Chromatographic Study of Methanol Adsorption on Activated Carbon

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Introduction

Importnace of Adsorption Reaction

- Air pollution control
- Catalytic reaction
- Lots of gas-solid reaction in industrial processes

Experimental Method for Adsorption

- Packed bed experiment
- TGA experiment
- Measuring the partial pressure
- Chromatographic study

Some Features of Chromatographic Study

Advantage

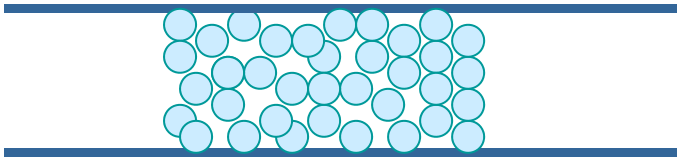
- Little Time to Experiment
- Easyness of Experimental Apparatus
- Quantitative Determination of Reaction Parameters
- Small Amount of Adsorbent
- Reusable of Adsorbent

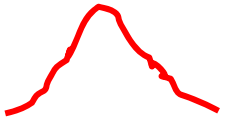
Disadvantage

- Limitation to the Region of Linear Adsorption
- Requirement of Physical Properties
  Surface area, Pore volume, Porosity,...

Concept of Chromatographic Study

Adsorbent Column





pulse input
C_o

Elution Curve
$C_e(t)$

Assumptions for the Chromatographic Study

- Isothermal Condition of Column
- Constant Void Fraction and Interstitial Velocity
- Linear Adsorption of Adsorbate
- Constant Size of Spherical Particle
- One Dimensional Dispersed Flow

Governing Equations of Packed Column

$$\frac{\partial C}{\partial t} = E_Z \frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - \frac{3D_e}{R}\frac{1-\varepsilon_b}{\varepsilon_b}\left(\frac{\partial c_i}{\partial r}\right)_R \qquad \text{Column}$$

$$\varepsilon_p \frac{\partial c_i}{\partial t} = D_e\left(\frac{\partial^2 c_i}{\partial r^2} + (2/r)\frac{\partial c_i}{\partial r}\right) - \rho_P \frac{\partial c_a}{\partial t} \qquad \text{Particle}$$

$$D_e\left(\frac{\partial c_i}{\partial t}\right)_R = k_f\left(C - (c_i)_R\right) \qquad \text{Diffusion rate}$$

$$\frac{\partial c_a}{\partial t} = k_a\left(c_i - \frac{c_a}{K_A}\right) \qquad \text{Adsorption rate}$$

$C = c_i = c_a = 0$ at t=0 $\qquad C = 0$ at $x = \infty$

$C = C_1(t)$ at x=0 $\qquad \frac{\partial c_i}{\partial r} = 0$ at $r = 0$

Definition of Moment

- Definition of n-th Moment

$$m_n = \int_0^\infty C_e(t) \cdot t^n dt$$

- n-th Absolute Moment

$$\mu_n = m_n / m_0 = \frac{\int_0^\infty C_e \cdot t^n dt}{\int_0^\infty C_e dt}$$

- n-th Central Moment

$$\mu_n' = \frac{\int_0^\infty C_e \left(t - \mu_1\right)^n \cdot t^n dt}{\int_0^\infty C_e dt}$$

Moment Analysis of Elution Curve of Pulse Input

$$\mu_1 = (z/u)[1+\delta_0] + (\mu_1)_{pulse}$$

$$\mu_2' = \mu_2 - \mu_1^2 = (2z/u)[\delta_{ax} + \delta_f + \delta_d + \delta_{ad}]$$

$$\delta_0 = [(1-\varepsilon)/\varepsilon](\varepsilon_p + p_p k_a)$$

$$\delta_{ax} = \frac{Ez}{u^2}(1+\delta_0)^2 \qquad \delta_f = \frac{1-\varepsilon}{\varepsilon}\frac{R}{3k_f}(\varepsilon_p + \rho_p K_a)^2$$

$$\delta_{ad} = \frac{1-\varepsilon}{\varepsilon}\frac{\rho_p K_a^2}{k_a} \qquad \delta_d = \frac{1-\varepsilon}{\varepsilon}\frac{R}{15D_e}(\varepsilon_p + \rho_p K_a)^2$$

Table 1. Properties of Activated Carbon
(Calgon, BPL 4×10 granule)

True Density	2.0×10^3	$[kg/m^3]$
Particle Density	0.85×10^3	$[kg/m^3]$
Particle Porosity	0.63	
Surface Area(BET)	992	$[m^2/g]$
Particle Size	0.20 mm, 0.34mm, 0.93mm	
Total Pore volume	0.75×10^{-3}	$[m^3/kg]$

Table 2. Characteristics of Packed Column and Operating Conditions

Packed Length	[m]	0.07
Column I.D.	[m]	4.37×10^{-3}
Particle Size[m]		0.20, 0.34, 0.93
Sample Weight	[g]	0.50, 0.43 0.43
Column Porosity	[-]	0.48 0.52 0.51
Gas Flow Rate	[ml/min]	30, 50, 70, 90
Temperature	[°C]	70, 100, 130

