Hydrogen Recovery from CH$_4$ – H$_2$ Gas Mixture by Adsorption Using Coconut Shell-Based Activated Carbon

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Abstract. In this study, attempts have been made to utilize biomass residue to recover hydrogen from CH$_4$ – H$_2$ gas mixture, which might be applied for hydrocracking process in oil refineries. Part of this attempt is to produce an activated carbon based on coconut shell, which is processed through chemical and physical activation using 25% ZnCl$_2$ followed by activation at 800°C with N$_2$ flow for an hour to increase its surface area. The resulted BET surface area and iodine number are 432.26 m$^2$/g and 644.80 mg/g, respectively. A detailed experimental study has been made for the adsorption of pure methane and hydrogen at 20°C, as well as CH$_4$ – H$_2$ mixture at 10, 20 and 30°C; each isotherm condition undergoes a variety of pressure ranging from 1 – 6 bars. Measurements were made using volumetric technique and gas chromatograph analysis. The highest adsorption is obtained for pure methane followed by CH$_4$ – H$_2$ mixture with 1:9 ratio and pure H$_2$. For gas mixture, the total adsorption increases with the increase of pressure in each isotherm; in which the higher temperature has lower adsorption ability. The adsorption result shows that methane has 2.7 times higher adsorption capacity than hydrogen and almost all methane in the mixtures is adsorbed by the activated carbon, therefore, the coconut shell based activated carbon produced from this research can be applied as the adsorbent in the separation process of CH$_4$/H$_2$ mixture.

Keywords: Hydrogen, methane, recovery, adsorption, activated carbon

1. Introduction

In recent years, various aims to increase efficiency are done in oil refineries in order to minimize the total cost of oil refining. One of the efforts is to minimize the hydrogen usage, as hydrogen is a major contributor to the high cost of oil refining process for both hydro treating and hydrocracking processes. This efficiency may be achieved through a recovery process, in which residual hydrogen from a unit is captured to be reused as the feed in the same unit. Various methods can be used to recycle hydrogen, but most of the prominent method is adsorption due to its low energy consumption and low operating cost.

Activated carbon is the most preferred type of adsorbent as it has advantages such as good resistance from humidity, high adsorption capacity at certain temperature and easy to regenerate [1]. The Indonesian potential of activated carbon market in the country exceeds 2000 ton per month, however approximately 500 ton of them needs to be imported, for most of the local made activated carbon does not meet the specified qualification for industrial grade used by oil refineries.

The objective of this study is to produce a biomass-based activated carbon that can be used to recover hydrogen from CH$_4$ – H$_2$ gas mixture, a gas mixture that is likely to be found in hydrocracking unit. In pursuit of that objective, we utilize coconut shell to produce activated carbon. The reasoning
behind coconut shell usage is its high carbon content and its abundance in nature. To increase the adsorption ability of activated carbon, chemical and physical activation is done. In this experiment, ZnCl$_2$ is chosen as the chemical activating agent, because of its lower cost compared to another activating agent, such as H$_3$PO$_4$ and KOH. Furthermore, ZnCl$_2$ can also act as a hydrating agent by adsorbing water that encloses the surface of activated carbon [2].

In this study we examine the adsorption ability of the coconut shell-based activated carbon for pure methane and hydrogen at 20$^\circ$C, as well as CH$_4$ – H$_2$ mixture at 10, 20 and 30$^\circ$C, with a variety of pressure ranging from 1-6 bar. The expected outcome of this study is to produce an alternate activated carbon for oil refinery industries that is more cost effective.

2. Methodology

Methods employed in this study consist of activated carbon preparation and characterization followed by adsorption measurements for pure methane and hydrogen at 20$^\circ$C, as well as CH$_4$ – H$_2$ mixture at 10, 20 and 30$^\circ$C, each with pressure variation ranging from 1-6 bar.

2.1. Carbon preparation and characterization

Crushed coconut shell is washed with water to dispel dirt, and then dried in an oven at the temperature of 110$^\circ$C for an hour to evaporate its water content. Next, this material is put into a furnace at 400$^\circ$C for an hour to produce a charcoal-like material. After that, this carbonized coconut shell is sieved to a particle of 100 meshes using magnetic stirrer at 85$^\circ$C for an hour. The slurry is then dried in the oven, followed by activating inside the reactor at 850$^\circ$C while flowed with N$_2$ at 100ml/minute for an hour. Sample is then cooled down to 30$^\circ$C and washed with distilled water until it reached a relatively neutral pH. Finally, this sample is dried in the oven.

