

Bioethanol Synthesis from Extracted Cashew Apple Juice and Its Application in Bioethanol-Gel Production

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Abstract

In an attempt to create accessible energy and safe cooking conditions, this investigation reports the preliminary findings on the feasibility of producing bioethanol from cashew apples and its application in producing BioEthanol Gel (BEG) for cooking activities. Bioethanol was produced from the fermentation of Extracted Cashew apple Juice (ECJ), both with the addition of baker's yeast and through spontaneous fermentation (without yeast). The fermented ECJs were distilled, and the recovered bioethanol was used for the blending of BEG with Carboxymethyl Cellulose (CMC). The physicochemical properties of the distilled bioethanol fall within established ethanol standards. The percentage of ethanol distilled by both fermented juices is similar (10.50 and 10%), while the concentration of the ethanol distilled was 60%. The optimal gel-to-bioethanol ratio of 2.80 yielded the longest combustion time of 112 s and the lowest ash residue of 0.033 g. This approach demonstrates that cashew apple juice can be effectively processed into ethanol, and that bioethanol gel offers a practical safety advantage over liquid ethanol for cooking applications.

Keywords: Bioethanol gel; Cashew apple; Caloric value; Moveable heat test; Thickener

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1. Introduction

Bioethanol is a key renewable energy source that serves as a key component in blending with petroleum products to reduce fossil fuel dependence and emissions, and also can be modified into a clean cooking fuel, which directly supports SDG 7 (Affordable and Clean Energy) by offering a bio-based, accessible, cheap, and environmentally friendly alternative. This energy source is gaining prominence in households, particularly compared to other options like solar, electricity, or LPG, especially in some parts of Africa [1 – 3]. Cooking activities are essential tasks performed by both the rich and poor to meet the nutritional, dietary, and individual preferences, and clean cooking is a central pillar of SDG 7, which aims to ensure affordable, reliable, sustainable, and modern energy access for everyone by 2030. The common traditional method of sourcing for energy used for cooking activities has raised safety concerns across the globe because, according to a World Health Organization report referenced [4], [5], about 91% of the world's population is from low-income countries that rely on firewood or its derivative (charcoal) as an energy source for cooking activities.

The safety concern emanating from the incomplete combustion of these energy sources leads to the release of harmful air pollutants, not limited to particulate matter, volatile organic compounds, and carbon monoxide. The havoc wreaked on health through the use of these traditional energy sources internationally has been reported: In sub-Saharan Africa, Particulate matter and carbon monoxide concentrations emitted from the use of firewood as a source of cooking energy are as high as 1574 $\mu\text{g m}^{-3}$ and 22 ppm, values greater than the permissible threshold [6]. A similar outcome was reported in Indonesia and Mexico [5], [7] where it was reported that exposure to firewood pollutants has a direct link to respiratory problems such as respiratory

infection, chronic obstructive pulmonary disease, and cough, and ultimately a reduction in the labor force. It has been reported that about 3.90 million deaths were attributed to the use of traditional energy sources, a figure greater than any other environmental risk and twice the amount that can be experienced in urban population air pollution inventory [5]. The women and children (born and unborn) are majorly affected by this method and control measure; cooking using the traditional cooking method was reported [8], [9]. This method will only reduce the contact of users with the method. Still, it will not eradicate the problem on a larger scale; therefore, an eco-friendly energy source for cooking activities should be sought.

Ethanol gel, a concentrated form of ethanol, suitable for cooking and heating applications, offers convenience, safety, and cleanliness compared to liquid ethanol fuels [10]. Bioethanol Gel was produced from the mixing of bioethanol with a thickener or viscosifier [11]. Some of the identified thickeners are CMC [11], calcium acetate [12], cellulose [13], carrageenan, and Carbopol. Researchers around the world have explored various formulations and production methods for BEG, aiming to optimize the performance, stability, and affordability of this biofuel utilization. Previous studies have demonstrated the feasibility and potential benefits of BEG as a sustainable cooking fuel, highlighting its role in reducing indoor air pollution and improving household energy access in underserved communities [11], [14]. The primary compounds used for ethanol are obtained from different sources.

