REFERENCES

Bamrungket, M. (2001) Water removal from natural gas via clinoptilolite. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University.

Brosillon, S., Manero, M.H., and Foussard, J.N. (2001) Mass transfer in VOC adsorption on zeolite: experimental and theoretical breakthrough curves, Environmental Science and Technology, 35, 3571-3575.

Campbell, J.M. (1992) Gas Conditioning and Processing. Oklahoma: Campbell Petroleum.

Chahbani, M.H. and Tondeur, D. (2001) Pressure drop in fixed-bed adsorbers. Chemical Engineering, 81, 23-34.

Chaikasetpaiboon, P. (2002) Experimental and Mathematical Modeling of A Multi-Bed Gas Adsorber. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University.

Chua, H.T. (2002) Adsorption characteristics of silica Gel + water systems. Journal of Chemical and Engineering Data, 47, 1177-1187.

Cohen, A.P. (1992) Desiccants. Encyclopedia of Chemical Technology. 6, 1031-1053.

Howe-Grant, M. and Kroschwitz, J.I. (Eds.). (1992) Adsorption. Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed., 1, 493-521.

Howe-Grant, M. and Kroschwitz, J.I. (Eds.). (1992) Solid Desiccants. Kirk-Othmer Encyclopedia of Chemical Technology. 4th ed., 7, 1042-1050.

Keller II, G.E., Anderson, R.A., and Yon, C.M. (1987) Handbook of Separation Process Technology, 645-619.

Lertviriyakijskul, S. (2000) Charecterization of water and hydrocarbon adsorption properties of sol-gel alumina. M.S. Thesis, The Petroleum and Petrochemical College, Chulalongkorn University.

MaCabe, W.L., Smith, J.C., and Harriott, P. (1993) Unit operation of Chemical Engineering. Singapore: McGraw-Hill.

Ruthven, D. M. (1984) Principle of Adsorption and Adsorption Process. New York: Wiley.

Sánchez, J.R., Palermo A., and Aldao, C.M. (1996) Monte Carlo study of thermal desorption curves of water from zeolite type A. Langmuir, 12, 36-39.

Sherman, J.D. and Yon, C.M. (1992) Adsorption, Gas separation. Encyclopedia of Chemical Technology. 1, 529-569.

Speight, J.G. (1993) Gas Processing: Environmental Aspects and Methods. Oxford: Butterworth-Heinemann.

Suyadal, Y., Erol, M., and Oğuz, H. (2000) Deactivation model for the adsorption of trichloroethylene vapor on activated carbon bed. Industrial and Engineering Chemistry Research, 39, 724-730.

Thipkhunthod, P. (2001) Experimental and predictions of water and hydrocarbon adsorption on activated alumina prepared via sol-gel. World Congress of Chemical Engineering 6th. Melbourne.

Yang, R.T. (1987) Gas Adsorption by Adsorption Process. London: Butterworths.

Zwiebel, I. (1969) Fixed bed adsorption with variable gas velocity due to pressure drop. Industrial and Engineering Chemistry Research Fundamentals, 8, 803-807.

APPENDICES

Appendix A Bed void fraction of each adsorbent layer.