Fig. 1 Typical Gas Chromatogram

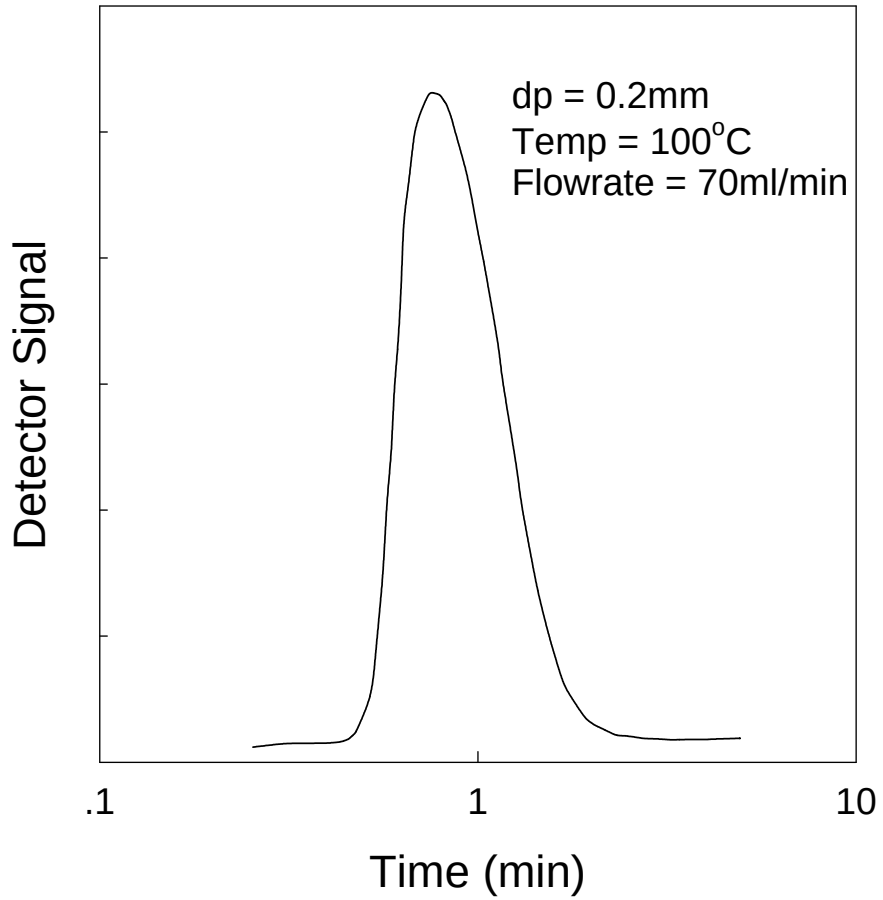


Fig. 2 Effect of the Injection Amount of CH_3OH on the Fisrt Absolute Moment

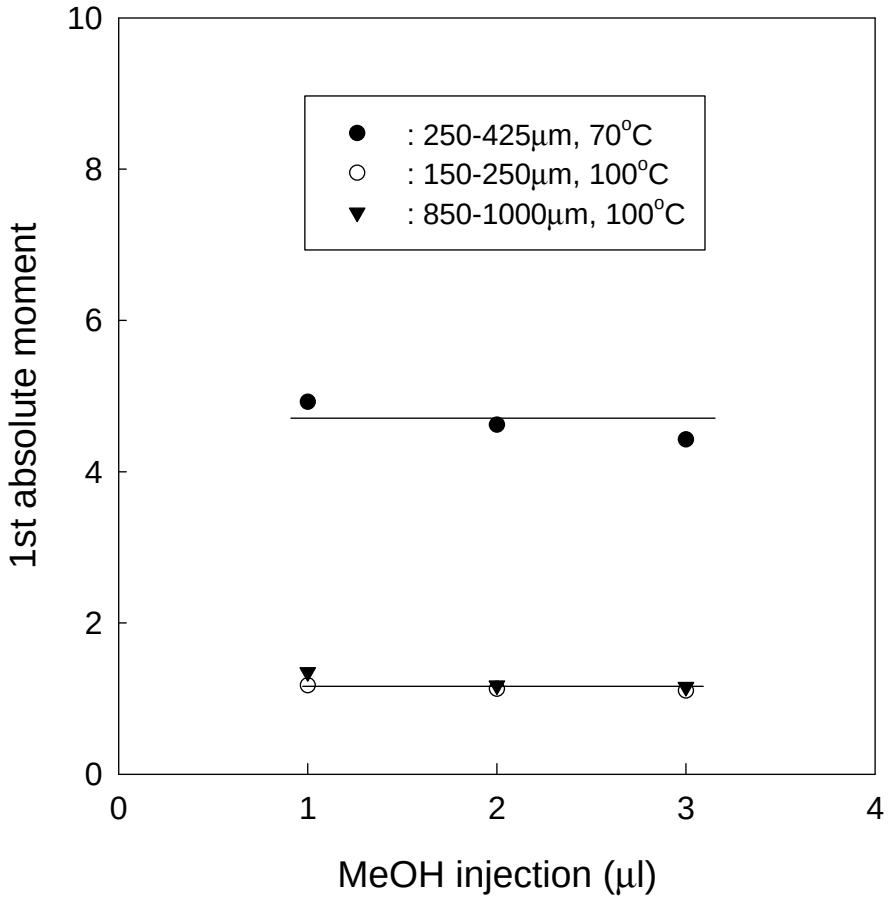


Fig. 3 Fisrt Absolute Moment of Methanol on Activated Carbon

