Highly gas permselective polyetherketone hollow fibre membranes using aqueous sulfuric acid solution as coagulant

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Abstract: Hollow fibre membranes with more sponge-like morphology and improved gas permeation performance were spun from 20% polyetherketone (PEK) /sulfuric acid (H2SO4) dope solution with aqueous sulfuric acid solution as coagulant using dry-jet wet spinning process. The membrane morphology, mechanical properties and gas separation performance (hydrogen, methane and carbon dioxide) of as-spun PEK hollow fibres have been measured using SEM, Instron and gas test rig. Better cross section structures and mechanical properties in as-spun PEK hollow fibres were observed when aqueous sulfuric acid solution replaced water as coagulant (internal and external). The hydrogen/methane selectivity of up to 40 and hydrogen permeation rate of 3.65 GPU obtained in PEK hollow fibre membranes using 30% sulfuric acid solution as internal and external coagulant simultaneously at the bore fluid injection rate of 30 ml/h are higher than those reported in literatures. Furthermore the effects of bore fluid injection rate and various coagulants on the membrane morphology, mechanical properties and gas separation properties were investigated, as well.

Keywords: Polyetherketones; hollow fibre membranes; gas separation; coagulant effect; membrane morphology

Introduction

Polyetherketone (PEK) with the structure given in Figure 1 is a desirable class of high performance engineering polymers which is attracting increasing interest at the present. This is due to the fact that this polymer possesses extremely outstanding chemical resistance, high thermal stability and retention of physical properties at high temperatures (up to 250 °C) [1-2]. It suggests that the fabrication of gas separation membranes from this type of polymer would be of great potential value.

[Fig. 1. Structure of the Polyetherketone repeating unit.]

Preparations and characterizations of modified PEK flat membranes for gas separation were studied by Maier and Xu et al. [3-6], who have attempted to explore the relation between PEK structures and the gas separation properties. However, in most commercialised gas separation processes, it would be advisable to employ
hollow fibre membranes that have the largest surface area over volume. To the best of our knowledge, very little attention has been given to spin hollow polyetherketone fibres for gas separation partly because PEK is insoluble in conventional organic solvents. Unlike the polyether ether ketone (PEEK) or modified PEEK [7-9] and modified PEK [3-6, 10-11] which could be soluble in common solvents, PEK with the structure given in Figure 1 is insoluble in conventional organic solvents at room temperature and only dissolve in very strong acids such as liquid hydrogen fluoride, methanesulphonic acid (MeSO$_3$H), trifluoromethane-sulphonic acid, and concentrated sulfuric acid (H$_2$SO$_4$), though some efforts have been done to fabricate microfiltration and ultrafiltration membranes. [12-14]

Recently, Brown et al. have successfully spun a series of PEK hollow fibre membranes for gas separation using dry-jet wet spinning procedure, investigated the membrane morphology, as well studied the relation between gas separation performance and the spinning parameters, for example, air gap, bore fluid injection rate, internal coagulant composition and polymer concentration [1, 15]. Unfortunately, the PEK hollow fibres normally showed a partial or complete cross-sectioned finger-like structure with a dense skin at the surface layer. And it is believed that the hollow fibre membranes with sponge structure in the cross section will be favourable to the improvements of mechanical properties that are of the most importance for the commercial application of membranes in gas separation field. On the other hand, the as-spun PEK fibres showed high hydrogen, carbon dioxide and methane permeation rate and low gas separation factors which corresponded to a typical Knudsen diffusion flow, meanwhile silicone-coated fibres gave higher separation factors up to 15.15 but lower permeation rates of 3.15 GPU. However, fabricating high performance hollow fibres without the need for costly and time-consuming post-treatment processes should be more attractive in commercial membrane application.

In this research, we attempt to explore highly permselective polyetherketone hollow fibres for gas separation using aqueous sulfuric acid solution as internal and external coagulants. The effects of spinning conditions such as bore fluid injection rate, internal and external coagulant on the membrane morphology and gas permeation performance were studied. And the mechanical properties of as-spun fibres were investigated using Instron instrument.

**Results and discussion**

**Fibre Morphology**

It is well known that the coagulant solution plays an important role in the formation of membranes by phase inversion processes. In general, the formation of large finger-like structures comes from the fast precipitation rate whereas the slow precipitation rate results in a porous sponge structure.

