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The Influence of Activated Carbon as Adsorbent in Adsorptive – Distillation of Ethanol–Water Mixture

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Abstract. This study observed the use of activated carbon adsorbent in adsorptive distillation to increase ethanol concentrations. The different ethanol influent concentrations considered were 90% v/v and 95% v/v, and the weight of activated carbon adsorbent used was 25 g and 50 g. The temperature was maintained at the boiling point under a pressure of 1 atm, and observational data were collected every 5 to 10 minutes and tested using a densitometer. The result of this study indicates that the distillation-adsorption technique using activated carbon exceeded its azeotropic point and produced fuel-grade ethanol that satisfied all requirements. The maximum water content in the ethanol-water mixture was found to be approximately 1% v/v. The highest ethanol concentration, 99.49% v/v, was achieved in 15 minutes utilizing 50 g of Calgon-activated carbon and beginning ethanol that was 95% v/v. Meanwhile, the lowest ethanol concentration of the other research variants was achieved with 25 g of Haycarb activated carbon and 90% v/v starting ethanol at 98.27% v/v.

Keywords: Activated carbon adsorbent; Adsorptive – Distillation; Ethanol – Water Purification

1. Introduction

The price of coal in October 2021 was US$ 270 per ton on ICE Newcastle. Meanwhile, the price of natural gas also increased to US$ 6 per MMBtu. The increase in commodity prices led to a global energy crisis in 2021. Indonesia was also affected, with fuel consumption reaching 75.27 million kl in 2021, consisting of 26.3 million kl of subsidized fuel and 48.97 million kl of non-subsidized fuel. Consequently, the dependency on fossil fuels has resulted in negative impacts on the environment, such as climate change and rising global temperatures. As a result, there’s a need for environmentally friendly alternative fuels. Bioethanol emerges as one such alternative, aligning with Indonesia's national energy policy and regulations promoting the use of alternative fuels to reduce dependency on fossil fuels.

As per Indonesia's National Energy Policy (KEN), the production of bioethanol is anticipated to rise from 1.5 million tons of oil equivalent (toe) in 2013 to 11 million tons toe by the year 2050. Bioethanol is a carbon-free fuel used in pharmaceuticals and cosmetics, but it needs to be anhydrous for fuel purposes to prevent engine corrosion. ASTM D4806 regulates that bioethanol used as fuel must have a maximum water content of

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1%, requiring further purification. Simple distillation is commonly used, but it cannot surpass the azeotropic point above 95% (Taufanny *et al.*, 2015). Therefore, a method is needed to surpass the azeotropic point and obtain ethanol concentrations higher than 95%. One of the methods for ethanol purification is adsorptive – distillation, where the vapor mixture produced from the distillation process is absorbed by an adsorbent. Adsorptive distillation offers several advantages, including high-purity separation, energy efficiency, selective separation, continuous operation, and compatibility with complex mixtures. However, it comes with certain drawbacks, such as sensitivity to temperature and pressure, requirements for maintenance, and the need for regeneration of adsorbent materials.

Previous studies have used zeolite 3A as an adsorbent to increase the ethanol concentration from 92% v/v to 99.5% v/v (Sudibandriyo and Putri, 2020; Taufanny *et al.*, 2015; Tadayon *et al.*, 2014; Mujiburohman, Sediawan, and Sulistyo, 2006). Additionally, another study used silica gel as an adsorbent to purify the IPA-water mixture, resulting in an increased concentration from 87.2% v/v to 99.5% v/v. The adsorptive-distillation method has proven to be effective in separating high-concentration ethanol-water (>95% v/v). Hence, it was chosen as the method in this research. Activated carbon as the adsorbent has a large surface area of approximately 300 – 3500 m^2/g, internal pore structure, high adsorption capacity (25-100% by weight), and the type of activated carbon affects the concentration of the resulting ethanol. Purification of ethanol using activated carbon as the adsorbent in the adsorptive-distillation method is a promising alternative fuel.

