Separation of n/iso-Paraffins by Adsorption Processes

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Abstract

The general objective of this work is to develop a conceptual tool for the separation of n/iso-paraffins using adsorption technology in view of the octane improvement of gasoline pools by the upgrading of light naphtha in petrochemical industry.

In chapter 1 the work performed in this area is reviewed since the development of synthetic zeolites by Union Carbide in the fifties. The 5A zeolite excludes branched paraffins and adsorbs linear paraffins.

Chapter 2 deals with the measurement of adsorption equilibrium isotherms of n-pentane and n-hexane (two of the major constituents of light naphtha) in pellets of 5A zeolite. A gravimetric apparatus using an electronic microbalance is developed. Isotherms of n-pentane and n-hexane were determined between 373 and 573K and up to 0.6 bar. The interpretation of equilibrium data is performed by the use of the "Multi-site-Langmuir" (MSL) adsorption model. The maximum adsorption capacity of n-paraffins is around 13g/100g_{zeo}. Heats of adsorption of n-pentane and n-hexane are 13.2 kcal/mol and 14.2 kcal/mol, respectively. Henry constants in the system 5A/n-pentane range from 0.28 g/g_{zeo} bar to 144 g/g_{zeo} bar between 573K and 373K, respectively. For the system 5A/n-
hexane the Henry constants range from 1.67 g/g\textsubscript{sat} bar to 14.36 g/g\textsubscript{sat} bar for the same temperature range.

Kinetics of sorption is studied in Chapter 3. A chromatographic ZLC (zero-length-column) apparatus is developed for the measurement of diffusivities in zeolite pellets. A ZLC model was developed to analyse kinetic data in such systems. The diffusivity data obtained for nC\textsubscript{4} and nC\textsubscript{6} showed that macropore diffusion is the controlling mechanism. The gravimetric apparatus is also used to study sorption kinetics and results agree with those from ZLC experiments. Between 473K and 573K pore diffusivities are 0.10 to 0.14 cm\textsuperscript{2}/s in the system He-nC\textsubscript{4}, 0.07 to 0.09 cm\textsuperscript{2}/s in the system N\textsubscript{2}-nC\textsubscript{6}, 0.11 to 0.13 cm\textsuperscript{2}/s in the system He-nC\textsubscript{6} and 0.06 to 0.08 cm\textsuperscript{2}/s in the system N\textsubscript{2}-nC\textsubscript{6}.

A mathematical model for the separation of n/iso-paraffins is developed in Chapter 4 based in equilibrium and kinetic data obtained in previous chapters. A fixed bed adsorption apparatus was developed; breakthrough curves with mixtures of n/iso-paraffins were measured and compared with the simulated ones. The effects of operating variables such as temperature, partial pressure of paraffins and flowrate are addressed between 448K and 573K and partial pressures of n-pentane and n-hexane up to 0.2 bar. Fundamentals of fixed bed adsorption of high concentrated solutions such as the effect of two linearly adsorbed species in presence on an inert are also studied in Chapter 4. It was found that roll-up can also appear in such systems.

A cyclic adsorption process for the separation based in Pressure Swing Adsorption (PSA) is studied in Chapter 5. A four step PSA cycle is implemented by the use of the mathematical model developed in Chapter 4. The effects of temperature, feed pressure and feed flowrate are studied using data of a patent assigned to IFP (Institut Français du Pétrole) where the unit operates at 573K with a high-pressure of 15 bar and low-pressure of 2 bar and total cycle time of 12min. The adsorbent productivity is 0.415 mol/min.kg\textsubscript{abs}.

Finally, a PSA laboratory unit was designed. The operating conditions of the laboratory unit are: temperature=573 K; high-pressure=5 bar, low-pressure=0.5 bar; adsorbent productivity= 0.351 mol/min.kg\textsubscript{abs}; cycle time=13 min. Experimental results obtained compare fairly well with the simulated ones. Also the implementation of a vacuum step increases the performance relatively to the cycle described by IFP.
These results show that the mathematical model developed is effective for the design and implementation of optimal operating conditions of adsorption units for the separation of n/iso-paraffins.
Resumo

O objectivo principal deste trabalho é o desenvolvimento de uma estratégia experimental e teórica para a separação de parafinas normais e ramificadas usando adsorção, com vista ao aumento do índice de octano das correntes de nafta leve na indústria petroquímica.

No Capítulo 1 resume-se o trabalho desenvolvido nesta área desde a descoberta da síntese de zeólitos pela Union Carbide nos anos 50. O zeolito 5A exclui parafinas ramificadas adsorvendo selectivamente parafinas normais.

O Capítulo 2 trata da medida de isotérmicas de equilíbrio de adsorção do n-pentano e n-hexano (dois dos maiores constituintes das correntes de nafta leve) em pellets de zeolito 5A. Desenvolve-se um equipamento gravimétrico usando uma microbalança electrónica. Determinam-se isotérmicas de adsorção entre 373 e 573K e até pressões parciais de 0.6 bar. Os dados de equilíbrio foram interpretados por um modelo denominado "Multi-site Langmuir" (MSL model). A capacidade máxima de parafinas normais é da ordem de 13g/100g Zoe. Os calores de adsorção do n-pentano e n-hexano são de 13.2 kcal/mol e 14.2 kcal/mol, respectivamente. As constantes de Henry no sistema 5A/n-pentano variam entre 0.28 g/g mol·bar até 144 g/g mol·bar entre 573 e 373 K, respectivamente. Para o sistema 5A/n-hexano as constantes de Henry variam entre 1.67 g/g mol·bar até 1436 g/g mol·bar para a mesma gama de temperatura.
No Capítulo 3 estudou-se a cinética de adsorção. Desenvolveu-se um equipamento cromatográfico para os estudos das difusividades em pellets de zeolito pela técnica ZLC (Zero-length column). Desenvolveu-se também um modelo matemático para o estudo da cinética em adsorventes bidispersos usando a técnica experimental ZLC. Os dados experimentais mostram que a difusividade nos macroporos é o mecanismo de difusão controlante para o n-pentano e n-hexano em pellets de zeolito 5A. O equipamento gravimétrico foi também usado para estudar a cinética de adsorção e os resultados são semelhantes aos da técnica ZLC. Entre 473 e 573 K a difusividade varia entre 0.10 e 0.14 cm²/s para o sistema hélio/n-pentano, entre 0.07 e 0.09 cm²/s no sistema azoto/n-pentano, entre 0.11 e 0.13 cm²/s no sistema hélio/n-hexano e entre 0.06 e 0.08 cm²/s no sistema azoto/n-hexano.

Um modelo matemático para a separação de parafinas normais e ramificadas foi desenvolvido no Capítulo 4 baseado nos dados de equilíbrio e cinética de adsorção. Um equipamento experimental para o estudo da dinâmica de adsorção em leito fixo foi também desenvolvido. Mediram-se “Breakthrough curves” com misturas de parafinas normais e ramificadas e compararam-se com as previstas pelo modelo. Estudaram-se os efeitos de variáveis operatórias como temperatura, pressão parcial de parafinas normais e caudal da alimentação entre 448 e 573 K e para pressões parciais de parafinas até 0.2 bar. Aspectos fundamentais da adsorção em leito fixo de misturas com altas concentrações de solutos foram também estudados no Capítulo 4, como por exemplo, o estudo do efeito da adsorção de dois componentes linearmente adsorvidos na presença dum inerte. Mostrou-se que o efeito de “Roll-up” pode também aparecer nestes sistemas.

No Capítulo 5 estudou-se um processo cíclico de adsorção baseado em “Pressure Swing Adsorption” (PSA) para a separação. O modelo matemático desenvolvido no Capítulo 4 serviu para implementar um ciclo PSA de quatro etapas. Os efeitos da temperatura, pressão da alimentação, fluxo da alimentação foram estudados usando dados experimentais de uma patente atribuída ao IPF “Institut Français du Pétrole” que descreve um sistema operando a 15 bar de pressão alta, 2 bar de pressão baixa, temperatura de 573 K e um tempo de ciclo de 12 min. A produtividade do adsorvente é de 0.415 mol/min·kg-m. Finalmente, desenvolveu-se uma unidade PSA no laboratório. As condições operatórias selecionadas foram: temperatura=568K; pressão alta = 5 bar; pressão baixa = 0.5 bar; produtividade do
adsorvente = 0.351 mol/min.kg; tempo de ciclo = 13 min. Os resultados experimentais obtidos são bem previstos pelo modelo. O ciclo desenvolvido no laboratório tem melhor desempenho que o ciclo descrito pelo IFP.

Estes resultados mostram que o modelo matemático desenvolvido ao longo deste trabalho, é efectivo para o estudo e implementação das condições operatórias óptimas das unidades de adsorção operando na separação de parafinas lineares e ramificadas por adsorção.
L’objectif de ce travail est le développement d’un outil conceptuel pour la séparation n/isoparaﬃnnes en utilisant la technologie d’adsorption, en vue de l’augmentation de l’indice d’octane de l’essence.

Dans le Chapitre 1 une revue du travail développé dans ce domaine est présenté à partir de l’introduction des zeolites synthétiques. Les zeolites 5A adsorbent les n-paraﬃnnes et excluent les iso-paraﬃnnes.

Dans le Chapitre 2 les mesures des isothermes d’adsorption du n-pentane et n-hexane sur pellets de zeolite 5A ont été décrites. La technique gravimétrique a été utilisée. Les isothermes entre 373 et 573 K et pressions jusqu’à 0.6 bar ont été décrites par le modèle MSL. La capacité maximale d’adsorption est de 13g/100g_\text{solv}_. Les chaleurs d’adsorption du n-pentane at du n-hexane sont 13.2 kcal/mol et 14.2 kcal/mol, respectivement. Les constantes de Henry pour le système n-pentane/zeolite 5A sont 0.28 g/g_\text{solv}_.bar et 144 g/g_\text{solv}_.bar entre 573 et 373 K, respectivement. Pour le système n-hexane/zeolite 5A les constantes de Henry sont 1.67 g/g_\text{solv}_.bar et 1436 g/g_\text{solv}_.bar pour les mêmes températures.

La cinétique d’adsorption a été étudiée au Chapitre 3. La technique ZLC a été utilisée pour la mesure de la diffusivité dans les particules de zeolite 5A. Un modèle a été développé pour
l’analyse des résultats. Entre 473 K et 573 K les diffusivités dans les pores sont 0.10-0.14 cm$^3$/s pour le système He-nC$_3$, 0.07-0.09 cm$^3$/s pour le système N$_2$-nC$_5$, 0.11-0.13 cm$^3$/s pour le système He-nC$_6$ et 0.06-0.08 cm$^3$/s pour le système N$_2$-nC$_8$.

Dans le Chapitre 4 un modèle pour la séparation n/iso-paraffines en lit fixe est décrit et vérifié expérimentalement. L’effet de conditions opératoires (T, pression partielle de nC$_3$, et nC$_8$ et débits) a été analysé. L’analyse théorique du comportement d’un lit fixe avec alimentation concentré et isothermes lineaires a été étudié.

La séparation par PSA a été l’objet du Chapitre 5. Un cycle à 4 étapes a été modelisé. Une unité expérimentale a été projetée et opérée à 573 K, P$_{in}$=5bar, P$_{out}$=0.5 bar et temps de cycle = 13 min. Les résultats expérimentaux sont bien prévus par le modèle et en accord avec les données du cas de base décrit dans le brevet de Minkkinen.

L’ensemble de la these supporté par modelization, simulation, et experimentation montre que les procédés d’adsorption sont efficaces pour la séparation n/iso-paraffines.
Agradecimentos

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List of Symbols

$A$  surface area of adsorbent, (m$^2$)

$A^{1-3}$  virial coefficients

$a_p$  specific area of the pellet, (m$^{-1}$)

$a_c$  specific area of column, (m$^{-1}$)

$b$  equilibrium parameter of linear isotherm, (mol/m$^3$)

$B_i$  adiabatic temperature rise for species i, ($=-\Delta H_{d,i}/C_{pi}T_i$)

$C_0$  initial concentration in the bulk fluid phase in the ZLC cell, (mol/m$^3$)

$C_{in}$  fluid phase concentration at the ZLC inlet, (mol/m$^3$)

$C_{out}$  fluid phase concentration at the ZLC outlet, (mol/m$^3$)

$C_p$  concentration of fluid phase in macropores, (mol/m$^3$)

$\tilde{C}_p$  dimensionless concentration of fluid phase in macropores, ($=C_p/C_0$)

$C_t$  total gas concentration in bed, (mol/m$^3$)

$C_{tf}$  total gas concentration of feed, (mol/m$^3$)

$\tilde{C}_t$  dimensionless total gas concentration, ($=C_t/C_{tf}$)

$c_{pg}$  heat capacity of gas, (J/mol.K)

$c_{ps}$  heat capacity of solid, (J/kg.K)

$D_{ax}$  axial mass dispersion coefficient, (m$^2$/s)

$D_c$  diffusivity in crystals, (m$^2$/s)

$D_p$  diffusivity in macropores, (m$^2$/s)

$D_{p,exp}$  measured (ZLC) diffusivity in macropores, (m$^2$/s)

$D_m$  molecular diffusivity, (m$^2$/s)

$D_K$  Knudsen diffusivity, (m$^2$/s)

$d_p$  pellet diameter, (m)
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tr>
<td>$F$</td>
<td>total molar flux, (mol/m$^2$.s)</td>
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<td>$F_f$</td>
<td>total molar flux of feed, (mol/m$^2$.s)</td>
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<tr>
<td>$F_H$</td>
<td>high-pressure feed molar flux, (mol/m$^2$.s)</td>
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<td>$F_L$</td>
<td>low-pressure feed molar flux, (mol/m$^2$.s)</td>
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<tr>
<td>$\bar{F}$</td>
<td>dimensionless molar flux, ($=F/F_f$)</td>
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<tr>
<td>$h_p$</td>
<td>film heat transfer coefficient, (W/m$^2$.K)</td>
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<tr>
<td>$h_w$</td>
<td>wall heat transfer coefficient, (W/m$^2$.K)</td>
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<tr>
<td>$\Delta H_i$</td>
<td>heat of adsorption of species i, (J/mol)</td>
</tr>
<tr>
<td>$H$</td>
<td>Henry's law constant, (kg/kg.atm)</td>
</tr>
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<td>$H_{ad}$</td>
<td>dimensionless Henry's law constant, ($=\rho_v RTH/M_w$)</td>
</tr>
<tr>
<td>$J_0(\beta_n)$</td>
<td>Bessel function of first kind and zero order</td>
</tr>
<tr>
<td>$J_1(\beta_n)$</td>
<td>Bessel function of first kind and first order</td>
</tr>
<tr>
<td>$k$</td>
<td>Boltzmann constant, (J/K)</td>
</tr>
<tr>
<td>$k_{\infty}$</td>
<td>pre- exponential factor, (kg/kg$_{ads}$-atm)</td>
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<tr>
<td>$K_{eq}$</td>
<td>equilibrium constant, ($\text{atm}^{-1}$)</td>
</tr>
<tr>
<td>$K_{eqi}$</td>
<td>equilibrium constant of species i, ($\text{atm}^{-1}$)</td>
</tr>
<tr>
<td>$k_e$</td>
<td>external film mass transfer coefficient, (m/s)</td>
</tr>
<tr>
<td>$K$</td>
<td>capacity factor ($=\left(1-c_p\right)H_{ad}/c_p$)</td>
</tr>
<tr>
<td>$K'$</td>
<td>ratio of equilibrium constants, ($=b_2/b_1$)</td>
</tr>
<tr>
<td>$K_{gl}$</td>
<td>global mass transfer coefficient, (m/s)</td>
</tr>
<tr>
<td>$k_i$</td>
<td>internal mass transfer coefficient, (m/s)</td>
</tr>
<tr>
<td>$K_{ax}$</td>
<td>effective axial bed thermal conductivity, (W/m.K)</td>
</tr>
<tr>
<td>$\ell$</td>
<td>length of ZLC cell, (m)</td>
</tr>
<tr>
<td>$L$</td>
<td>ZLC operating parameter, ($=\frac{1}{2} \text{Purge flow rate} \frac{R_p^2}{\text{P pellets Volume} \ \varepsilon_p D_p}$); Length of column, (m)</td>
</tr>
</tbody>
</table>
M          pressurisation rate, (s⁻¹)
M₀         amount of sorbate in the pellet at time zero, (mol)
Mₜ         amount of sorbate in the pellet at time t, (mol)
Mₘ         molecular mass of sorbate, (kg/mol)
n         number of active sites occupied by a molecule (MSL model)
nᵢ         number of active sites occupied by the molecule i (multicomponent MSL model)
nₙ         number of adsorbed molecules by unit area of adsorbent
Nₙₑf       number of film heat transfer units
            (=(1−εₜₐ)p, Lₜₐ/εₜₐνₜ, Cₜ, Cₚₑ)
Nₙₑw       number of wall heat transfer units
            (=a, Lₜₐ/εₜₐνₜ, Cₜ, Cₚₑ)
Nₙₑ         number of film mass transfer units,
            (=(1−εₜₐ)p, Lₜₐ, Kₚₑ, εₜₐν₂ₜ)
p         partial pressure of sorbate, (atm)
P         total pressure in the column, (atm)
Pₜ         high-pressure, (atm)
Pₜₙ         low-pressure, (atm)
Pe         particle mass Peclet number, (vᵢdₚ/Dₚₓ)
Peₜₙ       particle heat Peclet number, (CᵢₜCₚₑνᵢdₚ/Kₚₓ)
Peₙₑf      mass Peclet number for the column at feed conditions,
            (=vᵢL/Dₚₓ)
Peₙₑw      heat Peclet number for the column at feed conditions,
            (=CᵢₜCₚₑνᵢL/Kₚₓ)
Pr         Prandtl number, (=νCₚₑ/λₑ)
q         adsorbed phase concentration, (mol/m³); amount adsorbed (g/100gₚₑ)
qₚₓ         maximum adsorbed phase concentration, (mol/m³)
q―         averaged adsorbed phase concentration, (mol/m³)
qᵢ         averaged adsorbed phase concentration for species i, (mol/m³)
q̅         averaged dimensionless adsorbed phase concentration, (≡q/q₀)
\( \bar{q} \)  \hspace{1cm} \text{dimensionless adsorbed phase concentration, (} \equiv q/q_0 \text{)}

\( q_0 \)  \hspace{1cm} \text{adsorbed phase concentration in equilibrium with } C_0, \text{ (mol/m}^3\text{)}

\( q_{st} \)  \hspace{1cm} \text{isosteric heat of adsorption, (J/mol)}

\( q_{st0} \)  \hspace{1cm} \text{isosteric heat of adsorption at zero coverage, (J/mol)}

\( Q \)  \hspace{1cm} \text{volumetric flowrate, (ml/min)}

\( R \)  \hspace{1cm} \text{ideal gas law constant, (J/mol.K)}

\( r \)  \hspace{1cm} \text{radial coordinate inside crystals, (m)}

\( \bar{r} \)  \hspace{1cm} \text{dimensionless radial coordinate inside crystals, (} \equiv r/r_c \text{)}

\( r_c \)  \hspace{1cm} \text{crystal radius, (m)}

\( R \)  \hspace{1cm} \text{radial coordinate in pellet, (m)}

\( \bar{R} \)  \hspace{1cm} \text{dimensionless radial coordinate in pellet, (} \equiv R/R_p \text{)}

\( R_p \)  \hspace{1cm} \text{pellet radius, (m)}

\( Re \)  \hspace{1cm} \text{Reynolds number, (} \equiv \rho_g v_d \rho / \mu \text{)}

\( R_e \)  \hspace{1cm} \text{internal column radius, (m)}

\( s \)  \hspace{1cm} \text{dissociation parameter}

\( Sc \)  \hspace{1cm} \text{Schmidt number, (} \equiv \mu / \rho_g D_m \text{)}

\( Sh \)  \hspace{1cm} \text{Sherwood number, (} \equiv k_s D_p / D_m \text{)}

\( t \)  \hspace{1cm} \text{time, (s)}

\( T \)  \hspace{1cm} \text{temperature in bulk gas phase, (K)}

\( T_s \)  \hspace{1cm} \text{temperature in solid phase, (K)}

\( \bar{T} \)  \hspace{1cm} \text{dimensionless temperature in the bulk gas phase, (} \equiv (T-T_f)/T_f \text{)}

\( \bar{T}_s \)  \hspace{1cm} \text{dimensionless temperature in the solid, (} \equiv (T_s-T_f)/T_f \text{)}

\( T_f \)  \hspace{1cm} \text{feed gas temperature, (K)}

\( T_H \)  \hspace{1cm} \text{temperature in the high-pressure step, (K)}

\( T_L \)  \hspace{1cm} \text{temperature in the low-pressure step, (K)}
\( T_w \) temperature at the column wall, (K)

\( \tilde{T}_w \) dimensionless temperature at column wall, \((= (T_w - T_i)/T_i)\)

\( T_p \) tortuosity

\( u \) interaction energy, (J)

\( v \) superficial velocity, (m/s)

\( v_i \) interstitial velocity, (m/s)

\( x \) adsorbed phase mole fraction

\( y \) gas-phase mole fraction

\( y_i \) gas-phase mole fraction of species \( i \)

\( y_{iH} \) gas phase mole fraction at high-pressure step

\( y_{IL} \) gas phase mole fraction at low-pressure step

\( y_{if} \) gas-phase mole fraction at feed conditions

\( \bar{y} \) averaged gas phase mole fraction

\( Y \) ratio of mole fraction of adsorbable species and inert species

\( w \) concentration velocity, (m/s)

\( w_s \) shock velocity, (m/s)

\( w_i \) interaction parameter, (kJ/mol)

\( z \) axial coordinate in bed, (m)

\( \bar{z} \) dimensionless axial coordinate in bed, \((=z/L)\)

\( \gamma \)

**Greek symbols**

\( \alpha_{AB} \) separation factor

\( \beta_n \) roots of transcendental equation \( \beta_n J_1(\beta_n) - LJ_0(\beta_n) = 0 \)

\( \beta_{n,m} \) roots of transcendental equation

\[
\lambda_n = \sqrt{\beta_{n,m}^2 \gamma + 3K\gamma(1 - \beta_{n,m} \cot \beta_{n,m})}
\]
$\varepsilon$  energy constant for Lennard-Jones potential, (J)

$\varepsilon_b$  void fraction of the ZLC; porosity of bed

$\varepsilon_p$  particle porosity

$\gamma$  ratio of macropore and micropore diffusional time constants, ($=(D_{c}/r_c^2)/(D_{p}/R_p^2)$)

$\gamma'$  corrected ratio of macropore and micropore diffusional time constants, ($=(D_{c}/r_c^2).(1+K)/(D_{p}/R_p^2)$)

$\gamma_n$  Arrhenius number, ($=-\Delta H_i/RT_i$)

$\gamma_s$  activity coefficient of adsorbed phase

$\lambda$  integration constant

$\lambda_n$  roots of the transcendental equation $\lambda_n \cot \lambda_n + L - 1 = 0$

$\lambda_{c0}$  effective thermal conductivity of stagnant bed, (W/mK)

$\lambda_f$  fluid thermal conductivity, (W/mK)

$\lambda_s$  solid thermal conductivity, (W/mK)

$\mu$  gas viscosity, (kg/ms)

$\pi$  spreading pressure, (atm)

$\theta$  fractional coverage of adsorbent, ($=q/q_{\text{max}}$)

$\theta_i$  fractional coverage of adsorbent by species $i$, ($=q_i/q_{\text{max}}$)

$\theta_{if}$  coverage of adsorbent at $y_i$, ($=q_{if}/q_{\text{max}}$)

$\rho_a$  apparent density of solid, (kg/m$^3$)

$\rho_g$  gas density, (kg/m$^3$)

$\rho_s$  solid density, (kg/m$^3$)

$\tau$  dimensionless time, ($=v_{id}/L$)

$\tau'$  dimensionless time, ($=D_{p}t/R_p^2$)

$\tau_{\text{dif}}$  time constant for diffusion in macropores, ($=R_p^2/\varepsilon_p D_p$), (s)
\( \xi_h \)  heat capacity factor, \( \left( = (1-\varepsilon_b) \rho \varepsilon_c p_{ps} / \varepsilon_b C_{ps} \right) \)

\( \xi_{ml} \)  mass capacity factor, \( \left( = (1-\varepsilon_b) \rho \varepsilon_c q_{ml} / \varepsilon_b y_C C_{ml} \right) \)
In this chapter a brief history of n/iso-paraffins separation using molecular sieves adsorption technology is presented and the objectives for this PhD work are established.

1.1 History of the n/iso-paraffins separation by adsorption

Adsorption separation technologies are nowadays well-established processes in the field of chemical engineering. However, only in the last thirty-five years adsorption has been recognized as a key separation tool. The major step for the technological development was made possible by the synthesis of molecular sieves zeolites adsorbents in the early 1950's by Union Carbide Corporation (Cassidy, 1984).

Zeolites have a porous crystalline structure with a size scale similar to the kinetic diameter of molecules. The framework structure of zeolite A is shown schematically in Figure 1.1. It consists of an assemblage of SiO₄ and AlO₄ tetrahedra joined together in a regular arrangement. The eight cages located at the corners of the cube are joined through four-membered rings. This arrangement forms a large cage about 11.4Å accessible through eight-membered windows. In the sodium form (4A) there are 12 cations per cage obstructing the windows aperture. If the Na⁺ cations are exchanged with Ca²⁺ or Mg³⁺ the number of cations decreases and the effective aperture increases resulting in the 5A form (5A because the eight membered windows have a free diameter of near 5Å). The
dehydrated 5A form is capable of adsorbing significant quantities of normal paraffins at a considerable rate while excluding branched paraffins mainly due to the difference in kinetic diameters.

![Image of zeolite structure](image.jpg)

*Figure 1.1 Schematic representation showing framework structure of zeolite A.*

This characteristic of 5A zeolite is the basis of the successful application of this adsorbent in the separation of normal from branched paraffins. When a mixture of n/iso-paraffins is fed to an adsorber containing 5A zeolite a rich fraction of branched paraffins is produced while the normal ones are selectively adsorbed. Due to the close boiling points of paraffin isomers this separation by distillation is very energy consuming increasing the economic importance of the alternative adsorptive separation. For this separation the analogous of relative volatility in adsorption is defined by the separation factor,

$$
\alpha_{AB} = \frac{x_A / x_B}{y_A / y_B}
$$

(1.1)

where $x_A$ and $y_A$ are, respectively, the mole fractions of component A in adsorbed and fluid phases at equilibrium is practically infinite considering component B as a branched paraffin.
The exploitation of this technology took place in the late 1950's with the first IsoSiv units developed by Union Carbide Corporation (UCC) (Wilcher and Raghuram, 1991) operating with light straight-run naphtha (mainly C\textsubscript{5} and C\textsubscript{6} hydrocarbons) in the vapor phase. It is also based in Pressure Swing Adsorption (PSA), which was a recent development at that time. The first IsoSiv unit sketched in Figure 1.2 was used for solvent production (normal paraffins) and octane improvement of gasoline pools. The octane improvement of gasoline pools is based in the significant difference of the Research Octane Number (RON) between normal paraffins and branched and cyclic ones as can be seen in Table 1.1 where the RON number of some paraffins are shown. Branched paraffins have a much higher RON than the normal ones. For example, n-pentane has a RON of 61.7 compared to 92.3 for isopentane. The PSA unit sketched in Figure 1.2 was operated with two steps: Step 1 - Adsorption (bed 1) / Ccurrent depressurization+vacuum desorption+repressurization (bed 2); Step 2 - Reverse beds 1 and 2.

*Figure 1.2 Schematic diagram of the first IsoSiv unit operating under a PSA cycle (Yang, 1987)*
Table 1.1 Octane numbers of some pure components (Wilcher and Raghuram, 1991)

<table>
<thead>
<tr>
<th></th>
<th>RON</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅</td>
<td></td>
</tr>
<tr>
<td>i-pentane</td>
<td>92.3</td>
</tr>
<tr>
<td>n-pentane</td>
<td>61.7</td>
</tr>
<tr>
<td>C₆</td>
<td></td>
</tr>
<tr>
<td>2,2-Dimethylbutane</td>
<td>91.8</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>103.5</td>
</tr>
<tr>
<td>2-methylpentane</td>
<td>73.4</td>
</tr>
<tr>
<td>3-methylpentane</td>
<td>74.5</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>24.8</td>
</tr>
<tr>
<td>Methylcyclopentane</td>
<td>91.3</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>83.0</td>
</tr>
<tr>
<td>Benzene</td>
<td>120.0</td>
</tr>
</tbody>
</table>

In the middle of the 1960's the technology was extended to more heavy feedstocks mainly with 10 to 18 carbon number such as kerosine and gas oil boiling range materials. The most significant uses are the production of raw materials in the manufacture of biodegradable detergents and plasticizers from the high purity n-paraffins produced (Cooper et al., 1966). These units operate under isobaric conditions where the regeneration of the adsorption bed is performed with a displacement agent which is less adsorbable than the n-paraffins being desorbed, generally n-hexane (Cooper et al., 1966; Wilcher and Raghuram, 1991).

But, it is by the middle of the 1970's that the separation of n/iso-paraffins by adsorption is recognized as a potential technology in petrochemical industry. In the early 1970's the scientists of Shell Research B. V. in Amsterdam developed a new catalyst based in a strongly acidic zeolite or molecular sieve for the isomerisation of light virgin naphtha. The process was marketed under the name of Hysomer and the performance was to increase the RON number of light virgin naphtha from near 79 to 82. A schematic diagram of the process is shown in Figure 1.3. The integration of Shell's Hysomer process with Union
Carbide molecular sieve technology (Isosiv) results in the so-called Total Isomerisation Process (TIP) that was commercialized by Union Carbide. The first unit came on stream in 1975 with a performance of producing RON clear of 88 to 92. The process is sketched in Figure 1.4 where the arrangement of the isomerisation unit with the adsorption zone can be seen. The adsorption zone is constituted by two adsorbers: the adsorber in adsorption step produce high-octane branched paraffins, while the adsorber in desorption step is recycling to the isomerisation zone the normal paraffins retained in the 5A molecular sieve in the previous adsorption step. In 1993, 50 units have been licensed with a capacity in excess of 310000 BPSD (Wilcher and Raghuram, 1991). Different schemes and improvements of the TIP processes have been developed during the recent years. Some include the adsorption zone before the isomerisation one (Holcombe et al., 1991).

![Figure 1.3 Simplified flow diagram of the Shell Hysomer process (Symoniak, 1980)](image-url)
At the beginning of the 1990's, the IsoSiv units are licensed to UOP by the formation of the joint venture of the UOP and the CAPS of UCC. The vast majority of naphtha IsoSiv units today are based on isobaric adsorption-desorption cycles driven by the n-paraffins concentrations in the bulk phase. Figure 1.5 shows a sketch of such unit. A cycle comprises four steps (A1, A2, D1, D2) with the use of four beds. The continuous operation originates that either one adsorber is on each of the four steps; or two adsorbers are on the A-2 step and two on D-2 step. The sequence diagram is shown in Figure 1.6. The description of the four steps follows:

A1 step – The column completely regenerated is fed in upflow. The n-paraffins are adsorbed and the non-normals pushed the hydrogen retained in the void spaces from the previous desorption step. This step ends when the non-normals reach the outlet of the column.

A2 step – In this step the normals continue to be adsorbed to an extent determined by the partial pressure and molecular weight of the normals and operating temperature. During this step a rich fraction of non-normals is produced. The step ends before the mass transfer zone of normal paraffins reaches the top of the column.
D1 step – In this step desorption is started. The column is fed by the top (countercurrent to adsorption) by hydrogen purge gas cleaning the column from non adsorbed paraffins. The step is terminated when the non-normals reach a low –level at the bottom of the column.

D2 step – The hydrogen is continuously fed to the column in order to regenerate it from the normal paraffins adsorbed. The D2 step is terminated before the normals concentrations reaches that of purge gas.

\[ \text{Bed position } \]

\[ \text{feed A1 feed A2 feed feed H2+n H2+n } \]

\[ \text{iso's } \]

\[ \text{feed } \]

\[ \text{H2 } \]

\[ \text{iso's break } \]

\[ \text{H2 } \]

\[ \text{iso's } \]

\[ \text{feed } \]

\[ \text{H2+n } \]

\[ \text{H2+n } \]

\[ \text{H2+n } \]

\[ \text{H2+n } \]

\[ \text{H2 } \]

\[ \text{H2 } \]

\[ \text{H2 } \]

\[ \text{H2 } \]

\[ \text{H2 } \]

\[ \text{H2 } \]

\[ \text{n = normal components of feed} \]

\[ \text{iso's = non-normal components of feed} \]

Figure 1.5 Schematic diagram of steps of an IsoSiv unit operating under isobaric cycles (Wilcher and Raghuram, 1991).
Figure 1.6 Sequencing diagram of the IsoSiv unit sketched in Figure 1.5 (Wilcher and Raghuram, 1991).

Apart from this evolution at the UCC and UOP, ELF Acquitaine (Paris) developed a chromatographic process named N-ISELF which is shown in Figure 1.7 (Bernard et al., 1981). The technology can handle a material from C₄ to C₁₀ and operates under isobaric and isothermal conditions. The hydrocarbons are periodically introduced in a carrier gas (usually hydrogen) circulating in the system. Injection of hydrocarbons and switching between columns are accomplished by a valve system with an electronic controller. After an injection of hydrocarbons in a column, at first a mixture of isoparaffins leaves the bed followed by a product rich in normal paraffins. At the outlet of the bed the different hydrocarbons are discharged in different parts of the system by the electronic valve system. Three columns are necessary to ensure continuous operation. While one column is injected with the hydrocarbon/hydrogen mixture, another column will discharge isoparaffins and the third will discharge normal paraffins.

The problem of production of unleaded gasoline in order to reduce pollution by automotive cars is of great importance during these days. Recently two patents were assigned to IFP and UOP in order to improve the performance of the TIP processes. Holcombe et al. (1991) from UOP claimed an improvement to the IsoSiv process described previously by a close integration between the reactor and adsorber operations in TIP units. It is convenient to decrease the total adsorbent volume and there is no need of the A1 and D1 steps mentioned above. The hydrogen can also be running in the adsorber during the adsorption step. The invention enables improved integration of the two technologies of isomerisation and adsorption-desorption, by placing the isomerisation catalyst and the molecular sieve in the
same vessel. A typical composition of a feedstock suitable for processing in the TIP unit described by Holcombe et al. (1991) is shown in Table 1.2.

Figure 1.7 Schematic diagram of the chromatographic Elf NIsel process (Bernard et al., 1981).

Table 1.2 Typical composition of a feedstock for processing in a TIP unit (Holcombe et al., 1991, UOP).

<table>
<thead>
<tr>
<th>Components</th>
<th>Mole%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄ and lower</td>
<td>0-7</td>
</tr>
<tr>
<td>i-C₅</td>
<td>10-40</td>
</tr>
<tr>
<td>nC₅</td>
<td>5-30</td>
</tr>
<tr>
<td>i-C₆</td>
<td>10-40</td>
</tr>
<tr>
<td>nC₆</td>
<td>5-30</td>
</tr>
<tr>
<td>C₇ and higher</td>
<td>0-10</td>
</tr>
</tbody>
</table>
The IFP technology (Minkkinen et al., 1993) is based on the utilization of a high activity catalyst in the isomerisation zone. The system of recycling the low octane number species in the adsorption zone is also different. A two bed PSA cycle is used to produce components with high octane number and to recycle to the reactor zone low octane number constituents. It should be noted that the first IsoSiv units operates with a two bed PSA cycle; however in IFP patent there is no hydrogen running in the system and no vacuum. The low-pressure desorption step occurs at near 2 bar driven by a fraction of the isopentane rich vapour produced during the high-pressure feed step. The high-pressure adsorption step occurs at near 15 bar. The desorption of n-paraffins takes place under advantageous conditions from the energy point of view by combining a pressure drop and a stripping operation using an isopentane rich vapour. The charge composition to the isomerisation reactor described by Minkkinen et al. (1993) is shown in Table 1.3. After the isomerisation reactor the fraction of normal paraffins entering the adsorbers is 13.9 mole % of nC₅ and 4.6 mole % nC₆.

Table 1.3 Composition of a previously desulphurized light naphtha feed to be processed in the invention of Minkkinen et al. (1993). The RON number of this feedstock is 70.2.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Mole %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isobutane</td>
<td>0.4</td>
</tr>
<tr>
<td>Normal Butane</td>
<td>2.4</td>
</tr>
<tr>
<td>Isopentane</td>
<td>21</td>
</tr>
<tr>
<td>Normal pentane</td>
<td>29</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>2.2</td>
</tr>
<tr>
<td>2-2 dimethyl butane</td>
<td>0.5</td>
</tr>
<tr>
<td>2-3 dimethyl butane</td>
<td>0.9</td>
</tr>
<tr>
<td>2 methyl pentane</td>
<td>12.7</td>
</tr>
<tr>
<td>3 methyl pentane</td>
<td>10</td>
</tr>
<tr>
<td>Normal hexane</td>
<td>14</td>
</tr>
<tr>
<td>Methyl cyclopentane</td>
<td>5</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>0.5</td>
</tr>
<tr>
<td>Benzene</td>
<td>1.3</td>
</tr>
<tr>
<td>C₇+</td>
<td>0.1</td>
</tr>
</tbody>
</table>
In the future, certainly new developments of this separation will be made, especially by refinements in the isomerisation reactor and adsorption zone. This is due to the economical importance of this separation in petrochemical industries strategies. The demand of environmental protection with the restriction of lead in fuels clearly makes this technology of upgrading light straight run naphtha one competitive tool for that purpose.

1.2 Objectives of the PhD work

In parallel to these developments in industry, fundamentals of adsorption received a great attention from the scientific community. It is possible to encounter in books (Helfferich and Klein, 1970; Barrer, 1978; Rodrigues and Tondeur, 1981; Ribeiro et al., 1984; Ruthven, 1984; Yang, 1987, Karger and Ruthven, 1992; Suzuki, 1990), reviews (Keller, 1995) and specialized journals the basic underlying theory governing adsorption processes. However, the design of a process such as the separation of n/iso-paraffins is always a challenge for a chemical engineer since it combines the use of several developments of adsorption made during the years. Each year new ways of interpreting adsorption and new experimental techniques are developed. On the other hand, the basic data necessary to design such separation is never available due to the economic strategies of the specialized enterprises in the field. Only very few topics are published in patents and reviews. It is also on the interest of industrial companies that independent laboratories do the necessary research for the improvement of their technologies.

It is the goal of this work, to understand in an experimental and scientific basis the underlying phenomena of the separation of n/iso-paraffins for octane improvement of gasoline pools, making use of the most recently developments in experimental and modeling of adsorption in view of adsorber design. An adsorbent supplied by Rhone-Poulenc (5A zeolite pellets exchanged with calcium) similar to the employed in the units under operation of the trade mark IPSORB and previously described in IFP patent (Minkkinen et al., 1993) will be used.

In Chapter 2, the fundamentals of equilibrium of adsorption will be reviewed and applied for the separation of n/iso-paraffins. An electronic microbalance available at LSRE is set-up as an apparatus for the measurement of adsorption equilibrium isotherms of n-pentane and n-hexane in the 5A zeolite pellets. These normal paraffins are the main constituents of
light-straight run naphtha representing approximately 40% of the feed of the isomerisation rector and 20% of the feed of the adsorption zone. It is the n-paraffins adsorption capacity of the 5A zeolite that determines first the size of the adsorption vessels.

In Chapter 3, the kinetics of sorption is studied. The synthesized commercial molecular sieve zeolites are small crystals with dimensions in the order of 1-10 μm. To put this adsorbent for practical use it is necessary to aggregate the crystals in a macroporous pellet by the addition of an inert clay binder. This gives the necessary porosity and mechanical strength to the adsorbent. The arrangement offers generally two distinct resistances to mass transfer: the micropore diffusional resistance of the individual zeolite crystals and the macropore diffusional resistance of the extracrystalline pores. During this work the zero-length-column technique (ZLC) of Eic and Ruthven, 1988 is extended to the measurement of adsorption kinetics of normal paraffins in the composite zeolite pellets. A model for the interpretation of ZLC data is also developed. Experiments with the gravimetric technique are also performed.

Chapter 4 is devoted to study fixed bed adsorption with mixtures of n/iso-paraffins. An experimental set-up is developed for that purpose. A mathematical model is developed based in the data obtained in Chapter 2 and 3. This strategy can reduce significantly the number of experimental runs needed for the proper design of experimental units.

Chapter 5 deals with the cyclic operation of adsorption units. Especially the recent developments described in the IFP patent mentioned previously, where assessed. The PSA cycle described in IFP patent is studied and the model calibrated at the laboratory is used to simulate the cycle. A PSA unit was also designed where experimental results were obtained and a PSA cycle is suggested for the separation, that can be implemented in the several TIP schemes available.

References


Symoniak, M. F., Upgrade naphtha to ... fuels and feedstocks, *Hydrocarbon processing*, 110-114, May (1980)


Yang R. T., Gas separation by adsorption processes, Butterworth: Stoneham, 1987
2. Adsorption equilibrium

The equilibrium of adsorption is an important information needed for the design of an adsorber. The success of a given separation depends on the amount adsorbed at a certain temperature and pressure. A correct interpretation and quantification of adsorption equilibrium isotherms between sorbate and adsorbent, is an important step in the development of adsorption technologies for the separation and purification of gases and liquids using adsorbents. In this Chapter emphasis is given to the analysis of equilibrium data, referring some models existing in literature, and establishing at the same time a methodology of fitting the models to the experimental results. The methodology is illustrated with the choice of a suitable model for representing the equilibrium data obtained in this laboratory for n-pentane and n-hexane in pellets of 5A.

2.1 Theoretical

Adsorption isotherms

An adsorption equilibrium isotherm is an expression that relates the specific amount adsorbed of a certain species with the partial pressure of the species in the gas phase, at a fixed temperature. Theories of adsorption provide implicit and explicit relations between these variables.
Following IUPAC classification there are five distinct types of adsorption isotherms, which can be seen on Figure 2.1.

