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Absorption of CO2 from modified flue gases of power generation Tarahan chemically using NaOH and Na2CO3 and biologically using microalgae

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Abstract. This research was carried out on the absorption of CO 2 from the modified flue gases of power generation Tarahan using NaOH (sodium hydroxide) and Na2CO3 (sodium carbonate). The operation was conducted in a packed column absorber and then the output gases from the packed column was fed into photo-bioreactor for biological absorption. In the photo-bioreactor, two species of microalgae, N. occulata and T. chuii, were cultivated to both absorb CO 2 gas and to produce biomass for algal oil. The aims of this research were, first, to determine the effect of absorbent flow rate on the reduction of CO 2 and on the decrease of output gas temperature, second, to determine the characteristics of methyl ester obtained from biological absorption process. Flow rates of the absorbent were varied as 1, 2, and 3 l/min. The concentrations of NaOH and Na_2CO_3 were 1 M at a constant gas flow rate of 6 l/min. The output concentrations of CO_2 from the absorber was analyzed using Gas Chromatography 2014-AT SHIMADZU Corp 08128. The results show that both of the absorbents give different trends. From the absorption using NaOH, it can be concluded that the higher the flow rate, the higher the absorption rate obtained. The highest flow rate achieved maximum absorption of 100%. On the other hand, absorption with Na_2CO_3 revealed the opposite trend where the higher the flow rates the lower the absorption rate. The highest absorption using Na_2CO_3 was obtained with the lowest flow rate, 1 l/min, that was 45,5%. As the effect of flow rate on output gas temperature, the temperature decreased with increasing flow rates for both absorbents. The output gas temperature for NaOH and Na_2CO_3 were consecutively 35 oC and 31 oC with inlet gas temperature of 50 oC. Absorption of CO_2 biologically resulted a reduction of CO 2 up to 60% from the input gas concentration. Algal oil was extracted with mixed hexane and chloroform to obtain algal oil. Extracted oil was transesterified to methyl ester using sodium hydroxide as a catalyst. The results of in-situ transesterification method cannot be identified. Both microalgae achieved maximum yield at 2% catalyst concentration. Nannochloropsis occulata achieved the highest yield of algal oil that is 88.5%. The highest content of methyl ester from Nannochloropsis occulata was undecanoic acid methyl ester by 55.42% and the result from Tetraselmis chuii was palmitic acid methyl ester by 81.58%. Keywords: CO_2, chemical absorption, biological absorption, microalgae 21234567890 ‘’”” [3]ICBBogor 2017 IOP Publishing IOP Conf. Series: Earth and Environmental Science 141 (2018) 012023 doi :10.1088/1755-1315/141/1/012023 1. Introduction Pollution has caused a lot of [2]damage to the environment. One of waste that can be a threat to the environment is CO_2, which is increasingly increasing and can degrade air quality. Most of the CO_2 that is released into the environment is a result of human activities, for example on steam [1]power generation Tarahan in South Lampung. The amount per hour is not massive but, the buildup can occur if CO_2 is continuously released without further treatment. Action can be taken by absorption of CO_2 chemically and biologically. The biological absorption is carried out by using microalgae, where CO_2 will be absorbed by microalgae in the photosynthesis process. Besides reducing CO_2, this process can produce biodiesel using algal oil from microalgae. Microalgae have the lipid content of more than 30% and productivity of microalgae 200 times more than other vegetable sources, so it can be used as an alternative source of biodiesel [1]. On the other hand, the chemical absorption is applied using absorbents where absorbents are contacted with CO_2 in the absorber. Research on CO_2 absorption has been published in literature. Previous study [2], show that the initial absorption decreased at a flow rate of 0.2 l / min to 0.4 l / min, and then absorption increased at a flow rate of 0.4 l / min to 0, 6 l / min. The initial condition was due to unsteady process. He found that the greater the flow rate of fluid the lower the k_Ga due to the unsteadiness of flow. When the flow rates is steady