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Bioconversion and valorization of cassava-based industrial wastes to bioethanol gel and its potential application as a clean cooking fuel

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ABSTRACT

Bioethanol gel is gaining more attention for clean cooking fuel as green technology and partial replacement of burning the biomass for cooking purposes. The conversion of tapioca flour wastes to bioethanol and its production to bioethanol gel have not been performed. Tapioca flour industrial wastes are rich in sugar, and promising for the low-cost biomass for bioethanol production. The production of bioethanol from cassava peels and cassava pomace (*onggok*) and its bioethanol gel formulation were performed in this study. The research was carried out by treating tapioca starch wastes with pretreatment and hydrolysis, continued by applying eight fermentation treatments, and the bioethanol yields were analyzed quantitatively. Then, the bioethanol gel was formulated. The viscosity, calorific value, burning time, flame color, and ash content of the bioethanol gel were analyzed. It can be concluded that cassava-based industrial wastes were successfully converted to bioethanol with a 35% yield resulting in a 25% bioethanol concentration at a 2.64 g/L per h conversion rate. The efficiency of bioconversion was 86%, and reflux column distillation could increase the bioethanol concentration to 92%. Carboxymethyl cellulose (CMC) was an effective gelling agent and improved the viscosity at 1.338 mPa.s and burning time to 184 min. The ash content of all samples was lower than 5%, meaning that it is promising for further application as a household cookstove fuel.

1. Introduction

Cooking is essential in life, and there are still approximately 2.4 billion people in the world who rely on biomass such as firewood, charcoal, and crop residues as the primary source for traditional cookstoves (Rehfuess, 2006). Bioethanol production is now gaining attention because of its potential as green technology and partial replacement of burning the biomass and fossil fuels to reduce greenhouse gas emissions, inefficient combustion, and deforestation only for cooking purposes (Murphy and Kendall, 2015; Öhgren et al., 2007; Oketch et al., 2012; Rehfuess et al., 2006). Bioethanol gel is a clean cooking fuel and has several advantages, such as non-smoky, non-volatile, burns slowly with a high heat output, and its high viscosity minimizes the danger of its distribution to avoid an accidental spillage (Hermawan and Sudarmanta, 2018; Oketch, 2014). Bioethanol gel has shown great potential to meet household cooking needs and is now becoming popular in the community since it reduces the drawbacks of liquid ethanol for

distribution and utilization. Also, it is suitable for cooking, heating for fast food in restaurants, traveling, and catering (Ariyani, 2013; Hermawan and Sudarmanta, 2018). Moreover, the conversion of liquid bioethanol to the gel form is easy by adding a thickener agent, such as a carbopol and carboxymethyl cellulose (Ariyani, 2013).

One of the efforts to maintain bioethanol availability is converting lignocellulosic wastes to bioethanol using the fermentation technique. The green bioethanol production by fermentation method usually employs *Saccharomyces cerevisiae*, *Zymomonas mobilis*, and *Pichia stipitis* (Cha et al., 2012; Inal & Yiğitoğlu, 2011). In this technique, the raw materials are usually obtained from sap, sugar palm, sweet potato, cassava, bamboo, rice straw, bagasse, and corn cobs. However, non-edible biomass is preferred to reduce the competition with food production. Therefore, some bioethanol productions recently used agro-industrial wastes, including cassava peels, banana peels, pineapple peels, and flour industrial wastes (Baeyens et al., 2015; Binod et al., 2010; Lee et al., 2012; Yang et al., 2019).

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In this case, the flour industrial wastes are favorable since the world demand for tapioca flour increases by 10% every year. In Indonesia, the production of tapioca tubers is nearly 20 million tons from 1.93 million hectares per year. Indonesia is also the world's second-largest tapioca starch producer, which produces not less than 2 million tons per year, with Lampung Province holding over 80% of the total production. The cassava productivity can reach 100 tons/ha (Sukara et al., 2020; Unteawati and Mutaqin, 2018). Tapioca starch production is divided into three categories, i.e., traditional factory, semi-traditional factory, and modern factory. Most modern and semi-traditional factories have been well equipped to optimize starch factory waste utilization. In contrast, the traditional one still lacks in waste management, leading to increased tapioca industrial residues, such as cassava peels and cassava pomace.

Improper handling of these starchy wastes can cause environmental problems. Generally, the piles of cassava peels and pomace are dumped in a pond next to the factory. Then, many farmers who raise cows, chickens, and ducks take the waste and use them as animal feed. However, the farmers could not carry all wastes, leading to the unpleasant aroma, dirty, and clogging the drainage. The companies have conducted various efforts to reduce tapioca industrial residues by the bioconversion into value-added products, including organic fertilizers and low-grade Asia flour (Indrianeu and Singkawijaya, 2019). Nevertheless, the attempt to convert these wastes to biofuel is still limited. The starch-rich waste of tapioca flour industries or so-called *onggok* in the local Indonesian language is rich in sugar and can be utilized in bioethanol production. Also, the cassava peels is urgently potential lignocellulosic biomass for bioethanol synthesis. In this matter, *onggok* and cassava peels are potential alternative sources of starchy and lignocellulosic biomass to support the low-cost production process.