The fractional void in the packed column could be obtained from Figure A1.
The comparison of the bed voidages obtained by estimating from Figure A1 and
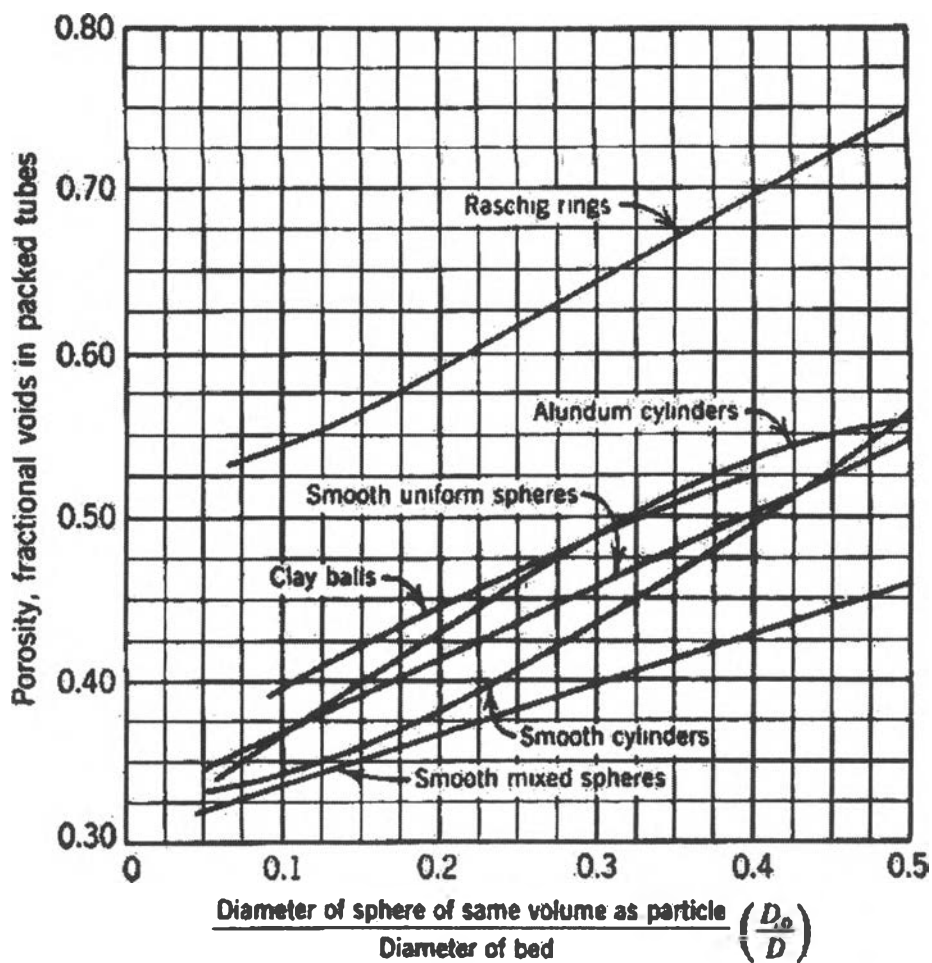determining by Chaikasetpaiboon et al. (2002) are shown in Table A1.

Figure A1 Porosity as a function of the ration of particle diameter to bed diameter
(Leva, 1947).

Table A1 The comparison of the bed voidage

	$\dfrac{D_0}{D}$ †	ε (Figure A1)	ε (Chaikasetpaiboon *et al.,2002*)
Silica gel	0.08	0.36	0.5994
Mol Siv 4A (1/8")	0.136	0.35	0.5081
Mol Siv 4A (1/16")	0.072	0.34	0.5337

†Bed diameter = 3.4 cm

Appendix B Calculations.

B.1 Axial dispersion coefficient

Dispersion in gaseous systems will occur when a concentration gradient exists in a packed bed and the turbulent diffusion due to the flow also contributes to the diffusive mass flux. The dispersion occurs in both radial and axial directions in the bed. The radial dispersion is not important when the ratio of bed-to-particle diameters is large. The dispersion coefficient is usually expressed terms of Peclet number ($Pe = 2R_p\mu/D_z\rho$), and:

$$\frac{1}{Pe} = \frac{1}{(Pe)_m} + \frac{1}{(Pe)_t} \tag{B1.}$$

where D_z is the axial dispersion coefficient, whereas $(Pe)_m$ and $(Pe)_t$ are the Peclet numbers for molecular and turbulent diffusion, respectively.

