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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.8, No.4, pp 1626-1631, 2015

Permeation of Acetone-Butanol-Ethanol (ABE) Using Blended Membrane PVA-Pectin

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Abstract: The blended membrane PVA-Pectin-Glutaraldehide (GA) for ABE permeation has been studied. Permeation studied using the blended membrane PVA-Pectin in mol ratio (1:1), (1:2) and (1:3) with glutaraldehide as crosslinker at various number of monomer (n) 60 and 120. Optimum Composition of membrane can exhibit the highest flux value of permeation ABE since early until equilibrium. The addition of GA do not increase the flux value, but improve the physical properties of PVA membrane. While the addition of pectin to PVA membrane and then crosslinked by GA can increase the flux value. Based on this research, PVA-Pectin-GA membrane is capable of increasing flux value from 0.64 to 1.04 L/m2.h (acetone), 0.25 to 0.32 L/m2.h (n-butanol) and 0.70 to 0.95 L/m2.h (ethanol) compared with PVA membrane. Comparison of the very high flux values indicate that PVA-Pectin-GA membrane is recommended for ABE permeation.

Keywords: PVA, Glutaraldehyde, Pectin, and ABE.

Introduction

Nowadays, industrial world is focusing on the invention of alternative fuels from biomass as a renewable energy source. This is due to the depletion of fossil fuel supplies, unstable prices of oil in the world and various problems which affecting oil production and distribution[1]. One of the alternative substituent or fuels additive which has been applied in various countries is ethanol[2]. Ethanol is environmental friendly fuels and is expected to reduce fuels import. The quite high of glucose content in agricultural waste or biomass can be decomposed become ethanol or other organic solvent such as acetone and butanol by fermentation method. In general, the fermentation of vegetable or agricultural materials has an ethanol product concentration about 5-10% (v/v), while the molasses fermentation can produce a concentration of ethanol about 8-12%[3]. Besides the ethanol, the sugar fermentation also produces other solvents namely butanol and acetone[4]. The concentration of product depends on the raw material, microorganism and fermentation methods[5].

Batch system of fermentation methods have been applied in many ethanol industry as it can produce a relatively high levels of ethanol. Unfortunately, product maximum concentration is attained at 12%, then it can lead to the death of inoculums or yeast, thereby the production process being hindered or stopped. So it is less efficient since it required relatively long operating times[6]. Increasing the efficiency of fermentation can be done by improving the product effectiveness by constantly reduced the product during the fermentation process, thus, the negative effect which caused by product may be reduced or increased the productivity by means of continuous fermentation[7]. Continuous fermentation is done by streaming the substrate and taking the product continuously, especially at a time when the limiting reactant approach the equilibrium. Substrate and inoculums are added together and continuously so that the exponential phase will be extended[8]. The taking of products continuously at any time is intended to make the fermentation process be continued.

The membrane is a thin layer to separate two phases which act as a selective barrier to matter displacement[9]. One of polymer that used as membrane in separation or purification process of an organic solvent is poly(vinyl-alcohol) or PVA. PVA has a high chemical stability, capable of forming a thin layer, cheap and hydrophilic. The high hydrophilic property of PVA leads to the low stability of PVA toward the water, so it is very easy to be swelling. Therefore, it needs to be modified to improve the characteristic of membrane by chemical methods, such as the formation of cross-links which able to generate membrane with high crystalinity degree and low swelling degree[10].

Besides the formation of crosslink, other method~~s~~ which is being developed to accelerate the permeation is blending method by mixing the non-covalent bond polymer to obtain a membrane with a mixture of component which has functional group as an active agent that helps to accelerate the process of permeation. Pectin is a type of natural hydrophilic polymer that can be added to the synthetic polymer PVA. The presence of pectin in the membrane mixture is expected to increase the functional group of carboxylic and hydroxide, which can form hydrogen bond with the sample (acetone, n-butanol and ethanol / ABE) thus the permeation rate, can be increased.

The aim of this research is to study the influence of pectin addition on the cross-linked basic polymer PVA with glutaraldehyde to the permeation of ABE.

Experimental

Material

All chemical used in this experiment were of analytical grade and purchased from Merck (Germany). The materials were acetone, ethanol, n-butanol, acetic acid, NaOH, aquabidest,filter paper, Pectin (from citrus WAKO pure for chemical industry), and PVA andglutaraldehyde.

