CHAPTER IV
RESULTS AND DISCUSSION

4.1 Adsorbents Characterization

4.1.1 BET Surface Areas

The specific surface areas of both adsorbents were determined by BET 3-Parameters Fit adsorption isotherm. The specific surface areas of NaX zeolite and NaY zeolite are 580 m^2/g and 549 m^2/g, respectively.

4.1.2 Thermo Gravimetric Analysis

The TGA results of both NaX and NaY zeolite adsorbents are shown in Figure 4.1.

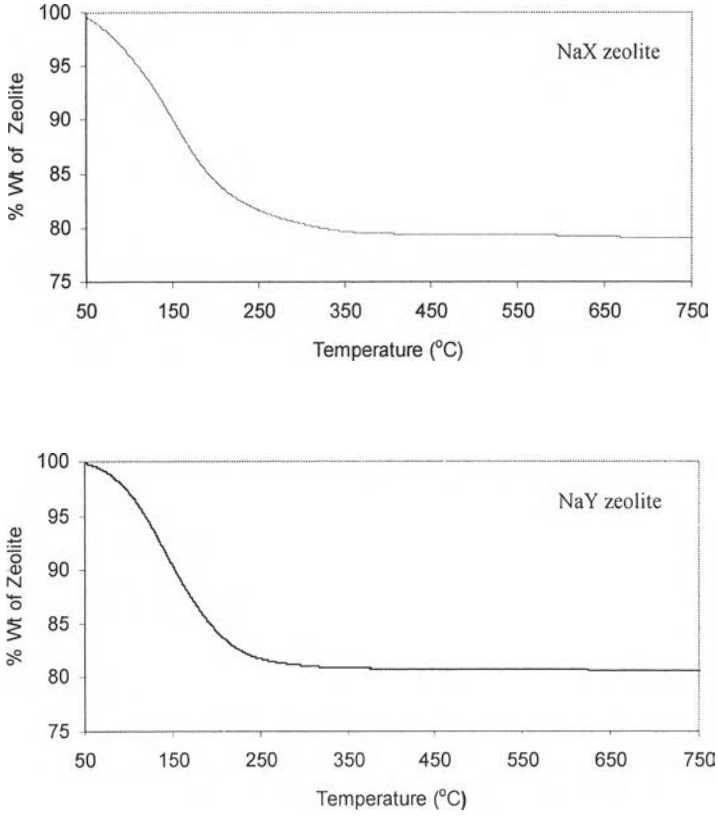

Figure 4.1 TGA results of NaX and NaY zeolites.

From the results, the water content in original NaX and NaY zeolites before treating are 20.43 and 19.17 % wt, respectively. From TGA results, it can be seen that at around 300 degree centigrade the water content of both zeolites is less than 3 percent, so both adsorbents should be treated at that temperature before using. Therefore, both zeolites were treated at 300 degree centigrade for 3 hours and kept in a desiccator before being used in the adsorption experiments.

4.2 Adsorption of Sulfur Compounds from Simulated Transportation Fuels

3-Methylthiophene and benzothiophene were used as representative sulfur compounds in gasoline where as dibenzothiophene was chosen as representative sulfur compound in diesel. Transportation fuels used in this study were simulated by using isooctane and decane as a model for gasoline and diesel, respectively. Thus, the simulated fuels containing sulfur compound were prepared by mixing benzothiophene or 3-methylthiophene with isooctane for simulated gasoline and dibenzothiophene with decane for simulated diesel.

4.2.1 Adsorption of 3-Methylthiophene in Isooctane on NaX and NaY Zeolites

Figure 4.2 shows the adsorption isotherms of 3-methylthiophene on NaX and NaY zeolites. Y-axis represents the amount of 3-methylthiophene adsorbed on zeolite and X-axis represents the equilibrium concentration of 3-methylthiophene in the system. From the results, the adsorption of 3-methylthiophene increases with increasing equilibrium concentration. Moreover, the adsorption data were found to be well fitted by Langmuir isotherm. As a result, the maximum capacity and adsorption affinity of 3-methylthiophene on both NaX and NaY zeolites could be obtained from Langmuir equation. The maximum capacity of NaX and NaY zeolite is 1.73 and 1.62 mmol/g, respectively. The adsorption affinity of NaX and NaY zeolite is 13.99 and 14.88 μmol/g, respectively. From the isotherms, we can see that at any equilibrium concentration NaX zeolite can adsorb 3-methylthiophene slightly

higher than can NaY. In addition, at higher concentration, the difference in the ability to adsorb 3-methylthiophene is greater. The results suggested that the acidity of the adsorbent is not a prominent factor in 3-methylthiophene adsorption as NaX has lower acidity than NaY, yet adsorbs more 3-methylthiophene. This is probably due to the fact that NaX has more exchangeable sites than NaY. It can be seen that, within the range of concentration studied, 3-methylthiophene adsorption on both zeolites still increases even at high concentration. This can be attributed to a relatively small size of 3-methylthiophene and a large number of sorption sites accessible for 3-methylthiophene adsorption.

