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Knudsen Number Sensitivity to Pressure Drop in a Nanoscale Membrane

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Abstract: According to the kinetic theory of gases, gas molecules are in constant random motion and frequently collide with one another and with the walls of their container. They continuously experience changes in velocity and direction. Between collisions, molecules move in a straight line at a constant velocity. The actual path length between two successful collisions of a molecule, known as a free path, cannot be established as its calculation requires the knowledge of the path of every molecule in a containment system. The average of all the path lengths between collisions is known as the mean free path (λ). Unlike free path, mean free path is measurable and it is a better measure of the random motion of gas molecules in a gaseous system which is very difficult to measure directly. However, the finding relating to pressure drop with Knudsen number (K_n) in a nanoparticle is limited. This study focuses on understanding the pressure gradient in a nonporous membrane structure and calculating the mean free path.

The Knudsen number of selected gases was plotted against pressure drop at 100^0C for the three gases and generated several plots. Each plot represents the profile of the respective Knudsen number of the gases in membranes with a pore size of 15nm, 200nm and 600nm respectively. The investigation established that there is an inverse relationship between K_n and Pressure. The correlation is strong as indicated by the R^2 of 0.89. The three gases show a dramatic relationship of K_n with pressure in the 15nm pore membrane. The rate of change or slopes of K_n with pressure is higher for all the gases in 15nm than for the 200nm and 6000nm pore sizes. K_n for H_2 has the most response to pressure in the 15nm with a response of -0.70 K_n/KPa, followed by CO_2 (-0.54 K_n/KPa) and Air (-0.37 K_n/Kpa). The lowest magnitude of K_n at the extended experimental pressure 300KPa is compared and a qualitative deduction can be drawn that the K_n/KPa parameter dampens as the pore size increases.

Keywords: Ceramic membrane, pore size, pressure, Knudsen number, mean-free path.

INTRODUCTION

Porous membranes have been used in the industry to successfully overcome the challenges such as distillation, ultrafiltration and pervaporation, they are more specifically used for gas separation, in which selectively and perselectivety give a higher ensure mechanical strength, for the past decade's gas transfer through the porous membrane have received much attention from various researchers (Mason, E.A. and AP, M., 1983). The transport of different constituents in a membrane is depended on the mechanism by which the constituents are transported. For example, in a porous ceramic membrane, the various constituents are transported because of the pressure difference established between the feed and permeate sides. In polymeric membrane systems in general the solution diffusion transport operates. Hence, in

one-dimensional diffusion of gas molecules in porous media involves molecular interactions between gas molecules as well as collisions between gas molecules and the porous media. As gas molecules travel through the porous media, one of three mechanisms can occur, depending on the characteristic of the diffusing gas species and the intrinsic microstructure of the porous media (Khayet, M. and Matsuura, T., 2004). The three mechanisms are molecular diffusion, viscous diffusion, and Knudsen diffusion. To distinguish among the three mechanisms, the Knudsen number (K_n) is typically used as described in the literature below.
In this search work we calculate the mean free path (MFP) of a nonporous membrane at different pressure, the gaseous system (fluid) in which molecules are moving is a continuum or a continuous medium; that is, a medium whose properties, such as temperature, pressure, density, and velocity, may vary in a continuous manner (Dadzie et al. 2008).

LITERATURE REVIEW

Based on these fluid properties and the diameter of the molecules as well as their population, the mean free path of molecules is derived and expressed mathematically (Bird, G.A., 1983) (Jennings, S.G., 1988).

$$\lambda = \frac{1}{\sqrt{2\pi}\, d^2 P/_{KT}} \qquad 1$$

Where d= molecular diameter and N/V is the number of molecules per unit volume or the density of molecules or the number density and can be equated to P/KT by ideal gas law.
Where:
λ: Mean free path [m]
KT: Boltzmann constant (1.3807×10^{-23} [J/K])
T: Temperature [K]
d: Kinetic diameter of the molecule [m]
P: Absolute pressure [Pa]
According to this equation,

(i). λ varies inversely with N/V - the larger the number of molecules, the more they collide with one another; hence, the shorter the mean free path,
(ii). λ also varies inversely to the diameter of the molecules (d = 2r), implying that the larger the molecule, the smaller the mean free path (Roufosse, M. and Klemens, P.G., 1973).

