EQUILIBRIUM JOURNAL OF
CHEMICAL ENGINEERING
*Homepage:*https://jurnal.uns.ac.id/equilibrium

EJChE Equilibrium Journal of Chemical Engineering

The Effects of Fermentation Extent and Acid Concentration on Bioethanol from HVS Paper Waste

Rizka Mulyawan*, Rizka Nurlaila, Tsa Tsa Anindya Rakhim Ahmadi, Muhammad, Novi Sylvia, Agam Muarif

[a]*Chemical Engineering Department, Engineering Faculty, Universitas Malikussaleh, Lhokseumawe, Indonesia 24355*

*Corresponding author: rmulyawan@unimal.ac.id

DOI: *https://dx.doi.org/10.20961/equilibrium.v7i1.72732*

Article History
Received: 01-04-2023, Accepted: 07-05-2023, Published: 13-05-2023

Keywords:

Bioethanol, Fermentation, HVS paper, Sulfuric acid

ABSTRACT. Bioethanol is an alternative energy sourced from environmentally friendly raw materials from wastes that contain a lot of lignocellulosic such as HVS paper. Paper contains about 85% cellulose, 8% hemicellulose, 5% lignin and the rest is in the form of ash compounds. Bioethanol is ethanol produced from the fermentation of glucose (sugar) followed by a distillation process. This study aims to analyze the effect of a combination of fermentation time and concentration of sulfuric acid on bioethanol. The highest yield of beathanol was obtained at a hydrolysis concentration of 6.5% with a 7-day fermentation time of 3.45%. Bioethanol density that was close to standard was 3.5% acid concentration with 3 and 5 days fermentation. Moreover, at 3.5% acid concentration showed the closest bioethanol viscosity to the standard value with all conditions synthesized acidic bioethanol with pH ranged from 6 to 6.5.

1. INTRODUCTION

A lot of difficulties in meeting global energy needs, which are now met primarily by fossil fuels. The continuous use of fossil fuels creates significant issues, including economic ones related to ensuring their availability for the ensuing several decades as well as the issue of pollution brought on by emissions through combustion into the environment[1].

The production of biodiesel from products derived from palm oil, Jatropha curcas, or the development of bioethanol are just a few of the studies that have been done and resulted in alternative energy sources that can replace petroleum. The synthesis of bioenergy from biomass as a source of renewable raw materials, such as bioethanol, is an alternative that has benefits from both a social and environmental standpoint[2]. Paper waste is one rarely used source of biomass. Indonesia's annual per capita consumption of paper continues to rise, reaching over 220,000 tons. Hence, the foregoing concerns, including those related to energy and the environment, can be solved by using waste paper as a raw material for bioethanol production[3].

HVS paper is known to have compound as bioethanol resources, whcih is cellulose. The content of HVS paper is 85% cellulose, 8% hemicellulose and 5% lignin with trace amount ash compunds[4]. Hence, the use of wasted HVS paper as bioethanol resource has been intensely investigated. There are studies conducted regarding bioethanol synthesis from HVS waste paper. [5] investigated bioethanol synthesis by varying yeast concentration along with the fermentation period. Moreover, [6] varied sulfuric acid concentration from 2% to 5% (v/v) with the optimum condition of 4% (v/v) sulfuric acid concentration for 7 days fermentation period. During the fermentation process, Saccharomyces cerevisiae has been utilized as the microorganism in bioethanol production. The microorganism had been used for long time in bioethanol synthesis and it was even tested for industrial scale for bioethanol production[7]. From these studies, the effects of hydrolysis and fermentation processes are significant to the synthesized bioethanol

The primary component of plants, cellulose, is plentiful in a variety of plant species used to make paper. As glucose molecules are combined to form straight or branched chains by releasing water, starch or cellulose is created. Hemicellulose and lignin fibers are combined to create strong, smooth paper when using cellulose as the primary raw material for papermaking[8]. Considering previous studies in bioethanol synthesis from waste HVS paper that has not been combining varied sulfuric acid in hydrolysis and fermentation period. This serves as the background for examining the impacts of varying the acid hydrolysis concentration and fermentation time in using

HVS paper waste as a raw material for the production of bioethanol.

Synthesized bioethanol that is aimed to fulfil its role as energy replacement of non renewable energy needs to be characterized. Bioethanol characterization is aimed to determine its suitability to peform as biofuel. Bioethanol is characterized through its several properties such as density, acidity, viscosity and its content beside its yield which later determines the optimized process[9].

