PURIFICATION OF ETHANOL BY CONTINUOUS ADSORPTION METHOD USING ZEOLITE 3A AND CALCIUM OXIDE

Mukhtar Anas Ibrahim*, Muhammad Hafizh Musyaffa, Heriyanto Heriyanto, Haryadi Haryadi
Department of Chemical Engineering, Politeknik Negeri Bandung, Jl. Gegerkalong Hilir, West Bandung 40559, West Java, Indonesia
*email: mukhtar.anas.tkpb18@polban.ac.id

Received 4 May 2022
Accepted 23 June 2022

Abstract

The depletion of oil reserves and the increasing need for fuel have become a problem in the supply of energy sources. One of the efforts to maintain the availability of fuel is to use ethanol fuel grade as an alternative fuel. Continuous adsorption is one method that can purify ethanol up to a concentration of 99.5% (v/v). This study aims to increase the purity of ethanol using adsorbent zeolite 3A and calcium oxide (CaO) with a continuous adsorption method. The feed used is technical ethanol with a concentration of 96% (v/v). The equipment used is a continuous adsorption apparatus with a fixed bed column. Parameters measured during the process were ethanol concentration, feed flow rate, temperature, and pressure. Variations carried out were variations in feed flow rate (5 mL/min, 12 mL/min, and 18 mL/min) and the type of adsorbent (zeolite 3A and CaO). The best continuous adsorption process at 5 mL/min flow rate using zeolite 3A adsorbent with the ethanol product concentration rated up to 99.54% on pycnometer analysis and 99.33% on GC-MS analysis. While using CaO adsorbent, the best results were obtained at 5 ml/min rate, with the highest ethanol product concentration of 99.54% in the pycnometer and 99.33% on GC-MS.

***Keywords**: fuel grade ethanol, adsorption, zeolite 3A, calcium oxide*

Introduction

Petroleum is an element for humans as a source of energy that can be used in life, as evidenced by fossil fuels in Indonesia which continue to increase linearly by increasing the number of motorized vehicles from year to year. Badan Pusat Statistik (2021) stated that the number of motorized vehicles in Indonesia increased by 7.83% from 2020 as many as 136,137,451 units to 2021 as many as 143,797,227 units. Fossil-based fuels such as gasoline and diesel are still the primary sources of fuel used. Meanwhile, the availability of crude oil is estimated only to be used for the next 9.5 years when viewed from the available oil reserves in Indonesia of 2.44 billion barrels divided by the level of oil production of 700 thousand barrels per day (Kementerian Energi dan Sumber Daya Mineral, 2021).

There is a need for alternative fuels with abundant availability with quality equal to or better than the currently used fuel. One that meets these requirements is ethanol which is used as fuel. Based on SNI DT 27-0001-2006 fuel grade ethanol has a minimum concentration of 99.5% (v/v) (SNI, 2006). This is because the blended fuel containing water will corrode engine components (Koc. M., 2009).

The ethanol concentration from the fermentation process has a low concentration. The highest ethanol concentration based on research conducted by Cahyaningtiyas et al. (2021) fermenting sugarcane juice using Saccharomyces Cerevisiae produced ethanol concentration

10%. Ethanol needs to be purified by the distillation method, but this method is only able to increase the concentration of ethanol up to 89.43% (mole fraction), and 95.57% (mass fraction) at the boiling point mixture of 78.15 °C (Perry & Green, 1997). This is due to the ethanol-water azeotrope point. So, additional methods are needed to increase the concentration of ethanol to achieve fuel-grade standards.

There are several ways that can be used to obtain ethanol with concentrations above the azeotrope, namely extractive distillation, azeotropic distillation, membrane technology, and adsorption processes (Abdollahipoor et al., 2018; Miranda et al., 2020). Extractive distillation and azeotropic distillation have a weakness, namely the many requirements for the selection of the third type of component to be used. These requirements are high solvent absorption of ethanol, low solvent solubility in water, chemical stability, efficient techniques for ethanol recovery and solvent recycling, use of non-toxic solvents, and sustainable solvents for the process. The advantage of liquid-liquid extraction is the low energy requirement, but to obtain the product from the solvent is usually done by distillation so that it becomes less economical (Lee et al., 2021).

