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Synthesis and Characterization of Nano Hybrid Membrane PES-TiO_2 for Biogas Purification: Combination Effect of Ultra Violet and Cross-Linking

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Abstract: One of the alternative energy offered and can be used as a substitute for fossil energy is renewable energy. Examples of renewable energy are very abundant and can be developed in Indonesia is biogas. Biogas mostly contain CH_4 and CO_2. Membrane separation is one of the most suitable process to make biogas more pure. So, it must be advanced to improve the membrane performance. The objectives of the current research are to investigate the effect of combined UV irradiation and cross linking on nano hybrid membrane PES-TiO_2 on their performance to separate CO_2 that contain in biogas. The nano hybrid membrane PES-TiO_2 was fabricated by preparing the dope solution containing PES, NMP as solvent, and nano TiO_2. The membrane was casted by using NIPS method, with expose under UV lights for 1, 2, 3 min and followed by immersion in acetone-ethanol mixture for 24 hours. UV irradiation and cross linking treatments increased the selectivity and permeability of nano hybrid membrane PES-TiO_2 on CO_2/CH_4 gas separation. The effect either UV irradiation or cross linking addition, make the void larger than before, so the selectivity and permeability can increase. With the addition of cross linking ethanol-acetone solution can reduce agglomeration in the membrane. The combination of UV irradiation and cross linking treatments can increase significantly in nano hybrid membrane PES-TiO_2 performance for CO_2/CH_4 gas separation.

1 Introduction

One of the current global problems is the imbalance between consumption and available energy sources. The main factors causing the problem are the dependence on fossil energy and the lack of public attention to the current energy crisis. According to the National Energy Board of the Republic of Indonesia (2014), dependence on fossil energy, especially petroleum in the fulfilment of domestic consumption is still high at 96% (petroleum 48%, gas 18% and coal 30%) of total consumption and efforts to maximize utilization renewable energy cannot run as planned. On the other hand, Indonesia tends to face a decline in fossil energy reserves that continue to occur and cannot be matched by the discovery of new reserves [1]. This condition causes Indonesia to import energy for domestic needs.

The scarcity of fossil energy requires another energy source that can be used as an alternative to help meet global energy consumption. One of the alternative energies offered and can be used as a substitute for fossil energy is renewable energy. An example of a very abundant renewable energy that can be developed in Indonesia is biomass in the form of biogas.

Biogas is gas produced from the process of fermentation of organic materials by anaerobic bacteria that are resistant to airtight conditions. Biogas can be produced from organic waste which is a combustible gas dominated by methane and CO_2 gas. All types of organic materials containing carbohydrate, protein, and fat compounds can be processed to produce biogas [2]. In principle, making biogas is very simple, that is by entering the substrate in the form of animal or human waste into the digestive unit (digester) and then closed tightly and some time will form a gas that can be used as a source of energy [3]. The composition of biogas according to Seadi et al., consists of methane (50-75%), carbon dioxide (25-45%), and small amounts of water vapour, oxygen, nitrogen, ammonia, hydrogen, and hydrogen sulphide [4]. The purity of methane from the biogas product becomes important because it can affect the value of the resulting heat. According to Mustafa et al., the use of biogas also still has limitations due to the impurities of biogas containing large amounts of CO_2 (20-45 Vol%) and H_2S (0-1 Vol%) other than CH_4 main component (55-80 Vol%) [5]. The presence of CO_2 in CH_4 Very undesirable, this is because the higher CO_2 levels in CH_4 further decrease the CH_4 heat value

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indicated by the yellowish red colour of the resulting flames [6]. In addition CO_2 is also corrosive and acidic with its presence with water compounds present in storage tanks or biogas distribution [7]. Reduced CO_2 levels will significantly increase biogas products.