Bioethanol is a hydrocarbon compound produced from materials rich in glucose, or that can be converted to simple sugar for onward fermentation and distillation [15]. It was reported that bioethanol production was part of 63% of energy production (biofuel) plan for 2018 towards decarbonization in the energy sector [16]. The usefulness of bioethanol in the energy decarbonization process drew attention towards its production, promoting the switch from the first generation (sugarcane, corn, or starch) to second generation production to avoid competition with the food chain [17], [18]. The second generation of bioethanol favors the use of agricultural wastes or underutilized residues that contain sufficient sugars for conversion, with or without feedstock pretreatment. Lignocellulosic materials, including agricultural residues (e.g., corn waste), forest residues (e.g., lignocellulose), and underutilized crops, have been successfully adopted for bioethanol production due to the presence of both cellulose and hemicellulose, which can be converted into fermentable sugars. A lignocellulosic feedstock is pretreated to reduce lignin content [19]. The widespread availability and relatively low cost of ethanol make it an attractive option for cooking applications, especially in regions with abundant agricultural resources.

One of the suitable wastes for the synthesis of bioethanol is cashew apple. Cashew apple is a perishable, underutilized crop residue due to its high moisture content (85 – 90%) and is rich in sugar (50 – 200 g L⁻¹ of glucose and fructose), vitamin C, and amino acids, which are important for yeast assimilation and yeast growth [20], [21]. Nigeria is among the largest producers of cashews (other countries are Brazil, India, Mozambique, Tanzania, Guinea-Bissau, Indonesia, and Vietnam) [21], Nigeria contributed to the waste generated from cashew apples because it exported 100,000 tons of cashew nuts in 2019 alone [22], while most of the cashew apples are left at the cultivation areas to rot away. The reduction in the cost of processing the feedstock, the availability of the major components that can easily be converted to bioethanol, and the availability in large underutilized quantities favor the selection of cashew apple as a potential feedstock for bioethanol production. There are investigations where juice from cashew apples was used for the production of bioethanol or alcohol with satisfactory results.

Cassava was selected as the feedstock for the production of bioethanol. The problem associated with the use of cassava was competition with food chains, and another feedstock should be explored [23]. Cassava waste was used as a bioethanol source, but it required the use of sodium hydroxide and hydrochloric acid for pre-treatment before the main operation (hydrolysis, fermentation, and distillation) [11]. In the case of juice from the cashew apple, it is underutilized, which can be channeled towards bioethanol production and does not require major pre-treatment before fermentation. In this study, the reduction of solid waste through the production of value-added products was investigated, where the report of findings of the production of BEG from bioethanol synthesis from ECJ was presented. This study is expected to establish that bioethanol gel (BEG) offers an eco-friendly heating source for cooking, and to compare its safety considerations with those of liquid ethanol.

2. Materials and Methods

2.1 Materials and Equipment for Bio-Ethanol Gel

Freshly harvested mixed varieties of cashew apples were obtained from a local cashew plantation in the premises of Ladoke Akintola University of Technology (LAUTECH), Ogbomoso, into a sealed polythene bag and transported to the laboratory. Baker's yeast and Carboxymethyl Cellulose (CMC) were obtained from a vendor, are of analytical grade, and used without further purification. The equipment used are bomb calorimeter (IKA C200), Fourier Transform Infrared Spectrophotometer (FTIR) (Infrared spectrometer Varian 660 Mid-IR Dual MCT/DTGS Bundle with ATR), and Apparent viscosity apparatus (where capillary viscometer is placed inside a temperature controlled thermostatic bath).

2.2 Cashew Juice Extraction and Fermentation Process

The collected cashew apples were thoroughly washed and squeezed manually to extract the juice [24]. The fermented ECJ was carried out using the methodologies published [25]. Two Five hundred and fifty (500) ml of the extracted cashew juice were dispensed separately into 2 different airtight bottles, while 4% (v/v) of yeast was added to the ECJ in a bottle (S1), and the second bottle (S2) was fermented spontaneously (without the addition of yeast). The two ECJs samples are fermented at 32 °C [26] while the sugar and alcohol content were monitored at 2 h interval using Brix and alcohol refractometers.