2. Methods

2.1. Materials

The ethanol–water mixtures (90% v/v and 95% v/v) used in this research are ethanol–water of technical grade, along with deionized water purchased from the Plaza Kimia Store in Bogor City, Indonesia. The activated carbon adsorbents, Calgon Activated Carbon (iodine number 1050 mg/g) and Haycarb Activated Carbon (iodine number 860 mg/g), used in the adsorptive – distillation process, are products of Calgon Carbon Corporation and Haycarb Corporation, Catlettsburg, USA.

2.2. Activated Carbon Adsorbent Preparation Process

In the preparation process of this activated carbon adsorbent, the activated carbon particles were filtered using a Mesh Sieve apparatus to obtain a particle size of the activated carbon adsorbent between 8 – 10 mesh, with a total weight variation of 25 g and 50 g. The weight variations of the adsorbent were determined based on the height of the adsorber column and the bulk density of the activated carbon adsorbent used. The uniform-sized activated carbon adsorbent will undergo activation by being heated using an oven (heater) at a temperature of 200^{o}C and maintaining that temperature for 2 hours. This process aims to remove the moisture content present in the activated carbon adsorbent. Afterward, the activated carbon adsorbent is cooled and dried inside a desicator to reach room temperature (25^{o}C).

2.3. *Ethanol – Water Mixture Preparation Process*

In the preparation process of the ethanol-water solution, an initial ethanol concentration (Co) with variations of 90% v/v and 95% v/v is required. For each research, 500 mL of the desired initial ethanol concentration is obtained by diluting bulk ethanol of 96% v/v with deionized water until the desired ethanol concentration is achieved. After that, an analysis is conducted on the resulting ethanol mixture to adjust the desired initial ethanol concentration using a Density Meter: DMA 4100 M Anton Paar. Then, the ethanol mixture, which has been diluted with deionized water and adjusted to the desired concentration, will be stored in dark-colored glass containers to prevent contamination by light before being used in the main process, which is the adsorptive-distillation process.

2.4. Adsorptive – Distillation Process

The primary process in this research is the adsorptive-distillation process. It is initiated by heating a 500 mL mixture of ethanol and water with varying concentrations (90% v/v and 95% v/v) in a three-neck flask on a hot plate set to a temperature of 170°C. Once the temperature inside the three-neck flask reaches 78°C, as indicated by the thermometer, the ethanol-water mixture begins to boil. The vapor of the ethanol mixture then enters the arrangement of activated carbon adsorbents (with variations of 25 g and 50 g) within the adsorber column.

The vapor of the ethanol–water mixture enters the adsorber column, where it will be adsorbed by either Calgon Activated Carbon or Haycarb adsorbents. Meanwhile, the ethanol vapor will pass through the adsorbents and be condensed in the condenser column with the help of the water coolant, resulting in ethanol with a higher concentration than its initial state. The condensate (pure ethanol) obtained will be stored in Dark Duran Schott Bottles at intervals of 5 – 10 minutes, and its concentration will be analyzed using a Density Meter: DMA 4100 M by Anton Paar.