The Peclet numbers are correlated with Reynolds and Schmidt numbers. One of many empirical correlations has been suggested by Wen and Fan (1975):

$$\frac{1}{Pe} = \frac{0.3}{Re\,Sc} + \frac{1}{\left(1 + \dfrac{3.8}{Re\,Sc}\right)} \tag{B1.2}$$

for

$$0.008 < Re < 400 \quad \text{and} \quad 0.28 < Sc < 2.2$$

The molecular diffusion coeffient or bulk diffusion coefficient, D_m was determined from Chapman-Enskog equation.

$$D_m = 1.86 \times 10^{-3} T^{3/2} \frac{\left[(M_{w,A} + M_{w,B})/M_{w,A}M_{w,B}\right]^{1/2}}{p\sigma_{AB}^2\Omega_D} \tag{B1.2}$$

where

T =   absolute temperature

P	=	total pressure
$M_{w,A}$	=	average molecular weight of bulk species
$M_{w,B}$	=	molecular weight of adsorbate species
σ_{AB}	=	collision diameter from Lennard-Jones potential; and
Ω_{AB}	=	collision integral

B.2 Overall mass transfer coefficient

The overall mass transfer coefficient (k) was estimated by using the correlation, which was defined by Seader and Henley:

$$\frac{1}{kK} = \frac{D_P}{6k_f} + \frac{D_P^2}{60D_e} \qquad (B2.1)$$

where k_f is the mass transfer resistant of the adsorbate from the bulk fluid to the surface of the particle, which is called mass transfer film coefficient. It could be determined by Wakao-Funazkri correlation:

$$\frac{k_f D_P}{D_m} = 2 + 1.1 \left(\frac{D_P G}{\mu} \right)^{0.6} \left(\frac{\mu}{\rho D_m} \right)^{1/3} \qquad (B2.2)$$

The effective diffusivity, D_e can be obtained by:

$$\frac{1}{D_e} = \frac{\tau}{\varepsilon_P} \left(\frac{1}{D_m} + \frac{1}{D_k} \right) \qquad (B2.3)$$

where, τ is tortuosity factor. For straight, randomly oriented, and cylindrical pores, it may be approximated as $\tau = 3$ and 4 for 4A zeolite and silica gel, respectively (Yang, 1987). The intrapellet void fraction, ε_p for silica gel was 0.55 while for 4A zeolite was 0.48 (Howe-Grant, 1992). Knudsen diffusion coefficient, D_K is the diffusion coefficient related to mass transfer within a pore which occurs when the molecule in the fluid collide with the pore wall.

$$D_K = 9.7 \times 10^3 r_P \left(\frac{T}{M} \right)^{1/2} \qquad \text{(B2.4)}$$

where

r_p	=	mean pore radius (cm)
T	=	absolute temperature (K); and
M	=	molecular weight of diffusing species

Appendix C Comparison of humidity analyzers.

In the previous work (Chaikasetpaiboon, 2002), portable humidity analyzers, Cole Parmer Tri-Sense® Relative Humidity/Air Velocity/Temperature Meter, were used to measure the humidity level of the gas stream at the entrance and exit of the adsorber but those analyzers are not sensitive at low relative humidity. Therefore, a new humidity analyzer, CERMET II hygrometer (Michell Instruments Ltd.), was installed to be compared with the old analyzer.