2.3 Distillation of Bio-ethanol from ECJ

The steps reported by Ige and Adeleke [24] were adopted for the distillation of the fermented ECJ. The fermented ECJ was filtered and fed into the distillation unit to distill ethanol from the liquid mixture. The mixture was heated with a heating mantle at a regulated temperature (80 °C), and the vaporized gaseous fraction was condensed through a condenser before it was collected as a liquid. The alcohol level in the distilled liquid was further tested using an alcohol refractometer.

2.4 Preparation of Bio-ethanol Gel (BEG)

Carboxylmethyl Cellulose (CMC) was used as a thickener in this study, considering its benefits as highlighted [11]. The solution was prepared by mixing 0.25 g of CMC powder and varying masses of bioethanol with 5 ml of distilled water, stirred continuously till homogeneous solution was obtained [27]. One gram (1 g) of each of the resulting BEG was then combusted. The combustion time and mass of residue were recorded. The BEG blend with the longest combustion time and least residual weight was then chosen as the optimum blend and was selected for further tests and characterization. The combustion time and residue mass were each measured three times, and the mean and standard deviation were calculated for each data set.

2.4 Characterization of Bioethanol and BEG

In the characterization of the distilled bioethanol from ECJ and BEG, three different characterization steps were followed. The first was the physicochemical analysis of the distilled bioethanol and the test conducted with their respective methodologies: Density [24], pH [28], viscosity [29], and heating value [30]. The performance analysis tests conducted on the produced BEG involve the determination of combustion time [28], residue post-burning of gel [28], viscosity [29], density [24], caloric value [30], and movable heat test [28]. The other characterization conducted was Fourier-transform infrared spectroscopy (FTIR) [31] to check the functional group present in the bioethanol and BEG.

3. Results and Discussions

3.1 Fermentation and Distillation of Bio-ethanol from ECJ

The ECJ was subjected to a fermentation process for 24 h, and the behavior of both yeast and spontaneously fermented ECJ was presented in Fig. 1. The yields of alcohol distilled for both S1 and S2 are 10.50% and 10% (by the volume fed to the distillation unit). The concentration of the distilled alcohol was 60% from the alcohol refractometer. Fig. 1 shows that the initial sugar content in the ECJ was 15, while the ethanol content was zero at the initial stage of the fermentation. The sugar content is reduced during fermentation with an increase in fermentation time. The final observable sugar content was constant at 18 h (3%), and a further increase in time did not affect the sugar reduction. The alcohol level of the yeast-fermented (S1) and spontaneously fermented ECJ (S2) was similar, with the same residual sugar content of 3% at 18 h. On the other hand, the alcohol content increased with an increase in fermentation time for both the ECJ fermented with and without baker's yeast, with a maximum alcohol content of 20% after 18 h. Further, an increase in ECJ beyond 18 h does not have any observable effect on the alcohol content of the ECJ. It was observed that the obtained alcohol content was higher; this development could be a result of interference from dissolved solids and suspended solids. The primary aim was to establish that alcohol content increased with a reduction in sugar level, regardless of the treatment that the ECJ was subjected to. The authors acknowledge that a test like HPLC or DNS would have conclusively supported the fermentation process. Also, the experiment was not sterilized before the commencement of the experiment because the interest of this preliminary study is to check if spontaneous fermentation will be sufficient for the conversion of ECJ to ethanol.

