

Chapter 4

Results and Discussion

4.1 Characterization of Carbon Adsorbents

4.1.1 Effects of activation temperature

Carbon adsorbents from corncob which were activated isothermally with 50 wt% sulfuric acid at various temperatures between 150°C and 350°C, provided different specific surface area, as well as iodine number, as summarized in Table 4.1 [32]. The results suggested that the rate of activation was increased with an increase in temperature in the same manner as chemical reaction kinetics. With phosphoric acid, the activation temperatures affected the carbon adsorbent characteristics in the same manner as that with sulfuric acid.

Table 4.1: characteristics of carbon adsorbents from corncobs activated with sulfuric acid at various temperatures

T (°C)	BET			I ₂ no. (mg/g)
	area,(m ² /g)		volume,(l/g)	
	total	micropore	micropore	
150	32	6	23	184
200	116	74	33	223
250	176	105	47	234
300	236	170	77	244
350	495	309	144	264

Table 4.2: Effect of chemical reagent used for prepared carbon adsorbents

reagent	T (°C)	BET		I ₂ no. (mg/g)
		surface area, (m ² /g)	D _p , (Å)	
without reagent		4	59	164
H ₂ SO ₄	250	176	109	234
20% H ₃ PO ₄	300	509	22	296
50% H ₃ PO ₄	300	1112	29	521
ZnCl ₂	600	1174	53	1242

4.1.2 Effects of chemical reagents

Characteristics of carbon adsorbents from corncobs activated with a reagent, especially specific surface area, were different from that activated with another reagent, as summarized in Table 4.2. Zinc chloride could provide high specific surface area and iodine number, which was in that specification of activated carbons. While both phosphoric acid and sulfuric acid provided the iodine numbers less than the specification. However, the activation with phosphoric acid provided moderate up to high specific surface area from activation, while with sulfuric acid resulted in relatively low specific surface area. The results suggested that the activation with both sulfuric acid and phosphoric acid required additional energy or high temperature in order to activate corncob for producing high specific surface area.

4.1.3 Element analysis

With electron diffraction X-ray (EDX), major elements in carbon adsorbents were able to be analysed. It was found that all carbon adsorbents were composed of carbon and oxygen, as summarized in Table 4.3. Only a small fraction of applied reagent was found in the carbon adsorbents. The results suggested that all reagents were merely employed to promote the activation. In other words, such reagents performed as catalysts.

Table 4.3: Effect of chemical reagent used for prepared activated carbons to EDX

reagent	EDX,element %						
	C	O	Si	P	Cl	S	other
H ₂ SO ₄	51.79	47.12	0.38			0.43	0.28
20% H ₃ PO ₄	59.77	39.72		0.3			0.21
50% H ₃ PO ₄	56.91	39.57	0.75	2.64			0.13
ZnCl ₂	57.34	41.96			0.48		0.22

4.1.4 Functional groups

With IR spectrum, all carbon adsorbents from corncob constituted hydroxyl groups, carbonyl groups and ether groups on the surface, at the wave number 3500, 1600 and 1200 respectively as shown in Figure 4.1. However, the amounts of these functional groups could not be determined.

4.1.5 Scanning Electron Microscopy

All carbon adsorbents, as well as raw corncob, were inspected with scanning electron microscope (SEM). It was found that raw corncob contained relatively small fraction of pore as shown in Figure 4.2. The result corresponded with quite small specific surface area, based on nitrogen adsorption. After activation with selected reagents, a large number of pores were found on the external surface of other three carbon adsorbents. With sulfuric acid, the pore size, was relatively large in comparison with the others as shown in Figure 4.3. While the pores, which were produced with zinc chloride, were the smallest pores as shown in Figure 4.6, corresponding with the relatively high specific surface area. With phosphoric acid, the pores were quite straight, as shown in Figure 4.4, Figure 4.5. The results suggested that each reagent promoted the activation reaction in different mechanism.

4.1.6 particle density

Particle density of each carbon adsorbent was measured indirectly by measuring the pressure drop across the packed bed at various flow rate of carrier gas. The