![Diagram showing five types of adsorption isotherms](image)

**Figure 2.1 The IUPAC classification of adsorption isotherms.**

Isotherms of type I are characteristic of microporous solids (e.g. zeolites and activated carbon). There is a definite saturation limit corresponding to complete filling of micropores. In isotherms of type II and III the adsorbed quantity tends to infinite corresponding to multilayer adsorption. They are observed in adsorbents with a wide range of pores. Isotherms of type IV and V correspond respectively to isotherms of the type II and III when capillary condensation occurs.

Several models are available in literature based on different methods of interpreting the adsorption phenomena. In this work we only focus on the interpretation of isotherms of type I, since they are related with the main objective of this work (adsorption on microporous zeolites). Adsorption equilibrium can be modeled by using the principles of the classic thermodynamics of solutions, statistical thermodynamics and molecular theory. The adsorbed phase can be considered mobile according to the principles of classic thermodynamics (the adsorbate inside the microporous has the properties of a continuous compressed liquid and thermodynamic relations can be used). The molecular theory is generally associated with the concept of localized adsorption (there are distinct sites for adsorption owing the formation of a molecular field). The adsorbent can be considered as energetically homogeneous or heterogeneous; it is homogeneous when the energy of adsorption is a constant over all sites and heterogeneous when the energy of adsorption is not constant over all sites. Interactions between adsorbed molecules may exist or not.
The principles of the thermodynamic of solutions applied to the study of adsorption equilibrium have been explored by Gibbs (Ruthven, 1984), who obtained the following adsorption isotherm,

$$ A \left( \frac{\partial \pi}{\partial p} \right)_T = \frac{RT}{p} n_s $$

(2.1)

where $A$ is the surface area of the adsorbent, $\pi$ is the spreading pressure, $p$ is the partial pressure of sorbate, $R$ is the ideal gas law constant, $T$ is the temperature and $n_s$ is the number of adsorbed molecules by unit area of the adsorbent. The substitution of bidimensional equations of state representing the adsorbed phase in Equation 2.1 allows its integration, leading to adsorption isotherms directly applicable to experimental results. It should be noted that Equation 2.1 has no practical interest in the study of adsorption isotherms since the variable $\pi$ can not be measured experimentally. Yang (1987) presents several equations of state and the corresponding isotherms.

More recently Suwanayen and Danner (1980) obtained from thermodynamic relations an adsorption isotherm using the concept of vacancy solution theory. A vacancy is a vacuum entity occupying adsorption spaces that can be filled by adsorbate molecules. The equation representing the isotherms has the following form,

$$ K_{eq} = \frac{1}{p} \frac{\theta}{1-\theta} f(\gamma_s) $$

(2.2)

where $K_{eq}$ is an equilibrium constant, $\theta=q/q_{max}$ is the coverage of the adsorbent, $\gamma_s$ is the activity coefficient, $q$ is the adsorbed concentration, $q_{max}$ is the maximum adsorbed concentration and the term $f(\gamma_s)$ accounts for the non-ideality of the system. When the equation was derived for the first time the authors used the Wilson equation to represent $f(\gamma_s)$. Later Cochran et al. (1985) used the Flory-Huggins equation. It should be pointed that when $f(\gamma_s)=1$, the Equation 2.2 reduces to the Langmuir isotherm.

According to the thermodynamic of solutions, the adsorbed phase is considered mobile and the molecules can move freely in that phase. Other concept is based on the idea that molecules are localized in some sub-systems which interact more or less rapidly. If the dislocation is rapid, we recover the concept of mobile adsorption. If the dislocation does
not occur we reach another important concept in the interpretation of equilibrium of adsorption which is that of localized adsorption. Due to the crystalline structure of zeolites, which are constituted by several cages connected by channels, the concept of mobile adsorption can be exploited to obtain adsorption isotherms. Considering the global system as an ensemble of several cavities (sub-systems) connected by channels where exchange of molecules exists, Ruthven (1984) applied the concepts of statistical thermodynamics to obtain the following isotherm assuming also that the molecules inside the cages can interact among them,

\[
c = \frac{K_{eq}p + (K_{eq}p)^2(1 - 2b'/v)^2 + \ldots + ((K_{eq}p)^m/((m-1)!)) (1 - mb'/v)^m}{1 + K_{eq}p + (1/2!) (K_{eq}p)^2 (1 - 2b'/v)^2 + \ldots + (1/ m!) (K_{eq}p)^m (1 - mb'/v)^m} \tag{2.3}
\]

where, \(c\) is number of molecules per cavity, \(v\) is the volume of zeolite cavity, \(b'\) is the effective co-volume of sorbate and \(m\) is an integer always smaller than \(v/b'\).

A simple concept of interpreting the equilibrium of adsorption was the one followed by Langmuir (1918): the adsorbent is constituted by several active sites that can accommodate only one molecule, or if the molecule dissociates when adsorbs, each fragment occupies one active site. The adsorption defined in this way is called in the literature by localized adsorption with no interaction between adsorbed molecules. Langmuir derived the following isotherm based on the assumption of dynamic equilibrium between adsorbed and gas phase species supposing that a molecule when adsorbs does not dissociate,

\[
K_{eq} = \frac{1}{p} \frac{\theta}{1 - \theta} \tag{2.4}
\]

The same equation can be obtained using a bidimensional equation of state of the type \(\pi(A-\beta)=nRT\), where \(\beta\) is the effective molecular area) applied in Equation 2.1 giving rise to a thermodynamic consistent isotherm. Langmuir equation has only one parameter in terms of correlation of experimental data, since \(\theta=q/q_{max}\) and the parameter \(q_{max}\) (maximum adsorbed concentration) should be temperature independent and can be measured independently of the shape of the isotherm. Several experimental results have been described by this equation, letting the parameter \(q_{max}\) change with temperature. A correlation of this type does not give physical meaning to the model being the fitting purely
empirical. However, the Langmuir isotherm is the most used isotherm to interpret isotherms of type I.

When the physical validity of Langmuir isotherm is to be maintained, generally the experimental isotherm is not well described by the model. Several corrections of the model have been proposed, namely the isotherm of Fowler and Guggenheim (1939),

\[
K_{eq} \exp\left(\frac{2w_\theta}{RT}\right) = \frac{\theta}{p(1 - \theta)}
\]  

(2.5)

that takes into account possible interactions between adsorbed molecules through the parameter \(w_\theta\), which is negative for repulsion and positive for attraction.

More recently Nitta et al. (1984) using arguments of statistical thermodynamics and assuming that a molecule when adsorbs can occupy \(n\) active sites, developed the following isotherm,

\[
K_{eq} \exp\left(\frac{n\theta}{kT}\right) = \frac{\theta}{p(1 - \theta)^n}
\]  

(2.6)

where \(u\) is the interaction energy between adsorbed molecules (positive for attraction, negative for repulsion) and \(k\) is the Boltzmann constant. Sircar (1995) showed, using kinetic arguments of the Langmuir type, that the same isotherm can be obtained, neglecting the interaction term between adsorbed molecules (\(u=0\)). The theory of Nitta et al. can be extended to multicomponent systems and can be predictive, is also thermodynamic consistent and can predict azeotropes, making an advance and a progress relatively to IAST theory (Myers and Prausnitz, 1965) on this domain.

A more complete isotherm taking into account the effects of adsorbate size, chemical dissociation and molecular interactions has been recently proposed by Martinez and Basmadjian (1996). The adsorption isotherm is,

\[
K_{eq} \exp\left(\frac{n\theta}{kT}\right) = \frac{\theta^6}{p(1 - \theta)^n}
\]  

(2.7)
where s represents the dissociation parameter. This isotherm reduces to the Langmuir one when there is no dissociation \( s=1 \), no interactions \( u=0 \) and a molecule occupies only one active site when adsorbs \( n=1 \).

**Heat of adsorption**

The isosteric heat of adsorption is calculated from adsorption isotherms by the Clausius-Clapeyron equation. Considering a perfect gas we obtain,

\[
q_{st} = RT^2 \left( \frac{\partial \ln p}{\partial T} \right)_q
\]  

(2.8)

where \( q_{st} \) is the isosteric heat of adsorption, \( p \) is the partial pressure of sorbate and \( q \) is the concentration of sorbate in the adsorbed phase. It is possible to calculate the isosteric heat from two isotherms at fixed \( q \) by integration of Equation 2.8 obtaining,

\[
\ln \left( \frac{p_1}{p_2} \right)_q = \frac{q_{st}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]  

(2.9)

Generally, the heat of adsorption is reported as a function of amount adsorbed at a given temperature. Heats of adsorption are of great importance since they reveal important aspects of adsorption. The magnitude of the heat of adsorption indicates the strength of the bonding between sorbate and surface. An increase in heat of adsorption profile with coverage is characteristic of non-heterogeneous adsorbents with gas-solid energies of interaction. A decrease of heat of adsorption with coverage is characteristic of highly heterogeneous adsorbents with a wide distribution of gas-solid interaction energies. A constant heat of adsorption with coverage indicates a balance between the strength of cooperative gas-gas interactions and the degree of heterogeneity of gas-solid interactions (Dunne et al., 1996). The heat of adsorption is also important for the calculation of energy balances in packed columns, since it determines the temperature profile in the columns. For TSA (Temperature-Swing-adsorption) it can be defined as the energy required for regenerating the column. Physical adsorption from the gas phase is exothermic which may be shown from simple thermodynamic arguments (Ruthven, 1984); therefore \( q_{st} \) is negative.
Methodology for interpretation, quantification and modelling of adsorption equilibrium experimental data

When treating experimental data, it is necessary to verify the thermodynamic consistency of these data, by fitting experimental data using the virial isotherm as suggested by Kiselev (1971) and Barrer (1981). The virial isotherm is obtained by applying the bidimensional virial equation of state to the Gibbs isotherm (Equation 2.1) and has the following expression,

\[ H = \frac{q}{p} \exp \left( 2A_1q + \frac{3}{2}A_2q^2 + \frac{4}{3}A_3q^3 + \ldots \right) \]  \hspace{1cm} (2.10)

where \( H \) is the Henry's law coefficient and \( A^{1-3} \) are virial coefficients. This equation when extrapolated to \( q \to 0 \) reduces to Henry's law which is defined by,

\[ H = \lim_{p \to 0} \left( \frac{q}{p} \right) \text{ or } q = Hp \]  \hspace{1cm} (2.11)

According to the virial isotherm, it is possible to obtain the values of Henry constant when the data is represented in semi-log plots of the form,

\[ \log \left( \frac{P}{q} \right) = f(q) \]  \hspace{1cm} (2.12)

Extrapolating the data to \( q \to 0 \) and using the structure of Equation 2.10, Kiselev (1971) and Vavilis et al. (1981) used this methodology to calculate Henry's constants in systems where the adsorbate is strongly adsorbed at low partial pressures. These systems do not allow the measurement of reliable experimental data at low partial pressure, and using Equation 2.10 it is possible to extrapolate data to \( q \to 0 \) leading to the Henry constant. Once the Henry constant is obtained at several temperatures we can calculate the values of the isosteric heats of adsorption at zero coverage using the Vant'Hoff relation,

\[ H = k_\infty \exp \left( -\frac{q_{H0}}{RT} \right) \]  \hspace{1cm} (2.13)
Barrer (1981) suggests that when the concentration of the adsorbed species increases beyond the limit of validity of Henry's law, \( q \) can be substituted by an activity \( a_s = q \gamma_s \) and then Equation 2.11 takes the following form,

\[
a_s = \gamma_s q = Hp
\]  

(2.14)

where \( \gamma_s \) is the activity coefficient. According to Equation 2.14 the virial isotherm (Equation 2.10) gives the following activity coefficient,

\[
\gamma_s = \frac{Hp}{q} = \exp\left(2A_1q + (3/2)A_2q^2 + (4/3)A_3q^3 + \ldots \right)
\]  

(2.15)

Experimental data gives the Henry constant \( H \) and \( \gamma_s \). For example, when Langmuir isotherm is valid the activity coefficient is given by,

\[
\gamma_s = \frac{1}{1-\theta}
\]  

(2.16)

Several model isotherms can be tested by simply representing the experimental data in the form \( p/q \) versus \( f(q) \), i.e.,

\[
\frac{p}{q} = f(q)
\]  

(2.17)

When the Henry’s law is valid \( \gamma_s=1 \) and \( f(q) \) is independent of \( q \) and graphically we obtain a straight line parallel to the axis of the independent variable \( q \). Generally we do not test the experimental data expecting that the Henry's law is valid except if we use very small partial pressures of sorbate in some kind of systems. Due to its simplicity the first model to test should be the Langmuir model and a graphical representation of data in the form,

\[
\frac{1}{p} \frac{\theta}{1-\theta} = f(\theta)
\]  

(2.18)

should give a straight line parallel to the abscissa if the model is valid.

There are several models that are small corrections to the Langmuir one. In these models the l.h.s. of Equation 2.18 should be kept constant, being necessary to adjust the dependency of \( f(\theta) \) that better fits experimental data. For example, in semi-log plots the
Fowler isotherm (Equation 2.5) predicts that \( f(\theta) \) should be linear with \( \theta \), with positive or negative slope depending on the type of forces acting in the adsorbent. It should be noted that all tests should be valid at all temperatures. Other technique is that when choosing a model of Langmuir type we place only the equilibrium constants in the right hand side of the isotherms. If the model is valid we obtain a straight line parallel to the abscissa in plots of the type given by Equation 2.18. For example in the Fowler isotherm the exponential term should be in the l.h.s. of Equation 2.18. The intercept with the axis of the dependent variable always give the equilibrium constants. This technique of treatment of experimental data can be more useful than adjusting the isotherms with numerical methods in equations with more than two adjustable parameters, because the parameters can loose their physical meaning. By this technique we always control the validity of Henry’s law which is very important for the thermodynamic consistency of the models. On the other hand, we always validate the model graphically.

2.2 Experimental section

Materials and reagents

The adsorbent is extrudate 5A zeolite 1/16 in cylindrical pellets (Rhone-Poulenc, France) with length = 6 mm. The SEM analysis shown in Figure 2.2 reveals that the crystals have a mean cube side of 2 \( \mu \)m. Mercury porosimetry studies performed by V. G. Mata in our laboratory are reported in Table 2.1 (Rodrigues et al., 1996). The n-pentane is 99% purity (Merck, Germany). Nitrogen and Helium are type R and N50 respectively in AirLiquide (France) classification

| Table 2.1 Mercury porosimetry results in Rhone-Poulenc pellets of 5A zeolite. |
|-----------------|----------------|
| Intrusion volume (cm\(^3\)/g) | 0.24 |
| Apparent density, \( \rho_a \) (g/cm\(^3\)) | 1.13 |
| Solid density, \( \rho_s \) (g/cm\(^3\)) | 2.22 |
| Porosity, \( \varepsilon_0 \) | 0.35 |
Figure 2.2 SEM photograph of Rhone-Poulenc pellets magnified 4000x;

Gravimetric apparatus

The studies of equilibrium and rate of adsorption were performed in the gravimetric apparatus sketched in Figure 2.3. It has three major sections: weighing system, gas mixing system and data acquisition. Weighing measurements were performed with a flow C.I. Electronics (United Kingdom) microbalance (A) in which a cage with pellets inside is suspended in one of its arms (B). The cage is a cylindrical spring with 2mm-i.d x 3cm-high placed inside a glass tube of 4mm-i.d where the gas flows. In all experiments four pellets were put in the cage which corresponds to approximately 50 mg of hydrated sample. A Termolab (Portugal) oven (D) with a type K thermocouple at samples level (e) is monitored with a Shimadzu (Japan) PID controller (F). Flow of adsorbate plus inert always passes downward the cage of pellets.

Figure 2.4 shows a real view of experimental apparatus. Figure 2.5 shows a detailed view of the cell where the pellets are suspended.
Stream 1, inert plus adsorbate, was produced by bubbling nitrogen or helium in liquid adsorbate contained in a Scott (Germany) saturator (wb) immersed in a Techne (United Kingdom) thermostated bath (TB). The mixture produced could be further diluted by pure inert stream 2. Flow rates of streams 1 and 2 were established by Teledyne-Hastings (USA) mass flowmeters (FM) with the corresponding control unit (FMC). Different combinations of streams 1 and 2 and temperature in the bath permit different partial pressures of adsorbate in stream 3. Before entering the microbalance, total flowrate and partial pressure are checked in a soap bubble flowmeter (BS). Stream 4 (inert) is useful for making desorption steps in kinetic studies.

The electrical signal produced in the microbalance by weight changes is send to Robal C.I. Electronics control unit (R) and then to a Data Translation (USA) acquisition data board attached to a IBM PS/2 computer (Com). A PClab routine implemented in a MSofBasic language records the ADV signal. The software permits a graphic monitoring of weight changes with time.

**Procedure for gravimetric runs**

The zeolite sample was dehydrated by heating it from ambient temperature to 633K in 20 ml/min pure nitrogen or helium over a period of at least 16 hours. In the first step of a typical adsorption run, the inert stream 4 is switched to a pre-set mixture of paraffin and inert (stream 1 plus stream 2). Once the balance achieved a constant weight, valve 2 is closed and 3 open and another partial pressure of paraffin is established changing stream 1 and 2 ratios. Once the flowrate is constant in soap-bubble flowmeter another run is obtained by switching again valves 2 and 3. Each time valves 1 and 2 are switched an abrupt change in weight occur; this is the drag and buoyancy force effects of gas flow over the sample. True change in weight due to adsorption was corrected by a pre-calibration with inert as a function of flowrate and temperature.
Figure 2.3 Schematic drawing of experimental gravimetric apparatus for measuring equilibrium and kinetics of sorption.

Legend: A - Microbalance; B - Cage with pellets; BS - Bubble soap; Com - Computer; D - Radiant oven; e - Thermocouple; F - PID control of oven; FM - Flowmeter; FMC - Flowmeter control unit; m - Pressure manometer; R - Microbalance control unit; U - Gas exhaust; TB - Thermostated bath; wb - Wash-bottle; 1,2,3,4,5 - On-off valves
Figure 2.4 Real view of gravimetric apparatus

Figure 2.5 Detailed view of gravimetric cell
2.3 Isotherms of n-pentane on pellets of 5A zeolite

Figure 2.6 shows n-pentane experimental adsorption equilibrium isotherms on 5A zeolite pellets. Measurement of total loading of adsorbent was not possible since data were not reliable at temperatures lower than 373K. At temperatures higher than 573K another parasitic effect becomes important: an abnormal increase in weight occurs which does not correspond to physical adsorption because the initial weight of the sample was not recovered in the desorption step; also sample color changes. Probably some coking occurs.

![Graph showing adsorption isotherms](image)

*Figure 2.6 Adsorption equilibrium isotherms of n-pentane in pellets of 5A zeolite. Points are experimental results. Lines are calculated isotherms from Nitta et al. model. Absolute temperatures are quoted in each curve.*

The isosteric heat of adsorption $q_{st}$ versus the amount adsorbed $q$ is shown in Figure 2.7. The values of $q_{st}$ were calculated by Equation 2.8. The isosteric heat of adsorption is around 12.5 kcal/mol, which is close to published data by Ruthven (1984) and Vavlitis et al. (1981).
A suitable isotherm for a perfect gas in the gas phase at equilibrium with sorbed gas, from a thermodynamic point of view, is the virial isotherm (Kiselev, 1971; Barrer, 1981). According to the virial isotherm (Equation 2.10), semi-log plots of $p/q$ versus $q$ extrapolated to zero concentration give us Henry's constants, which are useful to check the consistency of molecular models isotherms. Figure 2.8 shows semi-log plots of $p/q$ vs $q$ for the experimental isotherms. Extrapolation is possible in the range of temperature 473K-573K but not at lower temperatures because high adsorbent loading at small partial pressures of sorbate makes extrapolation difficult. Table 2.2 summarizes Henry's coefficients obtained from extrapolation of data plotted in Figure 2.8 to zero concentration. It also includes Vavlitis et al. (1981) data for n-pentane sorption in single crystals of 5A zeolite for comparison with this work. Values of $q_{st}$ according to a Van't Hoff dependence of Henry's constants with temperature ($H=k_{st}\exp(-q_{st}/RT)$) are also shown in Table 2.2.
Table 2.2 Henry’s coefficients and isosteric heats of adsorption of n-pentane calculated from virial isotherm and Nitta et al. model (1984) according to experimental data of this work. Comparison with previous results of Vavilits et al. (1981) obtained from the virial isotherm.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>virial Isot. (This work)</th>
<th>Nitta et al. Isot. (This work)</th>
<th>virial Isot. (Vavilits et al. 1981)*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H (g/g.bar)</td>
<td>H (g/g.bar)</td>
<td>H (g/g.bar)</td>
</tr>
<tr>
<td>674</td>
<td>-</td>
<td>-</td>
<td>0.07</td>
</tr>
<tr>
<td>617</td>
<td>-</td>
<td>-</td>
<td>0.15</td>
</tr>
<tr>
<td>573</td>
<td>0.25</td>
<td>0.28</td>
<td>-</td>
</tr>
<tr>
<td>568</td>
<td>-</td>
<td>-</td>
<td>0.33</td>
</tr>
<tr>
<td>523</td>
<td>0.77</td>
<td>0.82</td>
<td>0.81</td>
</tr>
<tr>
<td>473</td>
<td>2.5</td>
<td>3.2</td>
<td>-</td>
</tr>
<tr>
<td>423</td>
<td>-</td>
<td>16</td>
<td>-</td>
</tr>
<tr>
<td>373</td>
<td>-</td>
<td>144</td>
<td>-</td>
</tr>
<tr>
<td>( q_m ) (kcal/mol)</td>
<td>12.4</td>
<td>13.2</td>
<td>11.6</td>
</tr>
</tbody>
</table>

*We consider 1 molecule/cav=0.45 mmol/g\text{lind} (Ruthven, 1984)

The virial isotherm is suitable for interpreting data from a thermodynamic point of view, but does not give insight into sorption events at the molecular level (Barrer, 1981). Because information concerning multicomponent adsorption will be needed in future we decided to model the equilibrium data.

For type I isotherms in IUPAC classification a suitable isotherm is represented by the Langmuir (1918) one (Equation 2.4). As stated previously experimental determination of \( q_{max} \) was not possible. According to Doetsch et al. (1974), 5A zeolite can accommodate 2 molecules of nC\(_7\) in is cavities and according to Ruthven (1984) 5 molecules of nC\(_3\). For nC\(_5\) this value could be 3 or 4 molecules. According to Ruthven (1984) 1 molecule/cav=0.45 mmol/g\text{lind} corresponding to three molecules of nC\(_5\) at 9.75 g_{nC5}/100 g_{ads}, and to four molecules at 13 g_{nC5}/100 g_{ads}. Looking at Figure 2.6 the isotherm plateau at 373K is located at almost 9.7 g_{nC5}/100 g_{ads}; assuming that the zeolite...
accommodates one more molecule when decreasing the temperature or increasing the partial pressure, a reasonable value for adsorbent saturation is 4 molecules per cavity. A plot of \(\theta/p(1-\theta)\) against \(\theta\) according to Langmuir equation with \(q_{\text{max}}=13g/100g_{\text{ads}}\) is shown in Figure 2.9a); if Langmuir equation is valid a straight line parallel to \(\theta\) axis is obtained, with intercept at zero loading that gives the equilibrium constant, which in turn multiplied by \(q_{\text{max}}\) gives the Henry's law coefficient. It can be seen that Langmuir equation does not represent well the experimental data.

![Graph](image)

\[q_{\text{mg/cc/100g_{ads}}}\]

\[p/q(\text{bar},g_{\text{ads}}/\text{g_{cc}})\]

Figure 2.8 Semi-log plot of \(p/q\) versus \(q\) for analysis of virial isotherm.

As stated previously Nitta et al. (1984) developed an equilibrium adsorption isotherm which is similar to the Langmuir one. They assumed localized adsorption in which the adsorbed molecule occupies a certain number of active sites, represented by the parameter \(n\). The isotherm expression is, neglecting the interaction term between adsorbed molecules in the original model:

\[
K_{\text{eq}} = \frac{1}{p} \frac{\theta}{(1-\theta)^{n}}
\]  

(2.19)
According to Nitta et al. (1984) \( \theta = q / q_{\text{max}} \) with \( q_{\text{max}} = A_s / n \), \( A_s \) is the total number of active sites in the adsorbent, in 5A zeolite \( A_s \) is of the order of 9 mmol/g. If \( n=5 \) we obtain \( q_{\text{max}}=1.8 \) mmol/g which corresponds to exactly 4 mol/cav. This value is acceptable as mentioned above. With \( n=5 \) and \( q_{\text{max}}=13 \) g/100 g ads only \( K_{\text{eq}} \) is unknown in Equation (2.19). Model validation follows the same pattern of Langmuir isotherm; in a plot \( \theta / p (1-\theta)^n \) versus \( \theta \) all isotherms should be straight lines parallel to the \( \theta \) axis; \( K_{\text{eq}} \) are the intercepts at zero loading. Figure 2.9b) shows a plot of \( \theta / p (1-\theta)^5 \) versus \( \theta \) and in Figure 2.6 Nitta et al. model is superimposed to experimental data. Henry’s coefficients obtained by the intercept at zero loading in Figure 2.9b) are shown in Table 2.2; they range from 0.28 to 144 g_C_3 H_8/g ads.bar between 573 to 373K respectively.

Figure 2.6 and Figure 2.9 b) clearly show that results predicted by Nitta et al. model are in good agreement with experimental data. All parameters calculated in a straightforward way have physical meaning, and only Henry’s coefficient is temperature dependent. The model of Nitta et al. can be extended to multicomponent systems and could predict azeotropes as pointed out by Sircar (1995) and Martinez and Basmadjian (1996), so in this work we will test this model in multicomponent systems.
Figure 2.9 Semi-log plot of $\theta/p(1-\theta)^n$ versus $\theta$ for adsorption of n-pentane in pellets of 5A zeolite. a) $n=1$ (Langmuir isotherm); b) $n=5$ (Nitta et al. isotherm)
2.4 Isotherms of n-hexane on pellets of 5A zeolite

Figure 2.10 shows experimental adsorption equilibrium isotherms for n-hexane on 5A zeolite pellets covering a temperature range between 373K and 573K.

Figure 2.10 Adsorption equilibrium isotherms of n-hexane in pellets of 5A zeolite. Points are experimental results. Lines are calculated isotherms from Nitta et al. model. Absolute temperatures are quoted in each curve.

The isosteric heat of adsorption $q_{st}$ versus the amount adsorbed $q$ calculated by Equation 2.8 is shown in Figure 2.11. The isosteric heat of adsorption is around 14.2 kcal/mol similar to the value obtained by Ruthven and Kaul (1996) for sorption of n-hexane in zeolite NaX. According to the virial isotherm, Figure 2.12 shows semi-log plots of $p/q$ vs $q$ for the experimental isotherms. Extrapolation to zero loading is possible in the range of temperature 523K-573K but not at lower temperatures because high adsorbent loading at small partial pressure of sorbate makes extrapolation difficult.
Figure 2.11 Isosteric heats of adsorption $q_{st}$ versus adsorbed phase concentration $q$.

Figure 2.12 Semi-log plot of $p/q$ versus $q$ for analysis of virial isotherm.
Table 2.3 summarizes Henry's coefficients obtained from extrapolation of data plotted in Figure 2.12 to zero concentration. Values of \( q_m \) according to the Van't Hoff dependency of Henry's constants with temperature \( (H=k_m \exp(-q_m/RT)) \) are also shown in Table 2.3.

Table 2.3 *Henry's coefficients and isosteric heats of adsorption of n-hexane calculated from virial isotherm and Nitta et al. model (1984) according to experimental data of this work.*

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Virial isotherm</th>
<th>Nitta et al. isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( H ) (g/g.bar)</td>
<td>( H ) (g/g.bar)</td>
</tr>
<tr>
<td>573</td>
<td>1.54</td>
<td>1.67</td>
</tr>
<tr>
<td>523</td>
<td>5</td>
<td>6.76</td>
</tr>
<tr>
<td>473</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>423</td>
<td>-</td>
<td>152</td>
</tr>
<tr>
<td>373</td>
<td>-</td>
<td>1436</td>
</tr>
<tr>
<td>(-q_m) (kcal/mol)</td>
<td>14.0</td>
<td>14.2</td>
</tr>
</tbody>
</table>

From the analysis of Nitta et al. isotherm it is necessary to measure \( q_{\text{max}} \); unfortunately this is not experimentally feasible. For the adsorption of n-pentane it has been shown that \( q_{\text{max}}=13g/100g_{\text{ads}} \) is an acceptable value. To maintain thermodynamic consistency Nitta et al. isotherm requires that \( n q_{\text{max}}/M_w = \text{const.} \) Since \( n=5 \) and \( q_{\text{max}}=13g/100g_{\text{ads}} \) for n-pentane adsorption, it follows that for \( n \) should be 6 for n-hexane adsorption. Figure 2.13 shows a plot of \( \theta/p(1-\theta)^n \) against \( \theta \). It can be seen on Figure 2.13a) that Langmuir equation does not represent well the experimental data. Figure 2.13 b) gives the representation of the model with \( n=6 \). Henry's coefficients obtained by the intercept at zero loading in Figure 2.13b) are shown in Table 2.3; they range from 1.67 to 1436 g_{mc}/g_{ads}.bar between 573 to 373K respectively. Figure 2.10 shows Nitta et al. model with \( n=6 \) superimposed to experimental data; results predicted by Nitta et al. model are in good agreement with experimental data. Again all parameters calculated in a straightforward way have physical meaning, and only the Henry's coefficient is temperature dependent. The parameters obtained are also in conformity with the ones obtained for n-pentane.
Figure 2.13 - Semi-log plot of $\theta/p(1-\theta)^n$ versus $\theta$ for adsorption of n-hexane in pellets of 5A zeolite. a) $n=1$ (Langmuir isotherm); b) $n=6$ (Nitta et al. isotherm)
2.5 The MSL model applied to the interpretation of sorption of n-paraffins in 5A zeolite.

In order to study the validity of the MSL model relatively to the adsorption of n-paraffins in 5A zeolite, experimental data published in literature from methane to n-decane was compiled. The isotherms of methane (Ruthven, 1976), ethane (Ruthven and Loughlin, 1971), n-heptane (Doetsch et al., 1974), n-octane (Vavlitis et al., 1981) and n-decane (Vavlitis et al., 1981) in 5A zeolite were plotted in molecules/cav as a function of pressure; to convert molecules/cav to g/g\textsubscript{ads} the relation 1 mol/cav=0.45 mmol/g Linde pellet was used (Ruthven, 1984). This is to put all the isotherms in the same basis. It should be noted that the amount adsorbed in g/g\textsubscript{ads} of crystals is different from the amount adsorbed in g/g\textsubscript{ads} of pellets due to the addition of inert clay binder to crystals necessary to form pellets. The isotherms of ethane (Ruthven, 1971), propane (Ruthven and Derrah, 1972) and n-butane (Ruthven and Loughlin, 1971) were studied in pellets and experimental results given in mmol/g\textsubscript{pellet}; therefore no transformation of data is needed.

As noted previously, to maintain thermodynamic consistency of the MSL model, the relation n.q\textsubscript{max}/M\textsubscript{w}=const should be obeyed. The maximum adsorbent capacity (q\textsubscript{max}) was fixed during the fitting of n-pentane and n-hexane isotherms in our laboratory in 13g/100g\textsubscript{ads}. The data of Pan et al. (1983) for adsorption of n-heptane and n-dodecane in 5A zeolite also shows values in the order of 15g/100g\textsubscript{ads} for the maximum adsorbed capacity in zeolite crystals. The relation n.q\textsubscript{max}/M\textsubscript{w}=const is kept constant during this study.

Isotherms of methane in 5A zeolite

The data of Ruthven (1976) were originally fitted with the statistical model of Ruthven (Equation 2.3). The Henry’s constants extracted from the original model are summarised in Table 2.4. The heat of adsorption is around 5.2 kcal/mol. The fitting procedure to experimental data shown in Figure 2.14 with the MSL model leads to different values of the Henry constant and heat of adsorption; however, isotherms are well described by the MSL model. Table 2.4 shows model parameters. The Henry constant predicted by the MSL model ranges from 0.833 g/g\textsubscript{ads}.bar at 195K to 0.055 g/g\textsubscript{ads}.bar at 253K; for the same temperature range the model of Ruthven leads to 1.26 g/g\textsubscript{ads}.bar to 0.060 g/g\textsubscript{ads}.bar. The value of the isosteric heat of adsorption in the MSL model is 4.6 kcal/mol. The value of the
parameter $n$ of the MSL model is 1.4. The value of 1.4 is different from the value predicted by the relation $nq_{\text{max}}/M_w = \text{const}$, which is 1.1 if the maximum adsorbent capacity is 13 g/100 g$_{\text{ads}}$; since the value of $n$ is equal to 1.4 the maximum adsorbent capacity in this case is 10.3 g/100 g$_{\text{ads}}$ to maintain thermodynamic consistency. This difference can be attributed to a different maximum adsorbent capacity of the sample used in the study performed by Ruthven. It was impossible from the data shown in the work of Ruthven to calculate the maximum adsorbent capacity in order to see if the value selected is correct.

![Graph showing amount adsorbed of methane vs. pressure at different temperatures](image)

*Figure 2.14* Equilibrium adsorption isotherms of methane in 5A zeolite (Data of Ruthven, 1976). Points are experimental data. Lines are MSL model predictions.

*Isotherms of ethane on 5A zeolite*

The data of Ruthven and Loughlin (1971) were originally fitted with the statistical model of Ruthven. Henry's constants extracted from the model are shown in Table 2.4. They range from 0.095 g/100 g$_{\text{ads}}$ to 17.5 g/100 g$_{\text{ads}}$ between 345 K and 230 K respectively. The heat of adsorption is 6.9 kcal/mol. Figure 2.15 shows the adsorption isotherms and the fitting with the MSL model isotherm. In the figure it is also plotted an isotherm shown by Glessner and Myers (1969) at 308 K. The value of the Henry constant shown in Table 2.4 is 0.31 g/100 g$_{\text{ads}}$. In the fitting procedure the parameter $n$ used is 2.4 originating that the maximum adsorbent capacity is 11.3 g/100 g$_{\text{ads}}$. These values were used in the fitting of the data of
Ruthven and Loughlin and Glessner and Myers. The MSL model isotherm predicts with accuracy the isotherms between 273-345 K but fails at the temperature of 230 K.

![Graph showing adsorption isotherms for ethane in 5A zeolite.](image)

Figure 2.15 Equilibrium adsorption isotherms of ethane in 5A zeolite (data of Ruthven and Loughlin (1971) (Δ) and data of Glessner and Myers (1969) (O)). Lines are MSL model predictions.

Isotherms of propane on 5A zeolite

Ruthven and Derrah (1972) show data of sorption of propane in 5A Davison C-521 pellets. In the work, the isotherm data was not fitted to any isotherm. The MSL model was used to fit the data and results shown in Figure 2.16. In the fitting procedure the value of \( n \) used is 3 maintaining the thermodynamic consistency of value predicted by the relation \( n q_{\text{max}}/M_w = \text{const} \) with \( q_{\text{max}} = 13 \text{g}/100\text{g}_{\text{ads}} \). Table 2.4 shows model parameters. The Henry constants range from 1.95 g/g\(_{\text{ads}}\)-bar to 4.81 g/g\(_{\text{ads}}\)-bar between 348 K and 323 K, respectively. The isosteric heat of adsorption is 8.1 kcal/mol, similar to that reported in literature (Vavlitis et al., 1981). Figure 2.16 shows that the MSL model predicts with good accuracy all adsorption behavior.
Figure 2.16  Equilibrium adsorption isotherms of propane in 5A zeolite (Data of Ruthven and Derrah, 1972). Points are experimental data. Lines are MSL model predictions.

Isotherms of n-Butane on 5A zeolite

Figure 2.17 shows data of Ruthven and Loughlin (1971) for the sorption of n-butane in Linde 5A molecular sieve pellets. The data were originally fitted by the Dubinin-Polanyi potential theory by the use of a characteristic curve. In Figure 2.17 the results predicted by the MSL model with the parameter $n$ equal to 4 are also plotted and are in good agreement with experimental data. Table 2.4 shows model parameters. The Henry constants range from 0.342 g/g$_{ads}$bar to 91.0 g/g$_{ads}$bar between 498K and 323K. The isosteric heat of adsorption also increases relatively to propane and is fixed in 10.2 kcal/mol. This value is also in good agreement with the value published by Vavlitis et al. (1981).
Figure 2.17  Equilibrium adsorption isotherms of n-butane in 5A zeolite (Data of Ruthven and Loughlin, 1971). Points are experimental data. Lines are MSL model predictions.

Isotherms of n-heptane in 5A zeolite

The sorption of n-heptane in 5A zeolite crystals was studied by Doetsch et al. (1974) in a gravimetric system. In the original paper the sorption data are plotted in logarithmic scales and it is difficult to recover the experimental points. The strategy followed was to plot the model isotherms used by Doetsch et al. to fit their experimental data with the model parameters shown in their work. Figure 2.18 shows such representation. Again it was necessary to convert mol/cav to g/gads since all the isotherm parameters were given in mol/cav. The relation 1mol/cav=0.45mmol/gLinde was used to convert the data for sorption in pellets which is our main objective. The experimental data of Doetsch et al. was fitted originally by two completely different models: i) one assumes that the sorption occurs in a system of independent pairs of equivalent sites with an interaction energy when both sites of a pair are occupied; ii) the other assumes sorption with negligible interaction between adsorbed molecules on a set of independent pairs of non-equivalent sites. The two models predict with good accuracy all adsorbed behavior. The evidence from experimental data of
the precise saturation limit of two molecules per cavity and the lack of variation of this limit with temperature is the basis for the two models approximation.

For the fitting procedure with the MSL model, once more the relation \( n.q_{\text{max}/M_w} = \text{const} \) is used for the calculation of parameter \( n \), which is for this case approximately \( n=7 \). Figure 2.18 shows the MSL model fitted to the experimental data of Doetsch et al.. It was found during the fitting procedure that to keep the consistency of parameter \( n \) it is necessary to introduce the interaction parameter \( n.u/k \) to the MSL model according to Equation 2.6 Chapter 2. The value of \( u/k \) is 379K suggesting an attractive relation between sorbed molecules. This value is comparable with the force constant \( (\varepsilon/k=399.3K) \) for \( n \)-hexane. The attractive nature between sorbed molecules seems to be controversial: according to the statistical model of Ruthven there is no need to account for the intermolecular attraction between adsorbed molecules in nonpolar sorbates, only the attractive potential of the framework which determines the Henry constant and the repulsive interaction between molecules due to their finite size are of importance. However, most of the localized adsorption models derived from statistical thermodynamics account for the attractive nature of adsorbed molecules and significant data were fitted using the attractive parameter (Nitta et al., 1984). An explanation for the need of introducing the parameter \( w \) in the fitting procedure is the increasing length of \( n \)-paraffins. After \( n \)-heptane, there is no space in the cage of 5A zeolite for more than two molecules; therefore, the conformation of sorbed molecules in the 5A zeolite cage leads to an attraction between sorbed molecules. In Figure 2.18 the data of IFP (Julian, 1993) for the sorption \( n \)-heptane in 5A zeolite pellets at a pressure of near 2 bar and at a temperature of 573K are also plotted. It is remarkable that the parameters obtained by the fitting procedure of the MSL model to the data of Dotsch et al. were able to predict the sorption data of \( n \)-heptane at such high-pressure and temperature. It seems that the MSL model is also effective for the correlation of data on sorption of \( n \)-paraffins in 5A zeolite. Table 2.4 summarises the model parameters. The values of the Henry constant obtained by the MSL model range from 228 g/g_{ads}bar to 2.43 g/g_{ads}bar between 439K and 573K. These values are very similar to the values obtained from the virial isotherm according to the treatment of Doetsch et al. as can be seen in Table 2.4. The values of heat of adsorption at zero coverage, obtained from the virial isotherm and the MSL model, are 16.5 kcal/mol and 16.9 kcal/mol, respectively.
Figure 2.18  Equilibrium adsorption isotherms of n-heptane in 5A zeolite (data of Doetsch et al., 1974 and IFP Jullian, 1993). Points are experimental data. Lines are MSL model predictions.

Isotherms of n-octane in 5A zeolite

Figure 2.19 shows experimental data for the sorption of n-octane in 5A zeolite crystals obtained by Vavlitis et al. (1981) between 523K and 668K and for pressures up to 14 torr. The author only extracts Henry constants from the data since the main objective of their work was to study sorption kinetics. The MSL model fitting of data keeping thermodynamic consistency of the parameters is also plotted in Figure 2.19. The parameter n used to represent the data is 8. Again it was necessary to introduce the parameter u/k in the fitting procedure. The value shown in Table 2.4 is 392K suggesting a strong attraction between sorbed molecules. The Henry constants shown in Table 2.4 predicted by the MSL model range from 39 g/ads.bar to 0.707 g/ads.bar between 523K and 668K. The values shown by Vavlitis et al. also summarized in Table 2.4 range from 50.7 g/ads.bar to 0.82 g/ads.bar from the same temperature range. The isosteric heats of adsorption summarized in Table 2.4 are equal in the two cases with a value of 19.2 kcal/mol.
Figure 2.19 Equilibrium adsorption isotherms of n-octane in 5A zeolite (Data of Vavlitis et al., 1981). Points are experimental data. Lines are MSL model predictions.