The significant limitations of current bioethanol production processes using the lignocellulosic biomass are biomass pretreatment technology, the cost of cellulolytic enzymes for hydrolysis, and the yeast strain performance for fermentation (Olofsson et al., 2008; Rajak and Banerjee, 2018). Also, the duration of fermentation usually takes 7–14 days. Our previous preliminary research result showed that *onggok* simple fermentation employing *S. cerevisiae* produced 6.2% ethanol after eight incubation days without distillation (Heriyanti et al., 2020). The conversion of cassava peels to bioethanol by fermentation was performed for 7–8 days (Oyeleke et al., 2012). Various fermentation periods for converting cassava peels and *onggok* to bioethanol, i.e., 7, 14, 21, and 28 days resulted in a 55% alcohol, optimum at seven days (Amalia et al., 2021). The conversion of bioethanol to bioethanol gel can be achieved by adding the gelling agent. For example, the bioethanol thickening process by adding carboxymethyl cellulose (CMC) was influential for gel fuel characteristics. The calorific value will increase by adding the amount of CMC (Hermawan and Sudarmanta, 2018). Reportedly, the research on the bioconversion of cassava-based industrial wastes, such as cassava peels and cassava pomace (*onggok*) to bioethanol and its bioethanol gel formulation and their characterization, have not been well recorded. Therefore, in this research, the tapioca flour industrial starchy wastes and lignocellulosic bioethanol generation comprise three steps: pretreatment to degrade starch and lignin with alkaline, the hydrolysis of polymers process using acid into fermentable sugars, and the fermentation process using microorganisms. Simple pretreatment and fermentation should be performed for bioethanol production to reduce the cost, and the use of these chemicals can reduce the cost of pricy enzymes (Sutiyono et al., 2017). The improvement of bioethanol yield production from *onggok* and cassava peels by separate hydrolysis and fermentation (SHF), reflux column distillation to extract more bioethanol, bioethanol gel formulation from bioethanol produced, and bioethanol gel characterization were conducted in this study.

2. Materials and methods

2.1. Materials

Cassava peels and cassava pomace or *onggok* were obtained from the local tapioca flour industry PT Suryapati Kencana, Pati, Indonesia. *Saccharomyces cerevisiae* IPA1 was derived from the culture collection kept in 30% (v/v) glycerol stock at $-20\text{ }^{\circ}\text{C}$ in the Laboratory of Integrated Science, Universitas Negeri Semarang, Indonesia. It was initially obtained from a local bioethanol industry in Central Java and purified and maintained. The isolate was identified by sending the isolates to the Laboratory of Microbiology and Biochemistry, Universitas Negeri Semarang, Indonesia. According to conventional yeast identification methods, it was identified based on the morphology, sporulation, and fermentation characteristics (Kreger-van Rij, 2013). The isolate was also tested for the ability to use mannitol and maltose in the medium. The isolate did not grow on these sugars; therefore, it was considered to be *S. cerevisiae*. All chemicals include CMC, ethanol, yeast growth media, were purchased from local distributors of Merck (Germany), Oxoid (England), HiMedia (India) with analytical grade.

2.2. Cassava-based industrial wastes chemical characteristics

Cassava peels were washed from soil and other contaminants. Then it was cut into 2–5 cm and washed to eliminate sand and other contaminants. The peel was air-dried and ground to 0.40–0.45 mm. *Onggok* was air-dried and ground to get a smaller powder size. Both samples were kept in clean and tight containers before analyses. The chemical compositions of samples were determined using the test method following the Technical Association of the Pulp and Paper Industry (TAPPI). The water content, ash content, and moisture content were measured. The amount of lignin, cellulose, hemicellulose, and holocellulose were assessed following respective standard methods: T222 om-06, Chlorination, and Kurschner-Hoffner Methods. All experiments were conducted in triplicates (Aripin et al., 2013).