Pervaporation is a process of separating a mixture using membrane technology. The principle of pervaporation is permeation membrane and evaporation (Fan et al. 2016). Pervaporation has been used to separate ethanol-water mixtures using nano-pore hydroxy sodalite zeolite membranes. (Kazemimoghadam & Rigi, 2018). The weakness of this process is the cost of producing membranes, especially inorganic membranes, which are very expensive (Davey et al., 2016). The last method that can be used to purify ethanol is the adsorption process. Adsorption is the process of absorbing the material (adsorbate), which in this case is water or water vapour from ethanol, on a solid surface (adsorbent). In this research, a continuous adsorption process was carried out in the liquid phase without a heating process to suppress energy requirements. Based on research conducted by Lourentius S. (2012), the continuous adsorption process in the liquid phase using Malang natural zeolite adsorbent obtained an ethanol concentration value of 99.9–100%(w/w).

In this research, zeolite 3A and calcium oxide were used as adsorbents because both adsorbents were effective in producing fuel-grade ethanol. Based on the research of Mekala et al. (2022), Zeolite 3A is a better adsorbent and is also effective for absorbing water in an ethanol-water mixture under azeotropic conditions when compared to zeolite 4A. The highest concentration obtained was 99.9443% using zeolite 3A as adsorbent. In addition, based on research by Sergio & Dwikurniawan (2011), distillation and adsorption methods were carried out to make absolute ethanol using zeolite 3A and obtained ethanol fuel grade at a concentration of 99.7%. As for calcium oxide adsorbents, this is evidenced by research by Villarul et al. (2017) in the dehydration process of bioethanol derived from nirah nipah fermentation using the distillation-adsorption method using calcium oxide adsorbents, the highest concentration of ethanol is 99.7%. We use CaO as adsorbent because it has abundant availability. CaO is placed in a desiccator before use to prevent CaO from turning into $Ca(OH)_2$.

Research Methods

Tools and materials

The equipment used in this research includes a set of adsorption process tools as shown in Figure 1, thermometers, stopwatch, oven, ball mill, sieve shaker, analytical balances, gas cromatography and mass spectroscopy (Shimadzu QP Ultra 2010), pycnometers, and commonly used glassware. The materials used are technical ethanol 96% (v/v), calcium oxide, and zeolite 3A.

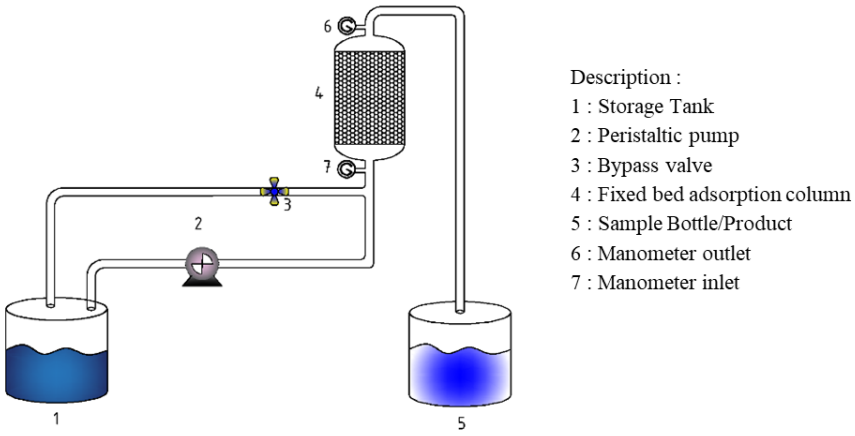


Figure 1. Schematic diagram of equipment for adsorption process

The adsorption column used in this research is stainless steel with a column height of 60 cm and a diameter of 2.79 cm. Material data for CaO and zeolite adsorbent components can be seen in Table. 1 and Table. 2.

