Methane Storage Performance in NiO Modified Soybean Straw Based-Activated Carbon

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Abstract. Adsorbed natural gas technology can be developed through the development of its adsorbent, especially activated carbon (AC). Biomass-based AC is possible to synthesize, especially by soybean straw which has cellulose content of 44-48 % and hemicellulose content up to 14%. Soybean straw-based AC with surface area 741 m²/g was used and through modifying process using metal oxide. The NiO-modification was done with a concentration variation of 0.5%, 1%, and 2%. Natural gas adsorption by synthesized AC was executed in the pressure range of 5-10 bars with interval 1 bar and temperature variation of 27°C, 31°C, and 35°C. The best non-modified AC was obtained with ZnCl₂ as an activator with S_BET of 741 m²/g and iodine number of 578 mg/g. The best modified AC was obtained with 2%-NiO modification with ZnCl₂ as an activator with S_BET of 632 m²/g and iodine number of 535 mg/g. The best adsorption capacity of synthesized AC reached 31.9 mg/g by modified AC on 10 bars and 27°C, and desorption/adsorption efficiency reaches 41.87% on 35°C, showing the effects of pressure and temperature on adsorbed natural gas.

1. Introduction
Utilization of natural gas as the main energy source can be one form of the implementation of the seventh point of Sustainable Development Goals, i.e. the creation of affordable clean energy use. The adsorbed natural gas (ANG) technology is a technology that allows the absorption of natural gas by porous solids which act as adsorbents at relatively low pressures (3.5 MPa). This method is more effective than compressed natural gas (CNG) which requires very high storage pressure, around 3000 psig [1] and liquefied natural gas (LNG) which requires a storage temperature of around -160 °C and complicated insulation technology [2]. Various factors influence the implementation of ANG, like the characteristics of the adsorbent, the loose capacity, the thermal effect of the adsorption heat, and the storage pressure [3].

Activated carbon has a very large surface area so it is suitable as an adsorbent or chemical reaction [1]. The surface area of commercialized activated carbon ranges from 1,000 to 2,000 m²/gram. The loading of metal oxides on activated carbon also affects the storage capacity and the release capacity of methane gas. Many studies have used lignocellulose material to produce AC, such as rice husk [4], pam leaf [5], almond shell [6], etc.

Soybean straw (Glycine max) waste has potential as an activated carbon raw material. Soybean straw has cellulose content in the range of 44-48%, hemicellulose content in the range of 12-15%, and the low number of ash and lignin [7]. In terms of quantity, according to Kementan RI, the abundance
of soybean straw waste is relatively large because soybean production per year in 2015 reached 963,183 tons and growth at 2.35% per year. During this time, this soybean straw waste has not been optimally used and is usually used as animal feed.

Adsorbed natural gas technology can be developed through the development of its adsorbent, especially activated carbon (AC). Biomass-based AC is possible to synthesize, especially by soybean straw. The high cellulose content makes this waste become popular raw material because it can produce good quality AC with a high surface area.

To increase quality, AC can be modified. Modified activated carbon is defined as adding chemical compounds to activated carbon to improve the performance of activated carbon in the adsorption and desorption processes. One of the activated carbon modification methods commonly used is metal oxide insertion. In this study, AC was modified with NiO. This method was expected to improve the adsorption ability of AC and increase methane storage with ANG technology.

2. Materials and Methods

2.1 Activated Carbon Modification
The AC used was produced in the previous study with a surface area of 741 m$^2$/g. Variation in the amount of loading metal oxide was done by inserting NiO in a portion of activated carbon produced and varied based on the amount of loading with variations of 0.5%, 1%, and 2%. The 10% Ni(NO$_3$)$_2$ solution was diluted into 0.5%, 1%, and 2% Ni(NO$_3$)$_2$ concentration solutions. The NiO solution mixed with AC samples and was stirred for 6 hours. This solution then decomposed in the furnace at 360 °C for 1 hour to obtain NiO-AC.

2.2 Activated Carbon Characterization
There are several characteristics of activated carbon that can be done to determine the pore structure, chemical composition, surface area, and absorption capacity of activated carbon made. These methods include iodine number calculation, Scanning Electron Microscopy (SEM), Energy-Dispersive X-ray (EDX), and Brunauer-Emmett-Teller (BET).