Apparatus

Apparatus used in this experiment were laboratory glassware, Thickness Mitutoyo 7301, Refractometer A. Kruss Optronic 88128, a set of chamber for sample transportand magnetic stirrer, Scanning Electron Microscopy (SEM) Hitachi SU8000, Gas Chromatography Shimadzhu 17-A DB-Wax analytical column (propylene glycol) (30 mx 0.25 mm).

Procedure

Fabrication of Cross-linkedPVA-Pectin Membrane withGlutaraldehyde (GA)

The cross-linked PVA-Pectin membrane with glutaraldehyde was made by mixing pectin in~~t~~ Petri dish (ø= 5cm) which contained 10 mL of PVA 2%, obtained mol ratio of PVA:Pectin = (1:1); (1:2) and (1:3) then it was stirred for a day up to homogeny. Cross-linking process was held by adding 1% acetic acid as catalyst and glutaraldehyde 35% (to get PVA molecules (n) = 60 and 120) into the mixture of membrane then re-stirring for 30 minutes. The mixture was incubated at room temperature for a day, and then at 80 °C for 5-6 hours. Finally, the temperature was lowered up to 40°C for a day to remove the remaining water.

ABE Permeation Using Membrane

The Permeation process was used feed of ABE solution and the receiver phase was filled by aquabidest. The permeation process was executed at room temperature. The mixture was then stirred until reach the equilibrium of sample concentration between feed and receiver phase. Each of phases was taken and analyzed by using spectrophotometry UV-Visible every 4 hours to monitor the amount of permeated samples.

Instrumentation used in this research was a set of permeation cell as shown in Figure 1. Prior to permeation process continuously, an advance composition (mol ratio of PVA: Pectin : Glutaraldehyde) and optimum thickness of membrane have to be selected. Optimum condition was determined based on the highest flux value of each samples. Flux value was calculated based on permeate volume which passed through the membrane per surface area of membrane at certain time, as in Equation[11]:

$$J = \frac{V}{A.t}$$

where :

J = flux ($L/m^2.h$)

V = volume of permeate (L)

A = surface area of membrane (m^2)

t = time (h)

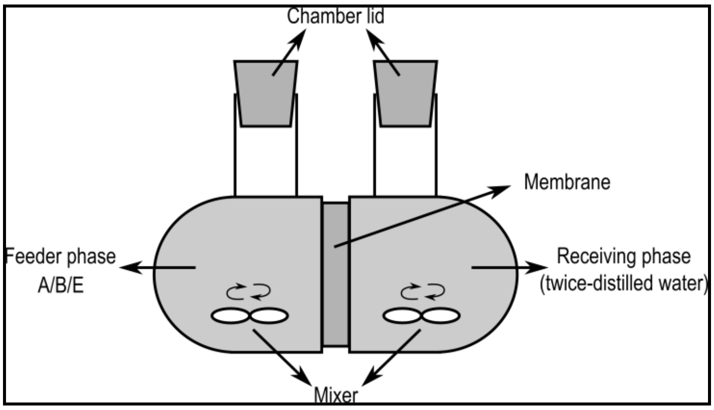

Figure 1.Permeation Cell

Result and Discussion

PVA-Pectin-GA membrane is non-porous membrane, so that the separation process based on solubility and difference of particle diffusion rate. The diffusion mechanism of ABE from feed phase to receiver phase includes absorption of ABE from sample mixture into the membrane, diffusion of ABE through the membrane and desorption of ABE to the receiver phase (aquadest). Both feed and receiver phase were stirred during the permeation process. Stirring in the feed phase has function as a pressure or diffusion energy toward membrane. This pressure can increase the permeation rate (flux) and decrease the separation factor. Meanwhile, stirring function on the receiver phase to attract ABE that has passed through the membrane for apart to the receiver phase immediately. It only gives less effect on the permeation rate. The difference of sample concentration (ABE) at feed phase and receiver phase lead~~s~~ to permeate ABE molecule through the membrane, where the transfer starts from high concentration to low concentration. Generally, permeation rate will increase if the permeate concentration is higher and decrease until it reaches equilibrium[12].

