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Effect of Kaolin/pesf Ratio and Sintering Temperature on Pore Size and Porosity of the Kaolin Membrane Support

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Abstract: This study discusses the effect of kaolin/PESf ratio and sintering temperature on the pore size and porosity of the flat sheet kaolin membrane support. Inexpensive kaolin has been proposed as a replacement for Al_2O_3 , Ti_2O and ZrO_2 as a membrane material. In casting the support precursor, Polyethersulfone (PESf), solvent N-methyl-2-pyrrolidone (NMP) and kaolin were used as a polymer binder, solvent and ceramic powder, respectively. The morphology structure and pore size were observed under the Scanning Electron Microscope (SEM) and the porosity were obtained by calculation using weight loss, area and thickness data of the prepared support. The results showed that both of the membrane pore size and porosity linearly decreased from 20 to 8 μm and 26 to 11% , respectively when sintering temperature was increased from 1100 to 1500°C and kaolin/PESf ratio was increased from 1:1 to 3.5:1.

Key words: Ceramic membrane, kaolin/PESf ratio, tape casting, phase inversion, sintering

INTRODUCTION

The use of polymeric membrane is more developed, however, ceramic membrane has the advantages in application requiring high temperature, harsh chemical environment and high pressure condition which polymer membrane fails (Liu *et al.*, 2001).

Several studies on ceramic membrane preparation using ceramic material such as Alumina (Al_2O_3), Zirconia (ZrO_2), metal oxide or metal alloys were carried out by Tan *et al.* (2001) and Liu *et al.* (2003). However, the existing ceramic membrane was limited by the availability and type of the ceramic material used.

Low cost of raw clay has been a growing interest in material selection due to its superior characteristic which compensates high cost sintering process (Khider *et al.*, 2004). Kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$), is suitable for membrane preparation because they are easily molded, fine texture, grain size of 0.2-1 μm , white though fired, low shrink-swell capacity, high temperature stability and high chemical resistance (Mohammadi and Pak, 2003).

Preparation of ceramic membranes involves several steps; formation of particle suspensions, shaping of ceramic precursor and consolidation of the membrane precursor (Li, 2007). Defect free membrane support with 30% porosity and submicron pore size (1-15 μm) provides mechanical strength to the production of multilayered membrane.

By employing phase-inversion method asymmetric structure can be obtained in a single step (Tan *et al.*,

2001; Koonaphapdeelert and Li, 2007) developed the ceramic membrane by varying the ratio of alumina to polymer binder and sintered at elevated temperature. Their results showed that the ratio of the dope solution and sintering temperature were two important factors which influence the membrane pore size, porosity and mechanical strength prepared ceramic membrane. Liu and Li (2005) reported that the sintering process plays a prominent role to obtain desired morphology and microstructures.

Currently, there is limited report on fabrication of asymmetric ceramic flat sheet membrane support. Therefore, this study will focus on studying the effects kaolin/PESf ratio and sintering temperature on the ceramic membrane morphology, pore size and porosity.

MATERIALS AND METHODS

Raw materials: Commercial Kaolin (Aldrich) ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) powders with approximate 10 μm particle size was used as membrane materials. Polyethersulfone, (PESf) (Aldrich) and N-methyl-2-pyrrolidone (NMP) (Acros) was used for preparation of polymer binder. Tap water was used for coagulation.

Powder characterization: A laser diffraction particle size analyser LSST-portable (Sequoia) was used to determine the kaolin particle size distribution. The chemical composition of the kaolin powder was carried out using X-ray Fluorescence (XRF) Casio.

Table 1: The composition of the ceramic suspension

Kaolin/PESf ratio	Composition (g)		
	Kaolin	NMP	PESf
1.0:1	27.0	150.75	27
1.5:1	40.5	150.75	27
2.0:1	54.0	150.75	27
2.5:1	67.5	150.75	27
3.0:1	81.0	150.75	27
3.5:1	94.5	150.75	27

Membrane preparation: The 150.75 g of NMP was taken in one liter wide neck reaction flask and the 27 g of PESf was slowly added over a period of 30 min to form the polymer solution. The solution was kept vigorous stirred on a magnetic stirrer Yellow MAG HS 7 S2 (IKA) for 24 h at 60°C. Then, kaolin powder was subsequently added. The mixture was stirred for 48 h for homogenous mixing. The dissolved solution was left at room temperature for 24 h in order to remove air bubbles and then the viscosity of the dope solution was measured. Effect of kaolin ratio on the membranes, was investigated by keeping constant the concentration of PESf and NMP. Table 1 shows the compositions of the dope solutions.

The ceramic suspension obtained was poured onto a clean and smooth glass plate of 15×15 cm at the room temperature and cast using a casting knife. The thickness of the membranes was controlled within 1.5 mm by using adhesive tape at each side of the glass plate.

