Preparation and characterization of soybean straw activated carbon for natural gas storage

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Abstract. Adsorbed natural gas (ANG) can be developed through its porous adsorbent, especially activated carbon (AC) which has larger specific surface area. AC made of soybean straw is developed because of its abundance as agricultural waste in Indonesia and high lignocellulosic content. AC is produced in 500°C furnace for 1 hour with nitrogen gas flow of 200 mL/minute. For AC production, variations of chemical activating agents utilizing $ZnCl_2$ and KOH and the concentration NiO as modification substance are made in this paper. Characterizations are made through iodine number, SEM, EDX, and nitrogen adsorption-desorption for obtaining data of adsorption capacity, surface topography, main composition, and particles specification. $ZnCl_2$ activated carbon shows better result with iodine number of 577.73 mg/g and S_{BET} of 741.26 m^2/g, and the second-best is found in 2%-NiO-modified $ZnCl_2$ activated carbon with iodine number of 534.79 mg/g and S_{BET} of 632.24 m^2/g. It is concluded that development of soybean straw as activated carbon precursor is still needed to obtain larger S_{BET} and better adsorption capacity.

1 Introduction

One of the Sustainable Development Goals declared by United Nations on 2015 is creating clean and affordable energy. To create one, utilization of conventional energy can be either optimized or reduced. Optimization of natural gas use as main source of conventional energy is quite promising since carbon dioxide emission of natural gas is lower (53.06 kg CO_2/MMBtu) than any other two types of conventional energy; crude oil produces 72.19 kg CO_2/MMBtu and coal produces 98.21 kg CO_2/MMBtu [5].

Natural gas use can be supported by optimizing the storage method to be effective and safe, so that adsorbed natural gas technology is considerable as the storage method. Adsorbed natural gas (ANG) is one of the natural gas storage forms besides compressed natural gas (CNG) and liquefied natural gas (LNG). Different from the latest two, ANG technology utilizes adsorbent as the storage media, resulting much lower storage pressure than CNG and more effective vessel design than LNG. ANG is perceived to be able reduce the risk of natural gas storage with high pressure and more explosion chance such as CNG [6]. This technology accommodates natural gas adsorption in lower pressure so that it should be supported by appropriate adsorbent.

One of the adsorbents that is clicked with the need of ANG implementation is activated carbon since the specific surface area can reach in the range of 1,000 to 2,000 m^2/gram [7]. Activated carbon can also be modified by metal oxide as the support of adsorption and desorption properties though the modification process will slightly reduce the adsorption capacity [8].

Activated carbon can be produced when the precursor contains large composition of carbon. From this statement, biomass is possibly utilized as activated carbon precursor since the carbon content is high in a form of organic polymer (e.g. cellulose, hemicellulose, lignin). One of the promising biomasses that can be utilized as activated carbon is soybean straw (*Glycine max*) since the range of cellulose is 44-83% and lignin of 5-14% [9]. Quantitatively, soybean straw production rate is positive, reaching 2,35% per year, and Indonesia's domestic soybean production reached 963,183 ton in 2015 [10].

This research will execute the synthesis of activated carbon with soybean straw *(Glycine max)* and conducting the modification process utilizing nickel oxide as the supporting material. Since there is previous research that synthesizing activated carbon from soybean straw utilizing zinc chloride as activating agent [1] and to the very best knowledge there has not been yet potassium hydroxide-activated precursor for activated carbon, this research will do one. Nickel oxide loading will also be varied to see the effect of the supporting material to the adsorption capability. Characterizations of the best activated carbon will be executed quantitatively and qualitatively to see the differences of the non-modified activated carbon to the modified one. It is expected that this research will be able to synthesize soybean straw-based activated carbon which is appropriate to be implemented in adsorbed natural gas technology.

