



## LIGNOCELLULOSIC MATERIAL FROM MAIN INDONESIAN PLANTATION COMMODITY AS THE FEEDSTOCK FOR FERMENTABLE SUGAR IN BIOFUEL PRODUCTION

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### ABSTRACT

Since the long history of Indonesia, the majority of Indonesian residence are working as farmers as the primary job. Plantation in Indonesia supplies the world market in remarkable amount. There are several main commodity holding important role in Indonesian agriculture: rice, sugarcane, coffee, cocoa, cassava, and tobacco. Those products are cultivated in a large amount almost in each district and consequently generating a large amount of agricultural waste from the post-harvesting process. The residue of those commodity were studied in this paper, including rice husks, sugarcane bagasse, spent coffee ground, cocoa pod husks, cassava peels, and tobacco stalks. They contain mostly cellulose of 29.1 - 57.4 % and hemicellulose of 7.49 - 35.5 % which are convertible to fermentable sugar. The lignin content in the range of 10.9 - 27.3 % which produces inhibitors in sugar and alcohol production. The utilization of this feedstock to produce biobutanol and bioethanol requires delignification process to prevent the inhibitor formation. Sequentially, hydrolysis is necessary to convert the cellulose and hemicellulose to fermentable sugars completely by using enzymatic or chemical process. Finally fermentation can be performed to produce bioethanol by yeast or biobutanol by *Clostridium sp.* The uniformity of the main constituent and the physical characteristic have made them potential to be efficiently utilized in heterogeneous mixture to produce large capacity of biobutanol and bioethanol.

**Keywords:** lignocellulose, sugarcane bagasse, cassava peel, rice husk, cocoa pod husk, spent coffee ground, tobacco stalks, biobutanol, bioethanol.

### INTRODUCTION

Indonesia is well known as one of the agricultural countries in the world. Since the long history of Indonesia country foundation until nowadays, the majority number of Indonesian residence are working as farmers as the main job [1, 2]. In spite of the large number of its population, Indonesia could implement self-sufficiency for the country food needs [3]. Passed by the volcano line, located in the equator with high sunlight exposure, and surrounded by the ocean with high rainfall, Indonesia became highly productive area for farming and plantation [4].

Plantation in Indonesia supplies the world market in remarkable amount [5]. This country has a climate which supports the growth of diverse types of plant [6]. Beside consumed for the national demand, product commodity from plantation also contributes significantly for country revenue by the export [7]. There are several main commodity holding important role in Indonesian agriculture: rice [7, 8], sugarcane [9], coffee [10], cocoa [11], cassava [7], and tobacco [12]. Those products are cultivated in a large amount almost in each district and consequently generating large amount of agricultural waste from the post-harvesting process [13, 14].

Meanwhile the energy demand around the world is increasing due to the population growth and the development of technology. Transportation as one of the largest fuel consuming activity has a specific requirement for the engine to work and well maintained [14]. Gasoline is used commonly for the vehicle with moderate size, mostly used for living needs. As the petroleum resources

are depleting, biobased renewable resources is getting attention to compensate the limited availability of gasoline [15]. Bioethanol has been used as the mixture with gasoline [15, 16, 17, 18] and biobutanol is known to be the compatible substitute for gasoline [19, 20, 21].

The waste from the main plantation commodity mentioned above can be utilized for the more valuable product. They contain mostly fibre and lignin with some other active compound or having active structure. The main constituent, fibre, is potential feedstock for the fermentable sugar to be converted to bioethanol or biobutanol [22, 23, 24, 25]. These lignocellulosic resources are abundantly available and still not optimally utilized yet [13, 14]. In order to establish an effective and efficient technology to produce fermentable sugar for bioenergy production, the availability and properties of the material need to be studied.

This paper discusses about the availability, production, properties, and application of rice husk, sugarcane bagasse, spent coffee powder, cocoa pod husk, cassava peel, and tobacco stalk as the feedstock for fermentable sugar in bioethanol and biobutanol production.

### MATERIALS AND METHODS

#### Sample preparation

The samples characterized in this experiment were rice husk, sugarcane bagasse, spent coffee powder, cocoa pod husk, cassava peel, and tobacco stalk collected from the plantation area in Jember District, East Java



Province, Indonesia. Five kilograms of raw materials were washed with water to clean up the soil, dust, and other impurities. They were cut into small pieces with the size of 1 - 2 cm. Moisture content was reduced to approximately 10% by sun drying for 3 days. Dried samples were grinded to the powder and filtered with the size of 40 mesh.

