

Synthesis N-Doped Activated Carbon from Sugarcane Bagasse for CO₂ Adsorption

Randy Yusuf Kurniawan, Irsandi Dwi Oka Kurniawan, Lukman Atmaja, and Nurul Widiastuti

Abstract—Nitrogen-doped activated carbon (SBACN) was synthesized from sugarcane bagasse waste as a carbon source and urea as nitrogen source through potassium hydroxide (KOH) activation for 2 h at high temperature via two step methods. The synthesized SBACN was characterized using X-Ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Fourier Transform Infrared (FTIR). The results showed that the SBACN has low degree crystallinity and graphitization with highly developed micropores due to synergistic activation effect of KOH and urea. These characteristics provide an important contribution to carbon dioxide adsorption capacity, which can reach up to 11,20% wt and this value is higher than pristine activated carbon. The results indicating that the presence of this nitrogen functionalities is found to have a beneficial influence on the carbon dioxide adsorption characteristic in standard condition and exhibit considerable potential in solid adsorption.

Keywords—Nitrogen-doped Nitrogen-doped Activated Carbon, Sugarcane Bagasse, KOH and Urea Activation, CO₂ Adsorption.

I. INTRODUCTION

The Carbon dioxide (CO₂) is one of the greenhouse gases that contributes the most to the occurrence of the greenhouse effect. About 70% of carbon dioxide gas is produced as a by-product of activities carried out by humans. Over the past two decades, the greenhouse effect caused an increase in the average temperature of the earth's surface around 0.8 ° C with an increase in the concentration of CO₂ in the atmosphere from 280 ppm to 400 ppm until May 2013. The CO₂ gas increase is estimated to reach 1550 ppm by 2030 if CO₂ gas emissions are not controlled. In addition to causing global warming, carbon dioxide dioxide that exceeds the normal limit (350 ppm) can endanger health and cause acid rain which adversely affects environmental equilibrium. Therefore, an effort is needed that can control emissions CO₂ gas in the air [1][2].

The technology that is widely developed to control CO₂ gas emissions is Carbon Capture and Storage (CCS), which is a method of separating carbon dioxide from the air through the process of capturing CO₂ gas on a large scale and then flowed and stored into a porous material so that CO₂ gas will not be released back into the atmosphere.

The CCS method is between absorption, cryogenic distillation, membrane and adsorption. The absorption method has a high efficiency (> 90%) but requires high costs and energy consumption for the regeneration process of the absorbent. Whereas the cryogenic distillation method is carried out with the principle of condensation which occurs at low temperatures (-161°C) without involving solvents so that it requires high energy to decrease CO₂ gas. Therefore, from the various CCS methods, the adsorption method is considered to be a potential method to be applied in reducing CO₂ gas emissions because it has the advantage of requiring low costs and energy because generally the adsorption process takes place temperature and pressure [3][4].

The adsorption method has a high adsorption and desorption rate, therefore the adsorbent is easy to regenerate, has high mechanical and thermal stability and

produces high adsorption capacity [3]. The adsorption process is divided into 2 parts, namely chemisorption and physical adsorption (physisorption). Physical adsorption of adsorbate (CO₂ gas) can be easily adsorbed on the surface of the adsorbent (activated carbon) through the Van der Waals force, so generally the adsorbent used will be easy to regenerate. While in chemical adsorption, there is an interaction between the adsorbate and the adsorbent on the surface which makes it difficult to regenerate [4].

CO₂ gas adsorption methods can be carried out using porous materials namely mesoporous silica [5] zeolite [6], porous carbon [7], and Metal Organic Framework (MOF) [8]. From some of these materials, activated carbon is considered as a potential material to be used as CO₂ gas adsorbent because of its high surface area and thermal stability, high adsorption-desorption kinetics and low cost in production. Activated carbon with a high surface area has higher CO₂ gas adsorption ability than carbon nanotubes and carbon nanofiber [9]. Therefore, in this study activated carbon was used as CO₂ gas adsorbent material.

The material that is widely developed for CO₂ gas adsorption is activated carbon because of its high surface area and thermal stability, high adsorption-desorption kinetics and low cost production [9]. Activated carbon can be prepared from biomass waste such as oil palm shells, coconut shells, date seeds, and bagasse. In some of these biomass wastes, bagasse is a type of biomass that has the potential to be developed as raw material for the production of activated carbon because it is abundant in Indonesia, reaching 7.68 million tons of bagasse per year and contains lignin-cellulose biopolymers consisting from hemicellulose, lignin and cellulose which can be used as carbon sources [10][11]. Sugarcane bagasse has high hemicellulose content compared to other lignin-cellulose components which reaches 53.4% by weight therefore the bagasse can be converted into activated carbon through two step methods [12]. The average energy of CO₂ gas adsorption on activated carbon is -13.07 kJ/mol, therefore to get a high adsorption capacity it is necessary to increase the temperature and pressure [13]. Alternative method that can be used to increase the interaction between gas-solid by adding heteroatom to the activated carbon matrix. Strong interaction between heteroatom on activated carbon and CO₂ gas is expected to increase CO₂ gas adsorption capacity [14]. In previous studies several