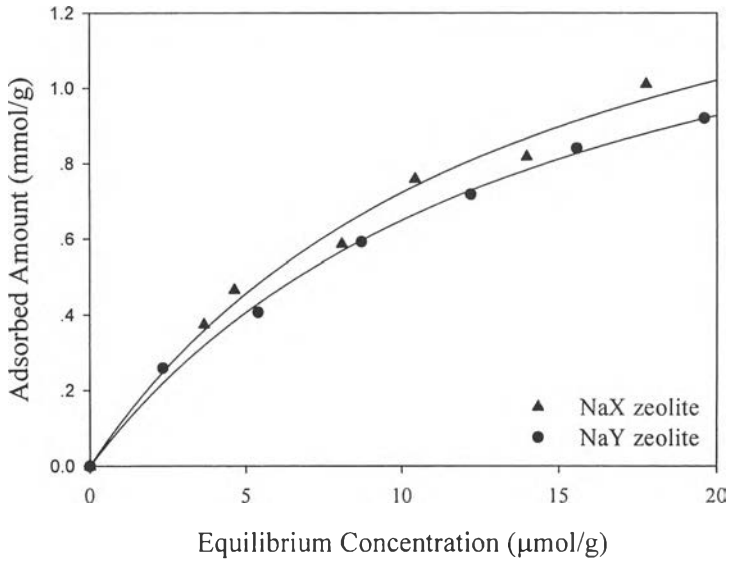

Figure 4.2 Adsorption isotherms of 3-methylthiophene in isooctane on NaX and NaY zeolites at 25 degree centigrade and fuel to adsorbent weight ratio of 85.
(Lines are curve-fitting using Langmuir isotherms)

4.2.2 Adsorption of Benzothiophene in Isooctane on NaX and NaY Zeolites

Figure 4.3 shows the adsorption isotherms of benzothiophene on NaX and NaY zeolites. Y-axis represents the amount of benzothiophene adsorbed on zeolite and X-axis represents the equilibrium concentration of benzothiophene in the system. From the results, a general trend can be observed that initially the adsorption of benzothiophene increases with increasing equilibrium concentration and then

become relatively constant. The adsorption data were found to be well fitted by Langmuir isotherm as also shown in the figure. As a result, the maximum capacity and adsorption affinity of benzothiophene on both NaX and NaY zeolites could be obtained from Langmuir equation. The maximum capacity of NaX and NaY zeolite is 1.22 and 1.22 mmol/g, respectively. The adsorption affinity of NaX and NaY zeolite is 0.80 and 1.50 μmol/g, respectively. From the isotherms, we can see that at any equilibrium concentration NaX zeolite can adsorb higher amount of benzothiophene than can NaY, especially in low concentration region. However, the amounts of benzothiophene adsorbed on NaX and NaY zeolites are quite close at higher equilibrium concentration. This can be attributed to higher sorption sites in NaX as compared to NaY. This results in higher surface energy of NaX and, consequently, higher interaction with the surface compound. Furthermore, nearly the same amounts of benzothiophene adsorbed on NaX and NaY zeolites observed at higher concentration may be due to the size of the solute and the steric hindrance. At low concentration, the effect of steric hindrance can be neglected since there are plenty of active sites available for solute molecules to adsorb. In contrast, at high concentration the effect of steric hindrance resulting from adsorbed molecules may become important.

