown in Table 3. Lampung province is the largest cassava producer, also with the highest root productivity. In this province there are 58 active tapioca-processing companies (Siregar, 2006), with annual capacities vary from 400 up to 15,000 tons of tapioca starch per year.

There was no clear information regarding the use of cassava in Indonesia. However, the data from BPS – Statistics Indonesia (2007) in Table 4 revealed that there

Table 3. Cassava production (ton) in 10 provinces in Indonesia (2006 – 2010).

Source: Ministry of Agriculture of Republic of Indonesia (2009, 2011).

Table 4. Industrial products of cassava in Indonesia (calculated based on data from Statistics Indonesia, 2007).

Table 5. Export and import of tapioca from and to Indonesia (BPS – Statistics Indonesia, 2010).

were 13,414,105 kg of dried cassava (gaplek and chips), 8,814,835 kg of cassava flour, and 1,195,617,247 kg of tapioca flour produced. This means that the amount of cassava used for dried cassava, cassava flour and tapioca flour were only 0.15, 0.11 and 26.01%, respectively. The rest of cassava produced (73.74%) might be consumed fresh or processed for snack foods, such as crackers, cake, cookies, and fermented cassava, and/or processed for bioethanol.

There are mainly three types of tapioca industry in Indonesia, home industry which produces less than 1 ton of tapioca flour per day, small-scale industry, with capacities ranged around 1 up to 4 tons per day and large-scale industry with capacities more than 4 tons per day. Almost all tapioca produced from these industries was used domestically. Data in 2007 show that of the total tapioca flour produced, only 10,720,484 kg (0.9%) was exported. The amount of tapioca exported was also decreased from 2005 to 2009 (Table 5), while there was not significant changes in the amount of tapioca imported. The imported tapioca might be that of special grade tapioca for specific purposes, such as for pharmaceuticals.

CHARACTERISTICS OF CASSAVA PULP

Cassava pulp contains approximately 68% starch (dry

Table 6. Estimation of potentially ethanol produced from cassava pulp.

¹⁾ Conversion factors from cassava root to tapioca flour and to cassava pulp are assumed 0.23 and 0.20, respectively; $^{2)}$ Density of ethanol is 0.789.

basis) and 27% fiber (dry basis) (Sriroth et al., 2000). Other researchers reported that the starch and fiber content of cassava pulp was 61.84 to 69.90% and 10.61 to 14.35%, respectively (Srinorakutara et al., 2004). Small scale tapioca industry produced cassava pulp with higher starch content (79.45%) containing 21.36% amylose (Hermiati et al., 2012). Besides starch, some other carbohydrates (cellulose, galactan, xylan, rhamnan, arabinan, and mannan) are present in cassava pulp (Kosugi et al., 2009; Hermiati et al., 2012). Starch granules in cassava pulp are trapped in fibrous cell wall structure of the material which consists of these carbohydrates. This nature hinders extraction of this starch without pre-gelatinization treatment or other physical, mechanical or chemical or treatment. Fresh cassava pulp contained 72 to 85% of moisture (Sriroth et al., 2000; Pandey et al., 2000). Since water is the major component of wet cassava pulp, the material could be easily degraded by micro-organisms. The low protein content and high fiber content in cassava pulp make the material not suitable for feed unless it is treated or mixed with other raw materials rich in protein. Since starch is another major component of cassava pulp, conversion of the material through hydrolysis of starch and followed by sugar fermentation process could be advantageous. The low fat and ash content in cassava pulp is an additional advantage for fermentation process.