2. MATERIALS AND METHODS

2.1 Materials and Equipments

The utililzed materials in this study were as follows:

1. Waste HVS paper
2. Sulfuric acid (H_2SO_4)
3. Aquadest
4. Urea
5. NaOH
6. Filter paper
7. Yeast
8. NPK Fertilizer

Equipments used in this research were as follows:

1. Mixer
2. Oven
3. Thermometer
4. Erlenmeyer flask
5. Digital scale
6. Ostwald Viscometer
6. Hot Plate
7. Digital pH meter
9. Hydrolysis equipment
10. Distillation equipment
11. Fermentation equipment

2.2 Methods

The method of acid hydrolysis, followed by fermentation, was the methodology used in this study. Before being hydrolyzed, the waste paper was pretreated. The pretreatment process was converted into paper pulp with paper mass to water volume ratio 1 kg: 20 liter H_2O soaked for 24 hours.

2.2.1 Hydrolysis

In order to clean up the mixtures of cellulose with hemicellulose and lignin, hydrolysis process was conducted. The hyrolysis of waste HVS paper took place by mixing the pulp with varying concentrations of sulfuric acid mixtures; 3.5%, 4.5%, 5.5% and 6.5%. Hydrolysis process was conducted in 250 mL solution with 120ºC temperature for 120 minutes.

Prior the fermentation process, hydrolyzed solution was transformed into inoculum. It prepared by adding 0.1 gram urea and 0.1 gram NPK to 20 mL hydrolyzed solution. The prepared solution then heated to 120ºC for 15 minutes and cooled at room temperature for 24 hours[10].

2.2.2 Fermentation

The hydrolyzed pulp was cooled then filtered and neutralized with NaOH to reach pH 4.5. 180 mL filtrate that passed through the filter paer was fermented with 0.9 gram of urea and 0.9 gram NPK fertilizer along with 20 mL inoculum for 3, 5 and 7 days. Following the process, the fermented solution was distilled for 5 hours at 78-80ºC in order to separate it from water.

2.2.3. Bioethanol Characterization

Having synthesized the bioethanol, it was characterized though pH, density, viscosity, yield and its content through gas chromatography analysis. Viscosity analysis was performed by utilizing the Ostwald viscometer[11]. The density of bioethanol was managed through (1)[12].

$$\rho = m/v \quad (1)$$

Where ρ is density, m is mass of bioethanol and v is the volume.

Moreover bioethanol viscosity was determined by using (2)[12].

$$\eta_{bioethanol} = \frac{\rho_{bioethanol} \times t_{bioethanol}}{\rho_{water} \times t_{water}} \times \eta_{water} \quad (2)$$

Where η is viscosity, ρ is density and t is flow time.

3. RESULTS AND DISCUSSION

3.1 Hydrolytic Acid Concentration and Fermentation Period Effects on Yield of Bioethanol

Yield of synthesized bioethanol with varying acid concentrations in hydrolysis process and fermentation period is shown in Table 1.

Table 1. Synthesized Bioethanol Yields

Acid Concentration (%)	Fermentation Time (Days)	Bioethanol Yield (%)
3.5	3	0.692
	5	0.994
	7	2.1511
4.5	3	1.203
	5	1.309
	7	2.349
5.5	3	1.219
	5	1.326
	7	2.595
6.5	3	1.390
	5	1.689
	7	3.451

It can be seen that at constant acid fermentation period, bioetanol yield was also found to be affeceted by acid concentration in hydrolysis process. It was due to more reactants to break the structure of cellulose from waste HVS paper into glucose, which was converted into bioethanol in fermentation process[13]. Moreover, yield of bioethanol is linearly affected by fermentation period. This is in line with [14] that stated bioethanol yield is linearly proportional to fermentation duration. It was due to more time given for the yeast that contains *Saccharomyces* to digets cellulose that was provided from waste HVS paper which had been hydrolysed.

3.2 Hydrolytic Acid Concentration and Fermentation Period Effects on Bioethanol Density

Obtained bioethanol densities with varying acid concentration during hydrolysis process is shown in Table 2.

Table 2. Synthesized Bioethanol Densities

Acid Concentration (%)	Fermentation Time (Days)	Bioethanol Densities (gr/mL)
3.5	3	0.7844
	5	0.7868
	7	0.8014
4.5	3	0.8284
	5	0.8308
	7	0.8528
5.5	3	0.8322
	5	0.8402
	7	0.8652
6.5	3	0.8442
	5	0.8638
	7	0.8686

The synthesized bioethanol densities are figured in the Fig. 1.