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2 Experiment Methods

2.1 Materials

There were materials needed to do this research. Soybean straw (*Glycine max*) was the main precursor of activated carbon, taken from agricultural area of Tulungagung, East Java. Activating agents used for chemical activation were varied; the chemical activation used pro-analyst zinc chloride (ZnCl$_2$, Merck, purity >99%) and technical potassium hydroxide (KOH, purity >90%). Nitrogen (N$_2$) was utilized as the gas for carbonization process. Distilled water was used for solvent of activating agent and as the activated carbon washing media. Nickel nitrate hexahydrate [Ni(NO$_3$)$_2$.6H$_2$O] was the precursor of nickel oxide (NiO) that would be decomposed inside the muffle furnace.

2.2 Preparation of activated carbon

Preparation of activated carbon consisted of production process and modification of activated carbon with nickel oxide.

2.2.1 Activated carbon production

The production process was divided into three stages: chemical activation, carbonization, and washing. This process was started by main precursor drying inside the oven in the temperature of 105°C for 2 hours to eliminate minor water particulate. Dried main precursor was then crushed and blended into size of 14 mesh for making the chemical activating agent easy to react with cellulose of main precursor. Chemical activation was conducted inside the Beaker glass by mixing main precursor and activating agent with certain mass ratio as the optimum point (ZnCl$_2$:SS = 3:1, KOH:SS = 4:1). The main precursor was immersed for 24 hours with atmospheric condition (27°C, 1 atm) covered by plastic wrap to prevent any impurities reaction.

Immersed precursor was then dried inside the oven for 2 hours in the temperature of 105°C to remove excessive water content and make the carbonization process more effective and efficient. Carbonization process was executed in the tubular furnace in the temperature of 500°C for both immersed precursor for 1 hour. Gas flow of nitrogen was set 200 mL/minute. Carbonized precursor was then washed by distilled water while stirred over hot plate magnetic stirrer at the temperature of 60°C to remove ions and impurities resulted by oxidation. Washing process was stopped when the pH of activated carbon was in the range of 6 to 7. Washed activated carbon was dried in the oven in 105°C for 1 hour.

2.2.2 Activated carbon modification

The modification process was started by making 200 mL solution of nickel nitrate with different concentration; 0.5%, 1%, and 2%. 1-gram activated carbon was then mixed into the solution to impregnate nickel nitrate into the activated carbon. The mixture was stirred for 6 hours to homogenize the content of nickel nitrate impregnated. The impregnated activated carbon was then filtered and dried in the oven at 105°C for 1 hour. The dried activated carbon was then placed into muffle furnace to execute decomposition of nickel nitrate to nickel oxide. The muffle furnace was set at 360°C, above the starting decomposition point of nickel nitrate (350°C). The modified activated carbon was then stored in a 5-cm sample pack under atmospheric condition.

2.3 Characterization of Activated Carbon

Characterizations for the activated carbon synthesized along the process consisted of four; iodine number, scanning electron microscopy (SEM), energy dispersive x-ray (EDX), and specific surface area analysis

2.3.1 Iodine number

Iodine number is an analysis method to measure the adsorption capacity of 1-gram activated carbon to iodine. The steps of analysis were referred to the standard ASTM D4607-94, released in 2011. Substance needed for this analysis consisted of neutralized activated carbon (pH = 6-7), potassium iodide (KI) as iodine source, sodium thiosulfate for titration process, and distilled water for solvent.

2.3.2 Scanning electron microscopy (SEM)

Scanning electron microscopy was executed for illustrating the surface topography of activated carbon. The analysis was examined by JEOL JED-2300 Analysis Station. 0.1 gram of sample was used in the dry condition and no pretreatment was executed. The picture magnification was set at 1500x.

2.3.3 Energy-dispersive x-ray (EDX)

Energy dispersive x-ray was executed simultaneously with scanning electron microscopy analysis. This method was used for analyzing elemental composition of synthesized activated carbon. The device for this method was the same with SEM, JEOL JED-2300 Analysis Station. The analysis power was examined at 20 kV with energy range of 0-20 keV.

