PAPER • OPEN ACCESS

Preparation of activated carbon from waste plastics polyethylene terephthalate as adsorbent in natural gas storage

To cite this article: Yuliusman *et al* 2017 *IOP Conf. Ser.: Mater. Sci. Eng.* **176** 012055

Preparation of activated carbon from waste plastics polyethylene terephthalate as adsorbent in natural gas storage

Yuliusman[1], Nasruddin[2], A Sanal[1], A Bernama[1], F Haris[1], I T Ramadhan[1]
[1]Chemical Engineering Department, University of Indonesia, Kampus Baru UI Depok, Indonesia
[2]Mechanical Engineering Department, University of Indonesia, Kampus Baru UI Depok, Indonesia

E-mail: usman@che.ui.ac.id; yuliusman@yahoo.com

Abstract. The main problem is the process of natural gas storage and distribution, because in normal conditions of natural gas in the gas phase causes the storage capacity be small and efficient to use. The technology is commonly used Compressed Natural Gas (CNG) and Liquefied Natural Gas (LNG). The weakness of this technology safety level is low because the requirement for high-pressure CNG (250 bar) and LNG requires a low temperature (-161°C). It takes innovation in the storage of natural gas using the technology ANG (Adsorbed Natural Gas) with activated carbon as an adsorbent, causing natural gas can be stored in a low pressure of about 34.5. In this research, preparation of activated carbon using waste plastic polyethylene terephthalate (PET). PET plastic waste is a good raw material for making activated carbon because of its availability and the price is a lot cheaper. Besides plastic PET has the appropriate characteristics as activated carbon raw material required for the storage of natural gas because the material is hard and has a high carbon content of about 62.5% wt. The process of making activated carbon done is carbonized at a temperature of 400 ° C and physical activation using CO_2 gas at a temperature of 975 ° C. The parameters varied in the activation process is the flow rate of carbon dioxide and activation time. The results obtained in the carbonization process yield of 21.47%, while the yield on the activation process by 62%. At the optimum process conditions, the CO_2 flow rate of 200 ml/min and the activation time of 240 minutes, the value % burn off amounted to 86.69% and a surface area of 1591.72 m^2/g.

1. Introduction

Natural gas has the potential of reducing the gasoline consumption of Indonesia due to Indonesia's high reserve amounting to 103.3 trillion cubic feet.One of the problems in the use of natural gas is in the process of storage and distribution, because in normal conditions (pressure 1 atm) natural gas is in its gas phase so the storage capacity will be small henceinefficient to use. Currently, the technology that is generally used is Compressed Natural Gas (CNG) and Liquefied Natural Gas (LNG). However, because CNG requires a high pressure of 250 bar and LNG requires a low temperature (-161°C), it become harmful in their uses. Adsorbed Natural Gas(ANG) technology uses activated carbon as an adsorbent, causing natural gas to be able to be stored at low pressure of about 34.47 bar with large storage capacity [6].

Activated carbon in ANG is made from plastic waste PET (polyethylene terephthalate) due to its abundant availability in Indonesia. The amount of plastic waste PET in Indonesia reached 26,500 tons

per day, as stated by the Ministry of Environment of Indonesia. Aside from that, activated carbon made from PET has the greatest surface area compared to activated carbon from waste PVC (polyvinyl chloride) and tires [3]. This study, therefore, aims to make activated carbon from plastic waste PET by physical activation using a variation of the flow rate of CO_2 and to obtain the optimal activation time in terms of creating activated carbon with high surface area.

2. Experimental

2.1. Activated Carbon Preparation

PET plastic waste is cleaned of impurities and then dried. PET plastic waste is crushed and screened to obtain the size of about 1-3 mm. This study has fixed parameters such as temperature and carbonation time, activation temperature and the rate of N_2 gas. After tools and materials preparation then we do the carbonization process to increase the carbon content of the PET plastic waste by releasing flammable substances such as CO_2, CH_4, H_2. Carbonization is carried out at 400^oC with the gradual heating rate of 10 ° C / min, for 240 minutes. Then, the experiment proceeded with physical activation using CO_2 gas, at a temperature of 975^oC for 60 minutes.