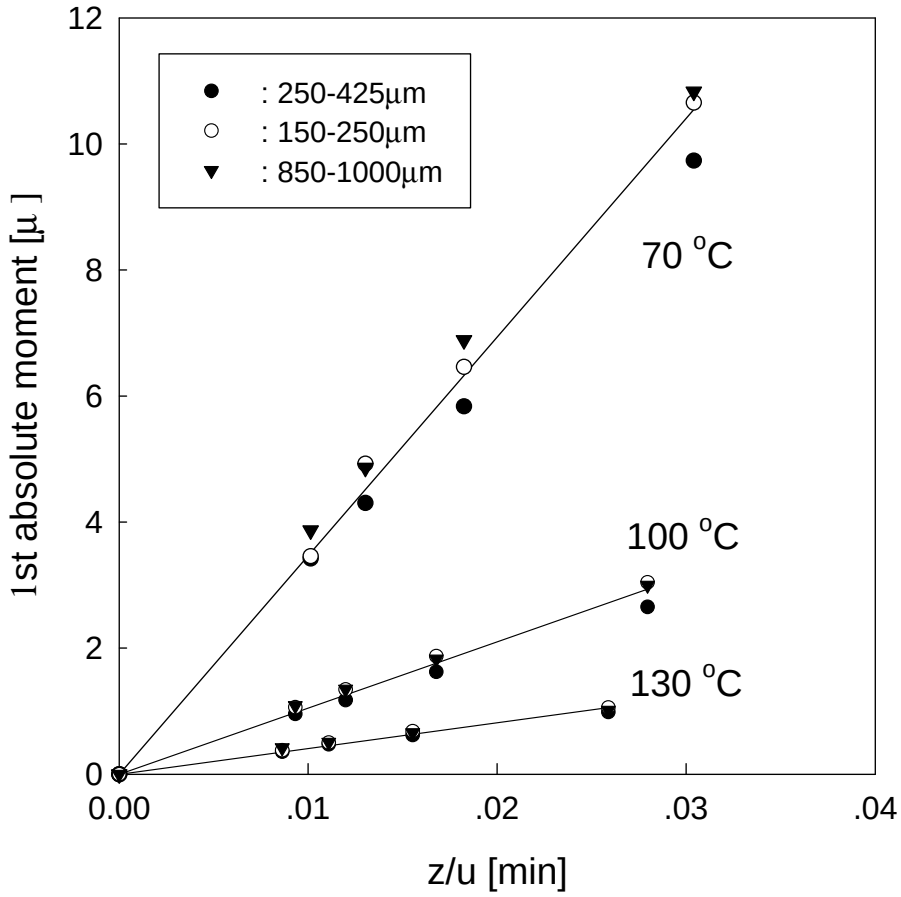


Fig. 4 Van't Hoff Plot of Adsorption Equilibrium Constant

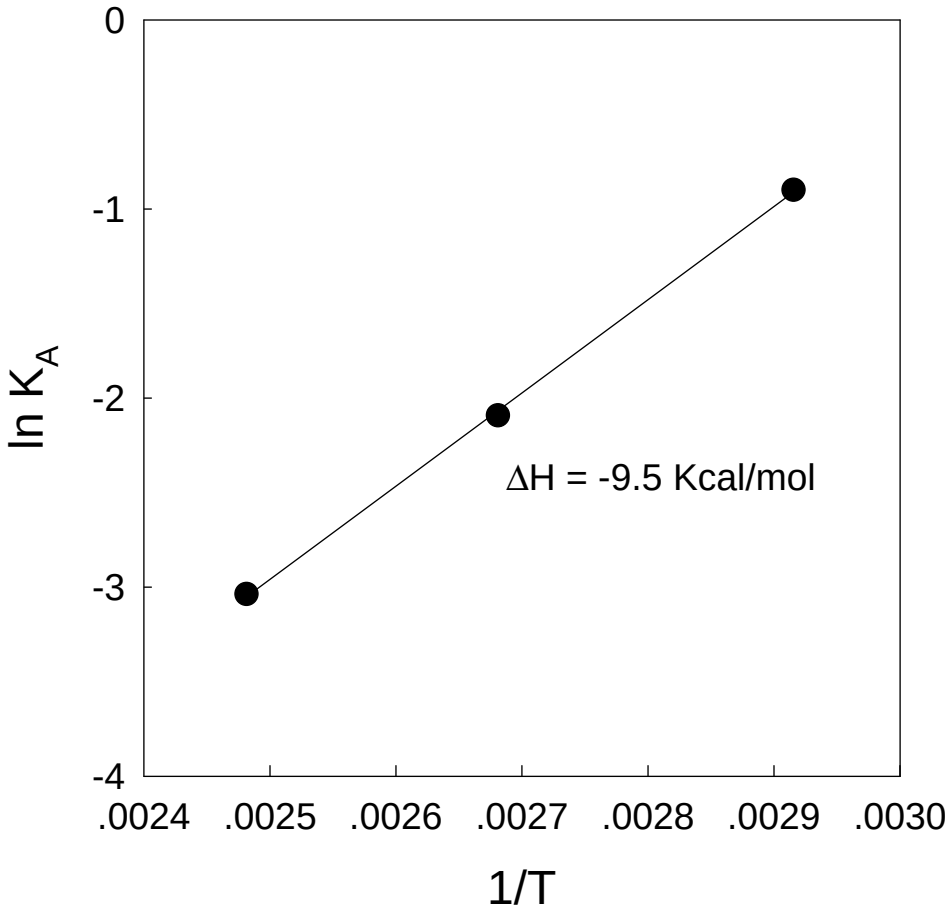


Fig. 5 Second Moment Plot of Methanol on Activated Carbon