Isotherms of n-Decane on 5A zeolite

Figure 2.20 shows experimental data for the sorption of n-decane in 5A zeolite crystals obtained by Vavlitis et al. (1981) at temperatures between 523K and 668K and pressures up to 1.6 torr. The MSL model is also plotted in Figure 2.20 using $n=10$ to keep thermodynamic consistency. Again the parameter $u/k$ is introduced; it is 392K which is equal to the value found in n-octane isotherms. The Henry constants shown in Table 2.4 predicted by the MSL model range from 390 g/g_{ads}.bar to 25.3 g/g_{ads}.bar between 523K and 596K. The values from Vavlitis et al. are in Table 2.4 and range from 407 g/g_{ads}.bar to 23.2 g/g_{ads}.bar for the same temperature range. The isosteric heats of adsorption are in both cases equal to 23.2 kcal/mol.
As a final conclusion, it was shown that the MSL model is effective for prediction of the sorption of linear paraffins in 5A zeolite. It is possible, by keeping the thermodynamic consistency of the parameters, to correlate data of sorption of methane at temperatures of near 195 K to sorption of n-decane at temperatures of near 668K. It is derived from the model the increasing heat of adsorption with chain length in a similar manner of previous published data. This evolution is plotted in Figure 2.21. The heats of adsorption range from 4.5 kcal/mol for methane up to 23.2 kcal/mol for n-decane. In Figure 2.22 it is shown the values of the Henry constants plotted as a function of the reciprocal of absolute temperature. The trends shown in Figure 2.22 are consistent, it is seen the increasing values of Henry constants as the temperature diminishes; when the paraffins increase their carbon number, higher is the slope of the straight lines indicating the increase in heat of adsorption. Other interesting aspect of the plot is that for the paraffins with higher carbon number the Henry’s constants are not so different as in the light paraffins. Since the Henry constant is a measure of the effects of sorbate-sorbent attractions it seems that for the hydrocarbons with higher carbon number these effects tend to be similar, which is not the case for the light paraffins. It was also found from the model that for paraffins higher than C7 there is a strong attraction between sorbed molecules. An explanation is that the space in the 5A cage is not enough for more than two molecules and only by attractive forces the adsorption content increases.
Figure 2.21 Isosteric heat of adsorption as a function of carbon number predicted by the MSL model for the sorption of n-paraffins in 5A zeolite pellets.

Figure 2.22 Temperature dependence of Henry constants predicted by the MSL model.
Table 2.4 MSL model parameters for the sorption of n-paraffins in 5A zeolite pellets

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### 2.6 Conclusions

A gravimetric apparatus was successfully built in order to measure adsorption equilibrium isotherms in adsorbent pellets. Data for the sorption of n-pentane and n-hexane in zeolite pellets were obtained in such equipment.

The adsorption equilibrium data was interpreted with a localized adsorption model in a homogeneous surface, assuming that a molecule when adsorbed occupies a certain number of active sites with no interaction between sorbed molecules.
The model was also used to analyze the sorption of n-paraffins from methane to n-decane based on published data. The model was able to predict all adsorption behavior keeping consistency in the model parameters. However, for paraffins with carbon number higher than six it is necessary to introduce another model parameter that accounts for the interaction of sorbed molecules.

These results are to be used in the studies of kinetics of sorption in Chapter 3, in fixed bed experiments in Chapter 4 and in the PSA studies in Chapter 5.

References


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Yang R. T., Gas separation by adsorption process, Butterworth, Stoneham (1987)
3. Kinetics of sorption

Commercial molecular sieve adsorbents are made from small crystals (typically 1-10 µm) of synthetic zeolites formed into pellets of convenient size (mostly cylindrical shape of 1.6 mm to 3.2 mm diameter) for industrial use, with the addition of an inert clay binder. This composite pellet offers two distinct resistances to mass transfer: the micropore diffusion inside the small crystals and the macropore diffusion on the pellet. There are several experimental techniques to measure the kinetics of sorption in these adsorbents. In this work we are interested in the gravimetric and ZLC technique (Zero-Length-Column). The gravimetric technique consists in the measurement of the uptake of sorbate in a particle exposed to a step change in the partial pressure of sorbate at the pellet surface. These experiments can be performed during the measurement of the experimental equilibrium data and have been extensively applied to the study of pellets. The ZLC is a differential bed of porous particles that is first saturated with the fluid mixture containing the absorbable species: at time zero the carrier gas flows through the ZLC and the desorption curve is measured in terms of concentration versus time. Eic and Ruthven (1988) introduced this technique in order to measure the micropore diffusion of the zeolite crystals.

In this chapter an extension of the ZLC technique to the measurement of diffusion in pellets is performed. A model for analyzing experimental data of ZLC experiments is developed taking into account the bidisperse nature of molecular sieve zeolites. A ZLC
apparatus is developed and experimental results of diffusion of n-pentane and n-hexane were obtained. These data are compared with the results obtained by the gravimetric technique during the measurement of equilibrium experimental data.

### 3.1 Introduction

A schematic diagram of a composite pellet is presented in Figure 3.1. The macropore diffusion has a time constant defined by $R_p^2/D_p$ and the micropore diffusion time constant by $r_c^2/D_c$. Assuming that the diffusion mechanisms are in series Ruckenstein et al. (1971) developed a bidisperse porous model applied to the measurement of transient diffusion in systems with linear isotherm. Based on such model Ruthven and Loughlin (1972) developed a criterion for the relative importance of the diffusion mechanisms, which is given by $\gamma'$:

$$\gamma' = \frac{(D_c/r_c^2)(1 + K)}{D_p/R_p^2}$$  \hspace{1cm} (3.1)

where $K = (1 - \varepsilon_p)H_{ad}/\varepsilon_p$ is the capacity factor and $H_{ad} (= p_t RTH/M_w)$ is the dimensionless Henry's constant or slope of the isotherm at the origin. Macropore diffusion is the controlling mechanism for $\gamma' > 10$; crystal diffusion is the controlling mechanism for $\gamma' < 0.1$. If $0.1 < \gamma' < 10$ both macropore and crystal diffusivity should be taken into account.

![Figure 3.1 Schematic diagram of a bidisperse porous adsorbent.](image-url)
At that time most of the measurements of transport diffusion was made by volumetric or gravimetric sorption uptake and chromatography in conjunction with the measurement of adsorption isotherms. It is well known that several transport mechanisms can be of importance in such systems making difficult the interpretation of kinetic data (Karger and Ruthven, 1992; Hufton and Ruthven, 1993) and may lead to erroneous results. In order to minimize such effects new techniques have been developed, such the ZLC technique of Eic and Ruthven (1988) and the Thermal Method of Grenier et al. (1995). With these techniques micropore diffusion in zeolites can be orders of magnitude faster than magnitude from the data measured by gravimetry or classical chromatography. Equilibrium and kinetics of sorption of paraffins up to n-Butane in 5A zeolite pellets have been widely studied by gravimetric uptake (e.g. Youngquist et al., 1971; Ruthven and Loughlin, 1971; Ruthven and Derrah, 1972; Zuech et al., 1983); however, for paraffins with higher carbon number only very few data are available (Eberly Jr., 1969; Silva and Rodrigues, 1997a,b).

To discriminate correctly between the importance of macropore or micropore diffusion, it is necessary to carry out experiments in pellets with different sizes but with the same crystal size (different \( R_p \), same \( r_c \)) or pellets with the same size but with different crystals (same \( R_p \), different \( r_c \)). If macropore diffusion is controlling, time constants for diffusion should depend directly on pellet size and should be insensitive to crystal size changes. If micropore diffusion controls the reverse is true. The influence of temperature is also important: when macropore diffusion is dominant the apparent time constant of diffusion defined by \( D_p/R_p^2(1+K) \) is temperature dependent in the same order of \( K \), which is independently obtained from the isotherm. This is so because pore diffusivity is weakly temperature dependent. The type of purge gas is also important: if micropore diffusion is dominant, gravimetric and ZLC desorption curves should be independent of the kind of purge gas.
3.2 Analysis of ZLC technique for diffusivity measurements in bidisperse porous adsorbent pellets

Since bidisperse porous adsorbents generally offer more than one diffusional resistance to mass transfer it is convenient to develop a mathematical model in order to analyse ZLC desorption curves.

The ZLC technique can be considered as a chromatographic method. Chromatographic methods have been used for the measurement of diffusivities in catalyst and adsorbent porous pellets; a review by Cresswell and Orr (1982) is recommended. These methods have advantages compared with gravimetric techniques, namely, the possibility of eliminating external mass transfer resistances and heat transfer effects. However, axial dispersion in the chromatographic bed can be a major drawback, which can disguise the information concerning the adsorption kinetics. Diffusion-cell techniques designed to avoid somehow axial dispersion effects have been recently reviewed by Park et al. (1997).

The Zero Length Column technique developed by Eic and Ruthven (1988) retains the main features of conventional fixed-bed chromatographic techniques and eliminates the effects of axial dispersion. The ZLC is a differential bed of porous particles which is first saturated with the fluid mixture containing the adsorbable species; at time zero the carrier gas flows through the ZLC at sufficiently high flowrate and the desorption curve is analysed in terms of concentration of adsorbate versus time. Essentially the ZLC technique differs from the shallow-bed technique (Sun, 1993), used for the measurement of film mass transfer at low flowrates, because it operates in the other extreme (high flowrate, negligible film mass transfer resistance).

The ZLC technique was initially used to measure the diffusivity of gases in zeolite crystals and results analyzed with simple models. Examples are: n-paraffins in offretite-eronite (Cavalcante et al., 1995), light paraffins in silicalite (Hufton and Ruthven, 1993) and C6 paraffins in silicalite (Voogd et al., 1991). The extension of the ZLC technique to liquid/solid systems has also been made by Ruthven and Stapleton (1993), Brandani and Ruthven (1995) and Rodriguez et al. (1998).
Chromatographic methods for the measurement of diffusivities in bidisperse pellets require complex model solutions in the time domain (Rasmussen, 1982). However, the use of the moment method greatly simplifies the analysis of experimental results. In the case of ZLC experiments, model equations are similar to those of a continuous stirred tank adsorber and the analysis is somewhat simpler than in fixed-bed chromatography.

Adsorption in bidisperse adsorbents was considered by Ruckenstein et al. (1971) who gave the analytical solution in the time domain for a step input in concentration in the infinite bath case. The solution was later extended by Lee (1978) for the finite bath case. More recently, a general model of adsorption/desorption in the time domain for bidisperse structured sorbents was presented by Do (1990) from which six degenerate models were derived.

The ZLC model is an extension of previous works; in fact, since the ZLC cell behaves as a continuous stirred tank adsorber, the concentration at the pellet surface is related with the outlet concentration of the ZLC. The boundary condition at the pellet surface in a ZLC is slightly modified if compared with the finite bath problem. For ZLC with zeolite crystals the solution initially obtained by Eic and Ruthven (1988) is similar to the diffusion problem in homogeneous adsorbents with film mass transfer resistance already solved by Crank (1957).

The objective of this part of the work is the analysis of ZLC methods for measurement of diffusivities in bidisperse porous adsorbents. The following steps are carried out to reach the objective:

i) development of a model for the ZLC accounting for macropore and micropore (crystal) diffusivity;

ii) analytical and numerical solutions of model equations;

iii) analysis of desorption curves based on the long time slope as a function of purge flowrate to identify regions with different controlling mechanisms.
Mathematical model

The mathematical model describing the ZLC system is based on the following assumptions:

i) The adsorbent pellet has a bidisperse porous structure containing macropores and crystals;

ii) Fick's law for diffusion is valid for macropore and crystal diffusion;

iii) Macropore and crystal diffusion are mechanisms in series;

iv) Adsorption in macropores is negligible;

v) Adsorption equilibrium in crystals is described by a linear isotherm;

vi) The ZLC cell is equivalent to a continuous stirred tank adsorber;

vii) The pellets and the microparticles have spherical geometry.

According to these assumptions model equations are:

*Mass balance for the adsorbable component in crystals:*

\[
\frac{\partial q}{\partial t} = D_c \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial q}{\partial r} \right) \quad (3.2)
\]

where \( q \) is the adsorbed concentration in crystals, \( r \) is the radial coordinate in the crystal, \( D_c \) is the diffusivity in the crystal and \( t \) is the time variable.

Boundary and initial conditions:

\[
r = 0; \quad \frac{\partial q}{\partial r} = 0 \quad (3.3)
\]

\[
r = r_c; \quad q = H_{ad} C_p \quad (3.4)
\]

\[
t = 0; \quad q = q_0 = H_{ad} C_0 \quad (3.5)
\]
Equations 3.3 and 3.4 are the symmetry condition at the center of the microsphere and the adsorption equilibrium at the macropore/crystal interface, respectively.

*Mass balance for the adsorbable component in a volume element of the pellet:*

\[
\varepsilon_p \frac{\partial C_p}{\partial t} + (1 - \varepsilon_p) \frac{\partial \bar{q}}{\partial t} = \varepsilon_p D_p \frac{1}{R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial C_p}{\partial R} \right)
\]  
(3.6)

where \( \bar{q} \) is the average adsorbed concentration in the crystal, \( R \) is the radial coordinate in the pellet, \( \varepsilon_p \) is the macropore porosity, \( C_p \) is the concentration in the macropores and \( D_p \) is the macropore diffusivity.

**Boundary and initial conditions:**

\[
R = 0; \quad \frac{\partial C_p}{\partial R} = 0
\]
(3.7)

\[
R = R_p; \quad \varepsilon_p D_p \frac{\partial C_p}{\partial R} \bigg|_{R=R_p} = k_e \left( C_{out} - C_p \bigg|_{R=R_p} \right)
\]
(3.8)

\[
t = 0; \quad C_p = C_o
\]
(3.9)

where \( k_e \) is the film mass transfer coefficient. Equations 3.7 and 3.8 represent the symmetry condition and the equality of fluxes at the pellet surface, respectively.

*Mass balance for the ZLC cell:*

Neglecting the accumulation term in the interparticle void fraction the mass balance for the adsorbate in the ZLC cell is:

\[
v_i C_{in} = v_f C_{out} + \frac{1 - \varepsilon_b}{\varepsilon_b} \varepsilon_p D_p \frac{3}{R_p} \frac{\partial C_p}{\partial R} \bigg|_{R=R_p}
\]
(3.10)

where \( v_i \) is the interstitial velocity, \( C_{in} \) is the fluid phase concentration at the ZLC inlet, \( C_{out} \) is the fluid phase concentration at the ZLC outlet, \( \varepsilon_b \) is the void fraction of the ZLC and \( \ell \) is the length of the ZLC cell.
Initial condition:

\[ t = 0; C_{\text{out}} = C_0; C_{\text{in}} = 0 \]  
(3.11)

Introducing dimensionless variables for concentrations in macropores, crystal and average concentration in crystal, respectively:

\[ \tilde{C}_p = \frac{C_p}{C_0}; \quad \tilde{q} = \frac{q}{q_0}; \quad \bar{q} = \frac{\bar{q}}{q_0} \]

and for time and space coordinates in crystals and pellet, respectively:

\[ \tau' = \frac{D_p t}{R_p^2}; \quad \bar{r} = \frac{r}{r_c}; \quad \bar{R} = \frac{R}{R_p} \]

the dimensionless model equations are now as follows:

**Mass balance in crystals**

\[ \frac{\partial \tilde{q}}{\partial \tau'} = \gamma \frac{1}{\bar{r}^2} \frac{\partial}{ \partial \bar{r}} \left( \bar{r}^2 \frac{\partial \tilde{q}}{\partial \bar{r}} \right) \]  
(3.12)

Boundary and initial conditions:

\[ \bar{r} = 0; \quad \frac{\partial \tilde{q}}{\partial \bar{r}} = 0 \]  
(3.13)

\[ \bar{r} = 1; \quad \tilde{q} = \tilde{C}_p \]  
(3.14)

\[ \tau' = 0; \quad \bar{q} = 1 \]  
(3.15)

**Mass balance in the adsorbent pellet**

\[ \frac{\partial \tilde{C}_p}{\partial \tau'} + K \frac{\partial \bar{q}}{\partial \tau'} = \frac{1}{\bar{R}^2} \frac{\partial}{\partial \bar{R}} \left( \bar{R}^2 \frac{\partial \tilde{C}_p}{\partial \bar{R}} \right) \]

(3.16)

Boundary and initial conditions:
\[ \bar{R} = 0; \quad \frac{\partial \bar{C}_p}{\partial \bar{R}} = 0 \]  

(3.17)

\[ \bar{R} = 1; \quad \frac{\partial \bar{C}_p}{\partial \bar{R}} \bigg|_{\bar{R}=1} = L \left( \bar{C}_{in} - \bar{C}_p \bigg|_{\bar{R}=1} \right) \]  

(3.18)

\[ \tau' = 0; \quad \bar{C}_p = 1 \]  

(3.19)

The model parameters are:

i) Adsorption equilibrium parameter \( K \) (capacity factor)

\[ K = \frac{1 - \varepsilon_p}{\varepsilon_p} H_{pd} \]  

(3.20)

ii) Diffusion controlling mechanism (ratio of time constants for macropore diffusion and crystal diffusion):

\[ \gamma = \frac{D_c / R_c^2}{D_p / R_p^2} \]  

(3.21)

Crystal diffusivity is the controlling mechanism for \( \gamma(1+K)<0.1 \): macropore diffusion is the controlling mechanism for \( \gamma(1+K)>10 \); if 0.1<\( \gamma(1+K)<10 \) both macropore and crystal diffusivity should be taken into account. The introduction of the parameter \( K \) for the analysis of the controlling results from the model structure of the pellet used; \( D_c \) is a diffusion parameter in the crystal and \( D_p \) is the diffusivity in macropores, the parameter \( K \) relates the different nature of the phases and it is necessary to compare the relative importance of diffusion parameters.

iii) ZLC parameter \( L \)

\[ \frac{1}{L} = \frac{3(1-\varepsilon_b)\varepsilon_p D_p}{v_l \varepsilon_b R_p^2} + \frac{\varepsilon_p D_p}{R_p k_e} \]  

(3.22)

The first term in the right hand side (r.h.s.) of the above equation is the ratio of space time in the ZLC, \((1-\varepsilon_b)\ell/\varepsilon_b v_l\), and the macropore diffusion time constant; the second term in the
r.h.s. is the ratio of film mass transfer time constant and macropore diffusion time constant, i.e., the reciprocal of Biot number.

**Analytical solution for linear adsorption equilibrium isotherm**

Model equations can be analytically solved for linear adsorption equilibrium isotherms, which is often the case in ZLC experiments. If we neglect the second term of the r.h.s of Equation (3.22), i.e. for negligible film mass transfer resistance, the outlet concentration of the ZLC is (see Appendix A1),

\[
\frac{C_{\text{out}}}{C_0} = 2L \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\beta_{n,m}} \frac{\exp \left( - \gamma \beta_{n,m}^2 \tau \right)}{\frac{\lambda_n^2}{\lambda_n} + L(L-1)} \left. \frac{d\lambda}{d\beta} \right|_{\beta=\beta_{n,m}}
\]  

(3.23)

where \( \beta_{n,m} \) and \( \lambda_n \) are obtained from the transcendental equations,

\[
\lambda_n \cot \lambda_n + L - 1 = 0
\]  

(3.24)

\[
\lambda_n = \sqrt{\beta_{n,m}^2 \gamma + 3K \gamma(1 - \beta_{n,m} \cot \beta_{n,m})}
\]  

(3.25)

and,

\[
\left. \frac{d\lambda}{d\beta} \right|_{\beta=\beta_{n,m}} = \frac{\gamma}{\lambda_n} \left( 2\beta_{n,m} + 3K(\cot \beta_{n,m} (\beta_{n,m} \cot \beta_{n,m} - 1) + \beta_{n,m}) \right)
\]  

(3.26)

**Numerical solution of the problem**

Alternatively numerical solutions can be obtained using orthogonal collocation (Villadsen and Michelsen, 1978). The solution is approximated by a sum of polynomials and the residuals made zero at the collocation points, i.e., the zeros of Jacobi polynomial \( P_{N}^{[\alpha,\beta]}(u) \), where \( N \) is the number of collocation points, \( u=\tilde{R}^2 \) or \( u=\tilde{r}^2 \) and \( s=2 \) for spherical geometry. The radial coordinates for the crystal and pellet are discretized and the resulting system of ODE's (ordinary differential equations) solved with an appropriate solver (See Appendix A2 for details).
Analysis of ZLC desorption curves

Desorption curves are calculated for the case of negligible film mass transfer resistance (high $k_f$). Simulated desorption curves, $C_{out}/C_0$ versus $\tau'$, are shown in a semi-log plot for easier data analysis. In Figure 3.2 the numerical solution is compared with the analytical solution (Equation 3.23) using 36 terms in the series. The values of the parameters are: $K=100$, $\gamma=0.001$ and $L=10$.

![Figure 3.2 Semi-log plot of curves $C_{out}/C_0$ versus $\tau'$: comparison between numerical and analytical solution (model parameters: $L=10$, $K=100$, $\gamma=0.001$)](image)

**Effect of L on the desorption curve, $C_{out}/C_0$ versus $\tau'$**

**Macropore diffusion control ($\gamma(1+K)>10$).** Figure 3.3 shows desorption curves for the limiting case of macropore diffusion control ($\gamma=1$ and $K=100$). For values of $L<0.1$ the desorption curves are straight lines with intercept equal to one; the concentration profiles in the macropores and in the crystals for $L=0.1$ at two different times are shown in Figure 3.4(a). The concentration profiles in the macropores and in the crystals are uniform at all times and so no kinetic information relatively to the diffusion processes can be obtained. In this case the time constant for the gas flow through the ZLC cell $(1-\varepsilon_b)\ell/\varepsilon_b v_1$ is much higher than the time constants for macropore and micropore diffusion; an equilibrium regime is then established.
Figure 3.3 Semi-log plot of curves $C_{out}/C_0$ versus $\tau'$ showing the effect of parameter $L$ for a macropore diffusion control (model parameters: $K=100$, $\gamma=1$)

For $1<L<10$ the desorption curves are straight lines at long times with intercept different from one. The concentration profiles in the macropores and in the crystals at two different times are shown in Figure 3.4b) for $L=1$. A smooth concentration gradient in the macropores exists; however, the concentration profiles in the crystals are uniform. This situation corresponds to the case where the ZLC time constant is of the same order of magnitude as the time constant for macropore diffusion.

A purely macropore diffusion regime occurs for $L>10$, where the slopes of the straight lines at long times shown in Figure 3.3 become independent of $L$ and the value of the intercept is inversely proportional to $L$. The concentration profiles in the macropores and in the crystals at two different times are shown in Figure 3.4c) for $L=10$. At short times there are sharp concentration gradients in the macropores; those gradients become smoother when time increases. In this regime only the macropore diffusion influences the desorption curve. However, experimental difficulties can arise because the concentration at the outer surface of the pellet becomes too small at short times making difficult the monitoring of the desorption curves. A trade-off between the most desirable high $L$ values and the feasible experimental conditions has to be found in order to measure macropore diffusion.
Figure 3.4 Effect of L on the concentration profiles in the pellet (□) and in the crystals (O) located at two different pellet radial positions (R/R_p=1 and R/R_p=0.36) for two dimensionless times. Case of macropore diffusion control (K=100, γ=1). a) L=0.1 (dimensionless times: τ'=16 and τ'=86); b) L=1 (dimensionless times: τ'=6 and τ'=16); c) L=10 (dimensionless times: τ'=6 and τ'=16)
Macropore -crystal diffusion control (0.1<\gamma(1+K)<10). Figure 3.5 shows desorption curves for various values of L when both diffusional mechanisms are important (\gamma(1+K)=1). Apparently the evolution of the desorption curves with L is similar to the macropore diffusion controlling case. An uniform concentration profile in the macropores at all times can still be found when the time constant of the ZLC, (1-\varepsilon_b) \ell / \varepsilon_b v_i is much higher than the diffusional time constants. This is sketched in Figure 3.6 a) for L=0.02. If the time constant of the ZLC, (1-\varepsilon_b) \ell / \varepsilon_b v_i is of the order of magnitude of the diffusional time constants the concentration profiles in the pellet display smooth gradients in the micropores and in the macropores. This is sketched in Figure 3.6b). Figure 3.6c) shows a purely diffusion regime for L=10, the concentration profiles are abrupt and as in the macropore diffusion controlling case the concentration at the pellet surface decreases rapidly in the early stages of the desorption curves.

![Figure 3.5 Semi-log plot of curves C_{out}/C_0 versus \tau' showing effect of parameter L for an intermediate macropore-crystal diffusional regime (model parameters K=100, \gamma=0.01)](image-url)
Figure 3.6 Effect of $L$ on the concentration profiles in the pellet ($\square$) and in the crystals ($O$) located at two different pellet radial positions ($R/R_p=1$ and $R/R_p=0.36$) for two dimensionless time. Case of intermediate macropore-crystal diffusion ($K=100, \gamma=0.01$). a) $L=0.02$ (dimensionless times: $\tau'=51$ and $\tau'=191$); b) $L=1$ (dimensionless times: $\tau'=11$ and $\tau'=51$); c) $L=10$ (dimensionless times: $\tau'=11$ and $\tau'=51$)
Figure 3.7 Semi-log plot of curves $C_{\text{out}}/C_0$ versus $\tau'$ showing effect of parameter $L$ for a crystal diffusion control (model parameters $K=100$, $\gamma=0.0001$)

Crystal diffusion control $\gamma(1+K)<0.1$. In the case of crystal diffusion control ($K=100$, $\gamma=10^{-4}$) the desorption curves for various $L$ values are shown in Figure 3.7. Comparing Figure 3.7 with Figure 3.3 similar trends on the evolution of the desorption curves with $L$ are observed either in macropore or crystal diffusion control cases. However, changes in desorption curves occur at smaller values of the parameter $L$ in the case of crystal diffusion control. In Figure 3.8a) the concentration profiles in the pellet for $L=0.001$ are uniform at all times. However, for $L=0.01$, i.e., when the time constant for the ZLC is of the same order of magnitude of crystal diffusion time constant there is a flat profile in the macropores and a smooth gradient in crystals (Figure 3.8b). For the crystal diffusion regime ($L=0.1$), Figure 3.8c) shows a sharp concentration gradient in the crystals.

The analysis of Figure 3.3, Figure 3.5 and Figure 3.7 shows that changing only the $L$ parameter in the ZLC technique is not enough to identify the controlling regime and consequently to measure both macropore and crystal parameters.
Effect of $\gamma$ on desorption curve

Let us analyse now the influence of $\gamma$ on desorption curves in ZLC operation. Figure 3.9 shows desorption curves for $L=1$ and $K=100$ and various $\gamma$. The effect shown in Figure 3.9 is expected in a system where $D_p/r_c^2$ is changed (for example, decreasing crystal size) and the purge flowrate and $D_p/R_p^2$ are kept constant. The evolution of the concentration history $C_{out}/C_0$ versus $\tau'$ with $\gamma$ displays two important features: i) as $\gamma$ diminishes, higher is the fall down of concentration in the cell at earlier times of the experiment; ii) the slope of the straight line at long times becomes smaller when $\gamma$ decreases. This is a consequence of the fact that micropore (crystal) diffusion becomes the controlling mechanism.

Analysis of model results for the measurement of diffusional parameters $D_p/R_p^2$ and $D_c/r_c^2$

The diffusional parameters $D_c/r_c^2$ and $D_p/R_p^2$, can be obtained by fitting the model solution to all experimental curves. This analysis should be made with caution, because various combinations of the parameters can represent the same experimental curve. It is also difficult to adjust the initial part of the curve; the initial fall down of concentration in the ZLC measured analytically may not represent correctly the concentration at the surface of the adsorbent (Huf ton and Ruthven, 1993; Voogd et al., 1991).

The analysis of the semi-log plots of $C_{out}/C_0$ versus $\tau'$ in Figure 3.3, Figure 3.5 and Figure 3.7 clearly shows that at long times they are well represented by a straight line in all diffusion regimes. Therefore, following Eic and Ruthven (1988) analysis for the measurement of intracrystalline diffusivity of zeolites, it is possible to simplify the treatment of experimental data if we use the information of the curves at long times. The solution of the model they developed is conveniently represented by a straight line when only the first term of the series is considered; the same is true in our model.
Figure 3.8 Effect of $L$ on the concentration profiles in the pellet (□) and in the crystals (○) located at two different pellet radial positions ($R/R_p=1$ and $R/R_p=0.36$) for two dimensionless time. Case of crystal diffusion control ($K=100, \gamma=0.0001$). a) $L=0.001$, dimensionless times: $\tau'=260$ and $\tau'=8510$; b) $L=0.01$, dimensionless times: $\tau'=260$ and $\tau'=760$; c) $L=0.1$, dimensionless times: $\tau'=260$ and $\tau'=760$
Figure 3.9 Semi-log plot of curves $C_{out}/C_0$ versus $\tau'$ showing the effect of the parameter $\gamma$ (model parameters: $L=1$, $K=100$).

Using the first term of the series represented by Equation 3.23 the straight lines at long times shown in Figure 3.3, Figure 3.5 and Figure 3.7 can be approximated by the following equation,

$$\ln \left( \frac{C_{out}}{C_0} \right) = \ln \left( \frac{2L}{\beta_{1,2} \left( \frac{\lambda_1^2 + L(L-1)}{\lambda_1} \right)} \right) - \gamma \beta_{1,1} \frac{D_p}{R_p^2} t$$

The intercept and the slope (Equations 3.28 and 3.29) contain the necessary information to obtain the model parameters.

$$\frac{2L}{\beta_{1,1} \left( \frac{\lambda_1^2 + L(L-1)}{\lambda_1} \right)} = \text{intercept}$$

$$\frac{\lambda_1}{\lambda_1} = \beta_{1,1} \frac{d\lambda_1}{d\beta}$$
\[ -\gamma \beta_{1,1} \cdot \frac{D_p}{R_p^2} = \text{slope} \]  

(3.29)

The model developed above should enable the calculation of three parameters, L, \( \gamma \) and \( \frac{D_p}{R_p^2} \) based on a single ZLC experiment. However, the expressions for the slope and intercept (Equations 3.28 and 3.29), have two additional unknowns \( \beta_{1,1} \) and \( \lambda_1 \), represented by the auxiliary Equations 3.24 and 3.25. Therefore, it is not possible in one single ZLC run to obtain all the unknowns, since we have a system of only four equations. If one of the diffusional time constants is known then it is possible to calculate the other one. Also based on some properties of the system a methodology to obtain the two diffusional time constants in bidisperse porous adsorbents can be suggested.

For a better understanding of the physical system and the developed model, we propose the following graphical analysis. For a given sorbate/adsorbent system in a ZLC cell the parameter K is known, for example from gravimetric measurements using a microbalance. For a given K the dimensionless intercept and slope of the model can be plotted as a function of the ZLC parameter L for various \( \gamma \). It is possible to identify in such a plot limiting crystal or macropore diffusion controlling regions.

It should be stressed that the above graphs require dimensionless slopes and intercepts, which involves the calculation of roots \( \beta_{1,1} \) and \( \lambda_1 \) as a function of L, \( \gamma \) and K. In Appendix A1, Table A1.1 shows the values of \( \beta_{1,1} \) as a function of L and \( \gamma \) for K=100 and Table A1.2 shows the values of \( \lambda_1 \) as functions of L.

In Figure 3.10 the dimensionless slope at long times of ln(Cout/C0) versus \( \tau' \), i.e., \( -\gamma \beta_{1,1}^2 \) is plotted as a function of L for various \( \gamma \). Several important features of the ZLC behaviour in a system with K=100 can be obtained from Figure 3.10:

i) There are two regions separated by a line represented by the values \( \lambda_1/(1+K) \) obtained for each L in which \( \lambda_1 \) is calculated by Equation 3.24. When the slope is proportional to L the system is at equilibrium and no diffusion parameters can be obtained. In a given system \( \gamma \) is fixed and there is always a value of L when operating the ZLC cell for which the system is at equilibrium.
ii) For each $\gamma$ there is a value for $L$ above which the slope has a constant value independently of changes on $L$. In a regime controlled by crystal diffusivity the dimensionless slope is proportional to $\gamma \pi^2$ (or $\pi^2 D / \tau^2$ in real time); in the region controlled by macropore diffusion the dimensionless slope is independent of $\gamma$ and tends to the limit $\pi^2/(1+K)$ (or $\pi^2 D_p / R_p^2 (1+K)$ in real time). When the two diffusional time constants are significant the slope changes with $\gamma$ but not in a proportional way and should be analyzed through $\gamma \beta_{1,1}^2$.

iii) The range of $L$ values required for the change in the slope from equilibrium regime to a diffusion controlled regime (constant slope) is nearly the same for all $\gamma$.

Figure 3.10 Dimensionless slopes of Equation 3.29 as a function of $L$ for various $\gamma$ and $K=100$. 
Figure 3.11 Intercepts from Equation 3.28 as a function of L for various $\gamma$ and $K=100$.

In Figure 3.11 the intercept given by Equation 3.28 is plotted as a function of L for various $\gamma$. Similarly Figure 3.11 shows that:

i) When the intercept is one, the system is at equilibrium and we can not obtain diffusional parameters. This region corresponds to that in Figure 3.10 where the slope is proportional to L.

ii) The range of L values for which it is possible to measure the diffusional parameters is larger for smaller $\gamma$. However, the intercept can be too small and experimental difficulties can arise.

iii) The intercept decreases proportionally to L in the region where the slope does not change with L.

Procedure for data treatment

After knowing the physical limits of the system through Figure 3.10 and Figure 3.11, we simulate one experiment for $K=100$, were results are described by,

$$\ln \left( \frac{C_{\text{out}}}{C_0} \right) = \ln(0.1) - 0.05t \quad (3.30)$$
Assuming that only $K$ is known a priori it is impossible to obtain the parameters $L$, $\gamma$ and $D_p/R_p^2$, from Equations 3.24, 3.25, 3.28 and 3.29. The strategy is to find sets of parameters that are solution of the problem, and analyse their physical validity.

Figure 3.12 shows the combinations of $D_c/r_c^2$ and $D_p/R_p^2$ that are solutions of the problem relatively to the information given in Equation 3.30. The calculation of a parameter set is simple: i) for an arbitrary $L$ we obtain $\lambda_1$ from Equation 3.24; ii) with Equation 3.25, $\gamma$ is calculated as a function of $\beta_{1,1}$ and inserted in Equation 3.28; iii) the measured value of the intercept allows the calculation of $\beta_{1,1}$ from Equation 3.28; iv) knowing $\beta_{1,1}$ we can back calculate $\gamma$ with Equation 3.25; and v) finally with $\beta_{1,1}$ and $\gamma$ and using Equation 3.29 for the measured slope we obtain $D_p/R_p^2$. By repeating this procedure for different values of $L$ we calculate different sets of the diffusional parameters.

![Graph showing $D_c/r_c^2$ vs. $D_p/R_p^2$](image)

*Figure 3.12* Sets of diffusional time constants $D_c/r_c^2$ and $D_p/R_p^2$ which are solution of Equation 3.30.

Figure 3.12 reveals several important details:

i) There are two asymptotic zones where one of the parameters becomes almost constant for significant changes in the other parameter. These zones correspond physically to macropore or crystal diffusion controlling regions. The crystal diffusion control case is characterized by large changes of $D_p/R_p^2$ for a constant value of $D_c/r_c^2$; for the macropore
diffusion control case the reverse is true. The relation between the asymptotic values of the
diffusional time constants is,

\[
\frac{D_e/\tau_e^2}{D_p/R_p^2} = \frac{1}{1 + K}
\]

(3.31)

This result can be explained easily. In fact, the solution of the diffusion equations assuming
Fick’s law is similar for diffusion in crystals and in pellets when macropore diffusion is
controlling. Only time constants are different and related by Equation 3.31. If K is high it is
also very difficult to distinguish in one experiment the two regimes in a pellet, even in
uptake experiments (Ruthven, 1984; Ruthven et al., 1986).

ii) We can calculate one time constant if the other is known. If we have a fair
estimate of one diffusion constant, located in one asymptotic zone we can calculate the
other time constant with confidence.

iii) If the estimate of one time constant is located in the intermediate zone of the
curve any tentative to obtain the parameters can have significant error.

We can conclude that more experimental information is needed to obtain the true set of the
diffusional parameters. Changing some property of the system and analyzing its response is
the only alternative to obtain both time constants. Two choices are possible:

1) Change of the purge flowrate, i.e., changing L for constant \( D_p/R_p^2 \) and \( \gamma \).

2) Change of the ratio of diffusion time constants, \( \gamma \).

Let us assume that when the purge flowrate is decreased four times, the response of the
system is:

\[
\ln \left( \frac{C_{out}}{C_0} \right) = \ln(0.38) - 0.037t
\]

(3.32)

The procedure leading to Figure 3.12 is now repeated; for Equation 3.32 we obtain the set
of diffusion constants shown in Figure 3.13. In Figure 3.13 we also represent the results
obtained from experiment corresponding to Equation 3.30, i.e., Figure 3.12. The set of
parameters is the same for both experiments. This fact is not surprising, because changing
the purge flowrate, does not change the diffusion time constants. We can conclude that changing the purge flow rate does not solve the question of measuring diffusional time constants.

![Graph showing D_p/R_p^2 vs D_c/t_c^2](image)

**Figure 3.13** Sets of diffusional time constants $D_p/R_p^2$ and $D_c/t_c^2$, which are solution of Equation 3.32 (D). Sets relative to Equation 3.30 (O) are also shown.

Using the second alternative, we increase $D_p/R_p^2$ by a factor of 10, keeping the flowrate and $D_c/t_c^2$ constants, the response of the system is:

$$\ln\left(\frac{C_{out}}{C_0}\right) = \ln(0.1) - 0.05t$$  \hspace{0.5cm} (3.33)

Again the procedure leading to Figure 3.12 is repeated and results shown in Figure 3.14. We also compare the set of parameters $D_p/R_p^2$ and $D_c/t_c^2$ to those from the experiment represented by Equation 3.30. Since we know that the parameter $D_p/R_p^2$ was changed (by a factor of 10) the problem has a unique solution because there exists only one $D_c/t_c^2$ at which the above solution is verified. An easy way of obtaining the true diffusional time constants is to divide the values of $D_p/R_p^2$ of the system represented by Equation 3.33 by 10, keeping $D_c/t_c^2$ constant. In this way the abscissa in Figure 3.15 has the same scale as Figure 3.12 (solution relative to Equation 3.30). If the intersection of the curves is unique, that point gives the true diffusional time constants.
Figure 3.14 - Sets of diffusional time constants $D_0/r_c^2$ and $D_p/R_p^2$ that are solution of Equation 3.33 (I). Sets relative to Equation 3.30 (0) are also shown.

Figure 3.15 Sets of diffusional time constants $D_0/r_c^2$ and $D_p/R_p^2$ that are solution of Equation 3.33 (I) represented in the same scale of abscissa of Figure 3.12. Sets relatives to Equation 3.30 (0) are also shown.

There are other ways of changing $\gamma$, such as: i) changing the crystal size, i.e., $D_0/r_c^2$ and ii) changing the purge gas. It is important to stress the relevance of the parameter $L$. There is a large range of $L$ values that do not allow the measurement of diffusion time constants,
because the system may be at equilibrium (see Figure 3.10 and Figure 3.11). The intercept may also be too small, and so difficulties will arise experimentally for measuring the long time straight lines. In a ZLC system, L is always limited; in fact L is simply:

$$L = \frac{1}{3} \text{Purge flowrate} \frac{R_p^2}{\text{Pellets volume} \ v_pD_p}$$  \hspace{1cm} (3.34)

The operator defines the r.h.s of Equation 3.34. For example, the purge flowrate in chromatographic equipment, should not be higher than 130 ml/min STP, otherwise there are problems in keeping the flame of the FID detector on. On the other hand, flowrates lower than 5 ml/min STP are unreliable. The pellet volume is also limited if we want to keep the ZLC as a differential bed. As an example: for pellets with $R_p = 0.12$ cm and purge flowrate in the range from 5 ml/min STP to 130 ml/min STP if the ZLC contains three pellets, then $1.1s^{-1} < LD_p/R_p^2 < 29s^{-1}$. Assuming $D_p/R_p^2 \approx 4s^{-1}$, $0.3 < L < 7.2$.

For $K = 100$, the observation of Figure 3.10 and Figure 3.11 tells us the type of system which can not be used in ZLC measurements. For example, from Figure 3.11, a system with $\gamma < 10^{-5}$ will always have intercepts which are too small.

For ZLC experiments with zeolite crystals, a criterion for the value of the diffusional time constant that can be measured is (Karger and Ruthven, 1992),

$$\frac{D_c}{r_c^2} < 0.05 \text{ s}^{-1}$$  \hspace{1cm} (3.35)

In bidisperse porous adsorbent pellets there is also a limitation for obtaining macropore diffusion time constant, which is by analogy:

$$\frac{D_c}{r_c^2} = \frac{D_p}{R_p^2(1 + K)} < 0.05s^{-1}$$  \hspace{1cm} (3.36)

Therefore for measuring diffusional time constants in bidisperse porous adsorbents with the ZLC technique, the system has to satisfy at least one of the conditions in Equation 3.36.
3.3 Experimental section

Gravimetric apparatus

The gravimetric apparatus is the same used for the measurement of adsorption equilibrium isotherms. It is sketched in Figure 2.3 of Chapter 2 (Adsorption Equilibrium).

ZLC apparatus

ZLC studies were performed in the apparatus shown in Figure 3.16. The section components are practically the same as in the gravimetric one, only the microbalance is replaced by a gas chromatograph.

Pellets, generally 3, are placed inside a small column (ZLC) directly attached to the FID GC (Carlo Erba GC 6000 Vega series, Italy). Figure 3.17 depicts in detail the ZLC cell. It is constituted by a small column with 2 mm internal diameter. It is a part of a “pack” necessary to adapt a packed column chromatograph to a wide bore column chromatograph and was sent by FISON. The connections to the small column are made by 1/16 in tube. The pellets occupy only a small fraction of the column length. Above the pellets there is free space that serves also as a way of fuel gas pass to the detector. This fuel gas never contacts with the pellets. Column saturation (stream 3; see Figure 3.17) and purging (stream 4; see Figure 3.17) were performed by two complete separate lines in order to avoid parasitic effects such as condensation on tube walls, inaccurate definition of zero time in the system (if purge gas passes by the same saturation line, pellets contact with purge gas at zero time could not be made with a free sorbate gas).

Procedure for ZLC technique

Sample dehydration was performed as in the gravimetric technique. Saturation of adsorbent was made with a very small partial pressure ($\approx 4 \times 10^{-8}$ bar) of nC$_5$ or ($\approx 2 \times 10^{-4}$ bar) nC$_6$ so adsorption is in the linear region of the isotherm. A typical experiment follows: after saturating the adsorbent with stream 3, streams 3 and 4 are switched in column, closing on-off valves 2 and 5 and opening 4, and the signal produced by the FID is recorded; at the same time needle valve 2' is opened a little to permit some back-flux of stream 3.
Figure 3.16 Schematic drawing of experimental ZLC apparatus for measuring sorption kinetics.

