Improved natural gas storage with adsorbed natural gas technology (ANG) using activated carbon from pineapple crown

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Abstract. Natural gas considered as alternative fuel that still has the enough availability in Indonesia. One of the utilizations of natural gas is ANG technology which based on adsorption principle. The adsorption of natural gas occurs in isotherms condition at 27 °C, 31 °C, and 35 °C and using low pressure up to 9 bar. Activated carbon were used from bio-based carbon from pineapple crown with IOD number 1337 mg/g and surface area 1190.799 m2/g which compared to commercial activated carbon with iod number 1727 mg/g. Bio-based carbon were prepared through chemical and physical activation. This study begins with making preparation for the ANG (Adsorbed Natural Gas) technology will be used, degassing process, measuring the void volume, storage capacity, and delivery capacity. The maximum storage of pineapple crown activated carbon reached 0.0397 kg/kg at 9 bar 27°C with desorption efficiency of 43.82% and commercial activated carbon reached 0.0429 kg/kg at 9 bar and 27°C and desorption efficiency of 43.82%.

1. Introduction
Indonesia's energy consumption continues to increase every year in both industrial, household and transport sectors. The annual increase of 3.99% from 555.88 million BOE in 2000 to 961.39 million BOE in 2014. This need will continue to increase in line with Indonesia's growing population and the ever-increasing population the utilization of natural gas in Indonesia is still considered less when natural gas reserves in Indonesia reached 103.35 billion barrels. Based on data from BPPT in 2016, the role of gas will increase to 13.8% by 2050, while the fuel reserves in Indonesia by 2015 have decreased 1.2% both potential reserves and proven reserves. The production of natural gas in Indonesia is up to 68 billion m3 but the consume is only 38 billion m3 [1].

The problem of natural gas utilization for transportation is in natural gas storage methods. Commonly used methods are CNG and LNG, whereas ANG is a new method in Indonesia in saving natural gas by utilizing activated carbon as storage medium. The LNG method can increase the volumetric energy density (VED) up to 64% but the cost for vessel is so high so need higher production costs. The CNG technology also need high cost because it needs multi-stage compressors [2]. Natural gas can be stored in an adsorbed phase in a porous material, this option being an alternative to...
CNG problems. In the ANG system the gas is stored in low pressure (3.5 - 4 MPa) and at room temperature [3]. The natural gas capacity is stored more in the tank containing the adsorbent. This happens because the tank containing the adsorbent has a high density rather than the gas equilibrium contained in the tank. There is also an increase in the quality of the storage because the gas volume in the empty tube increases due to the additional volume of the adsorbent. By using ANG technology this stored gas does not require high pressure.

The use of AC as adsorbent is a popular topic which always be developed. Renewable materials such as palm shells [4], palm kernel [5], banana peel wastes [6] etc are widely used. Other biomass that can be used is pineapple crowns. Pineapple crown is lignocellulosic materials which contained high cellulose which is good for AC raw materials. So, to increase the capacity of natural gas storage, activated carbon from pineapple crowns waste from previous study was used. From the iodine test of activated carbon was found that the AC had 1337 mg/mg surface area. Furthermore, the aim was to determine the adsorption and desorption capability of the commercial and pineapple crown wastes-based AC.

2. Experimental Details

2.1 Natural gas composition
Natural gas which used in this study are bought from SPBU Pertamina in Jalan Raya Bogor, Depok, West Java. Characterization of natural gas using chromatography are shown in Table 1.

| Component | Composition (%) |
|-----------|-----------------|
| CH₄       | 87.76           |
| C₂H₆      | 4.70            |
| C₃H₈      | 3.78            |
| C₄H₁₀     | 2.26            |
| CO₂       | 1.28            |
| N₂        | 0.22            |

2.2 Measurement of volume void
A void volume measurement is performed to determine the amount of tank volume not filled by activated carbon including the volume present between active carbon pore. The tank whose empty volume is measured is the adsorption tank (Measuring Cell). The void volume can be calculated using equation 1 below.

\[ V_{\text{void}} = n_{mc} \times R \times z_{mc} \times T_{mc} \]

whereas:
- \( V_{\text{void}} \) = void volume (cm³)
- \( R \) = 0.0821 L.atm/Kmol
- \( T_{mc} \) = adsorption vessel temperature (K)
- \( n_{mc} \) = delta npv
- \( z_{mc} \) = compression factor

The process occurs in 30°C and 7 bar of helium. Helium gas supplied to charging vessel until desired pressure and isotherm condition (30°C), connected valve then open until adsorption vessel and charging vessel reach isotherm condition in 15 minutes. Data obtained during the process then calculated to obtain the value for void volume. The z value was obtained from REFPROP 8 software assuming the helium gas was pure.

