EQUIJOST

Available online at www.equijost.com
Equity Journal of Science and Technology, 2021 8(1): 74 - 78
ISSN 2354-1814; E-ISSN 2682-5961
An Official Publication of Kebbi State University of Science and Technology, Aliero, Nigeria

Characterization of Bioethanol Fuel from Rice and Corn Straws: A Comparative Study

Abubakar K. Rabiu, Cosmos M. Elinge, Murtala M. Ambursa, Aminu K. Rabiu, Danladi S. Samaila
Department of Pure and Applied Chemistry, Kebbi State University of Science and Technology Aleiro, Nigeria
*Corresponding Author's email: rabiukokoa@gmail.com

Received: May 19, 2021: Accepted: July 15, 2021; Published Online: July 30, 2021

Abstract
In this study, the production and characterization of bioethanol from rice and corn straws were investigated. The bioethanol was produced through dilute acid hydrolysis, fermentation and distillation; and the distillates were purified by dehydration using zeolite 4A. The physicochemical and fuel properties of the bioethanol distillates including pH, refractive index, specific gravity, flash point, octane rating and calorific or heating value were evaluated. Further characterization of the biofuel was carried out using FTIR and GC-MS. The results indicated that octane number, calorific value, and specific gravity of the corn straw bioethanol obtained were significantly higher ($p<0.05$) compared to rice straw bioethanol. Meanwhile, no statistically significant difference ($p>0.05$) was observed in the flash point, refractive index, pH, pour and cloud points of the bioethanol produced from the two lignocellulosic substrates. Furthermore, the results reveal that pH, octane number, specific gravity and flash point are within the ASTM standards while refractive index, cloud and pour point were slightly outside the ASTM standard. This reveal potential of the feedstock as a source for Bioethanol production.

Keywords: Rice straw, Corn straw, Bioethanol, physicochemical properties, fuel properties

1. Introduction

Renewable energy based fuels, such as biofuel from biomass sources, have attracted a lot of attention of both researchers and government institutions as alternative fuel energy sources because they are biodegradable and produce less environmental pollution than the fossil based sources [1–5]. Moreover, fossil fuels are becoming increasingly expensive and their reserves are continuously being depleted [6]. Due to the economic importance of energy and its impact on the development of any nation, it has become necessary to secure and find more alternative sources of fuel energy [7].

Bioethanol is produced through the fermentation of sugar containing substrates such as sugar cane, sugar beet, lignocellulosic materials and or starch in grains of cereal crops [8]. It is one of the most important clean fuel and renewable energy source that has the potentials in the future for solving fuel shortages as well as environmental threats when compared with fossil based fuels [9]. During the first generation of bioethanol production, edible feedstocks such as sugarcane and corn were used thus, creating competition between food and fuel, causing rapid increase in food prices [5,10]. The second generation biofuels used non-edible feedstocks such as lignocellulosic substrates, agricultural wastes, forest waste and municipal wastes to mitigate the effect of competition between food and fuel thereby stabilizing the prices of food materials that were initially being used as primary feedstock for bioethanol production [11,12].

Lignocellulosic biomass are naturally abundant carbohydrates, which consist mainly, of cellulose, hemicelluloses and lignin polymers, with other smaller constituents of pectin, protein, extractives and ash [13]. Due to its natural abundance, lignocellulosic bioethanol production is certainly a good strategy of energy supply, particularly suitable for countries like Nigeria with huge forest and agricultural wastes [5,14]. For this reason, many research efforts have been made by various researchers [15,16]. Febrianti [17] reported the production of bioethanol using Tofu waste as feedstock in which 7.69 g/L of ethanol was produced. In another study, Teng-Chieh *et al.* [18] reported that pre-treatment of rice straw with 1% (w/w) sulphuric acid resulted in a maximal sugar yield of 83% ethanol at a reaction time of 1-5 min at 160 °C or 180 °C through enzymatic hydrolysis [18]. Similarly, Ja *et al.* [19] showed that pre-treatment of rice straw using aqueous-ammonia at moderate temperature increased the production of fermentable sugar and consequently higher bioethanol yield. Furthermore, Devendra and Rakesh [20] examined the effect of acid and alkaline pre-treatment methods of hydrolysis on lignocellulosic biomass (Rice straw, barley straw, wheat straw and corn cobs) and showed that acid pre-treatment was more effective and cheaper than alkaline.

