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REVIEW ARTICLE

Bioethanol Production from Rice Straw through Utilization of Agrobiomass Waste in Central Java Towards Clean Energy: a Review

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Abstract

Bioethanol is an alternative energy to replace fossil fuels from plants. Central Java is the second largest rice producer in the world in Indonesia, with the potential of rice straw waste which can be optimized into bioethanol. Rice straw contains abundant cellulose reaching 32-47%, hemicellulose reaching 19-27%, and lignin reaching 5-24%. Methods for making bioethanol from rice straw include pretreatment, hydrolysis, fermentation, and distillation. Lignin inhibits acid penetration before hydrolysis and microbial growth during fermentation, so it needs to be eliminated using alkaline pretreatment. Glucose production from alkali-pretreated rice straw can be hydrolyzed using chemical or enzymatic catalysts. Acid hydrolysis method using dilute H_2SO_4 with consideration of a shorter operating time. In addition, the price of enzymes is very high, and the operating time is very long, which will reduce product effectiveness. The acid hydrolysis method using 2% H_2SO_4 takes 30 minutes at 150 °C, which can produce a yield of 16%. Production of bioethanol from rice straw using separate hydrolysis and fermentation (SHF) methods. Saccharomyces cerevisiae, with a 24-hour fermentation time, produced a yield of 80.9% and a productivity of 0.172 g/L h. Distillation is used to remove impurities from liquids that have been polluted with rice straw-derived solutes with various boiling points. Vacuum distillation can produce a yield of 40% purity. Utilization of rice straw into bioethanol can reduce environmental pollution so that it supports clean energy.

Keywords: Bioethanol, rice straw, Central Java, clean energy

1. Introduction

Fossil fuels are non-renewable energy sources with complex problems, especially fuel oil prices, which have increased globally due to the energy crisis [1]. This phenomenon is caused by fossil reserves depleting with increasing age of exploitation, increasing market demand, restrictions on a production scale, and regulations regarding policies to reduce global air pollution levels [2]. This problem can be overcome by using alternative fuels as renewable energy sources that are more environmentally friendly, such as bioethanol [3]. Bioethanol is an alternative energy substitute for fossil fuels from plants containing starch and lignocellulosic plants [4]. The advantage of bioethanol compared to fossil fuels is the high oxygen content of bioethanol (35%), resulting in a clean fuel. The net result is environmentally friendly because carbon monoxide gas emissions are 19-25% lower than the oxygen content of fossil fuels, making it cleaner and more environmentally friendly [5].

Bioethanol source plants are divided into three groups, such as (1) starch-containing plants (such as cassava, oil palm, tengkawang, coconut, kapok, jatropha curcas, rambutan, soursop, malapari, and nyamplung); (2) sugar (such as molasses or molasses, palm sap, sugarcane sap, and sweet sorghum sap), and (3) cellulose fibers (such as sorghum stalks, banana stalks, straw, and wood) [6]. The most significant agro-biomass production was produced by rice straw (85.81%), followed by corn straw (5.84%), peanut straw (2.84%), soybean straw (2.54%), cassava shoots (2, 29%), and sweet potato straw (0.68%) [7], and gembili (21.44%) [8]. Central Java is Indonesia's second-largest rice producer, producing 9.36 million tons of dry-milled grain (GKG) with a land area of 1.69 million hectares [9]. Djoefrie and Dewi (2014) state that the rice harvest produces 55.6% straw and 44.4% grain, so the total straw waste in Central Java in 2022 will reach 5.2 million tonnes [10].

Central Java is located at $5^0$40'–$8^0$30' south latitude and $108^0$30'–$111^0$30' east longitude, with the sun shining all year round making this area's soil fertile and abundant natural resources. The average humidity in this area is relatively high, ranging from 69-83%, making it suitable for agricultural cultivation, such as pulses and paddy [11]. Regions with the highest paddy productivity in Central Java in 2022 are presented in Fig 1.