2.3. Cassava-based industrial wastes pretreatment and saccharification

Cassava peels were cut into small pieces ($5 \times 5\text{ cm}^2$) and soaked for three days in sterilized distilled water. Then, it was dried at room temperature ($30 \pm 2\text{ }^{\circ}\text{C}$) for five days. The cassava peels were then ground using a blender until a fine powder was obtained. *Onggok* was air-dried for 5 days and ground to get a smaller powder size to a moisture content of 10.5%. After drying, cassava peels powder and *onggok* powder were sieved using a sieve with 40 mesh size. Then, the powders were separately dried in an oven at $105\text{ }^{\circ}\text{C}$ for 2 h. Separately, the dry powders (125 g) were then treated by delignification by adding 3000 mL sterilized distilled water and 350 mL NaOH (10% v/v) (Heriyanti et al., 2020; Jung et al., 2018). Delignification was performed by heating and stirring at $160\text{ }^{\circ}\text{C}$ for 30 min. Subsequently, the mixture was filtered using a vacuum pump and filter paper (Whatman No. 1). The filtered residue was washed using sterilized distilled water until neutral pH was obtained. The process was then continued by drying the residue in an oven at $105\text{ }^{\circ}\text{C}$ for 2 h. The delignified powders were again ground and sieved to obtain a fine powder. Next, the hydrolysis of delignified cassava peels powder and cassava pomace powder was done by mixing 250 g of powder with 300 mL 15% (v/v) HCl. The mixture was heated at $100\text{ }^{\circ}\text{C}$ for 2 h (Sutiyono et al., 2017). The filtrate was further used for the fermentation processes. The amount of released glucose was measured using the glucose oxidase or peroxidase assay, whereas reducing sugar was measured using the dinitrosalicylic acid (DNS) method.

2.4. Yeast strain inoculum preparation

One scrap of 30% (v/v) of yeast glycerol stock was streaked on potato dextrose agar (PDA) and incubated at 30 ± 2 °C for 2 days. One yeast colony was inoculated into 10 mL potato dextrose broth (PDB) and incubated at 30 ± 2 °C for 24 h (150 rpm shaking). Then, 10 mL of culture broth was transferred into 90 mL fresh PDB to obtain 10% (v/v). It was then incubated at the same condition for 10 h, reaching OD_{600} at 1.5. The viability of the yeast cells was observed by cell count using the counting chamber, and at this absorbance, the cells reached 5×10^7 cells/mL. The yeast culture broth was withdrawn 10% (v/v) and transferred into a 90 mL fermentation medium.

2.5. Fermentation and bioethanol production

The fermentation for bioethanol production was performed by using the filtrate from the hydrolysis results as the substrate. The pH of the filtrates was adjusted to 4.5 by adding 6M NaOH solution. After pH adjustment, 0.5% (w/v) $(NH_4)_2SO_4$ was added, and the mixture was pasteurized at 80 °C for 15 min. Next, the substrates (90 mL filtrates) were prepared with various treatments in the fermentation process, as shown in Table 1. Then, the filtrates' fermentation was performed at room temperature (30 ± 2 °C) on a rotary shaker at 150 rpm for 7 days. The ethanol was then distilled using the reflux column method on the batch distillation initiated at constant reflux (reflux ratio 2). After the unit temperatures stabilized at a stationary state, the distillate samples were removed consecutively and continued until the ethanol was exhausted. The bioethanol concentration was measured by an alcohol meter. The data were presented as the mean of triplicates, and at least three parallel samples were applied in all analytical determinations.

2.6. Formulation of bioethanol gels

Carboxymethylcellulose (CMC) was used as the thickener agent. Three CMC concentrations (2.5%, 3.5%, and 4.5%) were prepared by mixing with distilled water and stirred continuously to reach boiling point. After boiling, the mixture was let to cool down to 60 °C. Then, CMC was mixed with bioethanol derived from the production and stirred for 4–6 h using a magnetic stirrer. After stirring, the mixture was rest overnight.

2.7. Characteristics test of bioethanol gels

Bioethanol gel was measured for its viscosity using viscometer spindle no 1 (Brookfield, model DVII, Engineering Lab, Middleboro, MA). The viscosity of sols was measured using Brookfield viscometer (model DVII, Engineering Laboratories, Middleboro, MA) at room temperature

Table 1
Fermentation treatments by varying filtrate composition and starter culture inoculation.

Code	Filtrate composition	Starter culture
T1	A mixture of 1:1 cassava peel and onggok filtrates	Not added
T2	Onggok filtrate	Not added
T3	A mixture of 1:1 cassava peel and onggok filtrates	Added 24 h before the incubation of the fermentation process
T4	Onggok filtrate	Added 24 h before the incubation of the fermentation process
T5	A mixture of 1:1 cassava peel and onggok filtrates	Added on the first day of incubation of the fermentation process
T6	Onggok filtrate	Added on the first day of incubation of the fermentation process
T7	A mixture of 1:1 cassava peel and onggok filtrates	Added 24 h after the day of incubation of fermentation process
T8	Onggok filtrate	Added 24 h after the day of incubation of fermentation process

and 20 rpm. The calorific value of bioethanol gel was measured using a calorimeter (Oxygen Bomb Calorimeter 6200, Paar, MO, USA). Then, the combustion test was performed to observe the burning time of the bioethanol gel. Ash content, fire color, and residues were observed during and after burning. The measurement experiment was carried out in triplicate.