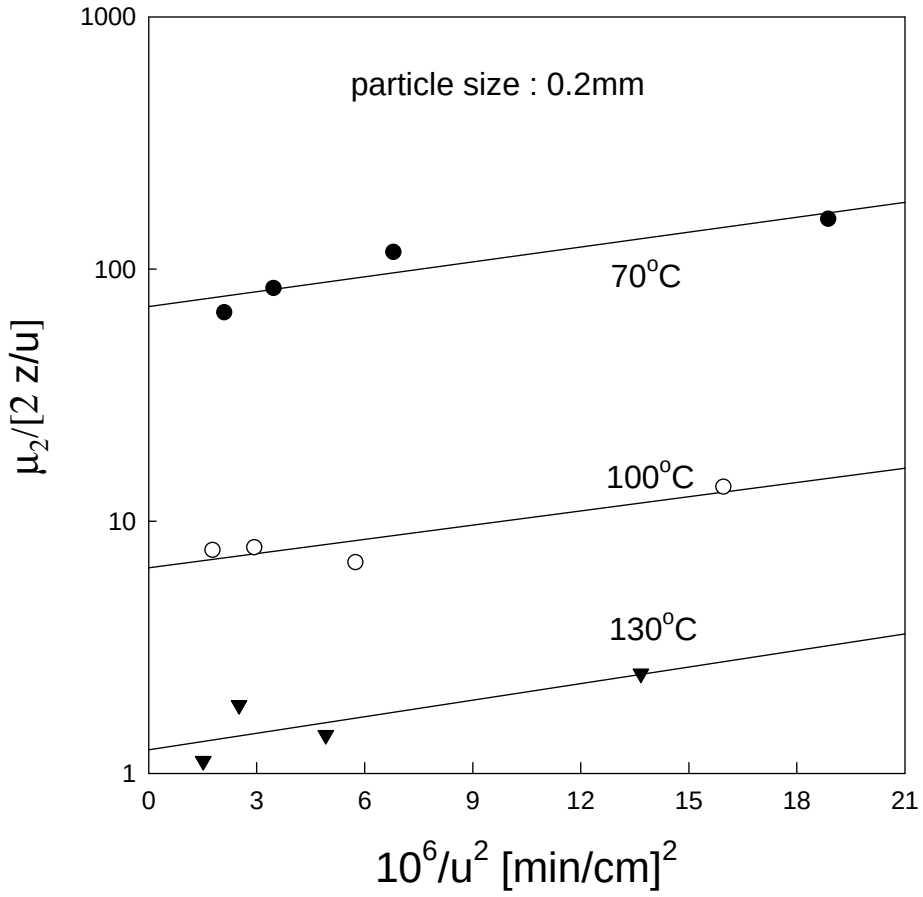


Fig. 6 Second Moment Plot of Methanol on Activated Carbon

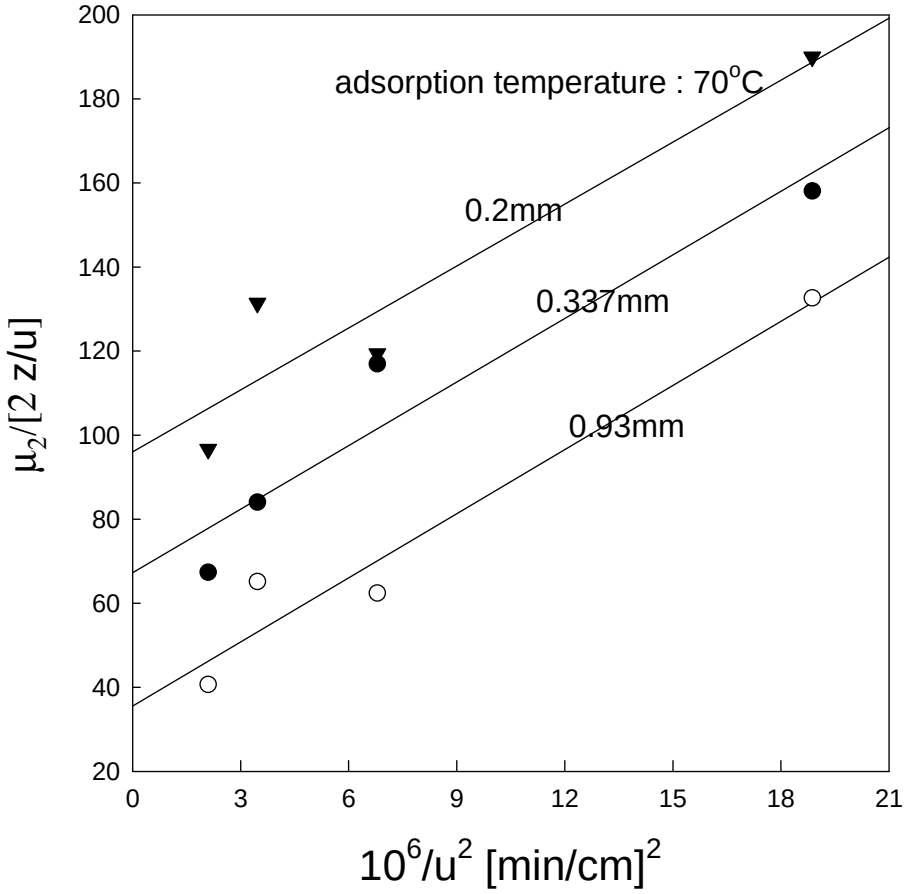


Table 3. Adsorption Equilibrium Constant For Methanol On Activated Carbon (BPL 4×10)