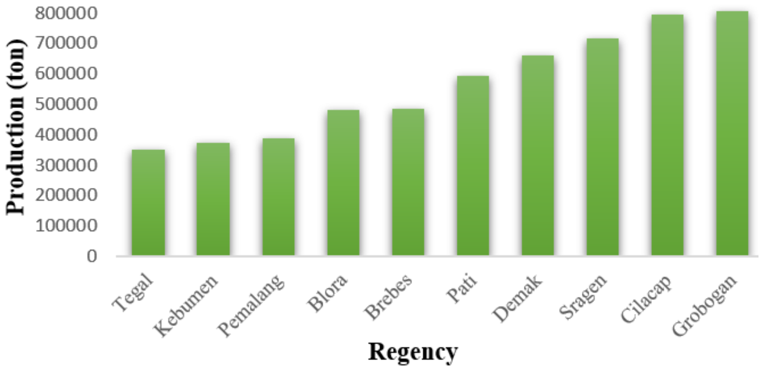

Figure 1. The Ten Largest Paddy Production in Central Java [12].

2. Selection of Raw Materials: Availability, Quantity of Production, and Continuity

Rice straw has several nutritional contents that can be processed into bioethanol, as shown in Table 1.

Table 1. Nutritional Label of Rice Straw [13]

Nutrition	Concentration (%)
Cellulose	32-47%
Hemicelluloses	19-27%
Lignin	5-24%
Ashes	18.8%
Glucose	41-43.4%
Xylose	14.8-20.2%
Arabinose	2.7-4.5%
Mannose 1.8%	1.8%

Rice straw contains abundant cellulose reaching 32-47%, hemicelluloses reaching 19-27%, and lignin reaching 5-24%, which can be optimized into bioethanol. Unfortunately, this abundant potential is not optimized correctly. Few people have used rice straws for animal feed, fertilizer, and industrial needs [14]. However, most farmers only burn straw in post-harvest fields without further processing [15]. It is dangerous because it can cause air pollution, soil pollution, respiratory infections, and global warming [16]. At the same time, rice straw contains cellulose which can be converted into environmentally friendly bioethanol [17], [18]. However, rice straw still contains 32-47% cellulose and 5-24% lignin, which is difficult to degrade and can interfere with the fermentation process into bioethanol. One way to overcome this is to do pretreatment of raw materials.

3. Production Process

3.1 Pretreatment Process

In the fermentation process, the cellulose content in rice straw is relatively high, 26.87%, and the lignin content in rice straw is 10.81% [19]. The first stage to produce bioethanol from straw is pretreatment, a process before the substrate can be fermented [20]. The pretreatment process to obtain pure bioethanol from rice straw uses fermentation and hydrolysis [21]. Lignin is present in rice straw and cellulose and can inhibit acid penetration before hydrolysis and microbial growth during fermentation. Therefore, lignin elimination is necessary [22]. The alkaline pretreatment method is aimed at increasing the digestibility of lignocellulosic biomass which can cause swelling of the biomass and increase of internal surface area, disruption of lignin structure, and decrease of crystallinity so that this method is better than acid/oxidative catalysts for breaking ester bonds between lignin, hemicellulose, and cellulose [23].

Rice straw comprises cellulose, hemicellulose, and lignin, which are connected by complex bonds and require a pretreatment process [24]. Hemicellulose and cellulose are rich in sugars that can be fermented into biofuels, but the presence of lignin, which does not contain sugar, can be a barrier that needs to be separated through delignification [25]. Delignification uses alkaline compounds, where alkaline compounds can disrupt the ether bonds in lignin. It will affect the separation of the lignin matrix and polysaccharides [26]. After pretreatment, monosaccharide sugars will be formed from hydrolysis, which will then be converted into ethanol through fermentation with the help of the yeast [27].