Research on hydrolysis of starch in cassava pulp to glucose has long been conducted (Kunhi et al., 1981; Ahmed et al., 1982; Srikanta et al., 1987, 1988; Sriroth et al., 2000). There were some other reports on this topic in the early 2000's (Wojciechowski et al., 2002; Chotineeranat et al., 2004; Kongkiattikajorn and Yoonan, 2004; Srinorakutara et al., 2004; Yoonan et al., 2004). More recent studies were reported by Kosugi et al. (2009), Rattanachomsri et al. (2009), Thongchul et al. (2010), Nair et al. (2011) and Hermiati et al. (2011, 2012). The sugars could be further used for different kinds of chemicals, such as lactic acid (John et al., 2006; Thongchul et al., 2010), fumaric acid (Carta et al., 1999), citric acid (Vandenberghe et al., 2000; Prado et al., 2005) , glutamic acid (Jyothi et al., 2005) or xanthan gum (Wojciechowski et al., 2004) through fermentation process using micro-organisms. Biotechnological potency of cassava pulp was reviewed by Pandey et al. (2000).

Cassava pulp could also be used as a medium for production of amylase enzyme (Ray, 2004; Swain and Ray, 2007), and for preparing composite materials (Matsui et al., 2004; Teixeira et al., 2009).

Potential utilization of cassava pulp for producing ethanol

One of important products that can be produced from cassava pulp is ethanol. Based on data of tapioca flour production in Table 4, it can be estimated the amount of cassava pulp produced, and thus potential ethanol produced from the pulp (Table 6). A large scale of tapioca plant having production capacity of 20 ton tapioca flour per day has a potency to produce 8.7 kL of ethanol per day. It is generally known that the economic scale of bioethanol production was at least 150,000 L ethanol per day. However, there were several types of bioethanol industry operated in Indonesia; home industry, cooperative industry, small-scale industry, and largescale industry, which produces 40 to 300 L, 400 to 1,000 L, 1,000 to 5,000 L and > 150,000 L of ethanol per day, respectively (Yudiarto, 2009, personal communication). These industries used molasses or cassava as raw materials. Only large scale industry produced 95 to 96% ethanol, and only one large industry produced 99.5% or fuel grade ethanol. The rest produced 90 to 95% ethanol. Therefore, production of ethanol from cassava pulp would be quite feasible, especially near tapioca industry.

Conversion of cassava pulp to ethanol can be accomplished through different kinds of processes, such as physical, chemical, biological process, or combinations of those processes. There were several studies concerning the utilization of the cassava pulp as a source of bioethanol through several methods of conversions. Most of studies involved acidic and enzymatic hydrolyses, solely or combined with other processes, such as hydrothermal process. Acids used mainly were inorganic acids, such as hydrochloric (Yoonan et al., 2004; Nair et al., 2011) and sulphuric acids (Srikanta et al., 1987; Yoonan et al., 2004; Srinokaruktara et al., 2006; Nair et al., 2011; Hermiati et al., 2011). The use of organic acid, that is, acetic acid or oxalic acid was also reported (Yoonan et al., 2004;

Hermiati et al., 2011), which resulted in lower yield of reducing sugars or glucose as compared to that used hydrochloric or sulphuric acids. Yoonan et al. (2004) found that sulphuric acid was the most effective for the hydrolysis, with maximum reducing sugar produced of 69.96%. Yield of ethanol from reducing sugar was 47% (theoretical yield 51%) or 0.23 g ethanol/g cassava pulp (oven dry). Hermiati et al. (2011) reported that microwave-assisted hydrolysis of cassava pulp in oxalic acid resulted in 75.69% glucose yield, while that in sulphuric acid was 80.80%.