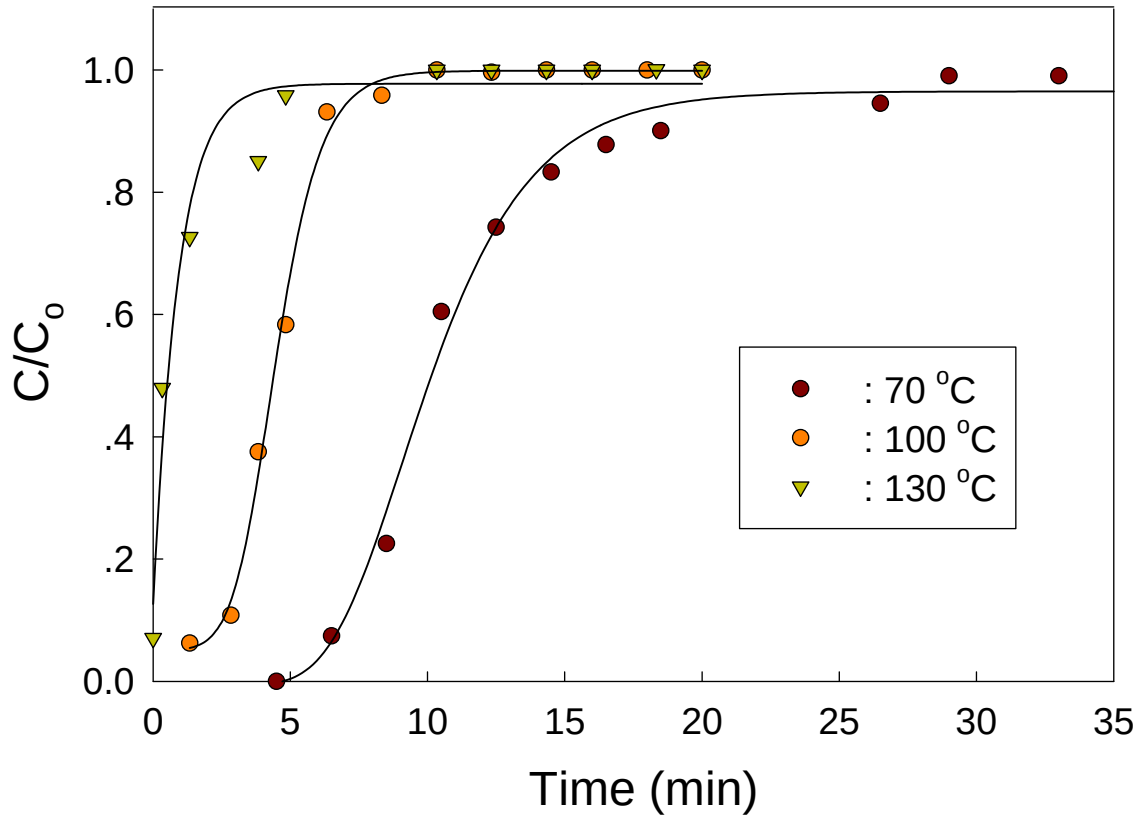
Temperature	[°C]	70	100	130
Equilibrium Constant (Moment)	[m^3/kg]	0.407	0.124	0.048
Equilibrium Constant (Packed)	[m^3/kg]	0.715	0.220	0.082

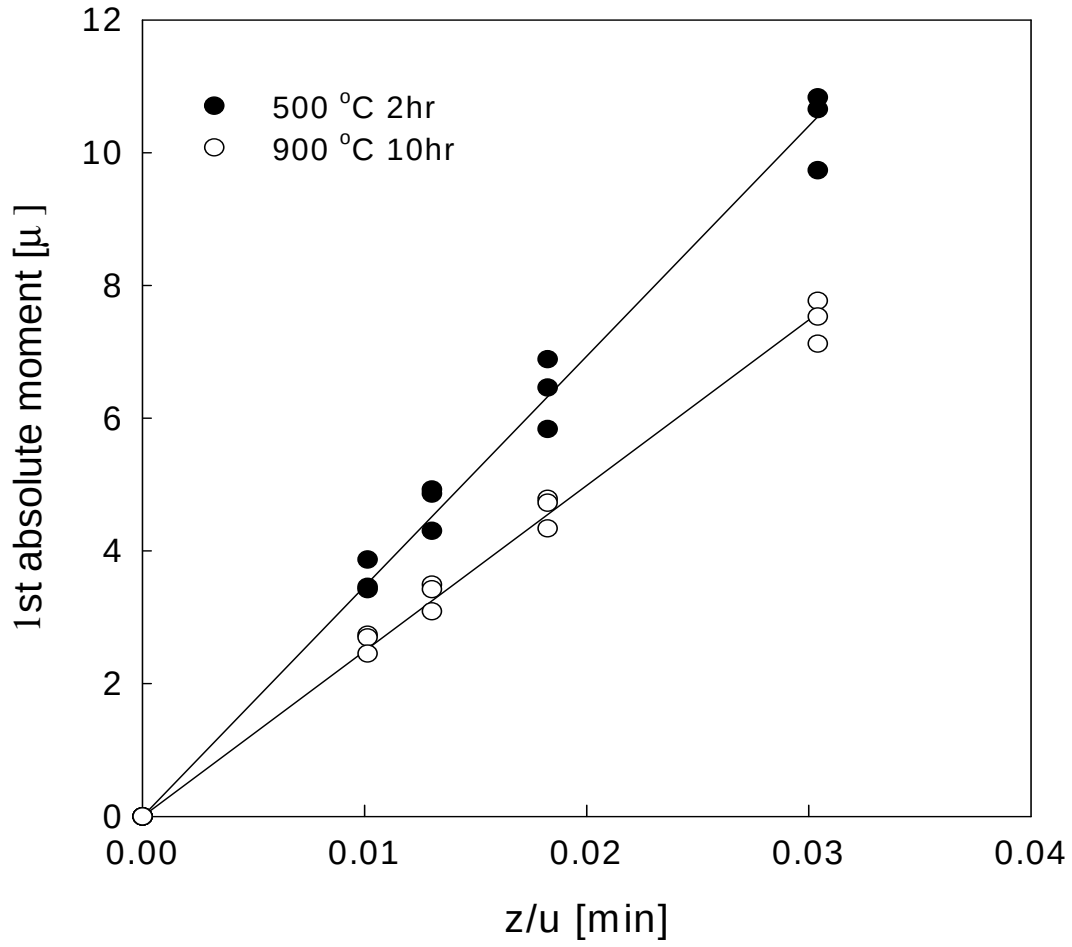
Table 4. Axial Dispersion Coefficient of MeOH On Activated Carbon (BPL 4×10)