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Figure 1. Powder of N-Doped Activated Carbon

heteroatoms that had been added to activated carbon were Boron (B) [15], Sulfur (S) [16] and Nitrogen (N) [17]. Nitrogen is a type of heteroatom which has the greatest effect on increasing interactions between CO₂ and carbon compared to other heteroatoms [18]. One important parameter in the N doping process on carbon is the maximum amount of nitrogen (% by weight N) that can be doped on carbon matrix. In the previous studies explain that the presence of excess nitrogen can actually cover the carbon pore which results in a decrease in the carbon surface area of 853 m²/g at an N ratio of 0.1% by weight to 609 m²/g at an N ratio of 0.3% by weight. However, N 0.3% has a higher CO₂ gas adsorption capacity than N 0.1% [19].

II. METHOD

A. Materials

Sugarcane bagasse was collected from Keputih, Surabaya. KOH (SAP), Deionised water, H₂SO₄ (98% p.a), Urea (p.a), N₂ gas with *high purity* (HP) (99,99% N₂), CO₂ with *Ultra High Purity* (UHP) (99,9999% CO₂).

B. Activated Carbon (SBAC) Synthesis

The activated carbon from sugarcane bagasse was synthesized via two step methods carbonization and activation. First, the sugarcane bagasse was cut into pieces, dried in oven (100°C) for 24 h. Subsequently, the dried sugarcane bagasse was carbonized for 2 h at 500°C at heating rate 3°C min⁻¹ in N₂ flow. After cooling, the obtained sample was denoted as SBC was mixed with KOH at ratio 1:3 (SBC:KOH). The mixture was further activated at 750°C for 2 h at a heating rate 3°C min⁻¹ under N₂ atmosphere. The obtained product were washed several times with deionized water to remove impurities and the dried at 105°C for 24 h. The obtained sample was denoted as SBAC.

C. N-Doped Activated Carbon (SBACN) Synthesis

The N-Doped activated carbon was synthesized via two step methods carbonization-doping and activation. First, the sugarcane bagasse was cut into pieces, dried in oven (100°C) for 24 h. Subsequently, the dried sugarcane bagasse and urea were mixed thoroughly at a ratio mass 1:1. The mixture was then carbonized for 2 h at 500°C at a heating rate 3°C min⁻¹ in N₂ flow. After cooling, the obtained sample was denoted as SBAN was mixed with KOH at ratio 1:3 (SBAN:KOH). The mixture was further activated at 750°C for 2 h at a heating rate 3°C min⁻¹ under N₂ atmosphere. The obtained product were washed

several times with deionized water to remove impurities and the dried at 105°C for 24 h. The obtained sampel was denoted as SBACN.

D. N-Doped Activated Carbon (SBACN) Characterization

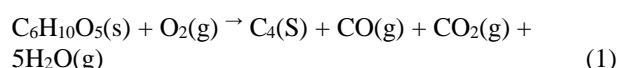
The powder X-Ray diffraction (XRD) analysis were employed to identify effect of N to crystallography activated carbon, Scanning Electron Microscope (SEM) to study the effect of N to morphology of activated carbon, specific surface area and pore distribution of SBACN was determined by adsorption-desorption N₂ (BET) using (*Quantachrome Autosorb iQ*) and the last to identify the kind of N bonding in the carbon matrix was used FTIR.

III. RESULTS AND DISCUSSION

A. Synthesis of SBAC and SBACN

N-Doped Activated carbon which successful synthesized can be shown at fig 1. In Figure 1 shows that the bagasse charcoal produced is still rough with non-uniform charcoal size. However, the bagasse charcoal is not coarser than the charcoal produced from the coconut shell. This is because the bagasse has a lower lignin content of 15%, while the coconut shell has a lignin content of 33.61%. Lignin compounds are natural polymers consisting of polyphenol molecules which function as binding to wood cells to each other, so that plant stems become hard and stiff [20].

