

CHAPTER IV RESULTS AND DISCUSSION

4.1 Effect of ozone treatment on activated carbon surface

Depending on the nature of activated carbon when immerse with water, two type of activated carbon can be resulted, H-type and L-type (Mattson and Mark, 1971, Hassler, 1974, Corapcioglu and Huang, 1987, and Bansal *et al.*, 1990).

The L-type activated carbon results from activation the carbons at low temperatures in air. The L-type behavior is expected to intensify after long exposure to the atmosphere even at ambient temperatures. These carbons are hydrophilic and take up a negative charge (OH^- ion) when immerse with water thus making water acid. On the other hands H-type carbons are hydrophobic and take positive charge when immerse with water.

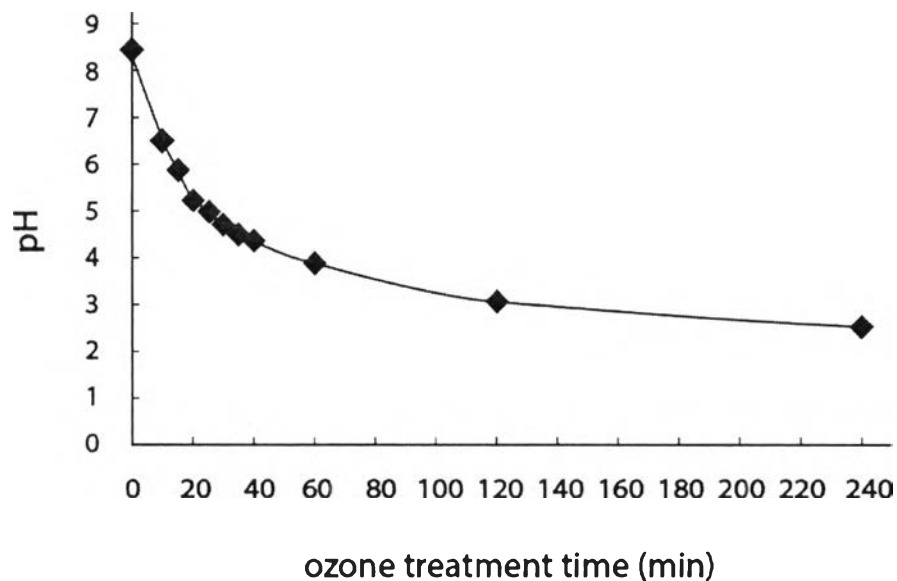


Figure 4.1 Relation between pH of activated carbon in water and ozone treatment time (min).

Figure 4.1 illustrates summaries relation between pH of activated carbon in water and ozone treatment time (min). It represented that all treated activated carbons

cause lower water pH when immersed. OH^- negative charge is absorbed by those treated carbons and these lower the pH of water. This suggests that oxidized activated carbons in this study are L-type activated carbon. This type of activated carbon can result have surface function groups which are carboxyl, carbonyl, carboxylic acid, anhydride, lactone, cyclic peroxide groups (Corapcioglu and Huang, 1987).

Furthermore, Figure 4.1 also shows variation in pH with an increase in ozone treatment time. In the first 20 min, the pH with an initial value of 8.4 rapidly decreases to 6, and slowly decreases to 2.5 at 240 min of ozonation. These results indicate that functional groups on activated carbon absorb OH^- negative charge on its surface and later leave positive charge in water. More acidity prominently appears on activated carbon with higher ozone treatment times which also mean that more functional groups were created at the surface of carbon as the time of ozonation lengthens. The negative species is confirmed through FTIR result in the next section.

4.2 Characterization of adsorbents

4.2.1 FTIR spectroscopy

FTIR spectroscopy is utilized to investigate the functional group on the surface of activated carbon.

Figure 4.2 shows the result from FTIR of non-treated and treated activated carbons

FT-IR results suggest the functional groups on activated carbons. The signal are as following, for carboxylic OH stretching $3400\text{-}2400\text{ cm}^{-1}$, C=O stretching $1710\text{-}1680\text{ cm}^{-1}$, C=C aromatic $1700\text{-}1500\text{ cm}^{-1}$, anhydride C=O stretching around 1820 and 1760 cm^{-1} , C \equiv C stretching at 2260 cm^{-1} . The spectra of ozonized samples can be analyzed in terms of functional groups as indicated above. The spectra suggest that the ozonation introduces functional groups on the surface area of carbon such as carboxylic and anhydride group. This FT-IR results also confirm that activated carbons are the L-type activated carbon with the carboxylic acid, anhydride functional groups (Corapcioglu and Huang, 1987). These functional groups are

clearly appeared as the time of ozonation lengthens corresponding to result in previous section.