The objective of the present study was to evaluate the physicochemical and fuel properties of bioethanol generated from corn and rice straws under mild conditions.

2. Materials and Methods

2.1 Materials

The rice and corn straws were collected from a farm in Gwadangaji village, Birnin-Kebbi, Kebbi State, Nigeria. *Saccharomyces cerevisiae* (Yeast) and Zeolite 4A were obtained from STK industries and Chinese Desiccant manufacturers, respectively. Sodium hydroxide and Sulphuric acid were both obtained from BDH and are analytical grade reagents.

https://dx.doi.org/10.4314/equijost.v8i1.12

2.2 Substrates Preparation

The rice and corn straws were air-dried and crushed using mortar and pestle. In the case of corn straw, grinding was performed using rice huller machine (Topex, made in madras). The samples were sieved through 2.0 mm mesh.

2.3 Hydrolysis and Fermentation

The hydrolysis of the substrates was carried out according to the method reported by Ademiluyi and Mepba [21]. Exactly 50 g each of the ground substrates were transferred into a 500 ml beaker and mixed with 400 ml of 3 M H_2SO_4. The mixture was heated on a magnetic stirrer for 105 min at 90°C. The pH of the hydrolyzed samples was maintained at 6.5 by adding drops of 2 M sodium hydroxide solution and monitored using pH meter. The hydrolysed samples were fermented using *Saccharomyces cerevisiae* in accordance with Ademiluyi and Mepba method [21]. The yeast was first activated by mixing 3 g of powdered yeast with 15 ml of water and 2 ml of the hydrolysed sample. The mixture was added to the bulk sample for fermentation to take place, and the resulting mixture was kept at room temperature (*ca.* 26 °C) for 96 h. The content was transferred into 500 ml conical flasks and airtight with cotton, aluminium foil and masking tape.

2.4 Distillation and Dehydration

The fermented samples were distilled at 55°C using rotary evaporator [5]. Zeolite 4A was used to remove residual water from the bioethanol distillate. The dehydration was carried out by mixing 50 g of zeolite 4A with the distillate and the content was stirred until homogenous mixture was attained. The bioethanol was recovered from the mixture by re-distillation using rotary evaporator. The procedure was repeated four times to obtain high purity bioethanol distillates.

2.5 Physicochemical Analysis of the Bioethanol

The physicochemical properties determined include specific gravity, pH and refractive index. The specific gravity of the bioethanol distillates was determined using Equation (1)[21]:

$$Specific\ Gravity = \frac{\text{Density of bioethanol}}{\text{Density of water}} \quad (1)$$

The density of the bioethanol and water was measured as reported by Ademiluyi and Mepba [21]. The weight of an empty pycnometer was first recorded and designated W_o. The pycnometer was filled with the bioethanol and the excess was wiped off. The weight of the pycnometer was again recorded (W_1). The density was calculated using Equation 2:

$$Density\ (\rho) == \frac{W_1 - W_0}{Volume} \quad (2)$$

The density of distilled water was recorded using the same procedure.

The pH values of the produced bioethanol distillate were determined using pH meter (Metrohm 827). The pH meter was first calibrated using two buffers (pH 4 and 7). The pH electrode was then inserted into a beaker containing 100 ml of the bioethanol and allowed to stabilize and the reading was recorded. The refractive index of the bioethanol distillates was measured using a refractometer. The lens of the refractometer was first cleaned with acetone, then a drop of the sample was placed at the centre of the prism. The light source, index arm and compensator drum were adjusted to align the sample through the eye piece. The refractive index value was then recorded [23].

2.6 Measurement of Fuel Properties of the Bioethanol

The fuel properties of the bioethanol distillates obtained from the rice and corn straws measured include pour point, cloud point, flash point, octane number and calorific value.