2.3 Adsorption capacity test
This test is intended to determine the natural gas adsorption ability of AC made from pineapple crown waste. Adsorption capacity calculated with volumetric method. The basis for volumetric measurement is pressure, volume and temperature.

The methods for adsorption capacity test are: (1) turn on the exhaust fan, (2) Perform a Circulating
Thermal Bath (CTB) to raise and maintain the temperature of the vessel to be constant, (3) Flow a certain amount of natural gas into the filling tank according to the desired pressure, (4) Wait until the temperature of the charging cell is stable. Then take note the temperature and pressure in the charging cell, (5) Open the charging valve connecting and measuring cell until the desired pressure, (6) Wait 15 minutes for the pressure in both tubes to stabilize, then record the final conditions for the temperature and pressure in both tubes. After adsorption equilibrium is reached, the amount of adsorbate adsorbed is measured from the change in pressure using real gas equation. The equation is stated in Equation 2.

\[ \rho = m \times V \]  

whereas:  
\( \rho = \text{gas density (kg/m}^3) \)  
\( m = \text{gas mass (kg)} \)  
\( V = \text{volume occupied by gas (m}^3) \)  

The value of gas density was calculated using REFPROP software.

2.4 Desorption test.
The desorption capability of the AC was also tested in this study. This test used the AC with the best surface area from the results of chemical activation and chemical-physical activation. The steps for desorption tests are: (1) Open the charging cell discharge valve until there is no more gas in the tank, (2) Record the amount of gas which released from “Coriolis”, (3) Open the discharge valve of the measuring cell until the pressure drops to atmospheric pressure, (4) Note the amount of gas that comes out in "Coriolis".

3. Result and Discussion

3.1 Activated Carbon
Activated carbon from pineapple crown are compared with commercial activated carbon. Activated carbon from pineapple crown denoted as KN1 and commercial activated carbon denoted as K1. Both characteristic from KN1 and K1 are shown in Table 2.

| Table 2. Activated Carbon Characteristics |
|------------------------------------------|
| Activated Carbon | K1 | KN1 |
| Raw material | Coconut shell | Pineapple crown |
| IOD number (mg/g) | 1727 | 1337 |
| Particle size (mesh) | 325 | 120 |

3.2 Void Volume Measurement
Prior to measuring the capability of natural gas storage, it was carried out the first test of the void volume of the activated carbon. The void volume is the volume not occupied by activated carbon and the amount of volume between the sidelines of activated carbon. This test is carried out by supplied some helium gas to the adsorbent vessel (measuring cell).

| Table 3. Activated carbon characteristic |
|-----------------------------------------|
| Trial | Void volume (cm\(^3\)) | K1 | KN1 |
| 1 | 295.369 | 291.147 |
| 2 | 294.086 | 291.193 |
| 3 | 294.745 | 292.478 |
| Mean | 294.734 | 291.605 |

From the Table 3, we can see that the commercial carbon (K1) has higher void volume than KN1. This shows that the density of K1 AC is higher. Because the density is proportional to the void volume of AC. Another reason is because the K1 has slightly higher surface area than K1. These matters are related
to the storage ability of AC [7].

3.3 Adsorption test
Adsorption test was done with pressure variation 5 up to 9 bar and temperature 27 – 35°C with increment of 4°C. 3 g of activated carbon was used on this experiment. The first process was degassing. Degassing was done to remove the volatile and unwanted matters in activated carbon before used. The degassing process was done as the first step of every variable. The process of transferring natural gas from the charging cell to the measuring cell was left for 15 minutes, at this stage, the adsorption of natural gas occurred to activated carbon.

The data obtained is storage capacity in mass of gas per mass of activated carbon. The following graph shows amount of gas adsorbed to pressure for K1 and KN1.

From the figure 2 shows that the highest capacity is obtained under high pressure and low temperature operating conditions, for K1 maximum storage capacity was obtained at 0.0429 kg / kg and in KN1 maximum storage capacity is obtained at 0.0397 kg / kg. There are no much differences in storage capacity between two activated carbons. The pore structure and surface characteristics of activated carbon are depending on the material and methods used in activated carbon production which results the differences in each type of activated carbon [8].