**Carbohydrate and lignin analyses**

Three hundred milligrams samples were added with 3 mL of 72% sulphuric acid in the pressure tubes and stirred until thoroughly mixed. The tubes were placed in the water bath 30 °C for 60 minutes and stirred every 10 minutes. After 60 minutes hydrolysis, 84 ml water was added into each tube to dilute sulphuric acid to 4%. Then the mixtures were filtrated. The filtrate were measured using UV-Vis spectrophotometer with the wavelength of 240 nm for lignin content analysis. Carbohydrate was analysed using High Pressure Liquid Chromatography (HPLC) with refractive index detector. HPLC was operated at 80 °C, 0.6 mL/minute flow for 35 minutes. Lignin content was calculated by the following equation:

$$\%Lignin = \frac{Abs \times V_f \times d}{\epsilon \times m \times L} \times 100\%$$

Where *Abs* is UV absorption, *V<sub>f</sub>* is filtrate volume in mL, *d* is dilution, *ε* absorptivity of the biomass in

*L/g.cm*, *m* is sample in mg, and *L* is pathlength of the UV-vis in cm.

Carbohydrate content was calculated by the following equation.

$$C_{anhydro} = C_{HPLC} \times Corr$$

Where *C<sub>anhydro</sub>* is concentration of polymerized sugar in g/L, *C<sub>HPLC</sub>* is sugar concentration from HPLC measurement in g/L, *Corr* is correction factor 0.88 for C-5 sugars (xylose and arabinose) and 0.90 for C-6 sugars (glucose, galactose, and mannose) [26].

**RESULTS AND DISCUSSIONS**

**Land availability and distribution**

Agricultural land availability for rice cultivation in Indonesia was increasing up to 14,116,000 ha in 2015 (Table-1). Rice as the main staple food of Indonesian, the distribution was spread in the location with high population. The distribution of the land was mainly in Java Island with 44.7% of Indonesian total rice cultivation area. The largest area of rice field was located in West Java, East Java, and Central Java with 14.5%, 14.4%, and 12.1% percentage of Indonesian field in 2015 respectively [7].

**Table-1.** Plantation area in Indonesia during 2012 – 2017 [7, 9-12].

Product	Cultivated area (1000 hectares)					
	Period					
	2012	2013	2014	2015	2016	2017
Cocoa	1,774	1,740	1,727	1,709	1,720	1,730
Cassava	1,129	1,065	1,003	949	NA	NA
Coffee	1,235	1,241	1,230	1,230	1,246	1,253
Rice	13,445	13,835	13,797	14,116	NA	NA
Sugarcane	442	470	477	454	458	426
Tobacco	270	192	209	209	156	185

Cocoa plantation in Indonesia was slightly decreasing until 2015 and increasing again in 2016. The majority of cocoa plantation area was cultivated by the residents with 96.0% of the area was public plantation in 2017. Plantation area was centralized in Sulawesi with 56.8% of Indonesian plantation. It was distributed in several provinces in Sulawesi with the largest area 16.8% in Central Sulawesi, 14.5% in South Sulawesi, and 15.0% in Southeast Sulawesi [11].

Indonesian coffee plantation area was also slightly decreasing until 2014 and increasing in 2016. Largest area of coffee plantation was in Sumatera Island with 63.6% of Indonesian plantation in 2017. South Sumatera was the area with the largest area of 21.1%, followed by Lampung with 12.9% and Aceh with 9.90%.

95.5% plantation area was owned and cultivated by public residents [10].

Cassava as the alternative staple food of Indonesian is being used for various purposes. The cultivation area was located mainly in Java with 46.6% of Indonesian cassava plantation. The province with the largest cultivation area was Lampung with 29.4%, Central Java with 15.9%, and East Java with 15.5% of total cassava plantation area [7].

The sugarcane plantation area in Indonesia was mostly located in Java with 62.5% of total plantation. 54.2% of the sugarcane plantation was the public plantation area. The largest sugarcane plantation was located in East Java, Lampung, and Central Java with the area percentage of 48.7%, 27.6%, and 8.86% respectively.



East Java was the centre of sugarcane plantation in Indonesia [9].