1. The effect of GA addition (monomer number of PVA crosslinks) on the ABE permeation.

All the studied solvent (acetone, n-butanol and ethanol) is a polar solvent, which can permeate and swell the membrane. That make a negative impact on the membrane selectivity and resistance, because it increases swollen and plasticized. The negative impacts can be reduced by adding crosslinker agent. The addition of crosslinker agent will improve the physical properties of membrane becomes more robust and not easily swell. The addition of crosslinker GA just give a little increasing of permeation flux value, because the main purpose of GA addition is to improve the physical properties of membrane. Reaction formation of crosslinking between the PVA by GA can be seen in Figure 2.

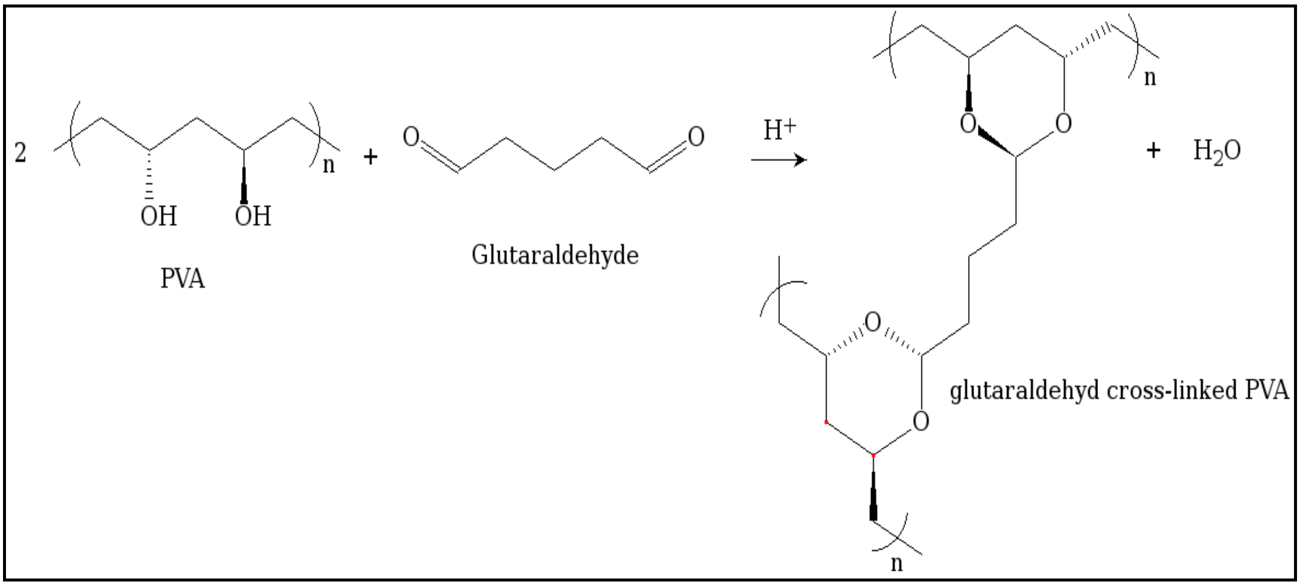

Figure 2.Cross-linking reaction of PVA with Glutaraldehyde[13].

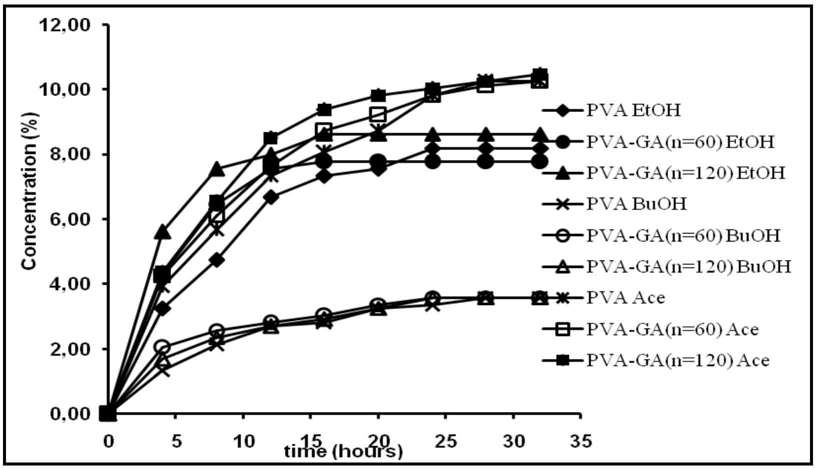

Figure 3.The relation of permeate concentration (%) versus time (hours) on the ABE permeation using three types of membranes: PVA, PVA-GA(60), and PVA-GA(120).