2.3.4 Nitrogen adsorption-desorption

Nitrogen adsorption-desorption was examined at 77 K (-195,15°C) by Micromeritics surface area analyzer. This method was used for analyzing microstructure of particle, in this case, activated carbon. Specific surface area used Brunauer-Emmett-Teller (BET) adsorption model. Other parameters such as micropore area, external surface area, micropore volume, and pore size were also obtained in this analysis method.
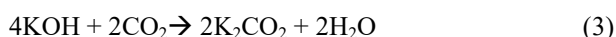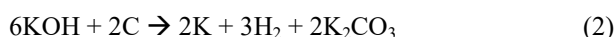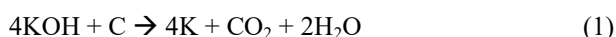
3 Results and Discussion

3.1 Production Yield

The average yield of soybean straw activated carbon with different activating agent is shown in Table 1.

Table 1. Average yield of activated carbon with different activating agent

Activating Agent	Yield, %
Zinc chloride	78.03
Potassium hydroxide	25.98

The result shows that precursor that is chemically activated by zinc chloride has significantly bigger yield than the one activated by potassium hydroxide. Different activating agent results different yield for the same precursor since the reaction nature of each chemical to the organic polymer consisted in the precursor (e.g. cellulose, lignin) is different. Organic polymer does not only consist of C atom but also O and other atoms. Basically, each activating agent decomposes the organic polymer into pure carbon and any kind of non-organic carbon substances such as tar, carbon dioxide, and carbon monoxide. Addition of nitrogen flow into the tubular helps preventing excessive oxidation of carbon which converts the organic polymer into non-organic substances and makes the carbon content lower. Zinc chloride selectively stripes atom O and H in a form of H_2O and H_2 rather than any non-organic carbon substances [1]. Potassium hydroxide has tendency to form ash and carbonates to be released from the char, following these chemical equations [2]:

$$4KOH + C \rightarrow 4K + CO_2 + 2H_2O \qquad (1)$$

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3 \qquad (2)$$

$$4KOH + 2CO_2 \rightarrow 2K_2CO_2 + 2H_2O \qquad (3)$$

Based on Equation (1) and (3), potassium hydroxide is also the dehydrating agent. Since the different tendency of reaction made by zinc chloride and potassium hydroxide, which potassium hydroxide forms more carbon impurities in a form of potassium carbonate and carbon dioxide, it can be concluded that zinc chloride accommodates better yield of activated carbon production rather than potassium hydroxide.

3.2 Iodine Number

Figure 1 shows iodine number of non-modified and nickel oxide-modified activated carbons from different activating agent and different concentration of nickel nitrate solution. The graph points two highest iodine number are owned by non-modified $ZnCl_2$ activated carbon (577.73 mg/g) and 2%-NiO-modified $ZnCl_2$ activated carbon (534.79 mg/g). KOH activated carbon results lower iodine number with the highest one is obtained by the non-modified with iodine number

529.51 mg/g. There is an enormous drop of iodine number from non-modified KOH activated carbon to 0.5%-NiO-modified activated carbon.
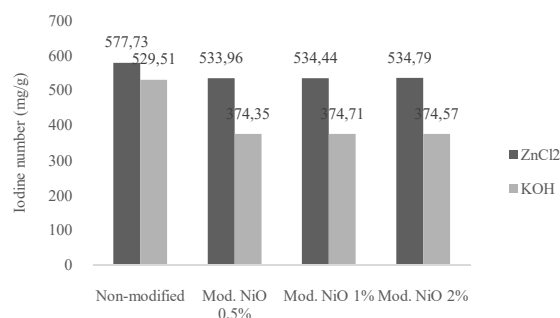
Fig 1. Iodine number of non-modified and modified activated carbon

