

## **BIOETHANOL PRODUCTION FROM COCONUT HUSK USING THE WET GAMMA IRRADIATION METHOD**

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### **ABSTRAK**

**PEMBUATAN BIOETANOL DARI SABUT KELAPA DENGAN METODE IRADIASI GAMMA BASAH.** Pemanfaatan sabut kelapa selama ini hanya digunakan sebagai bahan pembuatan kerajinan tangan seperti tali, sapu, keset, matras, dan lainnya ataupun hanya dibakar saja. Pembakaran sabut kelapa ini akan menimbulkan polusi udara. Padahal sabut kelapa bisa dimanfaatkan sebagai bahan baku pembuatan bioetanol sehingga meningkatkan nilai guna sabut kelapa. Salah satu cara pembuatan bioetanol dari sabut kelapa adalah dengan melakukan iradiasi terhadap sabut kelapa tersebut. Teknik dilakukan pada penelitian ini adalah dengan teknik iradiasi basah. Iradiasi basah dilakukan untuk mempercepat proses pembuatan bioetanol karena pada saat dilakukan iradiasi, selulosa telah terhidrolisis dan sudah terbentuk glukosa sehingga lebih efisien dalam waktu dan penggunaan bahannya sehingga tidak perlu dilakukan proses hidrolisis selulosa. Sampel sabut kelapa dalam keadaan basah karena telah dicampurkan dengan NaOH 4% diiradiasi menggunakan irradiator gamma STTN-BATAN Yogyakarta dengan dosis 30 kGy dan 50 kGy serta 0 kGy (atau tanpa iradiasi). Kemudian sampel difermentasi dengan jamur *Saccharomyces Cerevisiae* dari ragi tape sehingga terbentuk etanol. Etanol dimurnikan lalu dianalisa kadarnya dengan metode piknometri dan refraktometri. Hasilnya kadar etanol paling tinggi adalah yang tanpa iradiasi (0 kGy), ini disebabkan karena dosis yang digunakan rendah. Akan tetapi hal yang menjadi poin utama pada penelitian metode basah ini adalah pembuktian telah terhidrolisisnya selulosa dengan terbentuknya glukosa setelah sabut kelapa dalam keadaan basah diiradiasi, dan dengan analisa fehling A dan B terlihat endapan coklat yang membuktikan bahwa glukosa telah terbentuk.

Kata kunci: Bioetanol, Hidrolisis selulosa, Iradiasi gamma basah, Kadar etanol, Sabut Kelapa

### **ABSTRACT**

**BIOETHANOL PRODUCTION FROM COCONUT HUSK USING THE WET GAMMA IRRADIATION METHOD.** *The use of coconut husk has only been used as a material for making handicrafts such as ropes, brooms, mats, and others or just burned. The combustion of coconut husk can cause air pollution. In fact, coconut husk can be used as a raw material for bioethanol production so that the beneficial value of coconut husk will also increase. One way of bioethanol production from coconut husk is by irradiating the coconut husk. The coconut husk irradiation technique to be carried out in this study is the wet irradiation technique. Wet irradiation is carried out to accelerate the process of bioethanol production because at the time of irradiation, cellulose has been hydrolyzed and glucose has been formed so that it is more efficient in time and use of the material so that the cellulose hydrolysis process is not necessary. The coconut husk samples were wet because they were mixed with 4% NaOH and were irradiated using a gamma irradiator from STTN-BATAN Yogyakarta with a dose of 30 kGy and 50 kGy and 0 kGy (or without irradiation). Then the sample is fermented with the fungus *Saccharomyces Cerevisiae* from tape yeast to form ethanol. Ethanol is purified and then analyzed for concentrations using pycnometric and refractometric methods. The result is that the highest ethanol content is without irradiation (0 kGy), this is due to the low dosage used. However, the main point in this wet method research is evidence of hydrolysis of cellulose by the formation of gluoxane after irradiated wet coconut husk, and with Fehling A and B analysis, brown deposits are seen proving that glucose has been formed.*

Keywords: Bioethanol, Cellulose Hydrolysis, Coconut Husk, Ethanol Concentrations, Wet Gamma Irradiation

## INTRODUCTION

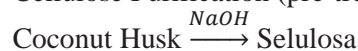
Bioethanol is a renewable energy that can be produced from the fermentation process of sugar or it can also be produced by synthesizing ethylene in a chemical reaction using hot steam [1]. Currently, most of the bioethanol is produced from molasses, corn syrup, or other food raw materials that have a high value. However, the use of the main raw material competes with its more primary use, called as a food source. Bioethanol can also be produced from materials containing lignocellulose. This material is abundant and has a high cellulose content, for example, agricultural waste. Agricultural waste has many benefits, including the fact that it does not interfere with the availability of food, is inexpensive, and is widely distributed across Indonesia [2].