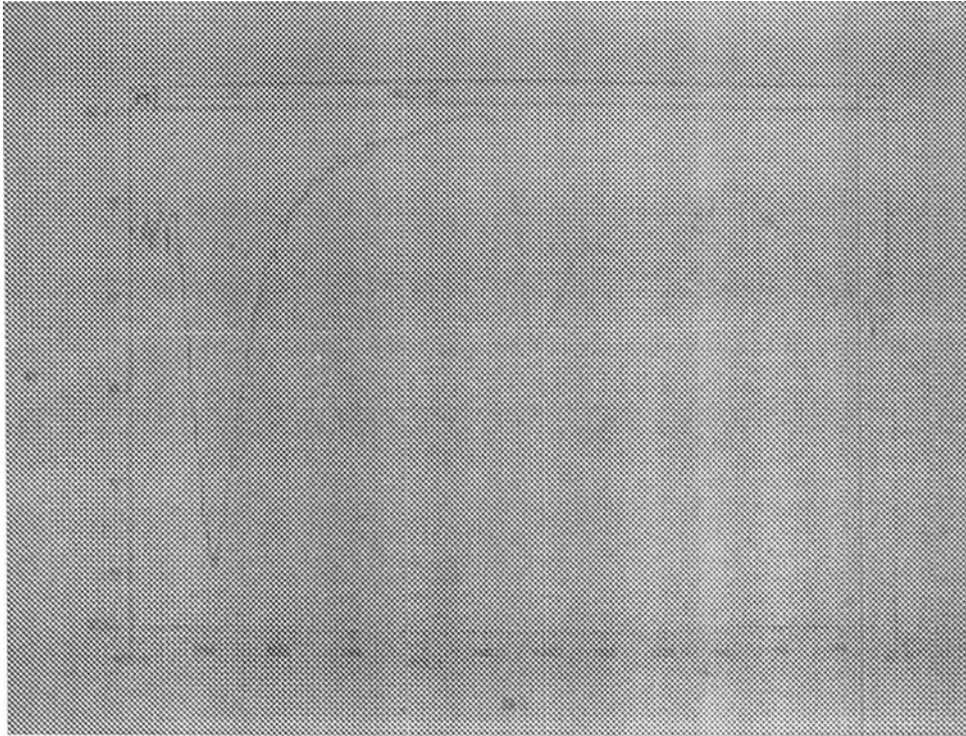


Figure 4.1: Spectrum of carbon adsorbent which activated with zinc chloride

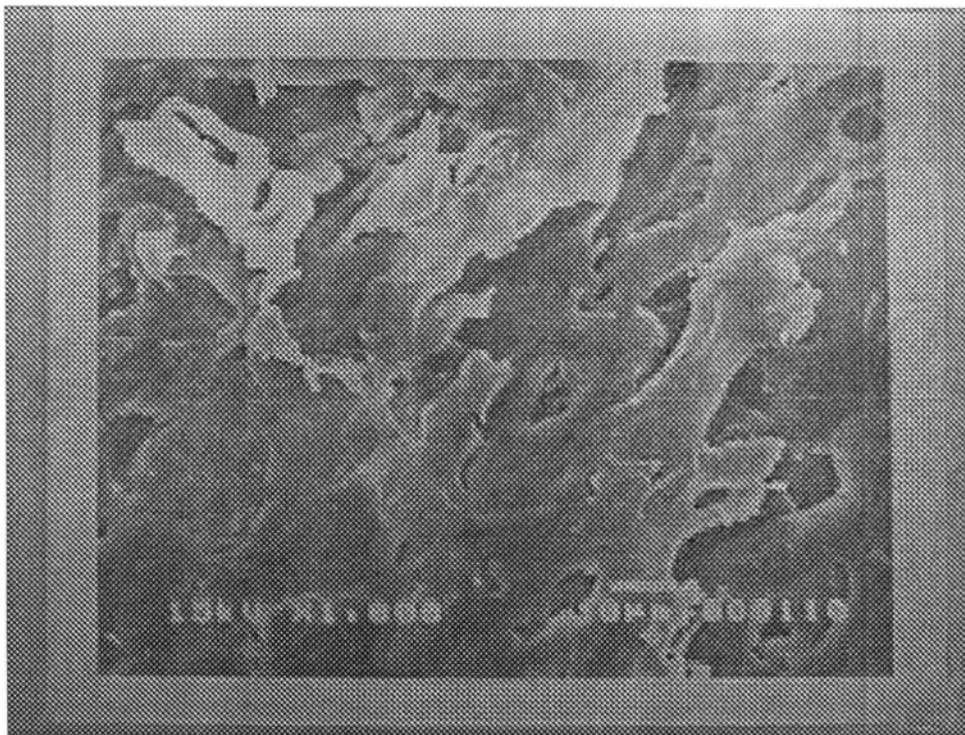


Figure 4.2: External surface of corncob

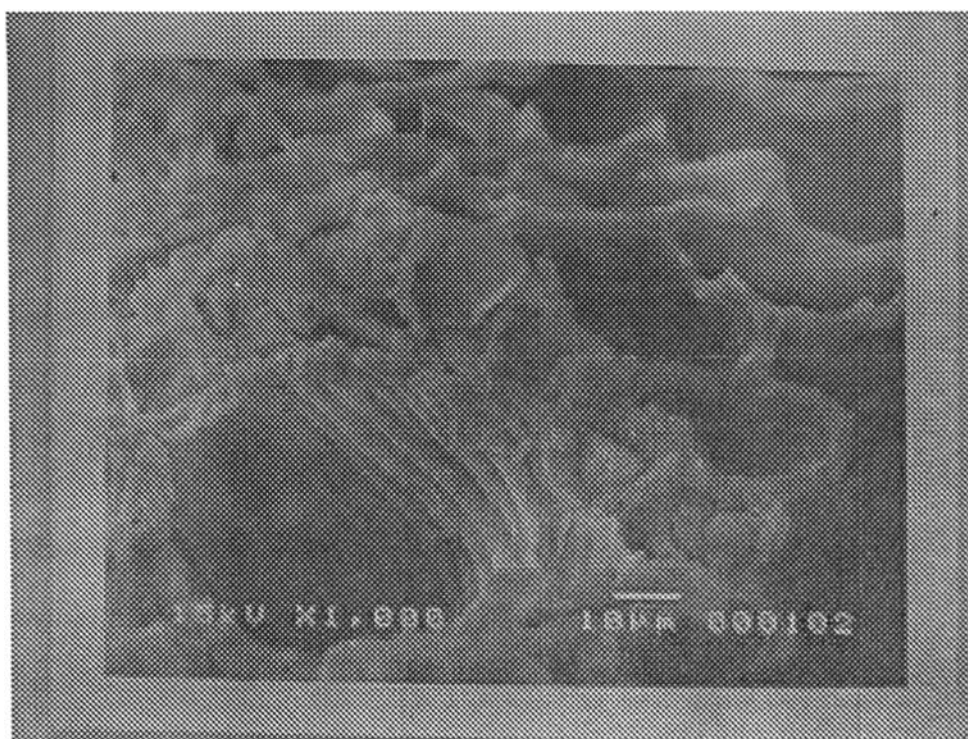


Figure 4.3: External surface of carbon adsorbent which activated with sulfuric acid

