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RESEARCH ARTICLE

Bioethanol Production from Corn Cob Trough Utilization of Agro-biomass Waste in East Java as Renewable Energy : a Review

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Abstract

The demand for energy from fossil fuels continues to surge along with the rapid development of industry and the economy. Efforts to reduce dependence on fossil energy, especially the limited petroleum, are crucial. Therefore, it is necessary to increase the utilization of other energy sources, especially bioethanol, which is renewable and environmentally friendly. The production of bioethanol is intensifying due to market stability, low costs, sustainability, its role as an alternative fuel, and the risk of fossil fuel depletion. Corn cob waste comprises various organic compounds, including 40-60% cellulose, 20-30% hemicellulose, and 15-30% lignin. These compounds can be transformed into various forms of bioenergy, including bioethanol, biogas, and bio-oil. The process of producing bioethanol from corn cobs involves pretreatment, hydrolysis, fermentation, and distillation. The production of bioethanol from corn cob waste consists of several stages: pretreatment, hydrolysis, fermentation, and distillation. Lignin impedes acid penetration before hydrolysis and inhibits microbial growth during fermentation, so it must be removed through alkaline pretreatment. Glucose production from alkali-treated corn cobs can be achieved through hydrolysis using chemical or enzymatic catalysts. Acid hydrolysis with 21% H_2SO_4 and 21% HCl is preferred due to its shorter operating time. On the other hand, the high cost of enzymes and the extended operating time diminish production efficiency. The acid hydrolysis method using 21% H_2SO_4 requires 1 hour, 2 hours, and 3 hours and uses 21% HCl at a temperature of 100°C with a yield of less than 10%. The production of bioethanol from corn cobs is carried out using the SHF and SSF methods. The SSF method yields a range of 1.94%-88.37%. The SHF method yields a range of 0.28%-0.57%. Distillation is employed to remove impurities from liquids contaminated by dissolved substances from corn cobs, which have varying boiling points. Vacuum distillation can achieve a purity level of 89%. Converting corn cob into bioethanol aids in reducing environmental pollution and promotes the use of clean energy.

Keywords: *Bioethanol, Corn Cob, East Java, Fermentation, Fossil Fuel*

1. Introduction

Fossil fuels are the main source of energy for industry as they are able to provide large and stable amounts of energy to support the operations of various industrial sectors, ranging from manufacturing to transportation [1]. The demand for energy from fossil fuels continues to surge along with the rapid development of industry and the economy [2]. This raises significant concerns, especially for countries still dependent on fossil fuels like petroleum, amidst the dwindling reserves of these energy sources [3]. To achieve global economic stability and reduce fossil fuel consumption, utilizing alternative energy sources from non-fossil materials, such as plant-based fuels as a renewable energy source, is a suitable solution [4].

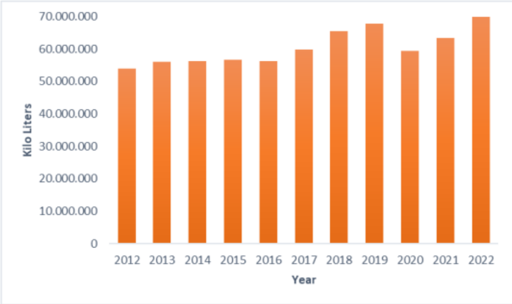

Figure 1. Total Fuel Oil Consumption Transportation Sector in Indonesia [5]

Efforts to reduce dependence on fossil energy, especially petroleum which will eventually be depleted due to limited deposits, require increasing the utilization of other energy sources, particularly bioethanol which is a renewable alternative energy source that produces lower carbon emissions than fossil fuels [6]. By capitalizing on its potential abundant resources, Indonesia can replace fossil fuels with bioethanol development that can support local economies, create jobs, and reduce carbon emissions, thereby contributing to global efforts to address climate change. [7]. Currently, there is an intensive effort to utilize materials containing coarse fiber with high carbohydrates, as all carbohydrate-containing materials can be processed into bioethanol [8].