3. Results and discussion

3.1. Chemical characteristics of cassava-based industrial wastes

The chemical composition of cassava peels and cassava pomace were analyzed and summarized in Table 2. The non-starch polysaccharide in cassava peels and cassava pomace are fibers, cellulose, hemicelluloses, and lignin (Djuma'ali et al., 2011). Cassava peels contain higher fibers and other components compared to cassava pomace. The high fibers component in cassava peels (65.4%) represents that the factory used aged cassava since fibers will increase following the age of the plant. The fiber components, including cellulose and hemicellulose, increase cassava-based wastes' capacity to absorb and hold water, resulting in high moisture content at nearly 50% and 60% in cassava pomace and cassava peels, respectively. Besides, cellulose and hemicellulose of cassava pomace were a little lower in this study than those previously reported (35.9%), but the lignin was commonly found in this level ($2.8 \pm 0.2\%$) (Kosugi et al., 2009; Rattanachomsri et al., 2009). Starch was the main polysaccharide in cassava pomace (more than 60% of dry matter). The drying as the preservation method prevents the gelatinization process, thus retaining the physical characteristics of starch, hemicelluloses, and lignin (Salvador et al., 2000). The ash substances of the waste were low, which supports easy hydrolysis (Djuma'ali et al., 2011). However, the lignin in cassava peels was high (17.3%), and this is the challenge in the step of delignification.

3.2. Pretreatment and saccharification of cassava-based industrial wastes

Several alternative substrates from various wastes could be utilized for bioethanol production, including starchy wastes and lignocellulosic biomass to take care of the residues in an environmentally sustainable process (Gutiérrez-Rivera et al., 2012; Ishola et al., 2014). Cassava-based industrial wastes, including cassava pulp, cassava pomace, and cassava peels, have been utilized as the alternative sources of starchy wastes for bioethanol production using fermentation technique due to its small lignocellulosic fibers' size and high starch content. Cassava peels and onggok contain sugars in the form of polysaccharides (starch, lignocellulose, hemicellulose), which are needed to be converted to simple sugars (glucose, maltose, or cellobiose). The conversion will allow the yeast to utilize the nutrients efficiently and transform them into bioethanol effectively.

Various pretreatments of lignocellulosic biomass have different effects, and lignin could be removed effectively in alkaline conditions (Steinbach et al., 2017). The composition of lignin in cassava-based industrial wastes was relatively low, especially in cassava pomace. Based on Table 3, the lignin content in the product was sharply reduced, with lignin removal efficiency at 80.9% in cassava peels and 73.6% in cas-

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Table 2
Chemical composition of cassava peels and cassava pomace (% w/w air-dried materials).

Component	Cassava peels	Cassava pomace
Fibers	65.4 ± 2.4	35.9 ± 1.1
Cellulose	37.6 ± 2.2	18.3 ± 0.3
Hemicellulose	37.1 ± 3.6	4.8 ± 0.1
Lignin	17.3 ± 0.5	2.8 ± 0.2
Ash	4.5 ± 0.2	1.9 ± 0.1
Moisture content	60.3 ± 3.2	48.1 ± 0.2

Table 3
Lignin content of cassava based-industrial wastes before and after delignification process and acid hydrolysis.

Biomass	Initial lignin concentration before delignification (% w/w)	Initial lignin concentration after delignification (% w/w)	Lignin concentration after acid hydrolysis (% w/w)	Lignin removal efficiency (%)
Cassava peels	17.3 ± 0.5 ^b	9.2 ± 0.3 ^b	3.3 ± 0.1 ^b	80.9 ± 2.7 ^b
Cassava pomace	2.8 ± 0.2 ^a	0.7 ± 0.1 ^a	0.1 ± 0.0 ^a	73.6 ± 0.1 ^a

Values in columns with different letter (superscripts) are significantly different ($P < 0.05$).

Values are mean ± SD for triplicate measurements.

sava pomace. Lignin is a large and complex structure present in the primary cell wall with cross-linked polymers of phenolic monomers, preventing the hydrolysis process (Pérez et al., 2002). In this study, physical grinding, heating, and stirring the biomass in an alkaline hydrolysis pretreatment process effectively enhanced lignin removal. Grinding has the purpose of reducing the cellulose crystallinity to improve biomass digestibility, whereas base hydrolysis utilizes lower temperatures and pressures compared to other pretreatment technologies (Mosier et al., 2005). Also, the alkaline pretreatment causes less sugar degradation compared to the acid processes. However, some lignin remains in the solids phase after the pretreatment, but this method is still regarded as potential since it promises cost-effective lignin pretreatment (Kumar et al., 2009).