Table 1. Specification of zeolite 3A

Model	3A
Color	Light gray
Nominal per diameter	3 angstroms
Shape	Sphere
Diameter (mm)	3–5
Size ratio up to grade (%)	≥98
Bulk density (g/ml)	≥0.70
Wear ratio (%)	≤0.20
Crushing strength (N)	≥85/piece
Static H_2O adsorption (%)	≥21
Ethylene adsorption (%)	≤3.0
Water content (%)	≤1.5
Typical chemical formula	$0.4K_2O$. $0.6Na_2O$. Al_2O_3 . $2SiO_2$. $4.5\ H_2O$ $SiO_2 : Al_2O_3 \approx 2$

Table 2. Specification of CaO

Material	Percentage (%)
Total CaO	84.17
Free CaO	79.83
$CaCO_3$	7.75
LOI	13.58
SIO_2	0.64
not dissolved	0.41
Al_2O_3	0.3
Fe_2O_3	0.52
K_2O	0.045
Na_2O	0.046
MgO	0.83
TiO_2	0.043
P_2O_5	0.004
H_2O-	<0.001
SO_3	0.041
Cl	<0.001

Preparation stage of adsorbent

The first stage is the adsorbent preparation stage. Zeolite 3A used has a size of 3–5 mm. Zeolite sizes 3–5 mm were chosen because these sizes are common zeolite sizes and are widely available in the commercial zeolite market. To adjust the size, CaO, which initially had the shape of a lump, was reduced to a uniform size with the zeolite to equalize the research variables. Thermal activation was carried out at 250 °C for 4 hours using an oven, this was based on the temperature of the 3A zeolite regeneration, then put in a tightly closed container (Gabruś et al., 2018). On the calcium oxide (CaO) adsorbent, grinding and sieving were

carried out with 2–4 mm. The sifted adsorbent is stored in a tightly closed container.

Experimental stage of continuous adsorption

The next step is a continuous adsorption experiment. This adsorption experiment phase begins by entering 3 liters 96% ethanol into the feed tank and inserting the adsorbent into the adsorption column, then calibrating the flow for each stream to be fed (5, 12, 18 mL/min). Then the adsorption process is carried out by flowing the feed ethanol using a peristaltic pump to the bottom of the adsorption column. The process is carried out at room temperature and atmospheric pressure. The ethanol solution will enter the adsorption column where the adsorbent has been previously inserted; in the water column, it will be adsorbed by the adsorbent while the ethanol will escape and flow into the product tank. Two variations were carried out, namely variations in the type of adsorbent (calcium oxide and zeolite 3A) and variations in the feed flow rate (5, 12, and 18 mL/min). Sampling was carried out every 5 minutes, and the ethanol concentration analysis was conducted.

Regeneration stage of adsorbent

The adsorbent that has been used needs to be regenerated. Regeneration of the adsorbent is carried out to restore the adsorption ability of the adsorbent that has experienced saturation. The regeneration process was carried out on 3A zeolite adsorbent by heating using an oven at 250 ^{o}C for 4 hours, this was done based on the 3A zeolite The highest regeneration efficiency of zeolite 3A adsorbent bed (RE) was at a temperature of 250 °C with an RE value of 65.7%, within 14000 seconds (3.9 hours) the value of total water content in zeolite adsorbent bed tended to stabilize with no significant reduction. significant, and after passing 16000 seconds (4.4 hours) the value of total water content in zeolite adsorbent bed was constant. (Gabruś et al., 2018). The heated adsorbent was put into a tightly closed container.

Analysis stage of product ethanol concentration

The last step is the analysis of the product ethanol concentration. Each sample of ethanol that has been adsorbed at a particular time is then analyzed to determine its concentration. This analysis uses the density approach and GC-MS (Gas Cromatography and Mass Spectroscopy), these two methods are based on research Walidah et al. (2015). GC-MS analysis was carried out on samples that had met the requirements for the ethanol concentration of SNI DT 27-0001-2006 based on the pycnometer approach. The tool used at this stage is a pycnometer calculation of the ethanol concentration with the sample density approach to standard ethanol.

A density test was carried out using a pycnometer. The pycnometer must be dry and clean, weigh the empty pycnometer and record the results (W_1), enter the distilled water, and weigh the empty pycnometer and record the results (W_2). Finally, empty and rinse the pycnometer with the sample to be measured from the lowest concentration, then weigh the empty pycnometer and record the result (W_3). When weighing the pycnometer, dry the outside of the pycnometer using filter paper and do not touch the pycnometer directly.

