GAS ADSORPTION AND SURFACE DIFFUSION ON 5Å MICROPOROUS ADSORBENT IN TRANSITION AND TURBULENT FLOW REGION

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Abstract: The flow of O_2, H_2 and CO_2 was in transition regime at relatively lower ΔT and then became turbulent at relatively higher ΔT when passed through the 5Å microporous zeolite adsorbent. Adsorption and surface diffusivity of all the gases that are being studied in these regimes increased with increase in ΔT. For the temperature difference from 5 to 115 K, the range of adsorption of O_2 was between 6.319×10^{-12} and 5.762×10^{-11} kg/s. The adsorption of H_2 was between 4.4×10^{-13} and 3.88×10^{-12} kg/s for the temperature difference ranging from 1 to 20 K. The adsorption of CO_2 was between 5.3×10^{-12} and 4.9×10^{-11} kg/s for the temperature difference ranging from 5 to 100 K. At pressure of 1 bar, CO_2 adsorption was the highest at all ΔT, followed by O_2 and H_2. The surface diffusivity increases with increase in ΔT. At a particular ΔT, the diffusivity increases asymptotically regardless of the flow regions.

Keywords: *Adsorption, diffusion, porous media, transition flow, turbulent flow.*

1. INTRODUCTION

Knowledge of the underlying physics governing gas phase transport in porous media is of considerable interest in many applications ranging from contaminant transport in soils to diffusion in porous membrane, adsorbents and catalysts. Diffusion, caused by random molecular motion, plays an important role in the permeation of membrane system. In gases, diffusion progresses at a rate of about 10 cm in a minute; in liquid, its rate is about 0.05 cm/min; in solids, its rate may be only about 0.00001 cm/min [1]. Experimental studies have shown that surface diffusion contributes significantly to the total diffusive flux in both mesoporous and microporous systems [2,3]. The contribution of surface diffusion increases as surface concentrations of adsorbed species increase from sub-monolayer to multi-layer coverages [4]. Experimental surface diffusivities are estimated from differences in transport rates for molecules and conditions that lead to significant or negligible surface transport. This indirect approach and the limited knowledge about molecule-surface interactions have prevented the separation of intrinsic surface mobility from morphological effects of surface connectivity within complex porous structures. Rutherford [5] showed that the micropore diffusion, characterized by the Darken relation, is rate limiting the adsorption dynamics of carbon dioxide in small 5Å pellets (zeolite 5Å). Steady state diffusion measured by permeation experiment is shown to consist primarily of a combined Knudsen and viscous mechanism with negligible adsorbed phase flux along the pellet present.

Adsorption involves preferential partitioning of substances from gaseous phase onto the surface of a solid substrate or adsorbent. The heat released from adsorption process is relatively low; < 1-5 times the latent heat of vaporization; hence no occûrrance of activation and dissociation of the adsorbed species. Adsorption is significant at relatively low temperature and pressure range [6]. Gases can adsorb on surfaces forming a monomolecular (unimolecular) layer, or may be two, three or more layers thick (multimolecular). It occurs rapidly and is reversible [7]. For gases at temperatures above their critical temperature, adsorption is confined to a monolayer [8]. Multilayer adsorption, being similar to condensation, is controlled by adsorbate–adsorbate interactions and it occurs when the temperature is close to the boiling point of the adsorbate at a given vapour pressure [9]. In the work of Takaba *et al.* [10], adsorption process was simulated using molecular dynamics model to describe the trajectories of molecules through membrane. The simulation considered the gas permeation of amorphous silica membrane under conventional canonical ensemble. However, the presence of surface diffusion was not well studied and was neglected when the number of permeated molecules and estimated the separation mechanism were studied. Very few authors have studied the characteristics of flows beyond the laminar regime in different locations of the porous media [2-7]. As most porous materials considered in traditional engineering applications present very small pores and the fluid speed is relatively small, the predominant regime is the laminar flow regime. However, high speed fluid flow through porous media (high Reynolds number) can lead to turbulent flow within the pores. In this work, the surface adsorption and diffusion of O_2, H_2 and CO_2 inside 5Å porous media in transition and turbulent regions are investigated.