The next step is the carbonization process. First the bagasse charcoal that has been cooled is mashed by using pestle and mortar. The refining process aims to reduce the size of sugarcane charcoal. The finer (smaller) size of bagasse, then the surface area of bagasse is contacted with heat when carbonization is also getting bigger. The bagasse carbonization process is carried out at a temperature of 500°C. The reactions that occur during the carbonization process are as follows [21]:



Based on the Reaction Equation 1, the carbonization process of bagasse produces carbon solids and other volatile compounds. Carbon products from the bagasse carbonization process are refined. Then the fine bagasse carbon is filtered using a 125 mesh filter. The refining and filtration aims to produce uniform sized carbon and reduce the particle size of the bagasse carbon. Particle size can affect carbon surface area. The smaller the particle size, the greater the surface area of carbon. Large surface area of carbon can affect the large storage capacity of hydrogen gas. Therefore, to find out the large surface area of carbon that has been produced from the carbonization process of the bagasse above can be done by measuring the surface area using the BET method. The test results using the BET method can be seen in Table 1. The results of testing the BET method on bagasse carbon showed that the surface area of sugarcane bagasse was very small at 22,5 m²/g. Large surface area on carbon can affect the formed pore structure. The smaller the surface area of carbon, the greater the pore structure produced. To enlarge the surface area of carbon produced from bagasse, it can be done with a chemically activated treatment.

Carbon activation in this study aims to enlarge the surface area of carbon by changing the macropore

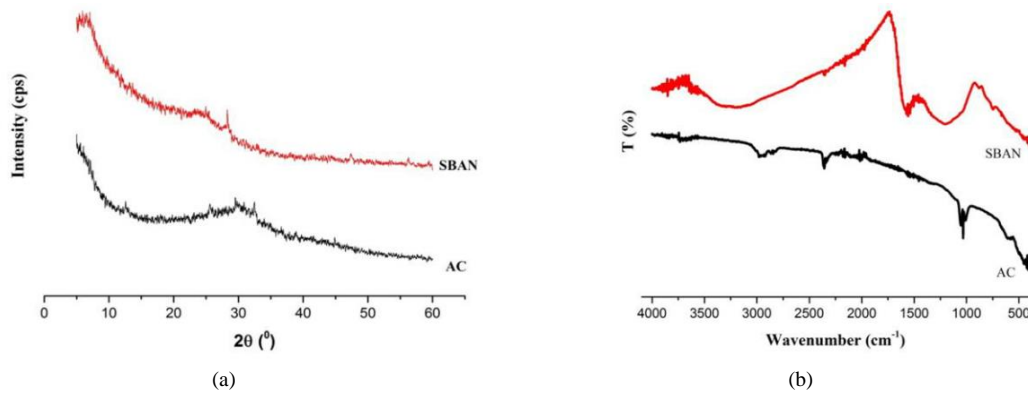


Figure 2. (a) Diffractogram (b) FTIR Spectra of SBACN and Pristine Activated Carbon from Sugarcane Bagasse.

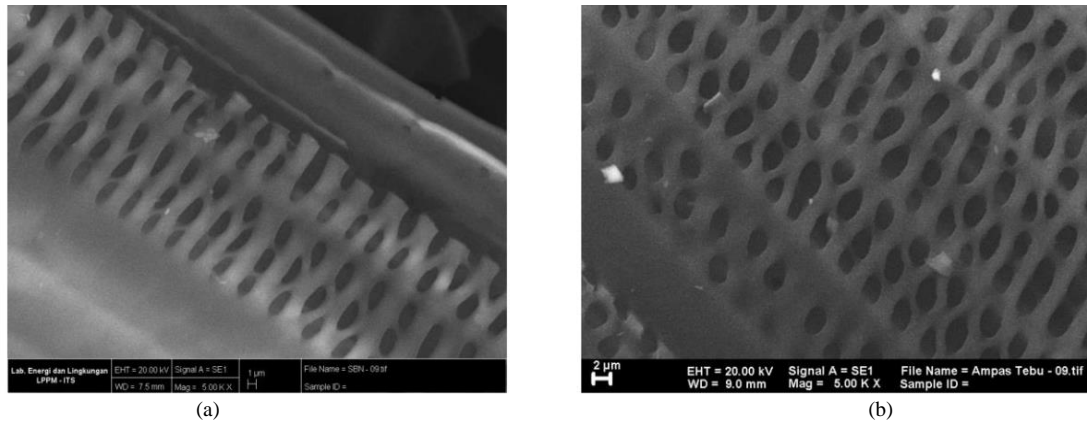


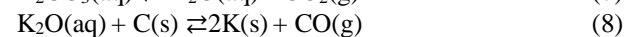
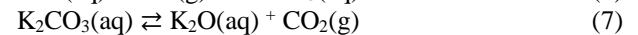
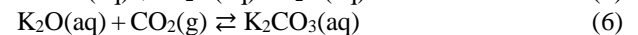
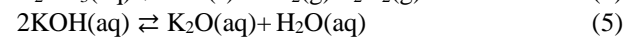
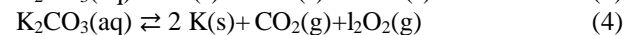
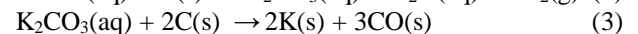
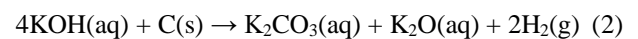
Figure 3. SEM Image of (a) SBAC (b) SBACN.