The pretreatment and hydrolysis aimed to obtain sugars in the form of glucose or disaccharides. The saccharification process of cassava peels and *onggok* produced reducing sugars for further application in the fermentation process. After the hydrolysis process of cassava peels and cassava pomace were performed, the filtrates were evaluated for reducing sugar concentration (g/L). Based on Table 4, the pretreatment and hydrolysis significantly affected the reducing sugar yield at 0.79 g/g dry cassava peels and 0.68 g/g *onggok*. Pretreatment and hydrolysis

Table 4
Reducing sugars concentration of cassava based-industrial wastes after pretreatment and hydrolysis processes.

Biomass	Initial reducing sugars before delignification (g/L)	Initial reducing sugars after delignification (g/L)	Reducing sugars concentration after acid hydrolysis (g/L)	Reducing sugar yield (%)
Cassava peels	0.11 ± 0.7 ^a	5.89 ± 0.33 ^b	10.87 ± 0.43 ^b	79.2 ± 1.2 ^b
Cassava pomace	1.25 ± 0.3 ^b	4.14 ± 0.72 ^a	9.93 ± 0.28 ^a	68.3 ± 0.9 ^a

Values in columns with different letter (superscripts) are significantly different ($P < 0.05$).

Values are mean ± SD for triplicate measurements.

Table 5
Analysis of bioconversion of cassava-based industrial wastes to bioethanol by simple fermentation using *S. cerevisiae* IPA1 at 10% (v/v) for 7 days at room temperature (30 ± 2 °C).

Treatment	Bioethanol yield (%)	Remaining sugar concentration (%)	Remaining HCl concentration (%)	Bioethanol concentration (%)	Bioethanol productivity rate (g/L per h)	Bioethanol conversion efficiency (%)
T1	22	3.62	0.13	14.28	1.32	41.21
T2	22	3.55	0.13	14.40	1.65	41.95
T3	25	3.52	0.12	14.15	1.08	41.03
T4	24	3.50	0.12	14.50	1.52	42.07
T5	35	2.15	0.08	25.85	2.64	86.26
T6	32	3.25	0.09	20.66	2.43	73.24
T7	30	3.32	0.10	15.75	1.97	44.11
T8	24	3.35	0.11	12.31	0.67	33.49

processes increased reducing sugar concentration compared to the initial concentration, as shown in Table 4. The initial reducing sugars after delignification of cassava peels and cassava pomace using alkaline solution were less than 6%. After acid hydrolysis, the reducing sugars increased up to 10%. Acids such as HCl and H₂SO₄ have been used for the hydrolysis of lignocellulosic materials. Acids are powerful agents but need dilution to reduce their toxicity, corrosive, and hazardous effects (Kumar et al., 2009). Dilute-acid pretreatment can improve the digestion of cellulose in some research, but the neutralization of pH is necessary when the enzymatic hydrolysis process is needed.

Similarly, the acid hydrolysis of cassava peels was performed with 7% HCl, and the degradation of hemicellulose and cellulose was effective (Widyastuti, 2019). Also, the acid hydrolysis of cassava pulp with H₂SO₄ for 30 min and followed by cellulase saccharification at 40 °C for 9 h resulted in glucose at 79.8% (w/w) (Akaracharanya et al., 2011). The purpose of hydrolysis is to obtain glucose where the H⁺ group of HCl will change the fiber from the biomass to the free radical group, bind with the OH⁻ group of the water molecule, and produce glucose. The amount of glucose produced depends on the concentration of the chemical used. However, the hydrolysis process would have been incomplete and leaving some lignocellulose components in the biomass with high crystallinity. In this research, the concentration of soluble sugars in the filtrate was still moderate, with glucose is the most soluble sugar, and the filtrate might contain unknown sugars, xylose, cellobiose, or maltose (Kongkiattakajorn and Somvorawean, 2011).

3.3. Bioconversion of sugars from cassava-based industrial wastes to bioethanol

The fermentation treatments by varying the substrate composition occurred for 7 days, resulting in Treatment 5 (T5) reached the highest bioethanol yield at 35%, whereas the bioethanol concentration before the distillation process was at 25.85%, as shown in Table 5. This result is in line with the previous research of bioethanol synthesis, which produced maximum bioethanol from red seaweed for 5–7 days (Candra et al., 2011). Similarly, another experiment using cassava peels as the carbohydrate source for bioethanol production was performed using *S. cerevisiae* with the highest ethanol production at 6% with 8 days fermentation time (Guntama et al., 2019). A shorter fermentation period was achieved in bioethanol production using cassava bagasse with enzymatic hydrolysis followed by fermentation and distillation, which was performed for only 24 h, and the average ethanol yield was relatively high at 30% (Martinez et al., 2018).

In this research, bioethanol production from cassava-based industrial wastes in various treatments for seven days was performed, and the method of batch distillation with a reflux column showed significant results. The reflux column distillation was significantly improved the bioethanol concentration. Also, the batch distillation method of separating bioethanol from the mixture was performed. The results showed that the method was effectively enhanced bioethanol concentration. The separation aimed to remove the impurities obtained from the fermentation process, affecting the quality of the bioethanol product.