The cloud and pour points of the bioethanol distillates were determined using ASTM D 2500 and ASTM D 5853 [24], while the flash point was measured using ASTM D 92 [25]. The octane number was determined using octane rating instrument on the basis of ASTM D 2699 Method [26], while the calorific value was determined using the ASTM D 4806 [5].

2.5 Fourier Transform Infrared (FTIR) Spectroscopic Analysis

The bioethanol distillates were characterized using FTIR (Shimadzu, FTIR-8400S). The bioethanol samples were scanned using the attenuated total reflection (ATR) technique at room temperature using 20 scans per sample with a resolution of 2 cm^{-1}.

2. 6 Data Analysis

The results of the fuel properties test and the physicochemical properties of bioethanol obtained from the two samples were compared using student T-test at 95% confidence level.

3. Results and Discussion

3.1 Physicochemical properties of the bioethanol

The results of the physicochemical measurements of bioethanol produced from rice and corn straws are presented in Table 3.1. The pH values of the bioethanol produced from rice and corn straws were 7.20 and 7.25 respectively, which are within the ASTM D6423 standard range [27]. The neutral pH recorded for both samples implies that the produced bioethanol distillate was of good quality. The specific gravity of the bioethanol from corn straw (0.8960 ± 0.007) was significantly higher than that of the rice straw (0.796 ± 0.007). The specific gravity for rice straw is within the ASTM standard (0.785 to 0.8099) while that for corn straw is slightly higher than the set limit. This means that the produced bioethanol does not have much water content and as such is suitable for use as fuel [28]. As shown in Table 3.1, the refractive index of the bioethanol produced from both substrates are similar ($p>0.05$), although the measured values are slightly less than that of the ASTM set limit of 1.36 [28]. This can be attributed to the difference in terms of feedstocks used [29]. Likewise, the colour of the two bioethanol distillates produced revealed a clear and colourless appearance, and thus confirms the characteristic appearance to be that of bioethanol.

Table 3.1: Physicochemical Properties of the Produced Bioethanol from Rice and Corn Straws

S/N	Property	Rice straw	Corn straw	P-value	ASTM Standard
1	Specific gravity	0.796±0.007	0.896±0.007	0.00006	0.794
2	Refractive index	1.3030±0.0061	1.2804±0.0514	0.52741	1.3568-1.444
3	pH	7.20±0.09	7.25±0.01	0.45	6.5-9.0
4	Colour	Colourless	Colourless		Clear without particle

SD = standard deviation of triplicate determinations

3.2 Fuel Properties of the Produced Bioethanol

The results of the fuel tests carried out on the bioethanol produced from rice and corn straws are presented in Table 3.2.The flash point of the bioethanol distillates from the two substrates are similar ($p>0.05$), but slightly higher than that of the ASTM set limit of 12-20 for bioethanol fuel ASTM D93 [5]. This implies that the produced bioethanol will be slightly less flammable than that of the bioethanol produced at ASTM standard limit. The difference may be attributed to the differences in the type of feedstock/substrates itself as reported previously [30].

The pour point of ethanol is the lowest temperature at which a liquid fuel loses its flow characterises [27]. It gives the lowest operational temperature of the fuel to determine its capability of usage in low temperate regions. From the result obtained (Table 3.2), it could be observed that the pour points of the bioethanol produced from the rice and corn straws are -4.00°C and -4.67°C respectively, which are slightly greater than that of the ASTM standard set limit of -5°C. These results suggest that the produced bioethanol can even be used in polar-regions where the temperature is less than -4°C [28]. However, no statistical significant difference was found between the two substrates ($P> 0.05$).

The cloud point is the temperature at which the cloud crystals will appear at the top of the fuel [28]. In other words, is the temperature at which solidification of heavier components of fuels resulting in a cloud of crystals within the liquid fuel first appeared [30]. The mean cloud point for rice straw is -7.47±0.35 which is lower than that of corn straw -8.20±0.10. However, the difference is not statistically significant at 95% confidence limit. The obtained values for the samples are higher than the ASTM standard limit for cloud point of bioethanol (-23°C). Thus, this implies that there is low tendency of formation of solidified waxes in the produced bioethanol, since lower cloud point indicates high tendency of formation of solidified waxes which may thicken the fuel and clogs the filters and injectors in engines.