Table 1. Flux value of the three membrane: PVA, PVA-GA(60), and PVA-GA(120) on ABE permeation

t= 12 hours	Aceton			n-butanol			Ethanol		
	PVA	PVA-GA (n=60)	PVA-GA (n=120)	PVA	PVA-GA (n=60)	PVA-GA (n=120)	PVA	PVA-GA (n=60)	PVA-GA (n=120)
C(%)	6.68	7.54	7.97	2.69	2.80	2.69	7.33	7.63	8.50
V	0.0027	0.0030	0.0032	0.0011	0.0011	0.0011	0.0029	0.0031	0.0034
F	0.64	0.72	0.77	0.25	0.26	0.26	0.70	0.73	0.82

In figure 3 and table 1 ~~shows~~ that ethanol has the highest flux than acetone and n-butanol, which means that ethanol permeated faster than acetone and n-butanol. This indicates that ABE can pass through the membrane, but due to the differences polarity of three samples on membrane, which causing the differences on flux permeation. Molecular size also affects the flux permeation. Based on the molecular size, ethanol molecule is smaller than acetone and n-butanol. The polarity of molecule will decrease because of the longer carbon chain, so that ethanol is easier to attract to the membrane than acetone and n-butanol. The polar membrane will also be easier to permeate polar molecule. The diffusion energy which was required to pass through the membrane will be greater for the bigger size of the molecule, so that from all molecules, ethanol reaches equilibrium in higher concentration, followed by acetone and n-butanol. n-butanol has the smallest flux value. This is due to the concentration factor, which ethanol and acetone has a concentration 20% while n-butanol is only 6%. The concentration differences is one of the driving forced which can lead to the permeation. The higher differences concentration between the feed with the permeate, The faster permeation occurs, the higher the flux value.

2. The effect of Pectin addition to PVA membrane on the flux of ABE permeation.

Pectin is a water-soluble polysaccharide (Water Soluble Polysaccharide) and the main constituent of D-galacturonic acid polymer, which is bounded by α-1,4-glycosidic. As well as PVA, pectin also hydrophilic, makes it easy to experience swelling if there are polar solvents, so it needs to be added crosslinker agent to strengthen its physical properties[14].

The results of ABE permeation from three membranes that be compared, i.e blended membrane PVA-Pectin-GA with each mole ratio (1: 1), (1: 2) and (1: 3) is shown in Figure 4. The concentration of ABE was increased on the receive phase at over time up to reach equilibrium permeation. The Equilibrium permeation is a condition where the sample concentration at receive phase can not be increased again or constant[15]. The permeation curves describe the equilibrium condition of three samples at the time of permeation up to 32 hours. The Calculation of ABE permeation flux from three membranes that have been studied shown in Table 2. Flux value is calculated at equilibrium condition.

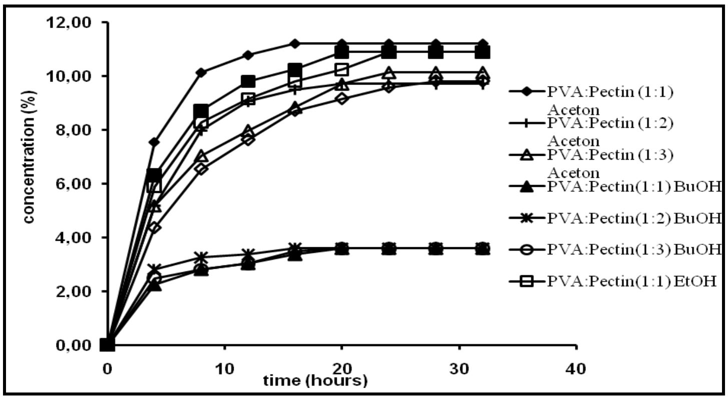

Figure 4.The relation of permeate concentration (%) versus time (hours) on the ABE permeation using three types of membranes: PVA-Pectin with mole ratio (1:1), (1:2) and (1:3) with addition GA as crosslinkerwith n=120.