Bioethanol is a type of ethanol produced through the conversion of biomass, and this technology has high economic value because it utilizes waste as its raw material [9]. To produce bioethanol, carbohydrates are the main substrate required because they are the only ones that can support fermentation [10]. Bioethanol is produced from biomass containing sugars, starch, and cellulose [11]. Bioethanol is used as a source of energy, mainly as a blend of gasoline. It can also potentially be used for producing sustainable aviation fuels [12].

Bioethanol, or ethyl alcohol (C_2H_5OH), is a clear, colorless liquid, soluble in water, ether, acetone, benzene, and all organic solvents [13]. This liquid has a characteristic alcohol smell, is environmentally friendly because it degrades naturally, has low toxicity, and does not produce significant air pollution if spilled [13]. The chemical and physical properties of ethanol are highly dependent on the hydroxyl group. At pressures > 0.114 bar (11.5 kPa), ethanol and water can form an azeotropic solution [14]. The use of bioethanol as fuel can be blended with gasoline in various compositions [11].

A differentiated technique of fermentation to transform bioethanol based on the hydrolysis process, are Separate Hydrolysis and Fermentation (SHF) and Simultaneous Saccharification and Fermentation (SSF) [15]. SSF (Simultaneous Saccharification and Fermentation) is an efficient approach for directly converting lignocellulosic materials into ethanol by combining the biocatalytic hydrolysis process of fermentation into a reaction phase in one reactor [16]. SSF has advantages in overcoming end-product inhibition, achieving relatively high ethanol yields, having a lower risk of contamination, and additionally being more economical on account of the use of a single bioreactor [17]. However, SSF has drawbacks, such as low enzymatic hydrolysis resulting in suboptimal sugar release, suboptimal yeast growth at high temperatures, and suboptimal fermentation results at lower temperatures [18]. Thus, SSF is influenced by several key factors, including reaction yeast strain, temperature, solid content, enzyme content, Ph, yeast addition ratio, and solid content [19].

Separate hydrolysis and fermentation (SHF) is a mode of bioethanol conversion in that every saccharification of the substrate from the fermentation of sucrose into bioethanol occurs as separate processes in different bioreactors [20]. The use of the SHF method is advantageous because it uses a small amount of enzymes and the ethanol formation time is faster [21]. The drawbacks of the SHF method include requiring two separate stages, making the process more complex and time-consuming, the production of inhibitors comparable to furfural also HMF that can inhibit enzyme activity and reduce sugar yields, and errors in enzyme selection that reduce process efficiency due to varying resistance to inhibitors [22]. Several factors need to be considered when using the SHF method, such as the amount of cellulase enzyme used during hydrolysis, the operating temperature for hydrolysis and fermentation, the initial substrate concentration in the fermentation process, the duration of the pre-hydrolysis phase before fermentation, and the presence of inhibitors that can hinder the process [23].

Corn cobs remain the component of corn herb left after the kernels have been removed and are one type of abundant lignocellulosic waste [24]. Lignocellulosic waste is defined as agricultural residues containing components such as cellulose, hemicellulose, and lignin [25]. The high cellulose content in corn cobs makes them a possible feedstock for bioethanol production because cellulose receptacles be hydrolyzed into monosaccharides like glucose, which can then be fermented into bioethanol. However, the resistant lignin in corn cobs requires pretreatment to increase the capability of enzymatic hydrolysis including bioethanol production [26]. Every utilization of corn cobs as waste involves stages of hydrolysis, fermentation, and distillation [27]. The effectiveness of exhaust gas emissions from bioethanol made from corn cobs can be seen through the significantly reduced HC levels [28]. In bioethanol production, it is important to ensure that the components in corn cobs that can be converted into ethanol are not damaged. Therefore, it is crucial to maintain low moisture during storage, perform proper pretreatment, optimize enzyme concentration, pH conditions, and temperature during enzymolysis, and use appropriate methods to enhance the capability of enzymatic hydrolysis moreover fermentation [29]. The effectiveness of corn cobs as a crude substantial product of bioethanol is also supported by their abundant availability as agricultural waste, among approximately 500 million tons produced annually worldwide[24]. Additionally, corn cobs have a good possibility as feedstock for industrial-scale bioethanol production, which receptacle be significantly enhanced using pretreatment methods like a co-solvent system based on ethylene glycol. This can achieve cellulose content as high as 91% and a lignin removal rate of 93% [30]. Therefore, corn cobs are highly potential raw materials for bioethanol manufacture receivable of their abundance, low cost, soaring energy smug, also lignocellulosic composition that allows for efficient bioethanol production after pretreatment to break down the resistant lignin structure [26].