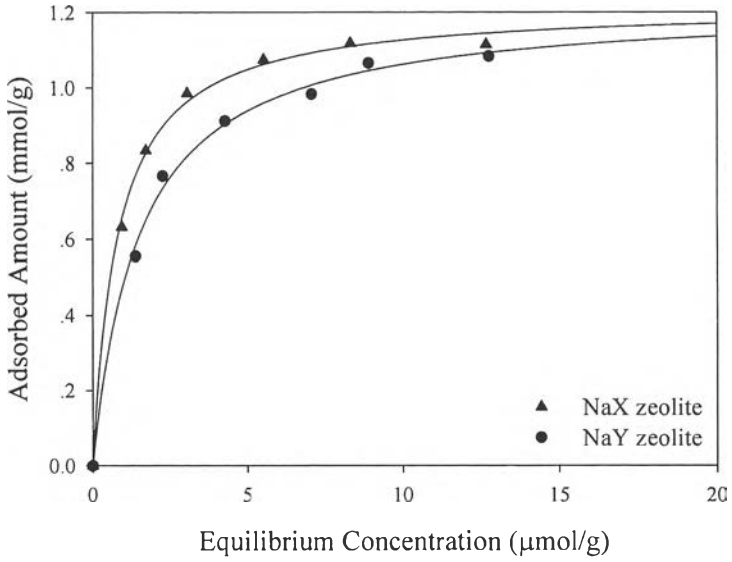

Figure 4.3 Adsorption isotherms of benzothiophene in isooctane on NaX and NaY zeolites at 25 degree centigrade and fuel to adsorbent weight ratio of 85.
(Lines are curve-fitting using Langmuir isotherms)

4.2.3 Adsorption of Dibenzothiophene in Decane on NaX and NaY Zeolites

Figure 4.4 shows the adsorption isotherms of dibenzothiophene on NaX and NaY zeolites. Y-axis represents the amount of dibenzothiophene adsorbed on zeolite and X-axis represents the equilibrium concentration of dibenzothiophene in the system. It can be seen that the adsorption of dibenzothiophene on both zeolites exhibits a Langmuir isotherm. As a result, the maximum capacity and adsorption affinity of dibenzothiophene on both NaX and NaY zeolites could be obtained from Langmuir equation. The maximum capacity of NaX and NaY zeolite is 1.18 and 1.18 mmol/g, respectively. The adsorption affinity of NaX and NaY zeolite is 0.70 and 0.75 μmol/g, respectively. From the isotherms, we can see that the adsorptions of dibenzothiophene are very similar for both NaX and NaY zeolites. This may be due to the influences from a number of sorption sites and the acidity of both zeolites. NaX has higher number of sites for solute adsorption but its acidity is lower than NaY. However, the effect of higher acid sites is not much

pronounced as seen previously in this study which may be the result of steric hindrance effect on the adsorption of big molecules such as dibenzothiophene. In addition, the effect of acid strength on dibenzothiophene adsorption is more significant when compared to 3-methylthiophene and benzothiophene adsorption since dibenzothiophene has two benzo functional groups in its structure. Therefore, dibenzothiophene has more π electrons that can be polarized or induced more easily when exposing to more acidic surface of NaY.

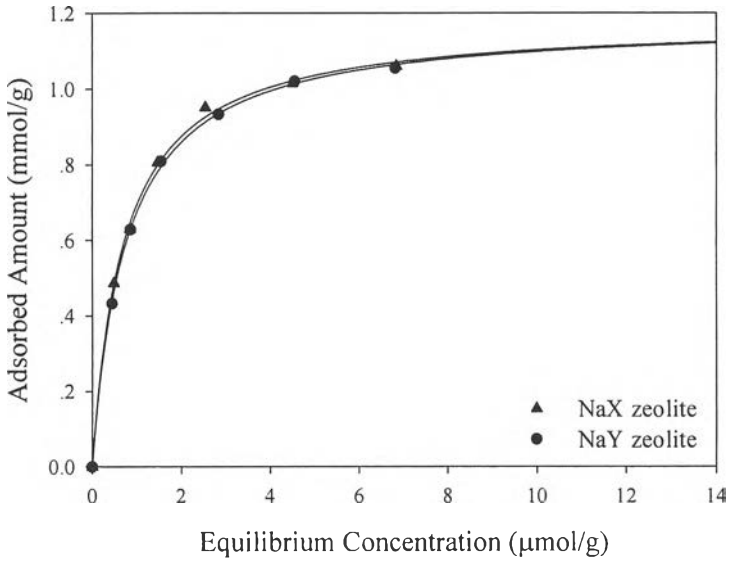

Figure 4.4 Adsorption isotherms of dibenzothiophene in decane on NaX and NaY zeolites at 25 degree centigrade and fuel to adsorbent weight ratio of 85.
(Lines are curve-fitting using Langmuir isotherms)