2. PROCEDURES

In this study, porous zeolite adsorbent with nominal pore size of 5Å (Zeosorb, Molsieb 5Å) was chosen to adsorb three different gases; oxygen, hydrogen and carbon dioxide, respectively. The weight and height of the adsorbent were 60 g and 6 cm respectively, while the diameter of the effective column which packed the adsorbent was 3.375 cm. The rate of adsorption in the porous media was determined by treating the process as condensation of vapour on a solid surface.

In analyzing surface adsorption and diffusion of the gases, few assumptions were considered to enable physical interpretation of data. The first assumption is that microporous material constitutes of a series of wider and narrower interconnected chambers. This assumption was practiced in the work of Gilron and Soffer [11]. The second assumption is that the media is homogeneous and its pores are of a perfectly cylindrical shape. The third assumption is that the heat of adsorption released is equal to the heat of condensation of vapor on a solid surface.

The following equations [12] were selected in this study.

For the laminar flow region,

$$\frac{\bar{h}_L(\upsilon_l^2/g)^{1/3}}{k_l} = 1.47\,\mathrm{Re}_\delta^{-1/3}; \qquad \mathrm{Re}_\delta \le 30 \quad (1)$$

For the transition flow region,

$$\frac{\bar{h}_L(\upsilon_l^2/g)^{1/3}}{k_l} = \frac{\mathrm{Re}_\delta}{1.08\,\mathrm{Re}_\delta^{1.22} - 5.2}; \qquad 30 \le \mathrm{Re}_\delta \le 1800 \quad (2)$$

For the turbulent region,

$$\frac{\bar{h}_L(\upsilon_l^2/g)^{1/3}}{k_l} = \frac{\mathrm{Re}_\delta}{8750 + 58\,\mathrm{Pr}^{-0.5}(\mathrm{Re}_\delta^{0.75} - 253)}; \qquad \mathrm{Re}_\delta \ge 1800 \quad (3)$$

$$h_{fg}' = h_{fg} + 0.68\,C_{p,l}(T_{sat} - T_s) \quad (4)$$

or in terms of the Jakob number,

$$h'_{fg} = h_{fg}(1 + 0.68Ja) \quad (5)$$

where,

$$Ja = \frac{C_{p,l}(T_{sat} - T_s)}{h_{fg}} \quad (6)$$

For laminar flow, the average convection coefficient is determined using the following equation,

$$\bar{h}_L = 0.943\left[\frac{g\rho_l(\rho_l - \rho_\upsilon)k_l^3 h'_{fg}}{\mu_l(T_{sat} - T_s)L}\right]^{1/4} \quad (7)$$

The heat transfer rate can be determined using,

$$q = \bar{h}_L\,A\,(T_{sat} - T_s) \quad (8)$$

The rate of adsorption can be determined using,

$$m = \frac{q}{h'_{fg}} \quad (9)$$

The existence of laminar flow is verified by calculating Re_δ using,

$$\mathrm{Re}_\delta = \frac{4m}{\mu_l b} \tag{10}$$

If $\mathrm{Re}_\delta \le 30$, the assumption of wave-free laminar flow is correct. If $\mathrm{Re}_\delta \ge 30$, a significant portion of the gas is either in the transition region or in turbulent region. Hence the wave-free laminar assumption may be poor. The calculation continues using,

$$\bar{h}_L = \frac{m\,h'_{fg}}{A(T_{sat} - T_s)} = \frac{\mathrm{Re}_\delta\,(\mu_l b)\,h'_{fg}}{4A(T_{sat} - T_s)} \tag{11}$$