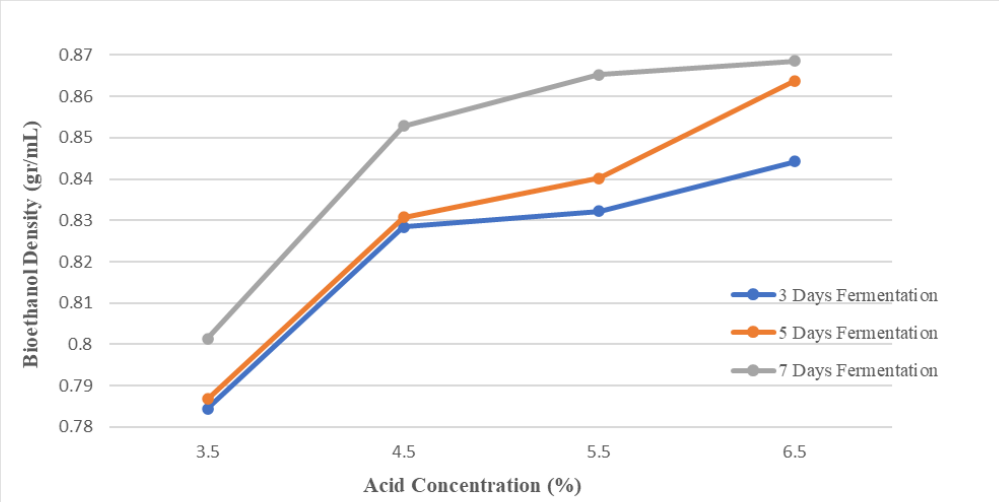

Figure 1. Synthesized Bioethanol Density

It can be seen from Fig. 1 that generally the density of synthesized bioethanol increased as acid concentration and fermentation period increased. Bioethanol produced close to standard bioethanol density, which is 0.7871 - 0.7896 g/mL [15], were the combination of 3.5 % acid concentration with 3 and 5 days fermentation period. On the other hand, bioethanol density produced from 7 days of fermentation exhibited different trend compared to others. This might be due to over fermentation period that passed the optimum conditions [16].

3.3 Hydrolytic Acid Concentration and Fermentation Period Effects on Bioethanol Acidity

Synthesized bioethanol acidity in this study was observed to be acidic. The pH of bioethanol pH was found to be varying from 6.0 to 6.5 as schown in Table 3. Acidic properties of bioethanol was due to acid formation from fermentation process [17].

3.4 Hydrolytic Acid Concentration and Fermentation Period Effects on Bioethanol Viscosity

Bioethanol viscosity is an important properties as biofuel. The role of viscosity is directly affecting its performance during machine test. The standard viscosity of bioethanol is 1.22 cP (centi Poise) [18]. The viscosity of produced bioethanol was observed and shown in Table 3.

Table 3. Synthesized Bioethanol Viscosities

Acid Concentration (%)	Fermentation Time (Days)	Bioethanol Viscosities (cP)
3.5	3	1.573
	5	1.147
	7	1.130
4.5	3	1.137
	5	1.130
	7	1.096
5.5	3	1.115
	5	1.104
	7	1.096
6.5	3	1.093
	5	1.071
	7	1.067

It can be seen from Table 3 that there was no exact viscosity that matched the standar bioethanol viscosity. The one that was closest to standar value was bioethanol that was synthesized from 3.5% acid concentration and 5 days of fermentation.

The property of viscosity showed the optimum condition for bioethanol production that follows the standardized property. Five days of fermentation duration with 3.5% acid concentration made synthesized bioethanol not too watery, thus these conditions might be considered to be the most optimum condition for bioethanol production regarding viscosity property.

3.5 Synthesized Bioethanol Content

According to the results from other parameters, the contents of synthesized ethanol focused on several samples. The effects of fermentation period was observed through 5 and 7 days of fermentation with 6.5% acid concentration. Beside that, acid concentration effects was observed by analysing 5.5% and 6.5% acid concentrations with 7 days fermentation period. Fig. 2 shows Gas Chromatography spectrums of synthesized bioethanol with the parameters of the spectrum are presented in Table 4.