Octane Number is another fuel property that is defined as the measure of fuel resistivity towards detonation and self-ignition [27]. In other words, it is a standard measure of the performance of an engine or the measurement of the knock resistance of fuel [6].The octane number measured for bioethanol produced from corn straw (102.67) was higher than that of rice straw (102.67). The difference between the two samples was statistically significant ($p<0.05$). However, both values are within the ASTM set limit of 96 and above, thus indicating good resistivity towards self-ignition or knock engine resistance.

Other fuel properties tested were the calorific value also known as the heating value or the energetic content of a fuel substance or food material. It is the amount of heat released during combustion of a specified amount of the fuel substance or food material [32]. The calorific values of the bioethanol produced from the two samples (rice and corn straw) are 6935.67±57.71 and 7175±116.40 respectively. The results indicate that the produced bioethanol distillates have heating values within the ASTM D 4806 acceptable specification. Furthermore, this test reveals that bioethanol produced from corn straw have higher amount of energy content than bioethanol produced from the corresponding rice straw ($p<0.05$).

3.3 FTIR Characterization

FTIR was used to identify the functional groups present in the samples. The FTIR spectra (Fig. 3.1) obtained in the present study showed similar features for both bioethanol produced from rice and corn straws. The presence of broad absorption peak between 3300 and 3500 cm^{-1} is indicative of the presence of OH group, which is usually assigned to OH stretching in alcohol [8]. The peaks at 1365 and 1080 cm^{-1} is attributed to C-O stretching and OH bending in ethanol [9].This result further confirms that bioethanol could be produced from both rice and corn straws.

Table 3.2: Fuel Properties of Bioethanol Obtained from Rice and Corn Straws

S/N	Property	Rice straw	Corn straw	P-value	ASTM Standard
1	Cloud point(°C)	-7.47±0.35	-8.20±0.10	0.07	-23.00
2	Pour point(°C)	-4.00±0.20	-4.67±0.45	0.10	-5.00
3	Flash point(°C)	20.37±0.21	20.37±0.85	1.00	93
4	Octane number	102.67±0.58	109.33±2.00	0.03	92 and above
5	Calorific Value (Kcal/kg)	6935.67±57.71	7175±116.40	0.05	6424-7094

SD = standard deviation of triplicate determinations

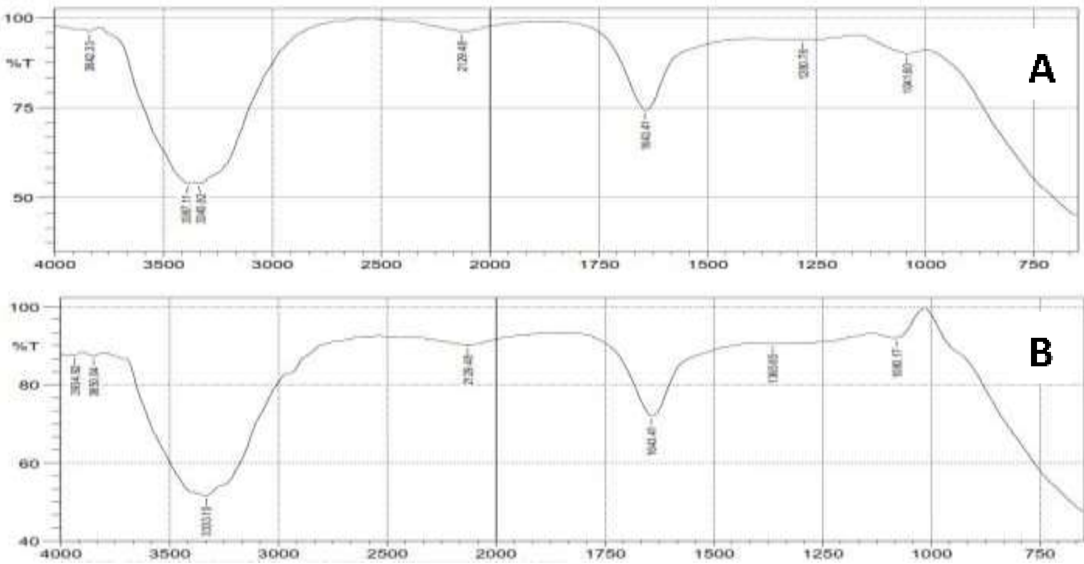

Figure 3.1: FTIR Spectra of Bioethanol Distillate Obtained from (a) Corn straw and (b) Rice straw.