The experiment was carried out to study the comparison of humidity analyzers with the constant feed flow rate was 130 ml/min, which was equivalent to the contact time of 34 seconds. The humidity level of the gas entering to the adsorber measured by the old analyzer was about 60%RH, but at the same line, the humidity level measured by CERMET II hygrometer was about 50%RH.
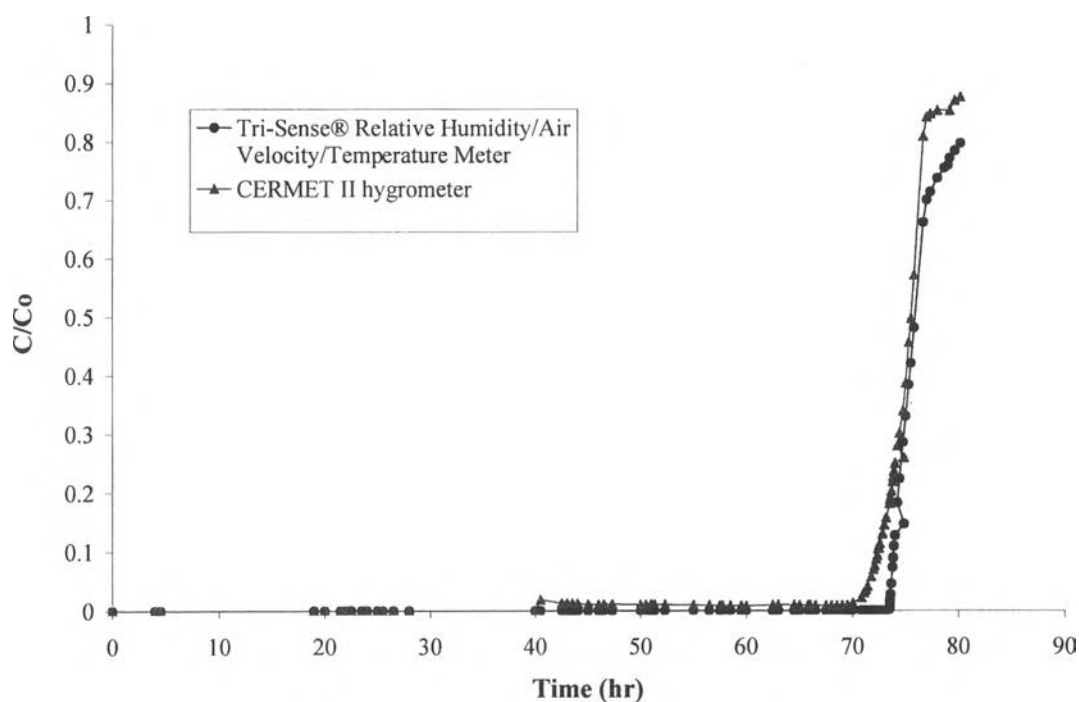
Figure C1   Comparison between CERMET II hygrometer(▲)and Tri-Sense® Relative Humidity/Air Velocity/Temperature Meter (◆): 50%RH and contact time 34 sec.

Two different breakthrough curves when comparing with the different analyzers are shown in Figure C1. The amount of time consumed for the outlet

water concentration to start appearing was about 70 hours and 73 hours for Tri-Sense® Relative Humidity/Air Velocity/Temperature Meter and CERMET II hygrometer, respectively. It was observed that CERMET II hygrometer was more sensitive than Tri-Sense® Relative Humidity/Air Velocity/Temperature Meter.