Tobacco plantation area was the smallest among those commodities. Tobacco plantation was centralized in Java with 82.6% of total plantation. East Java was the province with largest plantation area of 51.9%, followed by 25.2% in Central Java, and 11.4% in East Nusa Tenggara [12].

The plantation area of cocoa, cassava, and sugarcane was decreasing until 2015. However, observing this reduction, Indonesian government implemented the improvement for agricultural development. Indonesian government provided facility and infrastructure for agriculture so that the unplanted area could be grown again and even increased. Besides, the fertilizer crisis happened on this period was also controlled by government, supporting the farmer to activate the land [27].

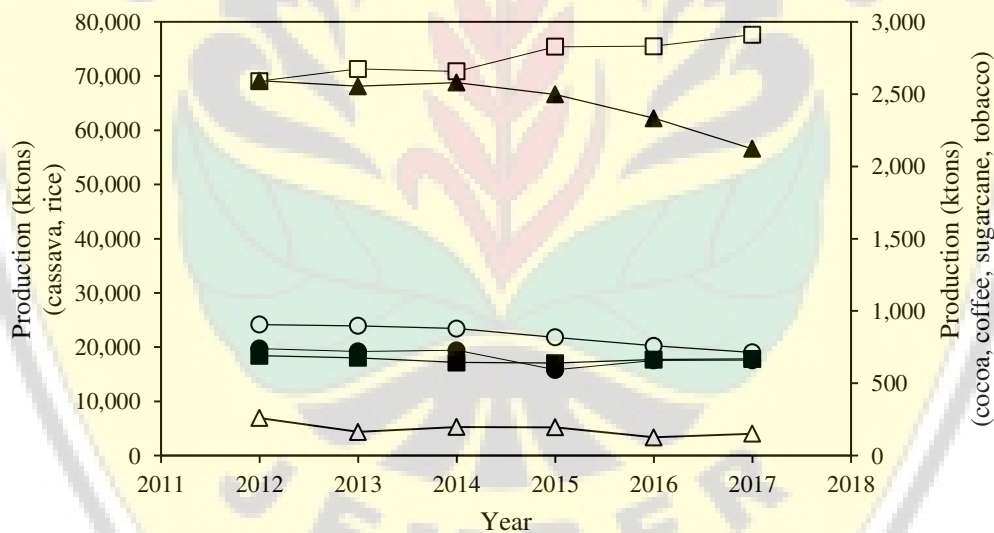
According to this data, East Java was the centre of agricultural land in Indonesia with the largest cultivation area of rice, the most planted commodity in Indonesia. Besides, East Java was also one of the provinces with largest cultivation area for other

commodities. Most of the cultivated area was public plantation which was managed by residents.

### Agricultural production

Indonesian agricultural product contributed 13.1% of gross domestic product in 2017. Most of the products are used for domestic consumption. Moreover the export of agricultural product in 2016 reached 5.4 billion rupiahs; it was increasing 23.5% in 2017. Agriculture has become the important sector to maintain food security, personal revenue, and national income [11, 28].

Figure-1 shows the agricultural production of rice, cassava, cocoa, coffee, sugarcane, and tobacco. Production of cocoa, coffee, and tobacco was relatively stable during 2012 - 2017. Rice production was increasing significantly from 69,056 kton in 2012 to 77,603 kton in 2017 [7]. While sugarcane production was decreased from 2,592 kton in 2012 to 2,121 kton in 2017 [9] and cassava was also decreased from 24,177 kton in 2012 to 19,045 kton in 2017 as the consequence of the decreasing plantation area [7].



**Figure-1.** Agricultural production of cocoa (closed circle), cassava (opened circle), coffee (closed square), rice (opened square), sugarcane (closed triangle), and tobacco (opened triangle)

The contribution of these commodities in the export sector was increasing. The unhulled rice export was increasing 5 times fold from 59 tons in 2015 to 291 tons in 2016. Cassava export was decreased 23.6% from 1226 tons in 2015 to 937 tons in 2016 [7]. Sugar export was also growing from 1,256 tons in 2016 to 2,032 tons in 2017 [9]. Coffee was exported 414,650 tons in 2016 and it increased to 467,800 tons in 2017 [10]. While cocoa export increased from 336,000 tons in 2016 to 354,880 tons in 2017 [11].