structure of carbon into a micropore structure. The activation method chosen is the chemical activation method. The advantages of chemical activation methods compared to physics activation methods include lower activation temperature, higher yield of activated carbon and more formed pores. The activator substance used in this study was KOH. KOH is a hydrating agent at high temperatures so that it can be used as an activator in the chemical activation process. KOH activators can increase the surface area in several studies. The large surface area will increase hydrogen adsorption capacity. KOH will be able to easily react with lignocellulose material on bagasse which has been carbonized beforehand [22]. This is different from acidic activators such as $ZnCl_2$, material which has lignocellulose compound is better mixed directly with $ZnCl_2$ activator without going through the previous carbonization process. This is because the lignocellulose material contains a lot of oxygen and acids will react well with functional groups containing oxygen [23].

The thing that must be considered in the activation process is the amount of activator added to carbon. The carbon/KOH ratio can affect hydrogen adsorption capacity. The number of suitable activators can increase the carbon dioxide adsorption capacity. However, if the number of activators is less or even excessive, it can reduce the adsorption capacity of CO_2 gas on carbon [23]. Therefore, in this study a variation of the carbon / KOH ratio was carried out to determine the right amount of KOH to the optimal CO_2 adsorption capacity of the bagasse activated carbon.

Carbonization is carried out at a temperature of $750^\circ C$. The temperature of $750^\circ C$ is the optimal temperature of carbonization in lignocellulose material [23]. If the carbonization temperature is too high it will damage the

pore structure formed on carbon. The pore structure is possible to be damaged at temperatures above $750^\circ C$ so that it can reduce porosity in carbon [24]. Chemical reactions that occur at the time of carbonization according to [25] are as follows:



Based on these reactions, the carbonization process produces several compounds including carbon dioxide gas, water vapor and carbonate compounds. At the time of carbonization, carbon dioxide gas can react again with KOH to produce carbonate compounds again. The above reaction also produces water vapor, because KOH is a hydrating agent. Potassium atoms formed during the carbonization process will experience good intercalation to develop and form micropores on carbon.

The use of KOH is considered more environmentally friendly than $ZnCl_2$ and H_3PO_4 [24]. Therefore, KOH is a type of activator that is widely used as a pore control agent. KOH activators are also considered to be more effective in producing activated carbon with micropore distribution and high surface area up to $3000 \text{ m}^2/\text{g}$. Serafin synthesized activated carbon through activation using KOH and obtained an adsorption capacity of 21.2% at 298 K and a low pressure of 1 bar [16]. Meanwhile, other studies obtaining carbon that was activated using KOH had a higher surface area of 6.91% higher when compared to activation using H_3PO_4 [25]. The mass ratio and activation temperature can be said to be optimal if it

TABLE 1.
SPECIFIC SURFACE AREA AND PARAMETER POROSITY OF SBAC
AND SBACN

Sample	SBET (m ² /g)	Vmikro (cm ³ /g)	Vt (cm ³ /g)
SBAC	212,76	0,062	0,112
SBACN	301,34	0,103	0,146

produces carbon with a high surface area and micropore distribution and of course produces a high adsorption capacity. This is because micropore is one of the most important factors in the gas adsorption process, so it is very important to produce adsorbent material with a high level of porosity (micropore) [26]. In the previous study, activated carbon prepared from rice husk ash and activated using KOH with a mass ratio of KOH / C 3: 1 at 750°C had a surface area of 1935.8 m²/g, micropore volume of 0.807 cm³/g and gas adsorption capacity CO₂ is 22.2% by weight at 30°C and a pressure of 1 bar [25]. Hidayatullah, synthesizes activated carbon from bagasse with variations of KOH/C 1:1 at 800°C activation temperature and obtained a small surface area of 178 m²/g. Another study conducted by Geng et al. 2015 obtained activated carbon material with a high surface area and micropore volume of 2613 m²/g and 0.269 cm³/g through activation using KOH with a ratio of 3:1 and activation temperature of 800°C. The resulting micropore volume is the largest volume value compared to activated carbon with variations of KOH/C 4:1 and 5: 1 at the same temperature.