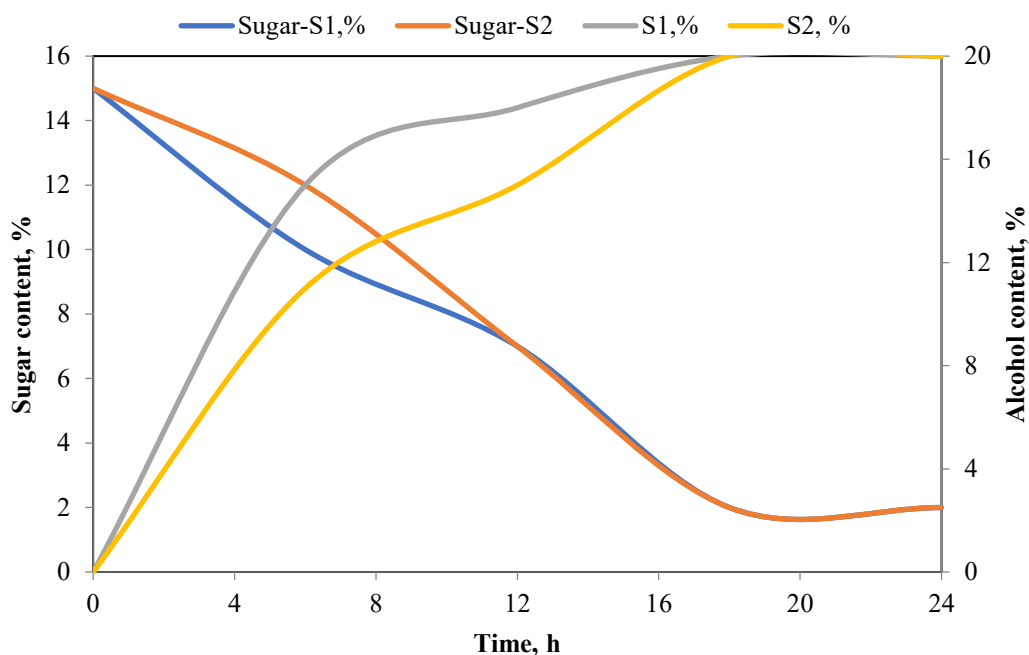


Fig. 1 The sugar content and alcohol content of the ECJ.

The percentage of bioethanol distilled from the fermented ECJ was 10.5% (for S1) and 10% (for S2) (S1 was used for the bioethanol gel production and characterization).

3.2 Characterization of the Distilled Bioethanol

The physicochemical properties of the distilled bioethanol from fermented ECJ were tabulated in Table 1. The values of the parameters considered in this investigation are favourably similar to the values obtained for bioethanol production from ECJ conducted elsewhere [24]. The result of the functional group in the distilled bioethanol was presented in Fig. 2. FTIR is used to determine the presence of functional groups in a particular substance. The functional groups present in any substance vibrate at different vibration frequencies, and functional groups are characterized at a specified vibration (that is, functional groups that represent a particular vibration will be absorbed at that dedicated frequency). In this case, the behaviour of bioethanol distilled from ECJ and bioethanol gel produced from the gel when Infrared was passed through them was presented in Fig. 2.

Table 1 Physicochemical properties of the distilled bioethanol.

Parameter	This Study	Ana et al. [24]
pH	4.78	5.33
Dynamic viscosity@20°C, mPa-s	1.733	2.88
Caloric value, MJ Kg ⁻¹	29.07	27.73
High Caloric value, MJ kg ⁻¹	31.32	