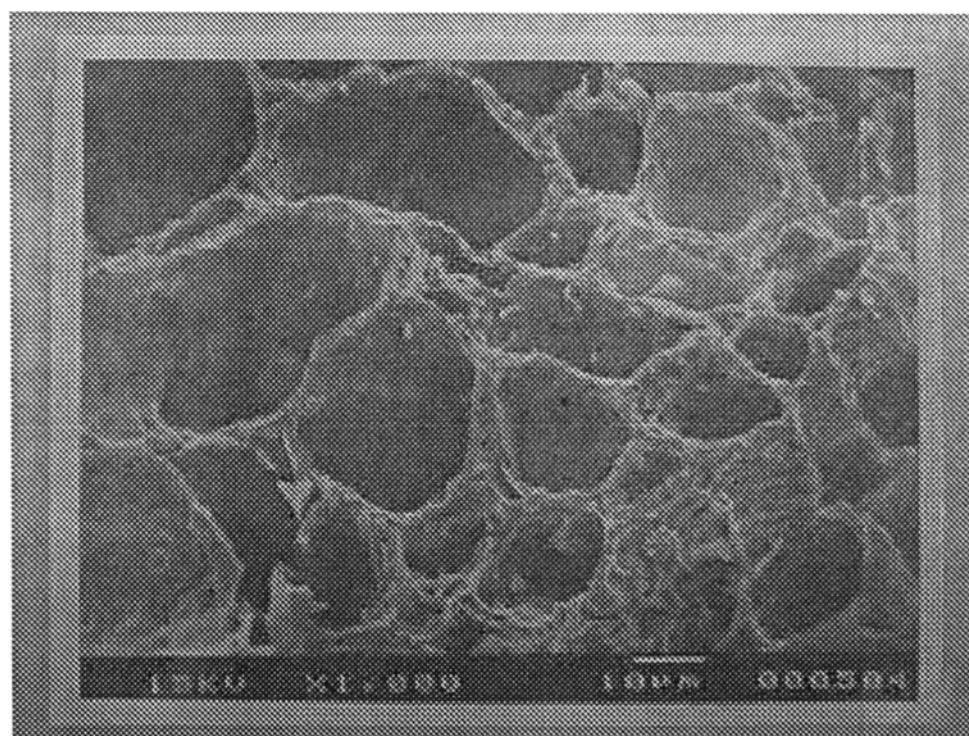


Figure 4.4: External surface of carbon adsorbent which activated with 20% phosphoric acid

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Table 4.4: Particle density of prepared carbon adsorbents

<i>reagent</i>	<i>sample weight</i> (g)	<i>column length</i> (cm)	ϵ	particle density (cm ³ /g)
H ₂ SO ₄	0.5837	10.4	0.2577	0.461
20% H ₃ PO ₄	0.6992	9.3	0.3477	0.458
50% H ₃ PO ₄	0.7342	12.3	0.3453	0.555
ZnCl ₂	0.3621	8.9	0.3171	0.363

results corresponded with equation 3.1. The porosity of the bed was determined from the intercept of the linear plot, as summarized in Table 4.4. Subsequently, the particle density could be determined from the bulk density, as summarized in Table 4.4.

4.2 First moment analysis

With chromatographic method, sample gas for adsorption experiments contained benzene vapor, toluene vapor and o-xylene vapor about 15.7%, 4.8% and 1.2% by volume, respectively.

4.2.1 Adsorption equilibrium constants

According to equation 2.14, the adsorption equilibrium constants were able to be determined from the slope of the plots of t_r versus L/v , which produced straight lines, as illustrated in Figure A.2.

Effects of activation temperatures

The adsorption equilibrium constant of corncob activated at temperature 150°C was the highest although the process provided the smallest specific surface area, as summarized in Table 4.1. The results demonstrated that the equilibrium constant did not correspond with the specific surface area.

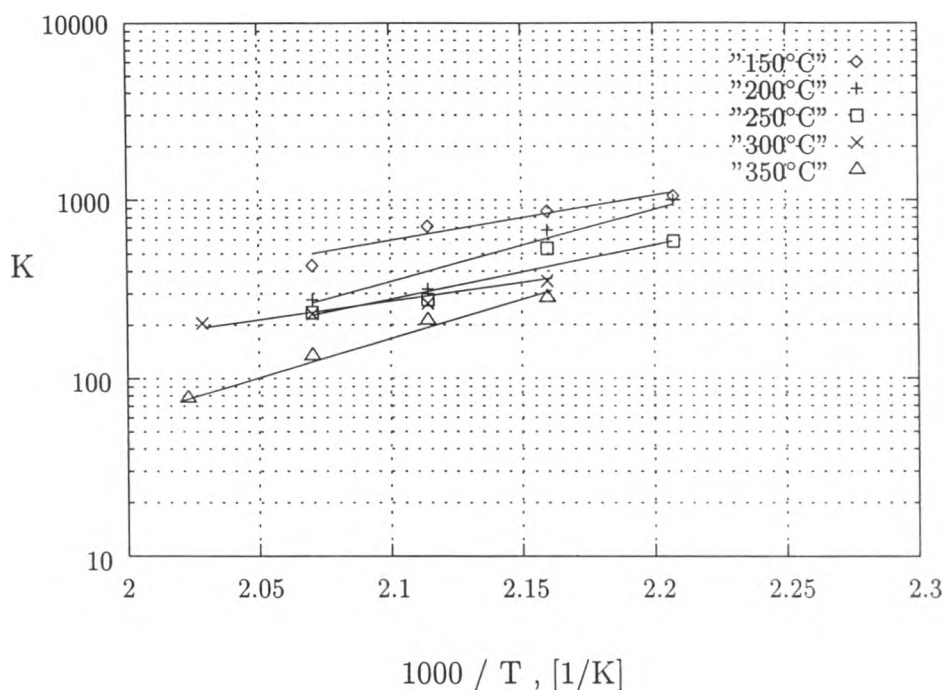


Figure 4.7: Adsorption equilibrium constants of toluene vapor on carbon adsorbents from corncob activated with sulfuric acid at various temperatures

