

Production of Bioethanol Gel from Sugar Cane Waste with Carbopol as Alternative Fuel

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Abstract: Bioethanol gel is an alternative fuel innovation with gel form, that ease packaging and distributing process. Bioethanol gel is modified bioethanol with carbopol as the thickening agent. Based on the result of the study, bioethanol gel as alternative fuel can be produced by hydrolyzing sugar cane waste and fermented with Saccharomyces cerevisiae for 4 days, producing bioethanol gel with 95% grade. Carbopol as thickening agent was added to bioethanol from sugar cane waste, producing bioethanol gel. Best result obtained with the variation of carbopol 1,8 g and NaOH 1 mL resulted to flowing gel. Characteristics of bioethanol gel are: flare time 237 seconds, residue 0,03 g, calorific value 33.064,25 kJ/kg, and 5 g of bioethanol.

1 INTRODUCTION

Indonesia is a country with high energy consumption in the world. Energy source that take the first place in consumption rank is petroleum which is a non-renewable energy source. One of the petroleum derivatives that are widely used in small industries and households is kerosene (paraffin).

At present government is trying to divert the use of kerosene to other fuels, such as gas. But this diversion has encountered many obstacles. For example, the number of fire cases because leaked gas from the tube. Therefore the conversion of kerosene does not have to be to gas fuel but also to another energy source, such as bioethanol which is more environmentally friendly and does not endanger the environment.

But bioethanol also has weakness in its physical properties. Bioethanol is volatile, have low surface tension, and low flash points. Causing bioethanol in liquid form can be dangerous (Robinson, 2006). For this, we need to modify the form of bioethanol. Bioethanol gel is a potential innovation for further development. The gel form ease packaging and distribution process. In production of bioethanol gel, thickener is needed in the form of powder such as calcium acetate, or other thickener such as xanthan gum, carbopol and various cellulose derivative materials (Tambunan, 2008).

Bioethanol gel has several advantages. They are easy to handle, packed, and stored for it does not easily spill and flow. Some advantages over other fuels where during combustion are not smoky, do not cause soot, and do not produce harmful gases. Bioethanol gel is non-carcinogenic and non-corrosive (Merdjan and Matione, 2003). Bioethanol gel innovation offers its own advantages over liquid forms of bioethanol both in terms of economy and security. Based on research conducted by Hanun (2018), states that bioethanol gel is more economical than paraffin.

Bioethanol gel provides a solution to the safety of the application of household energy use because it does not easily spill and evaporate (Lloyd and Visagie, 2007). Because bioethanol gel has more advantages compared to liquid bioethanol, the researchers hope to use bagasse as a source of carbohydrates that can be fermented into bioethanol and the addition of carbopol as gelling agent in the production.

2 MATERIALS AND METHODS

2.1 Materials

The materials used in this study include: bagasse, 3.5% HNO₃, NaNO₂, 2% NaOH, 2% Na₂SO₃, aquadest, 1.75% Na-Hypochlorite, 17.5% NaOH,

iodine solution, HCl 30%, 10% NaOH, benedict solution, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, KH_2PO_4 , $(\text{NH}_4)_2\text{SO}_4$, bread yeast, carbopol, NaOH 1N, soil oil, spiritus and gasoline.

2.2 Procedure

2.2.1 Bioethanol Making

Cellulose Isolation.

75 g of bagasse was putted into a beaker glass. Then 1000 mL of 3.5% HNO_3 and 10 mg NaNO_2 were added. The mixture is heated by thermostat for 2 hours at 80°C . Then filtered and the residue was washed with distilled water to $\text{pH} = 7$. To the residue, 375 mL of 2% NaOH and 375 mL of 2% Na_2SO_3 was added. The mixture was heated by thermostat for 1 hour at 50°C . Then it's filtered and washed with distilled water to $\text{pH} = 7$. The residue was added with 500 mL of Na-Hipochlorite 1.75%, then heated using a thermostat for 30 minutes at 100°C which then was filtered and washed with distilled water to $\text{pH} = 7$. 500 mL of NaOH 17.5% was added and heated by thermostat for 30 minutes at 80°C . Then filtered and washed the residue with distilled water to $\text{pH} = 7$. To the residue was added 500 mL of 1.75% Na-Hipochlorite and heated for 5 minutes at 100°C . It was filtered and washed with distilled water to $\text{pH} = 7$. After that the residue was dried in the oven at 60°C then let it cooled down in desiccator. Enough cellulose is putted onto a drip plate and then dripped with iodine 0.1 solution which will show positive cellulose test if there is no color change and FTIR analysis is performed.

Cellulose Fermentation.

