Hight Quality Bioethanol Characteristics of Rice Straw Raw Materials

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Abstract. Bioethanol is a renewable fuel derived from agricultural resources. This study aimed to examine the characteristics of bioethanol produced from rice straw, including ethanol concentration, methanol concentration, water content, copper (Cu) and chloride (Cl) levels, gum content, pH, heating value, density, viscosity, flash point, and octane number. An experimental method was employed, with the production process consisting of four stages: preparation, saccharification, three-day fermentation using 25 grams of Saccharomyces cerevisiae, and fractional distillation at four levels at 78 °C with 10 grams of zeolite rock adsorbent (70 mesh). Bioethanol quality tests followed ASTM standards (D5501 for ethanol, D550 for methanol, D1744 for water content, D1688 for Cu, D1613 for Cl, D381 for gum, D4806 for pH, D240 for heating value, D1298 for density at 20 °C, D445 for viscosity at 20 °C, D93 for flash point, and D2699 for octane number). The chemical analysis revealed 99.75% ethanol, 0.0024% methanol, 0.0019% vol water, 0.002 mg/kg Cu, 15.73 mg/l Cl, and 1.3 mg/100 ml gum. The physical analysis revealed a pH of 6.1 mg/L, a heating value of 6975 kcal/kg, a density of 0.781 g/cm^3, a viscosity of 1.26 cSt, a flash point of 15 °C, and an octane number of 105. Overall, the results confirm that rice straw bioethanol possesses superior performance and environmental advantages, making it a feasible substitute or additive for gasoline.

1 Introduction

The two important things that trigger world change are: (1) a logarithmic increase in the cruising speed of vehicles, namely increasing ten times every century, and (2) information technology that connects people in all parts of the world in seconds. As a result, the world becomes limitless, yet it feels increasingly narrow. On the one hand, increasing the speed of human movement enhances the economic growth rate, but on the other hand, fuel energy consumption increases by a factor of 100 every century. If the entropy of motion is uncontrolled, then not all energy contributes to economic growth. Most of the fuel energy still comes from fossil fuels, while reserves tend to become increasingly depleted. Global consumption of petroleum and liquid fuels from January 2019 to 2022 experienced fluctuations. In January 2020, there was a drastic decline to 80 million barrels of oil per day

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due to COVID-19, and then from July 2020 to July 2022, it continued to increase to 10380 million barrels of oil per day. Likewise, the trend in fuel consumption has started to increase since 2020. By July 2020, consumption of petalite had reached 16.8 million kiloliters, and diesel fuel had reached 9.9 million kiloliters. Previously, fuel consumption declined in 2020 due to the COVID-19 pandemic. Indonesia's oil consumption is expected to be 1.47 million barrels per day in 2021. According to British Petroleum data, this amount increased by 5.22% compared to the previous year, reaching 1.4 million barrels per day. Indonesia's oil consumption contributes 1.6% of the global total. Meanwhile, domestic oil consumption contributed 4.11% to the total in the Asia Pacific, which amounted to 35.81 million barrels per day. The trend shows domestic oil consumption has tended to fluctuate over the last decade. The highest oil consumption reached 1.62 million barrels per day in 2018. One of the latest renewable energy sources that can be used as a mixture or substitute for gasoline as a transportation fuel is bioethanol, which is processed from vegetable-based materials.

Meanwhile, Indonesia's oil production was recorded at 669,360 barrels per day in 2021. This value decreased by 6.74% compared to the previous year, which was 742,000 barrels per day. This means that Indonesia's oil balance remains in deficit. Therefore, Indonesia had to import 802,138 barrels of oil per day from abroad in 2022.