In other study using PET-based AC, with temperature 27 °C and pressure of 35 bar obtained 0.0586 kg/kg of maximum storage capacity [9]. The capacity is higher than this study but using higher pressure. Another study using AC which prepared with potassium hydroxide as chemical activator and resulted AC with 3052 m²/g surface area. The CH₄ storage capacity was 0.32 g/g at 3.5 MPa pressure [10].

The increase in adsorption along with the increase in pressure is due to the collision of natural gas with activated carbon depending on the amount of pressure applied, the higher the pressure the more carbon will be pounded and absorbed by the activated carbon [7]. While the rise in temperature results in decreased absorption capacity, this is influenced by the isothermal temperature of the adsorption process. This happens because in the adsorption process, adsorbate that flowed into the surface will pound into the carbon surface and condensed on the porous surface. So that at the low temperature of the adsorbate that is more and more condensed and result in more natural gas adsorption [7].

This study proves that activated carbon made from pineapple crowns can compete with commercial activated carbon sold in the market and able to increase the economic value of pineapple crown waste.
3.4 Desorption test
The desorption capacity shows how much natural gas can be released from the adsorbent to be utilized. The desorption process was carried out at a pressure of 9 bar from the gas adsorption test. The value of this leverage has a low value compared to the value of storage capacity because not all-natural gas can be released from the adsorbent. Released gas in adsorbent vessel recorded in coriolisis Siemens© SITRANS F C MASSFLO MASS 6000. Output data in coriolisis are shown in gram gas. Comparison of release capacities of carbon types K1 and KN1 can be seen in Figures 4 and 5.

![Figure 2. Desorption capacity of K1](image1)

![Figure 3. Desorption capacity of KN1](image2)

The graph shows the efficiency value of activated carbon in desorption process. From the figure 2 and 3 could be seen that the rise of efficiency was proportional to the rise of circulating thermal bath temperature.

The percentage of natural gas release generally ranges between 15 - 30% of storage capacity [11]. Of the two types of AC K1 and KN1, both have a minimum release capacity of 40%. This proves that activated carbon made from coconut shells and pineapple crowns can store and release natural gas properly. The amount of natural gas left in activated carbon can be affected by the type of particle. The larger the particle size, the more natural gas will remain in carbon [12].

3.5 Temperature profile in ANG vessel
The adsorption and desorption processes are strongly influenced by heat transfer so that the temperature profile when the adsorption process needs to be known to determine the pattern of heat transfer that occurs.
The extreme temperature changes will cause the absorbed molecule difficult to attach on the surface of the activated carbon. In the adsorption process, there is the possibility of adsorbent adsorption which is then followed by heat release. The temperature profile of the activated carbon K1 and KN1 can be seen in Figure 5.

![Temperature profile](image)

**Figure 4.** Temperature profile

Based on Figure 4 there is an increase in the temperature of each increase in pressure. This is because when the gas molecule attaches to the surface of the activated carbon through the ANG tube, there is the release of some heat energy. This is an exothermic process followed by an increase in temperature [13]. The thermal effect is one of the hardest challenges in ANG technology. The gas delivery during discharge or desorption is influenced by heat transfer. This matter causes the amount of gas delivered decrease when the flowrate of discharge is high. Because of this, the efficiency of desorption will decrease too which mean there is a large amount of gas still trapped in AC [10]. But recent research mainly focusses on how to overcome this and many MOF with flexible structure has been developed [14].

### 4. Conclusion

The higher the temperature at the time of the adsorption process the lower the storage capacity and the higher the pressure on the adsorption process will increase the storage capacity. While in the desorption process the higher the temperature the efficiency of natural gas release will increase.

a. Coconut shell-based commercial activated carbon (K1) have the largest storage capacity at $27 \, ^\circ \text{C}$ and a 9 bars pressure of $0.0429 \, \text{kg/kg}$ and the highest release efficiency of $43.83\%$ at $35 \, ^\circ \text{C}$.

b. Pineapple crown-based activated carbon (KN1) has the largest storage capacity at $27 \, ^\circ \text{C}$ and a 9 bars pressure of $0.0397 \, \text{kg/kg}$ and the highest discharge efficiency of $43.82\%$ at $35 \, ^\circ \text{C}$.

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