One of the agricultural wastes that have sufficient potential to become an alternative source of lignocellulose-based bioethanol is coconut husk. Coconut husk forms a major part of the weight of the coconut fruit (35%) and contains lignocellulose, including cellulose in the range of 26.60% to 43.44% [3]. If the production of coconut fruit in Indonesia reaches 3,250,000 tons/year, it will produce 1,137,500 tons of coconut husk/year. The use of coconut husk so far is mostly used as handicrafts such as ropes, mats, brooms, mattresses, car seat stuffing materials, etc., or for burning [4,5]. Burning coconut husk can cause air pollution and gas emissions in the atmosphere, as well as a decrease in the coconut husk's usefulness. Converting coconut husk to bioethanol has a number of advantages, including reducing waste from coconut plantations, reducing emissions from direct combustion, and increasing the usage value of coconut husk. In addition, this can also reduce the need for oil and gas imports if mass production is carried out and in a sustainable manner.

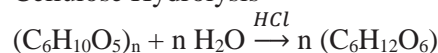
The cellulose content in coconut husk can potentially be used as a source of reducing sugar through chemical or enzymatic processes. The resulting sugar solution can be converted into a variety of products, including alcohol, acetone, butanol, and high-value products [6].

The manufacture of ethanol from coconut husk waste consists of 3 stages, namely [7]:

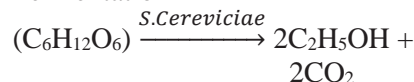
1. Cellulose Purification (pre-treatment)



2. Cellulose Hydrolysis



3. Fermentation



Constraints in the hydrolysis and fermentation processes are the presence of lignin content in the powder, high molecular weight, hydrogen bonds, and crystalline structures [8]. This inhibiting factor needs to be removed or reduced by the purification process (pre-treatment) [9].

At this purification stage, the coconut husk is mixed with NaOH before being irradiated (wet irradiation). It is different from the dry irradiation method which mixes the NaOH after first irradiating the coconut husk (irradiated in dry conditions). One such pre-treatment process is high-energy radiation to degrade lignocellulose (Figure 1) [10].

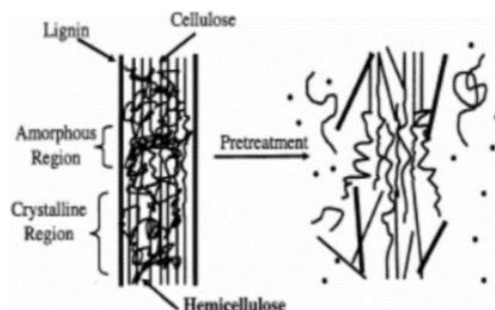


Figure 1. Schematic of Lignocellulosic Material Pretreatment

Gamma radiation will break the chain (degradation) and alter the microstructure of the husk, allowing the enzymatic hydrolysis process to speed up. The molecular weight of cellulose can be reduced by exposure to radiation. The lower the molecular weight of cellulose, the higher the radiation dose [11].

Pretreatment using gamma irradiation increases energy efficiency and is more environmentally friendly to reduce molecular weight, the crystallinity of cellulose, and increase the surface area of cellulose [12]. If

the raw material for coconut husk is mixed with dilute NaOH, it will cause cellulose to expand. The expansion of cellulose will increase the surface area of lignocellulose, reduce the degree of polymerization, reduce the crystallinity area, occur the separation of lignin and carbohydrate bonds, or decrease the level of lignin in lignocellulose. As a result, the cellulose hydrolysis process is not carried out during the fermentation stage. This is done in order to expedite the operation.

Previous research conducted by Darojati, et al. (2019) converted bioethanol from coconut husk using the wet irradiation method using high doses including 100 kGy, 150 kGy, 200 kGy, 250 kGy. The results showed that the highest ethanol content was at a dose of 150-200 kGy with ethanol concentration of 25-37% [13].