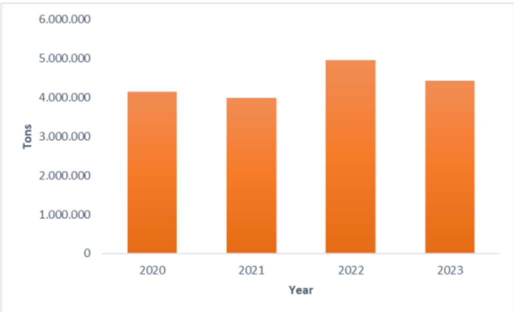

Figure 2. Corn Production in East Java Province [32]

Corn is one of the types of plants that can grow well in tropical regions such as Indonesia [31]. East Java Province is the largest corn-producing region in Indonesia. According to data from the Badan Pusat Statistik (BPS) in 2023, corn production in East Java in 2023 was 4.4 tons [32]. Corn contains about 30% waste in the form of corn cobs. Considering the corn production in 2023, East Java Province has the potential to produce around 1.3 tons of corn cobs [33]. This amount of waste is very significant and has great potential if utilized properly.

2. Raw Materials Selection

Tabel 1. Nutrition Label Content of Corn Cob

No	Nutrition	Concentration(%)	Reference
1	Cellulose	40-60	[34]
2	Hemicellulose	20-30	[34]

3	Lignin	15-30	[34]
4	Protein	2-3	[35]
5	Calcium	0,12	[35]
6	Phosphorus	0,04	[35]

The great opportunity to utilize corn cobs as raw material for products is quite attractive for development in terms of reducing waste by developing new products that can provide higher economic value [36]. Corn cobs have extraordinary potential due to their unique nutritional content. For example, they are rich in cell wall components, such as cellulose (40-60%), which can be processed into ethanol through hydrolysis and fermentation, and hemicellulose (20-30%), which also contributes to increasing ethanol yield and process efficiency. With this content, corn cobs become a potential raw material for optimization into bioethanol [37]. However, corn cobs still contain lignin (6-30%), which can inhibit the action of enzymes needed in the fermentation process, so its removal can accelerate the process and increase ethanol yield [38].

Protein in corn cobs (2-3%) can be hydrolyzed into amino acids, which are an important nutrient source for microorganisms used in the bioethanol fermentation process [39]. These amino acids help microorganisms to grow and reproduce well, thereby increasing fermentation efficiency and producing more bioethanol [40]. Calcium (0.12%) can help strengthen the cell walls of microorganisms used in the bioethanol fermentation process, making them more resistant to stress and pressure during fermentation, thereby enhancing process stability and resilience [41]. Phosphorus plays a vital role in essential cellular functions such as ATP synthesis and cellular structure stability, so adequate availability of phosphorus in the fermentation substrate can improve fermentation efficiency by accelerating the development of microorganisms [39].

3. Production Process

3.1 Pretreatment Process

Corn cobs are biomass waste containing lignin at 15%-30% [34]. The challenge in hydrolysis and fermentation of cellulose, whether using acids or enzymes, is due to its crystalline structure and the presence of lignin, which acts as a protective barrier for cellulose [42]. Lignin that protects cellulose is resistant to hydrolysis due to aryl-alkyl bonds and ether bonds [43]. Lignin, together with cellulose and other fibrous materials, forms the structural and cellular parts of plants [44]. Lignin is an aromatic polymer component that can interfere with the enzymatic hydrolysis process in ethanol production, thus requiring a delignification process [45]. Therefore, corn cobs need to undergo pretreatment to break down lignin and the crystalline structure of cellulose before proceeding to the hydrolysis and fermentation processes [46]. Besides breaking down lignin, the delignification process also increases the effectiveness of cellulose hydrolysis. The pretreatment stage is necessary to obtain high-quality cellulose [47].