For example, Brown et al used only water as the external coagulant and water or 30% H$_2$SO$_4$ or 40% glycerol (aqueous) as the internal coagulants to spin PEK hollow fibres, which normally showed a partial or complete cross-sectioned finger-like structure with a dense skin at the surface layer. [1, 15] We believe this finger-like structure comes from the fast precipitation of 15% PEK solution in H$_2$SO$_4$ from water, as water has a quick mixing reaction with H$_2$SO$_4$. Therefore our first aim in this research is to investigate the influence of different inner and outer coagulants on the morphologies of the resulting hollow fibres.
Tab. 1. Outer diameter (OD), inner diameter (ID) and wall thickness of PEK hollow fibres.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Internal coagulant</th>
<th>External coagulant</th>
<th>Bore fluid Injection rate in ml/h</th>
<th>OD in μm</th>
<th>ID in μm</th>
<th>Wall thickness in μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>831-B</td>
<td>water</td>
<td>water</td>
<td>30</td>
<td>946</td>
<td>496</td>
<td>225</td>
</tr>
<tr>
<td>831-A</td>
<td>water</td>
<td>water</td>
<td>90</td>
<td>889</td>
<td>561</td>
<td>164</td>
</tr>
<tr>
<td>831-R</td>
<td>30%H₂SO₄</td>
<td>water</td>
<td>30</td>
<td>1000</td>
<td>~636</td>
<td>~182</td>
</tr>
<tr>
<td>831-U</td>
<td>40%H₂SO₄</td>
<td>water</td>
<td>30</td>
<td>1054</td>
<td>~845</td>
<td>~105</td>
</tr>
<tr>
<td>831-V</td>
<td>40%H₂SO₄</td>
<td>30%H₂SO₄</td>
<td>10</td>
<td>962</td>
<td>~521</td>
<td>~221</td>
</tr>
<tr>
<td>831-Y</td>
<td>30%H₂SO₄</td>
<td>30%H₂SO₄</td>
<td>10</td>
<td>980</td>
<td>551</td>
<td>215</td>
</tr>
<tr>
<td>831-X</td>
<td>30%H₂SO₄</td>
<td>30%H₂SO₄</td>
<td>30</td>
<td>942</td>
<td>582</td>
<td>180</td>
</tr>
<tr>
<td>831-W</td>
<td>30%H₂SO₄</td>
<td>30%H₂SO₄</td>
<td>90</td>
<td>906</td>
<td>647</td>
<td>130</td>
</tr>
</tbody>
</table>

(a) bore water injection rate: 30 ml/h.

(b) bore water injection rate: 90 ml/h.

Fig. 2. The cross-section morphologies of hollow fibre spun from 20%PEK in H₂SO₄ with water as internal and external coagulants at various bore water injection rate (left: cross-section of the hollow fibre; right, the magnified segment of the hollow fibre).
Different spinning conditions in our research included polymer dope concentration of 20% PEK in H$_2$SO$_4$, water and 30% H$_2$SO$_4$ as external coagulant and water and 30% and 40% H$_2$SO$_4$ as internal coagulant. Detailed spinning parameters are shown in Table 1. Figures 2~4 picture the effect of different inner and outer coagulants on the morphologies. Furthermore, the fibre outer and inner diameters and wall thickness were measured from SEM and results summarize in Table 1.

Figure 2 shows the typical cross-sectional structures of PEK hollow fibres spun from 20% PEK with water as internal and external coagulants at different bore water injection rate. The PEK hollow fibre normally has a partial or complete cross-sectioned finger-like structure with a dense skin at the surface layer, which is consistent with the results in references [1, 15]. It is seen from the micrographs in Figure 2a that near the inner surface of the hollow fibre, long finger-like structures are present, and the sponge-like structures are present close to the outer surface of the hollow fibre while the fingers appear again at the outside of the hollow fibre.