0.5 g of cellulose bagasse was putted into a 250 mL erlenmeyer glass and 5 mL of distilled water was added. 8 mL of 30% HCl was added to the mixture. Erlenmeyer was covered with cotton and aluminum foil before it was heated in thermostat at 80°C for 1 hour. The mixture was cooled to room temperature, 10% NaOH was added to get $\text{pH} = 4-4.5$, and then filtered. 1 mL of filtrate was piped into a test tube and 5 mL of Benedict's solution was added. It was heated in a thermostat to form red brick deposits.

100 mL of glucose solution from hydrolysis of bagasse was poured into a 250 mL Erlenmeyer glass. 0,1502 g of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$; 0,1306 g of KH_2PO_4 ; and 1,2021 g of $(\text{NH}_4)_2\text{SO}_4$ was added. The mixture was sterilized using autoclave at 121°C for 1 hour and then cooled. Bread yeast was added as much as 6 grams. Fermented for 2, 4, and 6 days. The

fermented product was then distilled at 78°C and tested for ethanol using an alcohol hydrometer.

2.2.2 Making Bioethanol Gel

Thickener was added to bioethanol which has been obtained from bagasse to form bioethanol gel. 100 mL of bioethanol was poured into a beaker glass and stired with a speed of 1000 rpm, while 1.2 grams of carbopol was added slowly. The glass beaker was covered and the mixture was stirred continously for 45 minutes. Then 1 mL of 1 N NaOH is added to form the bioethanol gel. The same experiment was conducted with variation amount of carbopol (0.8 gr, 1 gr, 1.4 gr, 1.6 gr, and 1.8 gr) and 1 mL of NaOH.

2.3.3 Characterization

Stability and Flame Color Test for Bioethanol Gel.

5 grams of bioethanol gel was takken and putted into a porcelain dish and then burned. The color and flame of bioethanol gel combustion were observed and recorded.

Ignition Time Test.

1 and 5 grams of bioethanol gel was putted into a porcelain dish. Stopwatch was turned on when the attempt to burn bioethanol gel was performed and turned off when the flame appear.

Burned Bioetanol Gel Weight Test.

5 grams of bioethanol gel was putted into a porcelain dish and then burned until the gel cannot burn again (remaining ash and other solids). The residue then weighed, where the weight of the bioethanol gel that burns is the different between initial weight and final weight.

Heat Test.

Testing of heat value refers to Robinson (2006), carried out to determine the level of heat produced by each sample of bioethanol gel in units of calories (cal). The first step to measure the heating value was, bioethanol gel was burned in the C200 Kalorimeter Bomb where the combustion product is then cooled again to reach room temperature. The energy used to cool combustion products is equivalent to the energy available in fuel.

Movable Heat Test.

The transferred heat test or water boiling test was done to determine the effectiveness of the fuel in reference to Robinson (2006). Movable heat can be measured by inserting 100 mL of water into a beaker

glass and the initial temperature was measured. 15 g of bioethanol gel was putted into a porcelain then burned to heat 100 ml of water in a beaker glass. After boiling water, the heat transferred is calculated by calculating how much gel bioethanol is used for this process.

3 RESULTS AND DISCUSSIONS

3.1 Bioethanol Making

3.1.1 Cellulose Isolation

Isolation of cellulose bagasse through several stages. Starting from the delignification stage with addition of HNO₃ and NaNO₂, at this point impurities from bagasse are removed and cellulose was produced. Then proceed with pulping with NaOH and Na₂SO₃ with 1: 2 ratio, this process is delignification (removal of lignin) and will produce yellowish-white cellulose. For the removal of dyes on cellulose, bleaching with NaOCl is carried out. Hypochlorite ions which are strong oxidants will break ether bonds in lignin structure, consequently the color of cellulose pulp becomes white. To produce pure α-cellulose, 17.5% NaOH was added to dissolve β-cellulose and produce α-yellowish white cellulose. In other words, bleaching is needed to produce white α-cellulose.

The result of cellulose isolation from bagasse is white pulp, which 75g of bagasse is produced 10g α-cellulose. The cellulose obtained was tested qualitatively with iodine solution and showed positive results with no color change.

The FT-IR spectrophotometric test results also showed positive results by comparing wave number of bagasse cellulose and commercial cellulose. Figure 1 is the result of FT-IR spectroscopic test which shown spectrum with vibration peak in area of 3448.72 cm⁻¹ for -OH group, supported by emergence of vibrational peaks at wave number 2900.94 cm⁻¹ which shows C-H stretching groups, 1064, 71 cm⁻¹ which shows the ether group, and the glycoside bond in α-cellulose structure is found at wave number 1635.64 cm⁻¹ (Epriadi, 2017). Figure 1. showed that the results of FT-IR cellulose bagasse had similar wave numbers with commercial cellulose. Research on cellulose isolation has been carried out by several researchers including: coconut palm petiole (Xu et al., 2015), groundnut shells (Bano and Negi, 2017), and corncob (Gea, 2019).