The aim of this wet process, which uses low doses of 30 kGy and 50 kGy, is to see whether using a low dose in wet irradiation produces high concentrations of bioethanol, so it can be compared to the dry irradiation method, which requires high doses to produce high concentrations of bioethanol.

This study also compares whether the ethanol content obtained is in accordance with the bioethanol product with the standard quality of SNI 063565-2009.

## **METHODOLOGY**

Coconut husk was irradiated with a 12 kilo Curie Co-60 radiation source from the STTN-BATAN Yogyakarta category I branded Ob-servo Ignis Hungary gamma irradiator. The dose in kilogray units indicates the strength of this radiation pulse (kGy).

In this research, 30 kGy and 50 kGy doses were used. The process used in this study consists of several stages, including raw material preparation, gamma irradiation, fermentation, purification, and bioethanol concentrations analysis.

### **A. Raw Material Preparation**

Coconut husk is separated from the fruit and washed and dried. The dry coconut coir is ground into a fine powder and is screened with a mesh size of -40.

### **B. Gamma Irradiation**

The coconut husk is weighed at 50 g and split into 3 samples: 30 kGy, 50 kGy, and those

without irradiation. The coconut husk is placed in a special container and mixed with 750 ml of 4% NaOH to irradiate the coconut husk in a wet state before being irradiated. The glucose content in the sample was analyzed using the Fehling A and Fehling B methods to determine whether glucose had formed or not in the irradiated solution (black liquor). The black leachate solution was washed using 20% HCl to a neutral pH value.

### **C. Fermentation**

The sample was put into a 500 ml Erlenmeyer and 10 ml of pH 6.0 citrate buffer solution and nutrients (Urea 1 gram / NPK 0.25 gram) were added. Samples were sterilized using an autoclave at a temperature of 121°C for 15 minutes. After chilling the sample, 2.5 grams of *Saccharomyces Cerevisiae* enzyme was added to the Erlenmeyer. Samples were incubated in an incubator for 72 hours at 30°C.

### **D. Purification**

The fermented solution is subjected to a distillation process. The distillation process is carried out at a temperature of 80°C, because the boiling point of ethanol is 78°C and the boiling point of water is 100°C. The ethanol purification process is carried out by distillation. To prevent clogging during the distillation process, a solid-liquid separation must be performed prior to distillation. Filtration separates bioethanol from the fermentation method. The filtrate is distilled to remove any pollutants or impurities that may have accumulated during the fermentation phase [14].

### **E. Bioethanol Concentrations Analysis**

Analysis of ethanol concentrations was performed using two analyzes: pycnometer and a refractometer (refractive index).

## **RESULTS AND DISCUSSION**

The initial preparation performed in this study was to reduce the particle size so that when irradiation it was easier to form glucose, namely by sieving (sieving was done with a size of 40 mesh).

Before irradiation, coconut husk was dissolved in a strong alkaline solution of 4% NaOH. Selection of the strong base concentration of NaOH 4% based on the best conditions based on previous research. The

concentration of 1% NaOH can degrade lignin about 30% by weight of the substrate and is able to infiltrate the tissue and cause swelling so that the extractive substances in the fiber are easily soluble [15]. This process is called the delignification process.

In the delignification process, lignin reacts with NaOH solution which dissociates into  $\text{Na}^+$  and  $\text{OH}^-$ . The  $\text{OH}^-$  ion reacts with the H group on the lignin to form  $\text{H}_2\text{O}$ . This causes the O group to form free radicals and reactive with C to form an epoxy (C-O-C) ring, causing a series of groups to release bonds to the O group. The reaction produces two separate benzene rings, each of which has a reactive O group. This reactive O group reacts with  $\text{Na}^+$  to form phenolic salts and also dissolves in the alkaline solution so that the lignin is lost when rinsed with water [16]. The mixture of NaOH and coconut husk will turn blackish brown or often called black leachate (Figure 2). This shows that the degradation of lignin by NaOH. This degradation process results in the breaking of several bonds, including aryl-ether, carbon-carbon, aryl-aryl and alkyl-alkyl.