4.2.4 Comparison between the Adsorption of 3-Methylthiophene, Benzothiophene and Dibenzothiophene on NaX and NaY Zeolites

Figures 4.5 and 4.6 show the adsorption isotherms of three sulfur compounds on NaX and NaY zeolites, respectively. Y-axis represents the amount of sulfur compounds adsorbed on zeolite and X-axis represents the equilibrium concentration of sulfur compounds in the system. From both figures, it can be obviously seen that the adsorption of benzothiophene and dibenzothiophene on both

zeolites are higher than that of 3-methylthiophene at any equilibrium concentration. Especially at low concentration, both benzothiophene and dibenzothiophene are much better adsorbed by NaX and NaY zeolites than 3-methylthiophene. The preferential adsorption observed here suggested that the benzo functional group in benzothiophene and dibenzothiophene is an important in the adsorption of sulfur compounds on zeolite. It has been known that π electrons in benzene ring can form bond with zeolites (Hernandez *et al.*, 2003). In addition, Figure 4.5 shows that the adsorbed amounts of benzothiophene and dibenzothiophene on NaX are quite comparable, especially in low concentration range. This is likely due to the effects of the size and the molecular structure of the solute. Benzothiophene molecule is smaller than dibenzothiophene which has two benzene rings in the structure, thus hindering its adsorption on zeolite is due to steric effect. However, dibenzothiophene has more π electron which can interact preferentially with sorption sizes. In contrast to NaX, NaY can adsorb dibenzothiophene slightly higher than benzothiophene, especially at low concentration. This is probably due to high acidity of NaY which causes NaY to interact preferentially with dibenzothiophene as discussed previously. The results obtained in this part of study suggested that there are several factors affecting the adsorption of sulfur compounds on zeolites. This includes the properties of solute such as molecular structure and size and its polarity as well as the properties of the adsorbent such as number of sorption sites and acidity.

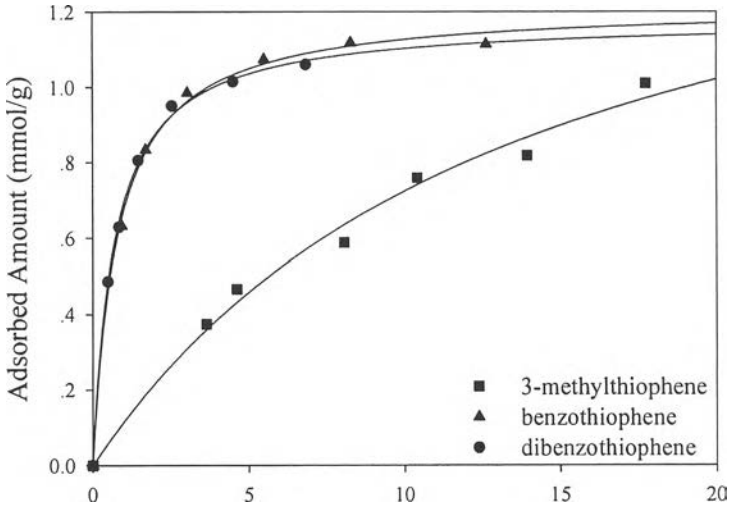

Figure 4.5 Adsorption isotherms of 3-methylthiophene and benzothiophene in isooctane and dibenzothiophene in decane on NaX zeolite at 25 degree centigrade and fuel to adsorbent weight ratio of 85.

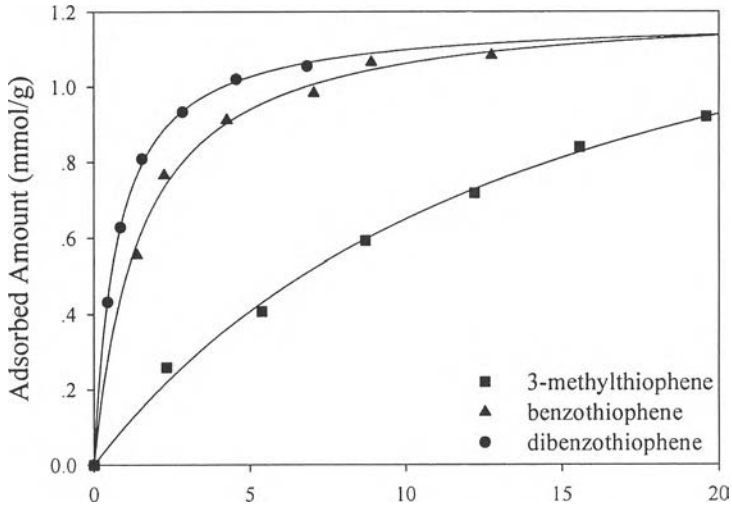

Figure 4.6 Adsorption isotherms of 3-methylthiophene and benzothiophene in isooctane and dibenzothiophene in decane on NaY zeolite at 25 degree centigrade and fuel to adsorbent weight ratio of 85.