Appendix D Simulation program.

```fortran
      PROGRAM BREAKTHROUGH CURVE PREDICTION
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc
c                                                                    c
c       This program was developed for solving the sets of the mass  c
c       and adsorption equations in order to construct the theoretical c
c       breakthrough curves. The method of lines (MOLs) with central c
c       finite difference approximation and fourth-order Runge-Kutta  c
c       method were employed to solve the partial differential equations. c
c                                                                    c
cccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccccc

      IMPLICIT NONE
      DOUBLE PRECISION C0,C,q,dt,KC,Kq,time,Csat,RH
      DOUBLE PRECISION v1,v,e_A,e_B,e_C
      INTEGER i,j,imax,jmax,n
      PARAMETER(imax=90,jmax=5000)
      DIMENSION C(imax,jmax),q(imax,jmax),v(imax,jmax)
      DIMENSION KC(4,imax,jmax),Kq(4,imax,jmax)

c       ................INITIAL CONDITION................
      dt = 0.008
      time=0
      j=1                      !at time = 0
      RH = 30
      Csat=1.2794E-03
      C0 = RH*Csat/100         !inlet concentration (mol/l)
      C(1,j)=C0
      v1= 0.25322091           ! Superficial velocity
      e_A=0.37
      e_B=0.35
      e_C=0.34
      v(1,j)=v1/e_A

      OPEN(5,file='velocity.dat')

      DO i=2,imax

         C(i,j)=0
         q(i,j)=0

      END DO

      OPEN(1,file='data1.dat')

      DO i=1,imax
         WRITE(1,101)time,i,j,C(i,j),q(i,j),v(i,j)
      END DO

         Call RK4(j,C,q,v,imax,jmax,KC,Kq,dt)

      GOTO 20

10    OPEN(2,FILE='DATA2.DAT')

      DO i=2,imax

         READ(2,102)time,C(i,1),q(i,1),v(i,1),(KC(n,i,1),n=1,4)
     1   ,(Kq(n,i,1),n=1,4)

      END DO
```

```
20      DO j=2,jmax

            DO i=2,imax

                v(1,j)=v1/e_A

                C(1,j)=C0

                C(i,j)=C(i,j-1)+(dt/6)*(KC(1,i,j-1)+2*KC(2,i,j-1)
     1                  +2*KC(3,i,j-1)+KC(4,i,j-1))

                q(i,j)=q(i,j-1)+(dt/6)*(Kq(1,i,j-1)+2*Kq(2,i,j-1)
     1                  +2*Kq(3,i,j-1)+Kq(4,i,j-1))

            END DO

            Call RK4(j,C,q,v,imax,jmax,KC,Kq,dt)

        END DO


C       ..............The Results....................

        DO j=1,jmax

            time=time+dt        !sec

        END DO

        CLOSE(2)
        OPEN(2,file='data2.dat')
        DO i=2,imax

            WRITE(2,102)time,C(i,jmax),q(i,jmax),v(i,jmax)
     1      ,(KC(n,i,jmax),n=1,4),(Kq(n,i,jmax),n=1,4)