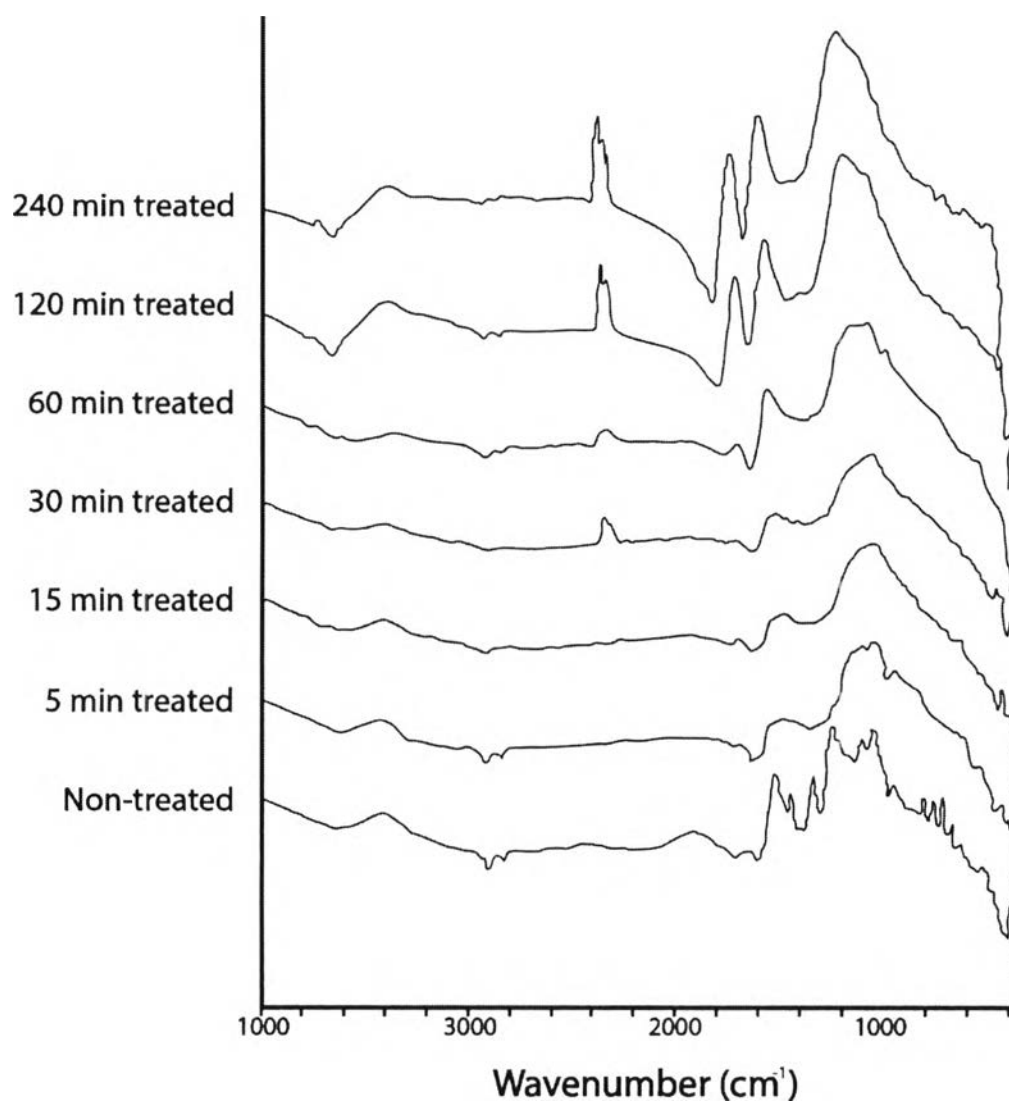


Figure 4.2 FTIR results of non-treated and treated activated carbons.

BET surface area analysis

The BET surface area (S_{BET}), micropore volume (V_{DR} , using DUBININ-RADUSHKEVICH or DR method), total pore volume, and average pore diameter were obtained by BET surface analyzer. The results are shown in Table 4.1.

Table 4.1 Physical BET surface properties of studied activated carbons

| Time of ozone treatment (min) | BET surface area (m ² /g) | V _{DR} (cc/g) | Total pore volume (cc/g) | Average pore diameter (Å) |
|-------------------------------|--------------------------------------|------------------------|--------------------------|---------------------------|
| 0 | 838 | 0.482 | 0.57 | 14.4 |
| 5 | 1042 | 0.597 | 0.72 | 14.6 |
| 10 | 1076 | 0.617 | 0.75 | 14.8 |
| 15 | 1080 | 0.620 | 0.75 | 14.8 |
| 20 | 1102 | 0.631 | 0.77 | 14.8 |
| 25 | 1130 | 0.640 | 0.77 | 14.8 |
| 30 | 1114 | 0.640 | 0.77 | 14.8 |
| 35 | 988 | 0.562 | 0.68 | 14.8 |
| 40 | 965 | 0.556 | 0.64 | 14.8 |
| 45 | 959 | 0.552 | 0.63 | 14.8 |
| 60 | 737 | 0.424 | 0.51 | 15.0 |
| 120 | 690 | 0.399 | 0.49 | 15.2 |
| 240 | 660 | 0.359 | 0.48 | 15.8 |

Figures 4.3 show that ozone treatment affects the physical properties of activated carbon. The BET surface area micropore volume total pore volume and the average pore diameter are changed with the ozone treatment time.

The untreated activated carbon has surface area 838 m² per gram. After treating with ozone for 5 min surface area is increased to 1042 m² per gram and continually increases with ozone treatment time, and reach the highest value 1130 m² per gram of activated carbon at 25 min of ozone treatment. The increasing of surface area is affected by the reaction between ozone and activated carbon surface.

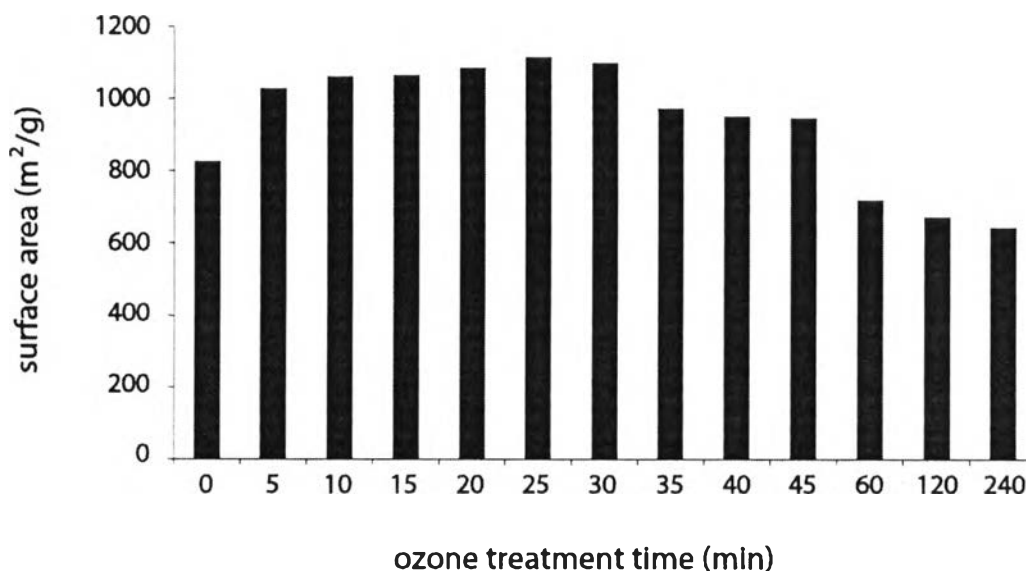


Figure 4.3 BET surface area (m²/g) of activated carbon as a function of ozone treatment time.