The difference of iodine number shows difference of adsorption capability of each activated carbon. Iodine adsorption is influenced by pore size, pH, and other deposits that either support or inhibit activated carbon adsorption capability. Non-modified activated carbon has more free pores than the modified ones that are not much blocked so that it can be assumed that the specified surface area is higher. Nickel oxide that comes from nickel nitrate decomposition at 360°C deposits at the micropore area of the particle so that amount of iodine that can be adsorbed is lower than the non-modified one. Nickel oxide has no record of interaction with iodine substance and/or particles, so iodine number basically does not define the adsorption capacity of activated carbon to different particulates.

Iodine number of modified zinc chloride activated carbon is bigger than modified potassium hydroxide activated carbon. The increase of nickel oxide concentration in zinc chloride activated carbon is proportional to the iodine adsorbed, but there is an optimum point of modified potassium hydroxide one. This can be assumed that the deposit position of nickel oxide into the pore and/or external surface of activated carbon plays important role to activated carbon adsorption capability. $ZnCl_2$ might have the deposit of nickel oxide mostly on the micropore side and a little on the surface, leaving mesopores and macropores of the activated carbon. Meanwhile, modification of KOH activated carbon utilizing nickel oxide covers mostly the external surface so remaining micropores, mesopores, and macropores result lower specific area and adsorption capability. Visually, it is discussed in subsection 3.3.

### 3.3 SEM and EDX characterization

SEM and EDX characterization consecutively describes visual appearance of activated carbon external surface and elemental composition of it. Table 2 shows the elemental composition of two types of activated carbon which has best iodine number based on the previous method of analysis. Figure 2 (a), (b), and (c), consecutively shows topography of external surface area of three types of activated carbon.

Table 2. Activated carbon elemental composition

Elements (%wt)	$ZnCl_2$, Non-Modified	$ZnCl_2$, 2%-NiO Modified
C	85.54	86.62
O	10.75	10.2
Zn	3.18	2.03
Cl	0.53	0.97
Ni	-	0.17
Total	**100**	**99.99**

The composition of both types of activated carbon have major composition of C atom that reach more than 80% of the whole mass. Zinc chloride, beside selectively removes H and O which leads to precursor dehydration during carbonization, also prevents tar and any other non-organic carbon substances [1]. The lesser atom C wasted in a form of non-organic carbon substances, the purity of C atom increases. Existence of Ni atom in modified $ZnCl_2$ activated carbon states that the modification method executed had succeeded a deposit in the activated carbon.

The topography of each type of activated carbon is not significantly different for Figure 2 (a) and (b) but so in Figure 2 (c). Figure 2 (a) and (b) consecutively show non-modified $ZnCl_2$ and 2%-NiO-modified activated carbon. The non-modified activated carbon plays a role as the precursor of the modified one so that it shows similar structure and arrangement of pores on external surface. Zinc chloride degrades the organic polymer, mainly cellulose, at carbonization process and conducts dehydration resulting chars and aromatization of the carbon skeleton, moreover creating pore structure [3]. The modification of zinc chloride activated carbon is visually succeeded since on Figure 2 (b) there is a blooming-like particle deposited on the surface which shows the particle of nickel oxide. The same illustration is shown in Nateghi*et al.* [4] who captures nickel oxide nanoparticles at magnification of 5000 times. Figure 2 (c) shows 1%-NiO-modified KOH activated carbon. It is concluded that the excessive modification of nickel oxide in KOH activated carbon covers most of the external surface area and dramatically decreases the adsorption capacity of it.
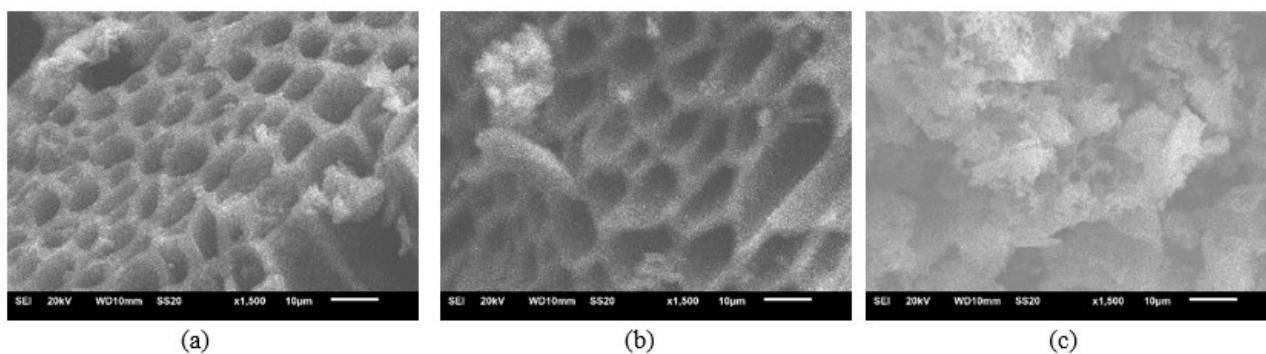
Fig 2. Topography of (a) non-modified $ZnCl_2$ activated carbon; (b) 2%-NiO-modified $ZnCl_2$ activated carbon, and; (c) 1%-NiO-modified KOH activated carbon

