# Core-shell polysiloxane-MOF 5 microspheres as stationary phase for gas-solid chromatographic separations

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**Effect of particle dimensions on pressure drop**

The pressure drop associated with a gas flowing through packed tubes, decreases with the voidage in the tube (ε) as well as the length of the tube. The relation between these properties and  Pressure drop is expressed by a correlation equation

$$\Delta P = \frac{2 f_m \times G_i{}^2 \times L_t (1-\varepsilon)^{3-n}}{D_P \rho_f \phi_s{}^{3-n} \times \varepsilon^3} \qquad ......Eq\text{-}1$$

Where,　　　　　$\Delta P$ = pressure drop, psi

　　　　　$L_t$ = depth of the packed bed, ft.

　　　　　$G = \rho V$ = mass velocity, lb h$^{-1}$ft$^2$

　　　　　$\rho$ = fluid density, lb ft$^{-3}$

　　　　　$D$ = effective particle diameter, ft.

　　　　　$\varepsilon$ = interparticle void fraction, dimensionless

$f_{m=}$ modified friction factor

n = Reynolds number

$f_s$ = shape factor

$\varphi_s$ = sphericity of the particle

By assuming a modified friction factor ($f_m$ = 2), Reynolds number (n = 2), and a shape factor ($f_s$ =1) for a perfect sphere, the pressure drops were calculated as a function of microsphere diameter and the resultant plots are presented in Fig. 1 The expanded portion is presented in the inset.
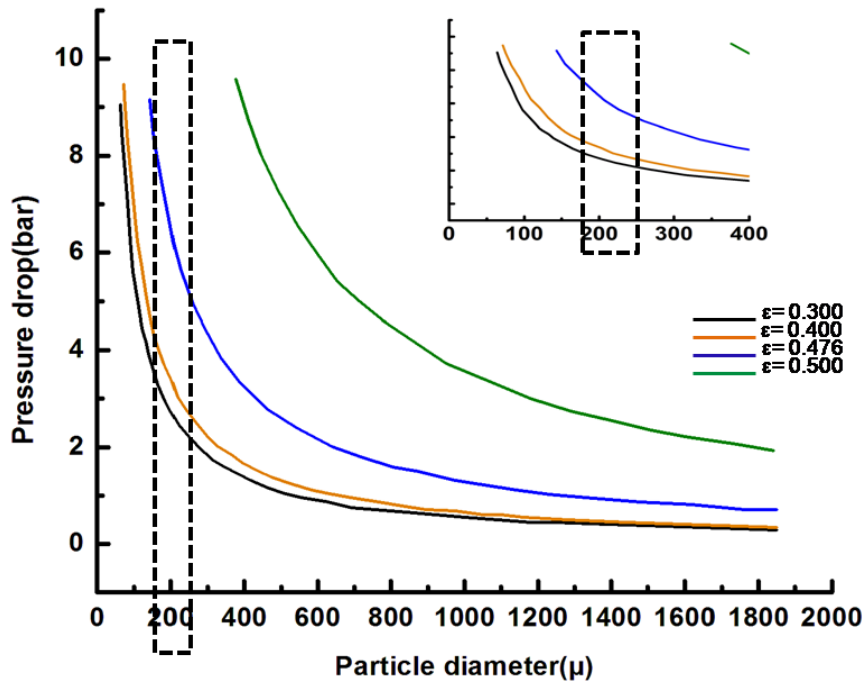


Fig. 1 : Pressure drops through a packed tube with a particle diameter ($D_P$) and voidage ($\varepsilon$) by equation 1. Inset shows an expanded view.

It can be seen that the pressure drop increases steeply with decreasing particle dimensions. The pressure drop associated with the particle range used in the present study is presented in the dashed box (250-177 µm). As is apparent, further decrease in the particle size would lead to

extremely high pressure drops which in turn would lead to operability issues in the gas chromatographic column. Further increase in packing efficiency (lower voidage) would further aggravate the pressure drop issue. It is for this reason, that chromatographic separations were performed on stationary phase with these dimensions (250-177 µm).

**Preparation of core microspheres**

The poly (dimethylsiloxane) (PDMS) core was prepared using a batch suspension polymerization process. A feed solution was prepared by dissolving vinyl terminated siloxane macromonomer (Elastosil M4644) in chloroform (60 % v/v) followed by the addition of requisite amounts of platinum based hardener (resin :hardener=10:1). The feed solution was introduced into a 1 L four-necked RB flask containing the suspending agent, PVA (1.5% w/v) through a rubber septum and was constantly stirred (600 rpm) at 45 °C. The polymerisation reaction was allowed to continue for 8 h. The reaction mixture was cooled and the microspheres were filtered, washed with water and dried under vacuum at 80 °C for 2 h. The extent of conversion was measured gravimetrically as the ratio of mass of microspheres to the amount of liquid macromonomer used for its preparation.