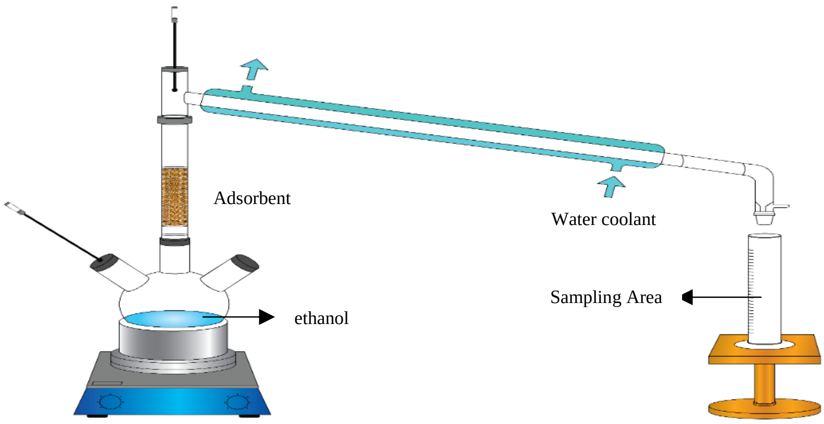

Figure 1 Scheme of adsorptive–distillation process

3. Results and Discussion

3.1. Results of Ethanol Concentration Profile Toward Time

This research utilizes the adsorptive–distillation process with the aim of increasing ethanol concentration. The initial ethanol concentrations in the liquid phase are 90% v/v and 95% v/v, and two types of activated carbon (Calgon and Haycarb) are used with weights of 25 g and 50 g. The highest ethanol concentration was obtained in the research variation using 50 g of Calgon-activated carbon with an initial ethanol concentration of 95% v/v, resulting in an ethanol concentration of 99.49% v/v. On the other hand, the lowest ethanol concentration is obtained in the research variation using 25 g of Haycarb activated carbon with an initial ethanol concentration of 90% v/v, resulting in an ethanol concentration of 98.27% v/v.

3.2. The Influence of The Type of Adsorbent on Ethanol Concentration

The results of the adsorptive–distillation process for the ethanol–water mixture under the first variable, which is the type of activated carbon adsorbent (Calgon and Haycarb), are shown in Figure 2.

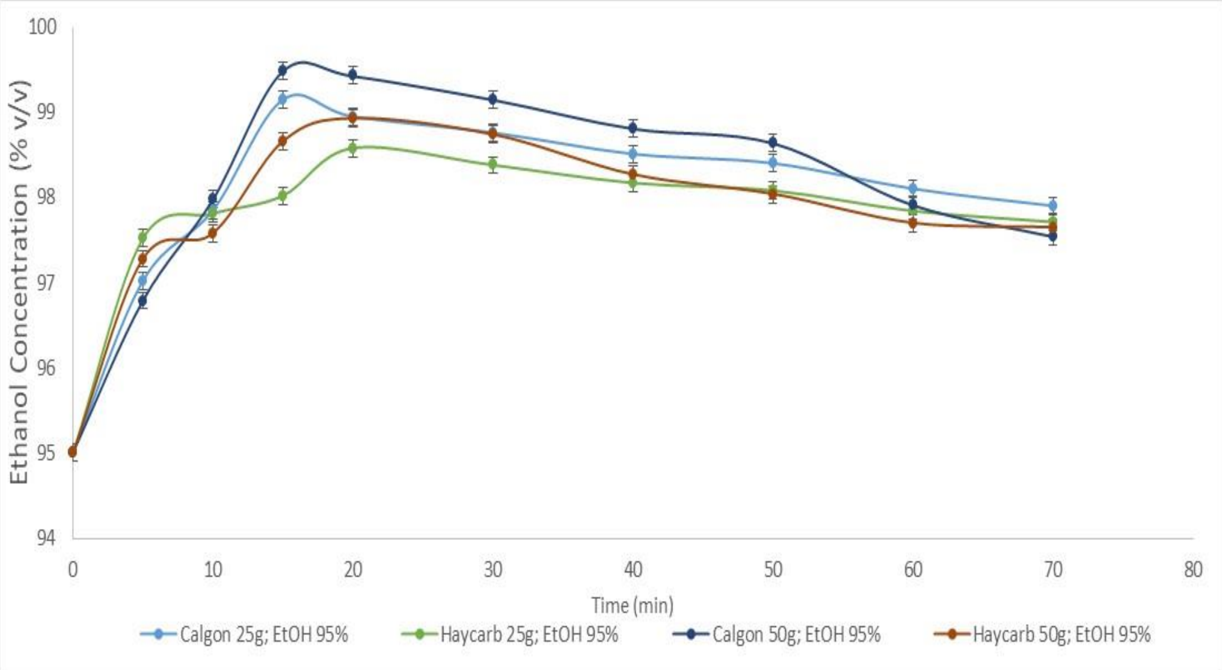

Figure 2 The comparison of results for the variations in activated carbon types at initial ethanol concentration 95% v/v, the weight of absorbent 25 g and 50 g