Effect of chemical reagent

The adsorption equilibrium constants of toluene vapor on all carbon adsorbents at temperature of 150°C-210°C were shown in Figure 4.8. In comparison with activating reagents, the equilibrium constant corresponded with the specific surface area, based on nitrogen adsorption. While the equilibrium constant did not agree with the specific surface area when they were compared with the effects of the concentration of phosphoric acid. Carbon adsorbent activated with 50% H_3PO_4 , contained more fraction of phosphorous atoms than that with 20% H_3PO_4 which illustrated in Figure 4.9. The presence of phosphorous atoms might prevent toluene molecules from being adsorbed on the surface, we expected that 50% H_3PO_4 has more polarity so it adsorbed less toluene molecule, with little polarity, than 20% H_3PO_4 . Consequently, the equilibrium constant for the former was lower than that for the latter.

For adsorption of benzene vapor, the adsorption equilibrium constants on all carbon adsorbents corresponded with the specific surface area. In addition, the

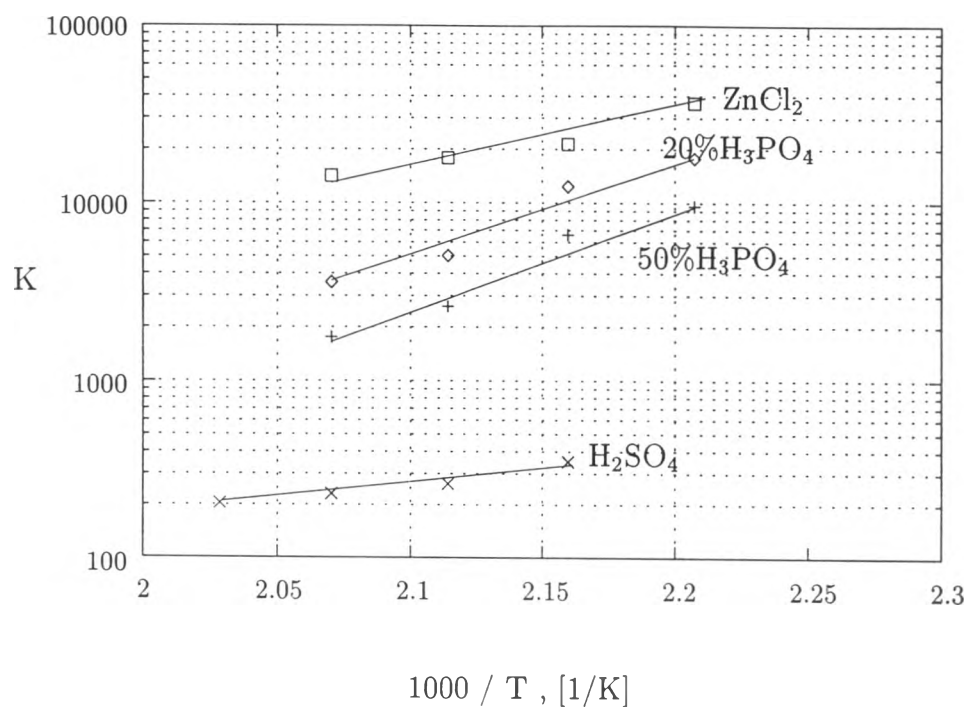


Figure 4.8: Adsorption equilibrium constants of toluene vapor on various prepared carbon adsorbents from corncob