The agricultural activity is becoming more advantageous with the support from government. The growing investment for innovation and technology in

agriculture has helped the farmer to enhance the productivity of their plantation. Moreover, the better management for quality controlling has made a significant impact so more farmers could produce the commodities qualified by the export standard [28]. Except for the sugarcane, where the growing cost was high, so that the imported one was more beneficial than growing domestically, other commodities are produced in the stable amount and especially for rice the production volume was enhancing. This will provide the sustainable amount of agricultural product during the long period for the lignocellulosic biomass feedstock [27].





Larger generation of agricultural products remain the large amount of agricultural waste. Sugarcane bagasse is generated 28% of overall sugarcane product [29], cassava peel exists up to 12% of the cassava root weight [30], tobacco stalks is produced approximately 5 ton / ha [31], rice product consists of 20% weight of rice husk [32], cocoa pod husk is 70% of the cocoa fruit [33], and coffee ground is assumed to have the same weight with the coffee bean product. Estimating the waste generation from this product in Indonesia it was obtained the number shown in Table-2. Huge amount of biomass is generated from this agricultural product up to total of 20, 459 ktons per year.

### Lignocellulosic biomass composition

Rice husks, cassava peel, cocoa pod husk, sugarcane bagasse, spent coffee powder, and tobacco stalks were studied in this research to understand the composition as the lignocellulosic feedstock. All of the samples were prepared as powder from the dried raw material. The chemical compositions of the main constituent of these materials are shown in Table-3.

Lignin is undesirable component in the biomass due to its degradation during hydrolysis process to inhibitor compounds. Furfural, hydroxyl methyl furfural (HMF), and formic acid is the main inhibitor compound formed from lignin decomposition [39, 40]. Cellulose is the polymer sugar consists of hexose as monomer sugars and hemicellulose consists of pentose sugars. Both of them are fermentable sugars for many types of alcohol producer strain. Lignin, cellulose, and hemicellulose are the main constituent in the lignocellulosic biomass.

Cellulose content was the largest component in tobacco stalks with composition of 48.62%. Lignin existed in a higher composition of 26.24% than hemicellulose of 7.49%. Another active compound from tobacco stalk is nicotine which may be utilized for insecticide. However, it demonstrated low antimicrobial activity that reduces the risk of being inhibitor during fermentation [41].

The main constituent of cocoa pod husk was cellulose with the composition of 29.93%. Hemicellulose content was 10.94% and the lignin content was 11.64%. Pectin is the other extractable component from cocoa pod husk which is an important material for food and medical product [42].

**Table-2.** Estimated lignocellulosic biomass generation in Indonesia 2017.

Product	Waste	Waste part of the product	Estimated waste generation <sup>a</sup>
Cacao	Cocoa pod husk	70% (33)	462
Cassava	Cassava peel	12% (30)	2,285
Coffee	Spent coffee ground	100%	669
Rice	Rice husk	20% (32)	15,521
Sugarcane	Sugarcane bagasse	28% (29)	594
Tobacco	Tobacco stalks	5 ton/ha (31)	929

<sup>a</sup> Estimated waste generation in kilotons

Sugarcane bagasse contained the highest composition of cellulose 57.38% and also of hemicellulose 34.52%. Lignin was contained 23.05% in sugarcane bagasse. Sugarcane bagasse stored the largest amount of carbohydrate as the feedstock for fermentable sugar.

Rice husk as the feedstock with the highest production amount is the most determining material among these products. The cellulose is the highest content in rice husk up to 34.52% followed by 25.68% lignin and 21.79% hemicellulose. High silica content is also detected

in rice husk which can be used as adsorbent, catalyst, glass, etc [43]. Currently rice husk is used as the planting media for home application.

Cellulose and hemicellulose content of cassava peel were 29.08% and 19.24% respectively. The lignin content in cassava peel was the lowest among these materials of 10.94%. Cassava peel, despite its hydrocyanic content, has been used for alternative food and cattle feed [44].