Legend: BS - Bubble soap; Com - Computer; Cr - Chromatograph; FID - Detector of chromatograph; FM - Flow-meter; FMC - Flowmeter control unit; m - Pressure manometer; TB - Thermostatic bath; U - Gas exhaust; wb - Washing-bottle; zlc - Zero-length column; 1, 2, 3, 4, 5 - On-off valves; 1', 2' - Needle valves
Figure 3.17 Schematic diagram of the ZLC cell.

A real view of the chromatograph and equipment used for ZLC experiments is presented in Figure 3.18. Figure 3.19 shows a detailed view of the ZLC cell.

Figure 3.18 Real view of ZLC experimental apparatus
Data treatment

The FID detector of the chromatograph is capable of linearly detect from few picograms to several milligrams of carbon based compounds. 20 attenuation levels are available in the electrometer of the gas chromatograph for the best resolution of the signal. Accordingly, when the attenuator is positioned in $2^0$ a current of 1pA is produced; when it is positioned in $2^{20}$ the current is 1048nA. At each attenuation level the signal is send to the Data Translation computer board from 0-10v and solved as a 12 bit (4096) code. The operating temperature limit of the detector is $330^\circ$C. When the ZLC desorption run starts a Basic program records the ADV signal coming from the electrometer of the gas chromatograph. Figure 3.20 shows a typical ZLC experiment recorded in ADV where an experiment starts
with an attenuation of 12; when the ADV signal reaches a value of around 450, the
electrometer is switched manually to an attenuation three times smaller. This is so to obtain
the best resolution of the 12 bit computer data board. Table 3.1 summarises typical
operating conditions of the detector in ZLC experiments.

**Table 3.1 Chromatograph operating conditions in ZLC experiments**

<table>
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<tr>
<th>Detector temperature</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Air</td>
<td>500 ml/min</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>25 ml/min</td>
</tr>
<tr>
<td>Oven temperature</td>
<td>ZLC study</td>
</tr>
</tbody>
</table>

![Figure 3.20 ADV signal as a function of time in a typical ZLC experimental run.](image)
3.4 Kinetics of sorption of n-pentane in pellets of 5A zeolite

For the present system an estimate of the relative importance of diffusional resistances can be made. For example at 573K: $D_m(\text{He-nC5})=1 \text{ cm}^2/\text{s}$; assuming tortuosity $\tau_p=4$ and particle porosity $\epsilon_p=0.35$ as common values in a zeolite pellet, the capacity factor $K$ calculated in the linear region of the isotherm is $K=760$; for a pellet with radius $R_p=0.08 \text{ cm}$ the apparent time constant for diffusion in macropores will be $D_p/(R_p^2(1+K))=0.05 \text{ s}^{-1}$. For crystal diffusion it is more difficult to obtain representative data because very different values are reported. Ruthven (1984) reported a value of $D_c/r_{c}^2=0.18 \text{ s}^{-1}$ for sorption of nC5 in 5A zeolite at 523K with crystals of 3.6 $\mu$m; activation energy for diffusion of C5 paraffins in 5A zeolite (Cavalcante et al., 1995) is in the order of 5 kcal/mol, which gives at 573K with $r_c=1 \mu$m, $D_c/r_{c}^2=0.09 \text{ s}^{-1}$. With this value $\gamma'$ is equal to 1.8 suggesting a system dominated by both diffusion resistances. In the work of Cavalcante et al. (1995) a value of $D_c=1 \times 10^{-8}$ cm$^2$/s at 573K is shown for a C5 paraffin in 5A zeolite, from which we calculate $D_c/r_{c}^2=1 \text{ s}^{-1}$ originating $\gamma'=20$, suggesting a macropore control system. Therefore no conclusion concerning the controlling diffusion mechanism can be drawn from previous data.

As stated previously in bidisperse porous adsorbents, it is important to carry out experiments in pellets with different sizes but with the same crystal size (different $R_p$, same $r_c$) or pellets with the same size but with different crystals (same $R_p$, different $r_c$). If macropore diffusion is controlling, time constants for diffusion should depend directly of pellet size and should be insensitive to crystal size changes. If crystal diffusion controls the reverse is true.

In the batch of pellets provided by Rhone-Poulenc the crystal size is around 1$\mu$m as can be seen in Figure 3.21. For a better study of diffusion some few pellets with the same size but with higher crystal size were requested to IFP. As can be seen in Figure 3.22 the crystals are around 3$\mu$m.
Figure 3.21 SEM photograph of Rhone-Poulenc pellets (magnified 10000x). These pellets correspond to the batch provided by RP for all the Ph D. work.

Figure 3.22 SEM photograph of Rhone-Poulenc pellets (magnified 10000x). These pellets were requested to IFP only to study the kinetics of sorption.

Effect of purge gas and purge flowrate on ZLC desorption curves

Figure 3.23a) and Figure 3.23b) show the effect of purge flowrate on desorption curves at 573K obtained by the ZLC technique for the systems N₂-nC₅ and He-nC₅, respectively. It is
apparent from the figures that desorption curves are sensitive to the nature of purge gas; desorption in the system He-nC$_3$ is faster than in the system N$_2$-nC$_3$. This is an indication that crystal diffusion is not the total resistance in the system, but no information concerning the controlling mechanism can be drawn.

**Effect of crystal size on ZLC desorption curves**

The effect of crystal size on desorption curves in the system He-nC$_3$ is shown in Figure 3.24; experiments are carried out with the same pellet size. Desorption curves are insensitive to crystal size variations, so it is clear that the controlling resistance to mass transfer is the macropore diffusion.

**Effect of temperature in ZLC desorption curves**

The effect of temperature on desorption curves for the system N$_2$-nC$_3$ is shown in Figure 3.25 revealing a strong temperature dependence of desorption time (which can be erroneously interpreted as an activated diffusion with activation energy in the order of the heat of adsorption), indicating clearly macropore diffusion control.

According to these results, a model for ZLC desorption curves taking into account only macropore diffusion is the relevant one. Assuming pellets and crystals as spheres that model could be obtained by a limiting form of the ZLC complete model for bidisperse adsorbents, or starting from the assumption that macropore diffusion is the controlling mechanism as Ruthven and Xu (1993) did.

Another approach is to consider the pellets as an infinite cylinder, from which the relevant solution for the ZLC model in a macropore control system is (Crank, 1975),

\[
\frac{C_{\text{out}}}{C_0} = 2L \sum_{n=1}^{\infty} \frac{\exp\left(-\beta_n^2 \frac{D_p}{R_p} t / R_p^2 (1 + K)\right)}{\beta_n^2 + L^2} \tag{3.37}
\]

where $\beta_n$ are roots of transcendental Equation 3.38

\[
\beta_n J_1(\beta_n) - LJ_0(\beta_n) = 0 \tag{3.38}
\]

In the above equations $J_1(\beta_n)$ and $J_0(\beta_n)$ are Bessel functions of the first kind $C_{\text{out}}$ is the outlet concentration of ZLC cell, $C_0$ is the concentration at time zero in the ZLC cell and,
The solution given by Equation 3.37 can be also derived from a limiting form of the model developed for bidisperse porous adsorbents (see Appendix A1).

Figure 3.23 Effect of purge flowrate and purge gas in semi-log plots of $C_{\text{out}}/C_0$ versus $t$ obtained in the ZLC system. a) $N_2$-$nC_5$ at 573K. b) $He$-$nC_5$ at 573K. Dashed lines are the representation of the first term of series model.
Figure 3.24 Effect of crystal size in pellets at 573K in the system He-nC₅: semi-log plot of $C_{out}/C_0$ versus time $t$ in the ZLC system. (□) Cube size 3.6 μm; (○) Cube size 2 μm.

Figure 3.25 Effect of temperature on desorption curves in the system N₂-nC₅: semi-log plot of $C_{out}/C_0$ versus time $t$ in the ZLC system. Dashed lines are the representation of the first term of series model.
According to Eic and Ruthven (1988) an easy way to determine model parameters is to use the information of desorption curves at long times. Model series represented in Equation 3.37 at long times resumes to,

$$\ln \left( \frac{C_{out}}{C_0} \right) = \ln \left( \frac{2L}{\beta_i^2 + L^2} \right) - \frac{\beta_i^2 D_p t}{R_p^2 (1 + K)}$$  \hspace{1cm} (3.40)

The experimental intercept and slope of straight lines at long times in the semi-log plots of desorption curves seen in Figure 3.23 to Figure 3.25 are related to Equation 3.40. Using intercept and slope information in conjunction with the definition of parameter L, the relevant equations to obtain the model parameters are,

$$\frac{2L}{\beta_i^2 + L^2} = \text{Intercept} \quad \frac{-\beta_i^2 D_p}{R_p^2 (1 + K)} = \text{Slope} \quad \frac{L e_p D_p}{R_p^2} = \frac{1}{2} \frac{\text{Purge flowrate}}{\text{Pellets volume}}$$  \hspace{1cm} (3.41)

where Intercep, Slope, Purge flowrate and Pellets volume are experimental information. Another way was to use the experimental values of the intercept and slope represented in Equation 3.40 and the transcendental Equation 3.38. The two methods should give the same parameters. Model parameters calculated by the first procedure are summarised in Table 3.2 for the systems He-nC₅, N₂-nC₅ at temperatures 473K to 573K.

Time constants of diffusion are weakly temperature dependent which is consistent with a macropore diffusion control; however, apparent time constants for diffusion defined by \(D_p/R_p^2(1+K)\) plotted versus \(1/T\) in Figure 3.26 for the system He-nC₅, are strongly temperature dependent with an activation energy of 13.8 kcal/mol which is of the order of heat of adsorption 12.5 kcal/mol. Time constants range from \(0.002 \text{s}^{-1}\) at 473K up to \(0.03\text{s}^{-1}\) at 573K.

In order to check if the gravimetric technique leads to similar results obtained by ZLC, gravimetric experiments in similar conditions of the ZLC were performed. The adsorbent was saturated with a small partial pressure of paraffin (\(= 4 \times 10^{-3} \text{bar}\)) in order to ensure the validity of Henry's Law and desorbed with a high purge flow rate (near 600 ml/min STP). Assuming that the model representing the ZLC apparatus can be applied to the gravimetric technique the relevant solution is (Crank, 1975)
Table 3.2 Summary of experimental conditions and model results of diffusion parameters in the ZLC technique.

<table>
<thead>
<tr>
<th>Q(ml/min)</th>
<th>Intercept</th>
<th>Slope (s⁻¹)</th>
<th>(\tau_{\text{diff}}) (s)</th>
<th>L</th>
<th>(\beta_1)</th>
</tr>
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<tr>
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<td></td>
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</tr>
<tr>
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<td>Avg 0.19</td>
<td></td>
<td></td>
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</tbody>
</table>

\[
\frac{M_t}{M_0} = 4L_i^2 \sum_{n=1}^{\infty} \exp\left(-\beta_n^2 D_p t / R_p^2 (1 + K)\right) / \beta_n^2 (\beta_n^2 + L_i^2)
\]  

(3.42)

where \(M_t\) is the amount of sorbate in the pellet at time \(t\), and \(M_0\) is the amount of sorbate in the pellet at time zero. If \(L \to \infty\) then Equation 3.42 reduces to (Crank, 1975),
\[
\frac{M_t}{M_0} = 4 \sum_{n=1}^{\infty} \frac{1}{\beta_n^2} \exp\left( -\beta_n^2 D_p t / R_p^2 (1 + K) \right)
\]

(3.43)

where \( \beta_n \) are calculated from \( J_0(\beta_n) = 0 \). For more than 70% uptake only the first term is relevant and the model resumes to,

\[
\ln \left( \frac{M_t}{M_0} \right) = \ln \left( \frac{4}{\beta_1^2} \right) \frac{\beta_1^2 D_p}{R_p^2 (1 + K)}
\]

(3.44)

In order to apply Equation 3.44, experimental data of \( M_t/M_0 \) versus time \( t \) in a semi-log plot should be a straight line at long times with slope \(-\beta_1^2 D_p R_p^2 (1+K)\) and intercept \(4/\beta_1^2\).

Figure 3.27 shows the effect of temperature on desorption curves obtained with a high purge flow rate of helium in order to guarantee a high value of \( L \) to validate Equation 3.44. Desorption curves are well described by the theory outlined above. The apparent time constants of diffusion \( D_p/R_p^2 (1+K) \) calculated from the long time slopes in Figure 3.25 are represented in Figure 3.26; they range from 0.0016 s\(^{-1}\) at 473K to 0.024 s\(^{-1}\) at 573K.

**Figure 3.26** Apparent time constant of diffusion \( D_p/R_p^2 (1+K) \) versus \( 1/T \) for the gravimetric and ZLC systems.
Both techniques gave the same order of temperature dependence in apparent time constants of diffusion; however, the values obtained by gravimetry are slightly smaller than those obtained by the ZLC technique. The results obtained by gravimetric and ZLC techniques show that at low adsorbent loading, the macropore diffusion time constant controls the mass transfer in the systems He-nc5 and N2-nc5.

Diffusion mechanisms in macropores are Knudsen diffusivity in series with molecular diffusion, and so the pore diffusivity is,

$$D_p = \frac{1}{T_p \left( \frac{1}{D_m} + \frac{1}{D_K} \right)}$$  \hspace{1cm} (3.45)

Table 3.3 summarizes the values of experimental pore diffusivity $D_p$ (obtained from values of $\tau_{diff}$ in Table 3.2), Knudsen diffusivity $D_K$ (average pore size of 0.17 µm as in Rodrigues et al. (1996)), molecular diffusivity $D_m$ (estimated by Chapman-Enskog equation) and tortuosity factors $T_p$ predicted by Equation 3.45. The values of $T_p$ are similar in both systems and do not change with temperature suggesting that Equation 3.45 represents with good accuracy the macropore diffusion mechanisms of this system.

![Graph](image)

*Figure 3.27 Effect of temperature in uptake desorption curves in the system He-nc5 obtained by the gravimetric technique.*
Table 3.3 Experimental and predicted pore diffusivities.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>( \tau_{\text{dif}} ) (s)</th>
<th>( D_{p,\text{exp}} ) (cm(^2)/s)</th>
<th>( D_{m} ) (cm(^2)/s)</th>
<th>( D_{k} ) (cm(^2)/s)</th>
<th>( T_{p} )</th>
</tr>
</thead>
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<tr>
<td>573</td>
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<td>0.27</td>
<td>1.5</td>
</tr>
<tr>
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<td>0.26</td>
<td>1.5</td>
</tr>
<tr>
<td>473</td>
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<td>0.07</td>
<td>0.21</td>
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<td>1.6</td>
</tr>
</tbody>
</table>

System He-nC\(_6\)

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>( \tau_{\text{dif}} ) (s)</th>
<th>( D_{p,\text{exp}} ) (cm(^2)/s)</th>
<th>( D_{m} ) (cm(^2)/s)</th>
<th>( D_{k} ) (cm(^2)/s)</th>
<th>( T_{p} )</th>
</tr>
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<tr>
<td>573</td>
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<td>0.75</td>
<td>0.25</td>
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3.5 Kinetics of n-hexane sorption in pellets of 5A zeolite

As in the n-pentane/5A zeolite system, an estimate of the relative importance of diffusional resistances can be made. For example at 573K: \( D_{m}(\text{He-nC}_6)=0.95\ \text{cm}^2/\text{s} \); assuming tortuosity \( T_{p}=4 \) and particle porosity \( \varepsilon_p=0.35 \) as common values in a zeolite pellet, the capacity factor K calculated in the linear region of the isotherm is \( K=3823 \); for a pellet with radius \( R_p=0.08 \ \text{cm} \) the apparent time constant for diffusion in macropores will be \( D_p/R_p^2(1+K)=0.0097\ \text{s}^{-1} \). For micropore diffusion in the work of Cavalcante et al. (1995) a value of \( D_c\approx1\times10^{-8}\ \text{cm}^2/\text{s} \) at 573K is shown for a nC\(_6\) paraffin in 5A zeolite, from which we calculate \( D_c/r_c^2\approx1\ \text{s}^{-1} \) and \( \gamma=103 \), which suggests a macropore diffusion controlled regime.

Effects of purge gas and purge flowrate on ZLC desorption curves

Figures 3.28 a) and b) show the effect of purge flowrate on desorption curves at 573K obtained by the ZLC technique for the systems N\(_2\)-nC\(_6\) and He-nC\(_6\), respectively. It is apparent from the figures that desorption curves are sensitive to the nature of purge gas; desorption in the system He-nC\(_6\) is faster than in the system N\(_2\)-nC\(_6\). This is an indication
that crystal diffusion is not the total resistance in the system, but no information concerning
the controlling mechanism can be drawn.

*Effect of crystal size on ZLC desorption curves*

The effect of crystal size on desorption curves in the system He-nC₆ is shown in Figure
3.29; experiments are carried out with the same pellet size. Desorption curves are
insensitive to crystal size variations, so it is clear that the controlling resistance to mass
transfer is the macropore diffusion.

*Effect of temperature in ZLC desorption curves*

The effect of temperature on desorption curves for the system He-nC₆ is shown in Figure
3.30 revealing a strong temperature dependence of desorption time, indicating clearly
macropore diffusion control.

According to these results, and just as in the nC₅/5Å system a model for ZLC desorption
curves taking into account only macropore diffusion is the relevant one. Model parameters
calculated by the procedure described previously are summarised in Table 3.4 for the
systems He-nC₆, N₂-nC₆ at temperatures 473K to 573K.

Time constants of diffusion are weakly temperature dependent which is consistent with a
macropore diffusion control; however, apparent time constants for diffusion defined by
D₀/Rₚ²(1+K) plotted *versus* 1/T in Figure 3.31 for the system He-nC₆, are strongly
temperature dependent with an activation energy of 14.6 kcal/mol which is of the order of
heat of adsorption 14.2 kcal/mol. Time constants range from 0.00035 s⁻¹ at 473K up to
0.0053 s⁻¹ at 573K. In Figure 3.31 we also plot data obtained for n-pentane at the same
experimental conditions.
Figure 3.28 Effect of purge flowrate and purge gas in semi-log plots of $C_{\text{out}}/C_0$ versus $t$ obtained in the ZLC system. a) $N_2$-nC$_6$ at 573K. b) He-nC$_6$ at 573K. Dashed lines are the representation of the first term of series model.
Figure 3.29 Effect of crystal size in pellets at 573K in the system He-nC₆: semi-log plot of \( \frac{C_{\text{out}}}{C_0} \) versus time \( t \) in the ZLC system. (□) Cube size 3.6 \( \mu \text{m} \); (○) Cube size 2 \( \mu \text{m} \).

Figure 3.30 Effect of temperature on desorption curves in the system He-nC₆: semi-log plot of \( \frac{C_{\text{out}}}{C_0} \) versus time \( t \) in the ZLC system. Dashed lines are the representation of the first term of series model.
Table 3.4 Summary of experimental conditions and model results of diffusion parameters in the ZLC technique.

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<thead>
<tr>
<th>Q(ml/min)</th>
<th>Intercept</th>
<th>-Slope (s⁻¹)</th>
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<tr>
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</tr>
<tr>
<td><strong>System He-nC₆</strong></td>
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<td></td>
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<tr>
<td>Temperature 573K</td>
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<td>0.112</td>
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<td>49</td>
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<td>0.151</td>
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<td>1.62</td>
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<td>91</td>
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<td>0.018</td>
<td>0.150</td>
<td>3.8</td>
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<tr>
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<td></td>
<td></td>
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<tr>
<td>Temperature 523K</td>
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<tr>
<td>55</td>
<td>0.56</td>
<td>0.0039</td>
<td>0.151</td>
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<td>Avg 0.15</td>
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<tr>
<td>Temperature 473K</td>
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<tr>
<td>122</td>
<td>0.32</td>
<td>0.0015</td>
<td>0.16</td>
<td>5.5</td>
<td>2.05</td>
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</table>
Figure 3.31 Apparent time constant of diffusion $D_p/R_p^2(1+K)$ versus $1/T$ for the system He-$nC_6$ and He-$nC_5$ obtained by the ZLC technique.

In order to check if the gravimetric technique leads to similar results obtained by ZLC, gravimetric experiments in conditions similar to those of the ZLC were performed. The adsorbent was saturated with a small partial pressure of paraffin ($= 1 \times 10^{-4}$ bar) in order to ensure the validity of Henry's Law and desorbed with a high purge flowrate (near 600 ml/min STP) in order to guarantee a high value of $L$ to validate Equation 3.43. Figure 3.32 shows the effect of temperature on desorption curves. Desorption curves are well described by the theory outlined above. The apparent time constants of diffusion $D_p/R_p^2(1+K)$ calculated from the long time slopes in Figure 3.32 range from 0.00086 s$^{-1}$ at 523K to 0.0028 s$^{-1}$ at 573K. Both techniques gave the same temperature dependence in apparent time constants of diffusion; however, the values obtained by gravimetry are smaller than those obtained by the ZLC technique. The results obtained by gravimetric and ZLC techniques show that at low adsorbent loading, the macropore diffusion time constant controls the mass transfer in the systems He-$nC_6$ and N$_2$-$nC_6$. 
Figure 3.32 Effect of temperature in uptake desorption curves in the system He-nC₆ obtained by the gravimetric technique. Absolute temperatures are quoted in each curve.

In Table 3.5 we summarize the values of experimental pore diffusivity $D_p$ (obtained from values of $\tau_{diff}=R_p^2/\varepsilon_p D_p$ shown in Table 3.2, Knudsen diffusivity $D_k$ (average pore radius of 0.17 $\mu$m as in Rodrigues et al. (1996), molecular diffusivity $D_m$ (estimated by Chapman-Enskog equation) and tortuosity factors $T_p$ predicted by Equation 3.45. The values of $T_p$ are similar in both systems and do not change with temperature suggesting that Equation 3.45 represent with good accuracy the macropore diffusion mechanisms of these systems.
Table 3.2 Experimental pore diffusivities of n-hexane on 5A zeolite pellets and tortuosities.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>( \tau_{\text{dif}} ) (s)</th>
<th>( D_{\text{p,exp}} ) (cm(^2)/s)</th>
<th>( D_m ) (cm(^2)/s)</th>
<th>( D_k ) (cm(^2)/s)</th>
<th>( T_\mu )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>System N(_2)-nC(_6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>573</td>
<td>0.22</td>
<td>0.08</td>
<td>0.25</td>
<td>0.25</td>
<td>1.6</td>
</tr>
<tr>
<td>523</td>
<td>0.26</td>
<td>0.07</td>
<td>0.21</td>
<td>0.24</td>
<td>1.6</td>
</tr>
<tr>
<td>473</td>
<td>0.31</td>
<td>0.06</td>
<td>0.18</td>
<td>0.23</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>System He-nC(_6)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>573</td>
<td>0.14</td>
<td>0.13</td>
<td>0.95</td>
<td>0.25</td>
<td>1.5</td>
</tr>
<tr>
<td>523</td>
<td>0.15</td>
<td>0.12</td>
<td>0.82</td>
<td>0.24</td>
<td>1.5</td>
</tr>
<tr>
<td>473</td>
<td>0.16</td>
<td>0.11</td>
<td>0.69</td>
<td>0.23</td>
<td>1.6</td>
</tr>
</tbody>
</table>

3.6 Conclusions

A mathematical model for analysing ZLC desorption curves in bidisperse porous adsorbents was developed. The model indicates that problems may arise in the measurement of the diffusional time constants, since experimental desorption curves may have the same shape in completely different controlling regimes. To overcome these difficulties, we suggest a recipe for data treatment. We believe that this strategy, applied to a system that falls in the physical limits of the ZLC technique, is enough to obtain all the diffusional characteristics of bidisperse porous adsorbents pellets.

Mass transfer of n-pentane and n-hexane in 5A zeolite pellets was dominated at low loading of the adsorbent by macropore diffusion. This conclusion was confirmed by two independent experimental techniques, namely ZLC and gravimetry. The pore diffusivity of nC\(_5\) in pellets of 5A zeolite ranges from 0.07 to 0.09 cm\(^2\)/s when temperature changes from 473K to 573K in N\(_2\) carrier gas; for the system He-nC\(_5\) the pore diffusivity in the same temperature range varies from 0.1 to 0.14 cm2/s. For the nC\(_6\) system the range from 0.06 to 0.08 cm\(^2\)/s, when temperature changes from 473K to 573K in N\(_2\) carrier gas. With Helium as a carrier gas the values of the diffusivities range from 0.11cm\(^2\)/s to 0.13cm\(^2\)/s.
References


Karger, J. and Ruthven, D. M., On the comparison between macroscopic and n.m.r. measurements of intracrystalline diffusion in zeolites, Zeolites, 9, 267 (1989)


4. Fixed bed adsorption

Mathematical modelling of separation processes coupled with the evaluation of physical parameters such as equilibrium and kinetics of sorption from independent experiments can reduce significantly the number of experimental runs for the proper design of adsorption units and selection of the optimal operating conditions.

The aim of the present chapter is the formulation of a model to simulate transient adsorption of n/iso-paraffins mixtures in fixed-bed processes. A mathematical model is developed and tested through experiments with mixtures of n/iso-paraffins. The physical parameters of the model were determined on the basis of the results of equilibrium and kinetics of adsorption (Chapter 2 and 3) and from correlations available on literature. The reliability of the model is tested by studying the effect of operating variables (temperature, flowrate and partial pressure of adsorbable species) on breakthrough and desorption curves measured in an adsorption unit packed with pellets of 5A zeolite.

Finally, fundamental aspects of fixed bed adsorption such as the effect of velocity changes in fixed bed adsorption are studied and exemplified by the adsorption of two linearly species in the presence of an inert.
4.1 Introduction

The efficiency of adsorption columns is measured by the width of the mass transfer zone. The efficiency is higher when the mass transfer zone is narrow. The mass transfer zone can be measured by the breakthrough curve, which is the effluent concentration at the outlet as a function of time, when an initially clean bed is subjected to an inlet stream of constant concentration. It can be shown (Rodrigues, 1981) that the shape of the mass transfer zone depends primarily on the nature of the isotherm. A favorable isotherm (e.g. Type I) coupled with kinetic dispersive effects leads to a self sharpening of the mass transfer zone. An unfavorable isotherm (e.g. type III) leads to a dispersive wave, which spreads out continuously as it propagates through the column. A favorable isotherm in adsorption is unfavorable for desorption and vice-versa. The effects of axial dispersion, mass transfer resistances and the variation in fluid velocity due to sorption can change the mass transfer zone. The effects of axial dispersion and mass transfer resistances always increase the width of mass transfer zones. The variation of fluid velocity due to sorption can lead to a sharpening of the mass transfer zone (Ruthven, 1984; Le Van et al., 1988). The number of transitions depends on the number of components fed to the column. Single transitions occur only when the system is composed by one adsorbable component plus inert or two adsorbable species without inert. In an adiabatic system the energy balance gives one additional transition (Pan and Basmadjian, 1970; Sweed, 1981; Jacob and Tondeur, 1983). In an isothermal operation two adsorbable species plus an inert or three adsorbable components lead to two transitions. When more than three components are present in the column multiple transitions can be obtained (Helfferich and Klein, 1970). A common feature of multicomponent fixed bed adsorption is that one component may exceed its feed concentration. This effect is generally called “Roll-up” and has been exemplified and explained by Glueckauf (1949) for the case of three components (two adsorbable species plus an inert; isothermal operation) in a system governed by favourable isotherms.

Analytical solutions of the mass balance equations can generally be obtained for the simplest cases of single transitions with linear equilibrium. Rodrigues and Tondeur (1981), Vermeulen (1984) and Ruthven (1984) gave a good review. However, the most important cases of adsorption are confined to non-isothermal multicomponent systems with favourable isotherms, where axial dispersion and pore diffusion effects are of importance.
In these cases only numerical solutions of the coupled partial differential equation can be obtained. The method of characteristics is a powerful technique but is limited only to first order partial differential equations; a study of an adiabatic adsorber governed by favourable isotherms with a lumped pore diffusion model has been done by Harwell (1980) using this technique. The method of orthogonal collocation (Villadsen and Michelsen, 1978) proved to be a powerful method to solve multicomponent fixed bed adsorber problems with nonlinear isotherms. It has been applied by Liapis and Rippin (1977) to describe multicomponent adsorption from a finite bath onto adsorbent particles in a system governed by the multicomponent Langmuir isotherm. Later Santacesaria et al. (1982) used this technique to solve multicomponent isothermal liquid separation of xylenes on Y zeolites. The extension to the gas phase separation of xylenes on Y zeolites was done by Morbidelli et al. (1985). In both cases the multicomponent Langmuir isotherm is used and a very efficient and robust solution of the complex coupled partial differential equations is reported. In this laboratory orthogonal collocation methods were used by Costa (1984) to solve a model for the adsorption of phenol on polymeric adsorbents, Leitão (1987) in the study of the Merox process and Quinta Ferreira (1988) in the analysis of fixed bed catalytic reactors containing large pores and bidisperse catalysts. The moving finite element method (Sereno, 1989) is also an effective strategy to solve fixed bed adsorption problems.

4.2 Mathematical model for fixed bed adsorption of n/iso-paraffins mixtures

The adsorption system considered is a non-isothermal, non-adiabatic column packed with pellets of 5A zeolite through which an inert gas flows in steady state. At time zero a mixture of n/iso-paraffins of known composition and an inert is introduced at the bottom of column. The mixture is fed until the column is saturated. Then countercurrent or cocurrent purge of the column with inert is carried out. The following additional assumptions are made:

1. Ideal gas law applies;

2. The pressure drop through the bed is negligible;

3. The flow pattern is described by the axial dispersed plug flow model;
4. The main resistances to mass transfer for adsorbable species are external fluid film resistance and macropore diffusion in series as pointed out in Chapter 3. External resistance and macropore diffusion can be combined in a global resistance according to a lumped model for the adsorbent particle as suggested by Morbidelli et al. (1982);

5. A resistance to heat transfer exists in the external fluid film around the solid;

6. The temperature dependence of gas and solid properties is neglected;

7. The column is adiabatic or isothermal or non-isothermal/non-adiabatic;

8. The adsorption equilibrium is described by Nitta et al.'s (1984) isotherm.

According to these assumptions model equations are:

**Ideal gas law**

\[ C_i = \frac{P}{RT} \]  \hspace{1cm} (4.1)

where, \( C_i \) is the total gas concentration in bulk gas phase, \( P \) is the total pressure, \( R \) is the ideal gas constant and \( T \) is the temperature in bulk gas phase.

**Mass balance to sorbate species**

\[ \varepsilon_b D_{ax} \frac{\partial}{\partial z} \left( C_i \frac{\partial y_i}{\partial z} \right) = \frac{\partial}{\partial z} (F y_i) + \varepsilon_b \frac{\partial}{\partial t} (C_i y_i) + (1 - \varepsilon_b) \rho_a \frac{\partial q_{li}}{\partial t} \]  \hspace{1cm} (4.2)

where, \( y_i \) is the mole fraction of sorbate species \( i \) in the bulk gas phase, \( F \) is the total molar flux, \( q_{li} \) is the average adsorbed phase concentration, \( \rho_a \) is the apparent adsorbent density, \( z \) and \( t \) are the axial coordinate and time, respectively, \( D_{ax} \) is the axial dispersion coefficient and \( \varepsilon_b \) is the bed porosity.

The boundary conditions are:

\[ z = 0; \ t > 0 \quad \varepsilon_b D_{ax} C_i \frac{\partial y_i}{\partial z} = F(y_i - y_{if}) \]  \hspace{1cm} (4.3)
\[ z = L; \ t > 0 \quad \frac{\partial y_i}{\partial z} = 0 \]  

(4.4)

where \( y_i \) is the molar fraction at inlet of the column and \( L \) the length of the column.

**Overall mass balance**

\[ \frac{\partial F}{\partial z} + \varepsilon_b \frac{\partial C_i}{\partial t} + (1 - \varepsilon_b) \rho_s \sum_{i=1}^{ncp} \frac{\partial \tilde{q}_i}{\partial t} = 0 \]  

(4.5)

where \( ncp \) is the number of components in the mixture.

The boundary condition is:

\[ z = 0; \ t > 0 \quad F = F_f \]  

(4.6)

where \( F_f \) is the total molar flux of feed.

**Mass transfer rate**

Since the accumulation of mass in gas phase can be neglected relatively to the solid phase the following equation is valid in a lumped particle system controlled by macropore diffusion (Morbidelli et al., 1982),

\[ \rho_s \frac{\partial \tilde{q}_i}{\partial t} = a_p K_{gl} C_i (y_i - \bar{y}_i) \]  

(4.7)

where \( \bar{y}_i \) is the average mole fraction of species \( i \) in the macropores, \( a_p \) is the specific area of particle and \( K_{gl} \) is the overall mass transfer coefficient which is defined by,

\[ \frac{1}{K_{gl}} = \frac{1}{k_e} + \frac{1}{\varepsilon_p k_i} \]  

(4.8)

where \( k_e \) is the external film mass transfer coefficient, \( k_i \) is the internal mass transfer coefficient (Glueckauf, 1955) and \( \varepsilon_p \) is the intraparticle porosity.
Adsorption equilibrium isotherm

It has been shown in Chapter 2 that the adsorption equilibria of n-pentane and n-hexane in 5A zeolite pellets are satisfactorily described by Nitta et al.'s model isotherm. Neglecting the interaction term between adsorbed molecules Nitta et al.'s multicomponent adsorption isotherm is,

\[ \theta_i = K_{eq}^i P y_i \left[ 1 - \sum_i \theta_i \right]^{n_i} \]  

(4.9)

where \( \theta_i = q_i / q_{max} \) is the coverage of adsorbent by species \( i \), \( q_i \) is the adsorbed phase concentration of species \( i \), \( n_i \) is the coefficient of the pure component isotherm for species \( i \), \( q_{max} \) is the maximum adsorbed concentration, \( K_{eq} = k_w \exp(-\Delta H_i / RT_i) \) is the equilibrium constant of species \( i \), \( -\Delta H_i \) is the heat of adsorption of species \( i \), and \( T_i \) is the adsorbent temperature.

Energy balance

a) Gas phase

\[ K_{ax} \frac{\partial^2 T}{\partial z^2} = \frac{F c_{pe}}{\rho_e} \frac{\partial T}{\partial z} + e_b C_v e_{tg} \frac{\partial T}{\partial t} + (1 - e_b) a_p h_p (T - T_i) + a_e h_w (T - T_w) \]  

(4.10)

where \( K_{ax} \) is the effective heat axial dispersion coefficient, \( T_w \) is the wall temperature, \( h_p \) is the film heat transfer coefficient, \( h_w \) is the wall heat transfer coefficient, \( c_{pe} \) is the heat capacity of the fluid phase and \( a_e = 2 / R_c \) is the specific area of column (\( R_c \) is the internal column radius)

The boundary conditions are:

\[ z = 0; t > 0 \quad K_{ax} \frac{\partial T}{\partial z} = F c_{pe} (T - T_f) \]  

(4.11)

\[ z = L; t > 0 \quad \frac{\partial T}{\partial z} = 0 \]  

(4.12)

where \( T_f \) is the feed gas temperature.
b) solid phase

\[ \rho_s c_p \frac{\partial \bar{T}_s}{\partial t} = a_p h_p (T - T_s) + \rho_s \sum_{i=1}^{n_p} \Delta H_i \frac{\partial \bar{q}_i}{\partial t} \]  

(4.13)

where \( c_p \) is the heat capacity of adsorbent.

Initial conditions

**Adsorption**

\[ t = 0; \forall z; \ y_i = \bar{y}_i = \bar{q}_i = 0; \ F = F_f; \ C_i = C_{if} \]  

(4.14)

\[ t = 0; T = T_s = T_w(z) \]  

(4.15)

**Desorption**

\[ t = 0; \forall z; \ y_i = \bar{y}_i = \bar{y}_{if}; \ F = F_f; \ C_i = C_{if} \]  

(4.16)

\[ t = 0; \bar{q}_i = q_i(y_{if}, y_{xf}, \ldots, y_{if}; T_s = T_s(z)) \]  

(4.17)

\[ t = 0; T = T(z); T_s = T_s(z); T_w = T_w(z) \]  

(4.18)

Dimensionless model equations

Introducing dimensionless variables for space \( \bar{z} = z/L \), time \( \tau = \tau_{if}/L \), molar flux \( \bar{F} = F/F_f \), averaged adsorbed phase concentration \( \bar{q}_i = \bar{q}_i / q_{if} \), total concentration \( \bar{C}_i = C_i / C_{if} \), and fluid, solid and wall temperature \( \bar{T} = (T - T_f)/T_f \), \( \bar{T}_s = (T_s - T_f)/T_f \), \( \bar{T}_w = (T_w - T_f)/T_f \), respectively, dimensionless model equations become:

**Overall mass balance**

\[ \frac{\partial \bar{F}}{\partial \bar{z}} + y_{if} \frac{\partial \bar{q}_i}{\partial \tau} + \frac{\partial \bar{C}_i}{\partial \tau} = 0 \]  

(4.19)

where \( y_{if} \) is the mole fraction of species \( i \) in the feed gas phase and \( \xi_{mi} \) is the mass capacity factor for species \( i \).
Boundary condition:

\[ \bar{z} = 0; \ t > 0; \ \bar{F} = 1 \]  \hspace{1cm} (4.20)

**Sorbate mass balance**

\[ \frac{\bar{C}_i}{P_{em}} \frac{\partial^2 y_i}{\partial \bar{z}^2} = \frac{\partial (\bar{F} y_i)}{\partial \bar{z}} + \frac{\partial (\bar{C}_i y_i)}{\partial \tau} + y_{it} \xi_n \frac{\partial \bar{q}_i}{\partial \tau} \]  \hspace{1cm} (4.21)

where \( P_{em} \) is the mass Peclet number for the column.

Boundary conditions:

\[ \bar{z} = 0; \ \tau > 0 \ \frac{1}{P_{em}} \frac{\partial y_i}{\partial \bar{z}} = \frac{\bar{F}}{\bar{C}_i} (y_i - y_{it}) \]  \hspace{1cm} (4.22)

\[ \bar{z} = 1; \ \tau > 0 \ \frac{\partial y_i}{\partial \bar{z}} = 0 \]  \hspace{1cm} (4.23)

**Mass transfer rate**

\[ y_{it} \xi_n \frac{\partial \bar{q}_i}{\partial \tau} = N_f \bar{C}_i (y_i - \bar{y}_i) \]  \hspace{1cm} (4.24)

where \( N_f \) is the number of mass transfer units.

**Adsorption equilibrium isotherm**

\[ \theta_{it} \bar{q}_i = K_{eq} (\bar{T}_s) P_{Y_i} \left[ 1 - \sum \theta_{it} \bar{q}_i \right]^{n_i} \]  \hspace{1cm} (4.25)

where \( \theta_{it} \) is the coverage of adsorbent at \( y_{it} \), and \( K_{eq} (\bar{T}_s) = K_{eq} (T_f) \exp \left[ - \gamma_f \bar{T}_s / (1 + \bar{T}_s) \right] \),

where \( \gamma_f = (-\Delta H_f) / RT_f \) is the Arrhenius number.
Energy balance

a) gas phase

\[
\frac{1}{Pe_{mf}} \frac{\partial^2 \tilde{T}}{\partial \tilde{z}^2} = \tilde{F} \frac{\partial \tilde{T}}{\partial \tilde{z}} + \tilde{C}_i \frac{\partial \tilde{T}}{\partial \tau} + N_{mf} (\tilde{T} - \tilde{T}_s) + N_{hw} (\tilde{T} - \tilde{T}_w)
\]  \hspace{2cm} (4.26)

where \(Pe_{mf}\) is the heat Peclet number for the column, \(N_{mf}\) is the number of film heat transfer units and \(N_{hw}\) is the number of wall heat transfer units.

Boundary conditions:

\[
\tilde{z} = 0; \tau > 0 \quad \frac{1}{Pe_{mf}} \frac{\partial \tilde{T}}{\partial \tilde{z}} = \tilde{F} (\tilde{T} + 1) - 1
\]  \hspace{2cm} (4.27)

\[
\tilde{z} = 1; \tau > 0 \quad \frac{\partial \tilde{T}}{\partial \tilde{z}} = 0
\]  \hspace{2cm} (4.28)

b) solid phase

\[
\xi_s \frac{\partial \tilde{T}_s}{\partial \tau} = N_{mf} (\tilde{T} - \tilde{T}_s) + \xi_s B_i \frac{\partial \tilde{q}_l}{\partial \tau}
\]  \hspace{2cm} (4.29)

where \(\xi_s\) is the heat capacity factor and \(B_i\) is the dimensionless adiabatic temperature rise for species \(i\).