Based on Figure 2 above, it can be observed that Calgon-activated carbon is more effective in adsorbing water from the ethanol-water mixture compared to Haycarb-activated carbon. The differences in specifications between the two, such as particle size, surface area, and iodine number, explain why Calgon is more effective. Calgon-activated carbon has a larger particle size that enhances the probability of water molecules coming into contact with the adsorbent surface, thereby facilitating a more efficient adsorption mechanism. The wider surface area provides a more extensive to amplified adsorption capacity as more active sites become available for water molecule attachment, resulting in greater water removal efficiency, and a higher iodine number signifies a greater number of micropores and an overall increased capacity for water adsorption also highly selective for water molecules due to their size and chemical properties.

Calgon-activated carbon has the largest surface area and pore volume compared to Haycarb-activated carbon. Research results also indicate that the maximum adsorption capacity increases with the increase in the surface area of the activated carbon. A larger surface area in activated carbon enhances its adsorption capacity, making it more efficient at capturing adsorbate substances due to the increased number of active sites and pores (Sudibandriyo, 2010). However, real-world considerations reveal that Calgon-activated carbon is generally more expensive than Haycarb-activated carbon when comparing equivalent weights, typically around 25 kg. Factors such as adsorption capacity, pore size distribution, and material purity should be considered to ensure the optimal selection of activated carbon that aligns with both technical and economic considerations.

3.3. The Influence of The Initial Ethanol Concentration on Final Ethanol Concentration

The results of the adsorptive–distillation process for the ethanol–water mixture under the second variable, which is the initial ethanol concentration (90% v/v and 95% v/v, are shown in Figure 3.