Oxygen complexes, formed by the reaction, later primarily desorb as CO₂ and CO (Kingsly and Davidson, 2006). The desorbed CO₂ possibly comes from the decomposition of carboxylic and CO is possibly from the decomposition of carbonyl, anhydride groups corresponding to functional group that found in L-type activated carbon. These gases later leave the surface and form new micropores which generally increased the specific surface area. Moreover, treated activated carbon with ozone gas is an exothermic process, therefore the reaction temperature is increased and the ozone reaction rate is accelerated similar to activation by CO₂ for activated carbon after carbonization processes. (You *et al.*, 1994). After 25 to 240 min of ozone treatment time surface area of activated carbon decreases from 1,130 to 660 m² per gram. The formation of oxygen functional groups increases as the time of exposure lengthens. These may obstruct gas to access pores at the entrance of the micropore (Valde's *et al.*, 2002). With these phenomena, specific surface area slightly decreases.

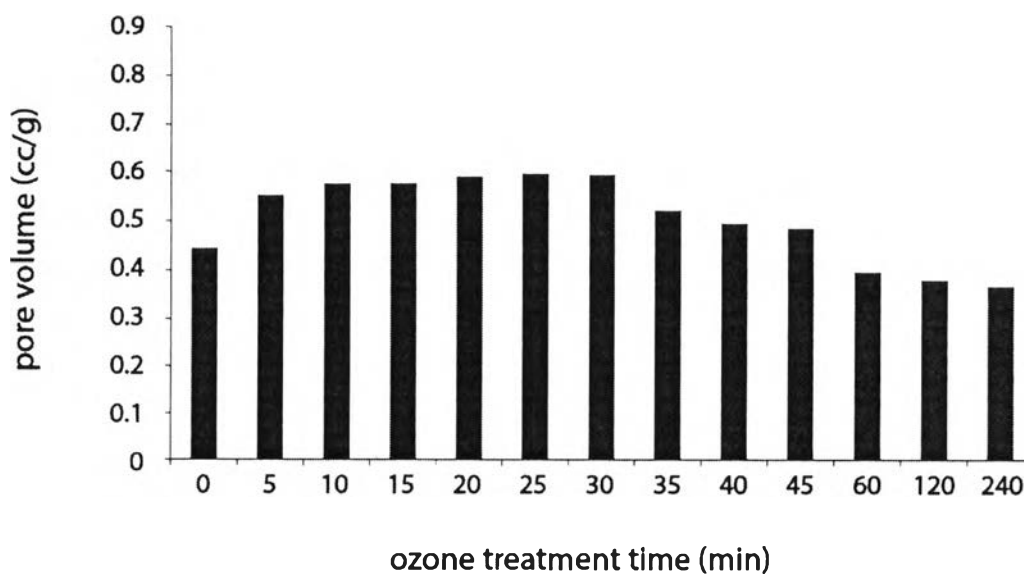


Figure 4.4 Pore volume (cc/g) of activated carbon as a function of ozone treatment time.

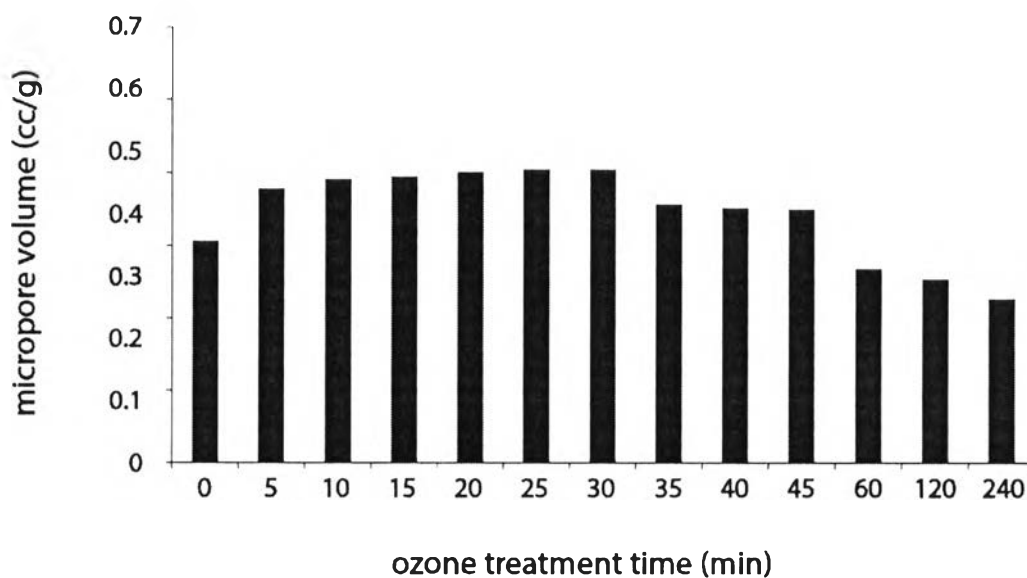


Figure 4.5 Micropore volume (cc/g) of activated carbon as a function of ozone treatment time.

From Figures 4.4-4.5, the pore volume and micropore volume have similar behavior corresponding to specific surface area. Non treated activated carbon

has total pore volume and micropore volume 0.57 and 0.48 cc/g, respectively. After treating with ozone for 5 min, total pore volume and micropore volume increase to 0.72 and 0.6 cc/g and continually increase, with the increase of ozone treatment time and reach the highest value 0.77 and 0.64 cc/g of activated carbon at 25 min of ozone treatment time. The increasing of total pore volume and micropore volume are affected by the reaction between ozone and activated carbon surface. This result insists that the chemisorption of ozone on activated carbon can develop porosity by slightly creating new micropore while carbon gas compounds are leaving the surface. Thus, this reaction generally increases specific surface area. After 25 min, total pore volume and micro pore volume slightly decrease with increasing of ozone treatment time. According to the FTIR result, as the time of exposure lengthens, there also generate oxygen containing functional groups onto carbon surface. This functional group may block some pores. It can be seen that ozone treatment cause pore blocking or pore etching phenomena because of increasing functional groups on activated carbon surfaces (Park and Jin, 2005). Resulting in a slightly reduction of micropore and pore volume including specific surface area.