Figure 2. Black Leachate

The doses used to irradiate black liquor in this study were 30 Kgy, 50 Kgy and 0 kGy (or without irradiation). Gamma irradiation in this pre-treatment aims to degrade the lignocellulose structure, especially breaking down cellulose chains (polysaccharides) into simpler chains (monosaccharides) so as to increase efficiency in the pre-treatment process of coconut coir into bioethanol. When cellulose is exposed to gamma radiation, free radicals are produced randomly. Each cellulose has two inter and intramolecular hydrogen bonds. These bonds stabilize the long, parallel chains of cellulose. Gamma irradiation will affect these bonds and cause the strength of the cellulose bonds to weaken which results in

cellulose degradation and increased degradability of lignocellulosic cell wall components.

The results of the analysis using Fehling A and Fehling B against irradiated black leachate show that there is a brown sediment at the bottom of the test tube. This shows that glucose has been formed by wet irradiation method without going through the cellulose hydrolysis process to produce glucose. So that the sample is directly carried out by the fermentation process to produce ethanol.



Figure 3. Glucose analysis using Fehling A and Fehling B methods

The fermentation process is carried out using instant tape yeast which is the fungus *Saccharomyces Cerevisiae*. The choice of *Saccharomyces Cerevisiae* fungus is because this fungus is non-pathogenic, non-toxic, easy to breed and requires simple nutrition. Fermentation is carried out under operating conditions such as temperature 30°C, pH 6, and the addition of nutrients. The nutrients used are NPK and urea. The choice of NPK and urea is because the fungus *Saccharomyces Cerevisiae* requires energy to survive which comes from nitrogen. Urea has a large nitrogen content, namely 46%, while NPK has a high phosphorus content which can trigger the growth of *Saccharomyces Cerevisiae* fungi during fermentation. The fermentation process can be said to be running or not, namely by the appearance of  $\text{CO}_2$  gas of the fermentation substrate and it smells bad. It indicates the fermentation process work well.

The ethanol content of bioethanol isolated from water via a purification process is then determined. The pycnometric approach is used to test for ethanol content in accordance with SNI 06-3565-2009. Bioethanol content testing, on the other hand, is done using the refractory method to obtain accurate and

reliable results. The results of the analysis of bioethanol concentrations using the pycnometric method are shown in Table 1.

Table 1. Bioethanol concentrations by pycnometer method (3 days fermentation)

Dose (kGy)	Density (gr/ml)	Bioethanol concentrations (%)
0	0.9851	10.5413
30	0.9947	3.0501
50	0.9946	3.0584

Table 1 shows that the highest bioethanol content produced is at the irradiation dose of 0 kGy. However, the bioethanol content obtained is still very small. This is due to several factors, namely the dose of irradiation, the hydrolysis process and the temperature of the distillation process. In another study using the dry irradiation method, the optimal dose to produce bioethanol is at a dose between 150 kGy-200 kGy, namely with an ethanol content of around 25-26%. The doses used in this study using the wet irradiation method were quite low, namely 30 and 50 kGy. This could be due to the fact that cellulose has not been completely degraded, so the conversion of cellulose from the beginning of the polysaccharide structure is split into monosaccharides which is not optimal so that the conversion of cellulose to glucose and ethanol is not optimal.

In testing with fehling A and fehling B, it is quite difficult to get a sediment that shows the formation of glucose or not. This can be due to the fact that the glucose that is formed is still very small, it can be caused by the possibility that the dose of irradiation used is quite small so that if you use a large dose, it is likely that a lot of glucose is formed. This can be proven in subsequent studies as an assessment of the effectiveness of the wet irradiation method in the formation of glucose without going through the cellulose hydrolysis process.

In this study, the heating temperature in the distillation process was between 80-87°C because at this temperature the maximum conditions where many distillates were formed. However, there is a possibility that the distillate formed is ethanol mixed with other compounds. So it is necessary to separate again in order to get pure ethanol.