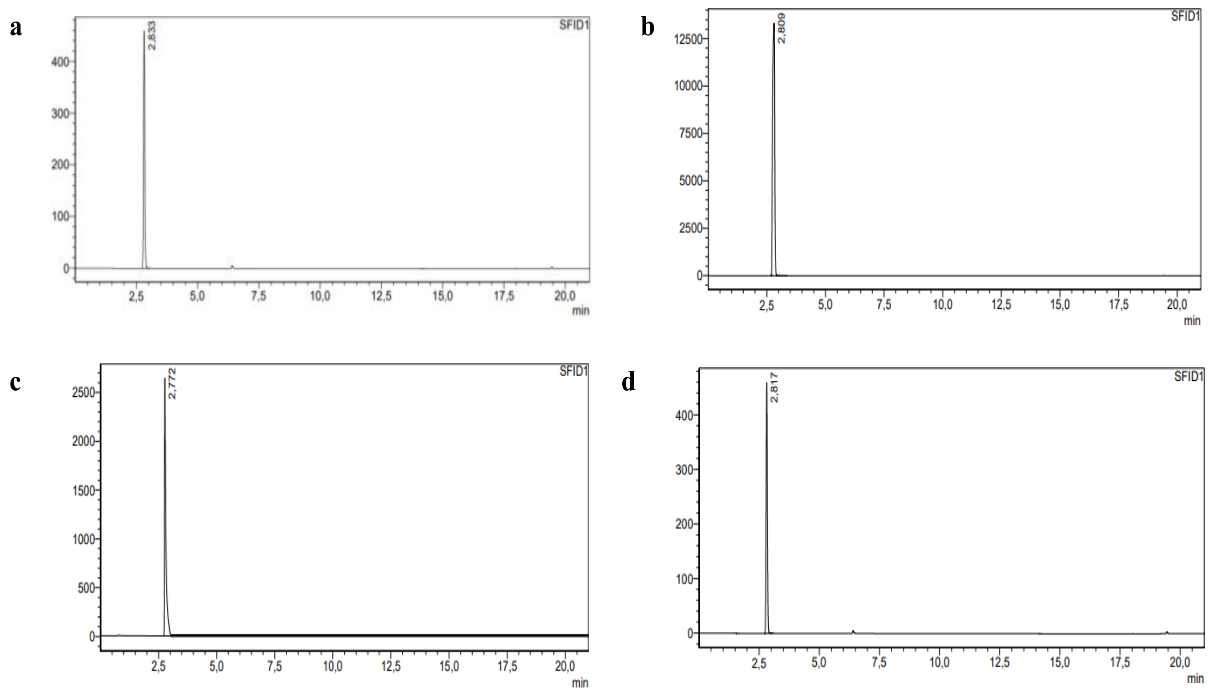

Figure 2. (a) Standard Ethanol GC Spectrum; (b) 6.5% acid concentration and 7 days fermentation Bioethanol GC Spectrum; (c) 6.5% acid concentration and 5 days fermentation Bioethanol GC Spectrum; (d) 5.5% acid concentration and 7 days fermentation Bioethanol GC Spectrum

Table 4. Bioetahnol GC Spectrum Details

Parameters	Ethanol	6.5% Acid; 7 Days	6.5% Acid; 5 Days	5.5% Acid; 7 Days
Time Retention	2.833	2.809	2.772	2.817
Area	87106371	78805237	10949949	1636815
Height	466831	13306111	2629479	459454
Concentration	99%	36.546%	26.410%	25.019%

Table 4 confirms that the the role of acid concentration during hydrolysis process and fermentation period is clearly exhibited. The concentration of ethanol was found to be linearly proportional to acid conectration; the higher acid concentration of acid in hydrolysis, the higher synthesized ethanol. Moreover, with the same acid concentration, fermentation time also linearly proportional to bioethanol produced to some extent.

4. CONCLUSION

The variations of acid concentration in hydrolysis process and fermentation duration was observed to influence bioethanol significantly. The influence of acid concentration and fermentation period were significantly affected the yield, density, acidity and viscosity of synthesized bioethanol.

This study suggest the significant role of waste particularly waste HVS paper for energy production such as bioethanol. It is suggested to explore on other waste for more valuable products synthesis.

REFERENCES

[1] C. N. Putri and B. Utami, "Pembuatan Bioetanol dengan Cara Hidrolisis Menggunakan Kertas Koran Bekas serta Pemurnian Menggunakan Agen Pengering (MgSO4, Na2SO4, dan CaCl2)," *JC-T (Journal Cis-Trans): Jurnal Kimia dan Terapannya*, vol. 1, no. 1, 2017.