Initial conditions

Adsorption

\[
\tau = 0; \forall \tilde{z}; y_i = \tilde{y}_i = \tilde{q}_l = 0; \tilde{F} = 1; \tilde{C}_i = 1
\]  \hspace{2cm} (4.30)

\[
\tau = 0; \tilde{T} = \tilde{T}_s = \tilde{T}_w (\tilde{z})
\]  \hspace{2cm} (4.31)

Desorption

\[
\tau = 0; \forall \tilde{z}; y_i = \tilde{y}_i = \tilde{y}_{i, rf}; \tilde{F} = 1; \tilde{C}_i = 1
\]  \hspace{2cm} (4.32)

\[
\tau = 0; \tilde{q}_l = \tilde{q}_l (y_{i, rf}, y_{2f}, ..., y_{rf}); \tilde{T}_s = \tilde{T}_s (\tilde{z})
\]  \hspace{2cm} (4.33)
\[ \tau = 0; \tilde{T} = \tilde{T}(\overline{z}); \tilde{T}_s = \tilde{T}_s(\overline{z}); \tilde{T}_w = \tilde{T}_w(\overline{z}) \]  

(4.34)

Model parameters are defined as:

**Mass Peclet number for the column**

\[ Pe_{mf} = \frac{v_{if}L}{D_{ax}} \]  

(4.35)

**Heat Peclet number for the column**

\[ Pe_{mh} = \frac{C_{if} c_{ps} \varepsilon_b v_{if} L}{K_{ax}} \]  

(4.36)

**Mass capacity factor**

\[ \xi_{mi} = \frac{1 - \varepsilon_b \rho_s \eta_{if}}{\varepsilon_b \eta_{if} C_{if}} \]  

(4.37)

**Heat capacity factor**

\[ \xi_{vh} = \frac{1 - \varepsilon_b \rho_a c_{ps}}{\varepsilon_b C_{if} c_{ps}} \]  

(4.38)

**Number of mass transfer units**

\[ N_f = \frac{1 - \varepsilon_b a_p K_{ef} L}{\varepsilon_b v_{if}} \]  

(4.39)

**Number of film heat transfer units**

\[ N_{hf} = \frac{1 - \varepsilon_b a_p h_p L}{\varepsilon_b C_{if} c_{ps} v_{if}} \]  

(4.40)
Number of wall heat transfer units

\[ N_{hw} = \frac{a_z h_w L}{\varepsilon_b C_p c_p v_{ef}} \]  \hspace{1cm} (4.41)

Adiabatic temperature rise

\[ B_i = \frac{(-\Delta H_i) q_{if}}{c_p T_i} \]  \hspace{1cm} (4.42)

Arrhenius number

\[ \gamma_{if} = \frac{(-\Delta H_i)}{RT_i} \]  \hspace{1cm} (4.43)

Non-linearity parameter of the isotherm

\[ \theta_{if} = \frac{q_{if}}{q_{max}} \]  \hspace{1cm} (4.44)

Numerical solution of model equations

The set of coupled partial differential equations shown in the dimensionless form was reduced first to a set of ordinary differential/algebraic equations (DAEs) applying orthogonal collocation technique (Villadsen and Michelsen, 1978) to the spatial coordinate. The collocation points were given by the zeros of Jacobi polynomials \( P_N^{(\alpha, \beta)} (z) \), with \( \alpha = \beta = 0 \). The resulting system was solved using a fifth order Runge-Kutta code (ODE’s) in conjunction with a Gauss elimination (Algebraic equations). Sixteen collocation points appeared to give satisfactory accuracy for all calculations performed. Details are given in Appendix A3.

Determination of model parameters involved in the adsorber model

The adsorbent is the same used in the study of equilibrium and kinetics of sorption. Table 4.1 summarizes the properties of the adsorbent.
Table 4.1 Adsorbent properties (5A zeolite, Rhone-Poulenc)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk density, $\rho_b$ (g/cm$^3$)</td>
<td>0.77</td>
</tr>
<tr>
<td>Apparent particle density, $\rho_a$ (g/cm$^3$)</td>
<td>1.13</td>
</tr>
<tr>
<td>Bed porosity, $\varepsilon_b$</td>
<td>0.32</td>
</tr>
<tr>
<td>Particle porosity, $\varepsilon_p$</td>
<td>0.35</td>
</tr>
<tr>
<td>Particle diameter, $d_p$ (mm)</td>
<td>1.6</td>
</tr>
<tr>
<td>Length (mm)</td>
<td>≈6</td>
</tr>
</tbody>
</table>

The axial mass dispersion coefficient ($D_{ax}$) was estimated from the correlation of Hsu and Haynes (1981),

$$\frac{1}{Pe_m} = 0.328 \frac{3.33}{ReSc \left(1 + 0.59(ReSc)^{-1}\right)}$$

(4.45)

where $Pe_m = \nu d_p / D_{ax}$ is the axial particle Peclet number, $Re = \nu d_p / \mu$ is the Reynolds number and $Sc = \mu / \rho_g D_m$ is the Schmidt number. The above correlation was obtained from experiments in a range $0.08 < ReSc < 1$, similar to that found in our work. Reynolds number in our system range from 0.6 to 1. The effective axial bed thermal conductivity ($K_{ax}$) was estimated by the correlation proposed by Votruba (1972),

$$\frac{1}{Pe_{hf}} = \frac{\lambda_{e}^0 / \lambda_f}{Re Pr} + \frac{14.5}{d_p \left(1 + \frac{A}{Re Pr}\right)}$$

(4.46)

with,

$$\frac{\lambda_{e}^0}{\lambda_f} = \left(\frac{\lambda_s}{\lambda_f}\right)^{0.28 - 0.737 \log \varepsilon_s - 0.057 \log \frac{\lambda_s}{\lambda_f}}$$

(4.47)

In the above equations $Pe_h = C_p v d_p / K_{ax}$ is the axial heat Peclet number particle number based on particle diameter, $\lambda_{e}^0$ is the effective thermal conductivity of stagnant bed, $\lambda_f$ is the fluid thermal conductivity, $\lambda_s$ is the solid thermal conductivity, $A$ is a constant ranging from 0 to 5 and $Pr = \nu C_p / \lambda_f$ is the Prandtl number. For cylinders a reasonable value of $A$ is 3.2 as pointed out by Votruba. The value of $\lambda_s$ is fixed in 0.3 W/m.K (Bourdin et al., 1996).
A typical value of $\lambda_e$ for the systems under study is 0.04 W/m.K (Reid, 1987), which gives a value of $\lambda_e^0$ around 0.32 W/m.K by the use of Equation 4.47.

Mass transfer inside the adsorbent was controlled by macropore diffusion as shown in Chapter 3. The intraparticle mass transfer coefficient ($k_i$) can be calculated according to a lumped model proposed by Glueckauf (1955),

$$k_i = \frac{5D_p}{R_p}$$  \hspace{1cm} (4.48)

where $D_p$ is the pore diffusivity and $R_p$ is the particle radius. Values of $k_i$ are in the order of 4.0 cm/s for the fixed bed studies of this work.

The external mass transfer coefficients ($k_e$) were estimated with the correlation of Wakao and Funazkri (1978),

$$Sh = 2.0 + 1.1 \text{Re}^{0.6} \text{Sc}^{0.35}$$  \hspace{1cm} (4.49)

where $Sh=k_e d_p/D_m$ is the Sherwood number. Values of $k_e$ are in the order of 3.0 cm/s for a flowrate around 150 ml/min (at 298K and 1 bar)

Only two parameters need to be estimated: the heat transfer coefficient between solid and bulk fluid and the heat transfer coefficient between the system and the surroundings. These parameters were obtained by matching the experimental curves.

### 4.3 Experimental section

The experimental set-up used for the study of fixed bed adsorption of mixtures of n/iso-paraffins is shown in Figure 4.1. It has four major sections: preparation of gases, adsorption column inside a furnace, analysis of gases and data acquisition. A description of experimental setup follows:

**Preparation of gases**

With three Teledyne-Hastings (USA) mass flow controllers (fm) nitrogen or helium are bubbled in Scott (Germany) saturators (wb) containing iso-pentane, n-pentane and n-hexane which are immersed in a controlled Techne (United Kingdom) thermostatic bath
(tb). The bubble soap (bs) allows the measurement of the gas flowrate at the outlet of the washing-bottle. With the measurement of the total flowrate at the outlet of the washing-bottle the partial pressure of the paraffin can be obtained. The rotameter (r) has the function of maintaining the adsorption column with the flux of an inert gas between experiments. This is to clean the adsorbent and to avoid its destruction at high temperatures; at the same time no electrical equipment is on.

Figure 4.1 Schematic diagram of experimental apparatus used for the study of fixed bed adsorption. Legend: c -Computer with data acquisition board; Cr -Chromatograph; f -Furnace; fb -Fixed bed; FID -Detector of gas chromatograph; fn -Flow meters; fnmc -Flow meters unit control; m - Pressure manometer; p -PID control of furnace; t -thermocouples; tb -Thermostated bath; wb -Washing-bottles 1,2,3,4,5,6,7,8,9 - on-off valves 10,11,12 -Needle valves.
Adsorption column and oven

The oven (b2) is the same described in Chapter 2 for the measurement of adsorption equilibrium isotherms. The column is in stainless steel with a diameter of 3.35 cm and 40 cm long. In the extremities two tampons Swagelock are adapted in order to connect the column to the gas tubes. Since the oven cavity (a2) is 22 cm long only, 20 cm were occupied by adsorbent (d2); the rest (20 cm) was filled with glass spheres (e2). In the extremities of the column two concentric rings (f2) with a mesh support for the adsorbent were used. Glass wool was also used in order to avoid dust passing to the rest of the installation. Two Omega (USA) thermocouples type K (tc) were inserted axially in the column, one near the middle of the column, and the other at the top. A schematic diagram of the arrangement of the column and oven is shown in Figure 4.2

*Figure 4.2 Schematic representation of adsorption column and oven.*
Analysis of gases

The analysis of the gases running in the column is performed with a Carlo Erba (Italy) gas chromatograph (cr) equipped with a FID detector. The chromatographic technique is based in the frontal chromatography since there is no competition between normals and iso paraffins (the iso-paraffins do not adsorb in the 5A zeolite). At the space time of the adsorber a rich fraction of isoparaffins is obtained and detected by the FID. This signal is constant until the first concentration wave of normals leaves the column. Since there is some selectivity between n-pentane and n-hexane it is possible to detect another signal corresponding to the evolution of the second wave produced in the adsorber.

When high flowrates and concentrations are running in the column it is not possible to send all the effluent to the FID. A special arrangement (y) that collects only a small fraction of the effluent was developed. This arrangement consists of two needle valves (10, 11). The fraction going to the chromatograph can be further diluted with helium if necessary (12). At the beginning of the experiments, the feed is bypassed (ya) to the end of the column allowing the regulation of the needle valves in order to obtain the best resolution in the FID detector for a given experiment.

Data acquisition

Data acquisition is performed with the interface already described in Chapter 2. A special program in Basic language was developed in order to monitor and record the temperature evolution in the adsorber and the signal produced in the FID.

Procedure

Before the first run the column was activated by purging with nitrogen during 24 hours from ambient temperature to 633K. The experiment starts by passing inert gas in the column upflow with a flowrate similar to the one used in adsorption. At the same time the mixture of n/iso-paraffins was produced in the washing-bottles and analysed in the chromatograph. Once the temperature in the column is constant the inert is replaced by the mixture through the switching of valves. The effluent of the column is sent to the chromatograph and continuously analysed. Since iso-pentane does not adsorb in 5A zeolite,
an increase of signal in computer was detected practically at the space-time. This signal is constant until breakthrough of n-pentane and n-hexane occurs. Desorption is performed in a similar manner by switching of valves that allows cocurrent or countercurrent purge with inert.

4.4 Fixed bed adsorption of mixtures of n-pentane/iso-pentane/nitrogen

Experimental adsorption runs were performed in order to study the influence of temperature, adsorbate partial pressure and flowrate on the performance of the adsorption unit. At the same time validation of the model is tested relatively to experiments made. Experimental conditions, model parameters and dimensionless model parameters are summarized in Tables 4.2, 4.3 and 4.4.

Effect of temperature

Figures 4.3 a), b) and c) show the effect of temperature in adsorption breakthrough curves for bed inlet temperature of 548K, 498K and 448K, respectively. The total flowrate (190ml/min at 298K), partial pressure of n-pentane (y_{nC5}=0.19) and total pressure (P=1bar) were kept constant during the experiments. The time evolution of the bed temperature profile during sorption process at two locations: Z =0.6 and column outlet is also shown. Here we should note that a significant difference in the temperature at the middle and outlet of the fixed bed exists at the beginning of experiments as can be seen in Figure 4.3. This is due to a parabolic profile existing in the oven. The maximum temperature is located at the middle of the oven, and decreases to both ends. Since fixed bed occupies the entire oven this effect reflects in a nonuniform temperature in the adsorber similar to that found in the oven. This profile is fixed and independent of adsorption in fixed bed. The existence of a parabolic profile inside the column apparently does not affect the sharp nature of breakthrough curves, which is expected since the isotherm of n-pentane is highly favorable at the partial pressure studied and the global mass transfer coefficient is quite high ($a_pK_g=30s^{-1}$ at 548K to $a_pK_g=24s^{-1}$ at 448K).

The adsorbed concentration increases when temperature decreases as a consequence of a high heat of adsorption of n-pentane of 13.2 kcal/mol predicted by Nitta et al.'s isotherm. As the temperature decreases more heat is generated during sorption as we can see from the evolution of temperature at the two locations selected; temperature at $Z =0.6$ increases near
7°K at 548K and 20°K at 448K. The final approach of breakthrough curve to the equilibrium value is slow as a consequence of the temperature increase owed to adsorption; only when temperature reaches its equilibrium value the breakthrough curve reaches the feed composition. Nevertheless, the equilibrium theory for adiabatic processes (Pan and Basmasdijan, 1970) could not be tested since our column is non-isothermal, non-adiabatic. It is clearly seen from Figures 4.3 a), b) and c) that both thermal and concentration waves appear at the end of column at the same time. This is expected since the parameter $\xi_m/\xi_b$ (which measures the relative velocity of thermal and concentration waves in an adiabatic system with a favorable isotherm) is lower than one at least in the experimental conditions used. Values of $\xi_m$ and $\xi_b$ for this system are reported in Table 4.4

**Table 4.2 Experimental conditions for fixed bed adsorption of n-pentane/i-pentane/nitrogen mixtures**

<table>
<thead>
<tr>
<th>Run</th>
<th>Fig.</th>
<th>$F_r$ (mol/m²s)</th>
<th>$T_f$ (K)</th>
<th>$y_{ics,f}$</th>
<th>$y_{ics,t}$</th>
<th>$P$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>4.3a</td>
<td>0.15</td>
<td>548</td>
<td>0.19</td>
<td>0.33</td>
<td>1.0</td>
</tr>
<tr>
<td>12</td>
<td>4.3b</td>
<td>0.15</td>
<td>498</td>
<td>0.17</td>
<td>0.33</td>
<td>1.0</td>
</tr>
<tr>
<td>13</td>
<td>4.3c</td>
<td>0.15</td>
<td>448</td>
<td>0.18</td>
<td>0.31</td>
<td>1.0</td>
</tr>
<tr>
<td>21</td>
<td>4.4a;4.5c</td>
<td>0.11</td>
<td>548</td>
<td>0.04</td>
<td>0.45</td>
<td>1.0</td>
</tr>
<tr>
<td>22</td>
<td>4.4b;4.6b</td>
<td>0.11</td>
<td>498</td>
<td>0.05</td>
<td>0.49</td>
<td>1.0</td>
</tr>
<tr>
<td>31</td>
<td>4.5b</td>
<td>0.11</td>
<td>548</td>
<td>0.09</td>
<td>0.44</td>
<td>1.0</td>
</tr>
<tr>
<td>33</td>
<td>4.5a</td>
<td>0.10</td>
<td>548</td>
<td>0.19</td>
<td>0.29</td>
<td>1.0</td>
</tr>
<tr>
<td>41</td>
<td>4.6a;4.7a;4.8</td>
<td>0.10</td>
<td>498</td>
<td>0.09</td>
<td>0.40</td>
<td>1.0</td>
</tr>
<tr>
<td>51</td>
<td>4.7b</td>
<td>0.14</td>
<td>498</td>
<td>0.11</td>
<td>0.40</td>
<td>1.0</td>
</tr>
</tbody>
</table>

In Figures 4.4 a) and b) a similar analysis of the temperature effect is performed except that a small partial pressure ($y_{ics}=0.05$) of n-pentane is used. The breakthrough curves are less abrupt than in the previous case which confirms that the shape of the isotherm is relevant in the system under study. Also temperature changes in column are less important since lower adsorption occurs.
Model predictions are in close agreement with experimental results as shown in Figure 4.3 and Figure 4.4. The values of the parameters concerning heat transfer at the wall and from solid to bulk fluid, calculated in order to match experimental curves, range from 14 to 15 W/m²K and from 6.7 to 9.2 W/m²K, respectively.

**Table 4.3** Model parameters for fixed bed adsorption of n-pentane/i-pentane/nitrogen mixtures

<table>
<thead>
<tr>
<th>Run</th>
<th>Fig.</th>
<th>( D_{ax} \times 10^5 ) m³/s</th>
<th>( K_{ax} ) W/mK</th>
<th>( k_i \times 10^2 ) m/s</th>
<th>( k_f \times 10^2 ) m/s</th>
<th>( K_{gf} \times 10^2 ) m/s</th>
<th>( h_p ) W/m²K</th>
<th>( h_w ) W/m²K</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>4.3a</td>
<td>9.1</td>
<td>0.35</td>
<td>4.4</td>
<td>3.5</td>
<td>1.06</td>
<td>9.2</td>
<td>15</td>
</tr>
<tr>
<td>112</td>
<td>4.3b</td>
<td>9.0</td>
<td>0.35</td>
<td>3.9</td>
<td>3.1</td>
<td>0.95</td>
<td>7.8</td>
<td>15</td>
</tr>
<tr>
<td>113</td>
<td>4.3c</td>
<td>8.4</td>
<td>0.35</td>
<td>3.4</td>
<td>2.8</td>
<td>0.83</td>
<td>6.7</td>
<td>14</td>
</tr>
<tr>
<td>121</td>
<td>4.4a; 4.5c</td>
<td>6.9</td>
<td>0.34</td>
<td>4.4</td>
<td>3.4</td>
<td>1.05</td>
<td>8.7</td>
<td>14</td>
</tr>
<tr>
<td>122</td>
<td>4.4b; 4.6b</td>
<td>6.4</td>
<td>0.34</td>
<td>3.9</td>
<td>3.0</td>
<td>0.94</td>
<td>7.5</td>
<td>14</td>
</tr>
<tr>
<td>131</td>
<td>4.5b</td>
<td>7.1</td>
<td>0.34</td>
<td>4.3</td>
<td>3.4</td>
<td>1.05</td>
<td>8.9</td>
<td>14</td>
</tr>
<tr>
<td>133</td>
<td>4.5a</td>
<td>6.5</td>
<td>0.34</td>
<td>4.3</td>
<td>3.3</td>
<td>1.03</td>
<td>8.6</td>
<td>14</td>
</tr>
<tr>
<td>141</td>
<td>4.6a; 4.7a; 4.8</td>
<td>5.8</td>
<td>0.33</td>
<td>3.9</td>
<td>2.9</td>
<td>0.93</td>
<td>7.3</td>
<td>14</td>
</tr>
<tr>
<td>151</td>
<td>4.7b</td>
<td>8.6</td>
<td>0.35</td>
<td>3.9</td>
<td>3.1</td>
<td>0.95</td>
<td>7.8</td>
<td>14</td>
</tr>
</tbody>
</table>

**Table 4.4** Dimensionless model parameters for fixed bed adsorption of n-pentane/i-pentane/nitrogen mixtures

<table>
<thead>
<tr>
<th>Run</th>
<th>Fig.</th>
<th>Pémf</th>
<th>Péhf</th>
<th>Nf</th>
<th>Nhaf</th>
<th>Nhwh</th>
<th>( \xi_{sm} )</th>
<th>( \xi_{sh} )</th>
<th>( \theta_{hf} )</th>
<th>( \gamma_f )</th>
<th>( B_{i \times 10^6} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>4.3a</td>
<td>44</td>
<td>3.0</td>
<td>655</td>
<td>221</td>
<td>21</td>
<td>222</td>
<td>998</td>
<td>0.21</td>
<td>12.1</td>
<td>3.7</td>
</tr>
<tr>
<td>112</td>
<td>4.3b</td>
<td>44</td>
<td>3.0</td>
<td>596</td>
<td>192</td>
<td>21</td>
<td>333</td>
<td>968</td>
<td>0.32</td>
<td>13.3</td>
<td>6.1</td>
</tr>
<tr>
<td>113</td>
<td>4.3c</td>
<td>44</td>
<td>2.8</td>
<td>565</td>
<td>175</td>
<td>22</td>
<td>404</td>
<td>919</td>
<td>0.45</td>
<td>14.8</td>
<td>9.8</td>
</tr>
<tr>
<td>121</td>
<td>4.4a; 4.5c</td>
<td>44</td>
<td>2.3</td>
<td>839</td>
<td>283</td>
<td>27</td>
<td>462</td>
<td>1040</td>
<td>0.09</td>
<td>12.1</td>
<td>1.6</td>
</tr>
<tr>
<td>122</td>
<td>4.4b; 4.6b</td>
<td>44</td>
<td>2.4</td>
<td>803</td>
<td>234</td>
<td>25</td>
<td>672</td>
<td>906</td>
<td>0.21</td>
<td>13.3</td>
<td>4.0</td>
</tr>
<tr>
<td>131</td>
<td>4.5b</td>
<td>44</td>
<td>2.5</td>
<td>821</td>
<td>266</td>
<td>25</td>
<td>329</td>
<td>982</td>
<td>0.15</td>
<td>12.1</td>
<td>2.6</td>
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<tr>
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<td>4.5a</td>
<td>44</td>
<td>2.1</td>
<td>821</td>
<td>302</td>
<td>28</td>
<td>221</td>
<td>1059</td>
<td>0.21</td>
<td>12.1</td>
<td>3.6</td>
</tr>
<tr>
<td>141</td>
<td>4.6a; 4.7a; 4.8</td>
<td>44</td>
<td>2.1</td>
<td>879</td>
<td>269</td>
<td>29</td>
<td>493</td>
<td>974</td>
<td>0.26</td>
<td>13.3</td>
<td>5.0</td>
</tr>
<tr>
<td>151</td>
<td>4.7b</td>
<td>44</td>
<td>2.9</td>
<td>620</td>
<td>196</td>
<td>21</td>
<td>451</td>
<td>953</td>
<td>0.28</td>
<td>13.3</td>
<td>5.3</td>
</tr>
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</table>
Figure 4.3  Effect of temperature on experimental breakthrough curves of n-pentane(O), temperature histories at bed exit (□) and temperature profiles at 12 cm from bed inlet (∆) for adsorption of a mixture of n/iso-pentane/N₂ in pellets of zeolite 5A. Lines are numerical solutions of the dynamic model with parameters given in Table 4.3 and Table 4.4.

a) Tₖ=548K, yₐₙₙₖ=0.19, Q=190ml/min (at 298 K), P=1atm.
b) Tₖ=498K, yₐₙₙₖ=0.17, Q=197ml/min (at 298 K), P=1atm.
c) Tₖ=448K, yₐₙₙₖ=0.18, Q=200 ml/min (at 298 K), P=1atm.
Figure 4.4 Effect of temperature on experimental breakthrough curves of n-pentane(○), temperature histories at bed exit (□) and at 12 cm from bed inlet (△) for adsorption of a mixture of n/iso-pentane/N₂ in pellets of zeolite 5A. The lines are theoretical curves calculated according to the numerical solution of the dynamic model with parameters given in Table 4.3 and Table 4.4.

a) T_f=548K, y_{nC5}=0.04, Q=141ml/min (at 298 K), P=1atm

b) T_f=498K, y_{nC5}=0.05, Q=144ml/min (at 298 K), P=1atm.

Effect of partial pressure of n-pentane in the feed.

The effect of n-pentane partial pressure in the feed at T_f=548K and constant feed flowrate is shown in Figures 4.5 a), b) and c) for partial pressures y_{nC5}=0.19, y_{nC5}=0.09 and y_{nC5}=0.04 respectively. The adsorbent capacity decreases at lower nC₅ partial pressure; breakthrough curves are sharper when the partial pressure of nC₅ increases.
Figure 4.5 Effect of partial pressure of n-pentane on experimental breakthrough curves of n-pentane (○), temperature histories at bed exit (□) and at 12 cm from bed inlet (Δ) for adsorption of a mixture of n/iso-pentane/N₂ in pellets of zeolite 5A. The lines are theoretical curves calculated according to the numerical solution of the dynamic model with parameters given in Table 4.3 and Table 4.4.

a) At $T_f=548 K$, $y_{nCS}=0.19$, $Q=130 ml/min$ (at 298K), $P=1 atm$.
b) At $T_f=548 K$, $y_{nCS}=0.09$, $Q=141 ml/min$ (at 298K), $P=1 atm$.
c) At $T_f=548 K$, $y_{nCS}=0.04$, $Q=141 ml/min$ (at 298K), $P=1 atm$. 
The stoichiometric time decreases when nC\textsubscript{5} partial pressure increases as a consequence of the favourable nature of adsorption equilibrium isotherm. In fact a simple global mass balance over the adsorption column leads to $t_\text{st} = (L/v_t)(1+\xi_\text{m})$. Sharper profiles with increasing partial pressures are observed and are a consequence of favourable isotherms which originates from the compressive waves according to the equilibrium theory. However, this effect is less pronounced as the partial pressure increases since the isotherm becomes more favourable. Sharper breakthrough curve is also a consequence of velocity changes due to adsorption as pointed out by Yang (1987). The same information is retained from temperature data: higher partial pressures lead to higher and narrow peaks; in contrast, lower partial pressures origin smaller and wider peaks. Figures 4.6 a) and b) show the same effect at $T_r=498K$ for a constant feed flowrate and for partial pressures $y_{nC5}=0.095$ and $y_{nC5}=0.056$ respectively. For a similar partial pressure, breakthrough curves are sharper than in the case at $T_r=548K$ since the isotherm is more favourable at 498K. Model results are also shown in Figure 4.5 and Figure 4.6 predicting with good accuracy the observed adsorber behaviour.

Effect of total flowrate

Figures 4.7 a), b) show the influence of the total flowrate on breakthrough curves at 548K. The total flowrate practically does not affect the shape of breakthrough curves, which is an indication that axial and heat mass dispersion coefficients are not limiting mechanisms in the system. This analysis can be clearly seen if we normalise the real time by the respective stoichiometric time; similar breakthrough curves are then obtained. Clearly breakthrough occurs faster at higher flowrate as indicated by the relation $t_\text{st} = (L/v_t)(1+\xi_\text{m})$; the proportionality between breakthrough time and flowrate indicates that constant pattern conditions are valid.

Again model predictions are in good agreement with experimental data relatively to concentration and temperature evolution.

Effect of purge flowrate in desorption

Figure 4.8 shows the effect of purge flowrate in the desorption of a bed saturated with n-pentane at partial pressure of 0.1 bar at 498K. In the Figure we also show the adsorption curve that was previously performed with a total flowrate of 130 ml/min. If desorption
were performed with a flow of inert similar to the total flowrate used in adsorption, the wash out of the column practically doubles the time of adsorption. To reach a cycle time of the same order one has to double the purge flowrate as could be clearly seen. This is expected for a system with a favourable isotherm since in desorption concentration waves are dispersive. In Figure 4.8 we show the comparison of heat effects at the middle of the column in adsorption and desorption. It is clear that heat effects are rather small in desorption compared to the ones in adsorption due to the dispersive effect caused by the unfavourable nature of the isotherm in desorption.

**Figure 4.6** Effect of partial pressure of n-pentane on experimental breakthrough curves of n-pentane (O), temperature histories at bed exit (∇) and at 12 cm from bed inlet (∆) for adsorption of a mixture of n/iso-pentane/N₂ in pellets of zeolite 5A. The lines are theoretical curves calculated according to the numerical solution of the dynamic model with parameters given in Table 4.3 and Table 4.4.

a) At \( T_r = 498K \), \( y_{nCS} = 0.09 \), \( Q = 127ml/min \) (at 298K), \( P = 1atm \).

b) At \( T_r = 498K \), \( y_{nCS} = 0.05 \), \( Q = 144ml/min \) (at 298K), \( P = 1atm \).
Figure 4.7 Effect of flowrate on experimental breakthrough curves of n-pentane (O), temperature histories at bed exit (□) and at 12 cm from bed inlet (△) for adsorption of a mixture of n/iso-pentane/N₂ in pellets of zeolite 5A. The lines are theoretical curves calculated according to the numerical solution of the dynamic model with parameters given in Table 4.3 and Table 4.4.

a) At $T_f=498K$, $y_{nCS}=0.09$, $Q=127\text{ ml/min (at 298K)}$, $P=1\text{ atm.}$

b) At $T_f=498K$, $y_{nCS}=0.11$, $Q=185\text{ ml/min (at 298K)}$, $P=1\text{ atm.}$
Figure 4.8  Effect of flowrate on desorption with nitrogen of a bed saturated with n-pentane (y_{nC5}=0.1) at T_f=498.15K, P=1atm and Q=130ml/min (at 298K).

(0) Desorption curve with Q=275ml/min (at 298K);

(7) Desorption curve with Q=130ml/min (at 298K);

The adsorption breakthrough curve with Q=130 ml/min (at 298K) (O) is also shown. Temperature profiles at 12 cm (adsorption) and 8cm (desorption) from bed inlet are also shown. The lines are theoretical curves calculated according to the numerical solution of the dynamic model with parameters given in Table 4.3 and Table 4.4.

4.5 Fixed-bed adsorption of mixtures of n-hexane/nitrogen

Similar experiments using n-hexane as the adsorbable species were performed. In Tables 4.5, 4.6 and 4.7 the experimental conditions, model parameters and dimensionless model parameters used in the following study are summarised.

Effect of temperature

Figures 4.9 a) and b) show the effect of temperature in adsorption breakthrough curves for bed inlet temperature of 513K and 469K, respectively. The total flowrate (160ml/min at
298 K), partial pressure of n-hexane \((y_{nC6}=0.028)\) and total pressure \((P=1\text{atm})\) were kept constant during the experiments. Breakthrough curves are rather sharp, which is expected since the isotherm of n-hexane is highly favorable at the partial pressure studied and the global mass transfer coefficient is quite high \((a_pK_g=24s^{-1} \text{ at } 513K \text{ to } a_pK_g=22s^{-1} \text{ at } 469K)\). The breakthrough time increases as the temperature decreases. This is due to an increase in the adsorbed phase concentration since adsorption is exothermic. The difference is significant due to the high heat of adsorption of n-hexane \((14.2 \text{ kcal/mol})\). As the temperature decreases more heat is generated during sorption as we can see from the evolution of temperature at the outlet of column; temperature increases near 7\(^{\circ}\)K at 513K and 15\(^{\circ}\)K at 469K. As in the case of n-pentane, the final approach of breakthrough curves to the equilibrium value are slow as a consequence of the temperature increase owed to adsorption. Model predictions are in close agreement with experimental results as shown in Figure 4.9. The values of the parameters concerning heat transfer at the wall and from solid to bulk fluid which are calculated in order to match experimental curves range from 13.1 to 16.8 W/m\(^2\)K and from 6.8 to 8.2 W/m\(^2\)K, respectively. These values are similar to the ones obtained using n-pentane as adsorbable species.

<table>
<thead>
<tr>
<th>run</th>
<th>Fig.</th>
<th>Experimental conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fr</td>
<td>T_f</td>
<td>y_{nC6}</td>
</tr>
<tr>
<td>(mol/m(^3)/s)</td>
<td>(K)</td>
<td>(bar)</td>
</tr>
<tr>
<td>211</td>
<td>4.10b</td>
<td>0.124</td>
</tr>
<tr>
<td>212</td>
<td>4.11a</td>
<td>0.341</td>
</tr>
<tr>
<td>213</td>
<td>4.10a</td>
<td>0.124</td>
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<tr>
<td>221</td>
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<td>222</td>
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<td>0.341</td>
</tr>
<tr>
<td>231</td>
<td>4.12</td>
<td>0.471</td>
</tr>
</tbody>
</table>

*Effect of partial pressure of n-hexane in the feed.*

The effect of n-hexane partial pressure in the feed at \(T_f=513K\) and constant feed flowrate \((161 \text{ ml/min at } 298 \text{ K})\) is shown in Figures 4.10 a) and b) for partial pressures \(y_{nC6}=0.103, y_{nC6}=0.028\). The adsorbent capacity decreases at lower nC\(_6\) partial pressure; breakthrough
curves are sharper when the partial pressure of nC₆ increases. The stoichiometric time decreases when nC₆ partial pressure increases as a consequence of the favourable nature of adsorption equilibrium isotherm. Higher partial pressures lead to higher and narrow peaks; in contrast, lower partial pressures origin smaller and wider peaks. These trends are similar to those found with n-pentane and the arguments used previously are valid in this system. Model results shown in Figures 4.10 a) and b) predict with good accuracy the observed adsorber behavior.

### Table 4.6 Model parameters for fixed bed adsorption of n-hexane/nitrogen mixtures

<table>
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<tr>
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<th>Fig.</th>
<th>Dₐx10⁵</th>
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<th>Kₑx10⁵</th>
<th>Kₑ₂x10⁵</th>
<th>hₚ</th>
<th>hₕ</th>
<th>hₓ³/K</th>
<th>W/m³K</th>
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<td>4.10b; 4.11b</td>
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<td>2.8</td>
<td>0.84</td>
<td>6.8</td>
<td>14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>212</td>
<td>4.11a; 4.12</td>
<td>24.1</td>
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<td>3.4</td>
<td>3.3</td>
<td>0.87</td>
<td>7.7</td>
<td>16</td>
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<td></td>
</tr>
<tr>
<td>213</td>
<td>4.10a; 4.9a</td>
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<td>0.32</td>
<td>3.4</td>
<td>2.8</td>
<td>0.84</td>
<td>6.9</td>
<td>13</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>221</td>
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<td>0.72</td>
<td>6.3</td>
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<td>4.12</td>
<td>24.1</td>
<td>0.33</td>
<td>3.4</td>
<td>3.3</td>
<td>0.87</td>
<td>7.7</td>
<td>16</td>
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<tr>
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<td>0.89</td>
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### Table 4.7 Dimensionless model parameters for fixed bed adsorption of n-hexane/nitrogen mixtures

<table>
<thead>
<tr>
<th>Run</th>
<th>Fig.</th>
<th>Pₑₘₑ</th>
<th>Pₑₜₑ</th>
<th>Nₑ</th>
<th>Nₑₕ</th>
<th>Nₑₙₑ</th>
<th>Nₑₙₑ</th>
<th>ξₑₑ</th>
<th>ξₑₕ</th>
<th>θₑₜₑ</th>
<th>γₑ</th>
<th>Bₑₜₑ</th>
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<tr>
<td>211</td>
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<td>619</td>
<td>606</td>
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<td>13.9</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>212</td>
<td>4.11a; 4.12</td>
<td>38</td>
<td>2.3</td>
<td>238</td>
<td>257</td>
<td>3</td>
<td>1422</td>
<td>3074</td>
<td>0.26</td>
<td>13.9</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>213</td>
<td>4.10a; 4.9a</td>
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<td>622</td>
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<td>550</td>
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<td>13.9</td>
<td>6.1</td>
<td></td>
</tr>
<tr>
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<td>1.1</td>
<td>678</td>
<td>436</td>
<td>55</td>
<td>644</td>
<td>2008</td>
<td>0.46</td>
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<td>8.8</td>
<td></td>
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<tr>
<td>222</td>
<td>4.12</td>
<td>38</td>
<td>2.3</td>
<td>238</td>
<td>257</td>
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<td>1422</td>
<td>3074</td>
<td>0.26</td>
<td>13.9</td>
<td>4.3</td>
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<tr>
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<td>175</td>
<td>198</td>
<td>25</td>
<td>1422</td>
<td>3074</td>
<td>0.26</td>
<td>13.9</td>
<td>4.3</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.9 Effect of feed temperature on experimental breakthrough curves of \( n \)-hexane, temperature histories at bed exit and temperature profiles at 12 cm from bed inlet for adsorption of a mixture of \( N_2/\text{nC}_6\) in pellets of zeolite 5A. The lines are theoretical curves calculated according to the numerical solution of the dynamic model with parameters given in Table 4.6 and Table 4.7.

a) \( T_f=513 K, y_{\text{nC}_6}=0.103, Q=161 \text{ml/min (at 298 K), } P=1 \text{atm}. \)

b) \( T_f=469 K, y_{\text{nC}_6}=0.103, Q=155 \text{ml/min (at 298 K), } P=1 \text{atm}. \)

**Effect of total flowrate**

Figures 4.11 a) and b) show the influence of the total flowrate on breakthrough curves at \( 513 \text{K} \) and \( y_{\text{n}}=0.028 \) for total flowrate 441 and 161 ml/min at 298 K, respectively. The
total flowrate practically does not affect the shape of breakthrough curves. Again, axial and heat mass dispersion coefficients are not limiting phenomena in the system. Model predictions are in good agreement with experimental data relatively to concentration and temperature evolution.

Figure 4.10 Effect of partial pressure of n-hexane on experimental breakthrough curves of n-hexane, temperature histories at bed exit and at 12 cm from bed inlet for adsorption of a mixture of \( N_2/nC_6 \) in pellets of zeolite 5A. The lines are theoretical curves calculated according to the numerical solution of the dynamic model with parameters given in Table 4.6 and Table 4.7.

a) At \( T_f=513K, y_{nC6}=0.103, Q=161ml/min \) (at 298 K), \( P=1atm \)
b) At \( T_f=513K, y_{nC6}=0.028, Q=161ml/min \) (at 298 K), \( P=1atm \).

Effect of purge flowrate in desorption curve

Figure 4.12 shows the effect of purge flowrate in the desorption of a bed saturated with n-hexane at partial pressure of 0.028 bar at 513K. In the figure we also show the adsorption
curve performed with a flowrate of 441 ml/min at 298 K. If desorption was performed with a flow of inert similar to the total flowrate used in adsorption, the wash out of the column practically doubles the time of adsorption. To reach a cycle time of the same order one has to double the purge flowrate as could be clearly seen in Figure 4.12.

Figure 4.11 Effect of flowrate on experimental breakthrough curves of n-hexane, temperature histories at bed exit and at 12 cm from bed inlet for adsorption of a mixture of \( N_2/nC_6 \) in pellets of zeolite 5A. The lines are theoretical curves calculated according to the numerical solution of the dynamic model with parameters given in Table 4.6 and Table 4.7.

a) At \( T_f=513K \), \( y_{nC6}=0.028 \), \( Q=441\text{ml/min (at 298 K)} \), \( P=1\text{atm} \).
b) At \( T_f=513K \), \( y_{nC6}=0.028 \), \( Q=161\text{ml/min (at 298 K)} \), \( P=1\text{atm} \).
Figure 4.12 Effect of flowrate on desorption with nitrogen of a bed saturated with n-hexane (y_{nCs}=0.028) at T=513 K, P_0=1 atm and Q=441 ml/min (at 298 K). The lines are simulated results.

4.6 Fixed bed adsorption of mixtures of n/pentane/n-hexane/isopentane/nitrogen

Since the PSA model involves multicomponent adsorption, fixed bed experiments at constant pressure with mixtures of n-pentane/n-hexane/isopentane/nitrogen of different compositions have been performed in the same fixed bed column in order to test the mathematical model as well as the multicomponent form of Nitta et al.'s isotherm. Table 4.8 and Table 4.9 summarise the operating conditions and model parameters. Figures 4.13 a), b) and c) show breakthrough curves for three different ratios of iC_5/nC_5/nC_6. Circles in Figure 4.13 represent the sum of nC_5 and nC_6 concentrations in the outlet stream measured experimentally, since the technique used to analyse the effluent stream of the column was the frontal chromatography. Because the concentration fronts of nC_5 and nC_6 are separated the experimental technique is effective for this system. The simulations (lines) represent the sum of concentrations and also the concentrations of individual species. It can be seen in Figure 4.13 that the mathematical model represents well the behaviour of the multicomponent system. Isopentane breaks just at the space-time of the adsorber. Roll-up
is clearly seen from the simulations. The time at which the concentration fronts of nC₅ and nC₆ reach the column exit are satisfactorily predicted by the mathematical model using Nitta et al.’s. multicomponent model isotherm with parameters of individual isotherms. In Figure 4.13 it can be seen only a slight increase in temperature at the passage of concentration fronts. This is so because normal paraffins are highly diluted in the feed.

**Table 4.8 Experimental conditions of multicomponent adsorption experiments in fixed bed**

<table>
<thead>
<tr>
<th>run</th>
<th>Fig.</th>
<th>F  (mol/m²s)</th>
<th>Tₐ  (K)</th>
<th>yₐC₅</th>
<th>yₐC₆</th>
<th>yₐC₅</th>
</tr>
</thead>
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<td>311</td>
<td>4.13a</td>
<td>0.23</td>
<td>513</td>
<td>0.026</td>
<td>0.012</td>
<td>0.363</td>
</tr>
<tr>
<td>312</td>
<td>4.13b</td>
<td>0.29</td>
<td>513</td>
<td>0.014</td>
<td>0.023</td>
<td>0.363</td>
</tr>
<tr>
<td>313</td>
<td>4.13c</td>
<td>0.21</td>
<td>513</td>
<td>0.025</td>
<td>0.027</td>
<td>0.348</td>
</tr>
</tbody>
</table>

**Table 4.9 Model parameters of multicomponent adsorption experiments in fixed bed**

<table>
<thead>
<tr>
<th>Run</th>
<th>Fig.</th>
<th>Dₓₓ×10⁻⁵ m²/s</th>
<th>Kₓₓ W/mK</th>
<th>kₓ×10² m/s</th>
<th>Kₓₓ×10² m/s</th>
<th>hₓ  W/m²K</th>
<th>hₓₓ W/m²K</th>
</tr>
</thead>
<tbody>
<tr>
<td>311</td>
<td>4.13a</td>
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<td>3.3</td>
<td>0.92</td>
<td>9.2</td>
</tr>
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<td>3.6</td>
<td>3.3</td>
<td>0.92</td>
<td>9.2</td>
</tr>
</tbody>
</table>
Figure 4.13 Breakthrough curves of mixtures of iC₅/nC₅/nC₆. Points are experimental data. Lines are model results. Experimental conditions and model parameters are shown in Table 4.8 and Table 4.9.

a) Feed composition: \( y_{\text{nC5}} = 0.025 \); \( y_{\text{nC6}} = 0.012 \); \( y_{\text{iC3}} = 0.363 \)
b) Feed composition: \( y_{\text{nC5}} = 0.014 \); \( y_{\text{nC6}} = 0.023 \); \( y_{\text{iC3}} = 0.363 \)
c) Feed composition: \( y_{\text{nC5}} = 0.025 \); \( y_{\text{nC6}} = 0.027 \); \( y_{\text{iC3}} = 0.348 \)
4.7 Fixed-bed adsorption of two linearly adsorbed components in presence of an inert

The isothermal adsorption of two adsorbable components plus inert carrier can be classified as a two-transition system (Ruthven, 1984). For such a system obeying Langmuir isotherms and when adsorbable species are present as trace components, Glueckauf (1949), using the method of characteristics, obtained concentrations profiles in a column (path followed in the diagram of characteristics). He was able to predict concentrations plateaus and the occurrence of sharp or diffuse boundaries by the application of a few simple rules. For trace and ideal Langmuir systems without axial dispersion or mass transfer resistance, Hellferich and Klein (1970) present an extensive treatment and generalization for multicomponent systems. When adsorbable species are present at high concentrations the assumptions of constant velocity on conservation equations are no longer valid and the complexity of the mathematical treatment increases giving rise to more difficulties in the understanding of such systems. Tsabek (1980) has presented a general mathematical treatment of such systems, using a model that includes mass transfer kinetics and axial dispersion. In subsequent analysis some special cases are studied, for the isothermal adsorption of three-component mixtures in systems governed by linear and Langmuir isotherms (Tsabek, 1981a,b; 1982a,b). Jacob and Tondeur (1981, 1983) have studied a special case of a non-isothermal system with one adsorbable species plus an inert. Le Van et al. (1988) gave a general criterion for the classification of transition type for isothermal monovariant systems (one adsorbable component in inert gas or two adsorbable species with no inert gas).