4.3 Effect of Temperature on Sulfur Compounds Adsorption

The effect of temperature on 3-mthylthiophene, benzothiophene, and dibenzothiophene adsorption by NaX and NaY zeolites was studied at three different temperatures, 25, 50, and 80 degree centigrade, as shown in Figures 4.7-4.9. Y-axis represents the amount of sulfur compounds adsorbed on zeolite and X-axis represents the adsorption temperature. The results revealed a general trend that the adsorption of 3-methylthiophene, benzothiophene, and dibenzothiophene on both zeolites decreases with increasing temperature which is similar to the work of Takahashi (2000). This can be expected from the fundamental of adsorption which is based on the concept of equilibrium constant which decreases with increasing temperature. When comparing NaX and NaY, it can be seen that the decrease in the adsorbed amount of sulfur compound on both zeolites is very similar. By increasing the temperature from 25 °C to 80 °C, it was found that the adsorbed amount on NaX decreases 50%, 21% and 15% and the adsorbed amount on NaY decreases 46%, 15% and 15% for 3-methylthiophene, benzothiophene and dibenzothiophene, respectively. Moreover, it was observed that the adsorption of 3-methylthiophene decreases to a much greater extent when compared to the adsorption of benzothiophene and dibenzothiophene. This result suggested that the bonding between 3-methylthiophene and sorption sites on the zeolites is weaker when compared to benzothiophene and dibenzothiophene. This may be due to the presence of benzo functional group in benzothiophene and dibenzothiophene's structure.

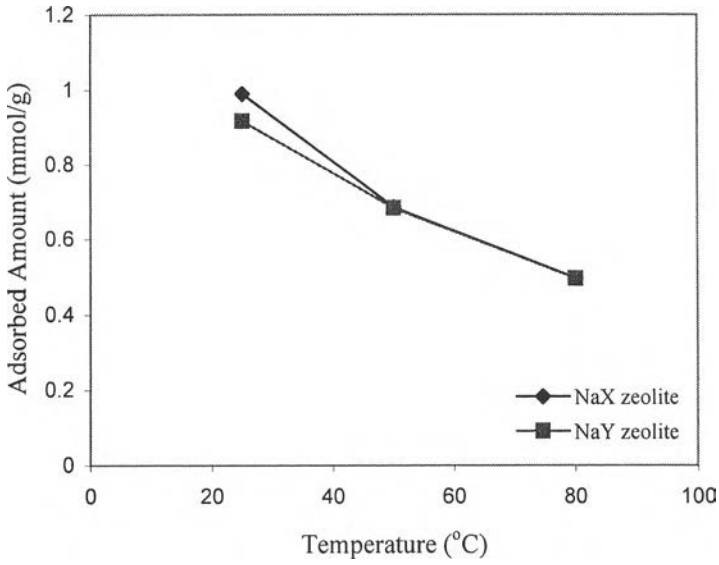

Figure 4.7 Effect of temperature on 3-methylthiophene adsorption over NaX and NaY zeolites at fuel to adsorbent weight ratio 85 with initial concentration at 3000 ppm.