The cast film was immediately immersed in distilled water at room temperature. Phase inversion starts and after 24 h the flat sheet ceramic membrane precursor was separated from the glass plate. The membrane was washed with tap water and dried at room temperature for 24 h. Membrane precursor thickness was measured by using digital micrometer (Mitutoyo, Japan).

Accordingly, the ceramic membrane precursors were heated using furnace Thermolyne 46100 at about 200 for 3 h, to removed water, then 500°C for 6 h to removed the organic polymer binder and sintered at temperature between 1000 to 1500°C for fusion and bonding to occur. Each step employs 1°C min⁻¹ of cooling and heating rate.

Membranes characterization

Determination of viscosity of casting solution: The 150 mL of the casting solution was filled into a 200 mL beaker and spindled for viscosity measurement using Brookfields Programmable HADV-IV⁺ Rheometer.

Scanning electron microscopy (SEM): Observation of the support was conducted using a scanning electron microscope (JSM-5610 LV-JEOL, Japan). The clear cross-sectional fracture was obtained by directly snapping the sintered ceramic membrane. These membrane samples were then positioned on a metal holder

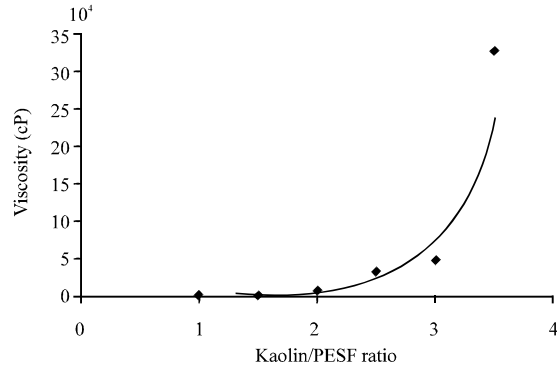


Fig. 1: Kaolin/PESf ratio vs. viscosities

and gold-coated using sputter-coating operated under vacuum. The SEM micrographs of cross-section of the kaolin membranes were taken at various magnifications.

Porosity measurement: The wet (unsintered) and dried (sintered) membrane was weighted. From the two weights the porosity of membrane was calculated using Eq. 1:

$$P(\%) = \frac{Q_0 - Q_1}{Ah} \times 100 \tag{1}$$

where, P is the porosity of membrane, Q₀ the wet sample weight (g), Q₁ the dry sample weight (g), A the area of membrane (cm²) and h is the thickness of membrane (cm) (Zheng *et al.*, 2006).

RESULTS AND DISCUSSION

Powder characterization: The chemical composition of the clay is given in Table 2 while the particle size is shown in Table 3. It reveals the clay powder is essentially formed of large amount of silica with alumina. The particle diameter ranges from 1 to 65 μm. More than 41% of the particles present a diameter <6 μm.

Effect of kaolin ratio to viscosity: Figure 1 showed effect of the kaolin to PESf ratio on the viscosity of dope solution. It was found that the viscosity increased exponentially with increasing kaolin ratio in the ceramic suspension. This is in good agreement with studies by Li (2007) who indicated that increases in viscosity are due to the increases of the solids volume fraction in kaolin suspension. In this study it was observed that membrane casting was easier at lower viscosity. However, at lower viscosity prepared precursor generally showed uneven membrane surface and inconsistent membrane thickness. It is safe to say that the compacts of the precursor particles which indirectly control the membrane thickness

Table 2: Chemical composition of kaolin (wt%)

Elements	Mass (wt%) according to			
	This study	Kingsbury <i>et al.</i> (2010)	Phelps and Watchman (2005)	Nandi <i>et al.</i> (2008)
Na ₂ O	0.39	NA	0.08	NA
MgO	0.25	00.03	0.20	NA
Al ₂ O ₃	38.09	37.27	38.1	39.5
SiO ₂	45.01	43.69	46.6	46.5
P ₂ O ₅	0.06	NA	NA	NA
SO ₃	0.04	NA	NA	NA
K ₂ O	0.19	NA	1.47	NA
CaO	0.19	00.38	0.19	NA
TiO ₂	0.83	00.09	0.07	NA
V ₂ O ₅	ND	NA	NA	NA
Cr ₂ O ₃	0.02	NA	NA	NA
Fe ₂ O ₃	0.50	00.64	0.69	NA
NiO	0.01	NA	NA	NA
CuO	ND	NA	NA	NA
ZnO	0.01	NA	NA	NA
Ga ₂ O ₃	0.01	NA	NA	NA
ZrO ₂	0.01	NA	NA	NA
MnO	ND	00.41	NA	NA
LOI	14.40	17.46	12.66	NA

NA: Not available, ND: Not detected

Table 3: Particle size distribution of clay

Diameter (µm)	Particle size distribution (%)
28-63	13
12-29	22
6-13	24
<6	41

were determined strongly by the viscosity of the ceramic suspension (Hsieh, 1996).