3.4 Nitrogen adsorption-desorption

Nitrogen adsorption-desorption method is conducted to characterize activated carbon's physical particle properties. Parameters included to the result of this analysis method are specific surface area (S_{BET}), micropore area, external surface area, micropore volume, pore width, and average particle size. Table 3 shows the value of parameters on both particles, non-modified $ZnCl_2$ activated carbon and the 2%-NiO-modified one.

**Table 3.** Particle characters based on some parameters

Parameters	$ZnCl_2$, Non-Modified	$ZnCl_2$, 2%-NiO-Modified
S_{BET} (m^2/g)	741.26	632.24
Micropore area (m^2/g)	562.79	467.94
External surface area (m^2/g)	178.47	164.30
Micropore volume (cm^3/g)	0.287	0.237
Pore width(nm)	2.136	2.169
Average particle size (nm)	8.094	9.490

This method results significant differences of the activated carbon based on the particle scale characterization. The S_{BET} values of both activated carbon is the highlight of this research due nitrogen adsorption can represent on how this synthesized activated carbon perform adsorption of gas, especially methane as main composition of natural gas to be stored. Non-modified $ZnCl_2$ activated carbon has larger S_{BET}than the modified one. This is because of the blockage happened in the modified activated carbon by nickel oxide. The blockage of nickel oxide occurs in the micropore side of the carbon so that total specific surface area owned by the modified activated carbon is lower than the non-modified one. This phenomenon is supported by other quantitative parameters on the table; there are value declines on micropore area and micropore volume regarded to NiO-modified activated carbon compared to the non-modified one. The external surface area value decline of modified activated carbon is caused by coverage of nickel oxide deposit, as shown in Figure 2 (b). Numerically, the S_{BET} values of both types of activated carbon are bigger than their iodine numbers, indicating that both activated carbon adsorb

gas particulate better than ions dissolved in the water. The average particle size values of both types state that the tested activated carbon has already been named as nanoparticle. Because of its small average particle size, these types of activated carbon have wider coverage to the adsorption system.