**Table-3.** Composition of main constituent in the materials.

Sample	Hemicellulose content <sup>a</sup> (%)	Cellulose content <sup>a</sup> (%)	Lignin content <sup>a</sup> (%)	Ash content <sup>b</sup> (%)	Bounded carbon <sup>b</sup> (%)	Density (g/L)
Tobacco stalk	7.49	48.62	26.24	67.86	24.04	0.220 [34]
Cocoa pod husk	10.94	29.93	11.64	27.59	48.49	
Sugarcane bagasse	35.52	57.38	23.05	17.92	67.29	0.625 [35]
Rice husk	21.79	34.52	25.68	49.71	41.90	0.480 [36]
Cassava peel	19.24	29.08	10.94	24.88	64.64	0.553 [37]
Spent coffee powder	27.34	46.40	27.34	1.935	17.64	0.524 [38]

<sup>a</sup> measured in dry matter basis.

<sup>b</sup> measured in carbonized matter basis.

Spent coffee powder conserved high carbohydrate content even after roasting and brewing. The cellulose and hemicellulose content were 46.40% and 27.34%. The lignin content was 27.34%. Spent coffee powder could be extracted for antioxidant compounds mainly caffeinic acid, ferullic acid, and chlorogenic acid [38].

These six materials have the similar constituents of cellulose as the main compound followed by lignin and hemicellulose. This similar characteristic made them possible to be used as heterogeneous mixture with similar handling. Lignin in the high composition requires pretreatment as an effort to improve fermentation effectivity. The density of these lignocellulosic materials are similar under 0.7 g/L indicating that this material would float on the solution. For this type of materials high

speed of agitation is necessary to be well mixed with the solution.

#### Utilization of lignocellulosic feedstock for fermentable sugar

High carbohydrate content of the lignocellulosic biomass is the promising potential to produce fermentable sugar. Biobutanol and bioethanol as the substitute of gasoline are focussed in this discussion. Several applications of single biomass have been reported by previous researchers. The main process for lignocellulosic materials to produce biobutanol and bioethanol are delignification, hydrolysis, and fermentation. Bioethanol production is summarized in Table-4 and bioethanol production is summarized in Table-5.

**Table-4.** Bioethanol production from lignocellulosic biomass.

Material	Delignification Reagent	Hydrolysis Reagent	Fermentation					Ref.
			Strain	Medium	Method	$C_E^a$	$Y_E^b$	
Sugarcane bagasse	HCl	HCl and ion exchange	<i>Candida shehatae</i> NCIM 3501	Yeast extract	Batch	8.67	0.419	46
Sugarcane bagasse	Steam and liquid hot water	Cellulase and $\beta$ -glucosidase	<i>Saccharomyces cerevisiae</i>	Yeast extract-peptone	SSF	7.84	0.690	47
Cassava peel	Steam	Cellulase	Ethanol tolerant <i>Bacillus cereus</i>	Yeast extract	batch	7.50	-	48
Cassava peel	H <sub>2</sub> SO <sub>4</sub>	Cellulase, xylanase, pectinase	<i>S. diastaticus</i> 2047 and <i>Candida tropicalis</i> 5045	Yeast extract	SSF	7.10	0.418	49
Cassava peel	-	Simultaneous saccharification and fermentation (SSF)	<i>Rhizopus nigricans</i> , <i>Spirogyra africana</i> , and <i>S. cerevisiae</i>	Hydrolysate	SSF	14.5	0.410	50
Cassava peel	HCl	<i>Glocophylum seplarium</i> and <i>Pleurotus ostreatus</i>	<i>S. cerevisiae</i> and <i>Zymomonas mMU</i>	Hydrolysate	Batch	12.5	0.220	51
Cassava peel	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	<i>S. cerevisiae</i>	Yeast extract	Batch	35.8	0.410	25
Cassava peel	NaOH	$\alpha$ -amylase	<i>S. cerevisiae</i>	Yeast extract	SSF with biogas endeavour system	27.0	0.486	52
Cassava stem and peel	Liquid hot water	<i>Rhizopus sp.</i>	<i>S. cerevisiae</i>	Yeast extract	SSF	5.03	0.132	53
Rice husk	NaOH and NaClO <sub>3</sub>	<i>Trichoderma reesei</i>	<i>S. cerevisiae</i>	Yeast extract	Batch	3.25	0.250	54
Rice husk	<i>Pleurotus ostreatus</i> and <i>Aspergillus niger</i>		<i>S. cerevisiae</i>	Nutrient broth	Batch	4.81	0.180	55
Rice husk	H <sub>2</sub> SO <sub>4</sub>	Cellulase, endoglucanase, cellobiase	<i>S. cerevisiae</i>	Mineral nutrient	Batch	4.42	0.110	56
Spent Coffee	H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> SO <sub>4</sub>	<i>S. cerevisiae</i>	Yeast extract	Batch	15.0	0.080	57
Spent coffee ground	H <sub>2</sub> SO <sub>4</sub>	Cellulase and glucosidase	<i>S. cerevisiae</i>	Yeast extract	Batch	25.0	0.430	58
Tobacco stalks	H <sub>2</sub> SO <sub>4</sub>	Cellulase and glucosidase	<i>S. cerevisiae</i>	Yeast extract	Batch	4.90	0.255	59