2.2. Characterization of Activated Carbon

Characterization of activated carbon was ensued by iodine number method with the concept of measuring the strength of adsorption of activated carbon in a solution of iodine. Iodine that is not absorbed in the activated carbon will be titrated using Sodium Thiosulphate ($Na_2S_2O_3$) until the solution becomes a pale-yellow color, then the solution is provided with an indicator which will change the color back to black and redo the titration process until the color becomes transparent. The less Sodium Thiosulphate is used, the greater the power of activated carbon adsorption. The equation for calculating the iodine number is as follows.

$$Adsorbed\ Iodine, \frac{mg}{g} = \frac{10 - \frac{V1 x N}{0.1}}{W} \times 12.69 \times \frac{V2}{10} \qquad (1)$$

where
V1	Use of sodium thiosulphate (ml)
V2	Volume of Iodine Solution (ml)
N	Normality of sodium thiosulphate
12,69	The amount of Iodine needed for a 1 mL sodium thiosulphate 0.1 N
W	Sample weight (gram)

To change the iodine number into surface area a linear regression equation is used that refers to ASTM D-4607-94. The equation is as follows

$$Iod\ Number = 0.6366\ x\ surface\ area + 174.34 \qquad (2)$$

In addition to iodine number, this study also used the characterization of SEM + EDX to see the morphology and composition of activated carbon.

3. Results and Discussion

3.1. Activated Carbon Preparation

3.1.1. Carbonization Process

Carbonization process aims to vaporize the compounds that are volatile which will create pores due to the loss of such compounds. Volatile compounds which are in PET plastic can be decomposed at a temperature of 480^oC comprising of water content that evaporates on 100^0C- 150^0C. Terephthalic Acid

(TPA) contained from PET are sublimate so that the TPA molecule will form CO_2, CO, and CH_4 gases [5]. This carbonization process lasted for 210 minutes that resulted in a smoke cloud. This happens because many volatile substances contained in plastic PET evaporated during carbonization. The results of the carbonization process produce % gain on average by 21.47%. These results correspond to the value that is a 17.4% fixed carbon value. This result is said to be good enough for the carbonization process because it can be said that almost all volatile compounds in PET has been lost.

3.1.2. Physical Activation Process

Activated carbon activation process is aimed at the formation of the macro pore structure and microporous activated carbon. In this study, physical activation is done by using carbon dioxide gas (CO_2), which will open the pores in activated carbon. Carbon dioxide gas serves as the activating gas where the gas will react with carbon so as to open the pores which will increase surface area. Aside from that, carbon dioxide gas also acts to prevent the entry of oxygen gas into the activator. A decrease in activated carbon formation can be viewed along with increased gas flow rate; it is in line with the principle of Le Chatelier's where an additional amount of reactant, in this case CO_2, will add to the result of the product and the bigger the amount of gas that reacts with carbon, the bigger the number of pores that will form. After getting a flow rate that produces the largest surface area, the activation process was repeated with variations of activation time using the optimal flow rate that has been obtained previously. It can be seen in Table 1, bigger reduction in the mass of activated carbon corresponds with increased activation time. This indicates that there had been a reaction and the formation of pores in activated carbon. However, the reduction of the resulting mass is less than the reduction in the process of CO_2 gas flow rate variation. This indicates that the reaction and the formation of pores in activated carbon are already approaching their optimum conditions.