Table 2. Flux value of the three membranes: PVA-Pectin with mole ratio (1:1), (1:2) and (1:3) with addition GA as crosslinker with n=120.

t = 12 hours	Aceton			n-butanol			Ethanol		
	(1:1)	(1:2)	(1:3)	(1:1)	(1:2)	(1:3)	(1:1)	(1:2)	(1:3)
C(%)	10.78	9.05	7.97	3.02	3.36	3.02	9.15	9.80	7.63
V	0.0043	0.0036	0.0032	0.0012	0.0013	0.0012	0.0037	0.0039	0.0031
F	1.04	0.87	0.77	0.29	0.32	0.29	0.88	0.95	0.73

ABE permeation across the membrane by forming hydrogen bonds between ABE and hydroxyl groups of PVA. The addition of pectin into the basic PVA membrane will increase the amount of hydroxyl and carbonyl group in the membrane. Both of these groups are called active group because it is able to form hydrogen bond with ABE, so it can pass through the membrane. The increasing of hydroxyl group also increased the transport rate of target compound of phenol by polyeugenol-Bisphenol A diglycidyl ether membrane[16]. This research shows the same result, if many ABE which form hydrogen bond with active group in the membrane, ABE permeation through the membrane will be faster. ABE permeation ~~is~~ also assisted by energy from stirring in feed phase. The hydrogen bond between ABE and active group is weak, so it is easy to disconnect by energy from stirring in permeate phase. Disconnection of hydrogen bond leads to ABE apart from the membrane and into the permeate phase. If ABE moved faster from feed phase to permeate phase, the membrane flux will be higher.

The approximation cross-linking reaction of membrane PVA-Pectin-Glutaraldehyde is shown in Figure 5.

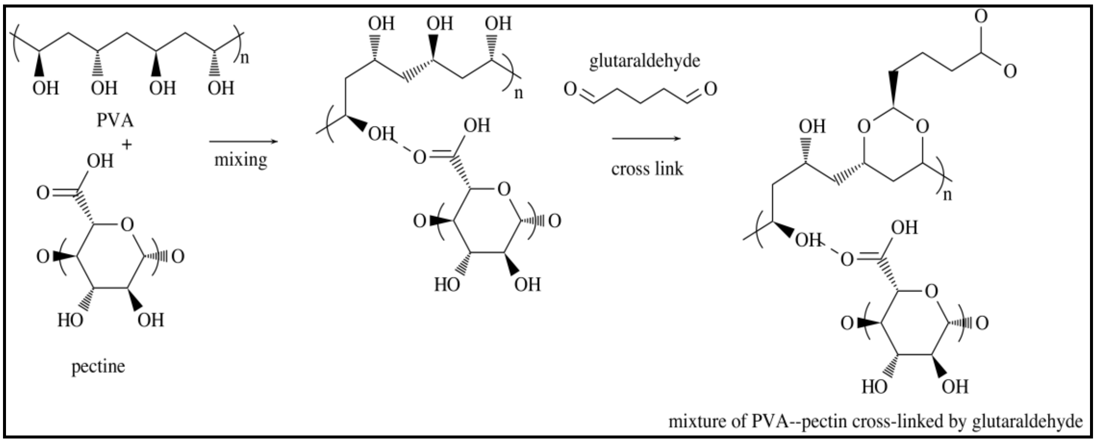

Figure 5.The approximation reaction between PVA, Pectin and Glutaraldehide

Based on the data above, membrane composition that provides the highest flux was obtained at the mole ratio of PVA: Pectin = (1: 2) for etanol and butanol, and (1:1) for aceton, with GA as crosslinker on n= 120. Table 3 shows that flux value of ABE permeation from two membranes PVA and PVA-Pectin-GA on optimum condition of each sample.

Table 3. Comparison of the flux values of two comparable membranes PVA and PVA-Pectin-GA on ABE permeation

Membrane	**Flux (L/m^2.hours)**		
	Acetone	**n-Butanol**	**Ethanol**
PVA	0.64	0.25	0.70
PVA-Pectin-GA	1.04	0.32	0.95

The addition of GA do not increase the flux value, but improve the physical properties of the PVA membrane.While the addition of pectin to PVA membrane and then crosslinked by GA can increase the flux value. Based on this research, PVA-Pectin-GA membrane is capable of increasing flux value from 0.64 to 1.04L/m^2.h (acetone), 0.25 to 0.32L/m^2.h (n-butanol) and 0.70 to 0.95 L/m^2.h (ethanol) compared with the PVA membrane. Comparison of the very high flux values indicate that PVA-Pectin-GA membrane is recommended on ABE permeation.

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