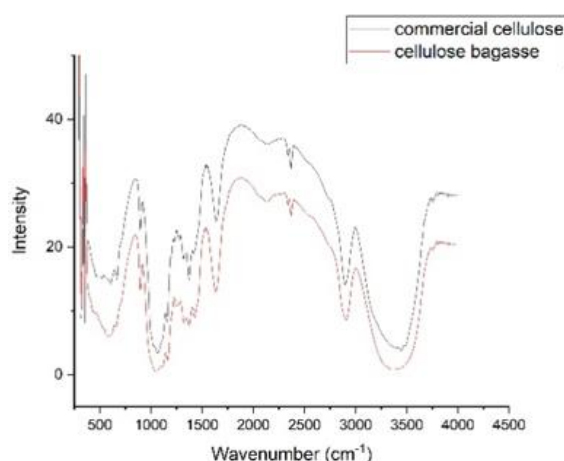


Figure 1: The spectrum of sugarcane pulp and commercial FT-IR cellulose.

3.1.2 Cellulose Fermentation

Obtained cellulose bagasse pulp is hydrolyzed with strong acid (HCl) for breaks the polymerization chain of cellulose into a monomeric unit glucose. The hydrolyzed cellulose is then neutralized by adding NaOH to pH 4–4.5. Neutralization was done to eliminate high residual acid from hydrolysis process so that a standard product is obtained at pH = 4–4.5. It is the optimum pH of *Saccharomyces cerevisiae* growth (Oktavia, 2013).

Table 1: Cellulose fermented bagasse.

Fermentation Time (Day)	Bioethanol Level (%)
2	9,6
4	18,2
6	10,4

The data above shown optimum time to produce bioethanol was until the 4th day. It's also shown in Irvan (2015)'s study, that the optimum day to produce bioethanol from bagasse was day 4 with 8 gram yeast producing 22.63% of ethanol.

The longer fermentation time, the more *Saccharomyces cerevisiae* cells multiply and more ethanol content is produced. This was a result of longer time make more number of active bacteria, multiply the ability to break substrate (Oktavia, 2013). However, on the 6th day *Saccharomyces cerevisiae* has died and the substrate to be consumed has been reduced.

Distillation in this study was carried out three times. By using simple distillation, the distillation will produce bioethanol for the first time with levels of 10–20% and 50–70% at second attempt.

Therefore, to get 90–95.5% levels, three repetitions of distillation are performed. After being distilled, the sample that was originally white will change color to clear and the aroma of alcohol is smelled.

3.2 Making Bioethanol Gel

Bioethanol gel is produced by mixing with carbopol and NaOH with slow stirring. The gel produced is clear, in this case carbopol only acts as a gelling agent without giving a color change to biethanol (Wibowo, 2010). Addition of NaOH functions is to neutralize acidic carbopol (Yogesthinaga, 2016).

The best bioethanol formulation is by adding 1.8 g of carbopol and 1 mL of NaOH. The form is thicker than other variations. The bioethanol produced can be seen in Figure 2.



Figure 2: Bioethanol gel.

3.3 Characterization

3.3.1 Stability and Flash Color Test for Bioethanol Gel

According to Turns (2000), fire is a continuous heat spread which is carried out by itself in a combustion zone that is localized at very high speeds. One characteristic of hydrocarbons combustion is appearance of blue flashes in the zone of rapid combustion in excess air conditions.

In the burning process, a good fire gives blue color. Red color is produced due to incomplete combustion process (Dewi, 2018). The flame of bioethanol gel (Figure 3) is blue with an unstable yellow to red tinge, and long-flaring flame. The red tinge increases with addition of carbopol and NaOH concentrations. According to Nugroho (2016), this caused by combustion without intermediaries so the fire seemed unstable. Turns (2000) also explained, a long and flaming fire caused by combustion conditions that are rich in fuel or the availability of oxygen needed is not appropriate.

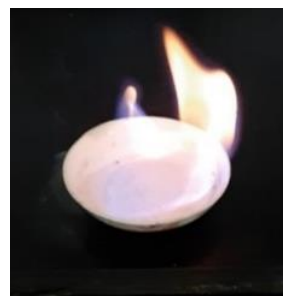


Figure 3: Bioethanol gel flame color.