<sup>a</sup> ethanol concentration in the fermentation media in g/L.<sup>b</sup> ethanol yield per biomass dry weight in g/g.

Sugarcane bagasse has been used for bioethanol and biobutanol production. Ethanol concentration of 8.67 g/L was produced using acid delignification with hydrochloric acid. Ion exchange was used to remove the small amount of inhibitors which is formed during hydrolysis [46]. Higher yield of ethanol was obtained at 0.690 using dual steam and hot water delignification

process. Saccharification and fermentation were performed simultaneously (SSF) using cellulase and  $\beta$ -glucosidase enzyme combination with *S. cerevisiae* in the yeast extract - peptone combination media. The hydrolysis and fermentation were optimized using these combinations [47].



Su *et al.* [60] attempted the sequential delignification using hot water, microwave, and fermentation using *Aspergillus niger* ATCC 1015, *Trichoderma reesei* ATCC 26021, and *Penicillium janthinellum* ATCC 44570. SSF was then performed using cellulase and xylosidase enzyme with *C. beijerinckii* NCIMB 8052. However, only 6.86 g/L butanol was obtained with the yield of 0.12 g/g. Even though the

inhibitor was not formed in detectable amount, the fermentation without nitrogen sources caused the low growth of bacteria and butanol production [60]. Butanol could be produced using *C. acetobutylicum* XY 17 immobilized on sugarcane bagasse in yeast extract - peptone - starch media without delignification and hydrolysis process. Remarkable concentration of butanol was obtained at 13.1 g/L with the yield of 0.16 g/g [62].

**Table-5.** Biobutanol production from lignocellulosic biomass.

Material	Delignification Reagent	Hydrolysis Reagent	Fermentation					Ref.
			Strain	Medium	Method	$C_B^a$	$Y_B^b$	
Sugarcane bagasse	Liquid hot water, microwave, <i>Aspergillus niger</i> ATCC 1015, <i>T. reesei</i> ATCC 26021, and <i>P. janthinellum</i> ATCC 44570	Cellulase and xylosidase	<i>C. beijerinckii</i> NCIMB 8052	Hydrolysate and P2 trace element	SSF	6.86	0.116	60
Sugarcane bagasse	NaOH	Gamma valero lactone	<i>C. acetobutylicum</i> XY16	Yeast extract-peptone-starch	Batch	14.3	0.203	61
Sugarcane bagasse	-	-	<i>C. acetobutylicum</i> XY17	Yeast extract-peptone-starch	Immobilized cells in bagasse	13.1	0.164	62
Tobacco stalks	Oxygen and steam	Cellulase and $\beta$ -glucosidase	<i>S. cerevisiae</i> and <i>C. butyricum</i>	Hydrolysate	Batch	8.0 (BuOH)	0.224	63
						12.9 (EtOH)	0.099	

<sup>a</sup> butanol concentration in the fermentation media in g/L.

<sup>b</sup> butanol yield per biomass dry weight in g/g.

Cassava peel has been widely studied for bioethanol production. Cassava peel contains relatively low lignin content of 10.94%. The highest ethanol concentration of 35.8 g/L was produced using sulphuric acid delignification and hydrolysis continued by batch fermentation using *S. cerevisiae*. The yield based on dry biomass weight was 0.410. High monomeric sugar concentration produced from severe sulphuric acid hydrolysis optimized the substrate availability for fermentation [25]. Simultaneous ethanol fermentation with biogas recovery improved ethanol fermentation up to 27%. Alkaline pretreatment with NaOH was studied, continued with SSF using  $\alpha$ -amylase to hydrolyze the starch and *S. cerevisiae* as ethanol producer. The biogas endeavour system had increased the fuel energy production up to 1.3 fold by the combination of ethanol and methane production [52].