2.3 Adsorbed Natural Gas (ANG) Test
AC with the best characteristics was then used as an adsorbent in an adsorbed natural gas (ANG) reactor. The parameter tested was the storage capacity and release of methane gas. The produced AC ability was compared with commercial AC. Storage capacity testing by adsorption mechanism was carried out at various operating pressures in the range of 5 to 10 bar at 1 bar intervals and maintained at isothermal conditions of varying ambient temperatures (27 °C, 31 °C, and 35 °C). Five grams of AC was used for every test.

3. Results and Discussion

3.1 Iodine number test
Analysis of iodine number is a method which states the adsorption capacity of 1 gram of activated carbon to iodine particulates. The relation between the iodine number and specific surface area can be determined by ASTM-4607-94 [8]. Figure 1 shows the iodine number of ACs, ZnCl$_2$ and KOH modified and unmodified, which next called by AC-a and AC-b respectively.
Figure 1 above shows the two highest iodine numbers achieved by AC-a unmodified (578 mg/g) and AC-a NiO 2% modified (535 mg/g). AC-b has a lower iodine number compared to AC-a, defined by the iodine number was 530 mg/g for the unmodified samples. This result indicated that ZnCl₂ was more effective as an activating agent to open the pore of soybean straw-based AC. The ZnCl₂ induced the decomposition process of lignocellulosic materials and restricted the formation of tar [7].

The number shows that non-modified AC has more free pores than modified AC. This is due to the closure of pores on the surface of AC due to the modified deposit, in this case, NiO. So, it can be assumed that the modified AC has a lower specific surface area than non-modified AC.

3.2 SEM, EDX, and BET Characterization

SEM analysis aims to present an illustration of the surface morphology of the particles. Activated carbon tested was AC-a which unmodified and modified with NiO 2%. The SEM morphological illustrations in this study were arranged at magnifications of 1500 times.

The two figures of the morphology of AC analyzed that AC-a had an evenly distributed pore distribution with relatively homogeneous pore sizes. In Figure 2 (b) in the upper left corner, there was a NiO deposit located right on the surface which tended to cover the pore of AC. The NiO seemed not completely mixed with the AC original pore which resulted in the lump closed the surface pore and reduce the active site of AC.
Energy Dispersive X-ray (EDX) is useful for observing the composition of activated carbon elementally. Table 1 presents the composition data of AC-a, both modified and unmodified.

**Table 1. EDX characterization results**

| Components (% wt) | Unmodified AC-a | NiO 2% modified AC-a |
|-------------------|-----------------|----------------------|
| 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 the two types of AC had the main composition of atom C which reaches more than 80% of the AC total mass. ZnCl₂ had selectivity to remove atoms in the form of H and O which directed the dehydration of raw materials during carbonization, also prevents the formation of tar and other non-organic carbon substances [7]. The presence of Ni atoms in the modified-AC indicates that the modification process has resulted in a deposit of activated carbon. BET analysis relies on nitrogen as an adsorbate which adsorbed and desorbed under 77K operating conditions. This analysis will produce pore characterization such as specific surface area (S\text{BET}), average pore size, pore-volume, and average particle size. Table 2 states the characterization of the two activated carbons through the BET test.

**Table 2. BET characterization results**

| Parameter                  | Unmodified AC-a | NiO 2% modified AC-a |
|----------------------------|-----------------|----------------------|
| S\text{BET} (m²/g)         | 741             | 632                  |
| Micropore area (m²/g)      | 563             | 468                  |
| External surface area (m²/g)| 178             | 164                  |
| Micropore volume (cm³/g)   | 0.287           | 0.237                |
| Pore width (nm)            | 2.136           | 2.169                |

NiO plugging occurred on the mesoporous side of carbon so the total specific surface area possessed by modified AC was lower than unmodified. This phenomenon was supported by other quantitative parameters shown in the table; there was a decrease in the value of the micropore area and the micropore volume.