It is the purpose of this section to study the special case of a three-component non-trace system (two adsorbable species plus one inert) showing, by a similar approach as to Glueckkauf (1949), some interesting features of fixed bed dynamics. A plug flow equilibrium model (no mass transfer resistance) solved by the method of characteristics, and an equilibrium dispersed plug flow model solved by orthogonal collocation are used. We also expect to bring some insight into the physical understanding of the fixed bed dynamics of high concentration solutes.
Plug flow model with equilibrium between gas and solid phase

The mathematical model is based on the assumptions of isothermal behavior of the system and constant gas-phase molar density (isobaric behavior for an ideal gas or constant total concentration $C_i$), no mass transfer resistance between bulk gas and solid phase and no mass axial dispersion. Accordingly to these assumptions the following equations can be written,

*Mass balance for inert species 0:*

$$\frac{\partial}{\partial z}(vC_0y_0^i) + \varepsilon_b \frac{\partial}{\partial t}(C_t y_0^i) = 0 \quad (4.50)$$

*Mass balance for adsorbable species 1:*

$$\frac{\partial}{\partial z}(vC_1y_1^i) + \varepsilon_b \frac{\partial}{\partial t}(C_t y_1^i) + (1 - \varepsilon_b) \frac{\partial q_1}{\partial t} = 0 \quad (4.51)$$

*Mass balance for adsorbable species 2:*

$$\frac{\partial}{\partial z}(vC_2y_2^i) + \varepsilon_b \frac{\partial}{\partial t}(C_t y_2^i) + (1 - \varepsilon_b) \frac{\partial q_2}{\partial t} = 0 \quad (4.52)$$

where $v$ is the superficial fluid velocity, $C_i$ is the total gas concentration (assumed constant), $y_0, y_1, y_2$ are mole fractions of inert, species 1 and species 2 respectively, $q_1$ and $q_2$ are the adsorbed phase concentrations of species 1 and 2 in equilibrium with bulk gas phase, $t$ is the time, $z$ is the axial coordinate in the bed and $\varepsilon_b$ is the bulk porosity.

*Adsorption equilibrium isotherm*

For linearly adsorbed species:

$$q_1 = b_1 y_1 \quad (4.53)$$

$$q_2 = b_2 y_2 \quad (4.54)$$

where $b_1$ and $b_2$ are equilibrium constants.

It is convenient to introduce the following variables,
\[ Y_1 = y_1/y_0, \quad Y_2 = y_2/y_0, \quad C_0 = C_0 y_0, \quad F_0 = v C_0 \quad (4.55) \]

where \( C_0 \) is the inert concentration and \( F_0 \) is the molar flux of inert in the system. Substituting these variables in Equations 4.50, 4.51 and 4.52 we obtain,

**Mass balance for inert species:**

\[ \frac{\partial F_0}{\partial z} + \epsilon_b \frac{\partial C_0}{\partial t} = 0 \quad (4.56) \]

**Mass balance for adsorbable species 1:**

\[ \frac{\partial}{\partial z} \left( F_0 Y_1 \right) + \epsilon_b \frac{\partial}{\partial t} \left( C_0 Y_1 \right) + (1 - \epsilon_b) \frac{\partial q_1}{\partial t} = 0 \quad (4.57) \]

**Mass balance for adsorbable species 2:**

\[ \frac{\partial}{\partial z} \left( F_0 Y_2 \right) + \epsilon_b \frac{\partial}{\partial t} \left( C_0 Y_2 \right) + (1 - \epsilon_b) \frac{\partial q_2}{\partial t} = 0 \quad (4.58) \]

Subtracting Equation 4.56 in 4.57, we get:

\[ F_0 \frac{\partial Y_1}{\partial z} + \epsilon_b C_0 \frac{\partial Y_1}{\partial t} + (1 - \epsilon_b) \frac{\partial q_1}{\partial t} = 0 \quad (4.59) \]

Also, by subtracting Equation 4.56 in 4.58, we obtain:

\[ F_0 \frac{\partial Y_2}{\partial z} + \epsilon_b C_0 \frac{\partial Y_2}{\partial t} + (1 - \epsilon_b) \frac{\partial q_2}{\partial t} = 0 \quad (4.60) \]

The adsorption equilibrium isotherms can be written as:

\[ q_1 = \frac{b_1 Y_1}{1 + Y_1 + Y_2} \quad (4.61) \]

\[ q_2 = \frac{b_2 Y_2}{1 + Y_1 + Y_2} \quad (4.62) \]

The separation factor defined as \( K'=(q_2/Y_2)/(q_1/Y_1)=b_2/b_1 \) is a constant. The equilibrium adsorbed phase concentrations \( q_1 \) or \( q_2 \) depend now on both \( Y_1 \) and \( Y_2 \) in a form similar to
the multicomponent Langmuir isotherm; however, the denominator in the modified isotherm Equations 4.61 4.62 is different from that of multicomponent Langmuir isotherm equation.

Equations 4.56, 4.59 and 4.60 are a set of three quasi-linear coupled differential equations. A method of solution can be found elsewhere (Jacob and Tondeur, 1983). Since Equations 4.59 and 4.60 plus 4.61 and 4.62 resemble the problem solved by Glueckauf in 1949 for adsorption of two solutes obeying a multicomponent Langmuir isotherm, a similar solution by the method of characteristics will be followed for this new type of equations. The key for solving the problem requires that we have a relationship of the type \( Y_2 = f(Y_1) \) which means that this relation does not depend of \( z \) and \( t \). As shown by Glueckauf this assumption involves a transition between two constant states which forms a Riemann's problem implying that (Rhee, 1981):

\[
\frac{dq_1}{dt} = \frac{dq_1}{dy_1} \left( \frac{dY_1}{dt} \right)
\]

(4.63)

\[
\frac{dq_2}{dt} = \frac{dq_2}{dy_2} \left( \frac{dY_2}{dt} \right)
\]

(4.64)

Using relations 4.63 and 4.64 Equations 4.59 and 4.60 can be written in a form of kinematic wave equations,

\[
w_1 \frac{dY_1}{dz} + \frac{dY_1}{dt} = 0
\]

(4.65)

\[
w_2 \frac{dY_2}{dz} + \frac{dY_2}{dt} = 0
\]

(4.66)

where the propagation velocities \( w_1 \) and \( w_2 \) are defined by,

\[
w_1 = \frac{\partial z}{\partial t} = \frac{F_0}{e_b C_0 + (1-e_b) \frac{dq_1}{dy_1}}
\]

(4.67)

\[
w_2 = \frac{\partial z}{\partial t} = \frac{F_0}{e_b C_0 + (1-e_b) \frac{dq_2}{dy_2}}
\]

(4.68)
As stated by Ruthven (1984) the concept of coherence recognized by Helfferich (1970) is implicit in Glueckauf approach. Coherence requires that the characteristic velocity for a given composition \((Y_1, Y_2)\) must be the same for the two species and therefore requires \(w_1 = w_2\), since,

\[
\frac{dq_1}{dY_1} = \frac{\partial q_1}{\partial Y_1} + \frac{\partial q_1}{\partial Y_2} \frac{dY_2}{dY_1}
\]

(4.69)

\[
\frac{dq_2}{dY_2} = \frac{\partial q_2}{\partial Y_2} + \frac{\partial q_2}{\partial Y_1} \frac{dY_1}{dY_2}
\]

(4.70)

and substituting relations 4.69 and 4.70 in Equations 4.67 and 4.68 we arrive to the result shown by Glueckauf (1949),

\[
\frac{\partial q_2}{\partial Y_2} \left(\frac{dY_1}{dY_2}\right)^2 + \left(\frac{\partial q_2}{\partial Y_2} - \frac{\partial q_1}{\partial Y_1}\right) \frac{dY_1}{dY_2} - \frac{\partial q_1}{\partial Y_2} = 0
\]

(4.71)

Equation 4.71 may be regarded as a quadratic defining the total differential \(dY_1/dY_2\). Since the modified isotherm of \(Y_1\) and \(Y_2\) are of normal type (\(\partial q_1/\partial Y_2\) and \(\partial q_2/\partial Y_1\) are both negative), Equation 4.71 has two real roots one being positive and the other negative. Accordingly, there will be two expressions for the speed of propagation of a concentration wave through the adsorption bed. In systems with linear isotherms the constant separation factor is constant, and for the modified isotherm of \(Y_1\) and \(Y_2\) it is also constant. Equation 4.71 can be written in the form,

\[
\left(\frac{dY_1}{dY_2}\right)^2 + \left(\frac{1}{K'} - \frac{Y_1}{Y_2} - \frac{K'-1}{K'Y_2}\right) \frac{dY_1}{dY_2} - \frac{1}{K'} \frac{Y_1}{Y_2} = 0
\]

(4.72)

where \(K' = b_2/b_1\). It can be shown that the only physically acceptable solution for \(Y_1 > 0\) and \(Y_2 > 0\) occurs when \(d^2Y_1/dY_2^2 = 0\), and therefore \(dY_1/dY_2 = \lambda\), where \(\lambda\) is a constant of integration. From Equation 4.72 after substitution of \(dY_1/dY_2 = \lambda\) we obtain the characteristic lines,

\[
Y_1 = \lambda Y_2 - \frac{(K'-1)\lambda}{1 + K'\lambda}
\]

(4.73)
Equation 4.73 represents two straight lines, one with positive slope (μ) and other with negative slope (v). The values of (μ) and (v) depend on the values of Y₁, Y₂ and K' and are the roots of the algebraic equation:

\[
\lambda^2 + \left( \frac{1}{K'} - \frac{Y_1}{K'Y_2} \right) \lambda - \frac{1}{K'Y_2} Y_1 = 0
\]  
(4.74)

Therefore, giving K', Y₁ e Y₂ it is possible to represent in a plot Y₂=f(Y₁) the characteristic equations,

\[
Y_1 = \mu Y_2 - \frac{(K'-1)\mu}{1 + K\mu}
\]  
(4.75)

\[
Y_1 = vY_2 - \frac{(K'-1)v}{1 + Kv}
\]  
(4.76)

These characteristic lines have a watershed point, which is obtained when the discriminant of Equation 4.74 is zero, i.e., when v=μ. At this watershed point v=μ=0 and the lines of the two families coincide with the Y₂ axis. The coordinates of this point are: Y₁=0; Y₂=K'-1.

The characteristics with positive slope leave the Y₂ axis always above the watershed point. The complete map of characteristics lines in the plane (Y₁,Y₂) is discussed in a later section.

Solving equations 4.75 e 4.76 for Y₁ and Y₂ we obtain,

\[
Y_1 = -\frac{K'(K'-1)\mu v}{(1 + K'\mu)(1 + K'v)}
\]  
(4.77)

\[
Y_2 = \frac{K'-1}{(1 + K'\mu)(1 + K'v)}
\]  
(4.78)

which gives the values Y₁ e Y₂ as a function of parameters μ e v.

Similarly from relations 4.61 and 4.62 we can get q₁ and q₂ as,

\[
q_1 = -\frac{-b_iK'(K'-1)\mu v}{(1 + K'\mu)(1 + K'v) + (K'-1)(1 - K'\mu v)}
\]  
(4.79)
\[ q_2 = \frac{b_2(K'-1)}{(1+K'\mu)(1+K'\nu) + (K'-1)(1-K'\mu\nu)} \] (4.80)

The propagation velocity of compositions \( Y_1 \) and \( Y_2 \) along the characteristics is obtained from Equations 4.67 or 4.68,

\[ w = \frac{\partial z}{\partial t} = \frac{F_0}{\varepsilon_b C_0 + (1-\varepsilon_b) \frac{dq_2}{dY_2}} \frac{F_0}{C_i \frac{C_i}{1+Y_1 + Y_2} + (1-\varepsilon_b) \frac{dq_2}{dY_2}} \] (4.81)

The derivative in the denominator can be obtained from the relation,

\[ \frac{dq_2}{dY_2} = \left[ \frac{\partial q_2}{\partial v_2} \right]_p \left[ \frac{\partial Y_2}{\partial v_2} \right]_p \] (4.82)

for the positive characteristic, and from

\[ \frac{dq_2}{dY_2} = \left[ \frac{\partial q_2}{\partial \mu_2} \right]_p \left[ \frac{\partial Y_2}{\partial \mu_2} \right]_p \] (4.83)

for the negative one.

**Shock Transitions**

In the case where shocks may exist Equations 4.57 and 4.58 are no longer valid. The correct mass balances are now difference equations. After some algebraic manipulation of those difference equations the propagation velocity of the shock can be written,

\[ w_s = \frac{\Delta(F_0 Y_1)}{\Delta(C_0 C_0 Y_1 + (1-\varepsilon_b)q_1)} = \frac{\Delta(F_0 Y_2)}{\Delta(C_0 C_0 Y_2 + (1-\varepsilon_b)q_1)} \] (4.84)

where \( \Delta \) denotes the difference between the concentration upstream and downstream of the shock.

It should be noted that the characteristic paths for a shock transition and simple waves are the same in this case. This is due to the linear nature of characteristics (Ruthven, 1984).
Conditions for the existence of simple waves or shocks

It has been shown in the mathematical treatment, that the system under study (adsorption of two components linearly adsorbed in the presence of one inert), is similar to the adsorption in systems with competitive isotherms governed by constant separation factors, where the variation of velocity is neglected (diluted systems). In such systems two rules have been formulated by Glueckauf (1949) and later proved by Helfferich (1970) which stated:

Rule 1: A concentration plateau $Y_1, Y_2$ is produced spontaneously in a boundary if the boundary in front of it travels along the positive characteristic of $Y_1, Y_2$, while the rear boundary travels along a characteristic where $dY_1/dY_2$ is negative or zero. (This eliminates any apparent ambiguity in the possible routes between two concentration states.)

Rule 2: Whenever the more strongly adsorbed solute increases in concentration along the column we have a diffuse boundary (simple wave) while where the concentration of the more strongly adsorbent decreases along the column we have a shock transition.

Dispersed plug flow model with equilibrium between gas and solid phase

Considering the axial dispersion term in the fluid mass balance equations 4.51 and 4.52 we can write,

Species 1 mass balance

$$\frac{\partial}{\partial z}(vC_1, y_1) + \varepsilon_b \frac{\partial}{\partial t}(C_1y_1) + (1 - \varepsilon_b) \frac{\partial q_1}{\partial t} = \varepsilon_b D_{aw} \frac{\partial}{\partial z} \left( C_1 \frac{\partial y_1}{\partial z} \right)$$  \hspace{1cm} (4.85)

Species 2 mass balance

$$\frac{\partial}{\partial z}(vC_1, y_2) + \varepsilon_b \frac{\partial}{\partial t}(C_1y_2) + (1 - \varepsilon_b) \frac{\partial q_2}{\partial t} = \varepsilon_b D_{aw} \frac{\partial}{\partial z} \left( C_1 \frac{\partial y_1}{\partial z} \right)$$  \hspace{1cm} (4.86)

Danckwerpts boundary conditions are used for equations 4.85 and 4.86.
Examples

In our study we first consider adsorption step inputs beginning with solute free bed. Three examples of breakthrough curves with equimolar mixtures of solutes are shown in Figure 4.14.

a) saturation of a clean bed with a concentrated mixture of solutes \( y_1=0.45, y_2=0.45 \), i.e., \( Y_1=4.5; Y_2=4.5 \);

b) saturation of a clean bed with a mixture with \( y_1=0.25, y_2=0.25 \), i.e., \( Y_1=0.5, Y_2=0.5 \);

c) saturation of a clean bed with a diluted mixture of solutes \( y_1=0.025, y_2=0.025 \), i.e., \( Y_1=0.0263; Y_2=0.0263 \).

Breakthrough curves of the reverse case (cleaning of the saturated bed) are shown in Figure 4.15.

a) \( y_1=0.45, y_2=0.45 \) and so \( Y_1=4.5; Y_2=4.5 \);

b) \( y_1=0.25, y_2=0.25 \) and so \( Y_1=0.5, Y_2=0.5 \);

c) \( y_1=0.025, y_2=0.025 \) and so \( Y_1=0.0263; Y_2=0.0263 \).

Points in Figures 4.14 and 4.15 are results of the dispersed plug flow model calculated with the orthogonal collocation technique. Lines are predictions of the plug flow model solved by the method of characteristics. All examples correspond to the same total molar flux at the inlet boundary of the column and to the same total gas concentration, only the relative molar fraction of species changes in these examples. Table 4.10 shows the parameters of the two models. Figure 4.16 and Figure 4.17 show the total molar flux variations accompanying concentration changes in Figure 4.14 and Figure 4.15.
Figure 4.14 Breakthrough curves, normalized mole fractions $y/y_f$ versus time, for adsorption with equimolar mixtures of adsorbable species. Points are results of the dispersed plug flow model. Lines are results of plug flow model.

a) Initial state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$
   Final state: $(y_1=0.45, y_2=0.45)$ or $(Y_1=4.5, Y_2=4.5)$

b) Initial state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$
   Final state: $(y_1=0.25, y_2=0.25)$ or $(Y_1=0.5, Y_2=0.5)$

c) Initial state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$
   Final state: $(y_1=0.025, y_2=0.025)$ or $(Y_1=0.0263, Y_2=0.0263)$
Figure 4.15 Desorption curves, normalized mole fractions $y_i/y_f$ versus time, of a bed saturated with equimolar mixtures of adsorbable species. Points are results of the dispersed plug flow model. Lines are results of plug flow model.

a) Initial state: $(y_1=0.45, y_2=0.45)$ or $(Y_1=4.5, Y_2=4.5)$
   Final state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$

b) Initial state: $(y_1=0.25, y_2=0.25)$ or $(Y_1=0.5, Y_2=0.5)$
   Final state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$

c) Initial state: $(y_1=0.025, y_2=0.025)$ or $(Y_1=0.0263, Y_2=0.0263)$
   Final state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$
Figure 4.16 Molar flux at the outlet of the bed, $F/F_r$ accompanying breakthrough curves in Figure 4.14. Points are results of the dispersed plug flow model. Lines are results of plug flow model.

a) Initial state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$
   Final state: $(y_1=0.45, y_2=0.45)$ or $(Y_1=4.5, Y_2=4.5)$

b) Initial state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$
   Final state: $(y_1=0.25, y_2=0.25)$ or $(Y_1=0.5, Y_2=0.5)$

c) Initial state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$
   Final state: $(y_1=0.025, y_2=0.025)$ or $(Y_1=0.0263, Y_2=0.0263)$
Figure 4.17 Molar flux at the outlet of the bed, $F/F_f$ accompanying desorption curves in Figure 4.15. Points are results of the dispersed plug flow model. Lines are results of plug flow model.

a) Initial state: $(y_1=0.45, y_2=0.45)$ or $(Y_1=4.5, Y_2=4.5)$
   Final state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$

b) Initial state: $(y_1=0.25, y_2=0.25)$ or $(Y_1=0.5, Y_2=0.5)$
   Final state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$

c) Initial state: $(y_1=0.025, y_2=0.025)$ or $(Y_1=0.0263, Y_2=0.0263)$
   Final state: $(y_1=0, y_2=0)$ or $(Y_1=0, Y_2=0)$
Table 4.10 Model parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bed length, L</td>
<td>0.20 m</td>
</tr>
<tr>
<td>Porosity, εₚ</td>
<td>0.4</td>
</tr>
<tr>
<td>Total molar flux at bed inlet, Fₚ</td>
<td>0.21 mol/m².s</td>
</tr>
<tr>
<td>Total gas concentration in the feed, Cₑ</td>
<td>21 mol/m³</td>
</tr>
<tr>
<td>Superficial velocity at bed inlet, vₑ</td>
<td>0.01 m/s</td>
</tr>
<tr>
<td>Axial mass dispersion coefficient, Dₓ</td>
<td>1.25x10⁻⁵ m²/s</td>
</tr>
<tr>
<td>Equilibrium parameter of species 1, b₁</td>
<td>4.072x10² mol/m³</td>
</tr>
<tr>
<td>Equilibrium parameter of species 2, b₂</td>
<td>2.036x10³ mol/m³</td>
</tr>
<tr>
<td>Ratio of equilibrium parameters, K'</td>
<td>5</td>
</tr>
</tbody>
</table>

Solution of the plug flow model by the method of characteristics

The solution of the plug flow model follows the development outlined above. Figures 4.18 a), b) and c) show characteristic paths in terms of variables Y₁ and Y₂ for three cases calculated using equations 4.74, 4.75 and 4.76. In all cases of Figure 4.18 points A and C represent the initial and final state, respectively, for the adsorption case. For desorption the reverse is true. Figure 4.18 a) also shows a map of several characteristics including the watershed point W(Y₁=0;Y₂=4). The characteristic lines with positive slope never intersect the Y₂ axis above the watershed point; the characteristic lines with negative slope never intersect the Y₂ axis below the watershed point.

The calculation of straight lines in the plane Y₁, Y₂ is simple:

i) giving the initial state we can calculate the two roots of Equation 4.74;

ii) with Equations 4.75 and 4.76 we can represent the two straight lines in the Y₁, Y₂ plane, one with negative slope (ν) and other with positive slope (μ);

iii) the same can be done for the points of the final state;
iv) the intersection of straight lines will give two intermediate states points B and D that represent concentration plateaus between transition states. The coordinates of points B and D shown in Figure 4.18 are represented by,

Point B: \[ Y_2=0; Y_1=-(K'-1)v_{FS}/(1+K'v_{FS}) \]  \hspace{1cm} (4.87)

Point D: \[ Y_2=(K'-1)/(1+K'\mu_{IS}); Y_1=0 \]  \hspace{1cm} (4.88)

where the subscripts IS and FS represent the initial state and final state, respectively.

For the adsorption cases, points A and C represent the initial and final state, respectively. According to rule 1 a new concentration plateau is produced at B and the stable boundary path is clearly A→B→C. For the desorption cases point C and A represent the initial and final state, respectively. Once again rule 1 states that the new concentration plateau is produced at D. The stable boundary path is C→D→A. For the adsorption cases, Rule 2 establishes that the transition between states A→B and B→C will be a shock. The movement of the shock between A→B in the bed can be calculated using for example Equation 4.84 in the form,

\[ w_s(A \rightarrow B) = \frac{F_0 Y_{IB}}{\varepsilon_b C_{0b} Y_{IB}+(1-\varepsilon_b)q_{IB}} \]  \hspace{1cm} (4.89)

and the movement of the shock between B→C can be calculated using Equation 4.84 in the form,

\[ w_s(B \rightarrow C) = \frac{F_0 Y_{IC}}{\varepsilon_b C_{0c} Y_{IC}+(1-\varepsilon_b)q_{IC}} \]  \hspace{1cm} (4.90)
Figure 4.18 Diagram of characteristic paths in terms of variables $Y_1$ and $Y_2$ connecting transition states of examples shown in Figure 4.14 and Figure 4.15. Points A and C represent the initial and final state for adsorption examples, respectively; for adsorption point B is the intermediate state. For desorption points C and A represent the initial and final state respectively; point D is the intermediate state. The point W represents the watershed point.

a) Map of several characteristics including Example a) in Figure 4.14 and Figure 4.15;  
b) Example b) in Figure 4.14 and Figure 4.15  
c) Example c) in Figure 4.14 and Figure 4.15
For the desorption cases, Rule 2 establishes now that the transitions between states C→D and D→A will be simple waves. The form and movement of these fronts are calculated using Equation 4.81 introducing the combination of concentrations $Y_1$ and $Y_2$ that connect points C→D and D→A. For example the movement of composition of point C moves accordingly to,

$$w(\text{point C}) = \frac{F_0}{\epsilon_b \frac{C_t}{1+Y_{1C} + Y_{2C}} + (1-\epsilon_b) \frac{dQ_{3C}}{dX_{3C}}}$$

(4.91)

**Solution of the dispersed plug flow model by application of the orthogonal collocation technique**

The set of coupled partial differential Equations 4.50, 4.53, 4.54, 4.85 and 4.86 was reduced first to a set of ordinary differential/algebraic equations (DAEs) applying orthogonal collocation technique (Villadsen and Michelsen, 1978) to the spatial coordinate. The collocation points were given by the zeros of Jacobi polynomials $P_N^{(\alpha,\beta)}(Z)$, with $\alpha=\beta=0$. The resulting system was solved using a fifth order Runge-Kutta code (ODE's) in conjunction with a Gauss elimination (Algebraic equations).

**Analysis of mathematical solutions**

Interesting features of the system can be seen in Figure 4.14 and Figure 4.15: as the molar fraction of adsorbable species increases in feed, an increasing roll-up in molar fraction of the less adsorbable species is seen in the breakthrough curve before the breakthrough of the most adsorbable component. A simple estimation of the intermediate plateau can be made: the amplitude of the plateau corresponds to the molar fraction of the less adsorbable species without the presence of the most adsorbable one. For the case in Figure 4.14 a) $Y_{\text{plateau}}=0.45/(0.45+0.1)=0.818$ (model prediction=0.840); for the case in Figure 4.14 b) $Y_{\text{plateau}}=0.25/(0.25+0.5)=0.3333$ (model prediction=0.35). The stoichiometric time of the second wave front is the same in the three cases and so independent of partial pressure of adsorbable species. However, the first mass transfer zone changes in time. As the partial pressure of adsorbable species increases, higher is the time to break the first mass transfer.
zone, leading to smaller plateau rich in the less adsorbable species. Another interesting feature is seen from the results of the dispersed plug flow model; it is well known that in a diluted system with linear isotherm axial dispersion leads to a spreading of the breakthrough curve. In these cases we see that the increasing concentration of adsorbable species leads to a self sharpening of breakthrough curves as can be seen in Figure 4.15. This behavior is similar to the effect of favorable isotherms in fixed bed adsorption. Since favorable isotherms are unfavorable for desorption, the reverse behavior is expected in desorption. This is seen in Figure where desorption is analyzed. Higher is the molar fraction of adsorbable species, higher is the spreading of breakthrough curves in contrast with adsorption. The first mass transfer zone breaks earlier as the molar fraction of adsorbable species increases. The completely cleaning of the bed is independent of initial molar fraction of adsorbable species in the bed and occurs at the same time.

4.8 Conclusions

The effect of temperature, partial pressure of sorbate and total flowrate in breakthrough curves of n/iso-paraffin mixtures was experimentally analysed and compared with model predictions. Temperature effects in fixed bed are of great importance when the partial pressure of normal paraffins in the feed increase. We report an increase of temperature in the order of 20°C for a partial pressure of n-pentane of 0.25 bar and for a feed temperature of 448K. Experiments were also instructive with regard to the influence of the nature of the isotherm in the dynamic behaviour of fixed-bed adsorbers.

All the parameters involved in the model were evaluated from independent experiments (adsorption equilibrium and kinetic parameters) or from correlations available on literature. Good agreement was found between experimental and the calculated values justifying the employment of the equilibrium adsorption isotherms obtained in Chapter 2 and the lumped model based in a macropore diffusion control (conclusion obtained from kinetic data in Chapter 3). The proposed mathematical model can be regarded as a useful tool for the description of cyclic processes, in order to design units where the separation of n/iso-paraffins will be performed.

Two different models are used to study the effect of velocity changes in a ternary fixed bed adsorption system (two adsorbable species plus an inert) governed by linear isotherms: a
dispersed plug flow model and a plug flow model with equilibrium between gas and solid phases. It is shown that velocity changes have a strong influence in the behavior of the system. In a ternary diluted system, an equilibrium model will lead to contact discontinuities but velocity variations causes shocks for adsorption and simple waves for desorption. Roll-up phenomena can be observed even with linear adsorption equilibria. In a dispersed plug flow model it is known that a diluted system leads to a spreading of mass transfer zones in adsorption; increasing velocity variations leads to increasing self-sharpening of mass transfer zones in a behavior similar of favorable isotherms. This fact leads to a reverse behavior in desorption where increasing velocity variations causes a higher spreading of mass transfer zones.

The work can be extended to systems containing n linearly adsorbed species and one inert where the modified isotherm is \( q_i = b_i Y_i/(1+\sum Y_i) \) following an approach similar to the one developed for Langmuir systems (at constant flowrate) although one should be careful in recognizing the difference in the denominator of both multicomponent isotherms.

Moreover, multicomponent Langmuir systems with variable flowrate can be worked out with the same change of variable \( Y_i = Y_i y_0 \) leading the modified adsorption equilibrium isotherm, \( q_i = Q_i b_i Y_i/[1+\sum (1+b_i) Y_i] \).

References


Quinta Ferreira, R. M. O., Contribution to the study of fixed bed catalytic reactors: effect of convection on large and bidisperse catalysts, Ph. D. Thesis, University of Porto, Portugal (1988)


5. PSA Separation of n/iso-Paraffins

In the previous chapter a dynamic model for the separation of n/iso-paraffins was presented. It provides a good representation of experimental data reported in a fixed bed column. In this chapter the model will be used to study a PSA unit for the n/iso-paraffins separation. A cycle presented by IFP and invented by Minkkinnen et al. (1993) was simulated. The performance of the cycle is studied by the combination of process variables (temperature, feed pressure, feed flowrate) and adiabatic or isothermal operation.

Finally, the model is used to design a laboratory unit under similar conditions of cycle time and productivity relatively to the patent. Process variables such as pressure ratio are selected in order to increase the performance of the cycle.

5.1 Introduction

Sorbent regeneration is a crucial step in cyclic adsorption processes. Regeneration by PSA invented by Skarstrom (1959) is accomplished by reducing the total pressure in the adsorber at constant temperature. This shift in pressure decreases significantly the time required to clean the adsorber compared to other processes such as inert purge stripping desorption where the regeneration is facilitated by adsorbate partial pressure reduction with the introduction of an inert gas. The combination of PSA with inert purge stripping can result in high efficient cycles, especially for bulk separations.
The PSA separation of n/iso-paraffins can be classified as a bulk separation of multicomponent gas mixtures governed by non-linear isotherms. Cen and Yang (1986) have performed pioneering studies in the mathematical treatment of similar systems, for a separation of a (50/50) H₂/CO mixture and Doong and Yang (1986) for a ternary mixture of H₂/CH₄/CO₂ in a five step PSA. Negligible pressure drop and axial dispersion, velocity variations, temperature effects and a lumped surface and pore diffusion model was used, giving rise to a representative description of experimental data. The Loading Ratio Correlation (LRC) was used for the prediction of multicomponent adsorption equilibria. More recently Lu et al. (1993) have performed simulations of the separation of helium and methane mixtures in a three step rapid PSA. The mathematical model accounts for velocity variations, pressure drop according to Ergun's law, axial dispersion, temperature effects, effect of dead volumes at both ends of column and includes conservation equations in particles. Details of bed dynamics at cyclic steady state and performance of PSA are addressed. Cen and Yang (1986) and Doong and Yang (1986) used finite differences schemes for the solution of mathematical models. Lu et al. (1993) used the PDECOL package based on orthogonal collocation in finite elements. Refinements for finite difference technique were recently introduced by Sun et al. (1996). Recently in this laboratory Mendes (1993) performed an experimental and modeling study of PSA nitrogen/oxygen separation from air in a two-column system using a Skarstrom cycle. The modeling equations were solved by finite difference schemes.

5.2 Study of PSA cycle assigned to IFP

PSA process description

The base case selected uses the patent data shown by Minkkinnen et al. (1993). In such process, isomerisation of C₅/C₆ normal paraffins with recycling of normal paraffins is described. The recycling is performed in a selective adsorption column containing 38 kg of 5A zeolite pellets. In the selective adsorption unit (length=4m; i.d=12.7cm) a PSA cycle takes place at 573K. The adsorption phase occurs at a total pressure of 15 bar with a duration of 6 minutes. The desorption phase is performed in 6 minutes at 2 bar countercurrently to adsorption with a fraction of the iC₅ rich product. To obtain continuous operation two columns are used. The effluent of the isomerisation reactor contains approximately 13.9 mole % nC₅ and 4.6 mole% nC₆. The performance of the unit is a
Research Octane Number (RON) product of 88 to 88.5 with less than 1 mole % of normal \( C_5/C_6 \). The desorption effluent recycled to the reactor contains approximately 27 mole % of \( nC_5 \) and 7.5 mole % \( nC_6 \).

To simulate the process described above we consider that the adsorption phase occurs in the pressurization with feed and high-pressure feed steps. Desorption is performed in blowdown and countercurrent low-pressure purge steps. As a base case we consider that the feed flowrate to the adsorption unit is the same as in the isomerisation reactor: 84.6 kg/h of a liquid containing a mixture of n/iso-paraffins. The iC_5 rich product flowrate used in desorption step is 31.8 kg/hr as cited by Minkkinnen et al. (1993). The PSA cycle simulation starts with the column free of n-paraffins.

**Mathematical model for PSA simulation**

In the isomerisation processes the feed entering the adsorption column may contain 30% of n-paraffins (Holcombe et al., 1980) or 20% (Minkkinnen et al., 1993). Therefore, velocity changes in fixed bed should be considered. On the other hand, due to the high heat of adsorption of normal paraffins (13.2 kcal/mol n-pentane and 14.2 kcal/mol n-hexane as stated in Chapter 2, temperature effects in the fixed-bed are of importance in this system. Generally the industrial adsorbers are adiabatic (Ruthven, 1984; Yang, 1987) so we expect a strong influence of temperature in the behavior of the system. Other important point is the adsorption equilibrium of normal paraffins. In Chapter 2 the isotherm proposed by Nitta et al. (1984) proved to be very useful in the description of n-pentane and n-hexane adsorption in 5A zeolite and in the multicomponent fixed bed adsorption study performed in Chapter 4.

Keeping in mind all these remarks the mathematical model developed and validated through experiments with mixtures of n/iso-paraffins in the fixed bed under constant pressure in Chapter 4 will be used in this work. Table 5.1 summarizes the mathematical model.
Table 5.1 Mathematical model for the study of PSA adsorption.

<table>
<thead>
<tr>
<th>Overall mass balance</th>
<th>( \frac{\partial F}{\partial z} + \varepsilon_b \frac{\partial C}{\partial t} + (1 - \varepsilon_b) \rho_s \sum_{i=1}^{\text{reactants}} \frac{\partial q}{\partial t} = 0 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass balance for adsorbable species</td>
<td>( \varepsilon_b D_{st} \frac{\partial}{\partial z} (C_t \frac{\partial y}{\partial z}) = \frac{\partial}{\partial t} (F y_i) + \varepsilon_b \frac{\partial}{\partial t} (C_t y_i) + (1 - \varepsilon_b) \rho_s \frac{\partial q}{\partial t} )</td>
</tr>
<tr>
<td>Mass transfer rate to the solid</td>
<td>( \rho_s \frac{\partial q}{\partial t} = a_p K_{ps} C_t (y_i - \bar{y}_i) )</td>
</tr>
<tr>
<td>Energy balance (gas phase)</td>
<td>( K_{st} \frac{\partial^2 T}{\partial z^2} = F c_p \frac{\partial T}{\partial t} + \varepsilon_b C_t c_p \frac{\partial T}{\partial t} + (1 - \varepsilon_b) a_p h_p (T - T_H) + a_c h_w (T - T_w) )</td>
</tr>
<tr>
<td>Energy balance (solid phase)</td>
<td>( \rho_s c_p \frac{\partial T}{\partial t} = a_p h_p (T - T_s) + \rho_s \sum_{i=1}^{\text{reactants}} (-\Delta H_i) \frac{\partial q}{\partial t} )</td>
</tr>
</tbody>
</table>

The following boundary conditions are used in order to represent the PSA process mentioned above.

**Step I (Pressurization)**

\[
P = (P_H - P_L)[1 - \exp(-Mt)] + P_L. \quad (5.1)
\]

where, \( P \) is the total pressure, the subscripts \( H \) and \( L \) represent the high-pressure and low-pressure conditions, respectively, and \( M \) is the pressurization rate.

\( z = 0: \)

\[
\varepsilon_b D_{st} C_t \frac{\partial y_i}{\partial z} = F (y_i - y_{iH}) \quad (5.2)
\]

\[
K_{st} \frac{\partial T}{\partial z} = F c_p (T - T_H) \quad (5.3)
\]

\( z = L: \)

\[
F = 0 \quad (5.4)
\]

\[
\frac{\partial y_i}{\partial z} = 0 \quad (5.5)
\]
\[
\frac{\partial T}{\partial z} = 0 \quad (5.6)
\]

**Step II (High-pressure feed)**

\[ P = P_H \quad (5.7) \]

\[ z = 0: \]

\[ F = F_H \quad (5.8) \]

\[ \varepsilon_y D_{st} C_i \frac{\partial y_i}{\partial z} = F (y_i - y_{iH}) \quad (5.9) \]

\[ K_{st} \frac{\partial T}{\partial z} = Fc_{pt} (T - T_H) \quad (5.10) \]

\[ z = L: \]

\[ \frac{\partial y_i}{\partial z} = 0 \quad (5.11) \]

\[ \frac{\partial T}{\partial z} = 0 \quad (5.12) \]

**Step III (Blowdown)**

\[ P = (P_H - P_L) \left[ \exp(-Mt) \right] + P_L \quad (5.13) \]

\[ z = 0: \]

\[ \frac{\partial y_i}{\partial z} = 0 \quad (5.14) \]

\[ \frac{\partial T}{\partial z} = 0 \quad (5.15) \]

\[ z = L: \]

\[ F = 0 \quad (5.16) \]
\[
\frac{\partial y_L}{\partial z} = 0 \quad \text{(5.17)}
\]

\[
\frac{\partial T}{\partial z} = 0 \quad \text{(5.18)}
\]

**Step IV (Low-pressure purge)**

\[ P = P_L \quad \text{(5.19)} \]

\[ z=0: \]

\[
\frac{\partial y_L}{\partial z} = 0 \quad \text{(5.20)}
\]

\[
\frac{\partial T}{\partial z} = 0 \quad \text{(5.21)}
\]

\[ z=L: \]

\[ F = F_L \quad \text{(5.22)} \]

\[
\varepsilon_b D_{ax} C_t \frac{\partial y_l}{\partial z} = F(y_{il} - y_i) \quad \text{(5.23)}
\]

\[
K_{ax} \frac{\partial T}{\partial z} = Fc_{pg}(T_L - T) \quad \text{(5.24)}
\]

**Numerical solution of model equations**

The set of coupled partial differential equations was reduced first to a set of ordinary differential/algebraic equations (DAEs) applying orthogonal collocation technique (Villadsen and Michelsen, 1978) to the spatial coordinate. The collocation points were given by the zeros of Jacobi polynomials \( P_n(\alpha, \beta) \) (\( \bar{z} \)), with \( \alpha=\beta=0 \). The resulting system was solved using a fifth order Runge-Kutta code (ODE's) in conjunction with a Gauss elimination (Algebraic equations). Sixteen collocation points appeared to give satisfactory accuracy for all calculations performed. Accordingly, there are 96 ODE's being integrated at the same time for two adsorbable species. The mass balance for adsorbable species gives \( 2 \times 16 = 32 \); the mass transfer rate to solid gives \( 2 \times 16 = 32 \); the energy balance (gas phase) 16
and the energy balance (solid phase) 16. Coupled with these 96 ODE's there are 16 algebraic equations resulting from the overall mass balance being solved by a Gaussian elimination.

**Determination of model parameters involved in the adsorber model**

The study of adsorption and diffusion of \textit{n}-pentane and \textit{n}-hexane in 5A zeolite pellets was performed in Chapter 2 and 3. The axial mass dispersion coefficient ($D_{ax}$) can be estimated from the correlation of Edwards and Richardson (Ruthven, 1984),

$$D_{ax} = 0.73D_m + \frac{0.5v_i d_p}{(1 + 9.49D_m / v_i d_p)} \tag{5.25}$$

where $D_m$ is the molecular diffusivity, $v_i$ is the interstitial velocity and $d_p$ is the particle diameter. The effective axial bed thermal conductivity ($K_{ax}$) was estimated with the correlation of Votruba (1972) as in Chapter 4.

Mass transfer inside the adsorbent was controlled by macropore diffusion for both \textit{n}-pentane and \textit{n}-hexane as reported in Chapter 3. The intraparticle mass transfer coefficient ($k_i$) can be calculated according to a lumped model proposed by Gluekauf (1955),

$$k_i = \frac{5D_p}{R_p} \tag{5.26}$$

where $D_p$ is the pore diffusivity and $R_p$ is the particle radius. Diffusion mechanisms in macropores are Knudsen diffusivity in series with molecular diffusion, and so the pore diffusivity is,

$$D_p = T_p^{-1} \left[ \frac{1}{D_m} + \frac{1}{D_K} \right]^{-1} \tag{5.27}$$

where $T_p$ is the tortuosity and $D_K$ is the Knudsen diffusivity. In PSA simulations we allow $D_p$ to vary with pressure and temperature.

The external mass transfer coefficients ($k_e$) was estimated with the correlation of Wakao and Funazkri (1978),
\[
Sh = 2.0 + 1.1 \text{Re}^{0.6} \text{Sc}^{0.33}
\] (5.28)

where \( Sh \) is the Sherwood number, \( \text{Re} \) is the Reynolds number and \( \text{Sc} \) is the Schmidt number. Similarly, the particle to fluid heat transfer coefficient was estimated by

\[
Nu = 2.0 + 1.1 \text{Re}^{0.6} \text{Pr}^{0.33}
\] (5.29)

where \( Nu \) is the Nusselt number and \( \text{Pr} \) is the Prandtl number.