The effect of increasing the feed macromonomer solution concentration on the particle size distribution of the resultant microspheres is presented in Figure S1. As is evident, the distribution shifts towards larger sized microspheres as the concentration of siloxane in the feed increases, which can be attributed to the increased polymerisable content in the hydrophobic dispersed droplets. Morphological investigations reveal the smooth texture of the siloxane microspheres (Figure S1, Inset). In all cases, complete conversion (> 98%) could be achieved, as evidenced by gravimetric analysis.
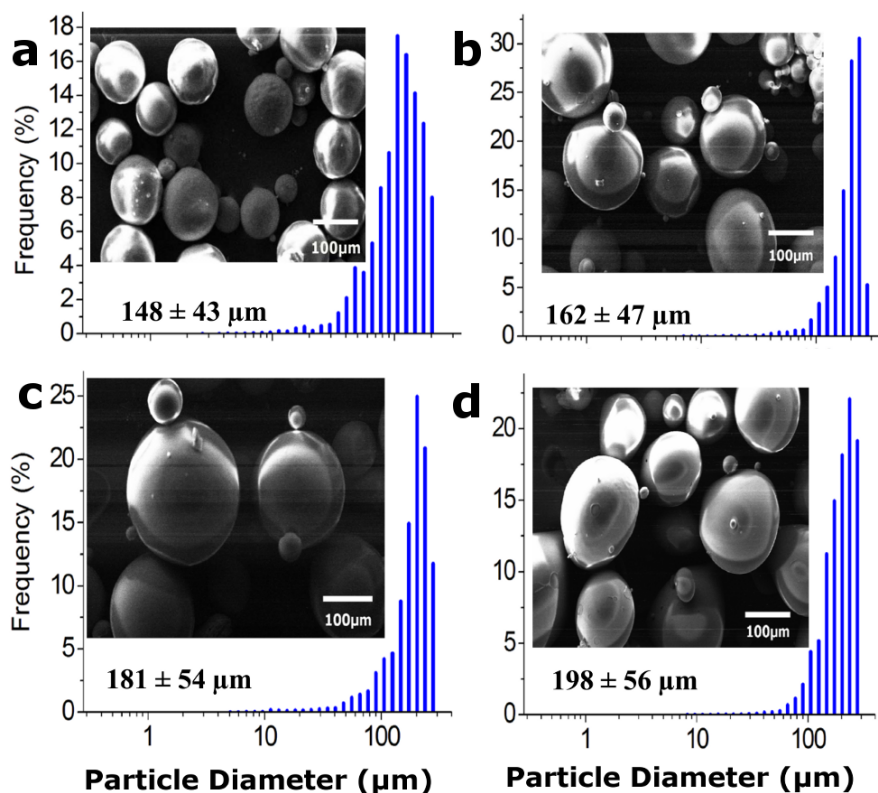
**Figure S1.** Effect of feed concentration on the particle size distribution and surface morphology of PDMS microspheres (stirring speed 600 rpm). a) 30% b) 40% c) 50% d) 60%

## Comparison of separation behaviour with commercially available packed column PORAPACK N and MS 5A.

The commercial column PORAPACK N and MS 5A was pre-conditioned at 150°C for 24 h using Helium as the carrier gas. Standard gas mixture containing 59.03% $H_2$, 20.05% $N_2$, 5.05% $CH_4$, 10.0% $CO_2$ and 5% CO (% v/v) (Sigma gases) was injected and the chromatogram was recorded while maintaining the following operating conditions:
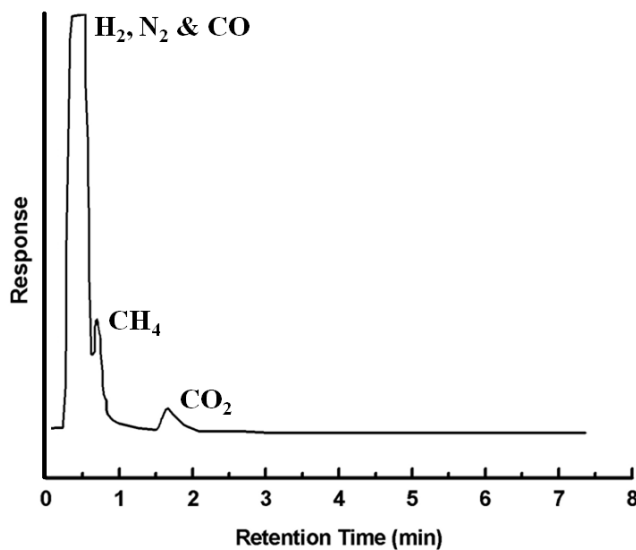
Injector temperature: 60 °C

Detector Temperature: 110 °C

Oven Temperature: 70 °C

TCD current: 70 mA

Flow rate: 30 ml/min

Gas chromatogram which presents the separation of the various components using PORAPACK N column is presented in Figure S2.