If Re_δ obtained from (10) is in the range of $30 \le \mathrm{Re}_\delta \le 1800$, then the flow is in the transition region. The new Reynolds number can be obtained by combining equation (2) and (11) to yield,

$$\frac{\mathrm{Re}_\delta\,(\mu_l b)\,h'_{fg}}{4A(T_{sat} - T_s)} = \frac{\mathrm{Re}_\delta}{1.08\,\mathrm{Re}_\delta^{1.22} - 5.2} \times \frac{k_l}{(\upsilon_l^2 / g)^{1/3}} \tag{12}$$

If $\mathrm{Re}_\delta \ge 1800$, then the flow is turbulent. The new Reynolds number can be obtained by combining equation (3) and equation (11) to yield,

$$\frac{\mathrm{Re}_\delta\,(\mu_l b)\,h'_{fg}}{4A(T_{sat} - T_s)} = \frac{\mathrm{Re}_\delta}{8750 + 58\,\mathrm{Pr}^{-0.5}\,(\mathrm{Re}_\delta^{0.75} - 253)} \times \frac{k_l}{(\upsilon_l^2 / g)^{1/3}} \tag{13}$$

Surface diffusivity is computed using,

$$D_s = 1.6 \times 10^{-2}\, e^{[0.45 \frac{(-\Delta H_{ads})}{mRT}]} \tag{14}$$

where

Ds = Surface diffusivity (cm²/s)

ΔH_{ads} = Heat of adsorption (gcm²/s² gmol)

R = Constant = 8.314×10^7 gcm²/gmol.K

m = 2 (for conducting adsorbent)

= 1 (for insulating adsorbent)

3. RESULTS AND DISCUSSION

3.1 Oxygen adsorption

The adsorption rate of oxygen in 5Å zeolite adsorbent against temperature differences, ΔT, where $\Delta T = T_{sat} - T_s$ is illustrated in Fig. 1. The adsorption increases as the temperature difference increases. For the temperature difference from 5-115 K, the range of adsorption is between 6.319×10^{-12} and 5.762×10^{-11} kg/s. The flow branches out and moves from a common point in the transition regime into turbulent regime with exception of the oxygen flow at pressure of 1 bar which remains in transition region. As the pressure increases, temperature difference, ΔT, needed for gas oxygen to achieve turbulent flow decreases.

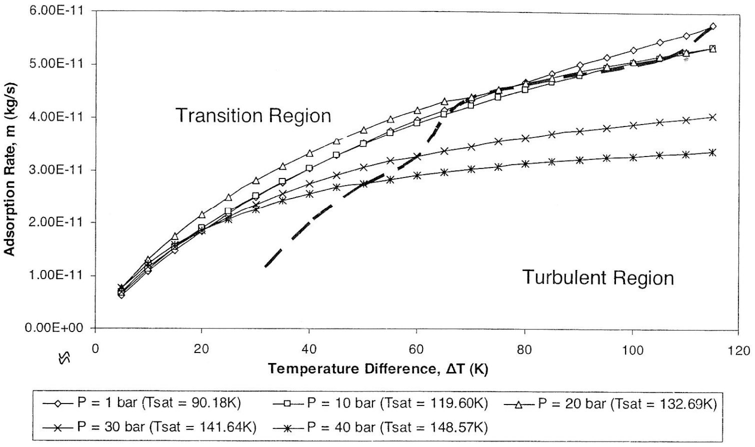

Fig 1: The rate of adsorption of oxygen on 5Å zeolite

In an isothermal, laminar flow process adsorption increases with increase in pressure. However, from this work the adsorption rate of oxygen decreases with increase in pressure. This is due to the fact that the saturation temperature increases at increased pressure. Assuming constant surface temperature, ΔT increase corresponds to increase in saturation temperature. Adsorption is reduced at higher saturation temperature because of greater gas mobility.