Bioethanol is a form of renewable energy that can be produced from vegetable-based materials (plants and fruit) which contain: (1) carbohydrates $(C_6H_{10}O_5)_n$, such as corn, cassava, sago, sweet potato, wheat, potatoes, sticky rice. (2) glucose $(C_6H_{12}O_6)$ such as molasses, sugar cane sap, coconut sap, palm sap, and cellulose. (3) cellulose $(C_6H_{10}O_5)_n$, such as banana tubers, sugar cane bagasse, sorghum straw, and rice straw. According to Amin et al. [1], rice straw contains 8.26% protein, 31.99% fiber, 77.00% NDF, 57.91% ADF, 23.05% cellulose, 19.09% hemicellulose, and 22.93% lignin. Lignocellulose is a complex biopolymer consisting of cellulose, hemicellulose, and lignin, which is difficult to degrade. As a result, not many microorganisms can utilise it as a raw material for producing bioethanol, necessitating a specific pre-treatment process. The main aim of pre-treatment is to break down the lignin structure, destabilize the crystalline structure of cellulose, and increase the porosity of the lignocellulosic material. Bioethanol is a type of alcohol produced from multilevel fermentation and distillation to obtain high-quality bioethanol. To carry out distillation, a high-quality absorbent is required, meaning that the absorbent material must have high porosity to absorb the maximum amount of water. Suitable absorbents include zeolite, pumice, and limestone. Zeolites are a group of alumino-silicate frameworks that occur in nature with high cation exchange capacity, high adsorption, and dehydration properties [2]. Meanwhile, according to Harjanti [3], clinoptilolite-type zeolite rock can be used as an adsorbent (separating water content from ethanol). The advantages of zeolite rock absorbents compared to pumice and limestone absorbents are that they have a hollow structure and even pore sizes and have the properties of dehydration (drying), ion exchange, catalyst, and filter [4]. The purpose of this research to analyze the properties characteristic of chemical and physical of bioethanol produced from rice straw raw materials. Bioethanol was produced through four stages, namely preparation, saccharification, fermentation, and distillation. The fermentation process was carried out for 3 days using 25 grams of Saccharomyces cerevisiae and stratified distillation was performed up to 4 levels at a temperature of 78°C with a zeolite rock adsorbent measuring 70 mesh and weighing 10 grams.

2 Materials and Method

2.1 Materials

Bioethanol (C2H5OH) is made from various kinds of vegetable base ingredients containing: glucose (C6H12O6) such as from molasses, sugar cane sap, coconut sap, palm sap, etc., (2) carbohydrates (C6H10O5) as in corn, cassava, sago, cassava, sweet potato, wheat, potatoes, white rice, sticky rice and various human staple foods, (3) cellulose (C6H10O5)n as in rice straw, rice bran, tuber bananas, sugarcane bagasse and others. The raw materials used in this research were rice straw.

Fig. 1. Rice straw.

Fig. 2. Rice straw pre-treatment.

Fig. 3. Zeolite rock pre-treatment.

Fig. 4. Zeolite rock adsorbent mesh 70.

2.2 Method

The process of producing bioethanol through four stages, namely, the preparation, saccharification, fermentation and distilation was carried out for three days at a temperature of 33°C and 25 grams of saccharomyces cerevisiae and stratified distillation up to 4 levels at a temperature of 78°C with zeolite adsorbent measuring 70 mesh with a weight of 10 grams. Pre-treatment using N- Methylmorpholine-N-oxide (NMMO), because pre-treatment using N-Methylmorpholine-N-oxide (NMMO) is more effective than acid pre-treatment or alkali pre-treatment because it can maintain the composition of the material lignocellulose, especially its hemicellulose constituents, plus NMMO is a suitable solvent for cellulose. The methods of testing the characteristics of bioethanol (chemical properties) with standardized ASTM (ethanol concentration D5501, methanol concentration D550, water content D1744, Cu content D1688, Chloride ion (Cl) content D1613, gum content D381). While the methods of testing the characteristics of bioethanol (physical properties) with standardized ASTM (pH value D4806, heating value D240, density to 20°C D1298, viscosity to 20°C D445, flash point D93, and octane number D2699). The control group includes rice straw material, pasteurised at 63°C for 30 minutes, followed by 3 days of fermentation with 25 grams of Saccharomyces cerevisiae. Stratified distillation was then carried out up to 4 levels at a temperature of 78°C using a 70 mesh zeolite adsorbent with a weight of 10 grams. Fractional Distillation Equipment Series. The experimental setup and instruments are illustrated in Figure 5.

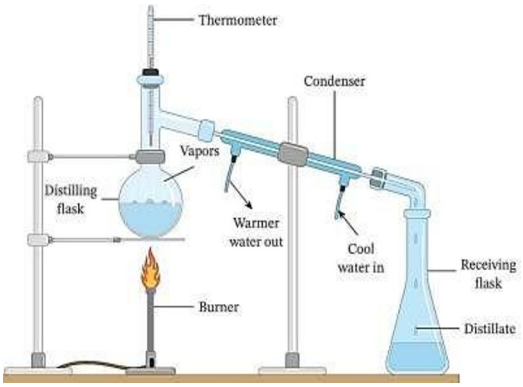

Fig. 5. The Setup of distillation equipment.