            WRITE(5,102)time,C(i,jmax),q(i,jmax),v(i,jmax)

            OPEN(3,file='30%&34sec(vnotconst).dat')
            IF(i.EQ.imax)THEN
                WRITE(3,102)time,C(i,jmax),q(i,jmax),v(i,jmax)
            ELSE
            END IF

        END DO

        CLOSE(2)
C       ...........Check Running Loop................................

        IF(time.LT.100) THEN
        GOTO 10
        ELSE
        GOTO 999
        END IF

C       .........Format for Input and Output Statements.......

101     FORMAT(F13.3,I3,I6,2E15.9,8E15.9)
102     FORMAT(F13.3,3E15.9,8E15.9)
999     STOP
        CLOSE(3)
        END


C       *******************************************************************
```

```
      SUBROUTINE RK4(j,C,q,v,imax,jmax,KC,Kq,dt)

      IMPLICIT NONE
      DOUBLE PRECISION CC,qq,C,q,dC_dt,dq_dt,dt,KC,Kq,v
      INTEGER i,j,imax,jmax
      DIMENSION C(imax,jmax),q(imax,jmax),dC_dt(imax,jmax)
      DIMENSION dq_dt(imax,jmax),KC(4,imax,jmax),Kq(4,imax,jmax)
      DIMENSION CC(imax,jmax),qq(imax,jmax),v(imax,jmax)

c     ..............Define Parameter.....................

      DO i=1,imax

         CC(i,j)=C(i,j)
         qq(i,j)=q(i,j)

      END DO

      Call ODEs_EQ(j,imax,jmax,CC,qq,dC_dt,dq_dt,v)

      DO i=2,imax

         KC(1,i,j)=dC_dt(i,j)
         Kq(1,i,j)=dq_dt(i,j)
         CC(i,j)=CC(i,j)+(dt/2)*KC(1,i,j)
         qq(i,j)=qq(i,j)+(dt/2)*Kq(1,i,j)

      END DO

         Call ODEs_EQ(j,imax,jmax,CC,qq,dC_dt,dq_dt,v)

      DO i=2,imax

         KC(2,i,j)=dC_dt(i,j)
         Kq(2,i,j)=dq_dt(i,j)

         CC(i,j)=CC(i,j)+(dt/2)*KC(2,i,j)
         qq(i,j)=qq(i,j)+(dt/2)*Kq(2,i,j)

      END DO

         Call ODEs_EQ(j,imax,jmax,CC,qq,dC_dt,dq_dt,v)

      DO i=2,imax

         KC(3,i,j)=dC_dt(i,j)
         Kq(3,i,j)=dq_dt(i,j)

         CC(i,j)=CC(i,j)+(dt)*KC(3,i,j)
         qq(i,j)=qq(i,j)+(dt)*Kq(3,i,j)

      END DO

         Call ODEs_EQ(j,imax,jmax,CC,qq,dC_dt,dq_dt,v)

      DO i=2,imax

         KC(4,i,j)=dC_dt(i,j)
         Kq(4,i,j)=dq_dt(i,j)

      END DO

      Return

      End
```

```fortran
c       ****************************************************************
        SUBROUTINE ODEs_EQ(j,imax,jmax,c,q,dC_dt,dq_dt,v)

        IMPLICIT NONE
        DOUBLE PRECISION c,q,dC_dt,dz,L,d2C_dz2,DL_A,v1,e_A,e_B,e_C,dq_dt
        DOUBLE PRECISION dC_dz,qstar,a1,b2,k1,db_A,db_B,db_C,a2,DL_B,DL_C
        DOUBLE PRECISION Csat,y1,y2,m1,m2,a3,b3,a4,a5,a6,n
        DOUBLE PRECISION v,dv_dz,Ct
        INTEGER i,j,imax,jmax
        DIMENSION C(imax,jmax),q(imax,jmax),dC_dt(imax,jmax)