3.2 Hydrogen adsorption

The adsorption rate of hydrogen in 5Å zeolite against temperature difference at different operating pressure is illustrated in Fig. 2. Since the saturation temperature of H_2 is extremely low in comparison to the other two gases, the maximum ΔT which can be analyzed for this study is only up to 20 K. The range of adsorption of H_2 is between 4.4×10^{-13} and 3.88×10^{-12} kg/s for the temperature difference ranging from 1 to 20 K. With the exception of pressure at 9 bars which remains in the transition region, the flow of hydrogen in the adsorbent changes from transition flow to turbulent flow as ΔT increases. This is due to the fact that at high pressure, the Reynold number decreased as a result of increase in the reduced viscosity and that the influence of the change/increase in ΔT was less significant compared to the increase in pressure.

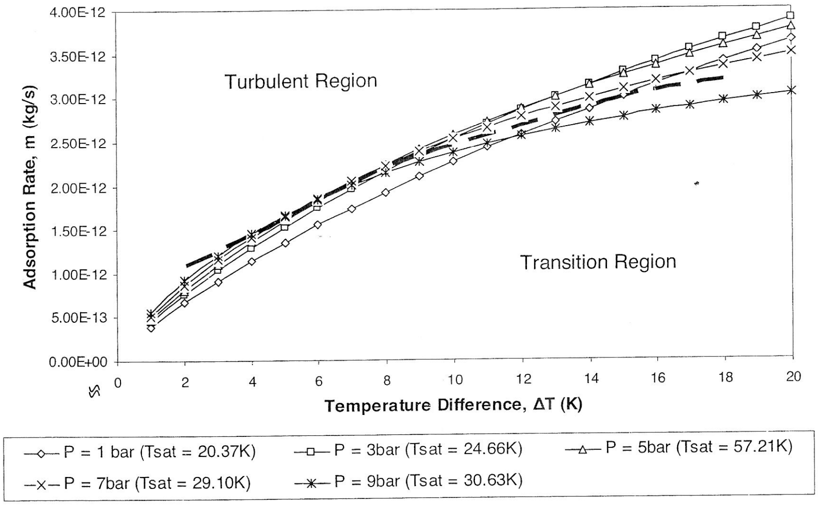

Fig 2: The rate of adsorption of hydrogen on 5Å zeolite

3.3 Carbon dioxide adsorption

The adsorption rate of CO_2 in 5Å zeolite against temperature difference and at different operating pressure is illustrated in Figure 3. The range of adsorption of CO_2 is between 5.3×10^{-12} and 4.9×10^{-11} kg/s for the temperature difference ranging from 5 to 100 K. The flow of CO_2 in the adsorbent changes from transition flow to turbulent flow as ΔT increases at all pressure. As the pressure increases, ΔT needed for CO_2 to reach turbulent state decreases. For instance, at 5 bars, the turbulence is achieved at ΔT = 70 K. As the pressure is further increased to 40 bars, the turbulence is reached at ΔT = 35 K.

3.4 Adsorption rate of different gases

Figure 4 illustrates the rate of adsorption of three gases species at different ΔT and constant pressure of 1 bar. Presure of 1 bar is selected for comparison due to the highest gas adsorption rate in the turbulent flow or at relatively higher ΔT after series of data analysis. The adsorption rate of CO_2 is the highest followed by O_2 and H_2. The incremental increase of CO_2 adsorption on the microporous adsorbent against that of O_2 and H_2 becomes more pronounced at higher ΔT or in the turbulent region. The highest adsorption rate of CO_2 was the highest probably due to its relatively lower critical temperature value compared to those of O_2 and H_2.