The density of ethanol can be calculated using equation 1.

$$\boldsymbol{\rho_{ethanol}} = \frac{(\mathbf{W_3} - \mathbf{W_1})}{(\mathbf{W_2} - \mathbf{W_1})} \times \boldsymbol{\rho_{water}} \qquad (1)$$

W1: empty pycnometer mass.
W2: pycnometer mass + water.
W3: pycnometer mass + ethanol

The data is processed with the equation obtained from the ethanol concentration data against standard density from the farmakope after obtaining the density of each sample.

Results and Discussion

Continuous adsorption process

The adsorption column used in this research was made and assembled from stainless steel pipes. The specifications of the columns used can be seen in Table 3. Determination of column dimensions is based on Lourentius (2012) research, which adsorbs water on ethanol using Malang natural zeolite. Lourentius used a 1.37 inch (3.48 cm) of diameter column with an adsorbent height of 30 cm and a feed flow rate of 2.22 mL/min. Synthetic zeolite 3A has a more uniform structure than natural zeolite, so the flow rate used in this research is higher, using flow rates of 5, 12, and 18 mL/min.

Table 3. Specification of adsorption column

Specification	Size
Height (cm)	60
Inside diameter (cm)	2.79
Outside diameter of column (cm)	3.34
Volume of adsorption column (cm^3)	366.63

The measurement of the ethanol concentration of the product was carried out using a density approach using a pycnometer. All samples resulting from the adsorption process were measured for density using a pycnometer. The density was calculated using equation 1 and then processed using the equation obtained from the regression between density and standard ethanol concentration from the Farmakope. The table alcoholmetric density and ethanol concentration from farmakope data can be seen in Table 4.

Table 4. Alcoholmetric table from Farmakope (Departemen Kesehatan Republik Indonesia, 2020)

Ethanol concentration v/v % (15.56 °C)	Density (g/mL) 25 °C
95	0.8092
96	0.8053
97	0.8011
98	0.7968
99	0.7921
100	0.7871

Based on the table above, density regression can be carried out on the ethanol concentration, and then the equation value is obtained. The equation of the regression results can be seen in equation 2.

$$y = 0.0044x + 1.2287 \qquad (2)$$

The concentration of the ethanol product can be calculated by entering the product density value against equation 2 as the Y value, and then the x value is obtained, which is the concentration of the ethanol product.

The adsorption process is carried out at atmospheric pressure because the measurements that occur at the inlet and outlet manometers do not increase the pressure. This event may occur due to the low feed flow rates (5, 12, and 18 mL/min). It can be seen in Figure 2.

Figure 2. Adsorption process equipment

Performance of calcium oxide adsorbent

The adsorption process using calcium oxide adsorbent was carried out at a temperature of 25 °C with an air pressure of 706.8 mmHg, which was carried out continuously on a stainless steel column with a diameter of 2.79 cm and a height of 60 cm for 90 minutes. The feed used is technical ethanol with a concentration of 95.9% based on a pycnometer analysis. The mass of calcium oxide used in one adsorption process was 288 grams. The product resulting from the adsorption process was analyzed for its concentration using a pycnometer. The following is a curve of product ethanol concentration on adsorption using calcium oxide against processing time. It can be seen in the concentration versus time curve for the calcium oxide adsorbent in Figure 3.

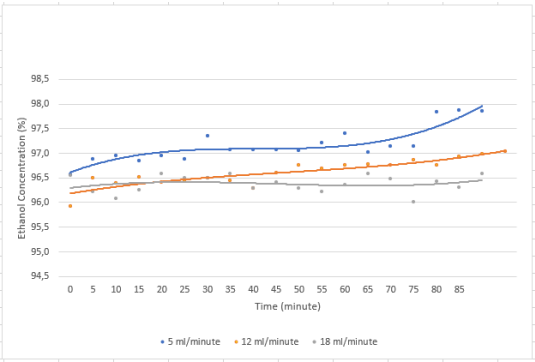


Figure 3. Curve of ethanol concentration against calcium oxide adsorption time

The pattern of changes in concentration that occurs in the adsorption process using calcium oxide adsorbent is generally similar in the three variations of the flow rate used. The increase in product ethanol concentration on the calcium oxide adsorbent did not increase drastically but increased slowly from the first sample to the last sample. In calcium oxide adsorbent, adsorption takes place chemically, where the adsorption process will run when a reaction occurs between calcium oxide and water to produce $Ca(OH)_2$. With this reaction, the concentration of water in the solution will decrease and increase the purity of the ethanol.