The ethanol concentration at a dose of 0 kGy was 10.5413%. Although the gamma irradiation pre-treatment was not carried out in this sample, the ethanol content was the highest higher than the sample that was subjected to gamma irradiation pre-treatment. There is a possibility that when the pH neutralization was carried out from the acidic pH using 20% HCl, a hydrolysis process had occurred in black liquor at a dose of 0 kGy so that glucose was formed at this 0 kGy dose. This is in accordance with the research conducted by Dwi et al. (2012), that the higher the HCl concentration, the smaller the glucose levels formed [17]. This proves that at a dose of 0 kGy, glucose is only formed during the neutralization process so that the final result is that the ethanol content at this dose is even higher than the other doses. If you look at the research conducted by Dwi, et al. (2012), who have also done without gamma irradiation, such as the 0 kGy sample but can get a glucose level of 14.27%, meaning that the 0 kGy sample can produce an ethanol content of 10.5413% is not impossible. When viewed from other studies, they can produce bioethanol by varying both the fermentation temperature, the duration of fermentation, the type of nutrients and others. However, there are no studies that have produced high levels of bioethanol (above 50%) if they do not use gamma irradiation pre-treatment.

The analysis results of bioethanol Concentrations using the refractometric method are shown in Table 2.

Table 2. Ethanol content Using refractometric method (3 days fermentation)

Dose (kGy)	Refractive index	T (°C)	T1 (°C)	Concentration s (%)
0	1.3330	20	27	7.5%
30	1.3320	20	27	5%
50	1.3325	20	27	6.25 %

Table 2 shows that the highest level remains in the sample with an irradiation dose of 0 kGy. Just like using the pycnometric method, the ethanol content in the sample with the kGy dose was higher than the sample with a dose of 30 kGy and 50 kGy. However, between the doses of 30 and 50 kGy, it was seen that the ethanol content increased in proportion to the dose. It is possible that if you

use a higher dose, the ethanol content produced will also be higher. In another study using the dry irradiation method, it was shown that the optimal dose to produce bioethanol is at a dose between 150-200 kGy with an ethanol content of around 36-37%. However, in this study the greater the dose used, the lower the ethanol content.

The results of this study are compared with the standard SNI 06-3565-2009 (Vegetable Ethanol) as in Table 3 to determine whether the wet irradiation process can produce bioethanol products with quality according to the SNI 063565-2009 standard. The bioethanol content obtained in this study did not meet the SNI 06-3565-2009 standards. This is caused by several factors, including:

1. The materials used are not carbohydrates or carbohydrate-producing materials, which are more easily formed into ethanol during the fermentation process, but rather wood / softwood fibers that must be treated in more detail and specifically.
2. Lack of addition of chemicals commonly used in the bioethanol manufacturing industry can also be a factor in the recovery of low bioethanol content.
3. The ratio of lignocellulosic substances is a factor in the low levels of bioethanol, whereas to obtain high yields the content of cellulose and hemicellulose must be high, otherwise the lignin content must be low.

Table 3. Comparison of Bioethanol Concentrations from Research Results with Standard SNI 06-3565-2009 (Vegetable Ethanol)

SNI 06-3565-2009	Method	Irradiation Dose (kGy)	Bioethanol Concentration	Annotation
96%	Pycnometry	0	10.5413 %	Not Eligible
		30	3.0501 %	
		50	3.0584 %	
	Refractometry	0	7.5%	Not Eligible
		30	5%	
		50	6.25 %	

## CONCLUSION

The highest ethanol concentrations is in unirradiated coconut husk (0 kGy). The use of dry or wet irradiation results in high ethanol concentrations when using high doses. Our wet irradiation can further accelerate the manufacturing process by not performed the hydrolysis of cellulose in the fermentation process. The concentrations of ethanol synthesized by irradiation is not in accordance with SNI 06-3565-2009 (Vegetable Ethanol) standards used in the market.

## REFERENCES

1. Chandel, A.K., E.S. Chan., R. Rudravaram, M.L., Narasu, L.V., Rao., and P. Ravindra, "Economics and Environmental Impact of Bioethanol Production Technologies", *Biotechnology and Molecular Biology*, Vol. 2, No. 1, pp. 14-32. 2007.
2. Rachmaniah, O., Febriyanti, L.S., and Lazuardi, K, "Pengaruh Liquid Hot Water Terhadap Perubahan Struktur Sel Bagas",

*Prosiding Seminar Nasional XIV-FTI-ITS*, 2009. Institut Teknologi Sepuluh November, Surabaya, pp. 31-40.