4. Conclusions

This study reveals that some of the fuel and physicochemical properties *viz.* flash point, octane number, calorific value, pH and specific gravity of the produced bioethanol distillates are within the ASTM standard limit, while others (cloud and pour point, refractive index) are slightly above the ASTM standard, but does not limit the quality of the fuel and that the difference could be attributed to the difference of the feedstocks. There was no statistically significant difference between the flash point, pour and cloud point, pH, colour and refractive index of the bioethanol obtained from rice and corn straws. However, the difference observed in values obtained for octane number, specific gravity and calorific value was statistically significant. The FTIR confirms the distillates to have the functional group of bioethanol. In addition, this study reveals the substrates (rice and corn straw) as potential feedstocks for bioethanol production and an alternate source of clean quality fuel.

Reference

1. Ibrahim HAH. Pretreatment of straw for bioethanol production. Energy Procedia. 2012;14(March):542–51.
2. Idrees M, Adnan A, Bokhari SA, Qureshi FA. Production of fermentable sugars by combined chemo-enzymatic hydrolysis of cellulosic material for bioethanol production. Brazilian J Chem Eng. 2014;31(2):355–63.
3. Chen WH, Pen BL, Yu CT, Hwang WS. Pretreatment efficiency and structural characterization of rice straw by an integrated process of dilute-acid and steam explosion for bioethanol production. Bioresour Technol [Internet]. 2011;102(3):2916–24. Available from:http://dx.doi.org/10.1016/j.biortech.2010.11.052
4. Akpan W, Offiong A, Ikrang E. Energy Characteristics of Ethanol-Diesel Mix for Automotive Use. Niger J Technol. 2015;35(1):80.
5. Yusuf AA, Inambao FL. Bioethanol production from different Matooke peels species: A surprising source for alternative fuel. Case Stud Therm Eng [Internet]. 2019;13. Available from: https://doi.org/10.1016/j.csite.2018.11.008
6. Kheiralla AF, El-Awad M, Hassan MY, Hussen MA, Osman HI. Effect of Ethanol−Gasoline Blends on Fuel Properties Characteristics of Spark Ignition Engines. Univ KHARTOUM Eng J. 2011;1(2):22–8.
7. Alrikabi NKMA. Renewable Energy Types. J Clean Energy Technol. 2014;2(1):61–4.
8. Mohanasrinivasan V, Anand E, SubathraDevi C, JemimahNaine S, Karthikeyan S. Bioethanol Production from Anacardium occidentale Fruit Juiceand Preparation of Blended Fuel Using In-house Developed Bioreactor. J Appl Environ

Microbiol [Internet]. 2015;3(2):44–8. Available from: http://pubs.sciepub.com/jaem/3/2/3