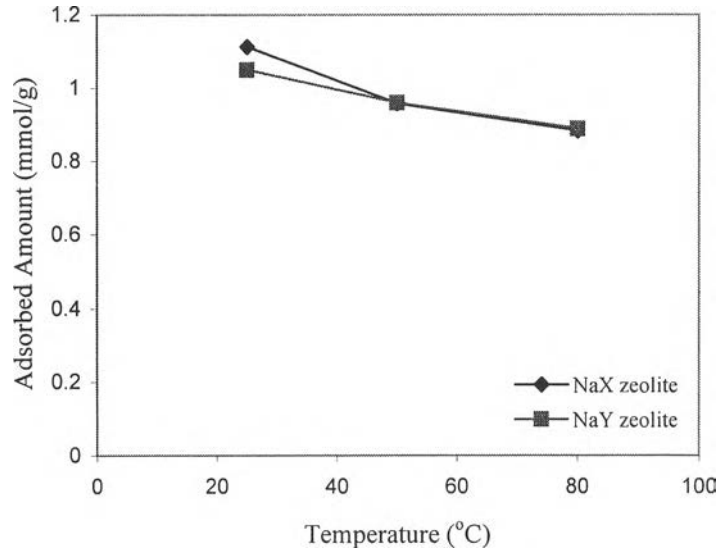

Figure 4.8 Effect of temperature on benzothiophene adsorption over NaX and NaY zeolites at fuel to adsorbent weight ratio 85 with initial concentration at 3000 ppm.

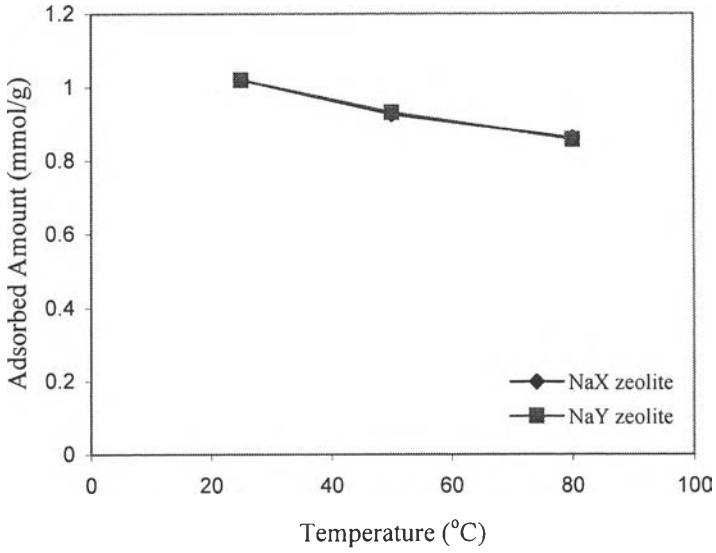

Figure 4.9 Effect of temperature on dibenzothiophene adsorption over NaX and NaY zeolites at fuel to adsorbent weight ratio 85 with initial concentration at 3000 ppm.

4.4 Effect of Fuel to Adsorbent Weight Ratio on Sulfur Compounds Adsorption

In order to investigate the effect of the fuel to adsorbent ratio, the adsorption of all three sulfur compounds was studied at three different fuel to adsorbent ratios, 20, 40, and 85, as shown in Figures 4.10–4.12. Y-axis represents the amount of sulfur compound adsorbed on zeolite and X-axis represents the fuel to adsorbent weight ratio. From the results, a general trend can be observed that the adsorption of 3-methylthiophene, benzothiophene, and dibenzothiophene increases with increasing fuel to adsorbent weight ratio. Similar results were also observed by Velu *et al.* (2003). This can be attributed to the fact that, by increasing fuel to adsorbent ratio, the number of moles of sulfur compound also increases with respect to the same weight basis of the adsorbent, and thus more sulfur can be adsorbed on the adsorbent. Moreover, as the fuel to adsorbent ratio was increased, the remaining concentration of sulfur compounds at equilibrium also increased. When considering the adsorption isotherms shown in the previous sections, at higher of equilibrium concentration of sulfur compounds in liquid phase, higher adsorbed amount on the adsorbent could be

obtained. It should be noted that, upon increasing fuel to adsorbent ratio, the adsorption of benzothiophene and dibenzothiophene increases to a higher extent when compared to the adsorption of 3-methylthiophene. For example, as the fuel to adsorbent ratio was increased from 20 to 80, the adsorbed amounts of benzothiophene and dibenzothiophene increased approximately three times where as only approximately 2 times increased in the adsorbed amount was observed in case of 3-methylthiophene. This is probably due to the preference of the adsorption of which NaX and NaY prefer to adsorb benzothiophene and dibenzothiophene than 3-methylthiophene as seen in the previous section. It was observed in this study that it is practically difficult to further increase the fuel to adsorbent ratio beyond the studied range since not only the adsorbed amount would not increase as much, but also the difference between initial and final concentrations may become too small to allow us to determine the adsorbed amount accurately.