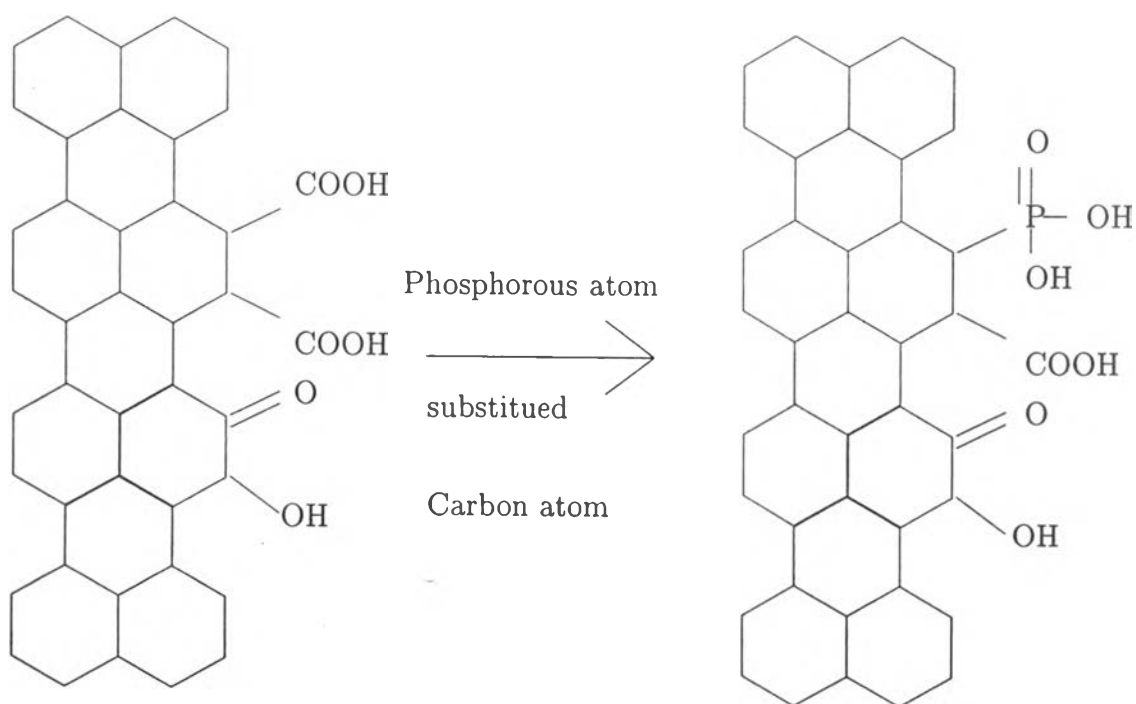


Figure 4.9: Open-type surface oxides on carbon surface when phosphorous atom substituted carbon atom

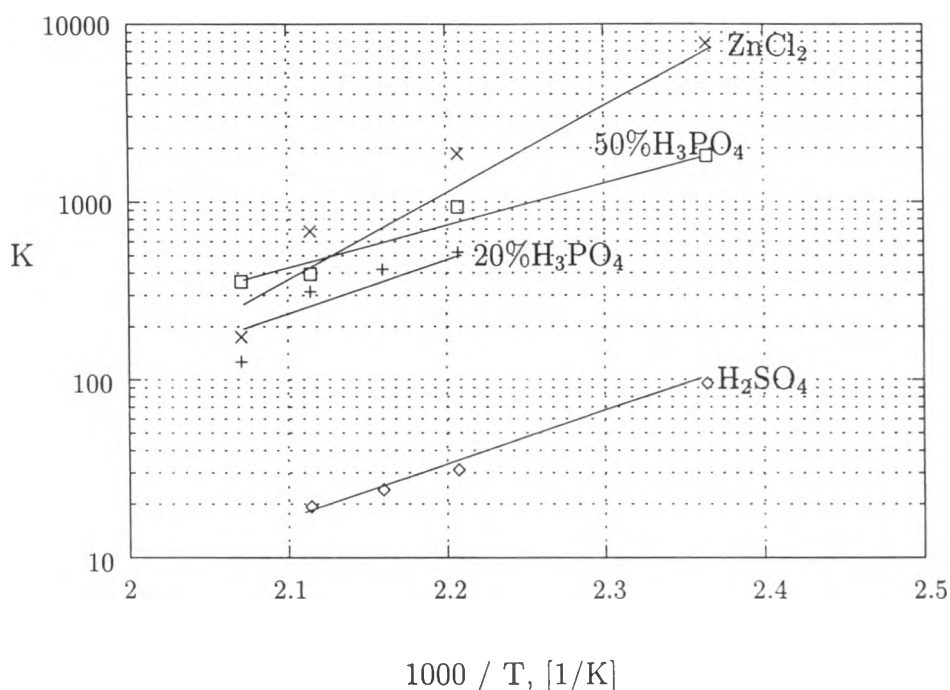


Figure 4.10: Adsorption equilibrium constants of benzene on various carbon adsorbents from corncob

presence of phosphorous atom did not affect adsorption of benzene vapor, which is non-polarity molecule. The results demonstrated the capability of activated corncob for each reagent in order to produce adsorption surface for benzene.

In contradistinction to the adsorption results of benzene and toluene, the equilibrium constant for o-xylene vapor on carbon adsorbents activated with zinc chloride was in between the adsorbents activated with other selected reagents as shown in Figure 4.11. The results suggest that the presence of phosphorous atoms might provide strong polarity of carbon adsorbent which prefer to adsorb polar adsorbate molecule such as o-xylene .

In comparison among the adsorbates, the adsorption equilibrium constant of benzene on each carbon adsorbent was the highest. While that of toluene was higher than that of o-xylene on the same adsorbents. The results demonstrated that the adsorbents produced from these reagents, contained non-polar surface and preferred adsorbing non-polar molecules to polar molecules as shown in Fig 4.12.

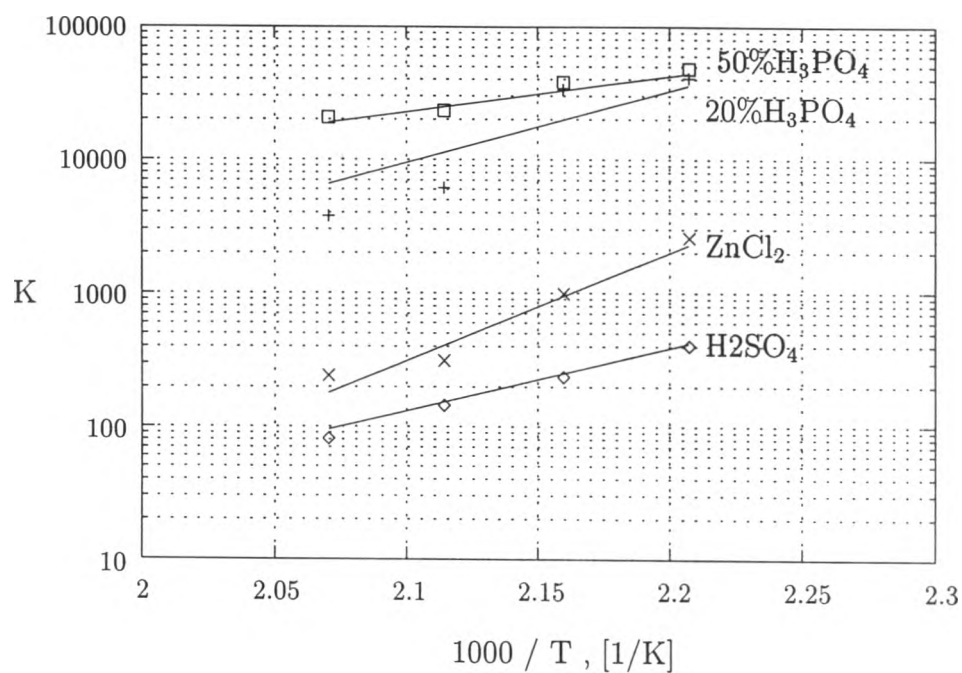


Figure 4.11: Adsorption equilibrium constants of o-xylene on various carbon adsorbents from corncob