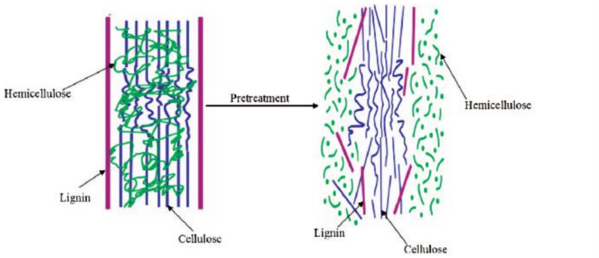

Figure 3. Schematic of Lignin Structure Destruction Process

Delignification is the process of separating lignin from the lignocellulose structure. The purpose of delignification is to reduce the lignin content in materials containing lignocellulose

[48]. During the delignification process, part of the lignin will dissolve. This process involves the saponification of intermolecular ester bonds surrounding xylan, hemicellulose, and other components like lignin and other hemicelluloses. Delignification damages the lignin structure and releases carbohydrate compounds [49]. The delignification process of corn cobs is carried out using NaOH solutions at concentrations of 0.5, 0.75, and 1 M, for 1.5, 2, and 2.5 hours at 80°C [50]. NaOH solution is chosen because it is effective in increasing cellulose extract yield [51] and is relatively cheaper compared to other chemical reagents [52]. NaOH functions as a delignification agent by degrading and breaking down the lignin structure, crystalline and amorphous parts, separating some lignin and hemicellulose, and causing the cellulose structure to swell [51]. Lignin degradation begins with the attack of hydroxide ions (OH-) from NaOH on the H atom attached to the phenolic OH group [53]. This H atom is acidic because it is attached to an O atom with high electronegativity. The more electronegative O atom pulls electrons from the H atom, making the H atom partially positive and easily released as an H+ ion [54]. This acidity is also influenced by the resonance effect of the alkyl group in the para position, making the H atom on the phenolic group more acidic [55].

3.2 Hydrolysis Process

The hydrolysis process is a chemical reaction that breaks a molecule into two parts by adding a water molecule (H_2O) to convert polysaccharides into simple monomers [56]. The hydrolysis process involves the transfer of OH- and H+ ions from H_2O to the substance being hydrolyzed [57]. In industry, this process is used to produce simple molecules such as glucose, maltose, and dextrin [58]. In general, an extended hydrolysis time results in a higher glucose content being generated [59].

$$(C_6H_{10}O_5)n + n\,H_2O \longrightarrow nC_6H_{12}O_6$$

Figure 4. Hydrolysis Process Reaction

The process of hydrolysis is influenced by the cellulose content in the raw material, hydrolysis pH, hydrolysis time, temperature, pressure, and acid concentration [60]. Hydrolysis methods can be carried out by acid hydrolysis, enzymatic hydrolysis, and acid-enzymatic hydrolysis [61].

Enzymatic hydrolysis can be performed with α-amylase, glucoamylase, and pullulanase [62]. Enzymatic hydrolysis is more advantageous compared to acid hydrolysis, as enzymes will specifically break glycosidic bonds, minimize color damage, and leave no residue [63]. In acid hydrolysis, the typical acids used in this process include acetic acid, phosphoric acid, hydrochloric acid, and sulfuric acid [64]. In acid-enzymatic hydrolysis, the process is carried out with acid hydrolysis first, followed by enzymatic hydrolysis by mixing the best acid hydrolysate with the enzyme solution [65].

Tabel 2. Comparison of Hydrolysis Processe Parameter [66]

Parameters	**Hydrolysis Process**		
	Acid	**Enzymes**	**Acid-Enzymes**
Technical Aspects			
Pressure (Kgf/cm^2)	3	1	1-3
Temperature (°C)	140-160	60-105	60-140
pH	2,3	4,5-6	1,8-2
Dextrose Equivalent	30-55%	90-95%	63-80%
Side Reactions	Have	-	Have
Corrosion Power	High	Low	High
Corrosion Power			
Acid Requirement	Much	Little	Much
Equipment Cost	Expensive	Cheap	Expensive

Energy	Big	Small	Average
Investment	High	Avarage	High
Environmental Aspects			
Pollutants	Acid	-	Acid