3.3.2 Ignition Time Test

The combustion time test aims to see the ability of bioethanol gel to burn until only part that cannot be burned again remains and is calculated for a long time until the fire is completely extinguished. The results of measurement of combustion length of bioethanol gel are presented in Table 2 and 3.

Table 2: Length of ignition test of 1 gram bioethanol gel.

Variation of NaOH (mL)	Variation of Carbopol (g)	Length of Ignition (seconds)
1	0,8	88
	1,0	95
	1,2	101
	1,4	109
	1,6	120
	1,8	180

Table 3: Length of ignition test of 1 gram bioethanol gel.

Variation of NaOH (mL)	Variation of Carbopol (g)	Length of Ignition (seconds)
1	0,8	180
	1,0	198
	1,2	215
	1,4	224
	1,6	233
	1,8	237

Data shown the best bioethanol gel burning time is 239 seconds (3 minutes 59 seconds) on the addition of 1.8 gram carbopol and 1 mL NaOH. From data, it can be concluded that more carbopol and NaOH additions able to withstand the burning rate of bioethanol gel.

Presence of carbopol and NaOH is a retaining factor so that the combustion becomes longer. Increased concentration of carbopol extend the flame because the vapor of bioethanol is trapped in carbopol and released slowly, makes it run out longer. When compared with liquid bioethanol, it can be seen that bioethanol gel has increased the

burning rate for a few seconds so it can be said that the evaporation of bioethanol is inhibited by the carbopol. Dewi (2018), has examined bioethanol gel and get the same results; ignition period is increased by addition of carbopol (1.5–2) grams.

3.3.3 Burned Bioethanol Gel Weight Test

This test is done to find out how much residue is produced. Residue is a part of fuel that not completely burn and left behind after the combustion, changes, or reactions are complete. The residual test results are presented in Table 4.

Table 4: Test for residual results.

Variation of NaOH (mL)	Variation of Carbopol (g)	Residue (g)
1	0,8	0,01
	1,0	0,01
	1,2	0,02
	1,4	0,02
	1,6	0,02
	1,8	0,03

The remaining residue is the amount of carbopol contained in the bioethanol gel which is ensnared together with in the form of a gel, the dried carbopol crust is brownish yellow. The data above shown varies of residue produced in burning process.

Wibowo (2010), stated that the more carbopol added to 70% ethanol caused the residue to increase, but this result was different in the bioethanol treatment with 95% concentration. Based on the results of the study, the increasing concentration of ethanol produces fewer residues.

3.3.4 Heat Test

Calorific value is the most important quality parameter for bioethanol gel as fuel. Calorific value is the amount of heat energy stored in fuel produced through combustion reactions. In fuel, the higher calorie value possessed, the better quality of fuel and higher combustion efficiency.

In this test, the best formulations were measured from length of ignition. The calorific value obtained from the measurement of the bioethanol gel calories with the Calorimeter Bomb. The data are presented in Figure 3.

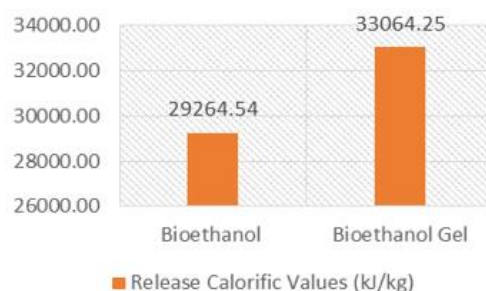


Figure 3: Heat Value Test.

Calorific value is closely related to the composition of carbon bound to a fuel. The higher carbon bound gives higher calorific value (Yulistina, 2001 in Oktavia, 2013).

From the results of measurements using Calorimeter Bomb, bioethanol gel heating value was higher than liquid bioethanol. This is due to addition of carbopol as a thickener, where carbopol is a thickener of Lubrizol production with a molecular formula $(C_3H_4O_2)_n$ and has an active group of polyacrylate acid that increased the calorific value (Dewi, 2018).

3.3.5 Movable Heat Test

A water boiling test is a test that determines the performance of bioethanol gel so it can be used as a household fuel. In this water boiling test, not all bioethanol gel formulas were used, but the best samples were taken, namely the addition of carbopol 1.8 g which was then compared with other fuels such as: spiritus, gasoline and kerosene. Heat transfer data can be seen in Figure 4.

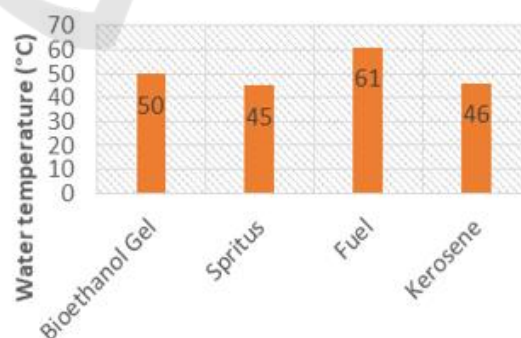


Figure 4: Heat transfer test.