Bioethanol must meet the standard of ethanol quality regarding the use of bioethanol for bio gel formulation. Also, the consideration of all production stages must be performed to calculate and reduce bioethanol production costs. The choice of the distillation method with low-energy consumption for its unit operation was presented in this research. The conventional distillation process has approximately 5–20% in total thermodynamic efficiency (De Koeijer and Kjelstrup, 2000).

On the other hand, the batch distillation using a single column employed in this research was feasible and appropriate for bioethanol production in a small production unit compared to the conventional distillation method. A low-cost ethanol recovery from banana culture waste using the reflux ratio at 2 in a batch distillation unit gave the maximum ethanol concentration at 67% (Coelho et al., 2012). Reflux is widely used in industries that use large-scale distillation columns and fractionators. Reflux refers to the portion of the overhead liquid product from the distillation column returned to the top of the column. The down-flowing fluid reflux in the column provides cooling and condensation of the upflowing vapor, increasing the distillation column's efficiency. This reflux column distillation technique is the same as simple distillation, only differs in the repeated condensation process.

As shown in Fig. 1, all treatments showed efficacy in bioethanol production, reaching a minimum bioethanol concentration at 55% and maximum at 93%. Treatment 5 (T5) and treatment 6 (T6) are significantly higher than other treatments, achieving 93% and 90%, respectively. The addition of starter culture on the day of fermentation (0 h) affected bioethanol production since yeast's growth was in the mid-log phase or ready to convert simple sugars to bioethanol in the filtrate medium. The starter culture can produce high quality and optimum bioethanol yield with consistency and may facilitate bioethanol industrial production (Luangkhlapho et al., 2014). In this research, *S. cerevisiae* IPA1 used was a defined starter culture obtained from a traditional bioethanol industry in Central Java, Indonesia. *S. cerevisiae* is defined as one of the widely used yeast strains, and even though it is at a household level, it could produce ethanol as the primary fermentation product. Various physiological characteristics, including generally regarded as safe (GRAS) for human consumption, its tolerance to a wide range of pH and optimum at acidic pH, also it is high tolerance the ethanol products make *S. cerevisiae* is advantageous and superior (Lin et al., 2014; Ortiz-Muñiz et al., 2010; Prasertwasu et al., 2014). *S. cerevisiae* grows well over a wide range of pH but grows better in acidic pH due to its ability to neutralize added H^+ to maintain pH homeostasis in acid stress (Chen et al., 2009). The buffering mechanism could help the cells to accommodate the rapid intracellular pH adjustment (Brandão et al., 2014). Cassava peels gave higher bioethanol at 16% after 7 days of fermentation mediated by *S. cerevisiae* (Isah et al., 2019). *S. cerevisiae* BY4743 was employed in the ethanol fermentation process using the hydrolysate from cassava peels for 36 h, and it gave an ethanol yield of

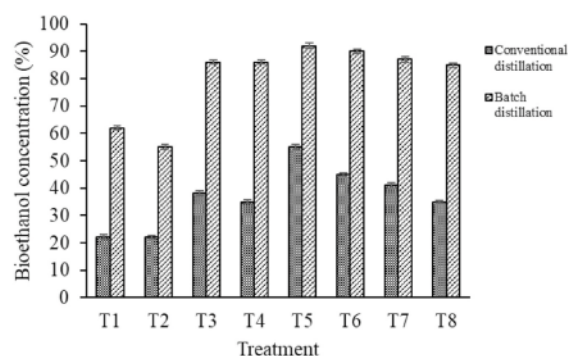


Fig. 1. Bioethanol production from various fermentation treatment parameters and comparison between conventional distillation and batch distillation methods.

0.53 g/g suggesting the cassava peels waste potential for bioethanol production (Aruwajoye et al., 2020).

3.4. The viscosity of bioethanol gels

Bioethanol products from various treatments were subjected to bioethanol gel formulation by mixing it with various carboxymethylcellulose (CMC) concentrations at 2.5%, 3.5%, and 4.5% (w/v). The results of the viscosity value determination are shown in Table 6.

According to Table 6, the higher the CMC concentration, the viscosity level of the bioethanol gel was also higher. In this study, the highest viscosity value was achieved by adding 4.5% CMC in Treatment 5 (T5) at 1.338 mPa s and the lowest value at 586 mPa s in T2 with 2.5% CMC added. The CMC level is inversely proportional to the water content used, which caused the increase in bioethanol gel viscosity. The higher the viscosity value of a solution, the higher the thickness. A high CMC concentration is needed to improve low bioethanol concentration due to the excessive water content in bioethanol products.