SLIPPAGE

When the radius of a molecule (r) is approximately equal to the mean free path (λ), such a molecule slides between the large molecules, and a phenomenon called slippage occurs. Slippage lowers the drag force, which causes the molecule to move faster (Julin et al. 2013). The slip correction factor is generally needed for molecules less than 10 μm in diameter.

KNUDSEN NUMBER {K_n}

The ratio of the mean free path length (λ) to a representative physical length scale, (Zhang, L.Z., 2008) e.g. the pore size diameter of a membrane (dp) is known as Knudsen number (Kn)

$$Kn = \lambda/dp \qquad 2$$

Where:
Kn: Knudsen number [dimensionless]
λ: Mean free path [m]

dp : pore size diameter [m]

The Knudsen number is used to determine whether statistical mechanics or continuum mechanics formulation of fluid dynamics should be used to model a situation. In a nutshell, Kn describes how the fluid "views" the particle, i.e. is the motion governed by the rules of molecules or of macroscopic objects.

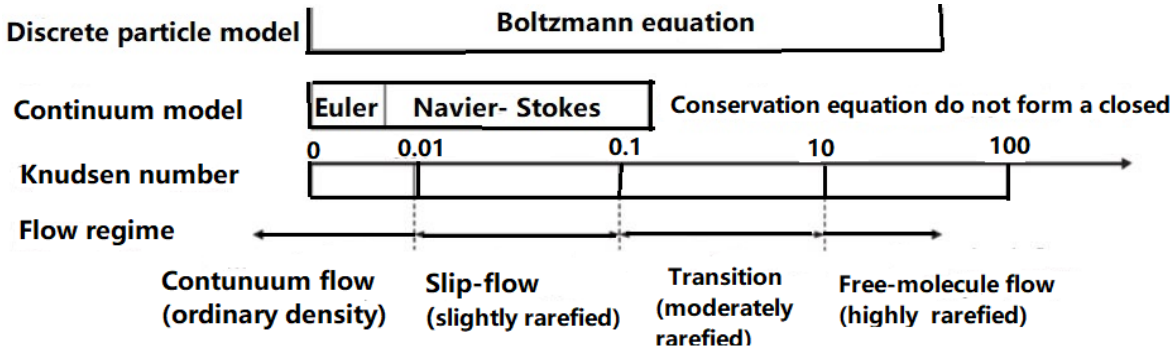

Figure 1 shows the flow of gases as described accorded to Boltzamam's equation

(i). If the Knudsen number is near or greater than one, the mean free path of a molecule is comparable to a length scale of the problem (i.e., the radius of the molecules), and the continuum assumption of fluid mechanics is no longer a good approximation. In such cases, statistical methods should be used.

(i). $K_n << 1$ ($K_n<0.1$)

Continuum regime: the fluid appears to the particle as a continuum, and the laws of continuum mechanics apply. No slip condition holds.

$K_n \approx 1$ ($0.1<K_n<10$)

Transition regime: transport is controlled by both continuum mechanics and kinetic theory. Slip correction is required

$K_n >> 1$ ($10<K_n$)

Free molecule regime: transport controlled by the kinetic theory of gases

EXPERIMENTAL

An experiment was conducted on a series of gas for H2 CO2 and Air on a radial inorganic ceramic membrane. The membranes are made of multiple layers of pore sizes (15, 200 and 6000nm), such that the most constricted pore was coated on the outer layer, while the inner layers are made of larger pore sizes and serve as (support).