3.2 Hydrolysis Process

Hydrolysis will occur in an acidic condition that randomly cuts the bonds [28]. Hydrolysis with strong acids can potentially reduce yeast performance because the pH is too low. Acid is a commonly used catalyst in the hydrolysis process of lignocellulosic biomass. Acid hydrolysis randomly breaks the substance bonds [28]. This method is often chosen due to its affordability and effectiveness in cellulose conversion [26]. However, hydrolysis under acidic conditions can generate toxic substances.

Additionally, some polysaccharides are sensitive to high process temperatures, requiring careful monitoring [29]. Another commonly used catalyst in hydrolysis is enzymes, which have lower utility requirements and do not produce toxic substances [30]. However, enzymes are relatively expensive [31]. The hydrolysis method discussed in this review is the Separate Hydrolysis and Fermentation method, where hydrolysis and fermentation are conducted sequentially and separately [27]. These are some previous studies regarding glucose production from alkali pretreated rice straw by hydrolysis using enzyme catalysts shown in Table 2 and chemical catalysts in Table 3.

Table 2. Glucose Production from Alkali Pretreated Rice Straw
by Hydrolysis using Enzyme Catalyst

No	**Enzyme Type**	**Concentration** (v/v)	**Condition**	**Yield (%)**	**Reference**
1	*Aspergillus niger* and *Trichoderma reesei*	Ratio 1:1	48 hour and 50°C	35	[32]
2	*Aspergillus niger* and *Trichoderma reesei*	Ratio 1:2	64 hour and 50°C	39	[32]

No	Enzyme Type	Concentration (v/v)	Condition	Yield (%)	Reference
3	*Aspergillus niger* and *Trichoderma reesei*	Ratio 1:3	64 hour and 50°C	53	[32]
4	*Aspergillus niger* and *Trichoderma reesei*	Ratio 2:1	64 hour and 50°C	30	[32]

Table 3. Glucose Production from Alkali Pretreated Rice Straw by Hydrolysis Using Chemical Catalyst

No	Chemical	Concentration (%)	Condition	Yield (%)	Reference
1	$H_2SO_4 + sCO_2$	1	160 ºC, 40 min	36,6	[33]
2	Carbon acid	0.05	200 ºC, 60 min	19,4	[34]
3	HCl	0.015	200 ºC, 60 min	19	[34]
4	H_2SO_4	2	150 ºC, 30 min	16	[35]

Based on data analysis from previous studies, it was found that the most effective method used is the acid hydrolysis method using dilute H_2SO_4 with consideration of a shorter operating time. In addition, the very high price of enzymes and very long operating times will reduce production effectiveness [36].

3.3 Fermentation Process

Fermentation is the primary bioethanol production process with the help of microorganisms such as yeast [37]. The fermentation process for ethanol production derived from lignocellulosic biomass can be categorized into two primary processes: separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF)[1]. Bioethanol production from rice straw uses the separate hydrolysis and fermentation (SHF) method. In the SHF method of bioethanol production, the hydrolysis and fermentation processes are performed in different reactors [38]. The advantages of SHF are that it creates ideal conditions for hydrolysis and fermentation by utilizing separate tanks, reduces the need for expensive chemicals, shortens residence time, and simplifies equipment requirements [39]. Therefore, the process is carried out using the Separate Hydrolysis and Fermentation method, in which enzymatic hydrolysis and fermentation are carried out separately sequentially [40]. The previous studies on bioethanol production from rice straw using the Separate Hydrolysis and Fermentation (SHF) method in the last ten years, shown in Table 4.