In order, the unmodified and modified AC pore width values were 2.136 nm and 2.169 nm, categorized as particles with mesoporous. Mesopore has a pore size between 2 and 50 nm. For better performance, AC should have a micropore structure that has a pore size of less than 2 nm [4]. This affected the performance of AC to absorb gas particulates in the pore because the gases had different widths on the molecular scale.

3.3 Natural Gas Adsorption Capacity Test

The whole process was preceded by void volume calculation. The void volume at measuring cell is the free part located at the top of AC and between the sidelines space between activated carbon. Void volume testing used helium gas because it belongs to the noble gas group; has higher stability than other gases. The natural gas used in this study was obtained from SPBU which contained 87.76% of methane (CH₄) gas. The results for the void volume test can be seen in table 3.
From table 3 above, commercial AC had the highest void volume. This indicated that the number of filling of natural gas will be greater when measuring cell filled with commercial AC.

Figure 3 shows the amount of gas adsorbed at different pressures and temperatures carried out by modified AC-a.

The variation of pressure in the isothermal system when natural gas adsorption on AC takes place shows the difference in the amount of natural gas that can be adsorbed. The phenomenon of increased adsorption capacity due to increased pressure, it can also be said that natural gas adsorption is physical adsorption [9] and there is a binding of gas molecules on the internal surface due to Van der Waals forces. Although NiO modified AC is neutral, nickel as a transition metal has electron acceptor properties and acts as Lewis acid so that methane which has Lewis alkaline properties will be attracted by acidic nickel [10].

Figure 4. The adsorption capacity of commercial AC-a
The same results also occurred for modified AC. The same pattern as unmodified AC showed that the process runs in the same conditions. The increase in temperature results in lower natural gas adsorption capacity, heat adsorption can affect the performance of natural gas storage in adsorbents [3] which in this case is caused by the exothermic nature of the adsorption so that an increase in temperature causes a decrease in the natural gas adsorbing capacity [11].

Pressure and temperature affect the adsorption capacity and release of activated carbon; the highest adsorption capacity is obtained at the highest pressure (10 bar) and the lowest temperature at variation (27 °C). The AC with the highest adsorption ability was the modified AC at an operating condition of 27 °C, 10 bars with an adsorption capacity of 31.9 mg/g.

3.4 Desorption Test
Table 5 provides an overview of the percentage efficiency of desorption/adsorption at 27 °C, 31 °C, 35 °C temperature and type of activated carbon, i.e. commercial (CAC), unmodified (UAC), and modified AC (MAC).

| T (°C) | Adsorption capacity (10 bar) [mg/g] | Desorption capacity (1 bar) [mg/g] | Efficiency (%) |
|-------|-----------------------------------|-----------------------------------|----------------|
|       | CAC | UAC | MAC | CAC | UAC | MAC | CAC | UAC | MAC |
| 27    | 38.4 | 31.9 | 30.9 | 18.5 | 12.6 | 10.4 | 48.24 | 39.62 | 33.23 |
| 31    | 35.8 | 29.1 | 27.9 | 17.9 | 11.9 | 9.6  | 49.87 | 40.66 | 34.10 |
| 35    | 31.8 | 27.0 | 26.0 | 17.0 | 11.4 | 9.4  | 51.77 | 41.87 | 36.97 |

Desorption is an endothermic process. Because of these characteristics, each type of AC at higher temperatures will release gases with a greater concentration than a lower temperature. The highest efficiency is achieved by CAC. CAC has a better surface structure with micropore which resulted in higher pore volume to store the methane gas.

4. Conclusion
Activated carbon made from straw waste has the potential to be further developed. The highest results obtained were non-modified AC with an S\textsubscript{BET} of 741 m\textsuperscript{2}/g and with an iodine number of 578 mg/g and 2% NiO modified AC with an S\textsubscript{BET} of 632 m\textsuperscript{2}/g with an iodine number of 535 mg/g. Pressure and temperature affect the adsorption capacity. The highest adsorption capacity was obtained at the highest pressure (10 bar) and the lowest temperature variation (27 °C). The highest number was detected in unmodified AC-a with 31.9 mg/g adsorption capacity. The highest efficiency was achieved by unmodified AC-a at 35 °C with an efficiency of 41, 87%. NiO impregnation should produce a better AC quality with the modified process. Further study is needed to obtain more optimal results.

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