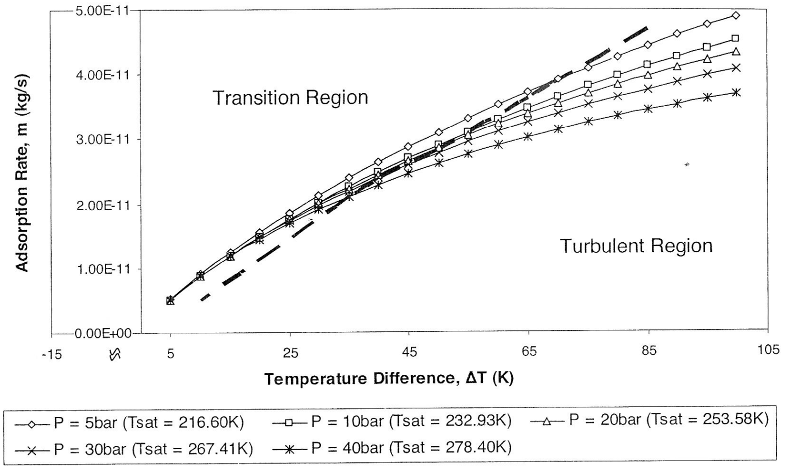

Fig. 3: The rate of adsorption of CO_2 on 5Å zeolite.

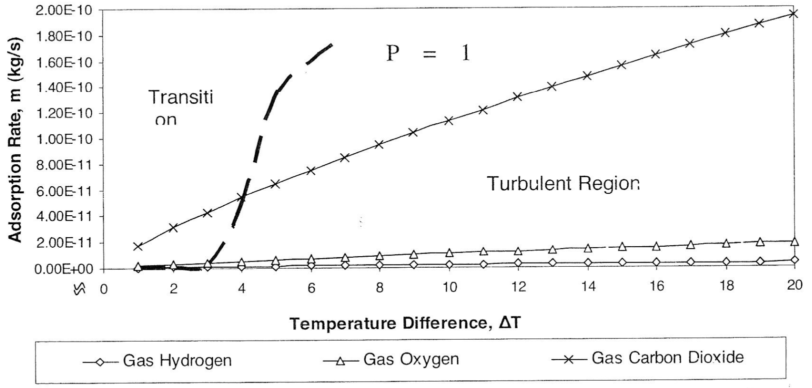

Fig. 4: The adsorption rate of different gases versus temperature difference

3.5 Surface diffusivity of oxygen

The surface diffusivity of gases is calculated using equation 14. The heat of adsorption has been corrected to account for the thermal advection. Figure 5 illustrates the surface diffusivity of O_2 against ΔT for pressure ranging from 1 to 40 bars. The surface diffusivity increases with increase in ΔT. At a particular ΔT, the diffusivity increases asymptotically regardless of the flow regions. In general, the surface diffusivity increases at relatively lower pressure and this is consistent with the experimental results of Chang and Lee [6].