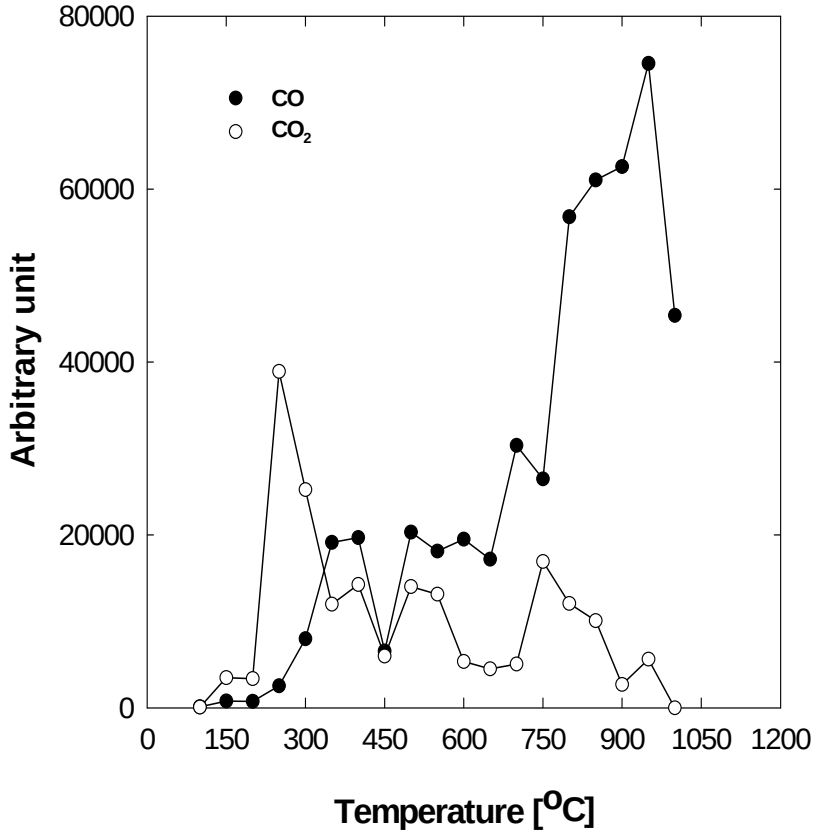
$\times 10^{-5}$ [cm^2/min]

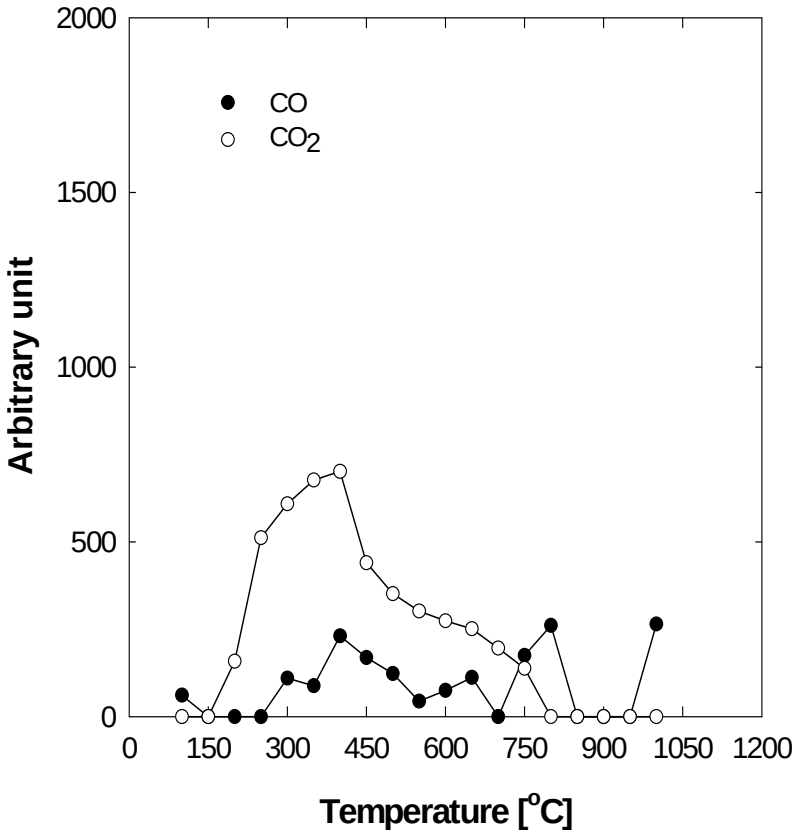
	0.2mm	0.34mm	0.93mm
70°C	1.77	2.55	1.91
100°C	1.62	2.72	3.17
130°C	1.12	0.99	-