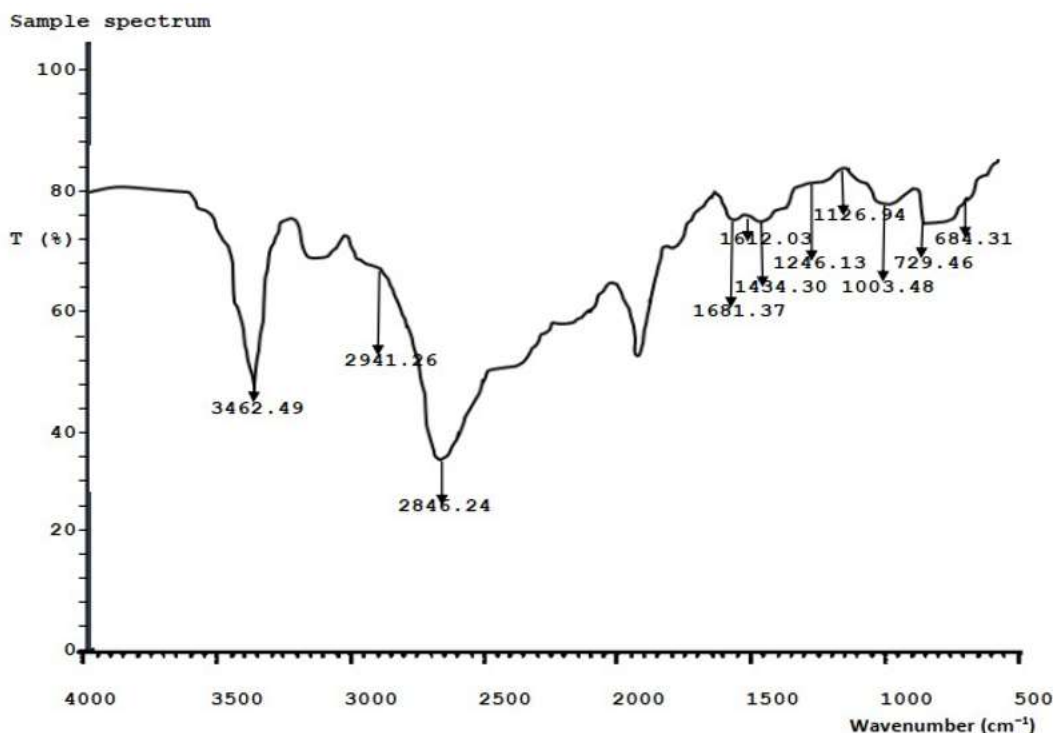


Fig. 2 FTIR spectrum of the distilled bioethanol.

In the bioethanol sample, the identified vibrations are hydroxyl (-OH), alkane (-CH), aldehydes (C=O and CH), aromatic (C=C), phenol (C-O), and alcohol (C-O). The functional groups are at the following wavelengths: hydroxyl group vibrated at 3462.49, 1241.13, and 1126.94 cm^{-1} which denotes the presence of alcohol, stretching alkane vibration was observed at a wavelength of 2941.26 cm^{-1} , stretching and conjugated aldehyde vibration were observed at 2846.21 cm^{-1} (C-H) and 1681.37 cm^{-1} (C=O), medium to weak aromatic vibration were observed at 1612.03 and 1434.3 cm^{-1} (C=C). Organic and inorganic vibrations were observed at wavelengths 1003.48 and 729 cm^{-1} . Some of the functional groups identified in our work were reported to be important to the characterization of bioethanol in previously reported bioethanol distilled from different biomass, such as marine microalgae [32], Saudi Arabia dates[33], and rotten watermelon and banana[34], rice and corn straw [35]. In all these investigations, the common functional groups are hydroxyl (OH), alkane (CH), and aldehyde (CO) in varied intensities.

3.3 Determination of Best BEG Blend

It was established that 4.50% of CMC was the best concentration for a bioethanol gel blend[11]. The bioethanol source considered in the research was from cassava, and the investigation failed to check the effect on the concentration of bioethanol in a fixed quantity of gel used for blending. The effect of varying the bioethanol blend with a fixed quantity of gel is presented in Table 2. The sensitivity was conducted for combustion time [28] of the BEG blend produced by varying the gel-bioethanol blend between 1 and 3. It was observed from the table that an increase in the volume of bioethanol blended with CMC increased the combustion time from 47 – 112 s. While the combustion time increased with an increase in the volume of bioethanol in the bioethanol gel, the mass of residue decreased from 0.0757 – 0.03367 g with an increase in the bioethanol-gel blend from 1 – 3. The obtained values at runs 4 and 5 are similar despite the slight increase in the bioethanol content in both experimental runs. The combustion time and residue of run 6 (CMC concentration of 3.50% and bioethanol-gel ratio of 2.80) are both inferior to the values obtained at gel-bioethanol of 3. It can be observed that the higher the ethanol concentration, the longer the combustion time and the less the residue left unburnt. The effect of bioethanol mass in all 6 different bioethanol gels does not affect the quality of the color of the flame produced from the respective BEG. Run 4 was selected as the best run in this investigation because it has the longest combustion time of 112 s and the least residue of 0.033 g at the lowest volume of

bioethanol (The mass of gel was kept constant while the mass of ethanol was varied for the six experimental runs). Run 4 was selected as the best run in this investigation and was used for further analysis or discussion going forward.

Table 2 Effects of variation of ethanol and CMC on the combustion characteristics of ethanol gel.