A higher sugar yield resulted from acid hydrolysis does not always correlate with ethanol production (Thongchul et al., 2010). In their study it was found that hydrolysate obtained from a short treatment time with a strong acid at a low acid concentration could produce high glucose content and almost no inhibiting by products, in contrast with that from a longer time of acid hydrolysis, which could not support the growth of the fungus R. oryzae to ferment the hydrolysate. Therefore, the formation of inhibitors, such as furfural, during the hydrolysis of cassava pulp is an important factor to be considered as well. Furfural concentration more than 1.5 g/l can inhibit the growth of S. cerevisiae, thus, it affects ethanol production (Modig et al., 2002). The inhibitors can be removed by using activated carbon after hydrolysis is completed. However, there is a new method reported that can suppress the formation of inhibitors, while at the same time increasing the glucose yield. The method uses activated carbon during the hydrolysis of cassava pulp under microwave irradiation. The addition of 1 g of activated carbon into 1g/20 ml suspension of cassava pulp in water and heated using microwave at 210°C f or 15 min resulted in 52.27% glucose yield with only 46.25 mg/100g hydroxymethyl furfural (Hermiati et al., 2012). Unfortunately, the result of fermentation of this hydrolysate has not yet been reported.

Previous enzymatic hydrolysis of cassava pulp was reported by Sriroth et al. (2000), Kongkiattikajorn and Yoonan (2004), Srinorakutara et al. (2004, 2006). The use of α-amylase and amyloglucosidase produced hydrolysate with reducing sugar yield of 52.85% (Kongkiattajorn and Yoonan, 2004). There was still around 50% of the material unutilized, therefore, it was suggested that some other hydrolytic enzymes were needed in the process. A study by Sriroth et al. (2000) revealed that the addition of cellulase and pectinase could increase the susceptibility of cassava pulp to αamylase. Srinorakutara et al. (2004, 2006) also used cellulase and pectinase beside α-amylase and amyloglucosidase (glucoamylase), which were added step wise to the substrate. Mixture of cellulase and pectinase was added first, followed by α-amylase, and finally glucoamylase. Maximum reducing sugar obtained was 6.2% (w/v). Recent study by Rattanachomsri et al. (2009) showed that the use of multi-enzyme secreted by Aspergillus niger produced a high yield of fermentable

sugars, equivalent to 716 mg glucose and 67 mg xylose/g cassava pulp. This yield was higher than that resulted from the process that used combinations of corresponding commercial enzymes (cellulase, pectinase, beta glucosidase, hemicellulase, amyloglucosidase, and α-amylase). However, Nair et al. (2011) reported that the use of commercial enzymes that contained cellulases, xylanases and hemicellulases in the hydrolysis of hydrothermally pre-treated cassava pulp could produce high yield of glucose, up to 706 g/kg cassava pulp.

According to Thongchul et al. (2010), either acid or enzymatic hydrolysis of cassava pulp produced a high glucose concentration (>100 g/L), however, acid hydrolysis produced a higher glucose concentration (85% of theoretical yield) than did enzymatic hydrolysis (less than 40% of theoretical yield) using cellulase, α-amylase and glucoamylase. This result of enzymatic hydrolysis did not agree with the results of enzymatic hydrolysis reported by other researchers (Jaleel et al., 1988; Rattanachomsri et al., 2009; Nair et al., 2011), which showed that enzymatic hydrolysis could hydrolyze almost all starch in the cassava pulp. This result was also different from that of Srinorakutara et al. (2006) and Wojciechowski et al. (2002) who found that both acid and enzymatic hydrolyses were almost equally efficient. However, it was suggested that economically, acid hydrolysis was more beneficial than enzymatic hydrolysis (Wojciechowski et al., 2002), while Srinorakutara et al. (2006) preferred enzymatic hydrolysis to acid hydrolysis due to the unwanted browning compounds and the higher cost of acid hydrolysis.

Some other researchers reported the use of hydrothermal process (Yamaji et al., 2006, 2007), hydrothermal combined with enzymatic hydrolysis (Kosugi et al., 2009), and microwave heating with activated carbon (Hermiati et al., 2012). The latest method provides one pot reaction for hydrolysis of cassava pulp and removal of fermentation inhibitors simultaneously.