**Results and discussion**

In order to study the dynamics and performance of the PSA unit we first simulate the cycle defined by Minkkinen et al. (1993) in adiabatic and isothermal conditions. Table 5.2 summarizes the characteristics of the adsorbent, column and operating conditions of the cycle described in the patent. Figure 5.1 shows a schematic diagram of the PSA cycle that includes four steps: Step I-Pressurization with feed; Step II-High-pressure feed; Step III-Blowdown; Step IV-Countercurrent low-pressure purge step.

**Bed dynamics at cyclic steady state**

Figure 5.2 shows bed profiles of concentration in the gas phase of \( nC_5 \) and \( nC_6 \) at the cyclic steady state (=50 cycles) for the adiabatic and isothermal cases, respectively, at the end of the four steps. Model parameters used in the simulations are shown in Table 5.3. It is clear from figures that the isothermal case is more efficient than the adiabatic one, since for the isothermal case in the high-pressure feed (Figure 5.2 II-a), the penetration distance of the first concentration front is smaller than in the adiabatic case (Figure 5.2 II-b). This is due to the effect of temperature gradients in the bed that decreases the adsorbent capacity, since adsorption is exothermic. Therefore, in isothermal conditions more feed can be treated for the same operating conditions. For non-isothermal, non-adiabatic conditions the concentration front should be located between the two limits studied in this paper.
Figure 5.1 Schematic diagram of PSA cycle described by Minkkinen et al. (1993)
Table 5.2 Column characteristics, adsorbent properties, operating conditions and process performance of cycle described in patent (Minkkinen et al., 1993)

<table>
<thead>
<tr>
<th>Column characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Length, m</td>
<td>4</td>
</tr>
<tr>
<td>Internal diameter, m</td>
<td>0.127</td>
</tr>
<tr>
<td>Adsorbent content, kg</td>
<td>38</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Adsorbent properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Extrudate 5A zeolite</td>
</tr>
<tr>
<td>Diameter, mm</td>
<td>1.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Operating conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Duration of adsorption phase (Press+feed), min</td>
<td>6</td>
</tr>
<tr>
<td>Duration of desorption phase (Blow+purge), min</td>
<td>6</td>
</tr>
<tr>
<td>Temperature of operation, K</td>
<td>573</td>
</tr>
<tr>
<td>High-pressure feed, bar</td>
<td>15</td>
</tr>
<tr>
<td>Low-pressure purge, bar</td>
<td>2</td>
</tr>
<tr>
<td>Feed flowrate and composition (mole %)</td>
<td>84.6 kg/hr</td>
</tr>
<tr>
<td></td>
<td>(81.5% iC₅; 13.9% nC₅, 4.6% nC₆)</td>
</tr>
<tr>
<td>Purge flowrate and composition (mole %)</td>
<td>31.8 kg/hr</td>
</tr>
<tr>
<td></td>
<td>(100% iC₅)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process performance</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>RON product</td>
<td>88 to 88.5</td>
</tr>
<tr>
<td></td>
<td>with less 1 mole % normals</td>
</tr>
<tr>
<td>Normal paraffins in desorption effluent (mole %)</td>
<td>27% nC₅; 7.5% nC₆</td>
</tr>
</tbody>
</table>
Figure 5.2 - Axial mole fraction profiles of normal paraffins and temperature at the end of the four steps of PSA cycle: a) Isothermal cycle b) Adiabatic cycle.

I - Pressurization; II - High pressure feed; III - Blowdown; IV - Low-pressure purge
Table 5.3 Experimental conditions and model parameters used in the numerical simulation of the cycle described by Minkkinen et al. (1993).

<table>
<thead>
<tr>
<th>High-pressure feed</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental conditions</strong></td>
</tr>
<tr>
<td>$F$</td>
</tr>
<tr>
<td>(kmol/m²·hr)</td>
</tr>
<tr>
<td>91.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{ax} \times 10^4$</td>
</tr>
<tr>
<td>(m²/s)</td>
</tr>
<tr>
<td>2.46</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Low-pressure purge</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Experimental conditions</strong></td>
</tr>
<tr>
<td>$F$</td>
</tr>
<tr>
<td>(kmol/m²·hr)</td>
</tr>
<tr>
<td>34.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{ax} \times 10^4$</td>
</tr>
<tr>
<td>(m²/s)</td>
</tr>
<tr>
<td>6.86</td>
</tr>
</tbody>
</table>

Other interesting features of bed dynamics are shown in Figure 5.2-II (High-pressure feed). In the high-pressure feed step, the first concentration wave ($nC_5$) is very sharp. The concentration of $nC_6$ presents a long tail. A roll-up phenomenon is clearly seen which is more important in the isothermal case (Figure 5.2-II-a). Due to the high heat of adsorption of $nC_5$ and $nC_6$ in 5A zeolite pellets, a positive peak of temperature in the order of 50 K exists in the column at the end of the high-pressure feed (Figure 5.2-II-b). This peak accompanies the first concentration wave. In the blowdown step (Figure 5.2-III) it is clear the increasing concentration of $n$-paraffins in the bed. Pentane and hexane mole fractions
increase four times relatively to inlet conditions in the feed. This is so because lowering pressure leads to a decrease of the adsorption capacity and therefore there is a high desorption of normal paraffins; since isopentane is not fed to the adsorber in this step the partial pressure of this component decreases. In the purge step (Figure 5.2 IV) the mole fraction in the gas phase of normal paraffins is reduced to values below the high-pressure feed conditions. Due to desorption a temperature sink zone in the bed below feed conditions appears near the feed end in the adiabatic case (Figure 5.2 IV-b).

The evolution of the system to the cyclic steady state in the high-pressure feed is shown in Figure 5.3 for the adiabatic and isothermal cases. In the adiabatic case (Figure 5.3 b) 70% of the bed is loaded in the first cycle. At the cyclic steady state, almost all the bed is loaded. In the isothermal case (Figure 5.3 a), the first cycle loads about 50% of the bed whilst 80% is saturated at the cyclic steady state. Other interesting feature is the progressive dispersion in the bed of the nC₅. In the first cycle the concentration front is sharper than in the cyclic steady state; however, the concentration front of n-pentane maintains the sharpness along the cycles. The behavior is similar in the isothermal and adiabatic cases.

**Process performance**

The main products in octane improvement of gasoline pools are the branched paraffins. In this study isopentane is the desired product. The process described by Minkkinen et al. uses isopentane to purge the adsorption column with the objective of recycling normal paraffins to the isomerisation reactor. According to this point the process performance relatively to the base cycle described previously will be assessed by the effect of purge to feed ratio of isopentane in terms of product recovery and purity in the high-pressure feed step. The following definitions are used:

**Purge to feed ratio (P/F) (molar basis):**

\[
P/F \text{ ratio} = \frac{\text{Amount of iC}_5 \text{ used in the purge step}}{\text{Amount of iC}_5 \text{ used in the feed step}}
\]  

(5.30)

**Recovery of iso fraction (molar basis):**

\[
\text{Recovery of iso fraction} = \frac{\text{iC}_5 \text{ produced in feed step - iC}_5 \text{ used in purge step}}{\text{iC}_5 \text{ fed in feed step}}
\]  

(5.31)
Figure 5.3 Evolution of axial mole fraction profiles of normal paraffins towards the cyclic steady-state in high-pressure feed. a) Isothermal cycle; b) Adiabatic cycle

Purity of iso fraction (molar basis):

\[
Purity_{iso} = \frac{\text{Amount of } iC_5 \text{ produced in feed step} - \text{Amount of normals produced in feed step}}{\text{Amount of } iC_5 \text{ produced in feed step}} \tag{5.32}
\]

Other performance criterion studied was the fraction of nC5 and nC6 in the desorption effluent recycled to the reactor in the low-pressure purge step with the definitions:

Fraction of nC5 recycled (molar basis):

\[
\text{Fraction of } nC_5 \text{ recycled} = \frac{\text{Amount of } nC_5 \text{ in effluent of purge step}}{\text{Amount of normals plus iso in effluent of purge step}} \tag{5.33}
\]
Fraction of nC₆ recycled (molar basis):

\[
\text{Fraction of nC}_6 \text{ recycled} = \frac{\text{Amount of nC}_6 \text{ in effluent of purge step}}{\text{Amount of normals plus iso in effluent of purge step}} \quad (5.34)
\]

The effects of operating temperature and high-pressure (step II) are studied and evaluated in terms of the definitions described above, all relatively to the base cycle described in the patent data. For the base cycle we compare the performance of an isothermal operation with the adiabatic one. Also the effect of feed flowrate is studied at 573K for \( P_H = 15 \) bar and \( P_L = 2 \) bar.

**Effect of feed flowrate**

The effect of feed flowrate in process performance can be studied in a plot of purity and recovery versus the purge to feed ratio. This study can be performed, by changing the purge to feed ratio at constant purge flowrate; i.e., by varying the feed flowrate or changing the purge to feed ratio at constant feed flowrate; i.e., by varying the purge flowrate. This is shown in Figure 5.4 d) for the adiabatic case. Depending on the relative flowrates of the purge to feed ratio we can obtain different process performances. It can be seen that for the same \( P/F \) ratio the process purity of the iso fraction is lower when \( F \) changes. This is due again to the favorable nature of isotherm. Once the bed is loaded to a certain fraction in the first cycle, the increase of purge flowrate does not allow the desorption of normal paraffins to a level that permits an efficient cleaning of the bed, since desorption is more difficult due to the unfavorable nature of the isotherm. As a conclusion, increasing the flowrate to a certain level relatively to the base cycle can give very low performance of the PSA process, due to a long bed coverage in high-pressure feed step II.

Due to these results, all studies of \( P/F \) ratio on process performance were made maintaining the feed constant accordingly to the value reported in Table 5.2, varying only the purge flowrate.
Figure 5.4 Effect of process variables on plots of purity and recovery of isopentane as a function of purge to feed ratio: a) Effect of feed pressure in adiabatic cycle; b) Effect of feed temperature in adiabatic cycle c) Effect of isothermal and adiabatic cycle; d) Effect of feed flowrate in adiabatic cycle. Symbol ◇ represents the base case.
Isothermal and adiabatic cases

The comparison between the isothermal and adiabatic cases for the base cycle (T=573 K; \(P_H=15\) bar; \(P_L=2\) bar) is shown in Figure 5.4 c). As expected the isothermal case has higher performance, since for the same purge to feed ratio higher recovery is obtained for the required product purity. Figure 5.5 plots the amount of normal paraffins (nC\(_5\) and nC\(_6\)) recycled to the reactor as a function of P/F ratio at 573 K and for \(P_H=15\) bar and \(P_L=2\) bar. Minkkinnen et al. report a value of approximately 27 mole% nC\(_5\) and 7.5 mole% nC\(_6\) recycled to the reactor in the low-pressure purge step for a P/F ratio near 0.45. From our simulations we obtain 21% for nC\(_5\) and 7.3% for nC\(_6\) in the isothermal case and 22% for nC\(_5\) and 7.8% for nC\(_6\) for the adiabatic case. These values show that our model is indeed effective to simulate the process. From Figure 5.5 it can be seen that as the P/F ratio decreases, the amount of normal paraffins in desorption effluent increases.

![Diagram](image)

*Figure 5.5 Normal paraffins in the desorption effluent of purge step as a function of purge to feed ratio. Operating conditions: \(P_H=15\) bar; \(P_L=2\) bar, \(T=573\) K.*
Effect of temperature in process performance

Figure 5.4 b) shows the effect of purge to feed ratio on product recovery and purity at two temperatures of operation ($T=573$ K and $T=523$ K) for the same $P_H=15$ bar and $P_L=2$ bar. It can be concluded that when temperature is lower the process performance is also lower. At first glance, we expect that when temperature decreases an higher performance will be obtained since the adsorbent has more adsorption capacity; however, due to the favorable nature of adsorption isotherms, as the temperature decreases isotherms become more rectangular and so the desorption step is more difficult. This is the reason why when temperature decreases we could not obtain higher process performance. This is an interesting feature of PSA bulk systems governed by favorable isotherms.

Effect of feed pressure

The effect of feed pressure is shown in Figure 5.4 a). It is clear that the process performance decreases significantly when the feed pressure decreases. For example, to obtain a pure iso-fraction at $P_H=10$ bar only $\approx 25\%$ of the iso fraction is recovered against $\approx 50\%$ at $P_H=15$ bar and $\approx 65\%$ at $P_H=20$ bar. A performance improvement of 25% is obtained between $P_H=10$ bar and $P_H=15$ bar; however, between $P_H=15$ bar and $P_H=20$ bar the performance increases only 15%. These results suggest that the base is cycle is probably near the optimum in terms of costs *versus* productivity.
5.3 Design and study of a laboratory pilot unit

The experimental apparatus was designed in order to operate a PSA cycle under the four steps described in IFP patent with a similar adsorbent productivity defined by the amount of feed mixture processed per unit amount of sorbent per unit time. For the case of the base cycle of IFP described previously the adsorbent productivity is 0.415 mol\text{non-normals}/min.kg_{ads}.

Description of experimental apparatus

A schematic diagram of the apparatus designed at the laboratory is shown in Figure 5.6 (This apparatus was designed in conjunction with Francisco A. da Silva and will also be used for his Ph D. work. Technical details of the equipment can be found in his Ph D. work).

![Diagram of apparatus designed at the laboratory](image)

*Figure 5.6 Schematic diagram of apparatus designed at the laboratory*

The adsorption column (AC) is in stainless steel with 80 cm long and 1.6 cm i.d.. It is placed inside a convective oven (CO) (dimensions 1.2x0.6x0.6 meter) which can operate
up to 400°C. The ventilation is maintained by two turbines. Three PID controllers perform the temperature control. This arrangement allows an uniform temperature in the column (+/- 1°C) eliminating the temperature gradient encountered in the experimental equipment used in Chapter 4 to study fixed bed adsorption. Two thermocouples type K (TT) were inserted in the column at 20 and 60 cm in order to detect the passage of mass transfer zones and measure the associated temperature effects. The direction of flow inside the column is controlled by solenoid valves (SV), which are placed outside the oven due to the high temperature of operation of the PSA cycle. A pressure transducer (PT) measures the pressure of the system. The pressure control of the system is set-up by a back-pressure regulator (BPR) designed to operate also at sub-atmospheric pressures. Sub-atmospheric pressures can be achieved by the vacuum pump (VC).

The feed of n/iso-paraffins injected by a piston pump (HPLC pump) is introduced at the bottom of the adsorber after being vaporized in the preheater (H) inside the oven. A balance (B) is used to control the amount of feed introduced in the column during the PSA runs. Before entering the column the feed can be diluted by an inert stream set-up by a mass flow controller (MGFC1). At the outlet of the bed and inside the oven the hydrocarbons are diluted by an inert stream (controlled by a mass flow-meter (MGFC2)) in order to prevent any hydrocarbon condensation into the lines and the pressure control device.

At the outlet of the back-pressure regulator a special arrangement allows the implementation of vacuum in the system. It is constituted by two solenoid valves (SV6 and SV7), a relief valve (RV) and a vacuum pump (VP).

A measured amount of ethane (MGFC3) is injected as an internal standard in the effluent of the column by a mass gas flow controller (MGFC3). Samples are collected by a 12 way VALCO sample injection valve (TS) and analyzed by a FID gas chromatograph (GC). A wide bore fused silica column with 25 m long is used to resolve the chromatographic data. Generally three minutes are necessary to analyze a sample containing ethane, isopentane, n-pentane and n-hexane.

All pipes are in stainless steel of ¼ in diameter except the lines connecting the injection valve, which are 1/16 in diameter. An exhausting system eliminates the gases from the experimental apparatus.
The solenoid valves, thermocouples, flow meters, piston pump, back pressure regulator, pressure transducer, injection valves and chromatograph are connected to an interface attached in a computer. Software allows the control of solenoid valves, set-point of flowmeters and back pressure, start and stop the pump and collection and injection of samples in the chromatograph. The chromatographic data is treated by a software named Maestro which automatically separates and integrates the areas of chromatographic peaks.

The performance of the PSA unit is characterized as follows:

i) The oven is capable of maintaining a uniform temperature of +/- 1°C between ambient temperature and 400°C.

ii) The maximum flow rate of the piston pump is 8.8ml/min. It supports a pressure of at least 30 bar.

iii) The maximum flowrate of nitrogen in the flowmeters is 5 L/min STP.

iv) The back pressure regulator was designed in order to operate between 0.1 and 5 bar under the flowrates specified above.

v) The solenoid valves were selected to support the pressure and give the minimum pressure drop at the flowrates used.

vi) The interface allows the reading of voltage signals between +/- 10volts; send voltage signals between +/- 10 volts and send 16 I/O digital signals. A software Genie allows the control and graphical view of all electric variables. It also permits the combination of the information to set-up the control operation of the PSA unit.

vii) The loops of the 12-way sample valve have 10μL and were chosen in order to give the best resolution of the chromatograms. It should be noted that n-pentane and iso-pentane are isomers with similar boiling points and so peaks separation is difficult. The combination of a *wcof fused silica 25mx0.53mm id* column with a coating of *cpsil 5CB df=5.0* for the volume of 10μl gave the best resolution of chromatograms.

Figure 5.7 shows a photograph of the lateral view of the equipment where the oven can be seen at the right, and at the left the back front of the gas chromatograph and the computer.
In the middle there is the vacuum pump and boxes where the electronic data acquisition interface is installed.

Figure 5.8 details the interior of the furnace, with the adsorption column, thermocouples and the two turbines.

*Figure 5.7 Lateral view of the PSA apparatus*

*Figure 5.8 View of adsorption column inside furnace.*
Experimental procedure

Before the first run, the column was activated by heating it from ambient temperature to 300°C in at least 24 hr. (see the procedure used for experiments performed in Chapters 2, 3 and 4).

A typical PSA cycle follows:

1) **Pressurization.** The set point of high-pressure is introduced in the back-pressure regulator (BPR). The feed injected by the pump (HPLC pump), is vaporized in the pre-heater and diluted by a nitrogen stream (MGFC1) before entering the column at the bottom of the adsorber. SV5 is closed and SV4 open.

2) **High-pressure feed.** At the outlet of the bed the hydrocarbons are diluted by a nitrogen stream (MGFC2) by opening the valve SV1. The valve SV7 is closed and SV6 open to by-pass the vacuum pump. When analysis of the effluent is performed a metered amount of ethane is injected trough MGFC3. The trapping system (TP) of samples is activated by the software control.

3) **Blowdown.** The set point of low-pressure is introduced in the back-pressure regulator (BPR). The mass gas flow controller 2 (MGFC 2) is stopped. The solenoid valves SV1, SV4 and SV6 are closed; SV5 and SV7 are open and the vacuum pump activated. The MGFC1 is now used to dilute the hydrocarbons coming out of the bed.

4) **Low-pressure purge.** The solenoid valve 1 is open and a selected amount of nitrogen purge is set-up in MGFC2

**Analytical section.** Before exiting the system through the exhausting system a part of the effluent passes through the VALCO trap system (TP), which can be seen in more detail in Figure 5.9. It is constituted by a 24-port valve that accommodates 12 loops and a 6-port injection valve. In Figure 5.9 a) the system is in trapping position. A small part of the effluent of the column is directed to the 12-loops valve through the 6-port valve and runs out of the system. At the same time the carrier gas passes to the capillary column through the 6-port valve. Each time the 12-loops valve is actuated a sample is trapped. The switching of the 6-port valve allows the analysis of samples. In Figure 5.9 b) the system is prepared to analyze the samples. The carrier gas passes by the 12-loop valve and the
effluent of the column runs out of the system through the 6-port valve. Each time the 12 valve is actuated a sample is injected in the chromatograph and analyzed. This trapping and analytical system can be actuated at any time of the PSA cycle.

Figure 5.9 Valco trapping and analytical system. a) Valves in trapping position. b) Valves in analyzing samples position
The measured amount of ethane introduced in the effluent of the column by MGFC 3 serves as an internal standard (p) for the calculation of the concentrations of n/iso-paraffins in the effluent stream. Table 5.4 shows the operating conditions of the chromatograph for the analysis of a typical sample.

*Table 5.4 Operating conditions of chromatograph*

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of column</td>
<td>65°C</td>
</tr>
<tr>
<td>Flowrate of carrier gas</td>
<td>10 ml/min</td>
</tr>
<tr>
<td>Detector temperature</td>
<td>250°C</td>
</tr>
<tr>
<td>Flowrate of hydrogen</td>
<td>34 ml/min</td>
</tr>
<tr>
<td>Flowrate of air</td>
<td>250 ml/min</td>
</tr>
<tr>
<td>Make-up nitrogen</td>
<td>45 ml/min</td>
</tr>
</tbody>
</table>

Figure 5.10 shows a chromatogram corresponding to a typical mixture of n/iso-paraffins. It can be seen the peaks corresponding to ethane, iso-pentane, n-pentane and n-hexane and the corresponding areas.

*Figure 5.10 Chromatogram of a mixture of n/iso-paraffins*
Since the amount of mass of ethane introduced in the effluent stream is known, the amount of n/iso-paraffins is calculated relatively to ethane. An example of the calculation of the mixture presented in Figure 5.10 follows:

i) The area of hydrocarbons calculated by the software Maestro is first corrected by introducing the relatively sensitivity value for the flame ionisation detector (Dietz, 1967). Table 5.5 shows relatively sensitivity values for the flame ionisation detector for the components present in the mixture.

<table>
<thead>
<tr>
<th>Table 5.5 Relative sensitivity data for hydrogen flame detector (data of Dietz, 1967)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative sensitivity (RS)</td>
</tr>
<tr>
<td>Ethane</td>
</tr>
<tr>
<td>Pentane</td>
</tr>
<tr>
<td>Isopentane</td>
</tr>
<tr>
<td>Hexane</td>
</tr>
</tbody>
</table>

To calculate the true fractional areas, each measured area is divided by the relative sensitivity to get the true area. The following relation can be used,

\[
A_{\text{real } i} = \frac{(A_{\text{meas } i})/RS_i}{\sum_i (A_{\text{meas } i})/RS_i}
\]  

(5.35)

where \((A_{\text{real } i})\) is the true area of component \(i\), \((A_{\text{meas } i})\) is the measured area of component \(i\) and \(RS_i\) is the relative sensitivity of component \(i\). For the example shown in Figure 5.10 the corrected areas are: \(\%nC_3=33.9\); \(\%iC_5=40.7\), \(\%nC_5=16.1\); \(\%nC_6=9.3\).

ii) Knowing the amount of one of the components present in the mixture, the values of the other components can be calculated relatively to the internal standard (p) using the relation,
\[
(\text{unknown amount of } i) = \frac{(A_{\text{rel}} \ i) (\text{known amount of } p)}{(A_{\text{rel}} \ p)}
\]

For the case shown in Figure 5.10 the mass flux of ethane introduced in the effluent stream was 0.553 gr/min; therefore, the mass fluxes of isopentane, n-pentane and n-hexane are:

\[
(\text{amount of } i \ - \ \text{pentane}) = \frac{(40.7) (0.553)}{(33.9)} = 0.663 \text{ gr/min}
\]  \hspace{1cm} (5.37)

\[
(\text{amount of } n \ - \ \text{pentane}) = \frac{(16.1) (0.553)}{(33.9)} = 0.263 \text{ gr/min}
\]  \hspace{1cm} (5.38)

\[
(\text{amount of } n \ - \ \text{hexane}) = \frac{(40.7) (0.553)}{(33.9)} = 0.152 \text{ gr/min}
\]  \hspace{1cm} (5.39)

**Selection of operating conditions of laboratory PSA unit**

In this section the operating conditions of the laboratory PSA cycle will be defined. A breakthrough curve at the high-pressure feed is performed in order to study the degree of bed loading at the first cycle. The mathematical model serves as a guide for the definition of the best operating conditions. PSA operating conditions will be selected on the base of these results.

Figure 5.11 shows a simulated and experimental breakthrough curve of a mixture of n/iso-paraffins at 568K and total pressure of 5 bar. Table 5.6 shows column characteristics and adsorbent properties. Table 5.7 reports the experimental conditions and model parameters.

The feed rate and content of n/iso-paraffins was selected in order to give an adsorbent productivity, cycle time and partial pressure of normal paraffins similar to the values found in the IFP patent already mentioned. In this case the productivity of non-normals was fixed in 0.351 mol/min.kg\text{ads} (0.415 mol/min.kg\text{ads} in the IFP patent). Figure 5.11 b) shows the associated temperature effects measured at two locations of the column. It can be seen from Figure 5.11 a) and b) that the experimental breakthrough curve and the simulated one are in good agreement. The roll-up of n-pentane is clearly seen and well predicted by the model. Also the time at which the two mass transfer zones break the column is well predicted; it seems that the multicomponent isotherm is indeed effective for this system. The temperature effects are shown in Figure 5.11 b), there is a significant increase in
temperature in the bed at the passage of mass transfer zones similar to that found in Chapter 4. It can be concluded that the column is non-adiabatic and non-isothermal. The temperature simulated curves were fitted to the experimental ones by adjusting the heat transfer coefficient at the wall and the heat transfer parameter from solid to bulk gas; the parameters obtained were 69 W/m².K and 19.3 W/m².K, respectively. The wall heat transfer parameter is approximately seven times greater than the value found for the fixed bed experiments performed in Chapter 4. This is due to the convective effect in the oven used for the PSA experiments. The particle to fluid heat transfer parameter is approximately two times greater, which can be explained from the higher flowrates of the experiment.

Table 5.6 Column characteristics and adsorbent properties of PSA laboratory experiments.

<table>
<thead>
<tr>
<th>Column characteristics</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Length, L (cm)</td>
<td>80</td>
</tr>
<tr>
<td>Internal diameter, d_c (cm)</td>
<td>1.6</td>
</tr>
<tr>
<td>Mass of zeolites, (g)</td>
<td>120</td>
</tr>
<tr>
<td>Adsorbent properties (5A zeolite)</td>
<td></td>
</tr>
<tr>
<td>Bulk density, ρ_b (g/cm³)</td>
<td>0.77</td>
</tr>
<tr>
<td>Apparent density, ρ_a (g/cm³)</td>
<td>1.13</td>
</tr>
<tr>
<td>Bulk porosity, ε_b</td>
<td>0.32</td>
</tr>
<tr>
<td>Particle porosity, ε_p</td>
<td>0.35</td>
</tr>
<tr>
<td>Pellet diameter, d_p (mm)</td>
<td>1.6</td>
</tr>
<tr>
<td>Tortuosity, T_p</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Figure 5.11 a) Breakthrough curve of a mixture of n/iso-paraffins at a temperature of 568K, total pressure 5 bar and feed flowrate 3.0 mol/hr. Points are experimental data. Lines are model predictions. b) Temperature evolution at two locations of the bed: L=20cm (25% of bed length) and L=60cm (75% of bed length).
Table 5.7 Experimental conditions and model parameters of breakthrough experiment.

<table>
<thead>
<tr>
<th>Experimental conditions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed flowrate and composition (mole %)</td>
<td>3.0 mol/hr</td>
</tr>
<tr>
<td></td>
<td>(10.8% nC₅; 4.7% nC₆</td>
</tr>
<tr>
<td>Pressure</td>
<td>5 bar</td>
</tr>
<tr>
<td>Temperature</td>
<td>295°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Model parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Axial mass dispersion, Dₘₑ (m²/s)</td>
<td>1.15 x 10⁻⁴</td>
</tr>
<tr>
<td>Axial heat dispersion, Kₑₑ (W/m.K)</td>
<td>5.8</td>
</tr>
<tr>
<td>Overall mass transfer coefficient, Kₑₑ (s⁻¹)</td>
<td>6.0</td>
</tr>
<tr>
<td>Film heat transfer coefficient, hᵣ (W/m²K)</td>
<td>19.3</td>
</tr>
<tr>
<td>Wall heat transfer coefficient, hₑₑ (W/m²K)</td>
<td>69</td>
</tr>
</tbody>
</table>

From Figure 5.11 a) it can be concluded that the first mass transfer zone breaks the column at near 480 s (8 min). This allows the definition of a high-pressure feed step around 6 min giving rise to a load of the bed of near 75% in the first cycle, which is closed to the value given in the patent (see Figure 5.3 (page 173) of the present chapter). It is necessary now to define the value of the low-pressure purge. The pressure ratio used in the IFP patent is $P_H/P_L=15/2=7.5$. Since the experimental laboratory unit allows the use of vacuum the value of 0.5 bar for the low-pressure purge will be selected given rise to a pressure ratio of $P_H/P_L=10$. This value is used in order to operate under a similar pressure ratio, but with the objective of increasing the performance of the cycle without the use of extreme vacuum which can increase significantly the costs of the process. A plot of the amount adsorbed of nC₅ and nC₆ as a function of nC₅ mole fraction in the gas phase at the feed pressure helps in the definition of the low-pressure in the PSA cycle. Figure 5.12 represents such a plot for four total pressure selected. Pressures of 3 bar and 0.4 bar correspond to the high pressure and low pressure in the IFP patent (in a base without non-normals); 1 bar and 0.1 bar correspond to the values selected to the laboratory unit (in a base without non-normals). From Figure 5.12 one can read the difference in loading of the adsorbent for nC₅
and nC₆ for the high and low-pressure. For a mole fraction of nC₅ equal to 0.75 the difference in the amount adsorbed between 3 bar and 0.4 bar is 1.36g/100gₐdₜ (IFP case). For the pressures of 1 bar and 0.1 bar the difference is 1.31g/100gₐdₜ (LSRE case). These values are similar. However, for nC₆ the results are different: between 3 bar and 0.4 bar the difference in loading is 0.9g/100gₐdₜ for the IFP case; between 1 bar and 0.1 bar the difference is 1.27g/100gₐdₜ for the LSRE case. From these results it can be concluded that the laboratory unit operating under a pressure ratio of Pₜₕ/Pₜₖ=5/0.5=10 will be more efficient especially for the desorption of nC₆ from the adsorbent.

![Graph showing the amount adsorbed as a function of nC₅ mole fraction in gas phase at four constant pressures.](image)

**Figure 5.12 Amount adsorbed of nC₅ or nC₆ as a function of nC₅ mole fraction in gas phase at four constant pressures. (-------) IFP case; (-----) LSRE case.**

**PSA experiments**

A cycle identical to the one defined in the IFP patent was selected in order to study experimentally the system. Table 5.8 summarizes the operating conditions. Four experiments were conducted in order to study the effect of purge to feed ratio on process performance. The feed pressure, temperature and flowrate are kept constant in all experiments. Only the amount of inert gas used in the low-pressure purge was changed. In Table 5.9 the amount of inert gas used in the low-pressure purge in the four experiments
and the values of purge to feed ratio are reported. The purge to feed ratio has the same
definition described above in the study of IFP patent (Equation 5.30). It is given on a molar
basis. Figure 5.13 shows a plot of the pressure variation between the four cycles. The
pressure evolution shown in the figure was measured experimentally and is constant in all
experiments.

Table 5.8 Fixed operating conditions of PSA laboratory unit.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressurisation time</td>
<td>0.5 min</td>
</tr>
<tr>
<td>Feed time</td>
<td>6 min</td>
</tr>
<tr>
<td>Blowdown time</td>
<td>0.5 min</td>
</tr>
<tr>
<td>Purge time</td>
<td>6 min</td>
</tr>
<tr>
<td>High-pressure feed, P&lt;sub&gt;H&lt;/sub&gt;</td>
<td>5 bar</td>
</tr>
<tr>
<td>Low-pressure purge, P&lt;sub&gt;L&lt;/sub&gt;</td>
<td>0.5 bar</td>
</tr>
<tr>
<td>Feed flowrate and composition</td>
<td>3.0 mol/hr</td>
</tr>
<tr>
<td></td>
<td>(10.8% nC&lt;sub&gt;5&lt;/sub&gt;; 4.7% nC&lt;sub&gt;6&lt;/sub&gt;</td>
</tr>
<tr>
<td></td>
<td>37.2% iC&lt;sub&gt;3&lt;/sub&gt;; 47.3% N&lt;sub&gt;2&lt;/sub&gt;)</td>
</tr>
<tr>
<td>Temperature of operation</td>
<td>295°C</td>
</tr>
</tbody>
</table>

Table 5.9 Amount of inert gas and purge to feed ratio used in the four PSA experiments at
the laboratory unit.

<table>
<thead>
<tr>
<th>RUN</th>
<th>Purge flowrate and composition</th>
<th>Purge to feed ratio, P/F</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.32 mol/hr (100% N&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>0.521</td>
</tr>
<tr>
<td>B</td>
<td>0.66 mol/hr (100% N&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>0.260</td>
</tr>
<tr>
<td>C</td>
<td>0.40 mol/hr (100% N&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>0.158</td>
</tr>
<tr>
<td>D</td>
<td>0.26 mol/hr (100% N&lt;sub&gt;2&lt;/sub&gt;)</td>
<td>0.103</td>
</tr>
</tbody>
</table>
Figure 5.13 Experimental pressure history in the four cycles defined for the PSA. I-Pressurization; II- High-pressure feed; III- Blowdown; IV – Low-pressure purge

Analysis of the PSA dynamic behaviour

The comparison of temperature between cycles is an interesting information in order to study the progress of the system towards the steady-state. Also the location of mass transfer zones can be assessed by these data.

Figures 5.14 a) and b) show a plot of temperature evolution at different cycles for RUN A (Purge with 500 ml/min STP of \( \text{N}_2 \)) at the high-pressure feed step. Interesting features of bed dynamics can be seen in Figure 5.14. The number of cycles to reach steady state is approximately four since the temperature profiles after this stage of operation are practically coincident. In the first cycle, the temperature increases near 15°C in the thermocouple situated at \( L=20 \) cm (25% of bed length) (see Figure 5.14a)) diminishing in subsequent cycles to reach approximately 10 °C at the cyclic steady state. This is due to the uncomplete regeneration of the adsorbent at the low-pressure purge step in this zone of the bed giving rise to a smaller adsorption in the next cycles. The thermocouple located near the top of the column (\( L=60 \) cm, 75% of bed length) gives the same information relatively to the evolution of the system to the steady state. In the first cycle the data indicates that the
mass transfer zone does not reach this zone of the bed. At the cyclic steady state the high-pressure feed step is stopped when the mass transfer zone reaches this zone, allowing the determination of the bed load reached in this experiment. Lines in the figures represent the mathematical model predictions. The mathematical model is able to predict the evolution trends of experimental data.

Figure 5.15 a) and b) show the same information but for RUN D (Purge with 100 ml/min STP). For this purge to feed ratio (P/F=0.103) it takes more time to reach the steady state. For example, in cycle 4 of RUN A (Figure 5.14a) the temperature evolution is practically the same as in cycles 8 and 9; however, for RUN D the cycle 4 is far away from the behavior of cycle 8 and 9, especially in the thermocouple at L= 60 cm. At cycle 8 or 9 it seems that the system is under the steady state as can be seen in Figure 5.15 a) and b). Compared with run A the experiment D shows other interesting features: there is a significant difference between the increase of temperature in the first cycle and subsequent cycles, since after cycle 1 the increase of temperature is only 6°C compared with 15°C at the first cycle. As noted previously this is due to the uncomplete regeneration of the bed that is more critical when the purge flowrate diminishes. This effect allows that the mass transfer zone penetrates deeply in the bed as can be seen from Figure 5.15b). For example, in RUN A the mass transfer zone passes the thermocouple situated at L=60 cm at near 330 s, but for RUN D the value is around 210 s. Again the mathematical model fit satisfactorily the temperature evolution towards the cyclic steady state.

Temperature histories for the two thermocouples over an entire cycle are also helpful in understanding the dynamics of the process. Figures 5.16 a) and b) show such plots for cycle 1 where the behavior of run A and D are compared. Figures 5.17 a) and b) show similar data for cycle 8 (near the steady state).

Figures 5.16 a) and b) show the same evolution of temperature in the two experiments in the high-pressure feed step. This is so because the same feed flowrate was used in the experiments. Since the purge flowrate is different between the two runs a significant difference in temperature is obtained in low-pressure purge. In RUN A the decrease in temperature is more clear than in Run D due to the higher desorption.

At the cyclic steady state Figures 5.17 a) and b) show for cycle 8 that the temperature excursions are significantly different. The temperature excursions in RUN A are higher
than in RUN D, since as noted previously there is a higher regeneration of the adsorbent. In Figure 5.17b) it is clearly seen the difference between the times at which the mass transfer zone passes this location of the column.

Figure 5.14 Evolution of temperature at several cycles for RUN A for the high-pressure feed step. a) Thermocouple located at L=20 cm from feed inlet; b) Thermocouple located at L=60 cm from feed inlet. Lines are model predictions. Points are experimental data (□ cycle 1; Δ cycle 4; O cycle 8; ◇ cycle 9)
Figure 5.15 Evolution of temperature at several cycles for RUN D for the high-pressure feed step. a) Thermocouple located at L=20 cm from feed inlet; b) Thermocouple located at L=60 cm from feed inlet. Lines are model predictions. Points are experimental data (☐ cycle 1; Δ cycle 4; O cycle 8; ◇ cycle 9).
Figure 5.48 Temperature histories over an entire cycle of a PSA experiment. a) Comparison between runs A (purge flowrate=500 ml/min STP) and D (purge flowrate=100 ml/min STP) for cycle 1 at the thermocouple at 20 cm from feed inlet. b) Comparison between runs A and D for cycle 1 at the thermocouple at 60 cm from feed inlet. Lines are model predictions. Points are experimental data (100 ml/min STP; O 500 ml/min STP)

I-Pressurisation; II- High-pressure feed; III- Blowdown; IV- Low-pressure purge
Figure 5.17 Temperature histories over an entire cycle of a PSA experiment. a) Comparison between runs A (purge flowrate=500 ml/min STP) and D (purge flowrate=100 ml/min STP) for cycle 8 at the thermocouple at 20 cm from feed inlet. b) Comparison between runs A and D for cycle 8 at the thermocouple at 60 cm from feed inlet. Lines are model predictions. Points are experimental data (□ 100 ml/min STP; ○ 500 ml/min STP)

I-Pressurisation; II- High-pressure feed; III- Blowdown; IV- Low-pressure purge
From the temperature data shown it is possible to conclude important points of the PSA system:

1) As the purge feed decreases more cycles are needed to reach the cyclic steady state.

2) The cyclic steady state is reached in at least nine cycles for the more critical experiments (runs C and D).

3) The decrease in purge feed increases the loading of the bed.

**PSA process performance**

The PSA process performance is measured in terms of purity and recovery as a function of purge to feed ratio. To calculate the purity of the iso fraction in the high-pressure feed step it is necessary to analyze the effluent of the column. In industrial operations it is important to calculate the purity only at the cyclic steady state. Since from the temperature data is possible to know when the cyclic steady state is reached, the effluent of the high-pressure feed is analyzed only at this stage of operation.

The molar flux of the hydrocarbons in the effluent of the column calculated from the analytical system described in page 185 is shown in Figure 5.50 for RUNS C and D. Figure 5.51 shows the concentration of hydrocarbons at the outlet of the column calculated from the relation \( C_i = \frac{F_{i,\text{meas}}}{\sum F_{i,\text{meas}}}.(P_{\text{exp}}/RT) \) where \( F_{i,\text{meas}} \) is the measured value of molar flux plotted in Figure 5.50 and \( P_{\text{exp}} \) is the measured experimental total pressure. Figure 5.52 plots the superficial velocity at the outlet of the column calculated by the relation \( v = \frac{\sum F_{i,\text{meas}}.RT}{A_c P_{\text{exp}}} \), where \( A_c \) is the column area. In RUNS A and B the normal paraffins do not break the column. In RUN C only a small fraction of n-pentane breaks the column as can be seen in Figures 5.18 and 5.19. Figure 5.50 b) and Figure 5.19 b) show that for RUN D a significant fraction of n-pentane and n-hexane breaks the column decreasing significantly the purity of the iso fraction. It is also seen in Figure 5.19 a) and b) that when the normal paraffins break the column the concentration of isopentane decreases. This is expected since the velocity and consequently the flowrate increases as can be seen in Figure 5.20.
Figure 5.53 shows a plot of the purity and recovery as a function of purge to feed ratio measured experimentally for the four runs performed. It can be seen that the purity decreases significantly for P/F ratios smaller than 0.25. When P/F ratio is 0.1 the purity decreases to approximately 96%. The results obtained for the IFP patent under a similar pressure ratio P/F=20/2=10 are also plotted in the figure for comparison. Figure 5.53 shows that comparing LSRE and IFP cycles, it can be concluded that the LSRE case is more efficient, since the breakdown in purity occurs for a smaller P/F ratio, so for the same level of purity, the recovery of the isofraction is higher in the LSRE case. This is expected since as shown previously in Figure 5.12 the difference in adsorbent loading between high-pressure and low-pressure is higher in the LSRE case. However, another effect accounts for this difference because the simulation in the IFP case is in adiabatic conditions and the LSRE case is in non-adiabatic non-isothermal conditions.

The flowrate of paraffins in the low-pressure purge step is shown in Figure 5.54 for experiments B, C and D at the cyclic steady state. Only the experimental results after 100 seconds of the beginning of the cycle are plotted. This is due to experimental difficulties in the analysis of the effluents of the column as can be seen in Figure 5.55, which represents an experiment where the adsorption column was replaced by a simple ¼ in tube.

It can be seen that near 100 seconds are needed to completely clean the system from the hydrocarbons after the beginning of the low-pressure purge step. The explanation for this behavior can be the condensation of hydrocarbons on tube walls that can disguise the true information of the adsorption column. This point is critical just after the beginning of the blowdown since the sudden decrease in pressure produces a high concentration of paraffins running in the effluent system.