        DIMENSION d2C_dz2(imax,jmax),dC_dz(imax,jmax),qstar(imax,jmax)
        DIMENSION dq_dt(imax,jmax),v(imax,jmax),dv_dz(imax,jmax)


c       ...............Define Parameter.....................

        L =8.8                      ! Total bed length
        dz = L/(imax-2)             ! Step size for length
        v1= 0.25322091             ! Superficial velocity
        Ct=0.040902639             ! P/RT

c       .........Parameter of Adsorber Zone-A (Silica gel)................

        db_A =0.74323242            ! Bulk density of adsorbent Zone-A
        DL_A=0.028249704            ! Axial dispersion through Zone-A
        e_A =0.36                   ! Void fraction of Zone-A

c       .........Parameter of Adsorber Zone-B (4ADG 1/8")...............

        db_B=0.656735544            ! Bulk density of adsorbent Zone-B
        DL_B=0.027733066            ! Axial dispersion through Zone-B
        e_B =0.35                   ! Void fraction of Zone-B

c       .........Parameter of Adsorber Zone-C (4ADG 1/16")...............

        db_C =0.656735544           ! Bulk density of adsorbent Zone-C
        DL_C=0.027170115            ! Axial dispersion through Zone-C
        e_C =0.34                   ! Void fraction of Zone-C

c       .......Adsorption Isotherm Constant Parameter.........
        k1 =1.004023607E-04*0.85    !Effective overall mass transfer coefici
ent

        j=j
c       ..........Zone-A (Silica gel)...............
        Csat=1.2794E-03
        a1=54.746/Csat              ! For Linear-Isotherm

        DO i=2,5

            qstar(i,j)=a1*C(i,j)

            dq_dt(i,j)=k1*(qstar(i,j)-q(i,j))

            d2C_dz2(i,j)=(1/(dz**2))*(C(i+1,j)-2*C(i,j)+C(i-1,j))

            dC_dz(i,j)=(1/(2*dz))*(C(i+1,j)-C(i-1,j))

            dv_dz(i,j)=-((1-e_A)/(e_A*Ct))*dq_dt(i,j)*db_A/1.8

            v(i,j)=dz*(dv_dz(i,j))+v(i-1,j)

            dC_dt(i,j)=DL_A*d2C_dz2(i,j)-v(i,j)*dC_dz(i,j)
1           -((1-e_A)/e_A)*dq_dt(i,j)*db_A/1.8-C(i,j)*dv_dz(i,j)

        END DO
```

```
C        ..........Zone-B (Mol Siv 1/8").................

         a2=3788.06620/Csat              !For Langmuir-Isotherm
         b2=203.58090/Csat

         y1=17.78440                     !For Exponential-Model
         a3=0.18400
         m1= 6.11160/Csat

         DO i=5,60

             If(C(i,j).GE.0.000255877) then

                qstar(i,j)=y1+a3*exp(m1*C(i,j))

             Else

                qstar(i,j)=(a2*C(i,j))/(1+b2*C(i,j))

             END If

             dq_dt(i,j)=k1*(qstar(i,j)-q(i,j))

             d2C_dz2(i,j)=(1/(dz**2))*(C(i+1,j)-2*C(i,j)+C(i-1,j))