then the value of k_Ga is greater. The k_La decrease with increasing the flow rate but then it is increase with higher flow rates. An optimum concentration in the CO_2 reduction process was obtained by previous study [3] that is 25% by weight of Na_2CO_3. The effect of the addition of boric acid (H_3BO_3) to the solution in has been determined where the best boric acid concentration was at 3% by weight with the CO_2 gas absorption of 67.81%. However it increased the absorption rate up to 2.4 times. Theoretically, chemical gas absorption is a process of mass transfer between two phases, gas and liquid, in which mass transfer occur when there is a driving force from one phase to another. The force of motion is a collision between molecules during mixing of fluid due flow rate velocity or forced mixing. Therefore, the greater the collision between molecules, the higher the absorption rate. The operating temperature affects the size of an absorber in the absorption operation. High temperatures affect the absorption capacity where the temperature enhances the reaction mechanism in the absorber [4]. Many research has been done by utilizing microalgae as a CO_2 absorbent with different types of microalgae. The commercial production of biodiesel derived from microalgae is still in the research and development stage, mainly due to the current prohibitive high costs associated with the biomass production and fuel conversion process. The schemes of research and development are optimizing parameters of operation 2such as the reaction time, the ratio of alcohol and microalgae lipid, catalyst concentration, and reaction temperature. In conventional trans-esterification, 8the extraction of lipid from microalgae was carried out by percolation using mixture of polar and non-polar solvents, such as methanol and chloroform. The oil was then trans-esterified into methyl ester in batch. Many research have 5been carried out to determine the best operating condition for th e extraction of microalgal oil. However, this method takes a long time and therefore it requires high cost. Therefore, the more attractive alternative is being developed, namely the in-situ method or trans-esterification of biodiesel without the extraction step. 3In this research, the experiment was carried out not only about the ability of alkaline solutions and microalga in reducing CO2, but also the potential of microalgae species in producing algal oil. 31234567890 ''"" ICBBogor 2017 IOP Publishing IOP Conf. 2Series: Earth and Environmental Science 141 (2018) 012023 doi :10.1088/1755-1315/141/1/012023 Previously, the studies were carried out separately either chemically or biologically. In this study, the absorption is carried out both chemically and biologically. The flow rates of the absorbent were 1, 2, dan 3 l /min. This is higher than the flow rate used by Hasnan et al. [2]. This is because the height of absorber in this study is larger than that applied by Hasnan et al. [2]. Similarly, as explained in previous research [5,6] high absorber and flow rates have an effect on overall mass displacement. 32. Materials and Methods 2.1 Chemical Absorption Materials The main equipment is packed column made from acrylic with a diameter of 7.5 cm and height of 127 cm). The packed column was filled with packing (based aluminum pipe mixture 2with a diameter of 8 mm, length of 2 cm and height of stuffing packing on columns 70 cm). Supporting equipment are a heater, air pump, gas flowmeter, liquid flowmeter, thermometer, and gas chromatography for analysis. The absorbent was 1 M NaOH and Na2CO3. They were made from 40 grams of NaOH crystal dissolved in 10 liters of water and 1.06 kg of Na2CO3 dissolved in 10 liters of water. Na2CO3 was mixed with the H3BO3 1as a catalyst of 3% weight. The CO2 from Aneka Gas Industri in Natar-Lampung