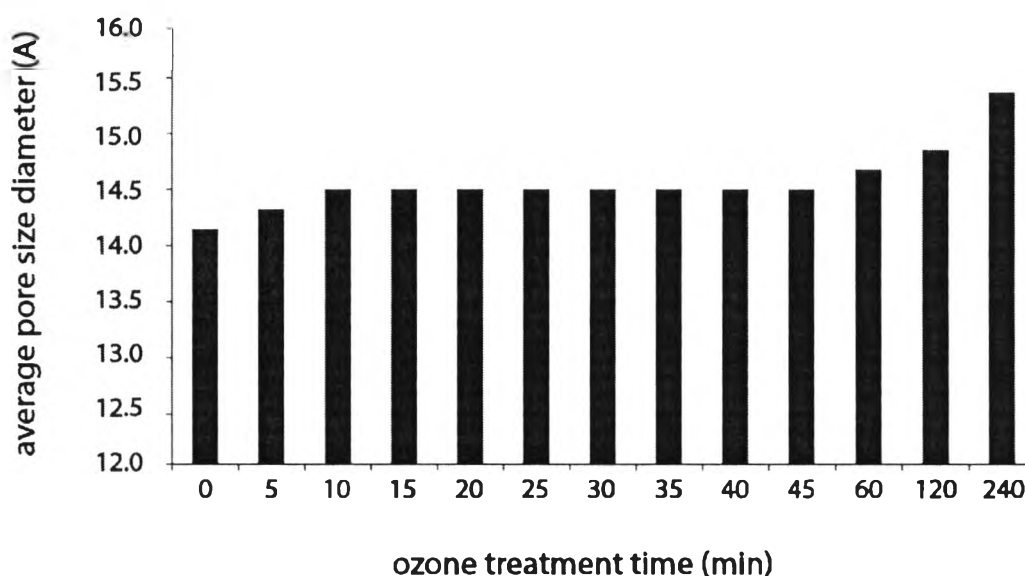


Figure 4.6 Average pore size diameter (Å) of activated carbon as a function of ozone treatment time.

Figure 4.6 shows average pore size diameter as a function of ozone treatment time. There is no significantly different in average pore diameter. This is possibly explained by the counter balance of two effects, the new formation of micropore and the widening of the existing pore.

4.3 Methane Adsorption by Ozone Treated Activated Carbons

Figures 4.7-4.10 are the relation between the amount of methane adsorption at 900 psia at 35°C as a function of BET surface area, micropore volume, total pore volume, and pore size diameter, respectively.

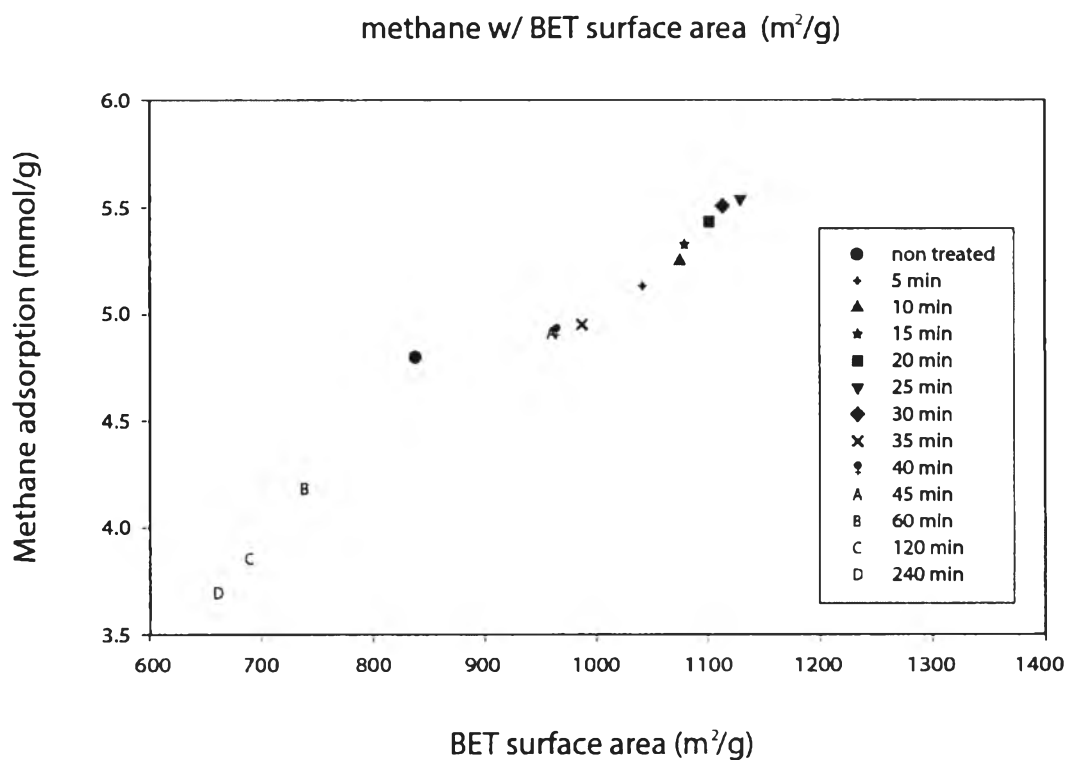


Figure 4.7 Methane adsorption (mmol/g) at 900 psia and 35 °C as a function of BET surface area (m²/g).

Figure 4.7 suggests that BET surface area directly affects the amount of methane adsorption. It can be observed that the activated carbons with high surface

area also have high methane adsorption, activated carbon with 25 min ozone treatment time with the highest surface area ($1130 \text{ m}^2/\text{g}$) has the highest methane adsorption. Following by others which have less BET surface area respectively. The surface of activated carbon has an active site that can absorb molecule of methane on its surface. The more surface area leads to more active site and more amount of methane adsorption. On the other hand activated carbon with 240 min ozone treatment time has only 660 m^2 , resulting in the lowest methane adsorption compare to other treated activated carbon. This result was corresponding to the physical properties of activated carbons in Table 4.1. Not only BET surface area affects to the methane adsorption, but other properties such as pore volume, micropore volume, and average pore size diameter also affect to amount of methane adsorption.