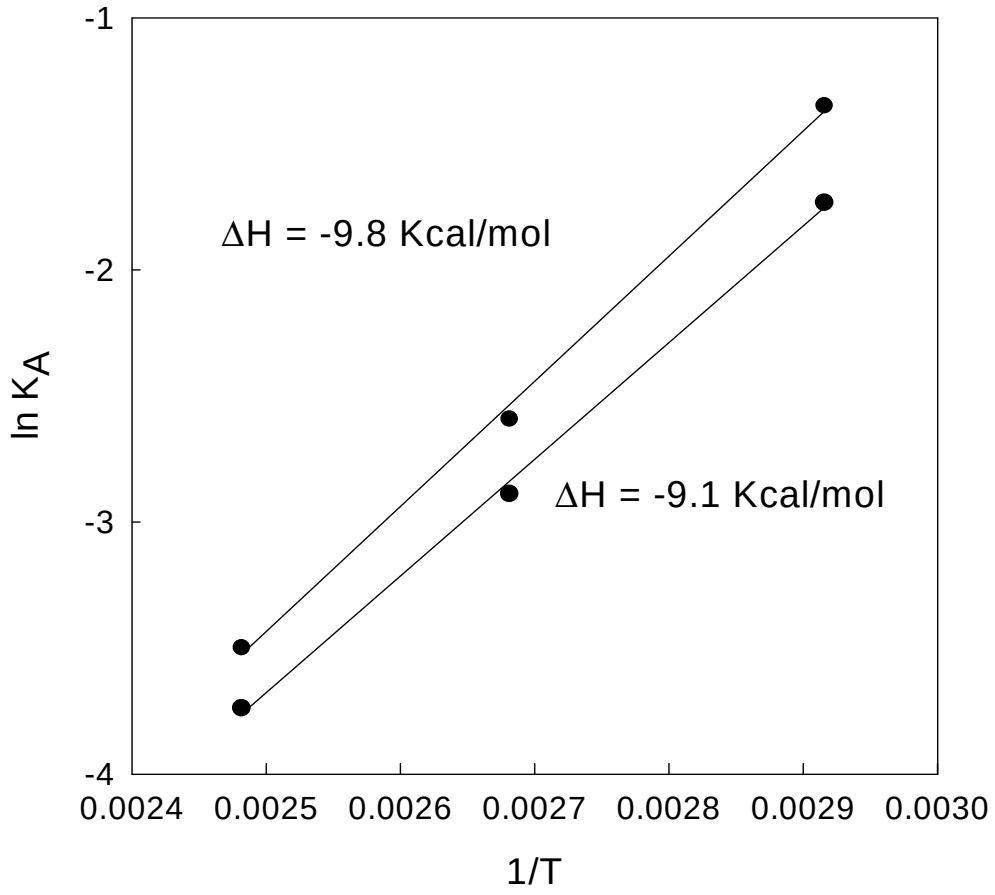
Fig. 6 Breakthrough Curves of MeOH over Activated Carbon