The ethanol product produced from the adsorption process using CaO adsorbent has relatively high turbidity. Turbidity comes from the CaO adsorbent, which collapses due to contact with the feed stream. Turbidity also comes from the $Ca(OH)_2$ reaction product of CaO and water, which is carried to the output stream. This becomes an obstacle when the sample is analyzed by pycnometer; for efforts to reduce the turbidity, the sample is left for one day so that the contaminants settle and are placed in a closed room so that they do not come into contact with outside air. After being allowed to stand for a day, a precipitate formed at the bottom of the sample bottle from the turbidity of the sample. This method can reduce the turbidity contained in the sample, but there is still a tiny amount of turbidity dissolved in the sample. The following is a sample image sedimented, which can be seen in Figure 4.

Figure 4. Samples of sedimented ethanol from the adsorption process using calcium oxide adsorbent

The continuous adsorption process using calcium oxide adsorbent increased the ethanol concentration until it passed the azeotrope point but could not reach the fuel grade ethanol concentration. The reaction between calcium oxide and water takes longer to reach the fuel grade concentration, so a longer contact time

between the adsorbent and feed is required. The method that can be used to increase the adsorption contact time is to increase the column height or decrease the flow rate used.

Although it cannot produce fuel-grade concentration until 90 minutes, the calcium oxide adsorbent can still absorb water until the adsorption process is stopped. This can be seen from the trend in the concentration curve to processing time which continues to rise until the last sample. The ability of the calcium oxide adsorbent to absorb much water is because the entire mass of calcium oxide can react with water so that the adsorption process can continue as long as the calcium oxide mass is still available in the column.

In the adsorption process using calcium oxide adsorbent, the smaller the flow rate used, the greater the ethanol concentration of the product produced. It happens because the adsorption contact time will be longer if carried out at a lower flow. The highest concentration obtained in the continuous adsorption process using calcium oxide adsorbent was 97.86%, obtained at a 5 mL/min flow rate on the sample at 85 minutes. The adsorption results using Calcium oxide adsorbent succeeded in increasing the ethanol concentration past its azeotrope point but could not reach the fuel grade ethanol concentration according to SNI DT 27-0001-2006.

The previous research that adsorbed water from bioethanol 96% using calcium oxide adsorbent was the research of Villarul et al. (2017) adsorbed using the vapour phase, where the feed was preheated at a temperature of 78 °C, then passed to a column containing calcium oxide adsorbent with a ratio of ethanol to adsorbent 1:2. The concentration of the results obtained from adsorption using the vapour phase reached 99.7%. This proves that using calcium oxide adsorbent in the vapour phase with heating proves that ethanol adsorption is better than that carried out in the liquid phase without heating.

Performance of zeolite 3A adsorbent

The adsorption process using zeolite 3A adsorbent was carried out under environmental conditions with a temperature of 25 ^{o}C and ambient air pressure of 706.8 mmHg, which was carried out continuously on a stainless steel column with a diameter of 2.786 cm and a height of 60 cm for 90 minutes. The feed used is technical ethanol with a concentration of 95.9% based on the results of pycnometer analysis. The mass of zeolite used in one adsorption process is 251 grams. The concentration versus time curve for zeolite 3A adsorbent can be seen in Figure 5.