Carboxymethyl cellulose (CMC) plays an essential role as a thickener agent (Santoso et al., 2018). CMC is a linear cellulose polymer ether. It is a biodegradable, colorless, odorless, and non-toxic emulsifier agent in the form of granules or powder that dissolves in water. It does not dissolve in organic solutions with a pH range of 6.5–8.0 and stable in the pH range 2–10. It can react with heavy metal salts to form an insoluble film in water, transparent, and not react with organic compounds. CMC is widely used in food, chemistry, petroleum, paper making, textiles, and building materials to form subtle textures. The viscosity of CMC can decrease with increasing ionic strength and decrease pH due to its polymer structure (Ariyani, 2013; Cândido and Gonçalves, 2016; Santoso et al., 2018; X. H. Yang and Zhu, 2007). CMC and carbopol are often used to effectively formulate bioethanol gels to improve their viscosity (Ariyani, 2013). CMC gave better characteristics in a bioethanol gel formulation, such as burning time, ash content, calorific value, and specific gravity compared to other samples using other thickening agents such as carbopol, and the price is considered more economical (Hanun and Sutjahjo, 2018).

3.5. The calorific value of bioethanol gels

The calorific value of bioethanol gels of all treatments with various carboxymethylcellulose (CMC) concentrations was measured, and the results are presented in Fig. 2.

The addition of CMC concentration and the high concentration of bioethanol gels can increase the calorific value. Bioethanol concentration in treatment 5 (T5) was 92%, whereas T6 was 90%, significantly gave the highest calorific value at more than 5000 kcal/kg. Besides, the calorific value also has a relationship with water content. High and low heat levels are very much influenced by water content. The low water

Table 6

The viscosity of bioethanol gel in different concentration of carboxymethylcellulose (CMC).

Treatment	Final bioethanol concentration %	Viscosity value (mPa.s)		
		2.5% CMC	3.5% CMC	4.5% CMC
T1	62	660.77 ± 1.22	762.55 ± 0.87	901.34 ± 0.22
T2	55	586.19 ± 0.79	676.51 ± 0.34	799.65 ± 0.76
T3	86	916.45 ± 0.76	1.057.58 ± 0.21	1.254.99 ± 0.34
T4	86	918.33 ± 0.68	1.046.57 ± 0.29	1.249.89 ± 0.77
T5	92	980.37 ± 0.65	1.131.32 ± 1.23	1.337.62 ± 0.39
T6	90	959.06 ± 1.02	1.106.21 ± 1.01	1.308.11 ± 0.14
T7	87	927.11 ± 0.99	1.069.31 ± 0.45	1.264.52 ± 0.33
T8	85	905.77 ± 0.94	1.045.22 ± 0.23	1.235.42 ± 0.46

Values are mean ± SD for triplicate measurements.

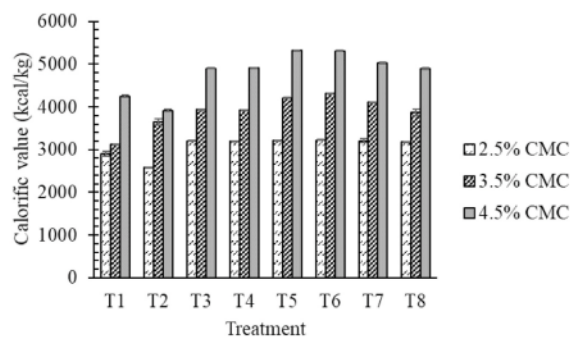


Fig. 2. The calorific value of bioethanol gels with various concentrations of carboxymethylcellulose (CMC) at 2.5%, 3.5%, and 4.5%.

content will be inversely proportional to the heat content produced in bioethanol gel testing (Ariyani, 2013; Hanun, 2018; X. H. Yang, 2007). Carbon and hydrogen in CMC can increase bioethanol gels' calorific value, where burning requires carbon to react with oxygen to produce heat. The carbon bonds in the fuel are mostly obtained from ethanol and CMC. Therefore, the higher the CMC concentration increased the heating value. This result is in line with the optimization results performed to obtain a high calorific value at more than 7000 kcal/kg of bioethanol gels by adding 2.5 g CMC to 96% bioethanol (Hermawan, 2018).

3.6. Burning time, color, and residue of bioethanol gels

The bioethanol gels were analyzed for burning time, color during burning, and residues left after burning. The results of the analysis are shown in Table 7.

Based on the results of the analysis with a bioethanol gel weight of 250 g, it can be seen that all treatments could ignite for a long time of about 180 min in treatment 5, 6, and 7 (T5, T6, T7). The flame color of the bioethanol gel burning was blue, and there was no relationship between carboxymethylcellulose concentration with flame color. However, CMC concentration affected the burning time due to the properties of CMC that bind to bioethanol. Bioethanol is a volatile compound, and when the vapor is mixed with oxygen, it could form a flammable mixture. Therefore, the higher the bioethanol concentration, the faster it evaporates into the air, and the combustibility is higher and faster. The presence of a CMC and water is the critical factor for a longer burning time. CMC holds the rate of bioethanol evaporation since it is trapped in the CMC and released slowly. The bioethanol gel combustion ability depends on bioethanol concentration and thickening agent used, and environmental factors. The environmental factors include the availability of a surface to evaporate bioethanol, temperature, vapor flow rate to the combustion area, and the oxygen around the combustion area (Ariyani, 2013; Hermawan, 2018). The results of this research

Table 7
Characteristics of bioethanol gels after burning.