Tabel 3. Production Etanol from Corn Cob

No	**Acid type**	**Operating conditions**	**Yield**	**Reference**
1	HCl 21%	2,5h and 100°C	0,21%	[50]
2	H_2SO_4 21%	1h and 100°C	4,65%	[67]
3	H_2SO_4 21%	2h and 100°C	5,53%	[67]
4	H_2SO_4 21%	3h and 100°C	10%	[67]

3.3 Fermentation Process

Fermentation is a method used to produce alcohol by precipitating a substance containing carbohydrates or a substance that, when precipitated, will generate carbon dioxide or amino acids under anaerobic conditions [68]. This process transforms monosaccharides into ethanol, resulting in chemical changes within the substrate or organic material due to the enzymatic activity of microorganisms [69]. The microorganisms involved in fermentation can be fungi or bacteria [70], with Saccharomyces cerevisiae being commonly utilized [71]. Saccharomyces cerevisiae can convert glucose, mannose, and galactose into ethanol [72].

$$(C_6H_{10}O_5)_n + n\,H_2O \xrightarrow{\text{Enzim selulose}} n(C_6H_{12}O_6)$$

Tahap Fermentasi

$$(C_6H_{12}O_6) \xrightarrow{\textit{Saccharomyces cerevisiae}} 2C_2H_5OH + 2CO_2$$

Figure 5. Reaction of the Fermentation Process

The goal of bioethanol fermentation is to effectively utilize organic materials, especially organic waste to generate bioethanol through the process of fermentation technology [68]. Fermentation can be categorized into two types based on the products: alcoholic fermentation, which produces alcohol as the final product, and non-alcoholic fermentation, which does not [72]. The process of fermentation can be significantly influenced by environmental elements like temperature, pH, incubation period, substrate concentration, microbial presence, and the accumulation of byproducts [72]. In bioethanol production, materials containing cellulose must first be hydrolyzed into glucose using acid, with the formation of glucose indicating the completion of the process, after which the material is ready for fermentation [73]. At the strt of fermentation, nutrients and cofactors crucial for yeast growth, including carbon, oxygen, nitrogen, hydrogen, phosphorus, sulfur, potassium, and magnesium, must be introduced at the beginning of the fermentation process [74]. To ensure optimal fermentation results, the hydrolysate with the highest sugar content will be used as the substrate, and the pH of the solution will be stabilized with NaOH [75]. The decomposition of a singular glucose molecule results in the production of two molecules of carbon dioxide and two molecules of ethanol [73]. The carbon dioxide produced results from the anaerobic catabolism of the sugar content [77]. The production of ethanol from lignocellulosic material involves two distinct processes: separate hydrolysis fermentation (SHF) and simultaneous saccharification and fermentation (SSF) [69]. SSF is considered superior to SHF due to faster ethanol production and higher ethanol concentrations [78].

Tabel 4. Production of Ethanol from Corn Cob

No	Microbal strain (hours)	Method	Time Fermentation (hours)	Productivity (g/L h)	Yield (%)	Reference
1	Saccharomyces cerevisiae TC-5	SSF	72	0.291	88.37	[78]
2	Saccharomyces cerevisiae	SSF	24	1.69	40.63	[79]
3	Saccharomyces cerevisiae	SHF	7	0.57	4	[69]
4	Saccharomyces cerevisiae	SSF	6	0.32	1.94	[70]
5	Saccharomyces cerevisiae	SHF	6	0.28	1.69	[70]

3.4 Distillation Process

The distillation process works by utilizing the difference in boiling points of components in liquid mixtures, especially those with a large enough difference in boiling point and vapor pressure [80]. This distillation process can achieve or enhance ethanol concentrations to over 95% [81]. The distillation process occurs when the mixture is heated and volatile components evaporate upwards, then cooled until they condense on the walls of the condenser [82]. The distillation process begins with heating water in a boiler until it vaporizes, and the steam flows towards the condenser to be cooled, resulting in the vapor condensing back into liquid form [83]. The resulting substance from this process is called distillate, while the remainder is referred to as residue [84]. Distillation is used to purify liquids contaminated by soluble substances from corn cobs with varying boiling points [85]. Apart from differences in boiling points, the factor of volatility differences, which is the tendency of a substance to become a gas, also affects distillation [86].