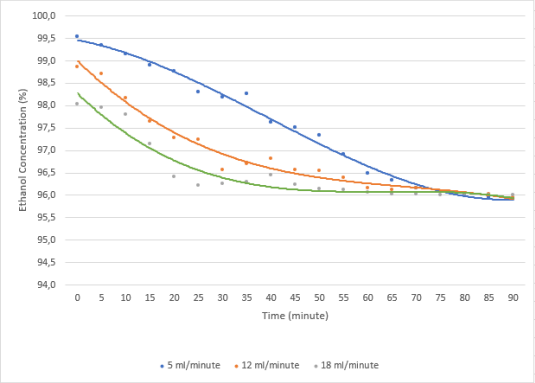


Figure 5. Curve of ethanol concentration against zeolite 3A adsorption time

Changes in ethanol concentration in the adsorption process using zeolite 3A as adsorbent at the three flow rate variations (5, 12, 18 mL/min) had the same pattern. The ethanol concentration will increase rapidly from the feed to sample concentration at minute 0. In zeolite 3A adsorbent, the adsorption process is physical adsorption, where water molecules will be adsorbed onto the surface of the zeolite pores, while ethanol molecules will not. A water molecule has a molecular size of 2.75 Angstrom and an ethanol molecule has a molecular size of 4.4 Angstrom. The zeolite adsorbent used must have a pore diameter larger than the diameter of the water molecule, but must

be smaller than the molecular diameter of ethanol, so the diameter of the zeolite adsorbent must be larger than 2.75 Angstrom, but smaller than 4.4 Angstrom (Perry & Green, 1997).

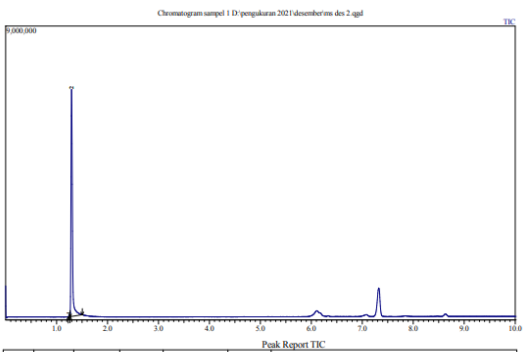
The feed that first encounters the fresh zeolite adsorbent will have a high concentration when it comes out of the bed. This happens because the pores in the zeolite adsorbent are empty when the adsorption process begins. As a result, water molecules in the feed can enter more easily into the porous zeolite so that the ethanol concentration of the resulting product increases drastically.

The ethanol concentration of the product decreased slowly with time. The pores in the zeolite are filled more and more as the processing time goes on; this reduces the ability of the adsorbent to absorb water molecules in the feed so that the ethanol concentration of the resulting product is lower than the concentration of the sample product at minute 0. The ability of the adsorbent to adsorb water continues to decrease until finally, the zeolite used is saturated and causes the product ethanol concentration to be the same as the feed concentration.

Three flow rate variations were carried out to find the best flow rate for increasing the ethanol concentration resulting from the adsorption process. Of the three variations of the flow rate used, the highest concentration of ethanol from the adsorption process was obtained at a flow rate of 5 mL/min. The smaller the flow rate used, the contact time between the adsorbent and the feed will increase. This causes the product ethanol concentration to be higher at low flow rates. This follows the opinion of Darjito et al. (2013), which states that the frequency of collisions between the adsorbent and the adsorbate will increase as the adsorption contact time increases.

The highest ethanol concentration based on pycnometer analysis of 99.54% was obtained in the sample that first came out of the adsorption column at a 5 mL/min flow rate. This concentration has complied with SNI DT 27-0001-2006 as ethanol fuel grade in terms of concentration.

The best adsorption operating conditions were at a feed flow rate of 5 mL/min with zeolite 3A as adsorbent, which resulted in a product ethanol concentration of 99.54% (v/v) with pycnometer analysis, so that the concentration according to fuel grade standards based on SNI DT 27-0001-2006 was 99.5% (v/v). After that, the sample concentration was measured again using GC-MS analysis. Based on the results of the Gas Chromatography (GC) analysis, it is known that there is one peak in the retention time of 1.245 for ethanol and 1.296. After that, analyzed by Mass Spectrometry (MS) to determine the type of molecule. From the results of the Mass Spectrometry analysis, it can be seen that the mass sample molecules are 46 g/mol (ethanol) and 32 g/mol (methanol). The results of the GC-MS analysis can be seen in Figure 6, Figure 7, and Figure 8.