Before used in the adsorption test, activated carbon is characterized to determine the surface area and iodine number of coconut shell-based activated carbon made in the previous step. BET method is used to measure the surface area using 0.3 gram of activated carbon samples, while iodine characterization is done to determine the iodine number, a characterization indicating the ability to adsorb an amount of iodine per gram of activated carbon (mg iodine/g activated carbon). 0.1 gram of sample is stirred and heated with 10 ml of iodine solution for 1 hour. After that, 5 ml of the mixed solution is titrated by Na$_2$SO$_3$. The volume of Na$_2$SO$_3$ used for titration is then inputted to iodine number calculation.

2.2. Adsorption Measurements and Modelling

The experimental apparatus for adsorption test is shown schematically in figure 1. The first step of adsorption measurement is to determine the void volume ($V_{void}$) of activated carbon, which is filled fully inside the sampling cylinder, by injecting a predetermined quantity of helium from a dozing cylinder with calibrated volume. This is done by opening valve 2 while closing valve 1 and valve 3 until the pressure in the dozing cylinder reached a certain pressure, when valve 2 is then closed. The equation is

$$V_{void} = n_{He} \left( \frac{Z_{He}RT}{P} \right)_{sampling}$$

where the amount of helium injected into sampling cylinder is

$$n_{inj} = \left( P_i \frac{1}{Z_{He,i}} - P_f \frac{1}{Z_{He,f}} \right) \frac{V_{dozing}}{RT}$$

$V_{dozing}$ is the volume of dozing cylinder, $P_i$ and $P_f$ represents initial and final pressure of dozing cylinder respectively, $R$ is universal gas constant and $Z$ is the compressibility factor. The measurement of void volume should be done several times to reduce the uncertainty of this value.

To measure the gas adsorption, a given quantity of gas, $n_{inj}$ is first injected into the sampling cylinder from dozing cylinder. This dozing cylinder is also used in making CH$_4$ – H$_2$ gas mixture. The amount of gas injected is determined by an equation analogous to equation (2), above. The condition of
the equilibrium is identified as the condition at which the pressure in the sampling cylinder is stabilized, or at around 30 minutes. The amount of unadsorbed gas, \( n_{\text{unads}} \), is calculated using the expression

\[
\frac{P(V_{\text{void}})}{Z_{\text{gas}}RT}_{\text{sampling}}
\]

where the pressure \( P \) was measured after equilibrium was reached in the sampling cylinder. The amount of adsorbed gas, \( n_{\text{ads}} \), is determined by difference as

\[
n_{\text{ads}} = n_{\text{inj}} - n_{\text{unads}}
\]

For gas mixture adsorption, the above equation is modified by adding the mole fraction of injected gas, giving the following equation

\[
n_{\text{ads}} = y_{i,\text{inj}} n_{\text{inj}} - y_{i,\text{unads}} n_{\text{unads}}
\]

The above steps are repeated for pure and gas mixture at three isotherms for a variety of pressure ranging from 1 – 6 bars to yield a complete adsorption isotherm.

\[
\text{Figure 1. Schematic diagram for adsorption measurement}
\]

The model used in this gas adsorption is based on Langmuir model. In order to determine the Langmuir model constant, the following expression is used

\[
n_{\text{model}} = n_{\text{max}} \frac{bP}{1 + bP}
\]

where \( n_{\text{model}} \) is the Gibbs adsorption model, \( n_{\text{max}} \) is the maximum adsorption capacity, \( b \) is Langmuir constant, and \( P \) is the pressure in sampling cylinder. The above expression is solved by guessing the value of \( b \) and \( n_{\text{max}} \). By using the value of \( n_{\text{model}} \) and \( n_{\text{ads}} \) from the experiment, %AAD (Absolute Average Deviation) is calculated in order to show any error on the experiment data.

\[
\%\text{AAD} = \frac{\sum |n_{\text{exp}} - n_{\text{model}}|}{n_{\text{exp}}} \times 100
\]

N in equation (7) is the number of points in one isotherm. Utilizing the solver feature on Microsoft Excel, the number of %AAD is minimized by changing the value of \( b \) and \( n_{\text{max}} \), giving the close values of Gibbs adsorption mole from the model and experiment.
3. Results and Discussion

3.1. Carbon preparation and characterization

The yield of activated carbon is calculated based on the mass of the activated carbon sample before and after entering the activating reactor. Coconut shell-based activated carbon produced in this study results the yield of 37.21%. Similar study by Mozammel at lower temperature shows higher yield, which justifies his claim that higher temperature leads to lower yield of product, as the carbonization that takes place at high temperature would produce more volatile matter that would escape easier [3]. However, the high temperature used in this experiment is needed to produce activated carbon with higher adsorption capability, characterized by its BET surface area and iodine number.