*Comparison of process performance with theoretical predictions*

The four experiments performed were simulated using the mathematical model previously described. The comparison between the experimental and simulated trends of the purity and recovery as a function of purge to feed ratio is shown in Figure 5.53. The agreement between theory and experiments is good. The breakdown in purity seems to be well predicted. For comparison the results previously obtained for the IFP patent are also plotted in the Figure 5.53. The increasing performance of the cycle studied in the laboratory
relatively to the IFP is mainly due to the implementation of vacuum in the low-pressure purge, operation in non-adiabatic conditions and the smaller value of productivity.

Figure 5.50 Molar flux of paraffins in the effluent of the high-pressure feed step versus time at the cyclic steady state (cycle 9). a) Run C (purge flowrate 150ml/min STP of nitrogen; b) Run D (purge flowrate 100ml/min STP of nitrogen). Lines are model predictions.
Figure 5.51 Concentration of paraffins in the effluent of the high-pressure feed step versus time at the cyclic steady state (cycle 9). a) Run C (purge flowrate 150ml/min STP of nitrogen; b) Run D (purge flowrate 100ml/min STP of nitrogen). Lines are model predictions.
Figure 5.52 Velocity at the outlet of the column versus time at the cyclic steady state (cycle 9). a) Run C (purge flowrate 150 ml/min STP of nitrogen; b) Run D (purge flowrate 100 ml/min STP of nitrogen). Points are experimental data. Lines are model predictions.
Figure 5.53 Purity and recovery of non normals as a function of purge to feed ratio. Points are experimental data and lines are model predictions.

The molar flux, concentration and velocity of the hydrocarbons in the effluent of the column are compared with the model in Figure 5.50, Figure 5.51 and Figure 5.52, respectively. The same trends are observed. Also, the breakthrough time is well predicted. An interesting point should be noted from these plots: the selectivity between n-pentane and n-hexane observed in Figure 5.11 for the breakthrough experiment is lost at the cyclic steady state. When n-pentane breaks the column also n-hexane breaks. In other words, it is more difficult to desorb the n-hexane from the system giving rise to its increasing content in the column. This is due to the more favorable nature of the adsorption equilibrium isotherm of n-hexane compared to n-pentane. From Table 5.7 it can be seen that the mass transfer rates are in the order of \(6.0 \text{ s}^{-1}\). Under these conditions mass transfer rate is high and the system becomes dominated practically by the influence of heat transfer limitations and adsorption equilibrium effects. The mass Peclet numbers are in the order of 800, so axial mass dispersion is also not important.
Figure 5.54 Molar flux of paraffins in the effluent of the column versus time at the low-pressure purge step. a) RUN D (purge flowrate of 100ml/min STP of nitrogen; b) RUN C (purge flowrate of 150ml/min STP of nitrogen; c) Run B (purge flowrate of 250ml/min STP of nitrogen).
Figure 5.55 Time needed to clean the gas sampling system after the beginning of the low-pressure purge step.

The flowrates of hydrocarbons in the effluent of the column at the low-pressure purge step are compared in Figure 5.54. Again the mathematical model shows the basic trends of all experimental observed behavior.

The agreement between experiments and theory suggests that the model contains the basic features of the real system.

5.4 Conclusions

A mathematical model for the separation of n/iso-paraffins by a four-step PSA has been developed. Equilibrium and kinetic parameters of the model were obtained from independent experiments in Chapters 2 and 3.

The PSA cycle described by Minkkinen et al. (1993) was simulated for isothermal and adiabatic conditions and consistent results were obtained. The process performance was studied in terms of recovery and purity as a function of purge to feed ratio. The effects of temperature, feed pressure and feed flowrate were studied. Decreasing the temperature of PSA operation relatively to the cycle described in the patent leads to lower performance. Also when feed pressure decreases from 15 bar to 10 bar the process performance goes down, but increasing the feed pressure from 15 bar to 20 bar does not improve much the
performance. Increasing the feed flowrate relatively to the base cycle decreases significantly the process performance.

A laboratory unit was successfully built in order to study experimentally the PSA cycle. Operating conditions similar to those in the patent were simulated in terms of cycle time, adsorbent productivity and high-pressure low-pressure ratio. The laboratory unit operates under a high-pressure of 5 bar and low-pressure of 0.5 bar, cycle time of 13 min and adsorbent productivity equal to 0.351 mol/min-kg_ads comparing to 0.415 mol/min-kg_ads of the IFP patent. The implementation of vacuum in the low-pressure purge increases the performance of the cycle relatively to IFP patent. The mathematical model was able to predict all PSA behaviors.

These results show that the mathematical model is effective for the design and implementation of optimal operational conditions of PSA units for the separation of n/iso-paraffins.

References


6. Conclusions and recommendations

In this chapter conclusions concerning the Ph D. work are established. Recommendations for future work are also addressed.

6.1 Conclusions of Ph. D. work

The basic underlying theory for the design of an adsorption separation process was reviewed and a methodology for gas adsorption process design established for the separation of n/iso-paraffins for octane improvement of gasoline pools. Experimental data necessary for the calibration of a mathematical model for simulating the separation of n/iso-paraffins in 5A zeolites have been obtained from independent experiments.

A gravimetric apparatus was developed and a procedure for measuring adsorption equilibrium isotherms in a flow microbalance system established. Isotherms of n-pentane and n-hexane have been obtained between 373K and 573K and for partial pressures up two 0.6 bar (Silva and Rodrigues, 1997a,b). An adsorption equilibrium model developed by Nitta et al. (1984) based on localised adsorption that assumes that a molecule when adsorbs occupies more than one active site describes with good accuracy the adsorption equilibrium data. Heats of adsorption are around 13.2 kcal/mol for n-pentane and 14.2 kcal/mol for n-hexane. Henry constants in the system nC_5-5A range from 0.28 g/g_{ads}.bar to 144 g/g_{ads}.bar
when temperature ranges from 373K and 573K. For the system nC$_6$-5A the values are 1.67g/g$_{ads}$,bar to 1436g/g$_{ads}$,bar for the same temperature range. This model was also used to correlate data published in literature for adsorption of n-paraffins up to n-decane in 5A zeolite. Again, maintaining thermodynamic consistency of the parameters it was possible to correlate the data. Heats of adsorption range from 4.5 kcal/mol in the system methane/5A zeolite to 23.2 kcal/mol in the system n-decane/5A zeolite. The MSL model is flexible and can be extended to multicomponent systems.

The kinetics of sorption of n-hexane and n-pentane in 5A zeolite pellets were studied using the ZLC technique (Eic and Ruthven, 1988) initially developed for the measurement of diffusivity in zeolite crystals and by the gravimetric technique. A ZLC apparatus for the study of diffusivity in pellets was developed and an experimental procedure established. Experiments between 473K and 573K have been conducted to study the effect of purge flowrate and crystal size of pellets in ZLC desorption curves. It was found that macropore diffusion is the controlling mechanism of diffusion of n-pentane and n-hexane in 5A zeolite pellets (Silva and Rodrigues, 1997a,b). This conclusion was confirmed by two experimental techniques, namely ZLC and gravimetry. The pore diffusivity of nC$_5$ in pellets of 5A zeolite ranges from 0.07 to 0.09 cm$^2$/s when temperature changes from 473K to 573K in N$_2$ carrier gas; for the system He-nC$_5$ the pore diffusivity in the same temperature range varies from 0.1 to 0.14 cm$^2$/s. For the nC$_6$ system they range from 0.06 to 0.08 cm$^2$/s, when temperature changes from 473K to 573K in N$_2$ carrier gas. With Helium as a carrier gas the values range from 0.11cm$^2$/s to 0.13cm$^2$/s. The tortuositities extracted from a model considering Knudsen diffusion and molecular diffusion in series are in the order of 1.6 in the systems n-hexane/5A and n-pentane/5A. A ZLC model for the study of diffusivity in bidisperse adsorbents such as 5A zeolite pellets has also been developed (Silva and Rodrigues, 1996). An analytical solution of the model by the method of the residues was obtained and compared with a numerical solution by orthogonal collocation. The flexibility of the analytical solution allows the establishment of a procedure for data treatment based on the long time straight lines of ZLC desorption curves. It is shown that using the first term of the series model, it is possible in two different runs where some property of the system such as temperature or crystal size or pellets size is varied, obtain the model parameters, namely the time constant for macropore diffusion $R_p^2/D_p/(1+K)$ and the time constant for micropore diffusion $r_c^2/D_c$. 
A non-isothermal, non-adiabatic fixed bed adsorption model accounting for bulk separations of mixtures with n/iso-paraffins has been developed. It is based on the assumption that macropore diffusion is the controlling mechanism of diffusion on the adsorbent particle. A lumped model for the adsorbent particle suggested by Morbidelli et al. (1982) is used. The fixed bed adsorption model is solved by the application of orthogonal collocation (Villadsen and Michelsen, 1978). A fixed bed apparatus for operating at high temperatures has been developed. Experiments with mixtures of iC₅/nC₅/nC₆ were carried out and the effect of operating variables such as, n-paraffins partial pressure, operating temperature and feed flowrate was studied (Silva and Rodrigues, 1997c). For multicomponent adsorption the extended Nitta et al. model isotherm was used. Good agreement was found between experiments and predicted results. These results proved that the mathematical model contains the basic features of the adsorption system. Also the multicomponent Nitta et al. model isotherm constructed with the single parameters isotherm proved to be an effective tool for the prediction of multicomponent equilibria. The breakthrough curves were obtained between 448 K and 573 K. Some experimental problems were found during the course of experiments due to the existence of a parabolic profile of temperature existing in the oven. However, in the simulations this profile was introduced in the mathematical model and results were in good agreement with experimental data. The breakthrough curves are of a sharp nature which can be explained from the high global mass transfer coefficient, in the order of 30s⁻¹. Accordingly, the shapes of breakthrough curves are primarily influenced by the adsorption equilibrium isotherm. This was proved by decreasing the partial pressure in feed resulting in an increase of the mass transfer zone of breakthrough curve. From these results, it is expected that diffusion inside the molecular sieve pellets in fixed bed adsorbers operating with mixtures of n/iso-paraffins are of secondary importance, at least for temperatures in the order of 573K and for high concentrated feed which is the main operating condition of industrial adsorbers. The problem will be in the regeneration of the adsorption vessels, since the isotherm becomes unfavorable in desorption and a long time for regeneration is necessary. This was also shown in the desorption curves studied. As an example, the time for the regeneration practically doubles the time for adsorption, if a similar purge flowrate of inert is employed in the desorption step for a case where a mixture of n/iso-paraffins is fed to an adsorber where the normals constitute 10% of the feed at 1bar and 523K (see Chapter 4, page 129). Accordingly, if the regeneration is performed with an inert at
isobaric conditions a significant quantity of inert should be employed. This is a reason why the implementation of a pressure swing can be a competitive strategy for this separation.

Fundamentals of adsorption such as the fixed bed adsorption of two linearly adsorbed species in presence of an inert were also studied. It was shown by a suitable variable change that this adsorption system is similar to the adsorption of two solutes in a trace system obeying a multicomponent Langmuir isotherm. It was proved with a treatment similar to that of Glueckauf (1949) by the use of the method of characteristics, interesting features of bed dynamics such as the effect of roll-up in a linear systems, only encountered in systems governed by favorable isotherms (Silva and Rodrigues, 1998b). It was also shown an increase roll-up in the system as the concentration of solutes in the feed becomes higher. The orthogonal collocation also used in the study proves that the increasing concentration of solutes also narrows the mass transfer zones. The similar structure of the system encountered with the change of variable relatively to the system governed by multicomponent Langmuir isotherm serves as base for extending this work for n solutes by a proper treatment of the equations encountered. There is in literature published work on trace systems governed by multicomponent Langmuir isotherms (Helferich and Klein, 1970) that can serve as a guide for the treatment of non-trace systems if the variable change is implemented.

The mathematical model developed and calibrated by the introducing of Nitta et al. model isotherm with parameters found from equilibrium data, and with kinetic parameters obtained from ZLC experiments were used to study a real system shown by Minkkinen et al. (1993) in a patent assigned to IFP. The PSA cycle described in patent which operates at 573K, with a high-pressure of 15 bar, total cycle time 12 min, low-pressure of 2 bar, and adsorbent productivity of non-normals of 0.415 mol/min kg ads (feed content of normal paraffins 19%) was simulated by the use of the mathematical model developed during the course of this work (Silva and Rodrigues, 1998a). The model was able to predict the PSA behavior since for the operating conditions reported in the patent, the simulations show that the cycle is possible and a good performances is obtained (for example, the bed coverage at cyclic steady state in the adiabatic cycle is near 95%). The effect of operating variables such as the high-pressure feed, temperature of adsorption, isothermal and adiabatic operation was studied in plots of purity and recovery of iso fraction at the high-pressure feed as a function of purge to feed ratio. Increasing high-pressure feed from 15 bar to 20
bar increases the recovery of the iso fraction from 50% to 60% when the breakdown in purity increases. Decreasing the high pressure feed to 10 bar decreases the recovery from 50% to approximately 25% which seems critical. The decrease in temperature from 573K to 523K decreases the recovery to approximately 40%; it should be noted that when temperature decreases, more adsorption occurs, so we expect at a first glance a more efficient cycle; however, the decrease in performance is clearly due to the higher difficulty in regenerating the bed since isotherms become more unfavorable in the desorption step. Also the isothermal cycle is much more efficient, for example when the breakdown in purity occurs the recovery increases from 50% in the adiabatic cycle to near 70% in the isothermal one. In comparing the simulated results with the patent ones Minkkinen et al. report an amount of approximately 27%mole nC₅ and 7.5 mole % nC₅ recycled to the reactor which compares with 21 %mole nC₅ and 7.3 %nC₅ predicted by the model. These results show that the model is indeed effective to simulate the process.

The mathematical model developed served also as a base to construct a laboratory pilot unit at the LSRE for studying a PSA cycle for the separation of n/iso-paraffins. A vacuum swing cycle was proposed for the separation under a pressure ratio similar to that found in the IFP patent. The high-pressure feed selected is 5 bar and the low-pressure 0.5 bar (the implementation of this high pressure/low pressure can be an advantage since there are reports (Magnoux et al., 1998) showing the coke formation with isopenatne at elevated pressures ≈15 bar). The adsorbent productivity of non-normals is 0.351 mol/min.kg_ads comparable to the IFP patent. The temperature of operation of the PSA lab unit is 568K.

The feed content of normal paraffins is 15.5%. A breakthrough curve at the high-pressure feed was performed and results compare fairly well with the simulated ones. Again the extended multicomponent isotherm of Nitta et al. predict with good accuracy the adsorption behaviour. By analysis of the breakthrough curve, the high-pressure feed time was selected in 6 min to give approximately 70% of bed utilisation in the first cycle of the PSA cycle. Four experiments were conducted to study the effect of purge to feed ratio on the purity and recovery of the iso fraction. When comparing the simulated results with the experimental ones it is concluded that the laboratory column operates under non-isothermal non-adiabatic conditions. During these experiments only the purge flowrate at the low-pressure purge step was varied. From the experimental results it is concluded that when the P/F ratio is smaller than 0.2 the purity of the iso-fraction goes down. However, comparing
with the IFP cycle for a similar high-pressure low-pressure ratio \( \text{Ph/Pl}=20/2 \) it was found that recovery in the lab unit is 70% compared with 60% for the IFP cycle when the breakdown of purity starts. The main conclusion is that the cycle proposed in this work can be a competitive one for the separation of n/iso-paraffins.

As a final conclusion, it can be said that a strategy for the design of a separation process using adsorption technology was developed. We believe that the results obtained here are representative of the system under study. This strategy can be applied to the simulation of other separation adsorption processes and the results shown here prove once more that mathematical modelling and simulation are useful tools for the design of industrial equipment in chemical engineering field.

### 6.2 Recommendations for future work

At the LSRE experimental apparatus are now available for the determination of physical parameters of adsorption systems such as equilibrium isotherms using gravimetry and kinetic parameters by the ZLC and gravimetric techniques. However, these techniques are restricted to single component systems. It is recommended in future work the development of experimental apparatus for the measurement of multicomponent sorption equilibria and kinetics of sorption. The differential adsorption bed apparatus (DAB) first developed by Carlson and Dranoff (1985) and later explored by Mayfield and Do (1991) and Hu et al. (1993) to the study of n-paraffins in activated carbon can be an interesting solution. The technique uses a gas mixing system, a differential adsorption bed, a desorption pump and a gas chromatograph for sample analysis. This technique can be easily adapted to the experimental equipment now available. Accordingly the investment to the set-up seems not to be high. A more refined technique but in principle similar to the DAB was recently shown by King and Do (1996). It is called Batch Adsorber FT-IR technique and take the advantages of using a infrared-detector that is convenient for systems where the kinetics is reasonably fast. This technique can be also a solution to study multicomponent adsorption systems.

Other interesting technique for the measurement of multicomponent adsorption equilibria is the use of the impulse response chromatography. This technique consists in using small and instantaneous perturbations (theoretically, Dirac impulses) in the composition of the
feed to a chromatographic column initially at equilibrium with that feed. The system response consists of a sequence of "peaks", the number of which is generally equal to the number of adsorbed components, and the moments of which are related to the isotherm derivatives. This technique was explored long ago to study the case of two components adsorbed with no inert. The generalisation for the study of any multicomponent systems seems to be difficult, due to mathematical and numerical complexity of the theoretical problem. However, two attempts recently drawn by Zhong and Meunier (1993) and Tondeur et al. (1996) are promising for the real application of this simple experimental technique. In the work of Tondeur et al. (1996) the case where all components are adsorbed is still not solved. This experimental technique can be also easily applied to the experimental apparatus developed during this work.

It is also recommended the study of the effect of the deposition of coke in the performance of the separation of n/iso-paraffins. The deactivation of the adsorbent results from the accumulation of carbonaceous materials on the adsorbent, which is a consequence of processing feed at elevated temperatures. This is more critical when heavy feeds are processed (especially in the separation of n-paraffins in the kerosine range). For example the kerosine Isosiv units include a regeneration step ranging from 15 to 30 days (Wilcher and Raghuram, 1981). It was found during the course of this work, especially in the PSA unit that the pellets near the zone where the feed was loaded changed his color significantly; they become gray. It is possible that a significant coke was deposited in the pellets. It can be interesting to study the drift of the performance of the molecular sieves by studying adsorption isotherms and kinetics of sorption in this coked pellets.

Relatively to the separation of n/iso-paraffins, the development of new adsorbents will make possible not only separate n-paraffins from branched and cyclic paraffins but also to separate by classes the branched paraffins and cyclic paraffins. It was shown in Chapter 1 in a table that between branched and cyclic paraffins there exists also different octane numbers. Studies of the separation of branched hexane isomers using zeolite molecular sieves have been conducted recently by Huddersman and Klimczyl (1996), showing that zeolite Beta (H, Na) is an effective separator of 2,3-dimethylbutane (RON 103.5) from 3-methylpentane (RON 74.5). This work opens the possibility of a better refinement of the technology of separating n/iso-paraffins for octane improvement on gasoline pools. It is necessary to investigate in future the abilities of other ion-exchanges beta zeolites or other
type of zeolites. These seem to be the most important developments in future relatively to
the objectives of the separation study during the course of this work. Experimental
apparatus are available for the determination of the physical parameters at the LSRE; the
advances will be certainly related with the discovery of new zeolite molecular sieves.

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Appendix A1. Analytical Solution of ZLC bidisperse model

Introducing the new variables,

\[ U = C'_p y; \quad u = q' x; \quad \bar{u} = \bar{q}' x \]

where,

\[ C'_p = \frac{C_0 - C_p}{C_0 - C_{in}}; \quad q' = \frac{q_0 - q}{q_0 - q_{in}}; \quad \bar{q}' = \frac{\bar{q}_0 - \bar{q}}{\bar{q}_0 - \bar{q}_{in}} \]

and for convenience \( x = \pi / r_c \) and \( y = R / R_p \). Using Laplace transforms relative to time defined by \( L(U(t)) = \bar{U}(s) = \int_0^\infty e^{-st} U(t) \, dt \), the model equation for the microsphere (Equation 3.12) becomes,

\[ \frac{d^2 \bar{u}}{dx^2} = \frac{s}{\gamma} \bar{u} \quad \text{(A1.1)} \]

Taking into account the corresponding boundary conditions we get:
\[ \tilde{u} = \frac{\sinh \left( \frac{s}{\gamma} \right)}{\gamma} \] (A1.2)

The average adsorbed concentration in the microspheres is calculated by

\[ \tilde{q}' = 3 \int_0^1 \left( \frac{q'}{x} \right) x^2 dx, \]
which after substitution of equation A1.2 gives,

\[ \tilde{q}' = 3 \frac{\tilde{U}}{\gamma} \left( \frac{s}{\gamma} \coth \left( \frac{s}{\gamma} \right) - 1 \right) \] (A1.3)

Applying Laplace transform to the pellet mass balance (Equation 3.16) we first obtain:

\[ \frac{d^2 \tilde{U}}{dy^2} = s \tilde{U} + Ks \tilde{q}' \] (A1.4)

Inserting Equation (A1.3) in the above equation we get

\[ \frac{d^2 \tilde{U}}{dy^2} = \left( s + 3Ks \left( \frac{s}{\gamma} \coth \left( \frac{s}{\gamma} \right) - 1 \right) \right) \tilde{U} \] (A1.5)

and using the corresponding boundary conditions we obtain:

\[ \tilde{U} = \frac{s}{\lambda \coth \lambda + (L-1)} \frac{1}{\sinh \lambda} \] (A1.6)

where

\[ \lambda = \sqrt{s + 3Ks \left( \frac{s}{\gamma} \coth \left( \frac{s}{\gamma} \right) - 1 \right)} \] (A1.7)

Equation (A1.6) provides the basis for the ZLC solution in the Laplace domain. If K=0 (no adsorption capacity) then \( \lambda = \sqrt{s} \) and the solution in the time domain is the one given by Crank (1975), and with parameter L later by introduced by Eic and Ruthven (1988) for the analysis of ZLC results with zeolite crystals,
\[
\frac{C_p - C_{in}}{C_0 - C_{in}} = \frac{2LR_p}{R} \sum_{n=1}^{\infty} \exp(-D\lambda_n^2 t / R_p^2) \frac{\sin(\lambda_n R / R_p)}{\lambda_n^2 + L(L-1) / \sin \lambda_n} \tag{A1.8}
\]

where \( \lambda_n \) are the roots of the equation \( \lambda_n \cot \lambda_n + (L-1) = 0 \). For ZLC cell we need to know \( C_p \) at \( R = R_p \).

The inversion of Equation (A1.6) can be simplified by introducing \( \beta = \sqrt{-(s/\gamma)} \); knowing that,

\[
\sin(\theta) = \frac{1}{\cosh(\theta)} \tag{A1.9}
\]
\[
\cot(\theta) = i \coth(\theta) \tag{A1.10}
\]
\[
\cot(-\theta) = -\cot(-\theta) \tag{A1.11}
\]
equation (A1.6) results in,

\[
\tilde{U} = L \frac{1}{\beta^2 \gamma \lambda' \cot \lambda' + (L-1) / \sin \lambda'} \sin(\lambda' y) \tag{A1.12}
\]

where,

\[
\lambda' = \sqrt{\beta^2 \gamma + 3K \gamma (1 - \beta \cot \beta)} \tag{A1.13}
\]

The inversion of Equation (A1.12) for time domain involves the determination of his singularities. Equation (A1.12) has a single pole for \( \beta^2 = 0 \) and an infinite number of poles for \( \lambda' \cot \lambda' + (L-1) = 0 \). The solution consists in the determination of the residues of the referred poles.

The residue for \( \beta^2 = 0 \) can be obtained by knowing that,

\[
\frac{\sin(\lambda' y)}{\sin(\lambda')} = \frac{\lambda' y - (\lambda')^3 / 3! + \ldots}{\lambda' - (\lambda')^3 / 3! + \ldots} = \frac{y - \lambda'^2 y^3 / 3! + \ldots}{1 - (\lambda')^2 / 3! + \ldots} \tag{A1.14}
\]

\[
\frac{\beta \sin(\beta)}{\sin(\beta)} = \frac{1 - \beta^2 / 2! + \ldots}{\beta - \beta^3 / 3! + \ldots} = \frac{1 - \beta^2 / 3! + \ldots}{1 - \beta^2 / 3! + \ldots} \tag{A1.15}
\]
the substitution of these relations in expression allows to obtain the pole for $\beta=0$, which is,

$$\lim_{\beta \to 0} \beta \tilde{U} = y$$

(A1.16)

The residues relatively to poles $\lambda' \cot \lambda'+(L-1)=0$ can be obtained using the Heaviside expansion theorem (Churchill, 1972). According to that theorem the residues of $\lambda' \cot \lambda'+(L-1)=0$ are obtained from,

$$\frac{2L}{\beta} \frac{\exp(-\gamma \beta^2 \tau)}{d \beta} \frac{\sin(\lambda' y)}{(\lambda' \cot \lambda'+(L-1)) \sin(\lambda')}$$

(A1.17)

The solution is the sum of the residue referent to the pole of $\beta=0$ with the infinite number resulting from Equation (A1.17). The solution is then,

$$U = y - 2L \sum_{\tilde{n}=1}^{\infty} \sum_{\tilde{m}=1}^{\infty} \frac{1}{\beta_{n,m}} \frac{\exp(-\gamma \beta_{n,m}^2 \tau)}{(\lambda_n^2 + L(L-1)) \frac{d \lambda'}{d \beta}_{|\beta=\beta_{n,m}}} \frac{\sin(\lambda' y)}{\sin \lambda'}$$

(A1.18)

and,

$$\frac{d \lambda'}{d \beta}_{|\beta=\beta_{n,m}} = \frac{\gamma}{2 \lambda'_n} (2\beta_{n,m} + 3K(\cot \beta_{n,m} (\beta_{n,m} \cot \beta_{n,m}-1) + \beta_{n,m}))$$

(A1.19)

where $\beta_{n,m}$ and $\lambda'_n$ are obtained from the transcendental equations,

$$\lambda'_n = \sqrt{\beta_{n,m}^2 \gamma + 3K \gamma (1- \beta_{n,m} \cot \beta_{n,m})}$$

(A1.20)

$$\lambda'_n \cot \lambda'_n + L - 1 = 0$$

(A1.21)

using the definitions $U = C'_p y$ and $C'_p = \frac{C_p - C_p}{C_0 - C_{in}}$, the expression (A1.18) results in,

$$\frac{C_p - C_{in}}{C_0 - C_{in}} = 2L \sum_{\tilde{n}=1}^{\infty} \sum_{\tilde{m}=1}^{\infty} \frac{1}{\beta_{n,m}} \frac{\exp(-\gamma \beta_{n,m}^2 \tau)}{(\lambda_n^2 + L(L-1)) \frac{d \lambda'}{d \beta}_{|\beta=\beta_{n,m}}} \frac{\sin(\lambda' y)}{\sin \lambda'_n}$$

(A1.22)
The ZLC solution for the case of negligible external mass transfer resistance is given by Equation (A1.22) for \( C_{in}=0, \gamma=1 \) and \( C_P=C_{out} \):

\[
\frac{C_{out}}{C_o} = 2L \sum_{m=1}^{\infty} \sum_{n=0}^{\infty} \frac{1}{\beta_{n,m}} \exp\left(-\frac{\gamma}{\beta_{n,m}} \tau' \right) \left( \frac{\lambda_n^2 + L(L-1)}{\lambda_n} \right) \frac{d\lambda'}{d\beta} |_{\beta=\beta_{n,m}}
\]

(A1.23)

Limiting cases can be analyzed from the solution given by Equation (A1.23):

a) **Macropore diffusion is the controlling mechanism.**

In this situation \( \beta \to 0, \beta \cot \beta = 1 - \beta^2/3 \); Equation (A1.19) then becomes

\[
\frac{d\lambda'}{d\beta} |_{\beta=\beta_{n,m}} = \sqrt{\gamma(1+K)}
\]

(A1.24)

and Equation A1.20,

\[
\lambda_n' = \sqrt{\gamma(1+K)} \beta_{n,m}
\]

(A1.25)

the solution is then:

\[
\frac{C_P - C_{in}}{C_o - C_{in}} = 2L \sum_{n=0}^{\infty} \exp\left(-\frac{\lambda_n^2}{1+K} \tau' \right) \sin(\lambda_n' \gamma) \sin \lambda_n'
\]

(A1.26)

The solution given by Equation (A1.26) is of the same form as in the case of diffusion in zeolite crystals alone (Eic and Ruthven, 1988) if we note that here the pore diffusivity is divided by the factor \((1+K)\) accounting for the adsorption capacity of the microspheres (crystals).

b) **Micropore diffusion is the controlling mechanism.**

In this situation \( \lambda \to 0, \lambda \cot \lambda = 1 - \lambda^2/3 \); with \((1+K)\gamma\) small Equation (A1.20) becomes

\[
\beta_m \cot \beta_m + (L/K \gamma - 1) = 0
\]

(A1.27)
and the solution is then,

\[
\frac{C_p - C_{in}}{C_p - C_{in}} = \frac{2(L/K\gamma)}{y} \sum_{m=1}^{\infty} \frac{\exp(-\gamma \beta_m n')}{(\beta_m^2 + (L/K\gamma)((L/K\gamma) - 1))} \sin(\beta_m y) \sin \beta_m
\]  

(A1.28)

The solution given by Equation (A1.28) is of the same form as in the case of diffusion in zeolite crystals alone (Eic and Ruthven, 1988) if we define \( L' = L/K\gamma \).

Table A1.1. \( \beta_{1,1} \) values as a function of \( L \) and \( \gamma \) for \( K=100 \)

<table>
<thead>
<tr>
<th>( \gamma )</th>
<th>0.001</th>
<th>0.01</th>
<th>0.1</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.00545</td>
<td>0.0172</td>
<td>0.0539</td>
<td>0.1561</td>
<td>0.2552</td>
<td>0.2814</td>
<td>0.3085</td>
</tr>
<tr>
<td>0.1</td>
<td>0.0172</td>
<td>0.05493</td>
<td>0.1704</td>
<td>0.4903</td>
<td>0.791</td>
<td>0.8693</td>
<td>0.9483</td>
</tr>
<tr>
<td>0.01</td>
<td>0.0545</td>
<td>0.172</td>
<td>0.534</td>
<td>1.4438</td>
<td>2.0881</td>
<td>2.2153</td>
<td>2.3291</td>
</tr>
<tr>
<td>0.005</td>
<td>0.0770</td>
<td>0.243</td>
<td>0.7487</td>
<td>1.8934</td>
<td>2.5045</td>
<td>2.6016</td>
<td>2.6824</td>
</tr>
<tr>
<td>0.001</td>
<td>0.1721</td>
<td>0.54</td>
<td>1.5529</td>
<td>2.7739</td>
<td>2.9996</td>
<td>3.0247</td>
<td>3.0443</td>
</tr>
<tr>
<td>0.0001</td>
<td>0.5396</td>
<td>1.57</td>
<td>2.829</td>
<td>3.1035</td>
<td>3.1274</td>
<td>3.1299</td>
<td>3.1319</td>
</tr>
<tr>
<td>0.00001</td>
<td>1.5653</td>
<td>2.834</td>
<td>3.1095</td>
<td>3.1377</td>
<td>3.1401</td>
<td>3.1404</td>
<td>3.1407</td>
</tr>
</tbody>
</table>

Table A1.2 \( \lambda_1 \) values as a function of \( L \)

<table>
<thead>
<tr>
<th>( L )</th>
<th>0.001</th>
<th>0.01</th>
<th>0.1</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_1 )</td>
<td>0.05476</td>
<td>0.1730</td>
<td>0.5423</td>
<td>1.5708</td>
<td>2.5704</td>
<td>2.8363</td>
<td>3.1102</td>
</tr>
</tbody>
</table>

References


Appendix A2. Numerical Solution of ZLC bidisperse model by orthogonal collocation

The orthogonal collocation technique is a well-established numerical method for solving partial differential equations. By this technique the unknown exact solution of a partial differential equation can be approximated as a sum of a series of orthogonal polynomials chosen to satisfy the boundary conditions. The trial function is substituted into the differential equation and the result called the residual is required to be zero at the collocation points, namely the root values for the highest order orthogonal polynomial in the trial function. Villadsen and Michelsen (1978) developed a comprehensive book where the underlying theory of collocation and practical examples of linear and non-linear problems are addressed. A collection of subroutines that help the reader to solve the majority of computational problems in differential equations can be found in the Appendix of the book.

Solution of the bidisperse pore model for the ZLC by orthogonal collocation

For the discretization Villadsen and Michelsen (1978) suggest that it is convenient to introduce the following change of variable in Equations 3.12 and 3.16 (see problem in Chapter 4 page 144 of Villadsen and Michelsen book),
\[ u = \bar{r}^2; \quad U = \bar{R}^2 \]

The mass balance in crystals becomes,

\[
\frac{\partial \bar{q}}{\partial \tau} = \gamma \left( 4u \frac{\partial^2 \bar{q}}{\partial u^2} + 6 \frac{\partial \bar{q}}{\partial u} \right) \tag{A2.1}
\]

and the mass balance in the pellet is,

\[
\frac{\partial \bar{C}_p}{\partial \tau} + K \frac{\partial \bar{q}}{\partial \tau} = \gamma \left( 4U \frac{\partial^2 \bar{C}_p}{\partial U^2} + 6 \frac{\partial \bar{C}_p}{\partial U} \right) \tag{A2.2}
\]

The boundary condition \( \partial \bar{q} / \partial \bar{r} = 0 \) at \( \bar{r} = 0 \) and \( \partial \bar{C}_p / \partial \bar{R} = 0 \) at \( \bar{R} = 0 \) are automatically satisfied in equations A2.1 and A2.2 respectively since \( \bar{r} \) and \( \bar{R} \) are only functions of \( u = \bar{r}^2 \) and \( U = \bar{R}^2 \).

As suggested by Villadsen and Michelsen (1978, pg145) the collocation points are chosen as the zeros of \( P^{[1,1/2]}_N(u) \). The interpolation polynomial is \( (u-1)P^{[1,1/2]}_N \). Applying the collocation technique Equations A2.1 and A2.2 take the following form,

**Micropore equation**

\[
\frac{d\bar{q}(i_{\text{mac}}, i_{\text{mic}})}{dt'} = \gamma \left( 4u(i_{\text{mic}}) \sum_{i_{\text{mic}}}^{N_{\text{mic}}+1} B(i_{\text{mic}}, j_{\text{mic}}) \bar{q}(i_{\text{mac}}, j_{\text{mic}}) + 6 \sum_{i_{\text{mic}}}^{N_{\text{mic}}+1} A(i_{\text{mic}}, j_{\text{mic}}) \bar{q}(i_{\text{mac}}, j_{\text{mic}}) \right) \tag{A2.3}
\]

Boundary condition:

\[ u = 1; \quad \bar{q}(i_{\text{mac}}, N_{\text{mic}} + 1) = \bar{C}_p(i_{\text{mac}}) \tag{A2.4} \]

**Macropore equation**

\[
\frac{d\bar{C}_p(i_{\text{mac}})}{dt'} + K \frac{d\bar{q}(i_{\text{mac}})}{dt'} = 4U(i_{\text{mac}}) \sum_{i_{\text{mac}}}^{N_{\text{mac}}+1} B(i_{\text{mac}}, j_{\text{mac}}) \bar{C}_p(j_{\text{mac}}) + 6 \sum_{i_{\text{mac}}}^{N_{\text{mac}}+1} A(i_{\text{mac}}, j_{\text{mac}}) \bar{C}_p(j_{\text{mac}}) \tag{A2.5}
\]
where \(A(i, j)\) and \(B(i, j)\) are the coefficients of the collocation matrices representing the differentiation weights at the collocation points, and,

\[
\tilde{q}(i_{mac}) = \sum_{j_{mac}=1}^{N_{mac}+1} W(j_{mac}) \tilde{q}(i_{mac}, j_{mic})
\]  

(A2.6)

Boundary condition:

\[
U = 1; \quad \tilde{C}_p(N_{mac} + 1) = \frac{-2}{L} \sum_{j_{mac}=1}^{N_{mac}} A(N_{mac} + 1, j_{mac}) \tilde{C}_p(j_{mac}) \left(1 + \frac{2}{L} (N_{mac} + 1, N_{mac} + 1)\right)
\]  

(A2.7)

(the macropore surface concentration \(\tilde{C}_p(N_{mac} + 1)\) has been expressed explicitly in terms of the concentration at the outlet of the film \((C_m)\) and as a function of interior macropore collocation points; this is using the boundary condition at \(\tilde{R} = 1\))

where, \(N_{mac}\) and \(N_{mic}\) is the number of collocation points in the macropores and micropores representing the degree of the Jacobi polynomial (number of interior interpolation points), respectively. For every \(i_{mac}\) collocation point there are \(N_{mic}\) collocation points in the micropores.

The collocation matrices \(A(i,j)\), \(B(i,j)\) were found from subroutines JCOBI and DFOPR with codes described in Villadsen and Michelsen(1978). The quadrature weights defined by the weighing vectors \(W(j)\) were found from subroutine RADAU described in Villadsen and Michelsen. The number of interior interpolation points \(N\) was chosen in order to give stability to the numerical integration of discretized equations. Generally three collocation points were used for the macropores and micropores. An example of implementation of a similar problem is described in the book of Villadsen and Michelsen in Chapter 4 page 145. The ordinary differential equations resulting from the discretization procedure were solved by a fifth order Runge-Kutta solver where the subroutines JCOBI, DFOPR and RADAU were implemented allowing the development of a package to solve bidisperse porous problems in adsorption.

References

Appendix A3. Numerical solution of fixed bed adsorption model by orthogonal collocation

After application of orthogonal collocation (Villadsen and Michelsen, 1978) Equations 4.19 to 4.29 assume the following form:

**Overall mass balance**

\[
\sum_{j=0}^{N_{sf}} A(i,j) \bar{F}(j) = -y_{uf} \bar{z}_{ma} \frac{d \bar{q}_{i}(i)}{d \tau} - \frac{d \bar{C}_i(i)}{d \tau} 
\]  
(A3.1)

Boundary condition:

\[
\bar{z} = 0, \tau > 0; \bar{F}(0) = 1 
\]  
(A3.2)

**Sorbate mass balance**

\[
\frac{d(C_i(i)y_i(i))}{d \tau} = \frac{C_i(i)}{P_{ef}} \sum_{j=0}^{N_{sf}} B(i,j)y_i(j) - \bar{F}(i) \sum_{j=0}^{N_{sf}} A(i,j)y_i(j) - y_i(i) \sum_{j=0}^{N_{sf}} A(i,j)\bar{F}(j) - y_{uf} \bar{z}_{mi} \frac{d \bar{q}_{i}(i)}{d \tau} 
\]  
(A3.3)

Boundary conditions:
\[ Z = 0, \tau > 0; \sum_{i=0}^{N_{x}} \frac{1}{Pe_{mf}} A(0, j)y_{x}(j) = \frac{\bar{F}(0)}{C_{x}} (y_{x}(0) - y_{x}(i)) \]  
\[ \text{(A3.4)} \]

\[ Z = 1, \tau > 0; \sum_{j=0}^{N_{x}} A(N + 1, j)y_{x}(j) = 0 \]  
\[ \text{(A3.5)} \]

**Mass transfer rate**

\[ \frac{d\tilde{q}_{i}(i)}{d\tau} = N_{f} \left( y_{i}(i) - y_{i}(i) \right) \]  
\[ \text{(A3.6)} \]

**Adsorption isotherm**

\[ \theta_{if} \tilde{q}_{i} = K_{eq} (\tilde{T}_{s}) P_{y_{i}} \left[ 1 - \sum_{i} \theta_{if} \tilde{q}_{i} \right]^{n_{i}} \]  
\[ \text{(A3.7)} \]

**Energy balance for the gas phase**

\[ \tilde{C}_{i}(i) \frac{d\tilde{T}_{i}(i)}{d\tau} = \frac{1}{Pe_{mf}} \sum_{j=0}^{N_{s}} B(i, j)\tilde{T}_{j}(j) - \tilde{F}(i) \sum_{j=0}^{N_{s}} A(i, j)\tilde{T}_{j}(j) - N_{hf} (\tilde{T}_{i}(i) - \tilde{T}_{w}(i)) - N_{b} \left( \tilde{T}_{i}(i) - \tilde{T}_{w}(i) \right) \]  
\[ \text{(A3.8)} \]

**Boundary conditions:**

\[ Z = 0, \tau > 0; \sum_{i=0}^{N_{s}} \frac{1}{Pe_{mf}} A(0, j)\tilde{T}_{j}(j) = \tilde{F}(0) (\tilde{T}(0) + l) - l \]  
\[ \text{(A3.9)} \]

\[ Z = 1, \tau > 0; \sum_{j=0}^{N_{s}} A(N + 1, j)\tilde{T}_{j}(j) = 0 \]  
\[ \text{(A3.10)} \]

\[ \tilde{T}_{w}(i) = \tilde{T}_{w}(Z(i)) \]  
\[ \text{(A3.11)} \]

**Energy balance for the solid phase**

\[ \frac{d\tilde{T}_{s}(i)}{d\tau} = N_{hf} (\tilde{T}(i) - \tilde{T}_{s}(i)) + \xi_{h} B_{j} \frac{d\tilde{q}_{j}(i)}{d\tau} \]  
\[ \text{(A3.12)} \]
where \( N \) is the number of internal collocation points and \( i=1,2,3, \ldots, N \). The 0 and \( N+1 \) points correspond to boundaries at \( \bar{Z} = 0 \) and \( \bar{Z} = 1 \), respectively.

The collocation matrices \( A(i,j) \) and \( B(i,j) \) were found from subroutines JCOBI and DFOPR with codes described in Villadsen and Michelsen(1978). The interpolation polynomial chosen was \( P_N^{(0,0)}(\bar{Z}) \). The number of interior interpolation points \( N \) was chosen in order to give stability to the numerical integration of discretized equations. Generally sixteen interior collocation points were used. This gives for a single adsorbable species 64 ODE's being integrated at the same time. 16 from the Mass balance to adsorbable species; 16 from the equation representing the Mass transfer rate, 16 from the Energy balance in the gas phase and 16 from Energy balance for the solid phase. At the same time there are 16 Algebraic equations being solved by Gaussian elimination from the equation representing the Overall mass balance.

References