3. Costa, Guy and Plazanet, Idelette, "Plant Cell Wall , A Challenge For Its Characterisation. " *Biological Chemistry*, Vol. 6, pp. 70-105. 2016.
4. Mahmud, Zainal and Ferry, Yulius, "Prospek Pengolahan Hasil Samping Buah Kelapa Pusat Praktikum dan Pengembangan Perkebunan." *Indonesian Center for Estate Crops and Development*, Vol. 4, No. 2, pp. 55-63. 2004.
5. Anggorowati. D.A and Dewi. B. K, "Pembuatan Bioetanol dari Limbah Sabut Kelapa dengan Metode Hidrolisis Asam dan Fermentasi dengan Menggunakan Ragi Tape", *Industri Inovatif*, Vol. 3, No. 2, September, pp. 9-13. 2013.
6. Fajar, A.A. "Biokonversi Lignoselulosa Limbah Sabut Kelapa Menjadi Bioetanol Menggunakan *Trichoderma Reesei*, *Zimomonas Mobilis* dan *Pichia Stipitis*". *Departemen Biokimia Fakultas*

- Matematika dan Ilmu Pengetahuan Alam*. IPB. 2014.
7. Joeh, Tina, Steam Explosions of Cotton Gin Waste for Fuel Ethanol Production, *Jurnal Kimia*. 1998.
  8. Hermiati, E., Mangunwidjaja, D., Sunarti, T. C., Suparno, O., and Prasetya, B. "Pemanfaatan Biomassa Lignoselulosa Ampas Tebu Untuk Produksi Bioetanol". *Litbang Pertanian*, Vol. 29, No. 4, pp. 121-130. 2010.
  9. Shin, S.J., Han, S.H., Park, J.M., and Cho, N.S, "Monosaccharides from Industrial Hemp (*Cannabis Sativa L.*) Woody Core Pretreatment with Ammonium Hydroxide Soaking Treatment Followed by Enzymatic Saccharification." *Journal of Korea TAPPI*, Vol. 41, No. 5, pp. 16-19. 2009.
  10. Xuan, D., Mai, V.Q., Duy, N.N., Phu, D.V., and Hien, N.Q, "Degradation of Chitosan By  $\gamma$ -Irradiation of Chitosan Swollen in Hydrogen Peroxide Solution." *Vietnam Journal of Science And Technology*, Vol. 52, No. 4, pp. 441-50. 2014.
  11. Charlesby, A., "The Degradation of Cellulose by Ionizing Radiation", *Journal Of Polymer Science*, Vol. 15, pp. 263-270. 1995.
  12. Sugiarto, Yusron., Mahfut, L.N., Rilek, N.W., Atrinto, A.C.P., and Khotimah, M, "Pengaruh Frekuensi Ultrasonik dan Konsentrasi Pada Proses *Pretreatment* Bioetanol Pelepah Sawit." *Jurnal Teknologi Pertanian*, Vol. 15, No. 3, pp. 213-22. 2014.
  13. Darojati. H. A, Putra. S, and Zulprasetya. F. P, "Pengaruh Iradiasi Gamma pada Konversi Biomassa Lignoselulosa Sabut Kelapa Menjadi Bioetanol" *Jurnal Teknik Kimia dan Lingkungan*, Vol. 3, No. 2. 2019.
  14. Puligundla, P., Smogrovicova, D., Obulam, V. S. R., and Ko, S. Very high gravity (VHG) ethanolic brewing and fermentation, *Journal of Industrial Microbiology*, Vol. 38, pp. 1133-1144, 2011.
  15. Asip, F., Wibowo. Y.P., and Wahyudi. R.T, "Konsentrasi HCl Pada Hidrolisa Sabut Kelapa Untuk Memproduksi Bioetanol" *Jurnal Teknik Kimia*, Vol. 22, No. 1, pp. 10-20. 2019.
  16. Sun, Y and Cheng, J, "Hydrolysis of Lignocellulosic Materials for Ethanol Production." *Bioresource Technology*, Vol. 83, pp. 1-11. 2002.
  17. Anggorowati, D.A., and Dewi, B.K., "Pembuatan Bioetanol Dari Limbah Sabut Kelapa Dengan Metode Hidrolisis Asam dan Fermentasi Dengan Menggunakan Ragi Tape" *Industri Inovatif*, Vol. 3, No. 2, pp. 9-13, 2013.