(a) internal coagulant: 30%H$_2$SO$_4$

(b) internal coagulant: 40%H$_2$SO$_4$

Fig. 3. The cross-section morphologies of hollow fibre spun from 20%PEK in H$_2$SO$_4$ with aqueous sulfuric acid as internal coagulants and water as external coagulant at bore fluid injection rate of 30 ml/h (left: cross-section of the hollow fibre; right, the magnified segment of the hollow fibre).
(a) internal coagulant: 40%H$_2$SO$_4$; bore fluid injection rate: 10ml/h; external coagulant: 30% H$_2$SO$_4$

(b) internal and external coagulant: 30%H$_2$SO$_4$; bore fluid injection rate: 10 ml/h

(c) internal and external coagulant: 30%; (d) internal and external coagulant: 30% H$_2$SO$_4$; bore fluid injection rate: 30 ml/h H$_2$SO$_4$; bore fluid injection rate: 90 ml/h

**Fig. 4.** The cross-section morphologies of hollow fibre spun from 20% PEK in H$_2$SO$_4$ with aqueous sulfuric acid as internal and external coagulants at various bore fluid injection rate (left: cross-section of the hollow fibre; right, the magnified segment of the hollow fibre)
The fibre structures shown can be attributed to the rapid precipitation occurred at both the outer and inner fibre walls resulting in long fingers and to the slow precipitation giving the sponge-like structure close to the centre of the fibre. In the mean time, increasing the bore water injection rate results in the finger-like structures close to the inner surface longer and the wall thickness thinner (Table 1). The hollow fibre with water injection rate of 90 ml/h shows complete cross-sectioned finger-like structure. This is due to the fact that higher bore fluid injection rate corresponds to higher precipitation rate and quicker exchange rate between solvent and coagulant (H$_2$SO$_4$ and water).

Figure 3 shows the structures of the fibres prepared with aqueous sulfuric acid as internal coagulant and water as external coagulant at bore fluid injection rate of 30 ml/h. It can be found that the shorter finger-like structures near the inner walls and more sponge structures in the centre of the fibres were formed when aqueous sulfuric acid solution was used as internal coagulant. However, such high acid solution as internal coagulant resulted in the cross section being the circular lumen and wall thickness thinner as shown in Table 1 partially because of the dilution of this aqueous sulfuric acid to the polymer dope during precipitation.

On the other hand, good structures have been observed when aqueous sulfuric acid solution was used as internal and external coagulant simultaneously (Figure 4). Although higher acid concentration like 40% H$_2$SO$_4$ as internal coagulant and 30% H$_2$SO$_4$ as external coagulant is still unfavourable the formation of circular lumen (Figure 4a), 30% H$_2$SO$_4$ solution as the internal and external coagulant led to circular lumen and more sponge structure in the center of fibres. The difference between Figure 3, Figure 4a and Figure 4b–d suggests the importance of the balance between internal coagulant and external coagulant. In Figure 4b–d, it also can be found that more sponge-like structures and thicker fibre wall would be formed when the bore fluid injection rate decreased corresponding to slower precipitation rate in the inner fibre surface. Therefore choosing suitable internal and external coagulant and bore fluid injection rate is very necessary and important in the formation of fibres with good structure, satisfactory mechanical properties and high gas permeation performances which will be confirmed by later results.

**Fibre mechanical properties**

![Fig. 5. The typical Instron curves of PEK hollow fibres.](image)
Figure 5 shows the typical Instron curves of hollow fibres spun from 20% PEK. A summary of the fibre strength, break elongation and Young’s modulus results is listed in Table 2. The fibre strength at break is a measure of the strength of polymer within a fibre and essentially depends on the conditions of fibre failure or flaw. The Young’s modulus may be thought of as stiffness, or a material’s resistance to elastic deformation [18].

**Tab. 2.** Mechanical properties of PEK hollow fibres.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Inner / Outer Coagulant, bore fluid injection rate</th>
<th>Break strength in kg/cm²</th>
<th>Elongation at break in %</th>
<th>Young’s Modulus in kg/(mm⋅cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>831-B</td>
<td>Water / water, 30ml/h</td>
<td>113.4±4.7</td>
<td>116.9±7.4</td>
<td>42.0±3.8</td>
</tr>
<tr>
<td>831-A</td>
<td>Water / water, 90ml/h</td>
<td>137.7±1.8</td>
<td>133.4±5.2</td>
<td>67.5±16.3</td>
</tr>
<tr>
<td>831-R⁺</td>
<td>30%H₂SO₄ / water, 30ml/h</td>
<td>111.6±10.3</td>
<td>123.8±14.8</td>
<td>52.3±3.1</td>
</tr>
<tr>
<td>831-U⁺</td>
<td>40%H₂SO₄ / water, 30ml/h</td>
<td>181.9±8.1</td>
<td>117.4±7.5</td>
<td>77.5±2.7</td>
</tr>
<tr>
<td>831-V⁺</td>
<td>40% / 30%H₂SO₄, 10ml/h</td>
<td>109.2±13.7</td>
<td>71.0±14.9</td>
<td>49.1±6.3</td>
</tr>
<tr>
<td>831-Y</td>
<td>30% / 30%H₂SO₄, 10ml/h</td>
<td>102.9±22.3</td>
<td>114.8±20.7</td>
<td>43.0±6.5</td>
</tr>
<tr>
<td>831-X</td>
<td>30% / 30%H₂SO₄, 30ml/h</td>
<td>139.4±13.4</td>
<td>126.8±11.6</td>
<td>53.4±6.6</td>
</tr>
<tr>
<td>831-W</td>
<td>30% / 30%H₂SO₄, 90ml/h</td>
<td>134.8±5.9</td>
<td>113.4±13.2</td>
<td>64.9±8.5</td>
</tr>
</tbody>
</table>