The gases were injected into the shell side of the membrane in a normal orientation, allowing the gases to pass through the support membrane at a different pressure. The steady-state was recorded for operating conditions of 0.2, 0.6, 1.0, 1.4, 1.8, 2.2, 2.6, and 3.00 bar at 100 degrees C.

The effect of transmembrane pressure drops was determined using the data obtained from the experiment. The inlet pressure used was in atmospheric Pressure (Atm.) for the operation condition, the inlet and outlet pressure from the experiment were recorded in Bars and the outlet was maintained at atmospheric pressure at 1atm and then converted to Pascal (1 bar is equivalent to 100.000pa). The pressure drop is the difference between the outlet and inlet

pressure in Pascal,). The pore size diameter (dp) of each membrane was used to calculate the Knudsen Number and the mean free path was calculated using equation 1. Respectively.

RESULTS AND DISCUSSION

The results indicate that the direction of fluid flow affects the permeation magnitude of the respective gases.

Table 1 Shows the result of pressure drop and Knudsen Number at 100º for a membrane pore size 15, 200 and 6000nm

Pressure drop (Pa) @ 100º	Kn = λ/dp (15nm)			Kn = λ/dp (200nm)			Kn = λ/dp (6000nm)		
	(H_2)	(CO_2)	(Air)	(H_2)	(CO_2)	(Air)	(H_2)	(CO_2)	(Air)
2.00E+04	7.71E+00	5.92E+00	4.03E+00	5.79E-01	4.44E-01	3.02E-01	1.93E-02	1.48E-02	1.01E-02
6.00E+04	5.79E+00	4.44E+00	3.02E+00	4.34E-01	3.33E-01	2.26E-01	1.45E-02	1.11E-02	7.55E-03
1.00E+05	4.63E+00	3.55E+00	2.42E+00	3.47E-01	2.66E-01	1.81E-01	1.16E-02	8.87E-03	6.04E-03
1.40E+05	3.86E+00	2.96E+00	2.01E+00	2.89E-01	2.22E-01	1.51E-01	9.64E-03	7.39E-03	5.03E-03
1.80E+05	3.31E+00	2.54E+00	1.73E+00	2.48E-01	1.90E-01	1.29E-01	8.26E-03	6.34E-03	4.31E-03
2.20E+05	2.89E+00	2.22E+00	1.51E+00	2.17E-01	1.66E-01	1.13E-01	7.23E-03	5.55E-03	3.77E-03
2.60E+05	2.57E+00	1.97E+00	1.34E+00	1.93E-01	1.48E-01	1.01E-01	6.43E-03	4.93E-03	3.36E-03
3.00E+05	2.31E+00	1.77E+00	1.21E+00	1.74E-01	1.33E-01	9.06E-02	5.79E-03	4.44E-03	3.02E-03