9. Gebrehiwot G, Jabasingh SA, Yimam A. Production of Cellulosic Ethanol from Wood Sawdust by Sulphuric acid Hydrolysis. 2017;7(3):30–5.
10. Lee RA, Lavoie J-M. From first- to third-generation biofuels: Challenges of producing a commodity from a biomass of increasing complexity. Anim Front. 2013;3(2):6–11.
11. Nwakaire JN, Ezeoha SL, Ugwuishiwu BO. Production of cellulosic ethanol from wood sawdust. Agric Eng Int CIGR J. 2013;15(3):136–40.
12. Naik SN, Goud V V., Rout PK, Dalai AK. Production of first and second generation biofuels: A comprehensive review. Renew Sustain Energy Rev. 2010;14(2):578–97.
13. Bajpai P. Pretreatment of Lignocellulosic Biomass for Biofuel Production. Green Chem Sustain. 2016;34:86.
14. Kumar P, Barrett DM, Delwiche MJ, Stroeve P. Methods for pretreatment of lignocellulosic biomass for efficient hydrolysis and biofuel production. Ind Eng Chem Res. 2009;48(8):3713–29.
15. Lee YG, Jin YS, Cha YL, Seo JH. Bioethanol production from cellulosic hydrolysates by engineered industrial Saccharomyces cerevisiae. Bioresour Technol [Internet]. 2017;228:355–61. Available from: http://dx.doi.org/10.1016/j.biortech.2016.12.042
16. Mahlia TMI. A Review of Bioethanol Production from Plant-based Waste Biomass by Yeast Fermentation. 2017;(February).
17. Campus D, Agricultural B, Campus D. Bioethanol Production From Tofu Waste. 2017;898–908.
18. Hsu T, Guo G, Chen W, Hwang W. Bioresource Technology Effect of dilute acid pretreatment of rice straw on structural properties and enzymatic hydrolysis. Bioresour Technol [Internet]. 2010;101(13):4907–13. Available from: http://dx.doi.org/10.1016/j.biortech.2009.10.009
19. Kyong J, Seop J, Woo M, Jin H, Choi I, Hyun T, et al. Bioresource Technology Ethanol production from rice straw using optimized aqueous-ammonia soaking pretreatment and simultaneous saccharification and fermentation processes. Bioresour Technol [Internet]. 2009;100(19):4374–80. Available from: http://dx.doi.org/10.1016/j.biortech.2009.04.026
20. Singh DP, Trivedi RK. Acid and alkaline pretreatment of lignocellulosic biomass to produce ethanol as biofuel. Int J ChemTech Res. 2013;5(2):727–34.
21. Ademiluyi FT, Mepba HD. Yield and Properties of Ethanol Biofuel Produced from Different Whole Cassava Flours. 2013;2013(40).
22. Eyankware O, Ulakpa C, Eyankware MO. Determination of Cloud and Pour Point of Crude Oil with Reference to Crude Transportation. Int J Sci Healthc Res. 2016;1(3):20–8.
23. Owuama CI, Ododo JC. Refractometric determination of ethanol concentration. 1993;48:415–7.
24. ASTM International. ASTM Standard D97-05. Stand Test Method Pour Point Pet Prod [Internet]. 2005;2:1–9. Available from: www.astm.org
25. ASTM International. D0092 Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester. Annu B ASTM Stand. 2005;1–10.
26. American A, Standard N. Standard Test Method for Motor Octane Number of Spark-Ignition Engine Fuel 1. 2003;i(November):1–68.
27. Sebayang AH, Masjuki HH, Ong HC, Dharma S, Silitonga AS, Mahlia TMI, et al. A perspective on bioethanol production from biomass as alternative fuel for spark ignition engine. RSC Adv [Internet]. 2016;6(18):14964–92. Available from: http://dx.doi.org/10.1039/C5RA24983J
28. Saka AA, Afolabi AS, Ogochukwu MU. Production and characterization of bioethanol from sugarcane bagasse as alternative energy sources. Lect Notes Eng Comput Sci. 2015;2218:876–80.
29. Tangka J, Berinyuy J, Tekounegnin, Okale AN. Physico-chemical properties of bio-ethanol/gasoline blends and the qualitative effect of different blends on gasoline quality and engine performance. J Pet Technol Altern Fuels [Internet]. 2011;2(2):35–44. Available from:http://www.academicjournals.org/journal/JPTAF/article-abstract/FC28FD49552
30. AJav E a, Akingbehin O a. A study of some fuel properties of local ethanol blended with diesel fuel. J Sci Res Dev. 2002;IV:1–9.
31. Akhil AG, K MAKP, Akhilesh S, A MAC, Khan S, Kanna R. Determination of Cloud And Pour Point of Various Petroleum Products. Int Ref J Eng Sci. 2017;6(9):1–4.
32. Toscano G, Foppa Pedretti E. Calorific Value Determination of Solid Biomass Fuel By Simplified Method. J Agric Eng. 2009; 40(3): 1.