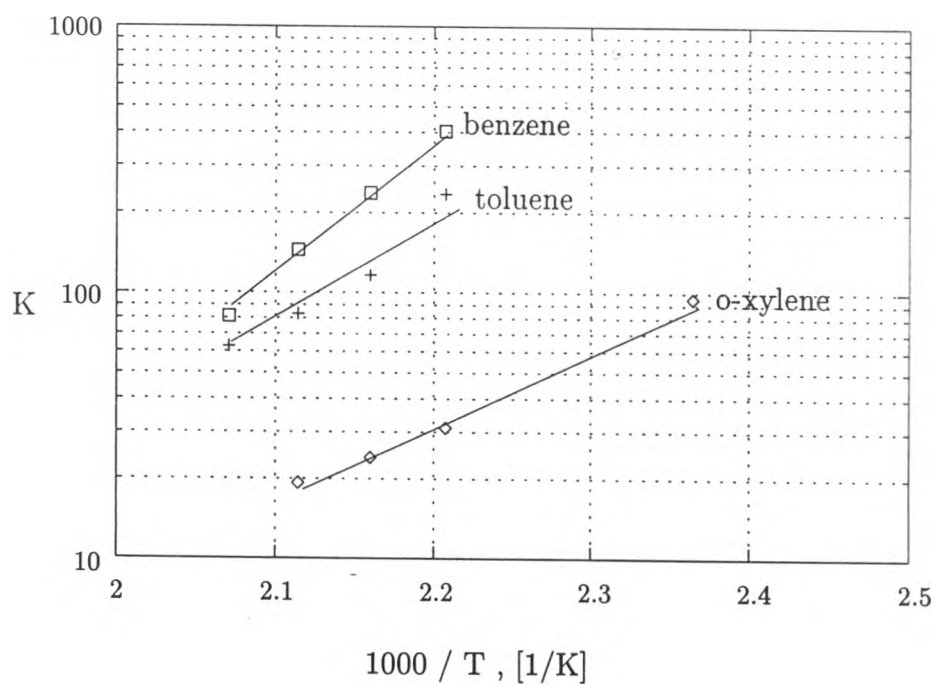


Figure 4.12: Adsorption equilibrium constants of benzene, toluene and o-xylene vapors on carbon adsorbent which activated with H₂SO₄

Table 4.5: Summary of heats of adsorption

<i>adsorbate</i>	<i>adsorbent</i>	ΔH , (kJ/mol)	other work
benzene	H ₂ SO ₄	54.09	
	50%H ₃ PO ₄	81.83	
	20%H ₃ PO ₄	48.39	
	ZnCl ₂	96.40	81.9 [34] 91.56 [7]
toluene	H ₂ SO ₄	33.58	
	50%H ₃ PO ₄	103.97	
	20%H ₃ PO ₄	109.85	
	ZnCl ₂	55.48	
o-xylene	H ₂ SO ₄	96.35	
	50%H ₃ PO ₄	160.63	
	20%H ₃ PO ₄	55.35	
	ZnCl ₂	151.15	

Table 4.6: Comparison the adsorption equilibrium constants of benzene (mol / g. Pa)

temperature (°C)	this experiment	other works
20	1.99×10^{-3}	2.77×10^{-3}
80	3.46×10^{-5}	4.71×10^{-5}
140	1.91×10^{-6}	1.99×10^{-6}
200	1.80×10^{-7}	2.00×10^{-7}

4.2.2 Heat of adsorption

The effects of temperature on the adsorption equilibrium constants corresponded with the van't Hoff equation (equation A.4). Consequently, the heat of adsorption was able to be determined from the slope of the corresponding linear plots, as shown in Figure A.3. The results were summarized in Table 4.5. In comparison with other works [7, 34], the heat of adsorption of benzene on corncob, activated with zinc chloride, was close to the results from other works, as shown in Table 4.6

In order to verify these indirectly measured adsorption equilibrium constants, the results were compared with the results of direct measurements with gravimet-

ric method. With the assumption of constant heat of adsorption, the equilibrium constants at low temperatures were able to be determined. The comparison results for the adsorption of benzene were shown in Table 4.6. The results were comparable.

4.3 Second moment analysis

4.3.1 Overall mass transfer coefficient

According to equation 2.16, the overall mass transfer coefficient were able to be determined from the intercept of linear plots. The results were summarized in Table 4.7.