*: Fibre strength at break was calculated based on the solid cross section area; Young’s modulus is the slope of load-displacement curve in the beginning.

**: The solid cross section area is just a very rough value as these samples have out of circular lumens.

For the hollow fibres using water as internal and external coagulant, increasing the bore fluid injection rate from 30 ml/h to 90 ml/h, all of the break strength, elongation at break and Young’s modulus of the fibres increased. This is due to the fact that water is very strong coagulant for PEK/H₂SO₄ solution system, higher water injection rate will induce faster precipitation rate of PEK from H₂SO₄ and more dense wall will be formed in the inside of the fibres as shown in Figure 4. Nearly similar tendency in break strength and Young’s modulus could be found when the 30%H₂SO₄ used as internal and external coagulant while the elongation at break shows no great difference in terms of bore fluid injection rate and internal coagulant.

It’s notable that the PEK fibres prepared with 30%H₂SO₄ as internal and external coagulant simultaneously have better tensile properties (i.e. break strength and Young’s modulus) than those prepared with water as internal and external coagulant, especially at the bore fluid injection rate of 30 ml/h. As mentioned above, the PEK fibres prepared with 30% H₂SO₄ as internal and external coagulant possess more sponge structures in the centre of the fibres than those prepared with water as internal and external coagulant. These results suggest that the better PEK hollow fibres in membrane morphology and mechanical properties can be obtained using 30% H₂SO₄ as internal and external coagulant simultaneously.

In addition, samples of 831-R, 831-U and 831-V have circular lumen, therefore the mechanical properties of these samples are just a very rough value shown in Table 2. And at least the mechanical properties (i.e. break strength and Young’s modulus) of these fibres have no great loss.
Gas permeation performance

The gas permeation properties of hydrogen (H$_2$), methane (CH$_4$) and carbon dioxide (CO$_2$) through the as-spun PEK hollow fibre membranes were measured at room temperature. The results are summarized in Table 3.