The CO₂ gas adsorption mechanism on activated carbon occurs through the weak Van der Waals interaction between CO₂ molecules and the surface of the activated carbon. CO₂ gas adsorption in activated carbon material is based on the principle of fissionation (physical adsorption) which is a reversible absorption of CO₂ molecules on the surface of the adsorbing material. The adsorption material acts as an adsorbent, while carbon dioxide acts as an adsorbate. CO₂ gas initially enters the pore on the surface of the adsorbent and occupies the pore on the surface of the adsorbent and occupies the active active blank on the surface [27]. Continuous filling finally makes CO₂ gas form a monolayer layer (4) above the surface of the adsorbent. If this condition is continued, CO₂ gas will form a multilayer layer until it reaches a saturation level [27]. If the adsorbed CO₂ gas has reached its saturation point, then the adsorption capacity will decrease due to the attraction between the surface and the adsorbate decreases as the adsorbent surface has been covered by the adsorbate molecule which has stuck to the surface of the adsorbate. The phenomenon of saturation is indicated by a graph that starts straight which shows the value of capacity (q) that begins to reach equilibrium (q_e). CO₂ gas adsorption capacity on activated carbon is determined by the gravimetric method [30], which is by observing changes in mass during the CO₂ gas adsorption process and then calculating the difference between the initial mass (mass before gas flow). Gravimetric measurements are expressed in% by weight according to equation (2.3). Where m_t is the sample mass after CO₂ gas adsorption while m₀ is the initial sample mass.

B. Characterization of SBAC and SBACN

Fig 2 (a) shows the XRD pattern for pristine activated carbon and N doped activated carbon (SBACN). The figures showed all samples show the broadened

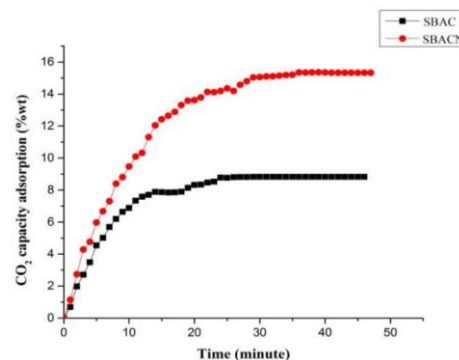


Figure 4. CO₂ adsorption isotherm of (a) SBAC (b) SBACN.

diffraction reflections, which were centered at around $2\theta = 31,2^\circ$ for activated carbon and $28,3^\circ$ for SBACN due to reflection to the (002) planes of graphite, showing their dominant features of amorphous carbon. For the SBACN sample, the (002) plane shift to smaller angle as compared with pristine activated carbon, indicating a low degree of crystallinity and graphitization on N-doped activated carbon, which may due to the existence of more pores and defects derived from the synergistic activation effect of KOH and urea. The FTIR spectra of pristine activated carbon and SBACN were shown in fig 2 (b). For SBACN, the peak at 1454 and 1538 cm⁻¹ attributed to N-CH₂ and C=N bonding suggesting that nitrogen atom not only exist in the surface of activated carbon but also exist in the SBACN polyaromatic structure. The peak at 3212 cm⁻¹ is due to N-H-O-H stretching [28].

In order to elucidate the role of urea as N source in the pyrolysis process, the SEM images of N-doped activated carbon are shown in fig 3, the SBACN displays a rough structure with interconnected porous network and hierarchical pore structure. Moreover, we can observe existence of large number of micropores from the SEM image. The previous study conclude that the addition of urea on activated carbon will displays very thin layered carbon morphology, show interconnected meso- and microporous network structure without obvious macropores rather than pristine activated carbon [28].

In this study, SBAC and SBACN were tested for CO₂ gas adsorption capacity. The process of measuring CO₂ gas adsorption capacity was tested by the gravimetric method, namely by observing changes in mass during the CO₂ gas adsorption process and recorded every 1 minute, then calculated the difference between the initial mass (mass before gas flow). The results of measurement of CO₂ gas adsorption capacity in SBAC and SBACN materials are then converted to weight percent. Before testing CO₂ gas adsorption capacity, SBAC and SBACN carried out the degassing process at 350°C for 3 hours to remove impurities and water vapor. After the degassing process the temperature is reduced to room temperature (30°C), then the CO₂ gas adsorption process begins with a flow rate of 10 mL/minute which is set using the Mass Flow Control tool. In this study the CO₂ gas adsorption process was carried out at 30°C until the mass of the adsorbent was constant. The Results of determined CO₂ gas adsorption capacity are shown in Figure 4. Based on Figure 4, the CO₂ adsorption capacity pattern in each sample has similarities as increasing hydrogen adsorption, which tends to increase. In the 0th minute until the 23rd minute there was a sharp increase, meaning that the CO₂