Table 4.7: Mass transfer coefficient of aromatics on various adsorbents

<i>adsorbent</i>	<i>adsorbate</i>	T(°C)	$k_{overall}$	k_{ext}
H ₂ SO ₄	benzene	150	4.48×10^{-2}	1.19×10^3
		180	1.12×10^{-1}	9.81×10^2
		190	2.35×10^{-1}	9.78×10^2
		200	2.57×10^{-1}	9.96×10^2
	toluene	180	2.48×10^{-2}	1.19×10^3
		190	2.84×10^{-2}	8.52×10^2
		200	6.74×10^{-2}	8.47×10^2
		210	7.64×10^{-2}	8.80×10^2
	o-xylene	180	1.03×10^{-2}	9.10×10^2
		190	2.14×10^{-2}	9.77×10^2
		200	3.77×10^{-2}	8.53×10^2
		210	5.82×10^{-2}	8.62×10^2
20% H ₃ PO ₄	benzene	180	4.19×10^{-2}	1.08×10^3
		190	5.64×10^{-2}	1.07×10^3
		200	7.23×10^{-2}	1.32×10^3
		210	4.22×10^{-1}	1.18×10^3
	toluene	180	4.52×10^{-3}	1.33×10^3
		190	1.46×10^{-2}	1.45×10^3
		200	1.30×10^{-2}	1.26×10^3
		210	1.20×10^{-2}	1.20×10^3
	o-xylene	180	2.97×10^{-3}	1.25×10^3
		190	3.77×10^{-3}	1.38×10^3
		200	1.11×10^{-2}	1.29×10^3
		210	4.10×10^{-2}	1.34×10^3
50% H ₃ PO ₄	benzene	150	1.06×10^{-1}	1.17×10^3
		180	1.11×10^{-1}	1.38×10^3

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<i>adsorbent</i>	<i>adsorbate</i>	<i>T(°C)</i>	<i>k_{overall}</i>	<i>k_{ext}</i>	
		200	2.16×10^{-1}	1.15×10^3	
		210	2.96×10^{-1}	1.0×10^3	
	toluene	180	1.86×10^{-2}	1.12×10^3	
		190	2.80×10^{-2}	1.21×10^3	
		200	7.99×10^{-2}	1.22×10^3	
		210	5.54×10^{-2}	1.15×10^3	
	o-xylene	180	3.14×10^{-3}	1.19×10^3	
		190	6.43×10^{-3}	1.26×10^3	
		200	6.95×10^{-3}	1.28×10^3	
		210	5.45×10^{-3}	1.26×10^3	
	ZnCl ₂	benzene	150	4.60×10^{-2}	1.28×10^3
			180	1.64×10^{-1}	1.28×10^3
190			6.98×10^{-2}	1.30×10^3	
200			2.48×10^{-1}	9.41×10^3	
toluene		180	1.13×10^{-2}	1.11×10^3	
		190	1.67×10^{-2}	1.20×10^3	
		200	1.94×10^{-2}	1.20×10^3	
		210	3.03×10^{-2}	1.13×10^3	
o-xylene		180	6.60×10^{-3}	1.13×10^3	
		190	9.60×10^{-3}	1.16×10^3	
		200	2.85×10^{-2}	1.16×10^3	
		210	7.86×10^{-2}	1.18×10^3	

Since the overall mass transfer coefficient was a combined coefficient of the external mass transfer coefficient with the pore mass transfer coefficient, the external one could be determined from the correlation of Sherwood number (equation 2.5), as summarized in Table 4.7. The external coefficients were higher than the overall coefficients at least four order of magnitude. The results suggested that the rate of adsorption was controlled by the pore diffusion. The overall mass transfer coefficients increased as an increase in temperatures corresponded with Arrhenius's equation. Subsequently, the overall mass transfer coefficient may be considered as adsorption rate constant which is analogous with chemical reaction kinetics. In other words the adsorption of benzene, toluene and o-xylene vapor on carbon adsorbents may be considered as first order reversible reaction between vapors and corresponding carbon surface. The activation energy of adsorption can be determined from the slope of the plot of $\ln k$ vs. $1000/T$, as summarized in Table 4.8.

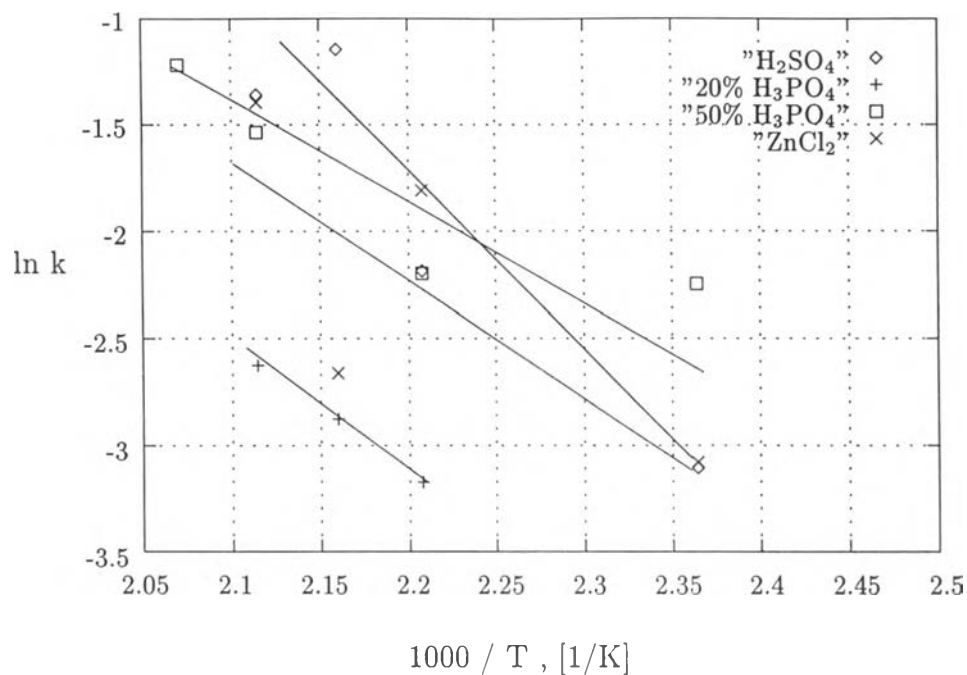


Figure 4.13: Overall mass transfer coefficient of benzene on various prepared adsorbents

4.3.2 Axial dispersion coefficient

Although an axial dispersion coefficient for each adsorption system could be determined from the slope of the linear plot according to equation 2.16, the result was much higher than the molecular diffusivity. That was a result of broad chromatogram even for a relatively short bed of adsorbents. Consequently, the obtained axial dispersion coefficients were not utilized.