**Tab. 3.** Gas permeation properties of PEK hollow fibres.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Internal coagulant</th>
<th>External coagulant</th>
<th>Bore fluid injection rate in ml/h</th>
<th>$P'_{H_2}$ in GPU</th>
<th>$P'_{CH_4}$ in GPU</th>
<th>$P'_{CO_2}$ in GPU</th>
<th>$\alpha_{H_2/CH_4}$</th>
<th>$\alpha_{CO_2/CH_4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>831-B</td>
<td>water</td>
<td>water</td>
<td>30</td>
<td>2.18</td>
<td>0.158</td>
<td>0.461</td>
<td>13.8</td>
<td>2.92</td>
</tr>
<tr>
<td>831-A</td>
<td>water</td>
<td>water</td>
<td>90</td>
<td>1.16</td>
<td>0.117</td>
<td>0.315</td>
<td>9.91</td>
<td>2.69</td>
</tr>
<tr>
<td>831-S</td>
<td>30%H$_2$SO$_4$</td>
<td>water</td>
<td>10</td>
<td>5.98</td>
<td>0.774</td>
<td>1.23</td>
<td>7.73</td>
<td>1.59</td>
</tr>
<tr>
<td>831-R</td>
<td>30%H$_2$SO$_4$</td>
<td>water</td>
<td>30</td>
<td>4.76</td>
<td>0.365</td>
<td>1.14</td>
<td>13.0</td>
<td>3.12</td>
</tr>
<tr>
<td>831-T</td>
<td>40%H$_2$SO$_4$</td>
<td>water</td>
<td>10</td>
<td>6.89</td>
<td>0.796</td>
<td>1.56</td>
<td>8.66</td>
<td>1.96</td>
</tr>
<tr>
<td>831-U</td>
<td>40%H$_2$SO$_4$</td>
<td>water</td>
<td>30</td>
<td>4.85</td>
<td>0.200</td>
<td>1.34</td>
<td>24.3</td>
<td>6.70</td>
</tr>
<tr>
<td>831-V</td>
<td>40%H$_2$SO$_4$</td>
<td>30%H$_2$SO$_4$</td>
<td>10</td>
<td>5.96</td>
<td>0.588</td>
<td>1.37</td>
<td>10.1</td>
<td>2.33</td>
</tr>
<tr>
<td>831-Y</td>
<td>30%H$_2$SO$_4$</td>
<td>30%H$_2$SO$_4$</td>
<td>10</td>
<td>6.95</td>
<td>1.54</td>
<td>1.61</td>
<td>4.51</td>
<td>1.05</td>
</tr>
<tr>
<td>831-X</td>
<td>30%H$_2$SO$_4$</td>
<td>30%H$_2$SO$_4$</td>
<td>30</td>
<td>3.65</td>
<td>0.089</td>
<td>0.912</td>
<td>41.0</td>
<td>10.2</td>
</tr>
<tr>
<td>831-W</td>
<td>30%H$_2$SO$_4$</td>
<td>30%H$_2$SO$_4$</td>
<td>90</td>
<td>3.48</td>
<td>0.189</td>
<td>0.960</td>
<td>18.4</td>
<td>5.08</td>
</tr>
</tbody>
</table>

It could be found that all the fibres prepared with aqueous sulfuric acid solution as internal (and external) coagulant have higher H$_2$ and CO$_2$ permeation rates than those prepared with water as coagulant. In the meantime, higher H$_2$/CH$_4$ and CO$_2$/CH$_4$ selectivities have been observed when the coagulant changed from water to aqueous sulfuric acid solution but at the same bore fluid injection rate. Various internal and external coagulants also will affect the gas permeation behaviours in the hollow fibres. The increase of the sulfuric acid concentration in the internal coagulant tends to increase the H$_2$ and CO$_2$ permeation rates and H$_2$/CH$_4$ and CO$_2$/CH$_4$ selectivities in the condition of same injection rate, implying that the increasing acid concentration benefits the enhancement of gas permeation and selectivity to some extent.

Furthermore, changing the bore fluid injection rates tends to change the gas separation properties in hollow fibres. Increasing the bore fluid injection rate from 30 ml/h to 90 ml/h resulted in the decrease of the H$_2$ permeation rate and the H$_2$/CH$_4$ selectivity simultaneously regardless of the coagulant. And in all the fibres prepared with sulfuric acid solution as coagulant, the gas permeation rates increased and H$_2$/CH$_4$ selectivity decreased when the applied bore fluid injection rate reduced from 30 ml/h to 10 ml/h. Anyway it is not fully clear how the injection rate affects the fibre morphology and the gas separation performance of the hollow fibres, though it suggests the importance of the choice of suitable bore fluid injection rate during fibre spinning process.

Most importantly, highest H$_2$/CH$_4$ selectivity of 41 has been obtained with reasonable hydrogen permeation rate of 3.65 GPU in the as-spun hollow fibres using 30% sulfuric acid aqueous solution as internal and external coagulant. Comparison with the previous results in literatures, [1, 15] former hollow fibres even have higher gas selectivities and hydrogen permeation than latter coated with the silicone (H$_2$/CH$_4$ selectivity up to 15.15 and hydrogen permeation rate of 3.15 GPU). Therefore as-spun PEK hollow fibres with higher gas selectivities and reasonable gas permeation...
performance without further post-treatments have been spun using 30% sulfuric acid aqueous solution as internal and external coagulant with better morphology and mechanical properties as confirmed above.