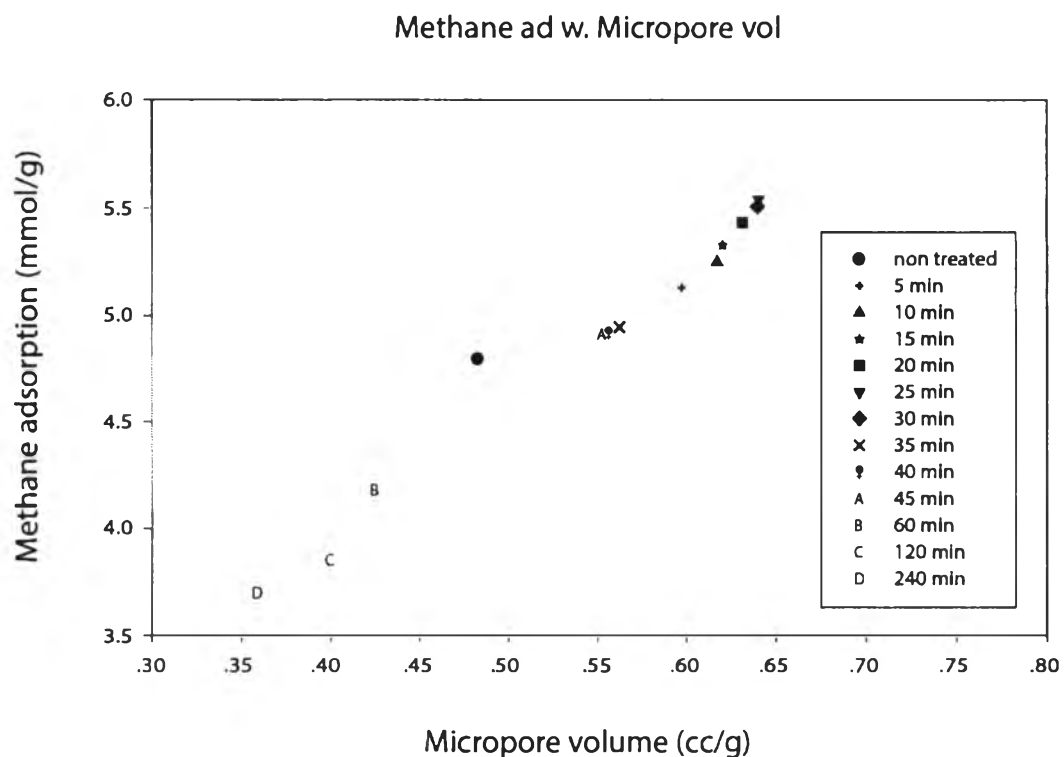


Figure 4.8 Methane adsorption (mmol/g) at 900 psia and 35 °C as a function of micropore volume (cc/g).

Figures 4.8-4.9 show the relation between the amounts of methane adsorption at 900 psia at 35°C as a function of micropore volume and total pore volume. From the result, the relation between the amounts of methane adsorption with micropore volume and total pore volume show similar behavior. Activated carbon with high micropore volume and pore volume also has high methane adsorption capacity which reaches the highest value 0.77 and 0.64 cc/g of activated carbon at 25 min of ozone treatment time. After 25 min, total pore volume and micropore volume slightly decrease with increasing of ozone treatment time. According to the FTIR result, as the time of exposure lengthens, there also generate oxygen containing functional groups onto carbon surface. This functional group may block some pores and also reduce the surface area leads to the reduction of amount of methane adsorption. Another reason is the size of CH₄ molecule is smaller than micropore (< 2nm), higher pore volume lead to higher amount of methane adsorption. Or it can be explained in term of DUBININ-RADUSHKEVICH equation (from eq. 3.2) that volume of gas adsorption is directly varied from pore volume.

Therefore BET surface area, micropore volume, and total pore volume play an important role in determining the amount of methane adsorption (Salehi *et al.*, 2007). However, the pore size of activated carbon is also an important parameter.

Figure 4.10 show the relation between methane adsorption (mmol/g) at 900 psia and 35 °C as the function of average pore size diameter (Å). According to previous study the optimum pore size diameter for methane storage is approximately 11.4 Å (Matranga *et al.*, 1992). Ozonation enlarges the pore site diameter of non-treated activated carbon from 14.4 Å to 15.8 Å in 240 min of ozone treatment. Activated carbons with 240, 120, and 60 ozone treatment time have the highest average pore size diameter much larger than optimum value 11.4 Å (Matranga *et al.*, 1992) As a result, increasing adsorption capacity in methane probably mainly because of the increases in the surface area, micropore volume and total pore volume. Another reason is there is not much difference between its pore size diameter values for the samples (Salehi *et al.*, 2007).

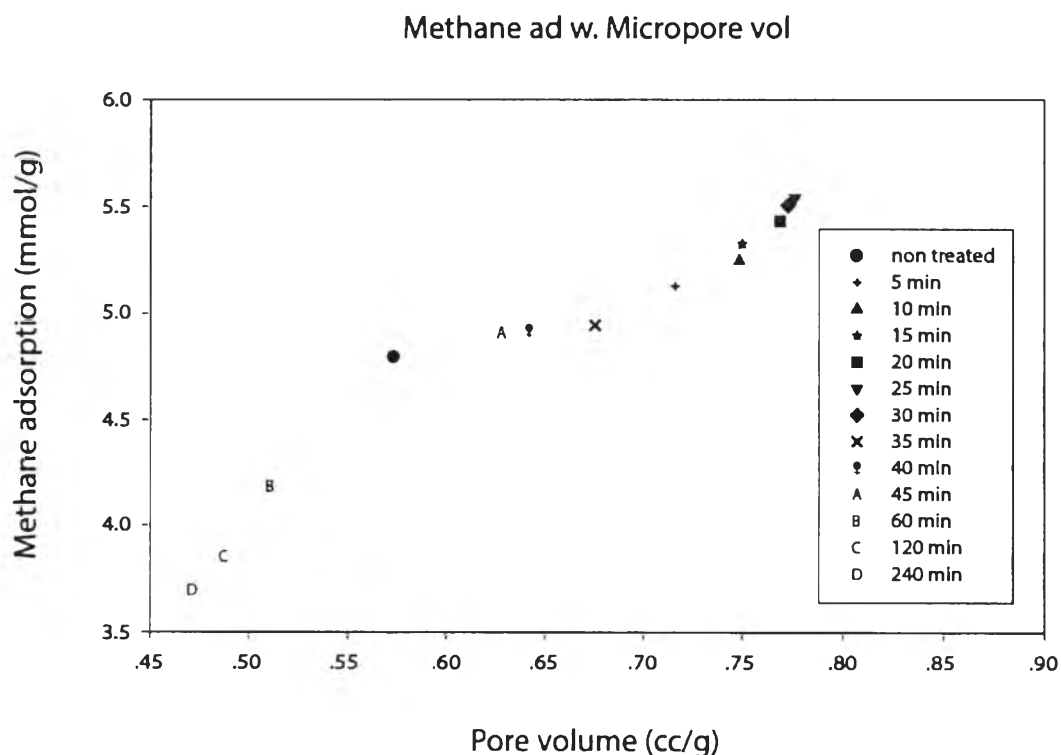


Figure 4.9 Methane adsorption (mmol/g) at 900 psia and 35 °C as a function of total pore volume (cc/g).