Flowchart of bioethanol production from rice straw raw material as shown in figure 6.

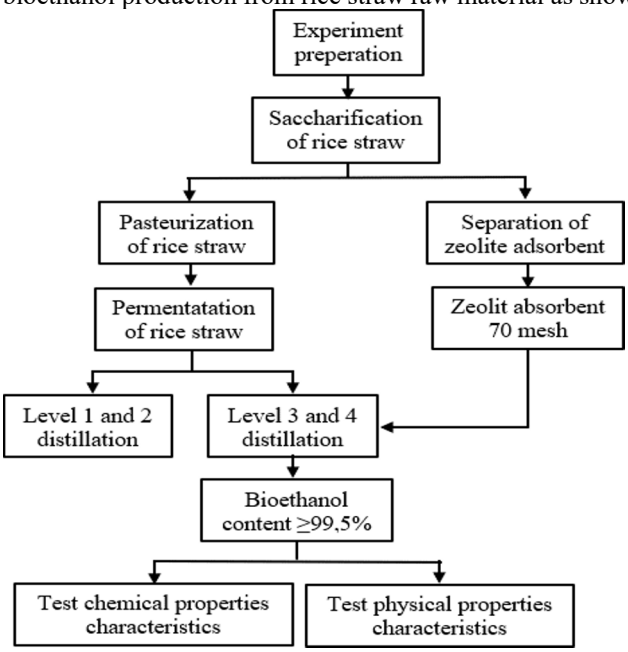

Fig. 6. Flowchart of bioethanol production from rice straw raw material.

3 Results and Discussion

3.1 The chemical properties

The laboratory test results for the chemical properties of bioethanol from rice straw raw materials are represented in Table 1.

Table 1. The results of the chemical properties test of bioethanol from rice straw raw materials.

No	Chemical Properties	Method	Bioethanol SNI Standart [5]	Laboratory Tests Bioetanol Rice Straw Raw Materials

1	Ethanol (C_2H_6O) content (%vol) min	ASTM D5501	99.50	99.75
2	Methanol (CH_3OH) content (mg/l) max	ASTM D5501	0.50	0.001
3	Water (H2O) content (%vol) max	ASTM D1744	0.70	0.002
4	Copper (Cu) content (mg/kg) max	ASTM D1688	0.10	0.002
5	Ion Clorida (Cl) content (mg/l) max	ASTM D512	30,0	15.86
6	Sulfur (S) contens (mg/l) max	ASTM D2622	20.0	0.04
7	Gum content (mg/100ml) max	ASTM D381	50,0	1.30

As shown in Table 1, the laboratory test results for the chemical characteristics of bioethanol from rice straw, obtained using a four-stage distillation, are presented. The ethanol (C_2H_6O) concentration reached 99.75%, meeting SNI specifications. This was mainly due to enzymatic activity, fermentation duration, and multistage distillation. Methanol (CH_3OH) content was extremely low at 0.001 mg/L, well below the SNI limit of 300 mg/L, due to high glucose consumption and yeast proliferation during fermentation [6]. This is attributed to sugar consumption and yeast growth during fermentation [7]. This result is noteworthy as it indicates a high level of safety and quality in the produced bioethanol. The fermentation and distillation processes likely played a crucial role in achieving such low methanol levels. Water (H2O) content was only 0.002%v (SNI max: 1.0%v), influenced by enzymes in fermentation and absorption during distillation. Lower enzyme amounts and larger pore sizes both helped reduce water content [4]. This reduction is influenced by enzyme efficiency and the quality of the pumice adsorbent used, which is highly porous. The use of minimal enzymes during fermentation reduces the water content in the bioethanol [8]. Furthermore, the larger and more porous the adsorbent, the greater its water absorption capacity, resulting in a lower water content. The copper (Cu) content was 0.002 mg/kg, far below the SNI limit of 0.1 mg/kg, likely due to the use of fermentation and distillation equipment. The fermentation and distillation processes play a crucial role in determining the retention of trace metals in bioethanol. Proper management of these processes can help minimize unwanted metal contaminants [9]. High levels of copper in biofuels can lead to corrosion of metal components in engines and storage systems. Copper can catalyze the oxidation of ethanol, leading to the formation of harmful byproducts that may damage engine parts over time [10]. Chloride ion (Cl) content was 15.86 mg/L, below the SNI limit of 40.0 mg/L, influenced by the hydrolysis rate (faster hydrolysis reduces chloride) [11]. Lower chloride ion levels are beneficial as chlorides can lead to corrosion of metal components fuel systems. High chloride concentrations can accelerate the degradation of materials, leading to reduced lifespan of engine components and increased maintenance costs [10]. Sulfur (S) content was very low at 0.04 mg/L, which is very low when compared to the standard (SNI) maximum of 50 mg/L, due to the low sulfur content in the rice straw raw materials. Some raw materials used in bioethanol production may contain higher natural sulfur concentrations, which can carry over into the bioethanol during production. By maintaining a sulfur level of only 0.04 mg/L, this bioethanol minimizes its environmental footprint and aligns with global efforts to reduces exhaust gas emissions from fossil fuels. The finally gum content was 1.30 mg/100 mL (SNI max: 5.0 mg/100 mL), The fermentation time and level distillation processes play a significant role in determining gum retention in bioethanol. The quality and type of feedstock used in bioethanol production can affect gum content. The process that follows the procedure bioethanol production will reduces the gum content.