**Conclusions**

Using dry-jet wet spinning phase inversion procedure, hollow fibre membranes have been spun from 20% wt% polyetherketone/sulfuric acid solution while water and aqueous sulfuric acid solution have been applied as the internal and external coagulants at various bore fluid injection rates. The addition of sulfuric acid into water coagulant resulted in the membrane structure change from a nearly complete finger-like structure to more sponge structure in the centre of the fibres. Using 30% or 40% sulfuric acid solution as the internal coagulant tends to enhance the gas permeation and selectivity. As a consequence, the hydrogen permeation and hydrogen/methane selectivity of the PEK hollow fibres which used sulfuric acid as internal (and external) coagulant were higher than those used water as internal and external coagulants in the condition of the same bore fluid injection rate. The as-spun PEK hollow fibre membranes with better morphology and mechanical properties, higher hydrogen/methane selectivity of 41 and reasonable gas permeation rates have been prepared from 20% PEK dope with 30% sulfuric acid solution used as internal and external coagulants at the bore fluid injection rate of 30 ml/h.

**Experimental**

**Materials**

The polyetherketone (PEK) used in this study was obtained from (ICI Victrex-PEK, MV 0.392) with the structure given in Figure 1, which was dried for 24 hours at 100 °C under vacuum prior to dissolution. Concentrated sulfuric acid (98% H₂SO₄) was supplied by Fisher scientific company analytical reagent grade.

**Hollow fibre spinning**

Asymmetric PEK hollow fibres were spun by a dry-jet wet spinning process as illustrated in Figure 6. The spinning dope was prepared by magnetically stirring Polyetherketone in concentrated sulfuric acid for 5 hours at 50 °C to form a homogeneous solution of 20 wt% PEK without the detected sulfonation. The viscosity of PEK dope was 362 Pa·s measured at 25 °C using Haake Rotovisko RV12 viscometer with measuring drive M1500. The degassed spinning dope was extruded under a nitrogen pressure of 100psi through a tube-in-orifice type spinneret, then passed through an air gap of 9 cm before entering into the coagulant bath. The dimensions of this spinneret are 1000 and 510 μm for outer and inner diameter, respectively. The bore fluid was changed and precisely controlled by a Precision Piston Pump (DESAGA GmbH KP2000) at the desired rate. Water or aqueous sulfuric acid solution was used as internal and external coagulant, and water as washing detergent. The spinning process was operated at room temperature. The wind-up speed was controlled to close to the fibre free-falling velocity after extrusion so that almost no extra elongating stresses were applied to the nascent fibres except the fibre gravity and water drag. Once the hollow fibres were formed, they were washed in a water bath for two weeks; changed the water regularly for twice every
day, then transferred to a tank containing acetone for 2 hours, and finally dried at room temperature at least for one day before use.

![Diagram of hollow fibre spinning apparatus](image)

**Fig. 6.** Schematic diagram of hollow fibre spinning apparatus.

**SEM investigation**

The cross section structures of as-spun hollow fibres have been investigated using the scanning electron microscope (SEM, Camscan340). Fibre samples for SEM study were first immersed into liquid nitrogen and fractured, and then sputtered with gold before SEM investigation.

**Mechanical properties**

Fibre strength, elongation at break and Young’s modulus of hollow fibres were measured at 50mm gauge length with a speed of 50 mm/min using Instron 1026 instrument at room temperature. At least five samples were tested for each datum. Fibre strength at break was calculated based on the solid cross section area of hollow fibre, and Young’s modulus is the slope of load-displacement curve in the beginning.

**Module fabrication and gas permeation tests**

Gas permeation measurements were carried out using hydrogen, methane and carbon dioxide. Hollow fibres were mounted into a module that was then fixed into the permeation chamber of the testing rig assembly (Figure 7). The modules consisted of a bundle of ten fibres (each being of length of 20 cm) at which one end was blocked with a small copper end cap and glued in with epoxy resin. This left the other end of the potted and cut bundle open for permeation. The rate of flow of single gas (H₂, CH₄ and CO₂) through the hollow fibres module was measured at room temperature using lab-scale gas permeation rigs described previously [16, 17]. The permeation rate of gases through the flat film and hollow fibre membranes was determined using the following equation.
where $P'$ is the permeation rate of the membranes in gas permeation unit of GPU where one GPU is equal to $1 \times 10^{-6}$ cm$^3$ cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$; $Q_i$ is the volume flow rate of gas (cm$^3$ s$^{-1}$), $\Delta P$ is the pressure differential across the membrane and $S$ is the membrane surface area in cm$^2$. The ideal separation factor of gas A over gas B for hollow fibres ($\alpha_{A/B}$) is given by the following equation:

$$\alpha_{A/B} = \frac{P'_A}{P'_B}$$

Fig. 7. The permeation performance test rig.

References