Selatan was made with concentration of 15% in air. The variables was the flow rates of the absorbent of 1, 2, and 3 l/min for both absorbents. Experimental set-up and Procedure Figure 1 shows the experimental schematic diagram for chemical absorption. 41234567890 ʻʻ"" ICBBogor 2017 IOP Publishing IOP Conf. Series: Earth and Environmental Science 141 (2018) 012023 doi :10.1088/1755-1315/141/1/012023 Figure 1. Schematic of CO_2 absorption tool setting The absorbent was pumped into to the top of the packed column as setting volumetric flow rates (1,2,3 l/min). In the same time, the mixture of 15% CO_2-air was fed at constant flow rate of 1 l/min and contacted counter-currently with the absorbent. Input gas mixture temperature was set to 50 oC. The operation was applied until steady state condition was obtained. The output gas of the packed column was fed into the foto-bioreactor for biological absorption using microalgae. Gas sampling was applied using sampling bag and injected it into CO_2 analyser (2014-AT Gas Chromatography Picture /SIMADZU Corp 08128). 2.2 Biological Absorption Foto-bioreactor was filled with 2 liter culture of microalgae which was cultured for 6 days. The microalgae was then cultivated after 6 days. In the same time, the concentration of the output gas of the packed column was analyzed and the temperature was also measured. Nannochloropsis oculata and Tetraselmis chuii were obtained from The Lab oratory of Marinculture Development, Lampung, Indonesia. They were cultured as explained above. After the cultivation, the microalgae was extracted in a soxhlet using chloroform: methanol and n-hexane as solvent [7]. As a result, algal oil was obtained. The alga oil was converted into methyl ester using sodium hydroxide in transesterification process with sulfuric acid as a catalyst. 51234567890 ʻʻ"" ICBBogor 2017 IOP Publishing IOP Conf. Series: Earth and Environmental Science 141 (2018) 012023 doi :10.1088/1755-1315/141/1/012023 3. Results and Discussions 3.1 Chemical Absorption 3.1.1 The Effect of Absorbent Flow Rates on CO_2 Absorption The effect of NaOH Flow Rate on CO_2 Absorption is shown in Figure 2. Figure 2. The effect of flow rates on the percentage of CO_2 absorption As can be seen from Figure 2, the absorption of CO_2 by NaOH is much greater than that of by Na_2CO_3. However, both absorbents gives different trend. As for NaOH, the higher the flow rates the higher the percentage of absorption. In contrast, as for Na2CO3 increasing the flow rates of absorbent decreasing the percentage of absorption. As for NaOH, the absorption of CO2 using NaOH increases with increasing flow rate is due to the increasing the flow rate means increasing the availability of absorbent for CO2 to dissolve as well as to react. This is in accordance with research [8] about the effect of flow rate of CO2 gas absorption. In the study, it was described that an increase in flow rate can increase the rate of absorption in the gas because the increase of gas flow rate will increase the value of gas mass transfer coefficient. The higher the value of mass transfer coefficient of the gas the higher the liquid absorption capacity of the gas. On the other hand, the absorption of CO2 using Na2CO3 shows that increasing the flow rates of absorbent decreasing the percentage of absorption. 3.1.2 The Effect of Absorbent Flow Rate on output gas temperature The effect of flow rates on output gas temperature is shown in Figure 3. As can be seen form the figure 3, the higher the flow rates the lower the percentage of output gas temperature. This means that the higher the flow rates the gas output temperature is increasing. Higher flow rates was expected to lower the gas output temperature, however the results show the opposite. This is because the higher flow rates means shorter contact time with the gas. Therefore, the gas outlet temperature is higher with higher flow rates than that of lower flow rates. 25.00 35.00 45.00 55.00 65.00 75.00 85.00 95.00 105.00 0.5 1 1.5 2 2.5 3 3.5 CO 2 absorption percentages Absorbent Flow Rates Laju Alir NaOH Laju Alir Na2CO3 Flow rates of NaOH Flow rates of Na2CO3 61234567890 ‘“” ICBBogor 2017 IOP Publishing IOP Conf. Series: Earth and Environmental Science 141 (2018) 012023 doi :10.1088/1755-1315/141/1/012023 Figure 3. The Effect of Absorbent Flow Rate on the percentage of reduce output temperature 3.1.3 Extraction of microalgal oil The lipids content or microalgal oil was extracted from microalgae in a soxhlet and show the results in Tabel 1. Table 1 Lipid Content extracted from Microalgaae Run Nannochloropsis oculata Tetraselmis chuii I 11.0% 10.3% II 13.0% 10.0% III 12.5% 10.0% Cultivation and harvesting processes affect the difference in the lipid. The culture was evaporated under vacuum to release the solvent using rotary evaporator. Then, the oil was obtained. It can be seen from the table that the oil extracted from N. oculata is much more that the oil from T. chuii. The 1algal oil was converted into methyl ester by means of transesterification. The reaction occurs in two stages, they are esterification and transesterification. Then, the oil produced from each algal species was mixed 2with a mixture of catalyst and methanol with stirring. Esterification must be carried out due to the high content of fatty acid, that is more than 5%. A Certain amount of algal biomass of each species was reacted methyl ester. 