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DEVELOPMENT OF A NOVEL ADSORPTION SEPARATION PROCESS OF BIO-BASED BUTANOL FOR THE ALTERNATIVE ENERGY SOURCES

Abstract:

Bio-based butanol has superior properties when compared to ethanol to be the gasohol and is gradually considered to be an important biofuel from the biomass fermentation. These properties include higher calorific value, low vapor pressure, low freezing point and miscibility with gasoline and diesel. DuPont (US) and BP (UK) announced their plans to produce bio-based butanol to be used as a new gasoline extender. Butanol can be produced by non-food products of fiber fermentation by Clostridium acetobutylicum or C. berijerinckii with acetone and ethanol as by-products. This acetone-butanol-ethanol (ABE) fermentation process used to be the main process for industrial production of butanol. The ABE solution concentration is around 20 g/L of which butanol is only 8-13 g. As expected, the energy cost for traditional distillation to recover butanol will be very high. The adsorption using silicalite (e.g. high Si/Al zeolites) is the most energy efficient method compared to pervaporation, gas stripping and liquid-liquid extraction. The results were observed that ZSM-5 zeolite has the highest selectivity for butanol adsorption. However, ZSM-5 still adsorbs minor ethanol and acetone. Therefore, the sorbent SAPO-34 was further used to adsorb ethanol and acetone. This novel multi-step adsorption process was applied to separate the bio-based butanol from the ABE solution and the purity of butanol can reach more than 99%. To reduce the fossil fuel crisis and the environmental impact, the promotion of the biofuels is considered gradually. In the latter part of nineteenth century, the first diesel engine was developed to run vegetable oils in Germany. Since the polymerization of unsaturated plant oil may cause the high viscosity of the oil, the use of plant oil in engine directly should overcome the contamination of filter and lubricant oil in the engine system. The proposed bio-based butanol made from the waste fiber fermentation and the property to be the biofuel compared to the fossil fuel is better, especially on the reducing of total carbon dioxide emission. The promotional and implementation projects of the plantation of Jatropha curcus for the alternative energy in tropical area of Indonesia will be introduced also. The Jatropha curcus seed oil can be made of biofuel and the fiber residue may become the feedstock for bio-based butanol.

Keywords:

Alternative Energy Sources; Biofuel; Butanol; ABE; Adsorption; Zeolite; Adsorption; Jatropha

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Introduction

To reduce the fossil fuel crisis and the environmental impact, the promotion of the bio-based energy is important recently. The almost none carbon loss technology for the bio-based butanol production is mature. The bio-based butanol to be used as the alternative energy sources will be popular gradually. Compared to ethanol, bio-based butanol provides 25% more energy and is immiscible with water (more easily to do separation and purification). Its property is close to gasoline and can be added more to gasoline.

The acetone–butanol–ethanol (ABE) fermentation process in the main process for industrial production of bio-based butanol has been applied until the mid-20th century. However, the highest yield of butanol concentration obtained in *Clostridial* fermentations was only around 20 g/L due to the butanol toxicity (Ezeji, Qureshi, Blaschek, 2004; Harvey, Meylemans, 2011). The mechanism of butanol toxicity is related to the hydrophobic nature of this compound and the primary effect of butanol appears to be on disruption of the phospholipid component of the cell membrane (Jones, Woods, 1986).

Bio-based butanol has superior properties when compared to ethanol to be the gasohol and is gradually considered to be an important alternative energy source from the biomass fermentation. The properties include higher calorific value, low vapor pressure, low freezing point and miscibility with gasoline and diesel result in the butanol becoming the potential biofuel. In 2007, DuPont (US) and BP (UK) announced their plans to produce bio-based butanol to be a new gasoline extender.A limited number of studies on the adsorption of butanol have been carried out using potato immobilized starch as an adsorbent (Khairul, Kamarudin, Hanapi, 2012). However, the immobilized potato starch not only adsorb butanol, but also adsorb the by-products, such as acetone and ethanol. Earlier studies obtained only in the equilibrium adsorption isotherm data. The rate of butanol adsorption from aqueous solution onto immobilized potato starch has not been discussed in the literature. The objective of this research is to propose a novel multiple-step adsorption process to separate butanol from ABE solution. Develop the regression models with R^2 values for the adsorption isotherm equations of butanol, acetone, and ethanol for further study. Selected sorbents to adsorb butanol, acetone, and ethanol for gas-phase single-component adsorption using gravimetric adsorption equilibrium apparatus can be used to verify the performance of the sorbent on butanol adsorption from ABE solution.

The yield of butanol in the fermentation broth of the ABE solution is very low ususally. The energy consumption in the traditional distillation process to separate the butanol from the fermentation broth will be high. Therefore, the selection of separation and purification method is considered important. The proposed multiple steps of adsorption and purification method was conducted in this work. The Zeolite with higher Si/Al ratio, ZSM-5 (Zeolite Socony Mobil-5), was chosen to adsorb butanol from the fermentation broth. However, minor acetone and ethanol were adsorbed into the ZSM-5 simultaneously. SAPO-34 (Small-Pore Molecular Sieve) was tried to adsorb the minor acetone and butanol from the desorbed butanol solution of ZSM-5. The high purity of the final product of bio-based butanol can be obtained by using the above novel multiple-step adsorption process.