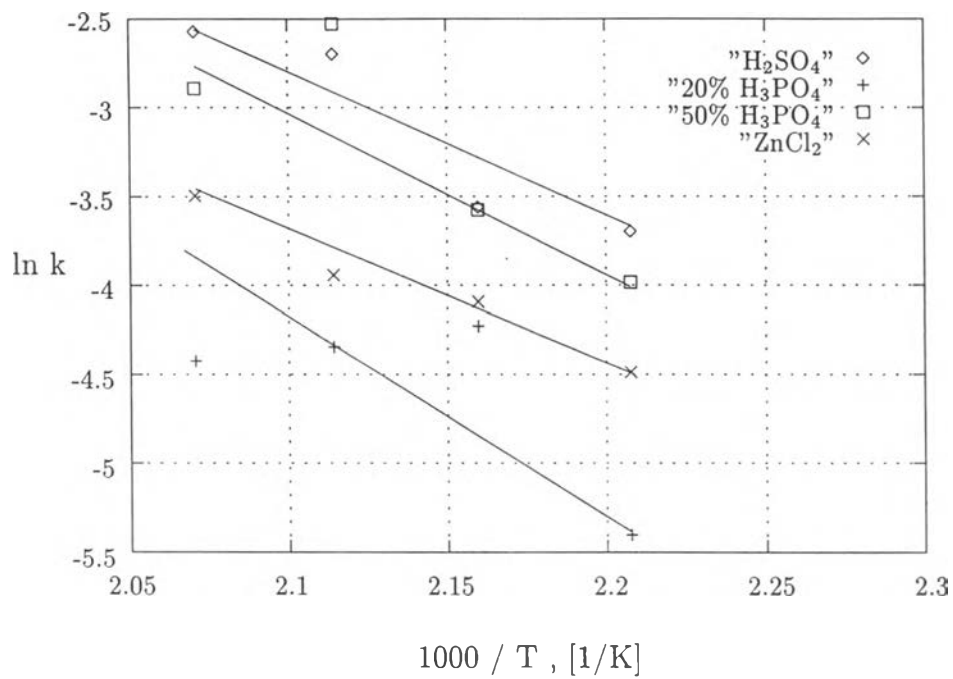


Figure 4.14: Overall mass transfer coefficient of toluene on various prepared adsorbents

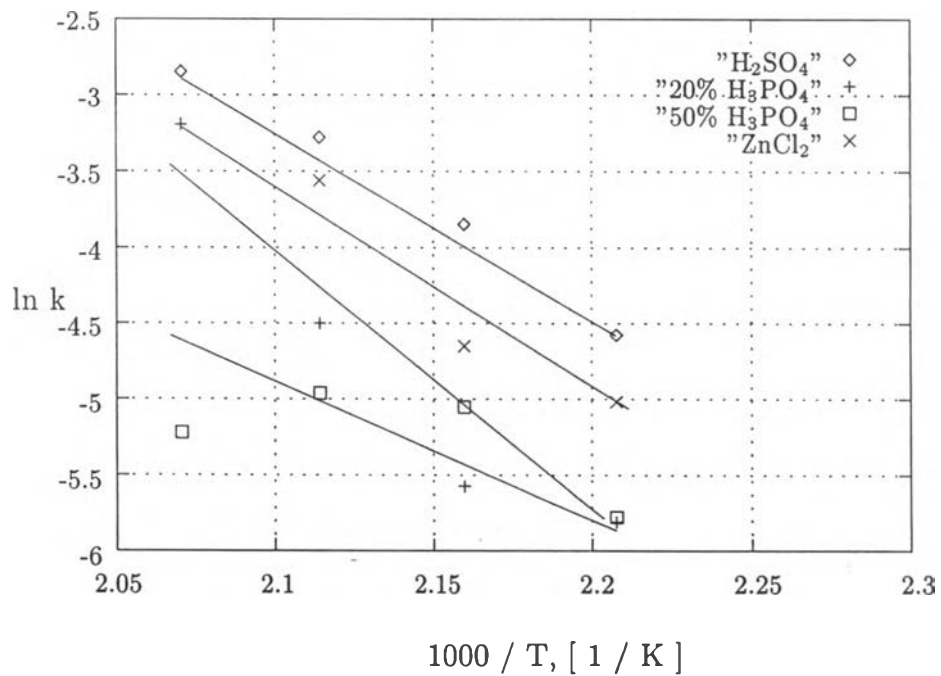


Figure 4.15: Overall mass transfer coefficient of o-xylene on various prepared adsorbents

Table 4.8: Summary of activation energy of adsorption

<i>adsorbate</i>	<i>adsorbent</i>	E_a , (kJ/mol)
benzene	H ₂ SO ₄	60.72
	50%H ₃ PO ₄	48.64
	20%H ₃ PO ₄	28.62
	ZnCl ₂	44.62
toluene	H ₂ SO ₄	77.03
	50%H ₃ PO ₄	52.38
	20%H ₃ PO ₄	79.20
	ZnCl ₂	56.74
o-xylene	H ₂ SO ₄	104.97
	50%H ₃ PO ₄	161.32
	20%H ₃ PO ₄	32.67
	ZnCl ₂	129.36