As a result, it is hard to define the relation between average pore size diameter and amount of methane adsorption activated carbon with ozonation in this experiment. According to table 4.1 There is no significantly different in the value of average pore size diameter for ozonation. This is possibly explained by the counter balance of two effects, the new formation of micropore and the widening of the existing pore. Increasing adsorption capacity in methane probably mainly because of the increases in the surface area, micropore volume and total pore volume. Another reason is there is not much difference between its pore size diameter values for the samples (Salehi *et al.*, 2007).

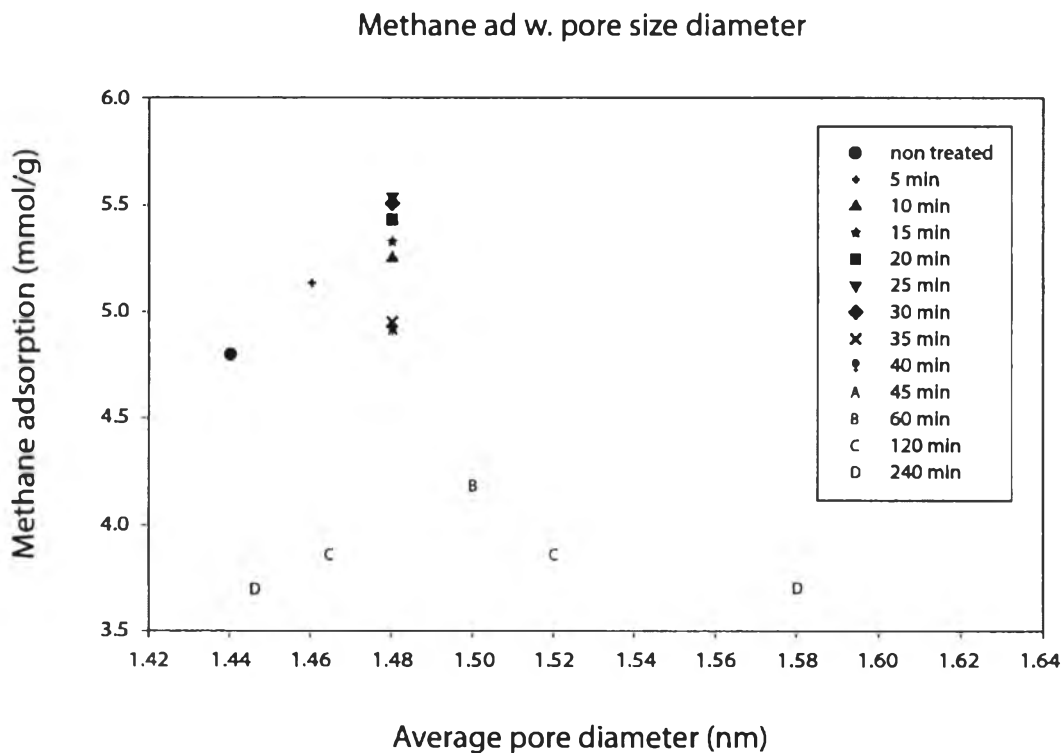


Figure 4.10 Methane adsorption (mmol/g) at 900 psia and 35 °C as a function of average pore size diameter (nm).

Figure 4.11 shows methane adsorption at 35 °C on activated carbon with different exposure of ozone; non-treated, 5, 10, 15, 20, 25, 30, 35, 40, 45, 60, 120, and 240 min with the pressure in the range of 0 to 900 psia obtain by volumetric methode. The methane adsorption isotherm was plotted between the amount of methane adsorbed (mmol) per gram of adsorbent (activated carbon) and equilibrium pressure of methane (psia).

The result shows that the amount of methane adsorption increases with an increase in the pressure. But the increasing trend is not significantly change at higher pressures. This is possibly attributed to the saturation of the adsorbent bed (Salehi *et al.*, 2007).