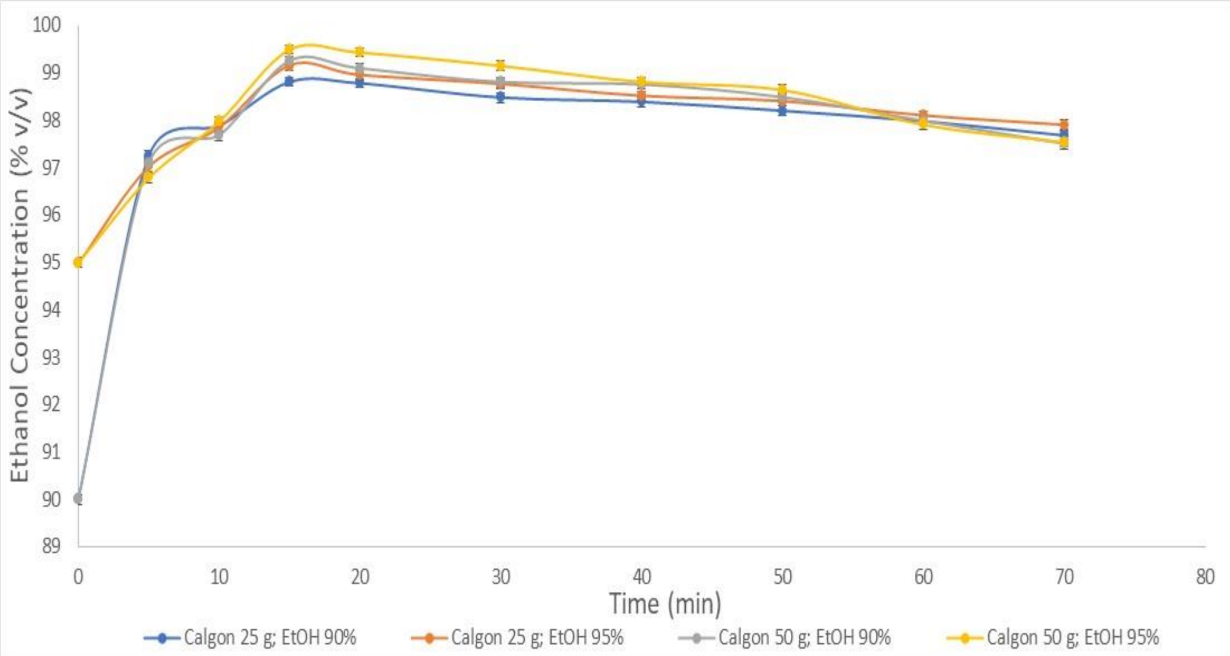

Figure 3 The Comparisons of results for the variations of initial ethanol concentration at calgon activated carbon 25 g and 50 g

Based on Figure 3 above, it can be observed that the initial ethanol concentration of 95% v/v yields a better curve compared to the initial ethanol concentration, resulting in a larger number of ethanol molecules undergoing adsorption (Laksmono *et al.*, 2019). However, increasing the initial ethanol concentration introduces complexities, and it results in a higher loading rate, indicating more ethanol molecules adsorbed per unit of time. Yet, this is accompanied by a decrease in the driving force for adsorbent surface diminishes. Additionally, the intensified adsorption process reduces mass transfer efficiency, leading to a shorter mass transfer zone (Rengga, Sudibandriyo, and Nasikin, 2017). Higher initial ethanol concentrations offer advantages through increased available ethanol molecules, but they also bring about trade-offs in terms of loading rate, driving force, and mass transfer efficiency. The optimal choice of initial ethanol concentration in an adsorption process necessitates careful consideration of these intricate dynamics to achieve the desired outcome.

The curves above suggest that as the initial ethanol concentration decreases, the curve tends to shift to the right. This shift indicates that the adsorbent requires more time to reach saturation (Sudibandriyo, Wulan, and Prasodjo, 2015). The adsorptive-distillation process at an initial ethanol concentration of 95% v/v experiences a faster decline in adsorption capacity compared to the initial ethanol concentration of 90% v/v. Although the saturation point in the initial ethanol concentration of 90% v/v and 95% v/v occurs at a relatively similar time based on research results, the curve shows that the low ethanol concentration continues to increase at around minute 40, while the high initial ethanol concentration starts to decrease from minute 30.

3.4. The Influence of Adsorbent Weight on Ethanol Concentration

The results of the adsorptive – distillation process for the ethanol–water mixture under the last variable, which is the weight of the adsorbent (25 g and 50 g), are shown in Figure 4.