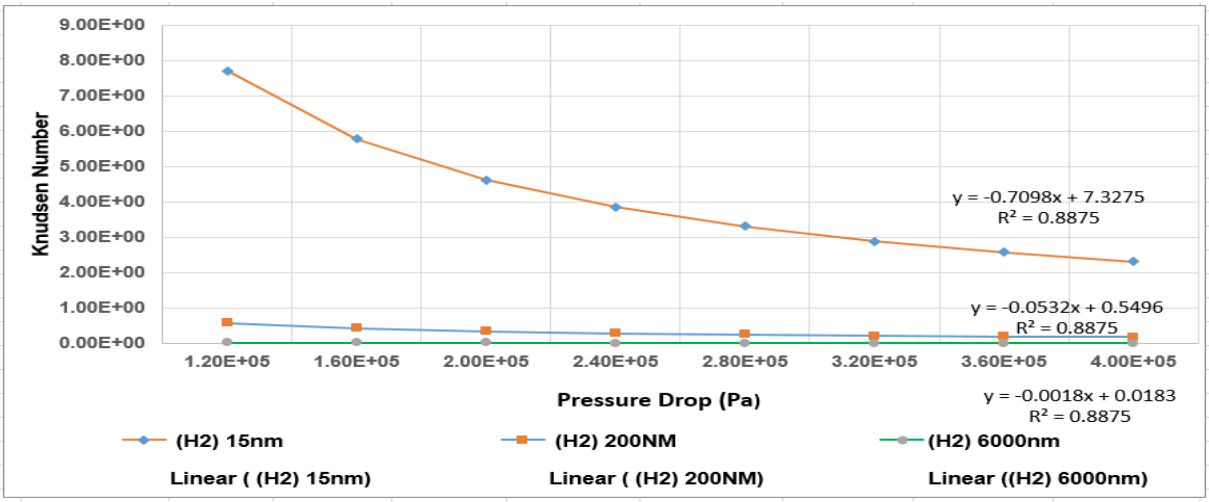

Figure 2: Shows pressure drop against Knudsen Number for membrane pore sizes 15, 200 and 6000nm. (k_n=λ/dp (100ºc for Hydrogen))SSS

The Knudsen number was plotted against pressure at 100C for the three gases in each. Each plot represents the profile of the respective Knudsen number of the gases in 15nm, 200nm and 600nm pressure gradient is considered in the linear direction. It shows that the friction factors decrease monotonically as the tangential momentum accommodation coefficient (TMAC) decreases and the channel aspect ratio increases. The effects of the aspect ratios on the pressure drop in the slip-flow region are shown in Figures 2,3 and 4. It is obvious shows that the pressure drop is higher for lower aspect ratios. The pressure drop in microchannel nanochannel decreases with an increase in the aspect ratios. The dimensionless heat transfer coefficient decreases with an increase in the Knudsen numbers and aspect ratios as well. This trend is shown in Fig. 2.3 and 4. The effect of the K_n number is to decrease the value of the dimensionless heat transfer

coefficient and this reduction increases significantly with an increasing K_n number. Figure 2.3 4 in 200nm and 6000nm, shows the effect of the volume flow rate on the average heat transfer from a microchannel/nanochannel heat sink. It is obvious that the average heat transfer increases with the increase in the volume flow rate and aspect ratio.

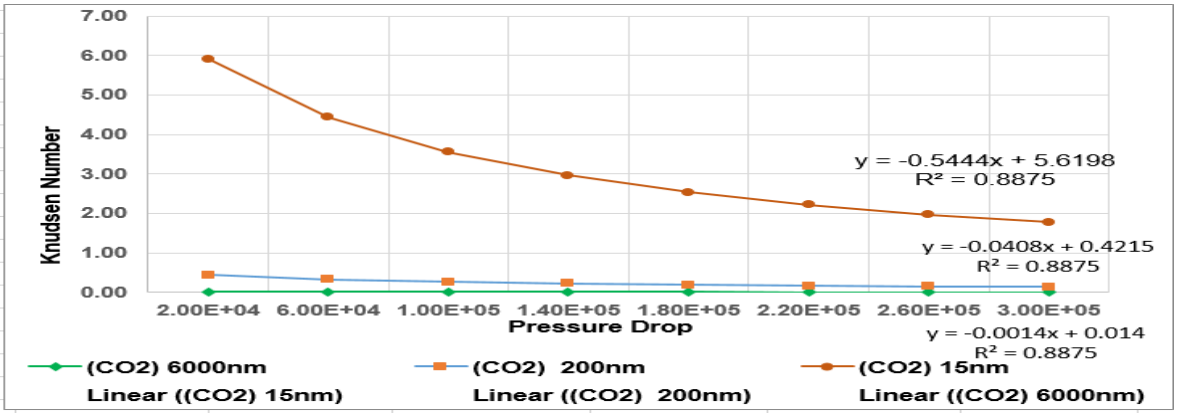

Figure 3: Shows Pressure drop against Knudsen Number for membrane pore sizes 15, 200 and 6000nm. (k_n=λ/dp (100ºc for CO2))