Many technologies have been developed for the purification of biogas from CO_2, such as CO_2 absorption, purification by using membranes, and CO_2 fixation by biological and chemical methods. From the several solutions offered, membrane technology for gas separation was chosen because of low energy requirements, low maintenance costs, and conditions that are not extreme.

There are three aspects to note in the membrane application for the separation of CO_2, the first aspect of membrane performance that includes the selectivity and permeability of the gas, the second aspect is the membrane resistance to the applied operating conditions such as temperature and pressure critical to have plastic properties, and the third aspect is availability material and cost to be used. The most widely used membrane material for CO_2 separation in the industry is the polymer. Polymers are chosen because they are relatively inexpensive and the manufacturing process is relatively easy compared to other materials. The most common types of membrane polymers used in gas separation processes are polyimide, cellulose acetate, and polyether sulfone (PES). PES was chosen because it has a higher resilience than polyimide and has a fairly high plastization pressure, which is 34 bar [8]. The PES membrane matrix, mostly uses a mixture of zeolites, carbon, silica, carbon nanotubes, or metal oxides as inorganic materials. One of the metal oxides used as inorganic materials in membrane manufacturing is TiO_2. TiO_2 was chosen because of its abundant presence in Indonesia, always stable when working at room temperature, and non-toxic [9].

The development of the fabrication and application of MMMs (Mix Matrix Membranes) containing inorganic particles in the polymer matrix for gas separation is still considered quite low compared to the polymer membrane, providing an opportunity for future membrane development. Success in improving membrane performance with mixed matrix concepts is limited to its use for gas separation, and morphological studies of prevailing membranes (e.g. asymmetric membranes, thin films of composite membranes).

Limited information in inorganic materials on the manufacture of polymer membranes makes the selection of materials in the membrane-making process into a problem that needs to be developed. Therefore, there is a need for better approaches and standards to identify the properties of inorganic materials, especially in terms of their ability as a separator [10]. So it is necessary to develop the ability of the membrane itself because basically membrane technology has a prospect that ensures for the future.

Therefore, in this research, the effort that can be done is by combining UV irradiation with cross linking using polyvinyl pirrolidone (PVP) and also mixture of ethanol and acetone and treatment by using thermal annealing on nano hybrid membrane PES - nano TiO_2 using material polyether sulfone (PES) to determine membrane characterization by determination of flux and selectivity, Scanning Electron Microscopy (SEM), and Fourier Transform Electron (FTIR) to obtain the best membrane performance in CO_2 purification in biogas.

2 Experimental

2.1. Materials Selection

Polyethersulfone (PES) powder was purchased from Solvay Advance Polymer USA.; N-methyl-pyrrolidinone (NMP) from Merck was used as the solvent due to its low toxicity. TiO_2 nanoparticle were prepared in Nano Center Indonesia with the average nanoparticles size is 50 nm.

2.2 Fabrication of asymmetric flat sheet mixed matrix membrane

The polymer solution was consisted of 20 wt-% PES, 80 wt-% NMP and 0.5 wt-% of nano TiO_2 in total solid. The homogeneous polyethersulfone was prepared according to the following procedure; 0.1 gram of TiO_2 nanoparticles and 20 gram PES were added to 80 mL NMP. This solution was further agitated by stirring at high speed for at least 4 hours. The membrane was casted by using NIPS method. The flat sheet membrane was prepared according to the dry/wet phase inversion technique. The solution was poured onto a clear, flat and smooth glass plate that was placed on the trolley. Stainless steel support casting knife was used to spread the solution to a uniform thickness. The casted membrane was exposed under UV lights for 1, 2, 3 min. The glass plate with the membrane film was then immersed in the water bath. During this process, solvent exchange occurred and solidified the membrane film to a complete membrane structure. To ensure all of the solvent in the membrane structure is removed, membranes were immersed in an aqueous bath for 24 hours, followed by cross linking added in ethanol-acetone (1:3) for 24 hours and air-dried for 60 minutes at room temperature.