3.2 The physical properties

The laboratory test results for the physical properties of bioethanol from rice straw raw materials are represented in Table 2.

Table 2. The results of the physical properties test of bioethanol from rice straw raw materials.

No	Chemical Properties	Method	Bioethanol SNI Standart [5]	Laboratory Tests Bioetanol Rice Straw Raw Materials
1	Density 20°C (g/cm^3) max	ASTM D1298	0.789	0.793
2	Kinematic viscosity 20°C (cSt)	ASTM D445	1.2-1.5	1.14
3	Flash point (°C)	ASTM D93	12-20	17
4	Boil point (°C)	ASTM D2892	80 max	74
5	Heating value (kcal/g)	ASTM D240	6424-7094	6987
6	pH (mg/l)	ASTM D6423	6.5-9.0	7.1
7	Octan number, min	ASTM D976	103	109

As shown in Table 2, the physical characteristics of bioethanol obtained from rice straw through a four- stage distillation process were evaluated. The density of the bioethanol, measured at 0.793 g/cm³, was slightly above the SNI reference value of 0.789 g/cm³. This property is influenced by several factors, including enzymatic activity, fermentation conditions, hydrolysis time, and ethanol concentration, with higher ethanol levels generally lowering density. The kinematic viscosity of 1.14 cSt exceeded the SNI specification. This value is affected by fermentation duration, the volume of starter applied, and the presence of hydroxyl (-OH) groups, which exhibit polar characteristics. The flash point of 17 °C fell within the SNI range of 12–20 °C and is dependent on the evaporation process, where rapid fuel evaporation leads to a reduced flash point [12]. The boiling point of bioethanol is 74°C, which complies with the SNI standard maximum of 80°C. The boiling point is affected by fuel composition and vapor pressure, higher vapor pressure results in boiling point higher. The heating value reached 6987 kcal/g, considered relatively high, mainly due to the carbon and hydrogen content of rice straw. Both higher carbon–hydrogen composition [13] and higher bioethanol concentration [14] contribute to an increase in heating value. The pH value was found to be 7.1 mg/L, which complies with the SNI requirements and is strongly influenced by the fermentation period. Longer fermentation increases alcohol formation and gas release but decreases the pH level [15]. Lastly, the octane number reached 109, exceeding the SNI requirement of 103, and this increase is attributed to the alcohol content of bioethanol, as higher alcohol concentrations yield higher octane numbers.

4 Conclusion

Based on the research objectives, the result, and discussion of bioethanol characteristics of rice straw raw material, it can be concluded that: The analysis of chemical properties shows that the concentration of ethanol is 99.75%, that of methanol is 0.0024%, that of water is 0.0019 % vol, that of copper is 0.002 mg/kg, that of ion clorida is 15.86 mg/l, and that of gum is 1.3 mg/100 ml. The analysis of physical properties reveals a density of 0.793 g/cm³, a kinematic viscosity of 1.26 cSt, a flash point of 17°C, a boiling point of 74 °C, a heating value of 6987 kcal/kg, a pH value of 7.1 mg/L, and an octane number of 109. Generally, bioethanol from rice straw raw material has physical and chemical properties that approach those of SNI standards, except that density and viscosity haven't met the SNI standard. The research results show the density of bioethanol from rice straw raw material is higher

compared to the density of SNI bioethanol. The next research suggestion to reduce density could be carried out starting from the 3rd distillation using an ethyl acetate mixture.

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