Table 1. Impact of time to process yield

Variable	Mass (g)		
Activation Time (minute)	Carbon (g)	Activation Carbon (g)	%Yield
120	10	6.46	64.6
150	10	6.2	62
240	10	6.2	62

3.2. Characterization of Activated Carbon

3.2.1. Burn Off

Burn Off is the value derived from the reduction of the initial mass of raw material to the final mass of activated carbon. Burn off value can be assumed as the formation of pore (volume) in the activated carbon. Calculation of burn off was done by using the following equation.

$$burnoff = \frac{initialmass - finalmass}{initialmass} x\ 100\%$$
(3)

The burn off value is in accordance with the number of volatile matter and ash content residing on PET plastic waste with a slight reduction due to small particles of activated carbon that got swept by the flowing gas. The resulting calculation implies that the value of % burn off at the optimum operating conditions, namely the CO_2 flow rate of 200 ml/min and the activation time of 240 minutes, is 86.69%; this corresponds to the amount of volatile matter content and ash from plastic waste PET which is 82.6 % and less than 0.1% [4]. Data from the burn off process: the initial mass of raw materials and the mass of active carbon after activation can be seen in the following table.

Table 2. Impact of time and gas flow rate of CO_2 to process' yield

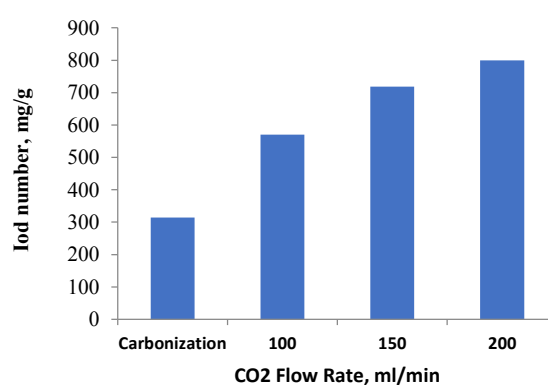| Gas Flow Rate (ml/minute)	Activation Time (minute)	Raw Material (g)	Activated Carbon (g)	% Yield
100	60	46,57	7,04	15,12
150	60	46,57	6,9	14,82
200	60	46,57	6,37	13,68
200	120	46,57	6,46	13,87
200	180	46,57	6,2	13,31
200	240	46,57	6,2	13,31

3.2.2. Iodine Number Testing
The surface area of activated carbon as an adsorbent is one of the most important parameter. Activated carbon adsorbent can be regarded as a good adsorbent if it has a high surface area. This is because the surface area of the adsorbent is one of the main factors affecting the adsorption process. For the measurement of the surface area of the activated carbon samples, iodine number method and BET method was used. Iodine number testing aims to determine the surface area of activated carbon through absorption of activated carbon to the solution of iodine. The values of iodine number obtained equates to the milligrams of iodine absorption capability per unit gram of activated carbon (mg/g). Iodine number obtained can be converted into the surface area using Equation 2.

Based on the graph in Figure 1, the surface area after physical activation is higher compared with the results of carbonization. The increase in surface area between the results obtained using physical activation with the results of carbonization with optimal flow rate of 200 ml/min is 799.7 mg/g so that it can be concluded that physical activation can magnify the width of the pores so as to increase the surface area. In regards to the variation of flow rate of CO_2, an increase in surface area corresponded from the increase of flow rate of CO_2 that indicates the high amount of CO_2 that reacted and opened the pores. The optimum flow rate is the flow rate with the highest surface area that is at a flow rate of 200 ml/min.
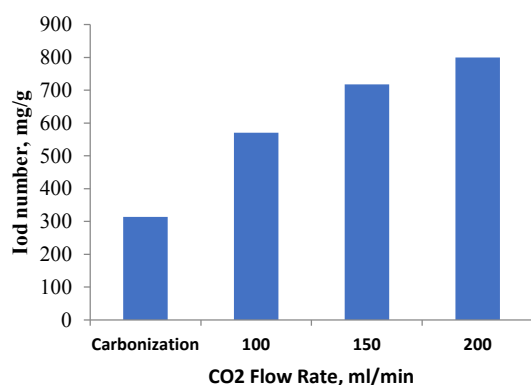
|	
Figure 1. Effect of gas flow rate of CO_2 to surface area	**Figure 2.** Surface area in different activation time