In this test we use the same weight of all materials, then measuring the temperature increased from the heating process with the initial temperature of water 25°C. The results of testing heat transfer can be concluded that bioethanol gel is able to

increase the temperature better than spiritus and kerosene but not compared to gasoline. In addition, bioethanol has other advantages, which are odorless and do not cause soot in process. The practical use of bioethanol gel is directly burned, unlike other fuels that use intermediaries such as axes (Nugroho, 2016).

4 CONCLUSIONS

Based on the results of the research it can be concluded that bioethanol gel as an alternative fuel can be produced from hydrolysis of bagasse pulp and then fermented with *Saccharomyces cerevisiae* for 4 days and adding carbopol as thickener. The best results were obtained with variations of carbopol 1.8 g and 1 mL NaOH with gel flowing forms. The characteristics of the bioethanol gel were: flame length 239 seconds (3 minutes 59 seconds), residue 0.03 g, heating value 33.064,25 kJ / kg, and 5 g bioethanol gel can raise the water temperature to 50 °C.

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REFERENCES

- Bano, S., Negi, Y. S., 2017. Studies on cellulose nanocrystals isolated from groundnut shells. *Carbohydr. Polym.* 157, 1041–1049.
- Dewi, R. K., Poespowati, T., Jimmy, 2018. Natrosol sebagai Salah Satu Bahan Pengental (Thickener) pada Produksi Bioetanol Gel dari Limbah Daun Tebu. *Indones. Chem. Appl. J.* 2, 1–6.
- Epriadi, R., 2017. Isolasi Nanoserat Selulosa dari Tandan Kosong Sawit (*Elais guinensis* jack) dengan menggunakan Tempo. Universitas Sumatera Utara.
- Gea, S., 2019. The Preparation of All-Cellulose Nanocomposite Film from Isolated Cellulose of Corncoobs as Food Packaging The Preparation of Cellulose Nanocomposite Film from.
- Hanun, V., Sutjahjo, D., 2018. Komparasi karakteristik bioetanol gel dengan pengental karbopol dan carboxymethyl cellulase (CMC) sebagai bahan bakar alternatif. *Tek. Mesin.*
- Irvan, Prawati, P., Trisakti, B., 2015. Pembuatan Bioetanol dari Tepung Ampas Tebu Melalui Proses Hidrolisis Termal dan Fermentasi: Pengaruh pH, Jenis Ragi dan Waktu Fermentasi. *Tek. Kim. USU* 4, 27–31.
- Lloyd, P. J. D., Visagie, E. M., 2007. A comparison of gel fuels with alternative cooking fuels 18, 26–31.
- Merdjan, R., Matione, J., 2003. Fuel Gel [WWW Document]. United State Patents Appl. Publ.
- Nugroho, A., Restuhadi, F., Rossi, E., 2016. Pembuatan Gel Etanol dengan Menggunakan Bahan Pengental Carboxymethylcellulose (CMC). *Jom Faperta* 3.
- Oktavia, T., Sumiyati, S., Sutrisno, E., 2013. Pemanfaatan Limbah Cair Cucian Beras sebagai Bahan Baku Pembuatan Bioetanol Padat Secara Fermentasi oleh *Saccharomyces cerevisiae*. Universitas Diponegoro.
- Robinson, J., 2006. Bioethanol as a household cooking fuel: a mini pilot study of the superblu stove in peri-urban Malawi. Loughborough University.
- Tambunan, L., 2008. Bioetanol Anti Tumpah 39, 24–25.
- Turns, S., 2000. An Introduction To Combustion: Concept And Applications, 2nd ed. McGraw-Hill Book Company Singapore, Singapore.
- Wibowo, W. A., Mulyono, T. S., 2010. Pembuatan dan Uji Pembakaran Ethanol Gel. *Ekuilibrium* 9, 67–71.
- Xu, C., Zhu, S., Xing, C., Li, D., Zhu, N., 2015. Isolation and Properties of Cellulose Nanofibrils from Coconut Palm Petioles by Different Mechanical Process 1–11.
- Yogesthinaga, Y., 2016. Optimasi Gelling Agent Carbopol dan Humektan Propilen Glikol dalam Formulasi Sediaan Gel Ekstrak Etanol Daun Binahong (*Anredera cordifolia* (Ten.) Steenis). Universitas Sanata Dharma.