Bioethanol production from rice husk was conducted by several researchers using alkaline, acid, and fungal pretreatment [54, 55, 56]. The lignin content of rice husk was quite high 25.68% caused low ethanol concentration in product. Interestingly, fungal pretreatment using *P. ostreatus* and *A. niger* succeeded to

reduce inhibitor formation and convert cellulose and hemicellulose with the ethanol yield of 0.180 g/g dry rice husk [55]. Fermentation with only hydrolysate with only mineral trace elements produced ethanol concentration 4.42 g/L, similar to the concentration using nutrient broth and yeast extract of 4.81 g/L and 3.25 g/L respectively [54, 56].

Spent coffee ground contains high cellulose content up to 46.40% and hemicellulose content up to 27.34%. 25 g/L ethanol was produced using cellulase and glucosidase. Fermentable sugar from coffee ground contains high amount of glucose yielding high ethanol yield up to 0.480 g/g spent coffee ground.

Tobacco stalks pretreated with sulphuric acid and hydrolysed by cellulase and glucosidase enzyme produced 4.9 g/L ethanol [59]. Pretreatment using oxygen and steam increased the ethanol concentration up to 12.9 g/L [63]. This was attributed to the formation of organic acid from lignin conversion by the additional oxygen preventing the furfural and HMF formation. This research was conducted using co-culture of *S. cerevisiae* and *C. butyricum* succeeded to produce butanol simultaneously of 8 g/L.





The most widely used delignification method was acid pretreatment. The addition of acid eased the sequential process with enzymatic hydrolysis which required acidic condition. Steam and liquid hot water methods were the second most used method. Although it is operated in severe condition, the minimization of chemical usage has been preferred for the more economical operation. Pretreatment with base has similar effectivity with acid pretreatment, but due to the high pH which needs more acid for the enzymatic hydrolysis, base pretreatment was not preferable. Fungal pretreatment has become an alternative for delignification with lower energy requirement, operated near ambient temperature. Simultaneously delignifying and hydrolysing fungus such as *P. ostreatus*, *A. niger*, *T. reesei* and *P. janthinellum* were effective to improve the fermentability of hydrolysate although they take longer time than high temperature pretreatment.

Enzymatic hydrolysis was commonly used to optimize the carbohydrate hydrolysis after delignification process. During delignification process, most part of the hemicellulose was degraded to pentose while cellulose was still remained. Cellulase was used to degrade the carbohydrate polymer and  $\beta$ -glucosidase to degrade the oligomer. In order to reduce carbon catabolite repression (CCR) in the hexose and pentose mixture, low enzyme dosage was used to produce cellobiose rather than glucose [23]. Cellobiose and pentose mixture could reduce CCR so the consumption of the substrate was optimized [64].

Fermentation for ethanol and butanol production had been investigated for many kinds of lignocellulosic feedstock. Inhibitors formed from lignin degradation may cause longer lag phase before strain growth. The inhibitors disturbed the stability of membrane formation in bacteria. Therefore, delignification process is necessary. Fermentation using lignocellulosic is also possible without delignification and hydrolysis. *C. acetobutylicum* XY17 had the ability to ferment various carbohydrate including cellulose and starch.

In Indonesia, bioethanol had been mixed with gasoline up to 15%. There are bioethanol manufacturers in Indonesia using sugar and molasses as the feedstock [65]. Lignocellulosic material as the abundant waste from agriculture with low cost is a large potential for bioethanol and biobutanol production. Similar process sequence for bioethanol or biobutanol production from delignification, hydrolysis, and fermentation for the sugarcane bagasse, rice husk, cassava peel, spent coffee powder, tobacco stalks, and cocoa pod husk is possible to be applied in the heterogeneous mixture of those materials. The optimum process still needs further study to meet the economical feasibility.

## CONCLUSIONS

Indonesia has a high potential for lignocellulosic material production. Large land availability and the increasing agricultural production generates a large amount of the lignocellulosic feedstock for fermentable sugar. Sugarcane bagasse, rice husk, cassava peel, spent coffee powder, tobacco stalks, and cocoa pod husk have

the uniform composition with cellulose, hemicellulose, and lignin as the main constituent. Delignification and hydrolysis process are necessary before fermentation for those materials. It is possible to utilize them effectively as heterogeneous mixture to produce biobutanol or bioethanol. Further investigation is needed to optimize the production process.

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