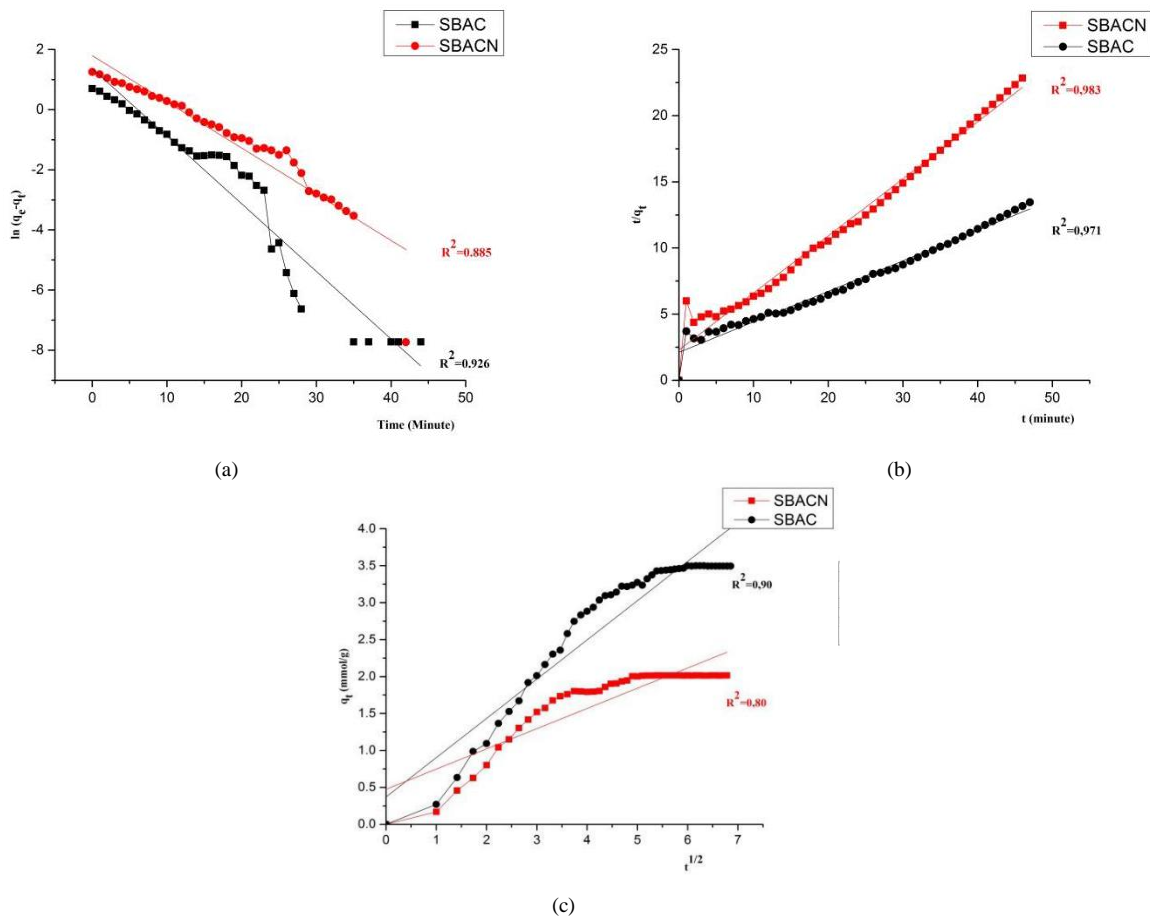


Figure 5. Graph of Isothermal CO₂ adsorption kinetic model: (a) pseudo-first order (b) pseudo-second order (c) intraparticle diffusion.

gas adsorption process took place quickly. This is because at the beginning of adsorption, CO₂ gas enters the pore and occupies an empty active side on the carbon surface. In this condition, the CO₂ gas adsorption process starts to run slowly because the empty active side has been filled by the incoming CO₂ gas first [24]. This process is seen in Figure 4, where from the 24th minute the increase in CO₂ adsorption capacity occurs slowly. If this condition is continued, CO₂ gas will form a multilayer layer until it reaches a saturation level [24]. The saturation level is indicated by the mass obtained constant.

The pristine activated carbon has a lower adsorption capacity than SBACN which suggest that pristine activated carbon displays more obvious mesoporous and macroporous character than microporous. The presence of pores less than 2 nm is an important parameter in adsorbing gas because the density of the gas will increase when it is in the micropore therefore the gas will not be easily released [29]. These results are also supported by testing using SEM where after doping, micropore distribution increases. These results suggest that both KOH and urea can act as efficient chemical activation reagents for improving the porosity and specific surface area of the carbon materials. The value of CO₂ gas adsorption capacity on SBAC and SBACN at temperature and space pressure respectively were 7.07 and 11.20 wt% (Fig. 3). This value is slightly smaller than that the porous carbon obtained from ammonia dopant of palm shell [30] and resin formaldehyde [31].