2.3 Gas Permeation Testing

The permeation test involved the use of gas permeation cell in which the membrane was placed on a sintered metal plate and pressurized at the feed side. Gas permeation rates were measured by a constant pressure system using a soap bubble flow meter. Fig. 1 illustrates the gas permeation cell set up. The cross-membrane pressure difference was maintained 1 bar. Pressure normalized gas permeation flux or permeance for gas I, (P/l)I, in (GPU), can be calculated as follows:

$$(P/l)i = Qi/\Delta P*A \qquad (1)$$

Where Qi is the volumetric flow rate of gas i, ΔP pressure difference across the membrane (cmHg), A is a membrane affective surface area (cm^2) and l is membrane skin thickness (cm). The ideal separation factor α i/j can be calculated by using the following equation:

$$\alpha\ i/j = (P/l)i : (P/l)j \tag{2}$$

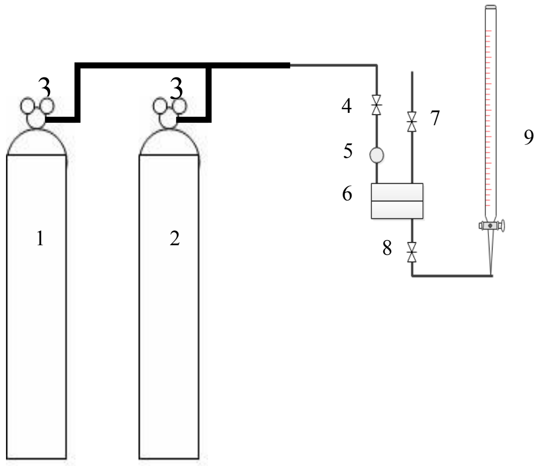

Fig 1. Instrumentation for Biogas Permeation

1. CO_2 tube
2. CH_4 tube
3. Regulator
4. Needle Valve
5. Pressure Gauge
6. Membrane module
7. Retentate
8. Permeate
9. Soap bubble flowmeter

3 Results and Discussion

3.1 Effect of UV irradiation on Nano Hybrid Membrane PES-TiO_2 for Biogas Purification

To observe the effect of the combination of the nano TiO_2 addition and UV modification, the membrane was fabricated with 0.5 wt-% nano TiO_2 loading and was exposed using UV light for 1, 2, and 3 minutes. Then the membrane is used to treat gas separation to evaluate the permeability and selectivity.

The addition of UV light to the PES + TiO_2 membrane increases the permeability of CO_2 and selectivity. CO_2 permeability and selectivity respectively are 104.10 GPU and 4.94 rise to 531.26 GPU and 7.53. This is because the UV-exposed PES + TiO_2 membrane undergoes a chain scission and crosslinking process. This phenomenon can cause membrane pores to form larger. Thus, raising the value of CO_2 permeability and selectivity [11].

The selectivity of the non-irradiated PES + TiO_2 membrane and UV light irradiance was obtained at values 4.94. Whereas in previous studies, PES polymer membranes without UV light irradiation had a selectivity of 8.33 [12]. This phenomenon is caused by the effects of UV light exposed to the polymer membrane. The UV lightinduced the polymer chains to restructure and grafting resulting on the denser polymer. The longer exposure of UV light on the membrane surface, it leads to the polymer chain degradation of polyethersulfone polymer [13-15]. As the consequences, the membrane pores will be larger, and the UV treatment increases the permeability. But this shows that the selectivity still obtained is far from standard.

According to Adib et al. the phenomenon occurs because there is a selective hole in the membrane layer which induces for the Knudsen diffusion mechanism resulting in low selectivity and high permeability [15]. This can be seen in Table 1. which shows that the permeability of CH_4 that escaped very large. While the desired mechanism in the separation of CO_2 and CH_4 is the mechanism of Molecular Sieving or Solution-Diffusion, where only or more CO_2 passes through the membrane whereas CH_4 is not expected to pass.