Peak Report TIC

Peak	R.Time	Area	Area%	Height	A/H	Name
1	1.245	91289	0.67	62963	1.45	Methanol (CAS) Carbinol
2	1.296	13498947	99.33	6951583	1.94	Ethanol (CAS) Ethyl alcohol

Figure 6. GC analysis for ethanol concentration of the product.

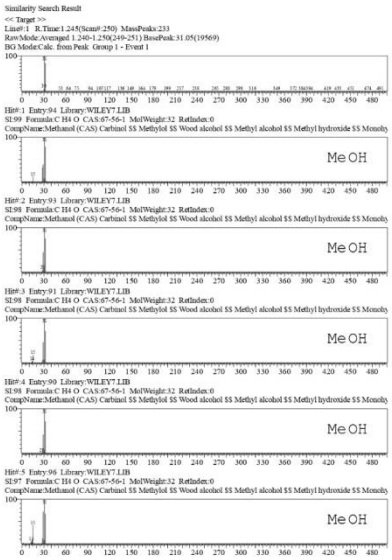


Figure 7. MS analysis for methanol of the product.

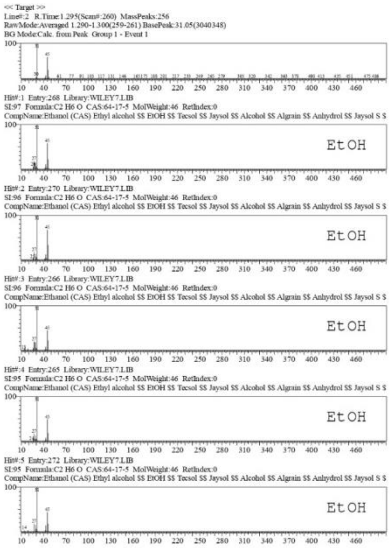


Figure 8. MS analysis for ethanol of the product.

From the results of the GC-MS analysis, it was found that the sample had an ethanol concentration of 99.33% based on the sample area. Methanol was also found in the sample content with a concentration of 0.67%. No water was detected in the sample analysis results, which indicated that all the water in the feed had been completely absorbed into the adsorbent. The sample can already be used as fuel because no water content can damage motorized vehicle engines.

Conclusion

Berdasarkan Based on the research that has been done, it can be concluded that in the process of increasing the concentration of ethanol using the continuous adsorption method using zeolite 3A and calcium oxide as adsorbents, the smaller the flow rate used, the higher the concentration of ethanol produced. Zeolite 3A adsorbent has a better adsorption ability than calcium oxide because it produces ethanol products with higher concentrations.

The best adsorption operating conditions were at a feed flow rate of 5 mL/min with zeolite 3A as adsorbent. The concentration of ethanol products produced was 99.54% (v/v) based on pycnometer analysis and 99.33% on GC-MS. The ethanol concentration product produced for the pycnometer analysis method is 99.54% (v/v), so that the concentration according to the standard fuel grade based on SNI DT 27-0001-2006 is 99.5% (v/v).

Acknowledgements

The researcher expresses his deepest gratitude to several parties, namely Bandung State Polytechnic who has provided laboratory facilities, Deputy Director 1 of Bandung State Polytechnic who has funded this publication. This research is supported by the analytical facilities of the Instrument Chemistry Laboratory at the Indonesia University of Education.

References

Abdollahipoor B, Shirazi SA, Reardon KF, Windom BC., 2018, Near-azeotropic volatility behavior of hydrous and anhydrous ethanol gasoline mixtures and impact on droplet evaporation dynamics, *Fuel Process Technol*, 181, 166–174.

Badan Pusat Statistik, 2021, Jumlah Kendaraan Bermotor, www.bps.go.id. Retrieved Mei 23.2022

Badan Standardisasi Nasional (BSN), 2006, Standar Mutu Etanol Sebagai Bahan Bakar. SNI DT 27-0001-2006.

Cahyaningtiyas, A., Sindhuwati, C., Kimia, J. T., & Malang, P. N., 2021, Pengaruh Penambahan Konsentrasi Saccharomyces Cerevisiae Pada Pembuatan Etanol Dari Air Tebu Dengan Proses Fermentasi. *Distilat: Jurnal Teknologi Separasi*, *7*(2), 89–94.