Tabel 5. Method of Distillation of Corn Cob

No	Metode	Time Fermentation (hours)	Yield (%)	Reference
1	Batch Distillation	96	44	[87]
2	Three-stage fractional distillation	6	82,3	[46]
3	Vacuum Distillation	4	89	[88]

Simple distillation has advantages aside from being cheaper and having an easy manufacturing process; in the cooling process between hot vapor and cooling water, they meet directly in counterflow [89]. This causes ethanol vapor to condense faster and flow back into liquid form. The purity level achieved by simple distillation is 44%, which means it has not yet reached industrial-scale bioethanol purity [87]. Fractional distillation or multistage distillation is a process of separating mixtures by evaporating and condensing their components in stages [90]. The purity level achieved by three-stage fractional distillation is 82.3%, which is superior to simple distillation. This differs from regular distillation due to the fractionating column and reflux process to achieve optimal separation of bioethanol and water [91]. Vacuum distillation is a method where liquids are vaporized at low pressure [8]. The purity level achieved by vacuum distillation is 89%, indicating it is the distillation method that produces the highest purity. The primary goal of vacuum distillation is to increase volatility and lower the boiling point of liquids because some compounds are sensitive to high temperatures and must be operated at low temperatures [92].

3.6 Application Bioethanol in East Java

Bioethanol can be used for basic chemicals, polymers, drugs, and fuels [93]. In the petroleum industry, bioethanol serves as a new renewable alternative fuel for internal combustion engines, replacing gasoline [94]. The conversion of bioethanol into complex hydrocarbon compounds is carried out through catalytic processes, such as ethanol dehydration to ethylene, which is then converted into gasoline via oligomerization or alkylation [95]. Bioethanol can be blended into gasoline at ratios of 5-10% (E5-E10) without requiring engine modifications, due to its higher octane number, thereby improving engine performance and reducing greenhouse gas emissions [96]. An example of bioethanol innovation is in the production of jet fuel through ethylene oligomerization reactions, which results in low carbon emissions [97].

In the petrochemical industry, bioethanol can be converted into hydrogen, methane, ethylene, and olefins [98]. Ethanol dehydration with acid catalysts such as alumina at high temperatures produces ethylene and water, which can be used for plastic synthesis and other chemicals such as ethylene oxide and ethylene glycol [99]. Bioethanol can also be converted into acetaldehyde and then into 1,3-butadiene, a raw material for elastomers, resins, and synthetic rubber [100]. Moreover, bioethanol can be converted into hydrogen for ammonia production, methanol, and hydrogen fuel cells [101].

In the cosmetics industry, bioethanol functions as an effective solvent, enhancing the penetration of active ingredients, acting as an antimicrobial agent, and serving as an alternative to petroleum-based solvents [102]. Bioethanol helps improve the stability and quality of cosmetic products and suppresses microbial growth [103].

In the pharmaceutical industry, bioethanol is used as a raw material for synthesizing various pharmaceutical compounds, such as olefins, aldehydes, ketones, and alcohols, through efficient catalytic processes [104]. Bioethanol also serves as an environmentally friendly solvent for chemical synthesis and active ingredient extraction, supporting more sustainable production practices [105]. As a solvent in drug formulations and plant extracts, bioethanol is safer because it produces lower carbon emissions compared to petroleum-based ethanol [106].

4. Conclusion

Bioethanol can be used as a new renewable alternative energy source that can be developed in many countries, including Indonesia. Previous research has evaluated the quality of bioethanol from corn cob waste as the main raw material. The opportunity for utilizing corn cob waste as a raw material for bioethanol is substantial because there is a large amount of unutilized waste. The bioethanol production process consists of three main stages: hydrolysis, fermentation, and distillation. Based on the review, the most effective method for bioethanol production from corn cobs includes 10% acid hydrolysis using 21% H_2SO_4 for 3 hours at 100°C resulting in a yield of 10%, SSF with Saccharomyces cerevisiae yeast for 30 hours resulting in a yield of 94.21%, and vacuum distillation yielding 89%. The use of corn cob waste for bioethanol production can help reduce fossil energy consumption and support clean energy.

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