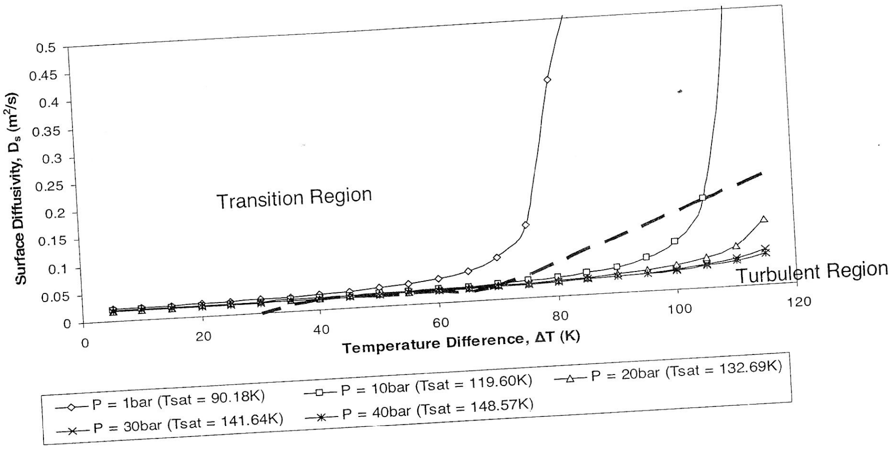

Fig. 5: Surface diffusivity of gas O_2 in 5Å zeolite

3.6 Surface diffusivity of hydrogen

Figure 6 illustrates the surface diffusivity of H_2 against ΔT for pressure ranging from 1 to 9 bars. The surface diffusivity increases with increase in ΔT. Comparing with Fig. 5, the turbulent region is reached at smaller ΔT for hydrogen than for oxygen. At a ΔT > 10 K, the diffusivity increases asymptotically in the turbulent region for all range of pressures. In general, the surface diffusivity for hydrogen is greater than that of oxygen. This is due to the fact that the saturation temperature of H_2 is extremely low and the critical diameter of hydrogen is smaller than oxygen.

3.7 Surface diffusivity of carbon dioxide

Figure 7 illustrates the surface diffusivity of CO_2 against ΔT for pressure ranging from 5 to 40 bars. The surface diffusivity increases with increase in ΔT. No asymptotic increase is observed for carbon dioxide. Again, the diffusivity is higher at relatively lower pressure. The highest diffusivity appears to be in the turbulent region for the range of pressure selected. The surface diffusivity for CO_2 is relatively smaller compared to that of H_2 and O_2 even at low pressure and high value of ΔT. This could be due to its greater molecular diameter and lower saturation temperature.

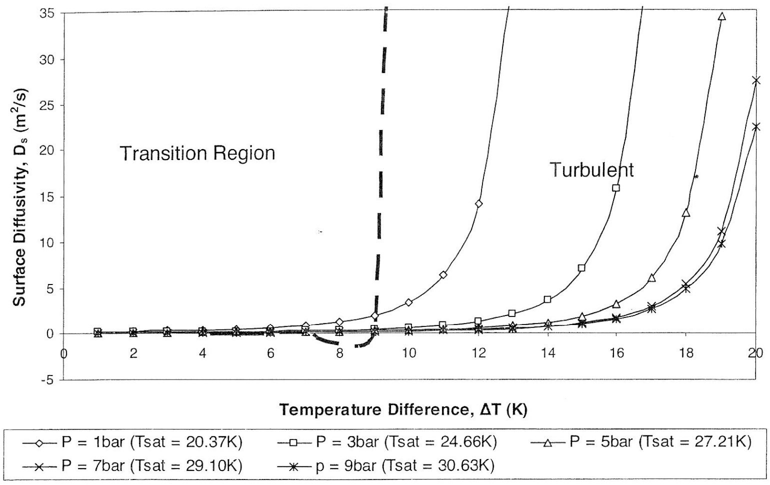

Fig. 6: Surface diffusivity of gas H_2 in 5Å zeolite.

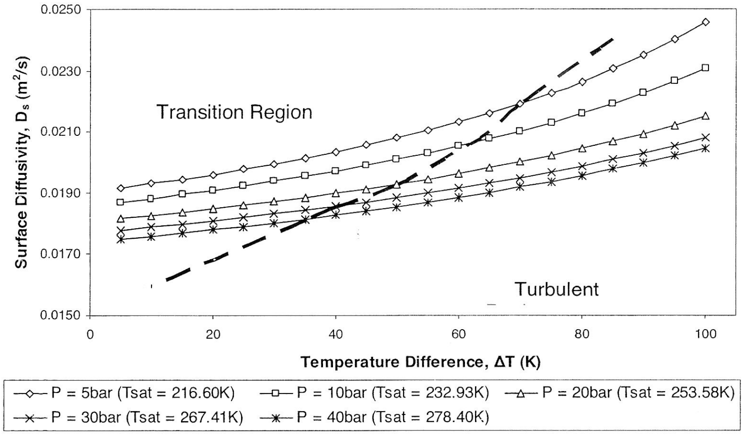

Fig. 7: Surface diffusivity of gas CO_2 in 5Å zeolite

4. Conclusion

The observation made is that the flow of O_2, H_2 and CO_2 gasesin porous media was either in transition or turbulent region depending on the value of temperature difference, ΔT. No laminar region exists inside the pore medium for all the gases. The results of this study are in contrast to the present assumption that the predominant regime in porous media is mostly laminar. The fluid adsorption and diffusion in porous media are strongly dependent on the temperature difference between the saturated temperature of the gas and the surface temperature of the pore. As the temperature difference increases, the flow of gas in porous media changes from transition region to turbulent region.