             dC_dz(i,j)=(1/(2*dz))*(C(i+1,j)-C(i-1,j))

             dv_dz(i,j)=-((1-e_B)/(e_B*Ct))*dq_dt(i,j)*db_B/1.8

             v(5,j)=v(5,j)*e_A/e_B

             v(i,j)=dz*(dv_dz(i,j))+v(i-1,j)

             dC_dt(i,j)=DL_B*d2C_dz2(i,j)-v(i,j)*dC_dz(i,j)
     1       -((1-e_B)/e_B)*dq_dt(i,j)*db_B/1.8-C(i,j)*dv_dz(i,j)

         END DO
C        ..........Zone-C (Mol Siv 1/16").................

         a4=3568.01720/Csat              !For Langmuir-Isotherm
         b3=200.22690/Csat

         y2=16.98320                     !For Exponential-Model
         a5=0.0562
         m2= 8.2131/Csat

         a6=28.0116                      !For Freundlich-Model
         n= 0.1405


         DO i=61,89

             If(C(i,j).LE.4.4778559E-04) then

                qstar(i,j)=(a4*C(i,j))/(1+b3*C(i,j))

             Else
                If(C(i,j).GE.7.9322018E-04)then

                qstar(i,j)=a6*((C(i,j)/Csat)**n)

             Else

                qstar(i,j)=y2+a5*exp(m2*C(i,j))
```

```
       End If

     END If

     dq_dt(i,j)=k1*(qstar(i,j)-q(i,j))

     d2C_dz2(i,j)=(1/(dz**2))*(C(i+1,j)-2*C(i,j)+C(i-1,j))

     dC_dz(i,j)=(1/(2*dz))*(C(i+1,j)-C(i-1,j))

     dv_dz(i,j)=-((1-e_C)/(e_C*Ct))*dq_dt(i,j)*db_C/1.8

     v(i,j)=dz*(dv_dz(i,j))+v(i-1,j)

     v(60,j)=v(60,j)*e_B/e_C

     dC_dt(i,j)=DL_C*d2C_dz2(i,j)-v(i,j)*dC_dz(i,j)
1      -((1-e_C)/e_C)*dq_dt(i,j)*db_C/1.8-C(i,j)*dv_dz(i,j)

  END DO

  i=imax
     qstar(imax,j)=qstar(imax-1,j)

     dq_dt(imax,j)=dq_dt(imax-1,j)

     d2C_dz2(imax,j)=0

     dC_dz(imax,j)=0

     dC_dt(imax,j)=dC_dt(imax-1,j)

     dv_dz(imax,j)=dv_dz(imax-1,j)

     v(imax,j)=v(imax-1,j)

  Return

  End
```
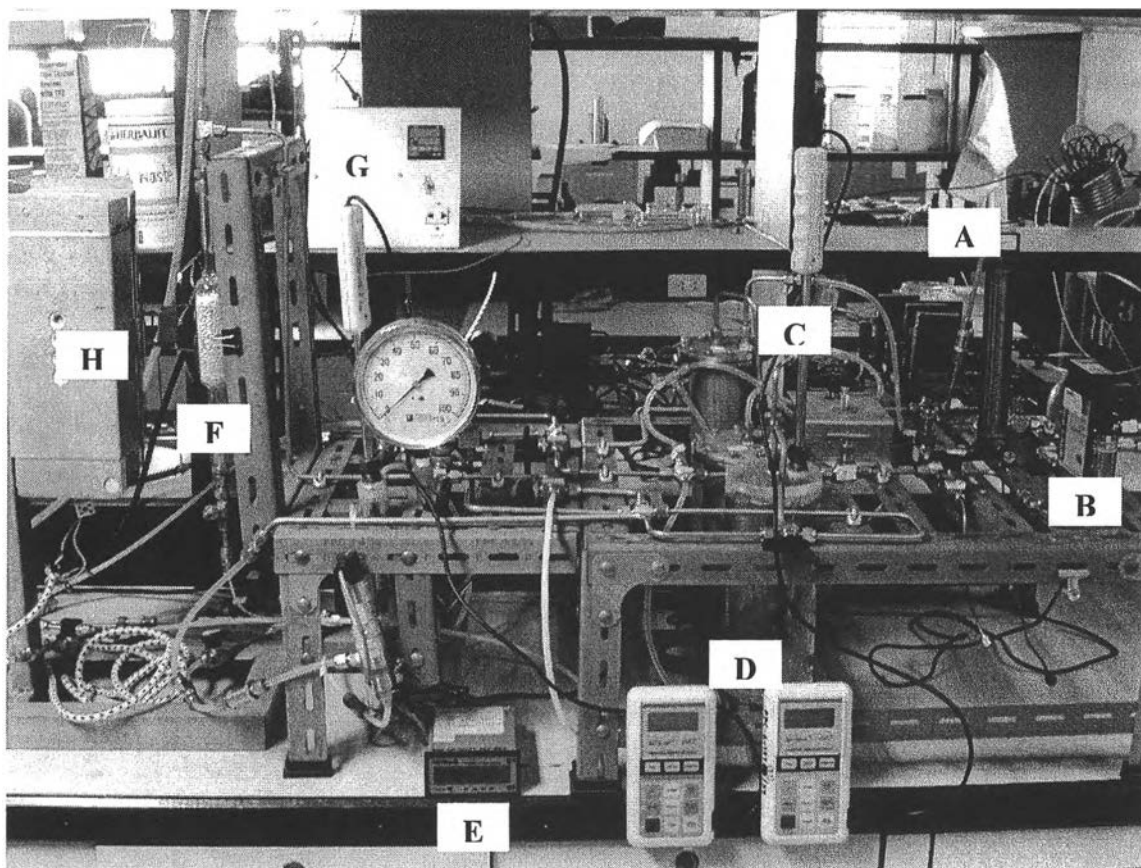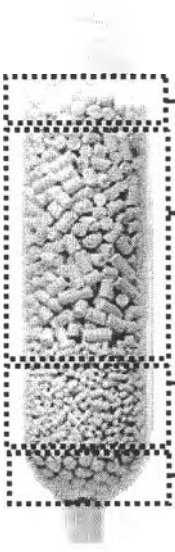
Appendix E Experimental setup.

Figure E1 Experimental Setup: A = Rotameter, B = Mass flow controller, C = Humidifiers, D = Humidifier analyzers (Parmer Tri-Sense® Relative Humidity/Air Velocity/Temperature Meter), E = Humidifier analyzer (CERMET II hygrometer) F = Adsorber, G = Temperature controller, H = Electric heater.

Appendix F Adsorber layout.

Table F1 Adsorber layout of the multi-layer adsorber used in the adsorption study

Adsorber Layout	Adsorbent Type	Height (cm)	Actual volume ratio[†] (%)
	Silica gel	0.4	4.3
	MolSiv (Zeolite) Type 4A with pellet size 1/8"	5.5	62.3
	MolSiv (zeolite) Type 4A with pellet size 1/16"	2.9	33.4
	Ceramic ball	*Inert material used as an adsorbent support	

Adsorber volume: 75 ml

[†] PTT Public Co.,Ltd.

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