Table 4. Production of Ethanol from Rice Straw Using the SHF Method

No	Microbial Strain	Time Fermentation (hour)	Yield (%)	Productivity (g/L h)	Reference
1	*Saccharomyces cerevisiae*	24	80.9	0.172	[41]
2	*Saccharomyces cerevisiae*	120	67.88	11.54	[42]
3	*Saccharomyces cerevisiae*	72	27.40	0.21125	[43]
4	*Saccharomyces cerevisiae*	29	73.5	1.17	[44]
5	*Saccharomyces cerevisiae NGY10*	24	49.7	2.073	[45]
6	*Saccharomyces cerevisiae*	32	5.1	0.1593	[46]
7	*Saccharomyces cerevisiae*	96	5.5	0.23541	[47]

No	Microbial Strain	Time Fermentation (hour)	Yield (%)	Productivity (g/L h)	Reference
8	*Mucor indicus, Rhizopus oryzae, Saccharomyces cerevisiae*	48	44	0.13	[48]
9	*K. marxianus*	24	23	1.4	[49]
10	*K. marxianus*	24	19	1.15	[49]
11	*K. marxianus NCIM 3465*	24	48	1.757	[45]
12	*C. glabrata NGY7*	24	48	1.992	[45]
13	*P. kudriavzevii NGY20*	24	47	1.81	[45]
14	*C. tropicalis NGY19*	24	43	1.81	[45]
15	*Candida tropicalis*	120	75.65	12.86	[42]

Based on data analysis from previous studies, it was found that fermentation with yeast *Saccharomyces cerevisiae* with a fermentation time of 24 hours was able to produce the most significant bioethanol yield with 80.9%. *Saccharomyces cerevisiae* is considered the safest and most widely commercialized microorganism, making it easy to find and abundantly available [50].

3.4 Distillation Process

Distillation is a method of separating liquids from a mixture based on the ability of the substances to evaporate due to differences in boiling points [51]. Distillation changes a substance from a liquid to a gas by heating the liquid, cooling the heated gas, and collecting the condensed liquid droplets [52]. The distillation process begins with heating the liquid to its boiling point, then flowing the steam into the condenser, after which the condensation results are collected as a liquid [53]. Distillation is used to remove impurities from liquids that have been polluted with rice straw-derived solutes with various boiling points [54]. These are some previous studies regarding the method of distillation of rice straw shown in Table 5.

Table 5. Method of Distillation of Rice Straw

No	Method	Yield (%)	Reference
1	Vacuum distillation	40	[35]
2	Double continuous distillation (crude and purified distillation)	3.92	[55]
3	Classic distillation method after 24h of fermentation using Forward Osmosis pre-treatment	10.3	[56]

Based on data from the distillation method from previous studies, it was found that the distillation method that produced the highest purity was vacuum distillation, with a yield of 40% purity. Vacuum distillation separates two components whose boiling point is very high by lowering the surface pressure to lower than 1 atm so that the boiling point is also low. In the process, the temperature used for distillation does not need to be too high [57]. Vacuum distillation is usually used to separate fractions that cannot be separated by atmospheric distillation [58].

3.6 Application Bioethanol in Central Java

Java Island is one of the largest oil producers in Indonesia. Currently, an oil refinery unit in Cilacap, Central Java, has a capacity of 384,000 barrels per day and is considered the largest oil producer owned in Indonesia. Products from the Cilacap refinery contribute about 34% of the national fuel demand and 60% of Java Island's fuel demand.

Based on the data analysis and considerations that have been carried out, bioethanol products from rice straw using a separate hydrolysis fermentation method could become one of the oil products of Cilacap Refinery. The consideration that has been carried including low cost of operation, production materials are not difficult to find, and the operating time does not take long for one cycle, so it does not hamper the productivity and effectiveness of the products to be produced and distributed.

4. Conclusions

Based on this review, it was found that the most effective method to be applied in the production of bioethanol from rice straw was the acid hydrolysis method using dilute H_2SO_4 with consideration of a shorter operating time, fermentation with Saccharomyces cerevisiae yeast with a fermentation time of 24 hours, and vacuum distillation. Through the utilization of rice straw in bioethanol, it can be a step to reduce environmental pollution so that it supports clean energy.

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