**Figure S2:** Gas Chromatogram showing the separation of $H_2$, $N_2$, CO, $CH_4$ and $CO_2$ (TCD detector) using PORAPACK N column

Gas chromatogram which presents the separation of the various components using MS 5A column is presented in Figure S3.
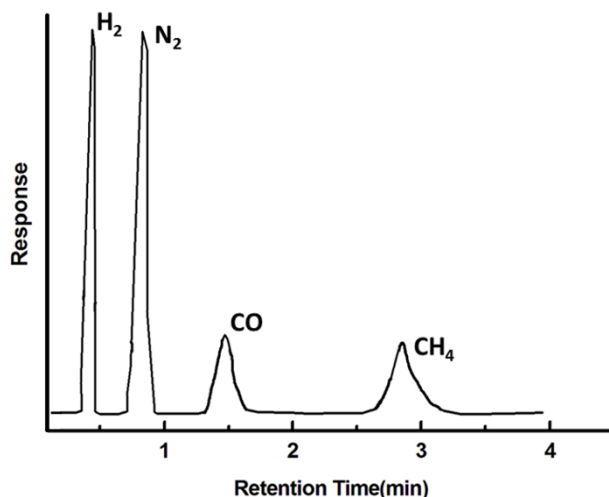
**Figure S3:** Gas Chromatogram showing the separation of $H_2$, $N_2$, CO, $CH_4$ using molecular sieve (MS 5A) column

**Operating conditions for the separation of gas mixtures using core shell PDMS-MOF 5 column**

The developed column of PDMS - MOF 5 was pre-conditioned at 200°C for 24 h using Argon as the carrier gas. Standard gas mixture containing (59.03% $H_2$, 20.05% $N_2$, 5.05% $CH_4$, 10.0% $CO_2$ and 5% CO, (% v/v) (Sigma gases) was injected and the chromatogram was recorded while maintaining the following operating conditions:

Injector temperature: 60 °C

Detector Temperature: 70°C

Oven Temperature: 110 °C

TCD current: 70 mA

Flow rate: 30 ml/min

Table S1: Retention time of the gaseous components present in the mixture ($H_2$, $N_2$, $CH_4$, $CO_2$ and CO) using core-shell PDMS -MOF 5 column

| S.No | Retention time (min) | Component | Amount (%v/v) |
|------|----------------------|-----------|---------------|
| 1 | 0.54 | $H_2$ | 59.04 |
| 2 | 0.81 | $N_2$ | 20.19 |
| 3 | 0.93 | CO | 5.00 |
| 4 | 1.79 | $CH_4$ | 5.04 |
| 5 | 4.49 | $CO_2$ | 10.24 |

**Operating conditions for the separation of natural gas mixtures using core shell PDMS-MOF 5 column**

The developed column of PDMS - MOF 5 was pre-conditioned at 200 °C for 24 h using Argon as the carrier gas. Standard gas mixture containing 79.37% Methane, 6.72% Ethane, 0.94% Iso-Butane, 0.53% Iso-Pentane, 1.31% n-Butane, 0.19% n-Hexane, 0.51% n-Pentane, 8.09% Propane and 2.34% $CO_2$, (%v/v). (Sigma gases) was injected and the chromatogram was recorded while maintaining the following operating conditions:

Injector temperature: 60 °C

Detector Temperature: 70 °C

Oven Temperature: 140 °C

TCD current: 70 mA

Flow rate: 30 ml/min

Table S2: Retention time of the gaseous components present in the natural gas mixture using core-shell PDMS -MOF 5 column.

| S.No | Retention time (min) | Component | Amount (%v/v) |
|---|---|---|---|
| 1 | 0.95 | Methane | 79.3 |
| 2 | 1.3 | Ethane | 6.72 |
| 3 | 2.2 | n-Propane | 8.09 |
| 4 | 3.1 | Carbon dioxide | 2.34 |
| 5 | 4.3 | Iso- Butane | 0.94 |
| 6 | 5.1 | n-Butane | 1.31 |
| 7 | 10 | n-Pentane | 0.51 |
| 8 | 11.9 | n-Hexane | 0.19 |