Run	Bioethanol ratio: Gel (g/g)	Combustion Time (s)	Residue (g)	Flame Color
1	1	47.5 ± 0.50	0.0757 ± 0.00116	Blue
2	2	91.03 ± 0.76	0.0553 ± 0.0022	Blue
3	2.40	95.0 ± 0.92	0.0464 ± 0.00053	Blue
4	2.80	112.33 ± 0.58	0.03367 ± 0.00116	Blue
5	3	112.33 ± 0.58	0.03367 ± 0.00116	Blue
6	*2.80	86.25 ± 0.71	0.0430 ± 0.0020	Blue

*The concentration of CMC was reduced from 4.50 – 3.50% for that run

3.4 Performance Parameters of the Produced Bio-ethanol Gel

Further tests were carried out on the chosen best fuel gel to determine its physicochemical properties. Bioethanol is a water-soluble, colorless, volatile, and combustible compound that requires a substance that will reduce its volatility without compromising its physicochemical behaviours, and that was the role of the gel prepared from CMC played in this study. The physicochemical properties of bioethanol increased with the blending of the bioethanol with CMC, as shown in both

Table 1 and Table 3. The caloric value of the bioethanol gel was 44.83 MJ kg⁻¹, as against the caloric value of bioethanol, which was 31.32 MJ kg⁻¹. The increase in caloric value of the bioethanol gel was attributed to the presence of carbon and hydrogen content in CMC. Also, combustion requires the combination of carbon and oxygen for the production of heat; the more the carbon content (from ethanol and CMC), the more the observed caloric value of bioethanol gel combusted. These findings are in line with the results observed from previous investigations related to bioethanol gel produced from different ethanol sources [11, 27, 28]. The obtained caloric value shows that the bioethanol gel produced has a fuel quality and higher combustion efficiency when compared with the values obtained for bioethanol.

Table 3 Performance properties of bio-ethanol gel.

	This study	Az-Zahra et al. [28]	Princewill et al. [14]	Amalia et al. [11]
Combusted weight	1 g	1 g	60 ml	4.50
Combustion time, s	112	180	28	
Residue, g	0.033	0.03	0.40	<0.05
Viscosity@20 °C, mPa·s)	2389			1338
Heating value, MJ kg ⁻¹	42.58	29.62		
High heating value, MJ kg ⁻¹	44.83	33.06		5000 Kcal Kg ⁻¹

It was a fact that bioethanol combusted when in contact with oxygen, and a BEG blend that will promote combustion without change in color, while all physicochemical properties are not compromised in the process of elongating the time it requires for bioethanol to burn. The color of the BEG flame produced from this study is presented in . The flame color was blue, and the combustion time of 1 g of bioethanol gel was 112 s, as shown in Table 3. Blending of bioethanol with a CMC gelling agent increased the combustion time of BEG and was also related to the residue ash content after completion of combustion of the bioethanol gel. The elongation of the burning time was a result of the evaporation of bioethanol blended with CMC, and the bioethanol content will slowly react with oxygen, thereby elongating the time it takes for oxygen to combust the total volume of bioethanol in the gel.



Fig. 3 Flame color of the produced BEG.

The residue ash content of the gel was low after the combustion of the bioethanol gel. From Table 3, it was observed that residue ash content is affected by the concentration of both the gel and bioethanol used for the bioethanol gel blend. For the selected bioethanol gel, the residue content was 0.033 g. Residue content is an important performance parameter that was linked to the thickener used for bioethanol production. CMC is a non-flammable compound that obviously burns with ash content as the residue; the presence of carbon in its chemical configuration supported combustion and led to the generation of burnt residue, which was expected to be low in order not to create another environmental problem (generation of solid residue). The value of the obtained residue content was similar to the residue ash content reported [11], [29]. Residue ash content of 0.03 g was recorded, where Carbopol was used as thickener, while a value less than 0.05 g was presented in a similar investigation where CMC was the source of the thickener used for the BEG produced.

The presence of the thickener, Carboxymethylcellulose (CMC), a colorless, odorless, and non-toxic gelling agent when dissolved in water [11] enhanced the properties of the BEG produced such as combustion time, ash content, calorific value, and density compared to other samples using another gelling agent such as Carbopol, and its price is considered more economical [36].