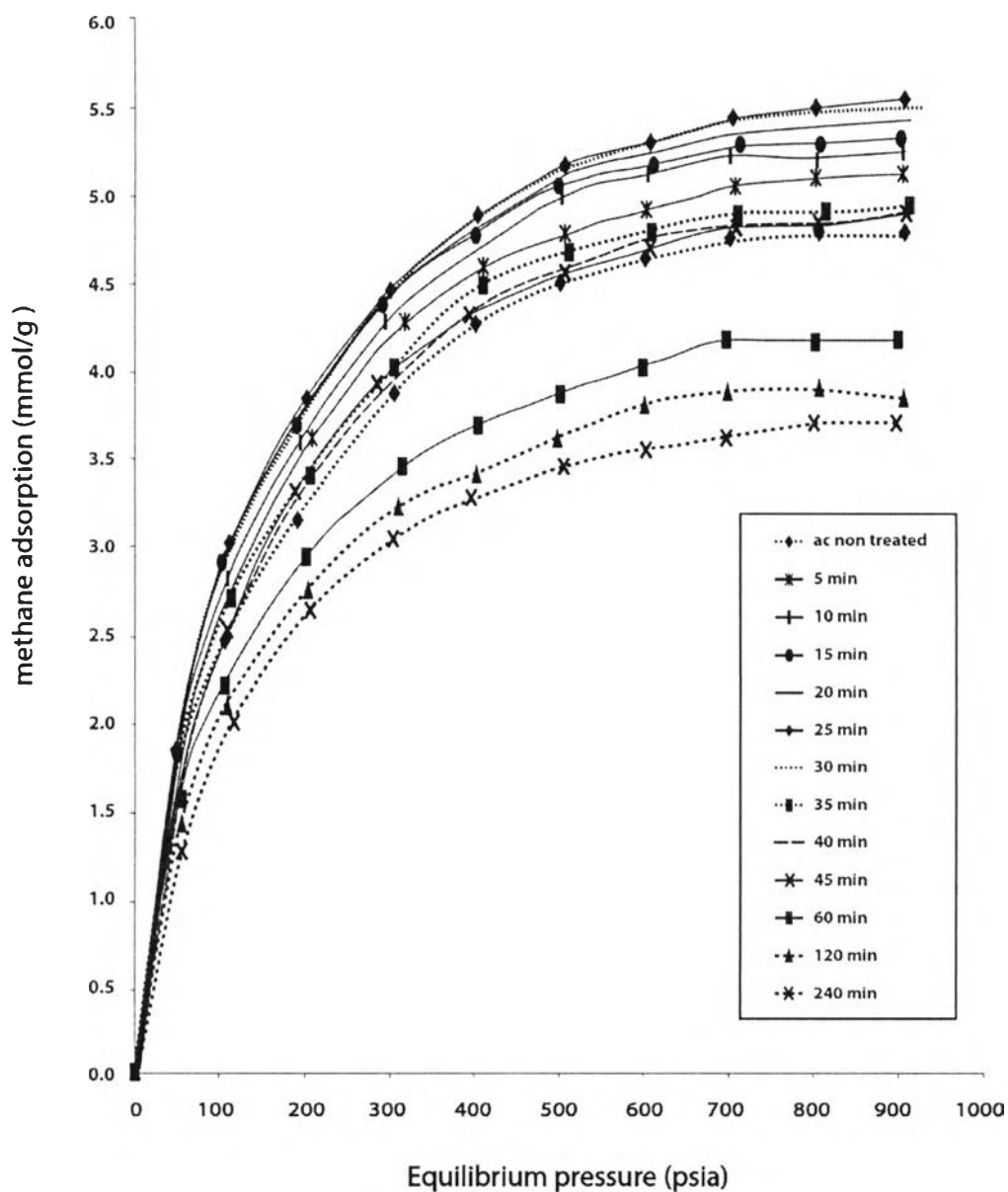


Figure 4.11 Methane adsorption (mmol/g) on activated carbons at 35 °C.

The methane adsorption capacity (mmol) per gram of activated carbon of 25 min of ozone treatment time show the highest methane adsorption, following by 30, 20, 15, 10, 5, 35, 40, 45, non-treated, 60, 120, and 240 min.

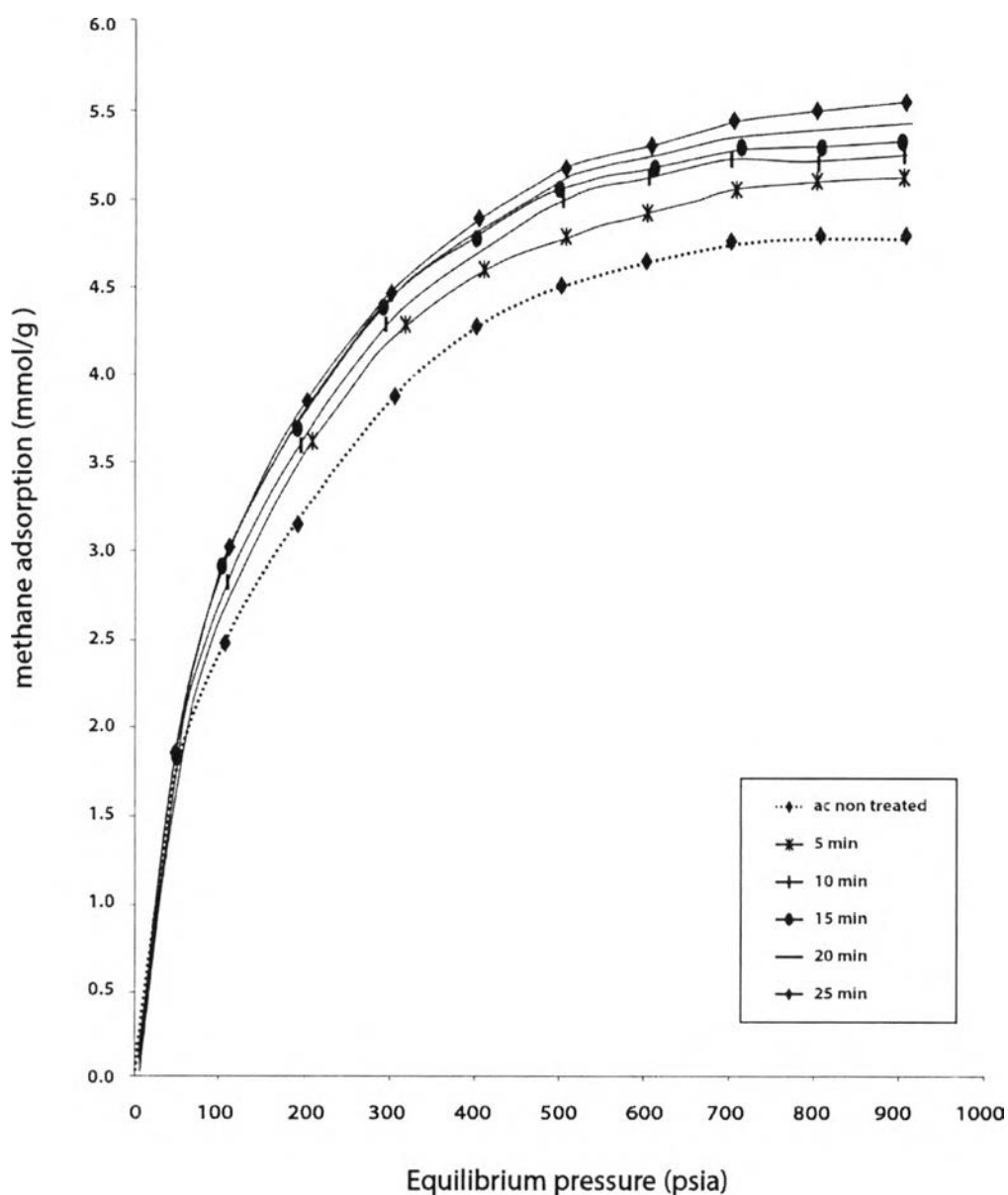


Figure 4.12 Methane adsorption (mmol/g) at 35°C on non-treated, 5, 10, 15, 20, and 25 min ozonation time.

Therefore, activated carbon adsorbed high amount of methane when it had a high BET surface area, micropore volume and total pore volume, which changed by the reaction of ozone. First 25 min ozonation expose time, surface oxygen complexes desorb primarily carbon gas compound which come from decomposition of surface functional group and create new micropore on the surface of carbon structure lead to an increase specific surface area. Corresponding to the physical properties in Table

4.1., specific surface area, total pore volume, and micropore volume increase with increasing ozone treatment time until 25 min. Consequently, these properties play an important role in methane adsorption (Salehi *et al.*, 2007) and lead to a high adsorption capacity of methane. It can summarize that methane adsorption increase with increasing ozone treatment time for first 25 min as show in Figure 4.12.