Results for surface area characterization of activated carbon sample using ZnCl$_2$ as chemical agent for activation shows that the BET surface area and iodine number of 432.26 m$^2$/g and 644.80 mg/g, respectively. This study shows better result compared to similar experiment in our previous works conducted at lower temperature, which resulted in the BET surface area of 300 m$^2$/g and 247 m$^2$/g respectively. Higher temperature of carbonization increases the surface area, this is because increase in temperature increases distillation of tar from the carbon thereby releasing more micro pores in the resultant product [4]. Another study using palm oil shell shows lower iodine number, 508 mg/g. This is due to the higher carbon content of coconut shell than those of palm shell.

3.2. Adsorption Measurements and Modeling

After injecting helium into the sampling cylinder for six times, the void volume of activated carbon is calculated to be 3.96 ml. Figure 2 shows the isotherm adsorption result at 20ºC for pure methane, hydrogen and CH$_4$ - H$_2$ mixture with 10% CH$_4$. The adsorption of pure CH$_4$ is the highest among the three, around 1.7 and 2.7 times higher than CH$_4$ - H$_2$ mixture and pure hydrogen, respectively. The detailed adsorption data is shown in table 1 and table 2.

![Figure 2. Adsorption of pure CH$_4$, pure H$_2$ and CH$_4$ - H$_2$ mixture at 20ºC](image)

| Pressure [Bar] | Gibbs Ads [mmol/g] | Pressure [Bar] | Gibbs Ads [mmol/g] |
|---------------|---------------------|---------------|---------------------|
| 0.795         | 0.049               | 0.987         | 0.033               |
| 1.661         | 0.109               | 2.158         | 0.061               |
| 2.774         | 0.186               | 3.016         | 0.100               |
| 3.951         | 0.257               | 3.992         | 0.134               |
| 4.832         | 0.403               | 5.112         | 0.156               |
| 5.928         | 0.476               | 5.819         | 0.175               |

Table 1. Adsorption of pure gas at 20ºC
Table 2. Adsorption of CH\(_4\)-H\(_2\) mixture at various isothermal conditions

| Pressure [Bar] | Gibbs Ads [mmol/g] | Pressure [Bar] | Gibbs Ads [mmol/g] | Pressure [Bar] | Gibbs Ads [mmol/g] |
|----------------|--------------------|----------------|--------------------|----------------|--------------------|
| 0.810          | 0.062              | 0.934          | 0.034              | 0.873          | 0.007              |
| 2.030          | 0.114              | 2.026          | 0.066              | 1.827          | 0.016              |
| 2.831          | 0.143              | 2.885          | 0.114              | 2.911          | 0.025              |
| 3.920          | 0.196              | 3.410          | 0.154              | 4.079          | 0.035              |
| 4.569          | 0.274              | 5.397          | 0.220              | 4.816          | 0.040              |
| 5.788          | 0.373              | 5.823          | 0.269              | 6.087          | 0.046              |

The reason why methane is easier to be adsorbed in the pores of activated carbon (approximately 16 Å) compared to hydrogen is because the molecular size of methane is bigger than hydrogen (3.8 Å and 2.8 Å, respectively). In these pores, hydrogen molecules are not attached on the surface and tend to stay in a bulk phase and thus only a small amount of hydrogen molecules are adsorbed [5].

Figure 3 represents the result of CH\(_4\)-H\(_2\) adsorption with 10% CH\(_4\) at different isothermal condition. The result shows that at an isothermal condition, highest adsorption is obtained at highest pressure of 6 bars. It could happen because the increase of pressure will increase the amount of molecular gas that is diffused to the surface then trapped in adsorbent pores to interact with carbon atom. Hence, the amount of gas adsorbed in the activated carbon will be higher [5,6].

At a constant pressure, higher adsorption obtained at a lower isothermal condition. This is consistent with Le Chatelier principle that stated at lower temperature, for exothermic process, decreasing temperature will increase the mole of gas adsorbed. From table 2, it could be seen that the maximum adsorption for mixture of CH\(_4\)-H\(_2\) mixture is 0.373 mmol/g at 10°C and 6 bar, which is 1.4 times higher than adsorption at 20°C and 8 times higher than adsorption at 30°C at the same pressure.