Table 1. CO_2 permeability and CO_2/CH_4 selectivity for different mixed matrix membranes before and after adding UV irradiation

Type	CO_2 Permeance (GPU)	CO_2/CH_4 Selectivity
PES + TiO_2	104.10	4.94
PES + TiO_2 + UV 1 min	531.26	7.53

In Table 2. We can see the performance of PES membrane for the separation of CO_2 from CH_4. The permeability values of CO_2 and selectivity tend to increase with increasing duration of irradiation. This is because the UV-exposed PES membrane undergoes a chain scission and crosslinking process. This phenomenon can cause membrane pores to form larger. Thus, raising the value of CO_2 permeability and selectivity [11].

However, the selectivity obtained in the experiments was very low when compared with previous experiments on PES membranes without irradiated UV light, ie, 8.33 [12]. While the selectivity shown in Table 2, selectivity does not reach a value greater than 3.75. Adib et al. assessed that the low selectivity of the research results was due to a selective hole in the membrane causing the gas flow mechanism occurring in the membrane to be Knudsen diffusion [15]. With the occurrence of Knudsen diffusion will increase CH_4 permeability and will reduce the selectivity. This can be seen in Table 1. which shows the permeability of CH_4 passes. While the desired mechanism in the separation of CO_2 and CH_4 is the mechanism of Molecular Sieving or Solution-Diffusion, where only or more CO_2 passes through the membrane whereas CH_4 is not expected to pass.

Table 2. CO_2 permeability and CO_2/CH_4 selectivity for different mixed matrix membranes before by adding UV irradiation

Type	CO_2 Permeance (GPU)	CO_2/CH_4 Selectivity
PES + TiO_2 + UV 1 min	531.26	7.53
PES + TiO_2 + UV 2 min	309.33	8.43
PES + TiO_2 + UV 3 min	1194.20	13.18

3.2 Effect of Cross Linking on Nano Hybrid Membrane PES-TiO_2 for Biogas Purification

Table 3. CO_2 permeability and CO_2/CH_4 selectivity for different mixed matrix membranes before by adding cross linker ethanol-aseton

Type	CO_2 Permeance (GPU)	CO_2/CH_4 Selectivity
PES + TiO_2 + UV 3 min	1194.20	13.17
PES + TiO_2 + UV 3 min + cross linking	1644.82	15.64

Based on Table 3, membrane with the addition of ethanol and acetone as cross linker or co-solvent and also internal coagulant together with water will lead to a denser and smoother membrane on its surface [16]. Addition of acetone in the casting solution with a ratio 3:1 with ethanol, results in the formation of a dense upper coating and a decline in the size and number of finger-like pores on the sub layer.

The immersion of membrane material in the organic solvent has been reported to be able to give effects to membrane transport properties [13]. This provides lower permeability and higher selectivity [17]. And also with the presence of acetone as the co-solvent can enhances the bridge formation between the compounds [18]. Based on the presence of ethanol and acetone as cross linker with ratio 1:3 can improve the membrane performance, so that the membrane surface will be denser, smaller pore, and the selectivity will increase.

3 Conclusion

Membrane nano hybrid PES with 0.5 wt-% nano TiO_2 as additive materials with 3 minutes of ultraviolet irradiation for biogas separation can increased the permeability of CO_2 and the selectivity of CO_2/CH_4. This phenomenon is caused by the effects of UV light exposed to the polymer membrane. Variations in ultraviolet irradiance from 1,2,3 minutes, while UV irradiation for 3 minutes has the highest permeability of CO_2 and selectivity of CO_2/CH_4. Besides that, combination between ultraviolet irradiance and immersion of membrane nano hybrid PES-nano TiO_2 into non-solvent solution ethanol-acetone (1:3) can increased the permeability of CO_2 and selectivity CO_2/CH_4 because the presence of acetone as the co-solvent enhances the bridge formation between the compounds.

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