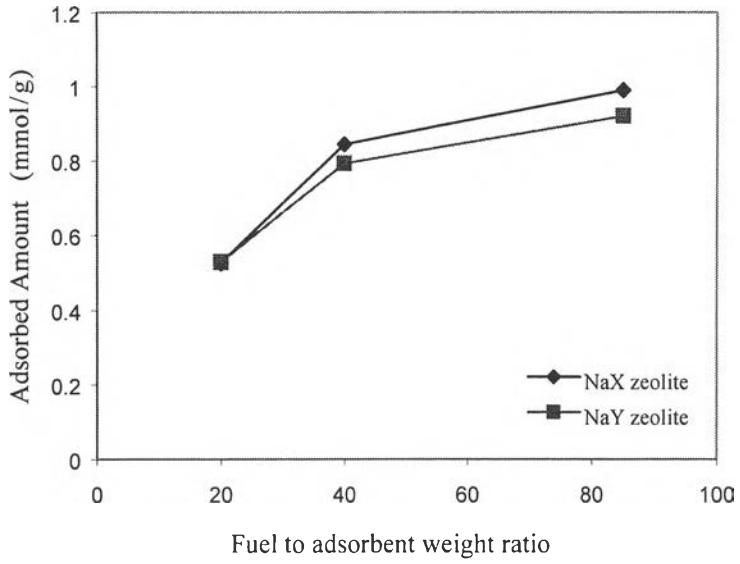

Figure 4.10 Effect of fuel to adsorbent weight ratio on 3-methylthiophene adsorption over NaX and NaY zeolites at 25 degree centigrade with initial concentration at 3000 ppm.

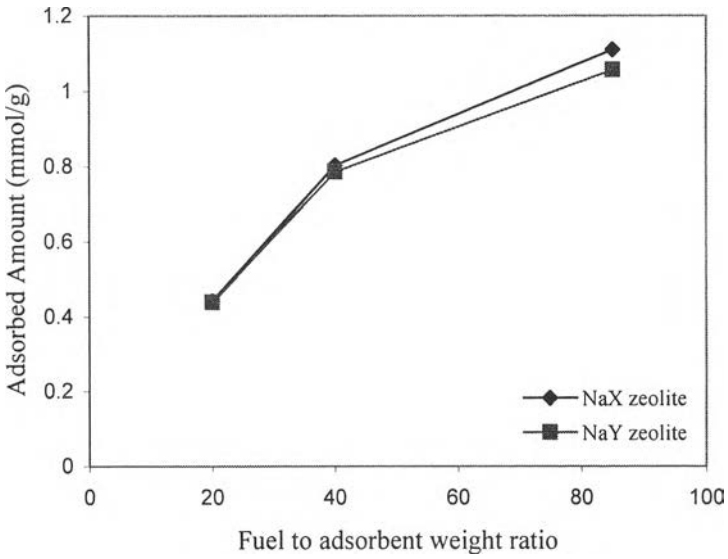

Figure 4.11 Effect of fuel to adsorbent weight ratio on benzothiophene adsorption over NaX and NaY zeolites at 25 degree centigrade with initial concentration at 3000 ppm.

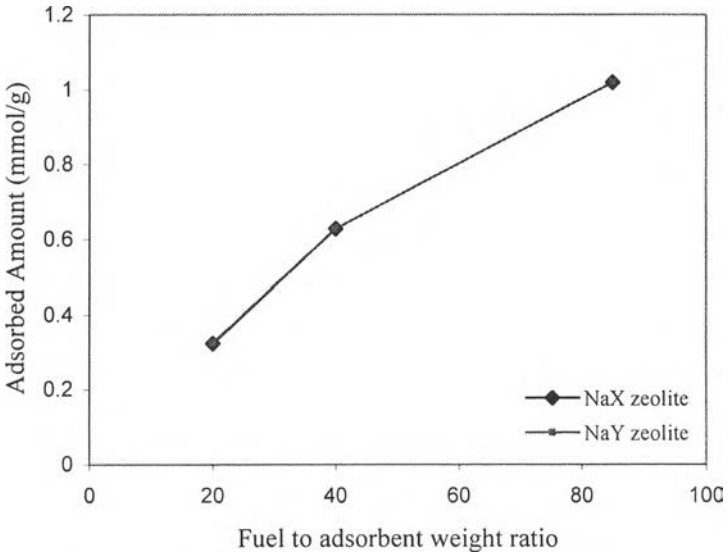

Figure 4.12 Effect of fuel to adsorbent weight ratio on dibenzothiophene adsorption over NaX and NaY zeolites at 25 degree centigrade with initial concentration 3000 ppm.