In general, all methane injected is adsorbed by the activated carbon. However, based on a chromatograph analysis, a small amount of methane can be found in the unadsorbed gas at certain condition. The detailed amount of methane found is shown in table 3. As shown in the table, at 5 and 6 bar, a small amount of methane is not adsorbed by the activated carbon. Higher pressure resulted in more unadsorbed methane, because at higher pressure the number of molecules increased. This addition of molecules causes a competition for methane molecules to be adsorbed on the surface of activated carbon, so that the unadsorbed methane is released in bulk phase.
Table 3. Unadsorbed CH$_4$ at various isothermal conditions

| Temp. [°C] | Unadsorbed CH$_4$ [%] At 5 bar | Unadsorbed CH$_4$ [%] At 6 bar |
|------------|--------------------------------|--------------------------------|
| 10         | 0.62                           | 1.21                           |
| 20         | 0.87                           | 1.27                           |
| 30         | 1.04                           | 2.17                           |

Figure 4 shows the comparison of adsorption between two different types of activated carbon: coconut shell and palm shell based activated carbon. Overall, it can be observed that coconut shell based activated carbon has higher adsorption capacity than the one made of palm shell. An especially big gap can be seen from the adsorption of pure methane, in which coconut shell based activated carbon is 2.1 times higher than of palm shell, whereas for pure hydrogen, the difference is only 1.4 times. This comparison can explain the selectivity of activated carbon. Coconut shell-based activated carbon is proved to have a higher selectivity than that of palm shell, which makes it a very potential material for CH$_4$ – H$_2$ separation process.

Figure 4. Adsorption Comparison with Other Activated Carbon

Isotherm adsorption for pure gas and CH$_4$ – H$_2$ mixture on figure 2 and figure 3 fits the Langmuir isotherm model that described physical interaction between adsorbate and adsorbent molecules. The experimental data as well as all model parameters are well represented by the model with AAD as shown in table 4. The $b$ parameter in Langmuir model, as expressed in equation (6), is a Langmuir constant that describes how strong gas molecules adsorbed to the surface. It relates with $Q$ that describes the enthalpy if adsorption or energy of adsorption. The equation for $b$ can be expressed as follows

$$
b = \left( \frac{\alpha}{k_d \sqrt{2\pi m k T}} \right) \exp \left( \frac{Q}{RT} \right) \tag{8}$$

where $\alpha$, $k_d$ and $m$ are constants. It could be seen in table 3 that the amount of $b$ increases by decreasing temperature and thus consistent with equation (8). The value of $n_{max}$ is also higher at lower isothermal condition. This value is related to the surface area of the adsorbent and the surface density of the adsorbate. Surface density of the adsorbate is higher at lower temperature [7].

Table 4. Langmuir Isotherm Model Parameter

| Temp. | $n_{max}$ | $b \times 10^3$ | %AAD  |
|-------|-----------|----------------|-------|
| 10    | 5.099     | 11.2           | 11.8  |
| 20    | 4.553     | 8.89           | 11.5  |
| 30    | 1.199     | 7.24           | 5.0   |
4. Conclusion
Activated carbon has been successfully created from coconut shell which has the BET surface area of 432 m²/g. The adsorption result shows that methane has 2.7 times higher adsorption capacity than hydrogen and almost all methane in the mixtures is adsorbed by the activated carbon. Therefore, the coconut shell based activated carbon produced from this research can be applied as the adsorbent in the separation process of CH₄/H₂ mixture.

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6. References
[1] Plaza M, Pevida C, Pis J, and Rubiera F 2011 Evaluation of the cyclic capacity of low-cost carbon adsorbents for post-combustion CO₂ capture. Energy Procedia 4 1228-1234
[2] Allwar A B and Nawi M 2008 Textural characteristics of activated carbon prepared from oil palm shells activated with ZnCl₂ and pyrolysis under nitrogen and carbon dioxide Journal of Physical Science 93-104
[3] Mozammel H M, Masahiro O, and Bhattacharya S 2007 Activated charcoal from coconut shell using ZnCl₂ activation Biomass and Bioenergy 22 397-400
[4] Joshi R.R 2015 Optimization of conditions for the preparation of activated carbon from lapsi (choerospandias axillaris) seed stone using ZnCl₂ Journal of Institute of Engineering 11(1) 128-139
[5] Sudibandriyo M 2011 High pressure adsorption of methane and hydrogen at 25°C on ativated carbons prepared from coal and coconut shell. International Journal of Engineering and Technology 11 (2) 79-85
[6] Sudibandriyo M, Wulan PDK, Prasodjo P 2015, Adsorption capacity and its dynamic behavior of the hydrogen storage on carbon nanotube, International Journal of Technology 6 (7) 1128-1136
[7] Sudibandriyo M, Mohammad S A, Robinson R L Jr, Gasem K AM 2011 Ono–Kondo model for high-pressure mixed-gas adsorption on activated carbons and coals”, Energy & Fuels 25 (7) 3355–3367