Treatment	Burning time (min)			Flame color	Residue
	2.5% CMC	3.5% CMC	4.5% CMC		
T1	30.2 ± 2.1	47.5 ± 1.2	75.3 ± 1.1	Blue	++
T2	32.5 ± 2.2	42.3 ± 2.5	78.2 ± 1.5	Blue	++
T3	45.4 ± 1.3	76.4 ± 3.1	100.0 ± 2.1	Blue	++
T4	48.3 ± 1.3	78.2 ± 2.0	100.5 ± 2.0	Blue	++
T5	75.5 ± 1.5	101.2 ± 1.0	184.4 ± 3.4	Blue	+
T6	82.2 ± 3.2	103.5 ± 1.3	183.0 ± 2.5	Blue	++
T7	78.6 ± 2.4	120.5 ± 1.5	179.0 ± 3.2	Blue	+
T8	71.5 ± 1.4	86.0 ± 2.2	135.3 ± 2.1	Blue	+

Values are mean ± SD for triplicate measurements.

show that CMC could dissolve perfectly into bioethanol and water. In a bioethanol gel stove, the stove inlet diameter can affect the burning performance (Hermawan, 2018). The ash content determination was carried out to observe residue production. As shown in Table 4, the residues after burning the bioethanol gels were low to moderately produced. The ash content analysis result is presented in Fig. 3.

The ash content in various samples with each treatment showed significant results. The addition of a different CMC concentration gave the significant effect of burning the bioethanol gel produced. As presented in Fig. 3, the increase in the CMC concentration of each treatment is proportional to the increase in ash content. The non-flammable chemical nature of CMC causes residual combustion. The ash content in all bioethanol gels combustion treatments shows a good result of less than 5%. Therefore, this bioethanol gel formula can be further applied in heating as a household fuel.

4. Conclusion

Cassava-based industrial wastes, including cassava peels and cassava pomace (*onggok*), are rich in lignocellulosic biomass, which was effective as the source of sugars bioethanol production. Alkaline delignification and acid hydrolysis processes in cassava-based industrial wastes indicated a practical breakdown of lignocellulosic materials as saccharification converted it to sugars at 0.79 g/g dry cassava peels and 0.68 g/g *onggok*. The fermentation process using local strain *Saccharomyces cerevisiae* IPA1 effectively transformed wastes to bioethanol at conversion efficiency at 86% with 35% bioethanol yield, resulting in 25% of bioethanol concentration fermentation. The reflux column batch distillation could effectively increase the bioethanol yield and concentration up to 92%. Carboxymethyl cellulose was effectively enhanced the viscosity value of the bioethanol gels to 1.338 mPa s. Also, the lower the water content caused each sample to have a higher heating value. All treatments effectively ignited the fire with a maximum duration of up to 184 min, and the increase in CMC in each treatment was proportional to the increase in ash content. However, all treatments showed less than 5% ash content. These results suggested that the cassava-based industrial wastes is potential for bioethanol gel production in both small scale (traditional method) and large scale (industrial method) with further application as a household cookstove fuel.

Ethical approval

This article does not contain any studies with animals performed by any of the authors.

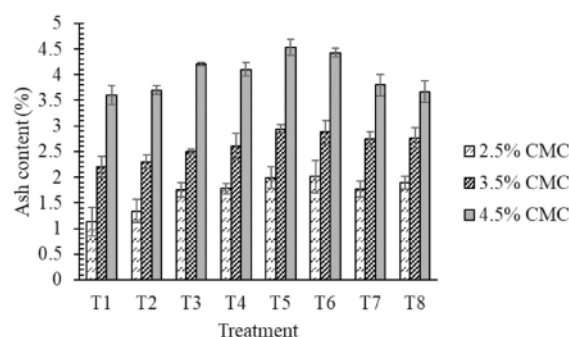


Fig. 3. Ash content as results of burning of bioethanol gels with various concentrations of carboxymethylcellulose (CMC) at 2.5%, 3.5%, and 4.5%.

CRediT authorship contribution statement

Andin Vita Amalia: Data curation, Visualization, Investigation, Software, Writing – original draft. **Fidia Fibrina:** Supervision, Writing - review & editing. **Talitha Widiatningrum:** Conceptualization, Methodology, Data curation, Supervision, Writing - review & editing. **Risa Dwita Hardianti:** Supervision, Writing - review & editing.

Declaration of competing interest

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the manuscript's contents, and there is no financial interest to report.

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