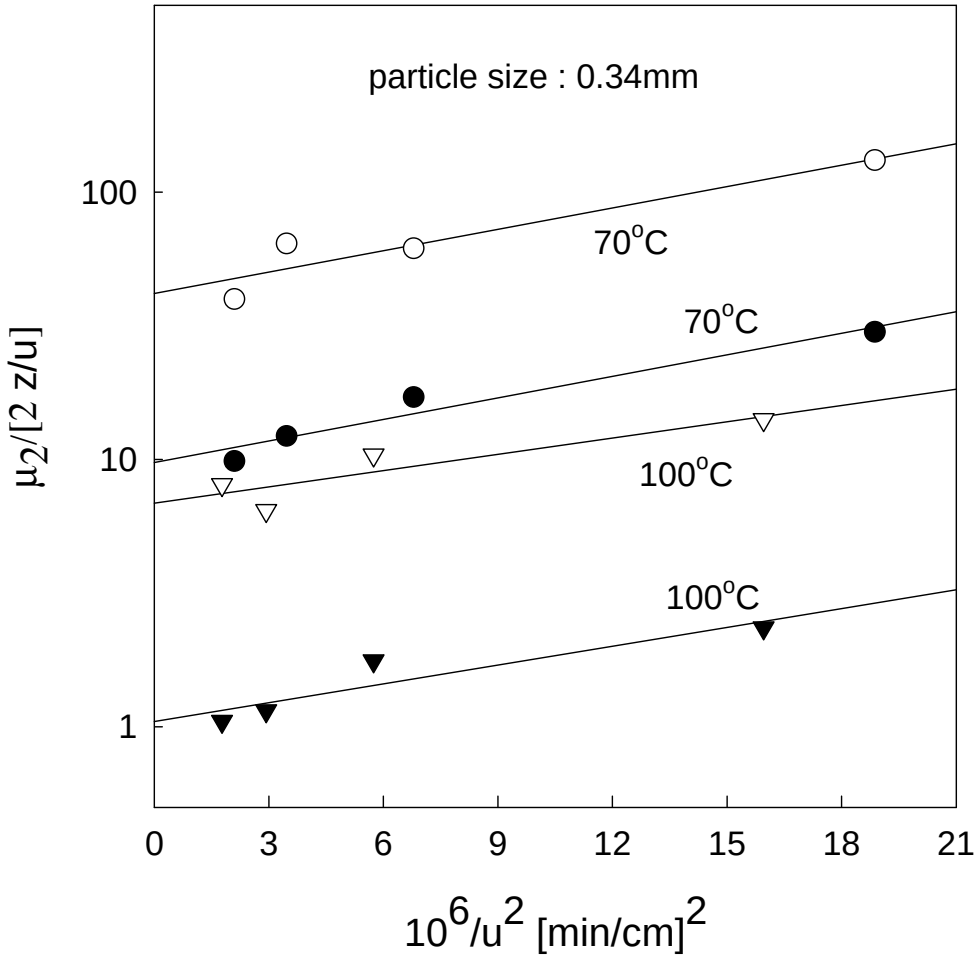


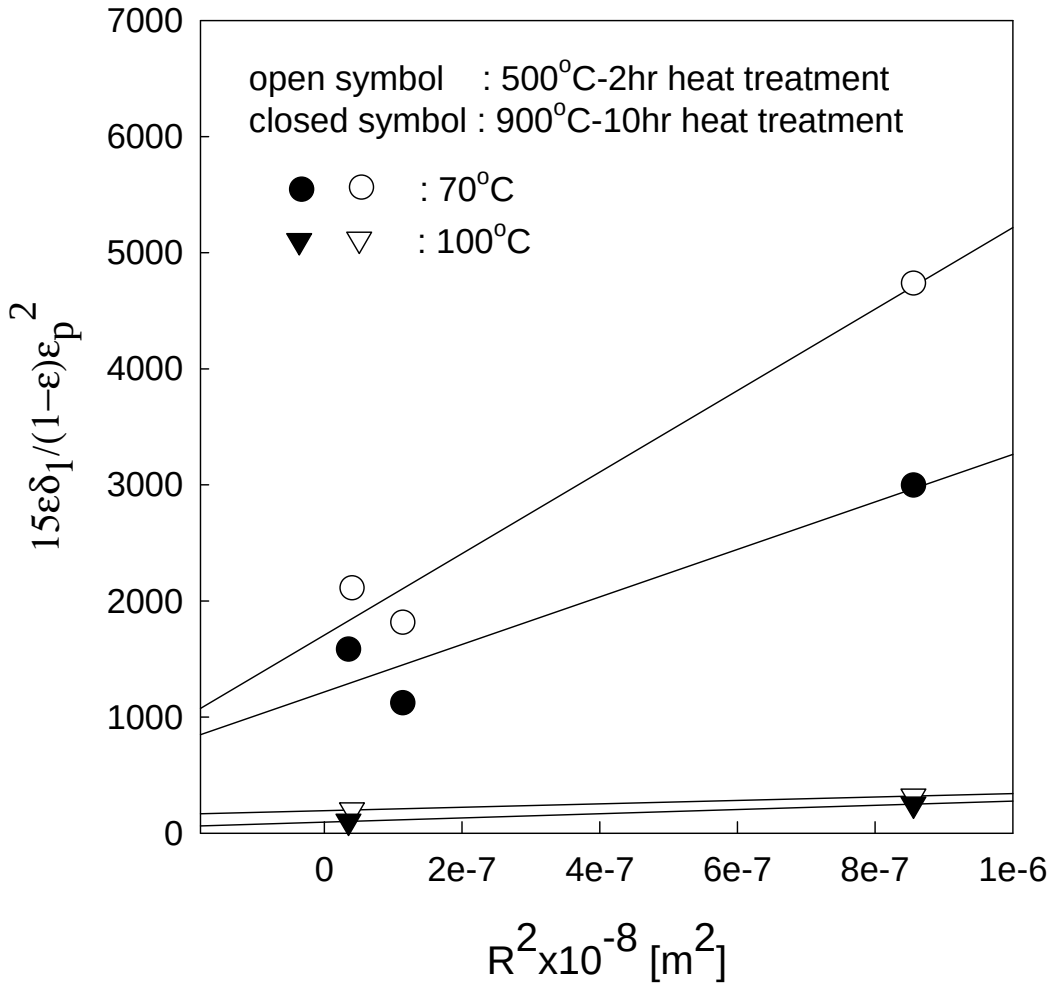

500 °C 2hr
900 °C 10hr
1st absolute moment [μ]
z/u [min]
0
2
4
6
8
10
12
0.00
0.01
0.02
0.03
0.04


80000
60000
40000
20000
0
Arbitrary unit
CO
CO2
0
150
300
450
600
750
900
1050
1200
Temperature [OC]


2000
1500
1000
500
0
Arbitrary unit
CO
CO2
0
150
300
450
600
750
900
1050
1200
Temperature [oC]


-1
-2
-3
-4
ln K_A
ΔH = -9.8 Kcal/mol
ΔH = -9.1 Kcal/mol
0.0024
0.0025
0.0026
0.0027
0.0028
0.0029
0.0030
1/T


particle size : 0.34mm
100
10
1
70°C
70°C
100°C
100°C
0
3
6
9
12
15
18
21
μ2/[2 z/u]
10^6/u^2 [min/cm]^2


open symbol : 500°C-2hr heat treatment
closed symbol : 900°C-10hr heat treatment
: 70°C
: 100°C
15εδ1/(1−ε)εp2
R2x10-8 [m2]
7000
6000
5000
4000
3000
2000
1000
0
0
2e-7
4e-7
6e-7
8e-7
1e-6

Summary of Diffusivities

Condition		Di/a^2 [s^{-1}]	$Da[m^2/s]$	D_{AB} [cm^2/s]
70 °C	500 – 2hr	0.0106	$1.152e^{-6}$	0.77
	900 – 10hr	0.0102	$3.288e^{-6}$	
100 °C	500 – 2hr	0.0198	$5.224e^{-6}$	0.88
	900 –10hr	0.0286	$4.182e^{-6}$	