[2] Y. Susmiati, "Prospek Produksi Bioetanol dari Limbah Pertanian dan Sampah Organik," *Industria: Jurnal Teknologi dan Manajemen Agroindustri*, vol. 7, no. 2, pp. 67–80, 2018.

[3] F. Fitria and K. Kasmudin, "Hidrolisis Kadar Glukosa Kertas Koran Menggunakan Gelombang Ultrasonik," *Jurnal Teknik Juara Aktif Global Optimis*, vol. 2, no. 1, pp. 56–61, 2022.

[4] A. Subyakto, F. Wasiyah, and L. Masruroh, "Utilization of HVS Paper Waste for The Manufacture of Oxalic Acid," *IPTEK The Journal of Engineering*, vol. 7, no. 2, pp. 66–70, 2021.

[5] P. Wahyu, C. Chairul, and Y. Yelmida, "Biokonversi Kertas HVS Bekas Menjadi Bioetanol Dengan Variasi Kondisi Hidrolisis Asam Dan Waktu Fermentasi," *Jurnal Online Mahasiswa (JOM) Bidang Teknik dan Sains*, vol. 6, pp. 1–10.

[6] C. Ramayanti and R. G. Ketty, "Bioethanol Production From Waste Paper Using Separate Hydrolysis and Fermentation," *Ind. J. Chem. Res*, vol. 5, no. 1, pp. 429–433, 2017.

[7] L. Favaro, T. Jansen, and W. H. van Zyl, "Exploring industrial and natural Saccharomyces cerevisiae strains for the bio-based economy from biomass: the case of bioethanol," *Crit Rev Biotechnol*, vol. 39, no. 6, pp. 800–816, 2019.

[8] C. M. Thaib, E. Gultom, and B. Aritonang, "Pembuatan Kertas Dari Limbah Kulit Durian dan Ampas Tebu Dengan Perbedaan Konsentrasi NaOH," *JURNAL KIMIA SAINTEK DAN PENDIDIKAN*, vol. 4, no. 1, pp. 1–11, 2020.

[9] G. A. Tenkolu, K. D. Kuffi, and G. T. Gindaba, "Optimization of fermentation condition in bioethanol production from waste potato and product characterization," *Biomass Convers Biorefin*, pp. 1–19, 2022.

[10] M. J. Pelezar and E. C. S. Chan, "Basics of Microbiology 2." UI Press, Jakarta, 2008.

[11] M. Asif, S. S. Kasim, S. Parveen, and A. A. Sheikh, "Effect of Electrolytic Concentration on Density and Viscosity of Ethanol-Water Mixed Solvent Systems," *International Journal of Chemical Engineering Research*, vol. 8, no. 1, pp. 47–50, 2016.

[12] F. B. Amtiran, F. K. Y. Serangmo, and I. Gauru, "Pembuatan bioetanol skala laboratorium sebagai bahan bakar alternatif untuk pengembangan energi terbarukan dari bahan baku serbuk buah bidara (Ziziphus Mauritiana)," *Jurnal Teknik Mesin*, vol. 2, no. 1, pp. 1–6, 2019.

[13] K. J. Dussan, D. D. Silva, E. J. Moraes, P. V Arruda, and M. G. Felipe, "Dilute-acid hydrolysis of cellulose to glucose from sugarcane bagasse," *Chemical engineering transaction*, vol. 38, 2014.

[14] D. Tri Retno and W. Nuri, "Pembuatan bioetanol dari kulit pisang," in *Prosiding Seminar Nasional Teknik Kimia "Kejuangan" 2011*, 2011.

[15] Dirjen Migas, "DEPARTEMEN ENERGI DAN SUMBER DAYA MINERAL REPUBLIK INDONESIA DIREKTORAT JENDERAL MINYAK DAN GAS BUMI," 2008.

[16] A. K. Azad, N. Yesmin, S. K. Sarker, A. Sattar, and R. Karim, "Optimum conditions for bioethanol production from potato of Bangladesh," *Advances in Bioscience and Biotechnology*, vol. 2014, 2014.

[17] S. Maicas, "The role of yeasts in fermentation processes," *Microorganisms*, vol. 8, no. 8. MDPI, p. 1142, 2020.

[18] M. Hidayati, K. D. Sapalian, I. Febriana, and Y. Bow, "PENGARUH pH DAN WAKTU FERMENTASI MOLASE MENJADI BIOETANOL MENGGUNAKAN BAKTERI EM4," *Publikasi Penelitian Terapan dan Kebijakan*, vol. 5, no. 1, pp. 33–40, 2022.