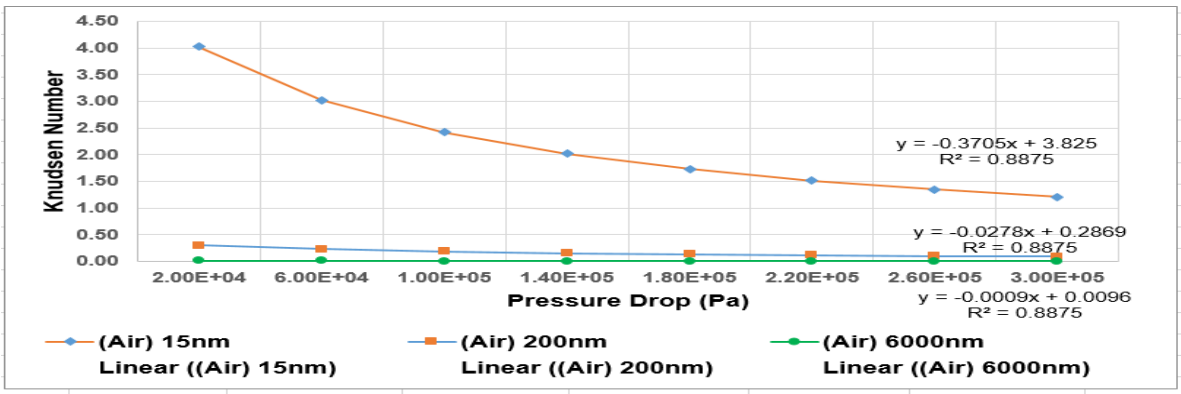

Figure 4 shows the Pressure drop against Knudsen Number for membrane pore size 15, 200 and 6000nm. (k_n=λ/dp(100ºc for Air)).

From Figures 2, 3, and 4 it is established that there is an inverse relationship between K_n and Pressure. The correlation is fairly strong as indicated by the R^2 of 0.89. The three gases show a dramatic relationship of K_n to pressure in the 15nm pore membrane. Such that the rate of change or slopes of K_n to pressure is higher for all the gases in 15nm than for the 200nm and 6000nm pore size. H_2 K_n number has the most response to pressure in the 15nm with a response of -0.70k_n/KPa, followed by CO2 (-0.54k_n/KPa) and Air (-0.37K_n/Kpa). The lowest magnitude of K_n at the extended experimental pressure 300KPa is comparing Figures 2, 3, and 4, a qualitative deduction can be drawn that the K_n/KPa parameter dampens as the pore size increases.

Pitching these plots (drawn from table 1) against the Knudsen regimes in Figure 1 gives an opportunity to characterise the gas dynamics in pores of different sizes and explore and apply the knowledge to industrial practice.

In Figure 2 and Table 1 for H_2 gas in 15nm and at the extended pressure of 20KPa to 300KPa, the value range of Kn is 7.8-2.3Kn. This implies that the flow fits into the transition (moderately rarefied) zone in Figure 1 The K_n profile (0.58-0.17kn) of H_2 in 200nm indicates that the H_2 is in the transition (slightly rarefied) phase. However, in the 600nm, the K_n profiles value ranges from s 0.019 and 0.0058K_n, suggesting that the flow experiences slip flow at lower pressure and then transitions into the continuum regime (0.0058Kn) as pressure increases to 300KPa. Similar results were obtained for Air and CO2 respectively.

4. CONCLUSION

It is demonstrated from the K_n characterisation that molecular weight was not an influencer for the dynamics to the extent of the operating conditions and pore sizes investigated in this study.

If the objective function of a process is to increase the K_n number, then from this study, it can be deduced that pore size is reduced below 15nm or pressured below the operating pressure of 20 KPa. That is further rarefication.

The work has also demonstrated that processes can use pore size rhythm to achieve different K_n regimes by stacking membranes in series or parallel to form a certain K_n rhythm. Such applications can find utility in processes such as catalytic reaction and gas separation to optimise and control process dynamics.

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