0 4 8 12 16 20 24 28 32 36 0 1 2 3 4 Absorbent Flow rates Percentage of reduce Temperature (%) 71234567890 ′′′′ 3ICBBogor 2017 IOP Publishing IOP Conf. 2Series: Earth and Environmental Science 141 (2018) 012023 doi :10.1088/1755-1315/141/1/012023 Figure 4. The effect of catalyst concentration on yield methyl ester of N. oculata 1and T. chuii Figure 4 showed that the yield of methyl ester increase with increasing of catalyst concentration up to 2,0%. 2The concentration of catalyst in this state is able to optimally break the bond on lipid and exchange with methanol, thus forming FAME and glycerol. The mechanism of reaction can be seen from the Figure 5 below. Figure 5. The mechanism 5of transesterification reaction with base catalyst [9] Figure 5 showed that the mechanism of the transesterification reaction takes 2 steps . 6The first step, NaOH catalyst will bind to alcohol and wait for the contact with triglycerides [10]. After contacting between alcohol and triglycerides, the Na+ ions help break the bond contained triglycerides. The disconnected ties react with alcohol and Na+ ions back to form a compound NaOH. N. Occulata T. Chuii Yield of methyl ester (%) 81234567890 ′′′′ 3ICBBogor 2017 IOP Publishing IOP Conf. 2Series: Earth and Environmental Science 141 (2018) 012023 doi :10.1088/1755-1315/141/1/012023 It also occurs in the second step, in order to obtain the compound of alkyl esters (biodiesel). 6In the third Step, H + ions produced from the break up of alcohol will bind to O=, thus forming glycerol. At a concentration of 1.5% catalyst, methyl ester produced is minimum. When insufficient amount of catalyst is available, the catalyst is not able to optimally promote the lipid break the bond, so the reaction is slow. It takes a little longer to achieve optimum yield. The highest yield in both microalgae is obtained in the catalyst concentration of 2%, that is 88.5% in microalgae N. oculata and

82.3% in microalgae T. chuii. Maximum yield of FAME obtained from N. oculata is slightly higher than that of T. chuii. 3.1.4 Characterisation of biodiesel by GC-MS The biodiesel produced from N. oculata and T. chuii were analyzed and compared with standards of fatty acids and methyl ester by gas chromatography analyzer. Based on Figure 6 and 7, there are two peaks that indicate the presence of methyl ester component on both microalgae. Figure 6 shows the result of GC-MS analysis from N. oculata. Figure 6. GC-MS result for Nannochloropsis oculata FAME Figure 7. GC-MS result for Tetraselmis chuii FAME The results indicated that the peak at R. time 31.390 corresponding to the presence of undecanoic acid methyl ester by 55.42% and at R. time 44.620 corresponding to the presence of glyceryl - 1,2 – isopropylidene – 3 - laurin by 44.58%. The GC-MS analysis result of Tetraselmis chuii methyl ester is shown in Figure 7. The first peak appeared at R. time 32.165 minutes. Based on the data bank of methyl ester, it shows that the peak is dodecanoic acid methyl ester by 18.42%. The second peak that appeared at the time R. 44.750 minutes corresponding to the presence of palmitic acid methyl ester by 81.58%. 91234567890 ‘’“” ICBBogor 2017 IOP Publishing IOP Conf. Series: Earth and Environmental Science 141 (2018) 012023 doi :10.1088/1755-1315/141/1/012023 4. Conclusions The absorption of CO_2 by NaOH is greater when compared with that of Na_2CO_3. This is because the solubility and reaction rate of CO_2 in or with each NaOH and Na_2CO_3 is different. The absorption of CO_2 with NaOH increases with increasing flow rate and the opposite is for Na_2CO_3. Extracted oil was transesterified to biodiesel using sodium hydroxide as a catalyst. Both of microalgae obtained maximum yield at 2% catalyst concentration. Nannochloropsis oculata gives the highest yield that is 88.5%. The highest content of methyl ester from Nannochloropsis oculata is undecanoic acid methyl ester by 55.42% and the result from Tetraselmis chuii is palmitic acid methyl ester by 81.58%.

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