Based on Figure 2, an increase of activation time corresponding to an increase of surface area proves that the formation of pores still happens up to the highest increase of activation time. A comparison of the activation time of 120 minutes with activation time of 60 minutes' shows that there's a significant increase in surface area. In contrast, there is no significant increase of surface area if a comparison was to be made between 180 minutes of activation time with 240 minutes of activation times; this signals

that the activation time is nearing its optimum value hence it is concluded that the optimum value of activation time to create activated carbon with the highest surface area is 240 minutes. From the results, it can be seen that the optimal value of operating conditions in terms of creating activated carbon with the main parameter of surface area is at temperature of 975°C, carbon dioxide gas flow rate of 200 ml/min, and activation time of 240 minutes that created a surface area of 1591,72 m^2/g.

3.2.3. SEM (Scanning Electron Microscopy) Characterization

SEM characterization of the activated carbon aims to look at the structural morphology of activated carbon as well as see the pores formed in the activated carbon. Characterization is done on carbon and carbonization results from the variation of the activation time to see the difference between the results of carbonization and physical activation. The results of the characterization of the samples can be seen in Figure 3a, 3b, 3c and 3d, with the magnification of FE-SEM is 5000 X.
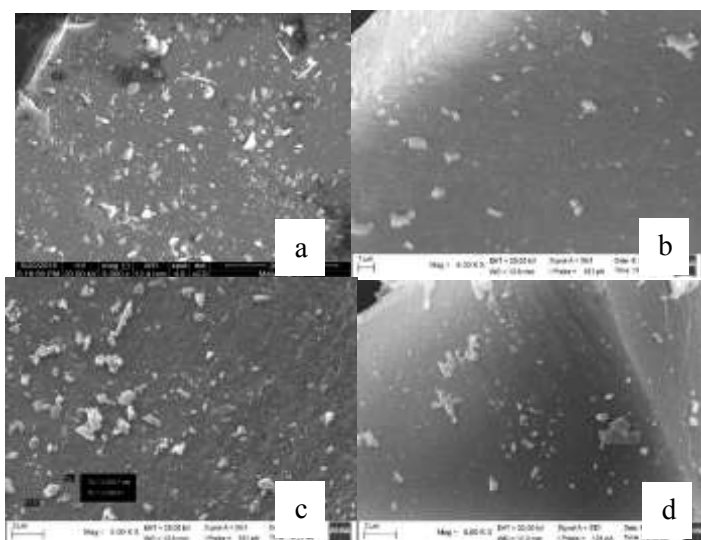
Figure 3. FE-SEM characterization results of; (a) carbonization result, (b) 120 minutes activation time, (c) 180 minutes activation time, (d) 240 minutes activation time

It can be seen in the results of FE-SEM characterization of the activated carbon samples that they do not show a lot of macro pores and are dominated by micro pores. This is due to the physical activation done using CO_2 gas in which the CO_2 gas maintained the condition of activated carbon by making it avoid O_2 gas that can cause burning and turn the activated charcoal into ash. CO_2 also reacts with carbon to form pores in activated carbon and increase the surface area of the activated carbon.

It can be seen that on activated carbon with an activation time of 120 minutes there's little to no impurities that can be seen on the carbon from carbonization which proves that the sample has reacted with CO_2 and open up the pores on the sample and also the higher heat in the activation process aids in removing impurities that are still trapped in the carbon sample. This happens because at a higher temperature, combustion process occurs better than at low temperatures. In the activated carbon with an activation time of 180 minutes and 240 minutes, it can be seen that there is a change on the surface of activated carbon in the sense of how it is more rugged than the activated carbon with a time of 120 minutes. This indicates that it has formed pores in activated carbon.