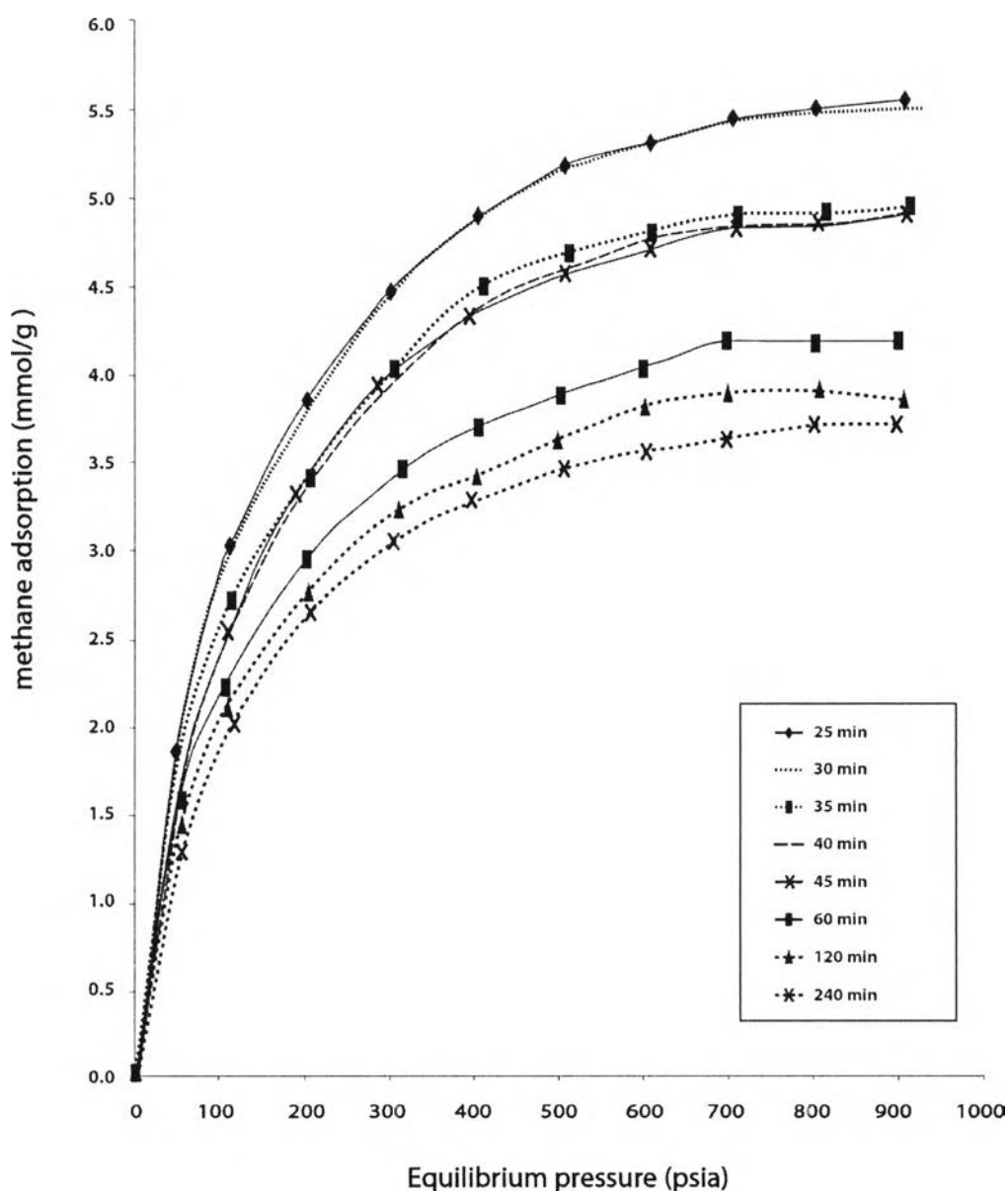


Figure 4.13 Methane adsorption (mmol/g) at 35°C. on 25, 30, 35, 40, 45, 60, 120, and 240 min of ozonation time.

Figure 4.13 shows the amount of methane adsorption of 25, 30, 35, 40, 45, 60, 120, and 240 min treated activated carbon with pressure increase up to 900 psia. In contrast, time of ozone treatment affect adverse to methane adsorption. As the time of exposure lengthens, after 25 min the pore were enlarged by the gasification of the carbon, with a resulting reduction in the surface area micropore volume and total pore volume. These lead to a decrease in adsorption capacity of methane.

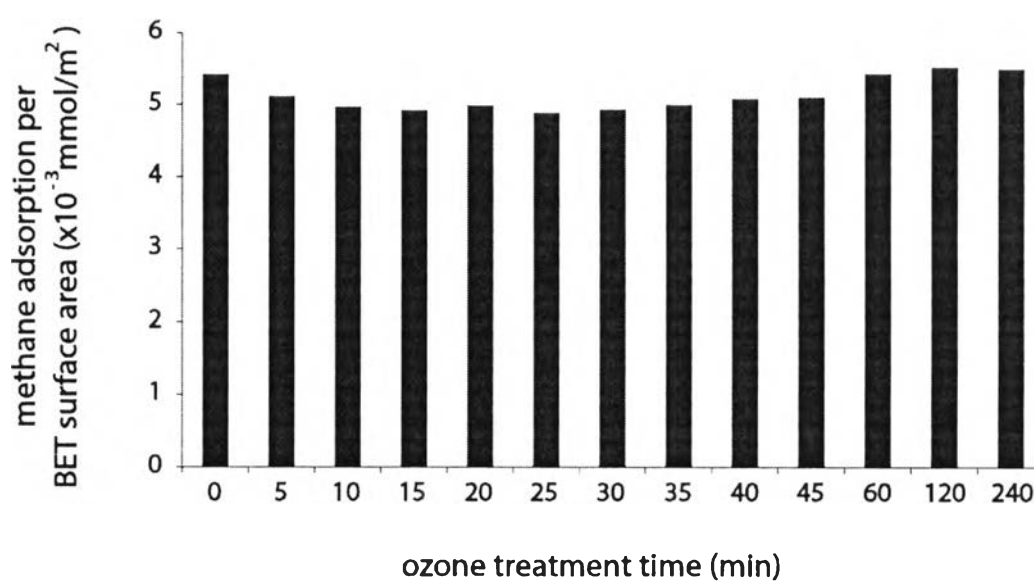


Figure 4.14 The amount of methane adsorption at 900 psia 35°C per BET surface area (mmol/m^2) as a function of ozone treatment time.