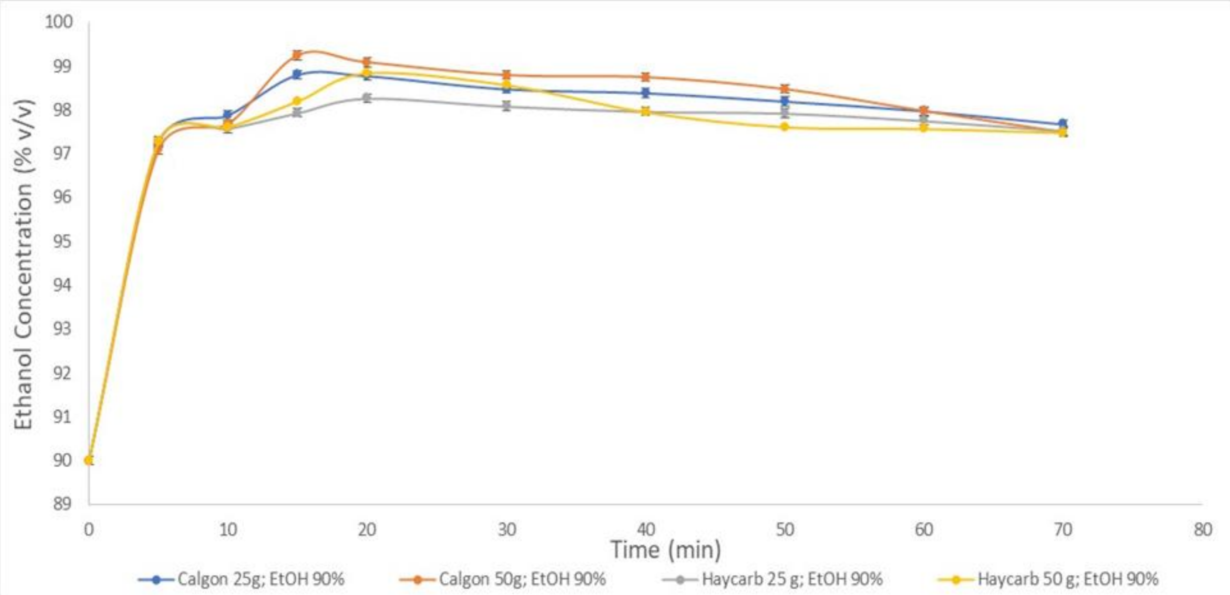

Figure 4 The comparisons result for the variations of adsorbent weight at Calgon and Haycarb activated carbon with initial ethanol concentration 90% v/v

The use of 50 g of activated carbon yields the best results compared to 25 g of activated carbon. When more activated carbon is introduced into the mixture, a surplus of these adsorption sites becomes available. This surplus enhances the adsorption process, allowing for a more efficient and extensive interaction between the activated carbon and the water molecules. As a result, a larger quantity of water is selectively removed from the mixture, reducing its concentration within the liquid phase (Laksmono *et al.*, 2019). Consequently, the remaining liquid phase contains a higher proportion of ethanol. The ethanol molecules, being less inclined to adhere to the adsorption sites compared to water, become less diluted as water is selectively removed. This leads to a significant increase in the ethanol concentration within the remaining solution. In comparison to other research variations, the increased amount of activated carbon leads to a faster adsorption curve and achieves a stable highest concentration. This is attributed to the positive influence of a larger quantity of activated carbon from the ethanol mixture in the water adsorption process.

The use of a larger quantity of activated carbon, specifically 50 g, results in a greater surface area and adsorption capacity compared to 25 g of activated carbon. This allows for better contact between water (adsorbate) and activated carbon (adsorbent). However, with a weight of 25 g, the activated carbon is unable to rapidly adsorb water from the ethanol mixture, leading to hindered mass transfer (Al-Asheh, Banat, and Fara, 2009). Therefore, the use of 50 g of activated carbon yields a higher final concentration of pure ethanol compared to using 25 g of activated carbon.

4. Conclusions

All variations of ethanol–water purification research using adsorptive – distillation processes with activated carbon adsorbents, such as Calgon and Haycarb, can surpass the azeotropic point, characterized by the final ethanol concentration obtained being greater than 95.6% v/v. The Calgon activated carbon (weighing 50 g) with initial ethanol concentrations of 95% v/v and 90% v/v can meet the requirements for Fuel Grade Ethanol, which include a water content in ethanol of less than 1% v/v and an ethanol concentration of approximately 99% v/v. The highest ethanol concentration is achieved when employing 50 g of Calgon-activated carbon with an initial ethanol of 95% v/v, resulting in concentrations of 99.49% v/v. Conversely, the lowest ethanol concentration is attained when using 25 g of Haycarb activated carbon and an initial ethanol of 90% v/v, yielding a concentration of 98.27% v/v. Calgon-activated carbon exhibits superior quality compared to Haycarb-activated carbon due to its larger surface area, higher adsorption capacity, and iodine number. The initial ethanol concentration has an impact on the final ethanol concentration, as higher initial ethanol concentrations allow for faster passage through the azeotrope point. Additionally, the quantity of activated carbon affects the final ethanol concentration, with greater amounts of activated carbon resulting in increased adsorption of water from the ethanol mixture.

Acknowledgments

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