3.2.4. EDX (Energy-Dispersive X-Ray Spectroscopy) Characterization

EDX characterization aims to determine the composition of activated carbon made in this study. Figure 4 shows that the resulting activated carbon holds elements other than carbon such as oxygen, sulfur, iron, and copper. The carbon content of raw materials is 63% whereas the activated carbon with optimal activation time reached 83.2%, which means an increase of 20.2%. This indicates that the

volatile matter has been greatly reduced, causing the formation of pores that provide increased surface area on the activated carbon.
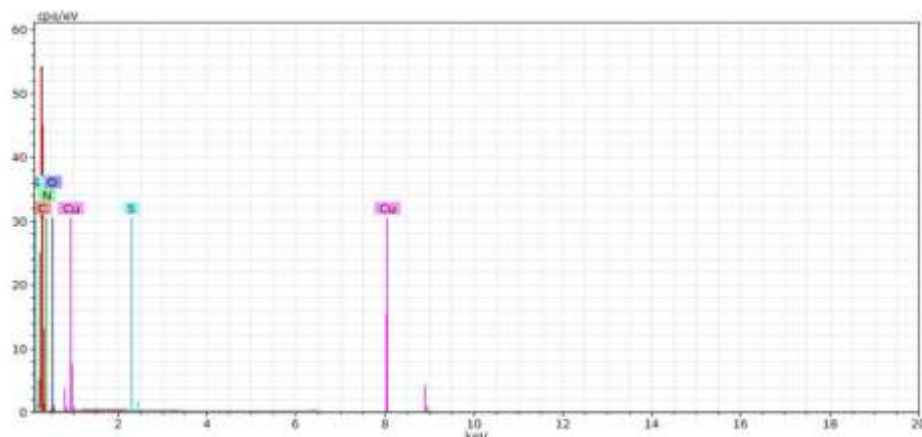
Figure 4. EDAX result of activated carbon with 240 minutes activation time

The physical activation treatment with CO_2 can significantly increase the carbon composition, which is about 7.4% when compared with activated carbon with the activation time of 240 minutes. This indicates that the reaction between carbon dioxide and carbon opened the pores on the sample. It can be seen in the results of EDX characterization which found that the carbon content in the activated carbon that is made has a corresponding value where, according to Duong (2008), the elements contained in the activated carbon equal to 85-95% of carbon and other elements are hydrogen, nitrogen, sulfur and oxygen. The iron contained in the activated carbon is a result of the physical activation container tube peeling off and going into the activated carbon, while the copper contained in the activated carbon is caused by the EDX testing sample container containing copper.

4. Conclusion

It can be concluded from the study entitled Preparation of Activated Carbon from Waste Plastics Polyethylene Terephthalate as Adsorbent Natural Gas Storage that:

The carbonization process obtained a yield of 21.47% and the physical activation process obtained a yield of 62%. Overall yield of 13.3% was obtained.Increasing the flow rate of CO_2 can increase the surface area of activated carbon produced. The optimum flow rate of CO_2 obtained at 200 ml/min.

Increasing activation time can increase the surface area of activated carbon produced. The maximum activation time is 240 minutes.The highest surface area was obtained when the gas flow rate of $CO_2$is 200 ml/min and activation time is 240 minutes, which is1591,72 m^2/g.Aside from carbon, other elements that resided within the activated carbon is oxygen, iron, and copper.

References

[1] Do D D 1998 *Adsorption Analysis: Equilibria and Kinetics* (London: Imperial College Press)

[2] Esfandiari A, Kaghazchi T and Soleimani M 2012 *J. Taiwan. Inst. Che. Eng.* **43** 631–637

[3] Lian F, Xing B and Zhu L 2011 *J. Colloid. Interface. Sci.***360** 725–730

[4] Melendi-Espina S, Alvarez R, Diez M A and Casal M D 2015 *Fuel. Proces. Technol.* **13** 351-358

[5] Rachmawati Q and Herumurti W 2015 *Jurnal. Teknik.ITS.***4**

[6] Samid D D 2011 *Optimasi Karakteristik Karbon Aktif Pada Sistem Adsorbed Natural Gas Dalam Kondisi Dinamis* (Depok, West Java: Universitas Indonesia)

[7] Yuliusman, Widodo W P, Yulianto S N and Rany A 2014 *The 9th Joint Conf. Che.* 130-134

[8] Yuliusman, Widodo W P, Yulianto S N 2015 *Int. J. Technol.* **6** 492-503