The lower CO₂ gas adsorption capacity on SBAC material when compared to SBACN because the effect of nitrogen adds to the active side while increasing the new

pore, resulting in additional surface area and micropore volume. the interaction of SBAC and SBACN carbon with CO₂ gas molecules as atoms has almost the same electronegativity, so that carbon bonds with CO₂ generally do not have large bonded dipole moments [17]. Therefore, hydrogen molecules can maintain their properties and do not change when the adsorption process takes place. Porous carbon has a hexagonal structure such as benzene with sp² hybridization. The hydrogen bond in the sp² hybridization system has a weak interaction, which results from dipole-dipole induction. The dipole moment produced is very small because the bond between H-H molecules originating from the amine group on the SBACN is quite rigid and the load density of the material bound to sp² is slightly uniform at the equilibrium of CO₂ adsorption, causing an increase in CO₂ molecules in low carbon [17]. Therefore in this study nitrogen modification was carried out.

In addition to the proportion of micropores that are higher than activated carbon (SBAC), the N atoms in SBACN also influence the adsorption capacity of the CO₂. CO₂ gas is a species of weak acid molecule that can interact with the free electron pair found on the N atom. This interaction is Lewis acid-base. In the previous study, N atoms were types of atoms which had a large influence on increasing CO₂ gas adsorption capacity through Lewis acid-base interactions where CO₂ acts as an acid while N is a base species that donates free electron pairs to CO₂ molecules [31]. This interaction causes more CO₂ gas to be adsorbed through chemical adsorption interactions. Therefore, the SBACN type of adsorption produced is a combination of physical and chemical adsorption. This

type of adsorption also causes the equilibrium adsorption point on SBACN to be longer than SBAC. In Figure 4, it can be seen that the SBACN equilibrium point occurred at the 23 minute while the SBAC at the 17 minute showed the equilibrium point. This shows that the SBAC adsorption occurs only involving the role of the pore while the role of SBACN N also helps the CO₂ gas adsorption process so that when CO₂ gas has filled the entire pore of activated carbon, then CO₂ will interact with the N atom. This gives an advantage over physical adsorption which only involves the role of porosity. The type of physical adsorption has a low adsorption enthalpy value which causes CO₂ gas to be more easily decomposed and this decreases its function as a gas adsorbent if applied on a large scale.

Increased CO₂ gas adsorption capacity on N-doped carbon is also caused by Lewis acid-base interactions. CO₂ is a weak Lewis acid that can interact with Lewis base species. The Lewis base will donate electrons to the CO₂ molecule. On this carbon, nitrogen will bind to C atoms by forming N-pyridinic, N-hydraulic and N-graphitic structures. N-pyridine contains a pair of free electrons that can be donated to CO₂ molecules and causes CO₂ to be oxidized to form CO molecules or formic acids. The addition of N to the surface of activated carbon can increase electronic conductivity and surface alkalinity. Increased resistance to the surface of activated carbon will increase interaction with Lewis acid species such as CO₂ [17].

Previous study was found that the addition of nitrogen atoms to activated carbon produced CO₂ gas adsorption capacity of 1.73 mmol/g at 25°C and 1 bar pressure. This value is higher than activated carbon without N doping which only produces CO₂ gas adsorption capacity of 1.22 mmol/g. Hao, et al., 2010 [36] reported that activated carbon N-doped from monolith had a higher CO₂ gas adsorption capacity of 3.3 mmol/g at 25°C than activated carbon that was prepared from melamine (2.25 mmol/g). The same results were also reported by [32] who found an increase in CO₂ gas adsorption capacity of 32% on N-doped activated carbon compared to activated carbon without N dopant.

The adsorption of CO₂ gas on N doped carbon occurs chemically through the presence of Lewis acid-base interactions. CO₂ is a weak Lewis acid that can interact with Lewis base species. The Lewis base will donate electrons to the CO₂ molecule. In general, N-pyridine contains a pair of free electrons that can be donated to CO₂ molecules and causes CO₂ to be oxidized to form CO molecules or formic acids. Niu also mentioned that the addition of N to the surface of activated carbon can increase electronic conductivity and surface alkalinity [17]. Increased resistance to the surface of activated carbon will increase interaction with Lewis acid species such as CO₂. If N is present in the carbon group in the form of amine, then the N reaction on the amine group with CO₂ gas molecules can be stated as follows:

The reaction can be seen in CO₂ gas which interacts with N atoms in the amine group to form a product in the form of ammonium carbamate and ammonium bicarbonate. The previous research found that one bidentate ammonium carbamate molecule can be converted into two bidentate ammonium bicarbonate molecules when water vapor is flowed into the system. The CO₂ gas adsorption

capacity of N doped carbon is also very dependent on the type of N bound to the carbon surface. Although N doping is carried out using materials containing N in high quantities, but if N is bound to carbon is a stable type of N quarter then of course, CO₂ gas cannot interact with that N which results in low adsorption capacity values. However, if N bound to the surface of the carbon forms a N-pyridin or hydraulic-like structure, then the structure will have an effect on the adsorption capacity of the CO₂ produced [33].

The mechanism of interaction between CO₂ molecules and N on N doped carbon can also occur through hydrogen bonds. The hydrogen bond occurs between O atoms in CO₂ molecules with H or N atoms on the carbon surface. The structure of graphite on carbon will bind hydrogen atoms in the form of C-H sp² so that this H atom can interact in the form of hydrogen bonds with O atoms on CO₂ molecules. In addition to H in the structure of graphite, if N also binds H to form an amine group then H can also interact with O atoms on CO₂ molecules. This hydrogen bond can be beneficial in terms of application because CO₂ gas adsorbed on the carbon surface will not be easily decomposed due to the higher bond energy value compared to the Van Der Waals interaction produced between the carbon pore structure and the CO₂ gas molecule. Therefore. The adsorption capacity will increase in the surface of activated carbon.

C. Kinetic Study of CO₂ adsorption on SBAC and SBACN

Adsorption kinetics study in this study aims to determine the effectiveness of hydrogen gas adsorption on activated carbon from bagasse. Several adsorption kinetics models have been calculated to determine the appropriate adsorption kinetics model, including: Pseudo Lagergren, Pseudo Ho, and intraparticle diffusion models.

Pseudo-first-order reactions are derivatives of second order assuming one reactant has a much higher concentration than the concentration of other reactants [34]. This kinetic modeling assumes that the reaction rate of the second order is as if it were first order. Therefore pseudo words appear in this order reaction because the concentration of one reactant does not seem to change [34][35]. Graph of pseudo-first order of SBAC and SBACN are shown in Fig. 5 (a).

In figure 5 (a) shows a graph of a pseudo-first order, which is a plot between $\ln(q_e - q_t)$ as an ordinate and time (t) as an abscissa. The quasi-order modeling in this study was that the concentration of the activated carbon adsorbent and activated carbon doped with nitrogen was assumed to be unchanged, because the concentration was too large compared to the CO₂ concentration as the adsorbate.

Second-order reactions are derivatives from first order based on equilibrium adsorption capacity, assuming the adsorption capacity is always proportional to the number of active sites of an adsorbent [34]. Pseudo-second-order kinetic equations show how the adsorption rate of an adsorbate depends on the adsorption capacity of the adsorbent not on the adsorbate concentration [36]. In this study, CO₂ adsorption capacity is always proportional to the amount of active nitrogen in SBAC and SBACN.

The plot between t/q_t and time (t) as shown in Figure 5 (b) is a pseudo second order graph. CO₂ gas adsorption rate is greater in SBACN material than SBAC. Addition

of N can increase CO₂ adsorption capacity so that CO₂ adsorption rate also increases. This shows that the adsorption process takes place faster with the addition of heteroatom N because nitrogen is the active side of the carbon framework.

The intra-particle diffusion kinetics model indicates the CO₂ adsorption process in the SBAN pore takes place in two stages, namely the mesopore diffusion stage and the micropore diffusion stage. At the mesoporous diffusion stage, CO₂ gas molecules are adsorbed on amorphous carbon on the outer surface of SBACN, while at the micropore diffusion stage, CO₂ gas molecules will be deposited on the surface in the SBACN which enters the carbon pore [34][37].

The plot between q_t as ordinate and $t^{1/2}$ as abscissa as shown in Figure 5 (c) is a graph of intra-particle diffusion. Based on Figure 5 (c), the initial process or mesoporous diffusion is rapid which then slows down when diffusing into the surface of micropore diffusion on SBACN nitrogen which enters the carbon pore [34][37].

IV. CONCLUSION

N-doped activated carbon has been synthesized from sugarcane bagasse via 2 two-step methods successfully provide higher porosity and CO₂ gas adsorption performances than activated carbon without dopant N. The incorporation of KOH and urea on carbon has positive synergistic to form microporosity and effective nitrogen-doping formation. N-doped activated carbon showed more microporosity intensity with the CO₂ gas adsorption capacity produced is 11,20% wt.

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