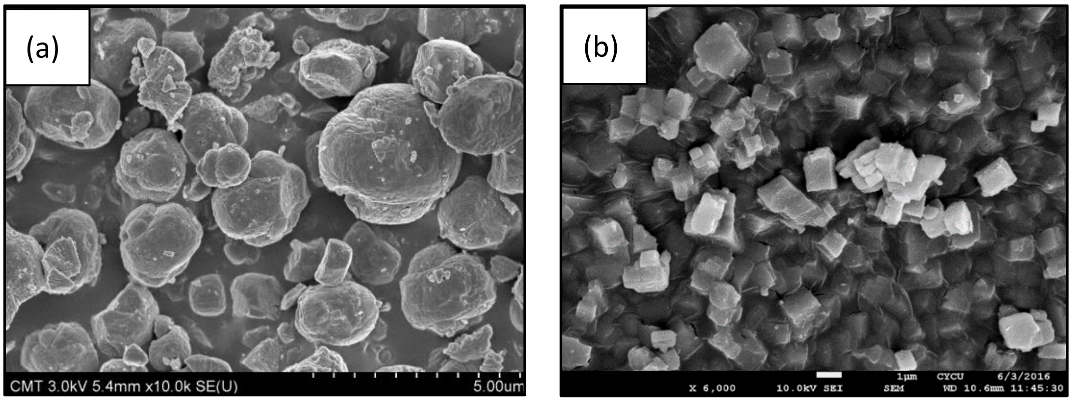
Results and Discussion

The adsorbents used in these experiments include ZSM-5 (Alfa Aesar Co.) and SAPO-34 (Tianjin Chemical Science Co.). The surface properties of the adsorbents can be found in Table 1. The SEM (Scanning Electronic Microscopy) images for the adsorbents microstructure were shown in Figure 1.

Table 1: The surface characteristics of ZSM-5 and SAPO-34

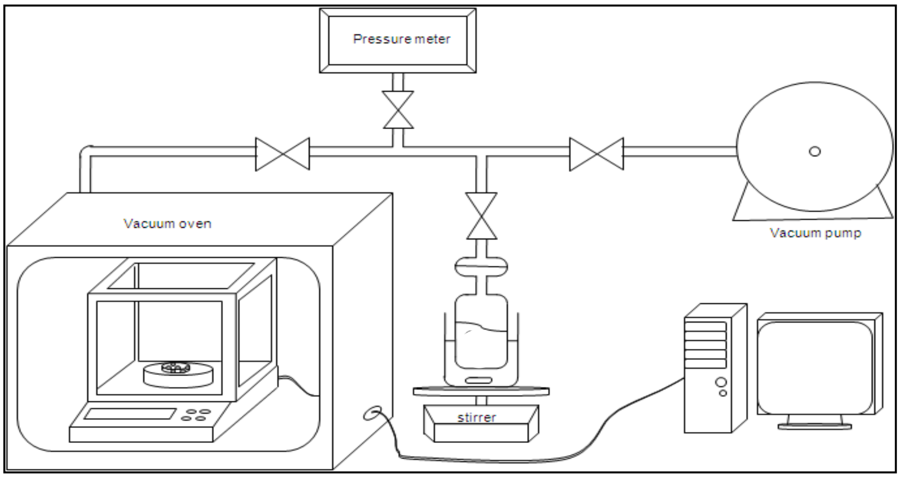
Adsorbent	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter(Å)
ZSM-5	355.11	0.20	22.65
SAPO-34	547.27	0.24	17.71

Figure 1: SEM images of (a) ZSM-5 and (b) SAPO-34



In the gas phase equilibrium study, the adsorbent was degassed under vacuum at 100 °C for 24h prior to each experiment. Then, it was placed on a microbalance, and the initial weight was recorded. The vacuum was started until the required level was reached. The appropriate volume of gas adsorbate was then allowed to pass through the system until the system reached the desired pressure. Pressure and weight were recorded soon after the balance stabilized. The described steps were repeated until the gas adsorbate reached its saturated vapor pressure in Figure 2. Plotting the pressure versus the adsorbed weight gave rise to the equilibrium isotherm curves.

Figure 2: Gravimetric adsorption equilibrium apparatus



Results and Discussion

In the liquid phase equilibrium study, the determination of the concentration of acetone, butanol, and ethanol in the aqueous phase was performance by means of GC (Thermo Electron Corporation, AS3000). The GC column was Innowax 19091 N-133 (30mx 0.20 mm, with coating of 0.10 μm) from Agilent Technologies Inc. Mobile carrier gas phase through the column was helium at 6mL/min. The temperature of the column was kept at 70°C.

According to the reports of adsorption and recovery of butanol using ZSM-5 was the first successful conducted process in the ABE solution. The concentration of acetoner, butanol, and ethanol concentrations before adsorption in the ABE solution were in 2.33 g/L, 9.02 g/L and 0.25 g/L, respectively. It was obtained that butanol adsorption capacities (uptake) range is from 85 mg/g to 120 mg/g (acetone adsorption uptake ranging from 1 mg/g to 4 mg/g; ethanol adsorption uptake ranging from 1 mg/g to 2 mg/g) in the ABE solution**.** In the desorption solution of ZSM-5, it was observed that the acetone adsorption uptake range is from 85 mg/g to 120 mg/g and ethanol adsorption uptake range is from 20 mg/g to 35 mg/g (butanol adsorption uptake ranging from 1 mg/g to 4 mg/g).

Conclusion

The proposed concept in this study for butanol adsorption and purification is the multiple-stage adsorption process. Most of the butanol was adsorbed by ZSM-5 from the ABE solution and the SAPO-34 was used to adsorb the minor contents of ethanol and acetone in the desorption solution of ZSM-5. The purity of the final product of bio-based butanol can reach more than 99 wt% by using the above novel multiple-step adsorption process. In the nineteenth century, the first diesel engine was developed to run vegetable oils in Germany. Since the polymerization of unsaturated plant oil may cause the high viscosity of the oil, the use of plant oil in engine directly should overcome the contamination of filter and lubricant oil in the engine system. The proposed bio-based butanol made from the waste fiber fermentation and the property to be the biofuel compared to the fossil fuel is better, especially on the reducing of total carbon dioxide emission.

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