One of the important parameter for activated carbon is pore width. This will affect the performance of activated carbon to adsorb gas particulate inside the pore since gas has different width in the molecular scale. Consequently, pore width values of non-modified activated carbon and modified one are 2.136 and 2.169 nm, categorized as particles with mesopores. Though the value is in the range of mesopores, the adsorption isotherm model follows adsorption isotherm type I since the value is so close to the limit of pore width which supports adsorption isotherm type I (< 2 nm) that the adsorption graphic similarly follows type I. Figure 3 and Figure 4 shows the adsorption isotherm plot of non-modified $ZnCl_2$ activated carbon and 2%-NiO-modified one, in sequence. When the nitrogen adsorption is being occurred and reaching relative pressure (P/P_o) value of one, it is detected that non-modified activated carbon adsorbs more N_2 with value of 255.97 cm^3/g STP rather than non-modified one with value of 221.61 cm^3/g STP.
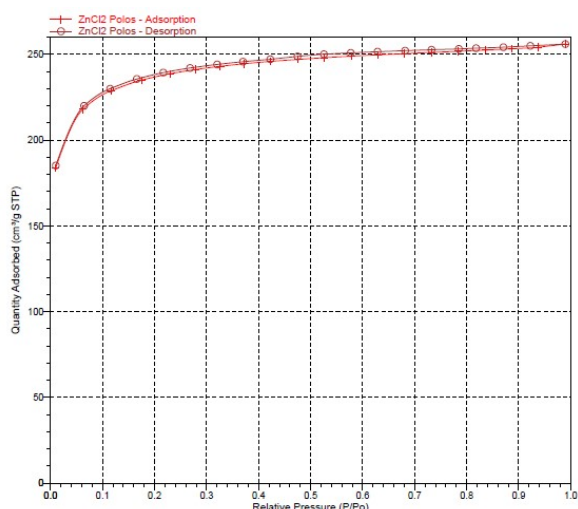
Fig 3. Adsorption isotherm plot of non-modified $ZnCl_2$ activated carbon
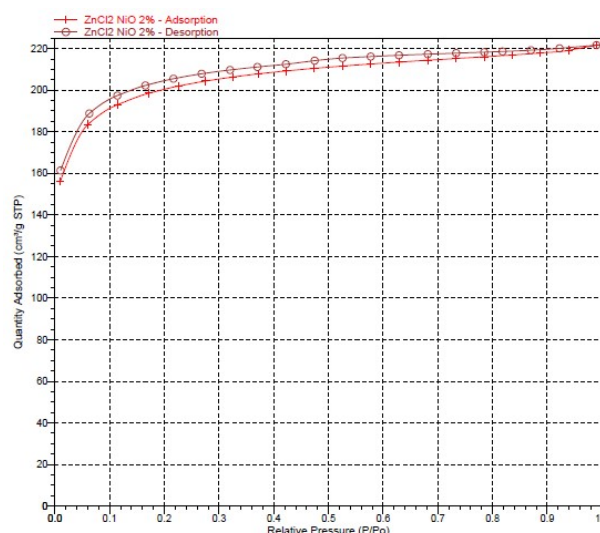
Fig 4. Adsorption isotherm plot of 2%-NiO-modified $ZnCl_2$ activated carbon

4 Conclusion

Through this research, it can be concluded that development of activated carbon production by soybean straw as main precursor is succeeded since the best properties of synthesized activated carbon is obtained by non-modified zinc chloride activated one, reaching S_{BET} value of 741.26 m^2/g. Chemical activation utilizing potassium hydroxide does not resulting better result in properties (iodine number) and economy (production yield). Best modified activated carbon is also obtained by zinc chloride-based activated carbon with amount of nickel oxide impregnated is 2%. Nevertheless, in this research, modification process also does not improve activated carbon adsorption capability, at least for iodine particulate and nitrogen. Further, existence of nickel oxide as the supporting metal oxide for activated carbon is supposed to be directly tested by pure methane or natural gas adsorption and compared to the non-modified one, since there is intense interaction between nickel oxide and methane. In the aspect of particle characterization, 2%-NiO-modified activated carbon owns S_{BET} value of 632.24 m^2/g; lower than non-modified one. Both types of activated carbon are supposed to be able to improve in the aspect of activating agent and modification utilizing different metal oxide that commonly used such as titanium oxide and magnesium oxide.

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