Fermentation of sugars produced from cassava pulp mostly were using yeast, especially S. cerevisiae (Yoonan et al., 2004; Kongkiattikajorn and Yoonan, 2004; Srinorakutara et al., 2004), even though there was also a study that used R. oryzae for this fermentation (Thongchul et al., 2010). Kunhi et al. (1981) reported a fermentation study of saccharified cassava pulp to ethanol using mineral salts and nitrogen enrichment during the fermentation. Jaleel et al. (1988) compared solid phase fermentation and hydrolysate fermentation of saccharified cassava pulp using yeast, and concluded that the former resulted in higher ethanol yield and productivity than did the later. Kosugi et al. (2009) also used S. cerevisiae, however, the yeast strain used was that displaying glucoamylase on its cell surface, which was constructed using a cell surface-engineering system based on agglutinin. It was reported that the use of this

strain could eliminate the use of amylolytic enzymes, and produced ethanol in 91 and 80% of theoretical yield from 5 and 10% of cassava pulp, respectively. Thermo-tolerant yeast, Candida tropicalis, was also used for the fermentation of sugars produced from hydrolysis of cassava pulp using multi-enzymes secreted by Aspergillus niger in a simultaneous saccharification and fermentation process (Rattanachomsri et al., 2009). From 4% (w/v) of cassava pulp, as much as 14.3 g/l ethanol was produced by this combined process after 30 h of fermentation.

Another important factor that should be considered in producing ethanol is initial sugar concentration in the hydrolysate that would be fermented to ethanol. According to Kunhi et al. (1981), the yield of ethanol, fermentation and plant efficiencies increased with the increase of initial sugar concentration up to 15%. Therefore, substrate concentration or solid/liquid ratio of the initial cassava pulp suspension is important. Most of the research reported used 5-10% cassava pulp suspension. In fact, in order to be able to get 15% sugar concentration, it needs at least 25% solid/liquid ratio of cassava pulp suspension. Recent study of cassava pulp hydrolysis in acid media under microwave irradiation by Hermiati et al. (2011) showed that glucose concentration increased with increased in substrate concentration, however, the glucose yield was decreased. After microwave treatment in 0.5% sulphuric acid for 10 min a total of 11% glucose in the cassava pulp hydrolysate was achieved by the use of 25% substrate concentration. An interesting technique for saccharification of cassava fibrous waste at high substrate concentration was reported by Srikanta et al. (1987) and Jaleel et al. (1988), where hydrolysis of starch present in cassava pulp was conducted in shallow layers in stainless steel trays, so that it facilitated the use of higher slurry concentrations. The method used acid, acid-enzyme, and enzyme saccharification. A complete conversion of starch to sugars was achieved by the use of 30% slurry concentration, 4% sulphuric acid, at 121 $\mathbb C$ for 30 m in (Srikanta et al., 1987). As much as 16.5% reducing sugar concentration could be produced from cassava pulp with the use of 30% slurry and combination of acid and enzymatic process (Jaleel et al., 1988). Other recent studies that used high substrate concentration in the hydrolysis of cassava pulp were not yet reported. Therefore, in order to obtain more economically feasible process, more research in higher substrate concentration of cassava pulp with the use of lower acid concentration, lower enzyme loading and shorter time is needed.

It is not easy to compare which conversion method was better or more efficient than the others, since studies conducted by researchers were varies in almost all treatments, starts from substrate concentrations, chemicals and enzyme loadings and process conditions. Further comprehensive studies, including financial analysis, are needed, so that the choice of a process is

not only based on glucose yield or glucose concentration, but also based on economic aspect consideration.

CONCLUSIONS

Cassava pulp contained carbohydrates, especially starch and cellulose, which are potential to be used for producing sugars, and further fermented to ethanol. The conversion process of cassava pulp to ethanol mostly involved chemical, enzymatic or microbial processes. Only a few used physical or mechanical process, i.e. hydrothermal process. Most studies conducted were focused on finding efficient methods to obtain as high glucose yield as possible, and only a few explored the glucose recovery from the process. The utilization of cassava pulp to produce ethanol 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. However, comprehensive studies are still needed to establish bioethanol industry from cassava pulp.

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