Davey, C. J., Leak, D., & Patterson, D. A., 2016, Hybrid and mixed matrix membranes for separations from fermentations. *Membranes*, *6*(1).

Departemen Kesehatan Republik Indonesia, 2020, Farmakope Indonesia Edisi VI, Jakarta, 2279.

Darjito, Triandi, Rachmat., Mardiana, Diah, 2013, Adsorpsi Ion Mg (II) Menggunakan Adsorben Kitin Terfosforilasi. *Malang : Jurnal Jurusan Kimia Universitas Brawijaya*, 2(1), 206.

Fan, S., Xiao, Z., Li, M., & Li, S., 2016), Pervaporation Membrane Bioreactor with Permeate Fractional Condensation and Mechanical Vapor Compression for Energy Efficient Ethanol Production, *Applied Energy*, 179, 939–947.

Gabruś, E., Witkiewicz, K., & Nastaj, J., 2018, Modeling of regeneration stage of 3A and 4A zeolite molecular sieves in TSA process used for dewatering of aliphatic alcohols. *Chemical Engineering Journal*, *337*, 416–427.

Kazemimoghadam, M., & Rigi, Z. A., 2018, Evaluation and synthesis of Nano-pore Hydroxysodalite (HS) zeolite membranes: Application to pervaporation of Ethanol/water mixture, *J. Water Environ. Nanotechnol.*, *3*(2), 173–190.

Kementerian Energi dan Sumber Daya Mineral, 2021, Cadangan Minyak Indonesia Tersedia untuk 9,5 Tahun dan Cadangan Gas 19,9 Tahun**.** *Siaran Pers Mentri Energi dan Sumber Daya Mineral* No: 028.Pers/04/SJI/2021, www.esdm.go.id, Retrieved June 15.2021.

Koc, M., Sekmen, Y., Topgul, T., Yucesu, H.S., 2009, The Effect of Ethanol Unleaded Gasoline Blends on Engine Performance and Exhaust Emissions in a Spark-Ignition Engine. *Renewable Energy*, Vol 34, 2102.

Lee, Y. H., Chen, C. H., Umi Fazara, M. A., & Mohd Irfan Hatim, M. D., 2021, Production of fuel grade anhydrous ethanol: A review. *IOP Conference Series: Earth and Environmental Science*, *765*(1).

Lourentius, S., 2012, Analisis Kesetimbangan Adsorpsi dan Kurva Breakthrough Pada Proses Dehidrasi Bioetanol Menjadi Fuel Gade Ethanol (FGE) Menggunakan Adsorpsi Zeolit Alam Malang. Surabaya. ISSN 1976-9427.

Mekala, M., Neerudi, B., Are, P. R., Surakasi, R., Manikandan, G., Kakara, V. R., & Dhumal, A. A., 2022, Water Removal from an Ethanol-Water Mixture at Azeotropic Condition by Adsorption Technique. *Hindawi Adsorption Science & Technology*, Vol. 2022.

Miranda N. T., Maciel Filho R., Maciel M. R. W., 2020. Comparison of complete extractive and azeotropic distillation processes for anhydrous ethanol production using aspen plus TM simulator, *Chem Eng Trans*, 80, 43–48.

Perry, R.H., & Green, D.W., 1997, Perry's Chemical Engineers' Handbook, 7th

Edition, Mc Graw-Hill Co, New York, section 13–11.

Sergio, J. & Dwikurniawan, H., 2011, Pembuatan Etanol Absolut dengan Distilasi dan Adsorbsi Menggunakan Molecular Sieve 3A. ITS, Surabaya.

Villarul, T.N., Chairul, Yenti S. R., 2017, Pemurnian Bioetanol Hasil Fermentasi Nirah Nipah Menggunakan Proses Destilasi-Adsorpsi Menggunakan Adsorben CaO. Pekanbaru : *Jom Fakultas Teknik Universitas Riau*, 4(2), 1–2.

Walidah, T., Chairul, Amun A. 2015. Pemurnian Bioetanol Hasil Fermentasi Nira Nipah dengan Proses Distilasi-Adsorpsi Menggunakan Bentonit Teraktivasi. *Jom Fakultas Teknik Universitas Riau*, 2(1), 1–6.