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NOMENCLATURE

Symbol	Definition	**Unit**
A	Heat transfer area of a pore	$[m^2]$
A_m	Membrane surface area	$[m^2]$
B	Circumference of pore	$[m]$
C_o	Initial concentration	$[mol.m^{-3}]$
C	Concentration	$[mol.m^{-3}]$
C_D	Dimensionless form of concentration	$[-]$
C_{pl}	Heat Capacity of liquid	$[J.kg^{-1}.K^{-1}]$
D	Diameter of pores in adsorbent	$[m]$
D_i	Ordinary Diffusion	$[m^2.s^{-1}]$
D_k	Knudsen Diffusion	$[m^2.s^{-1}]$
D_s	Surface diffusivity	$[m^2.s^{-1}]$
G	Acceleration due to gravity	$[ms^{-2}]$
h_{fg}	Heat of condensation	$[kJ.kg^{-1}]$
h_{fg}	Modified Latent Heat	$[kJ.kg^{-1}]$
$\overline{h}_L$	Average convection coefficient	$[Wm^{-2}.K^{-1}]$
J_a	Jakob number	$[-]$
K	Permeability of membrane	$[mol.s^{-1}][m][m^{-2}][kg^{-1}.m.s^2]$
K	Henry's adsorption constant	$[m^3.kg^{-1}]$
L	Length of pore	$[m]$
$\dot{m}$	Adsorption rate	$[kgs^{-1}]$
M	Empirical constant as in equation (14)	$[-]$
Pr	Prandtl numbers	$[-]$
$\overline{P}$	Average pressure in pores membrane	$[kg.m^{-1}.s^{-2}]$
Q	Heat transfer rate	$[W]$
q_p	Gas flow rate from the permeate stream	$[mol.s^{-1}]$
r	Radius of pore in membrane	$[m]$
R	Gas constant	$[kg.m^2s^{-2}.kgmol^{-1}.K^{-1}]$
Re	Reynolds number	$[-]$
Re_δ	Reynolds number at δ distance from boundary layers	$[-]$

T	Temperature	[K]
T_s	Surface temperature	[K]
T_{sat}	Saturated temperature	[K]
T	Time	[s]
t_D	Dimensionless form of time	[-]
t_{min}	Minimum time, under given flow conditions, to saturate a bed	[s]
u	Velocity	[ms^{-1}]
x	Distance traveled by gas in pore	[m]
x_D	Dimensionless form of distance traveled by gas in pore	[-]
Z	Length of adsorbent	[m]

Greek Letters

E	Membrane porosity	[-]
Δ	Distance of adsorbate of the boundary layers	[m]
T	Tortuous factor	[-]
v_l	Liquid velocity in axial direction	[ms^{-1}]
v	Gas velocity in axial direction	[ms^{-1}]
k_l	Thermal conductivity of liquid	[$Wm^{-1}.K^{-1}$]
ρ_l	Density of liquid	[kgm^{-3}]
ρ_v	Density of Vapour	[kgm^{-3}]
ρ_m	Density of membrane	[kgm^{-3}]
μ_l	Viscosity of liquid	[$N.sm^{-2}$]
ΔH_{ads}	Heat of adsorption	[$kg.m^2.s^{-2}.kgmol^{-1}$]
ΔP	Pressure difference	[$kg.m^{-1}.s^{-2}$]
ΔT	Temperature difference	[K]

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