3.5 FTIR Analysis of BEG

In the case of BEG (Fig. 4), the observed vibrations are hydroxyl (OH), alkane (CH), alkene (C=C), aromatic (C=C), amide III (C-N), and ether (C-O-C). The OH vibrations are observed at wavenumbers 3245, 1125, and 1051 cm^{-1} ; alkene was observed at 1639 cm^{-1} ; aromatic vibration was observed at 1534 cm^{-1} ; ether vibration was observed at 1210 cm^{-1} , and amide vibration at 1248 cm^{-1} . Amide, ethane, and ether vibrations were not observed in the bioethanol distilled, but can be found in the BEG, while ketone, phenol, and aldehyde vibrations appeared in the distilled bioethanol but disappeared in the BEG produced.

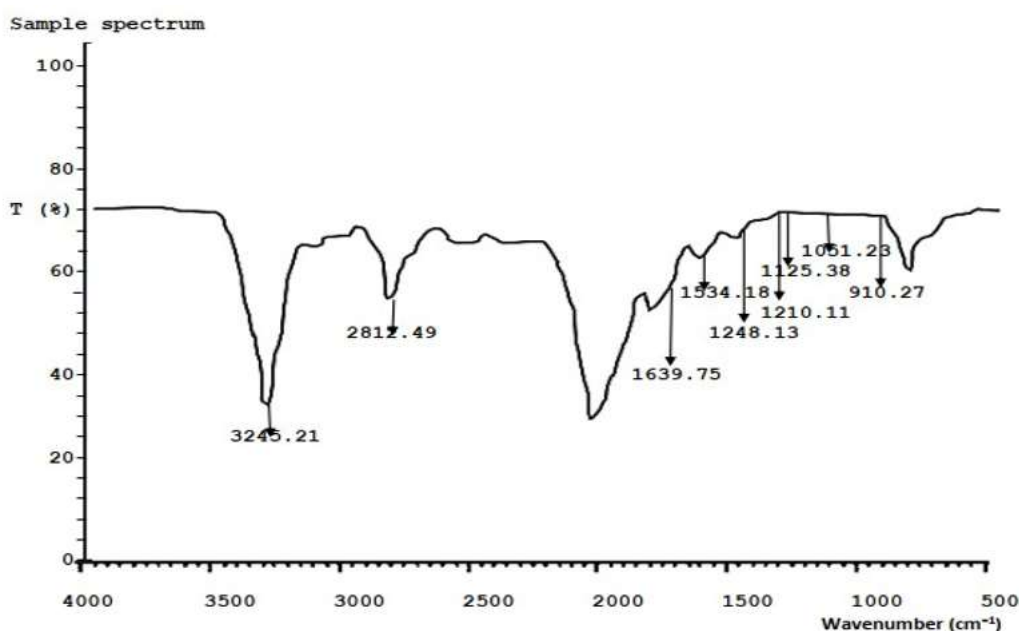


Fig. 4 FTIR spectrum of the BEG.

3.5 Movable Heat Test

A movable heat test is a water boiling test that determines the time it takes a 15 g bioethanol gel to elevate the temperature of 100 ml of water from its ambient temperature [28]. The result of the MHT test of the bioethanol gel was tabulated in Table 4. The temperature was noticed to increase from the heating process with the initial water temperature of 33 °C. The result of the heating test showed that the initial temperature of the water was raised by 23 °C in 1 min 41 s, which is faster and better than the result of MHT presented by Az-Zahra et al. [28], where the temperature of the water was increased from ambient temperature by 25 °C in 3 min and 59 s, and Carbopol was used as a gelling agent in their investigation.

Table 4 Result of MHT of the Produced BEG.

Study	Weight of BEG (g)	Volume of Water (ml)	Initial Water Temp. (°C)	Final Water Temp (°C)	Heating Time (s)
This study	15	100	33	56	101
Az-Zahra et al. [28]	15	100	25	50	237

4. Conclusion

This study demonstrates that ECJ can be fermented with or without baker's yeast, and the resulting distilled ethanol exhibits physicochemical properties that comply with established ethanol standards. The optimal bioethanol-gel ratio of 2.80 produced the longest combustion time of 112 s and the lowest ash residue of 0.033 g. Additionally, the modified hot time (MHT) of the synthesized bioethanol gel was notably faster, raising the temperature of water by 23°C in just 1 min and 41 s. This approach not only shows that waste cashew apple juice can be effectively processed into ethanol but also highlights that ethanol gel offers a practical safety advantage over liquid ethanol.

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