Effect of kaolin/PESf ratio and sintering temperature to Morphology: Figure 2 showed the produced asymmetric porous membrane cross sectional with 2.5:1 kaolin/PESf ratio before and after sintered at 1400°C. The structure near the outer surfaces consists of fingers like with narrow long voids while in the lower section a sponge like layer was observed. The finger-like structure was attributed from the rapid precipitation of the polymer near the surfaces, while slow precipitation produced the sponge-like structure (Koonaphapdeelert and Li, 2007; Li *et al.*, 2006). This asymmetric structure shown in Fig. 2a was visibly not clear because of the polymer binder presence inside the membrane precursor. In contrast, a clear asymmetric structure was obtained after sintering as shown in Fig. 2b. This showed that polymer had been burn off during sintering creating more visible asymmetric structure.

Similar result was also obtained by Liu *et al.* (2001). The result showed that near the outer and inner walls of the fibre precursor, short finger-like structure are present and that at the centre of the hollow fibre precursor, sponge like structure were posses. In which after sintering they obtained a similar but more visible structure.

Effect of Kaolin/PESf ratio and sintering temperature to pore size: Figure 3 and 4, shown that increase in

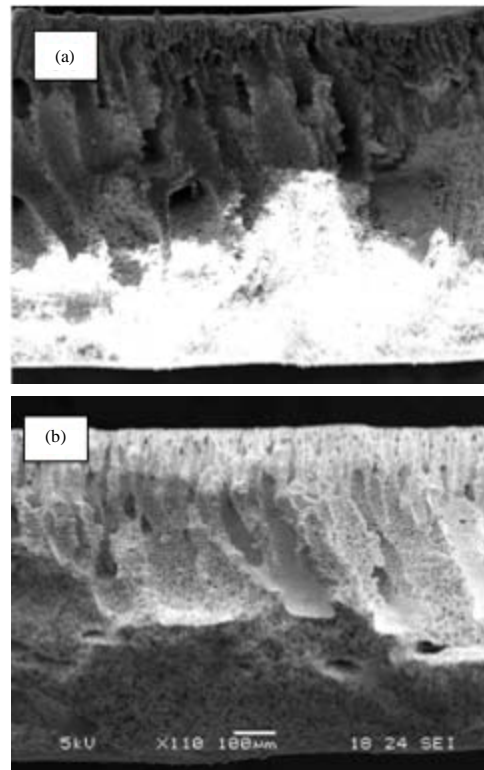


Fig. 2: SEM image of the kaolin member (a) before sintering and (b) after sintering (1400°C)

kaolin/PESf ratio from 1.0:1 to 3.5:1 of the kaolin suspension created a denser membrane. Pore size of the membrane found to decrease from 11 to 8 µm at 1400°C sintering temperature. Therefore, the kaolin content in ceramic suspension is found to affect the pore size of

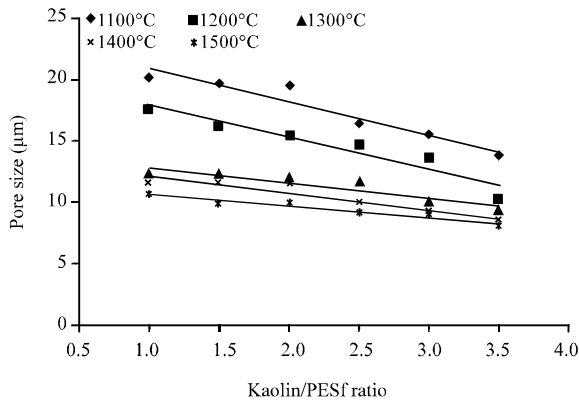


Fig. 3: Effect of kaolin/PESf ratio and sintering temperature on the membrane pore size: = 1100°C, = 1200°C, 1300°C, x = 1400°C and K = 1500°C

prepared kaolin membrane. The change in the microstructures was due to the lost of polymer content in the membrane precursor during membrane sintering. Following, the pore size of the membrane was found to decrease with sintering temperature. Figure 4a-f showed a clear asymmetric structure and smaller pore size at increasing sintering temperature.

Figure 5 showed sintered precursor in the temperature in the range of 1100 to 1500°C. For kaolin/PESf ratio 2.5:1, the pore size decrease from 16 to 9 µm. similar trend was observed for all other membranes prepared in this study. The changes obtained were due to the pore size shrinkage during the sintering. In addition, membrane pore size was affected by the grain growth in the membrane surface during the sintering process. Similar results were obtained by Jong *et al.* (2004). Their work on

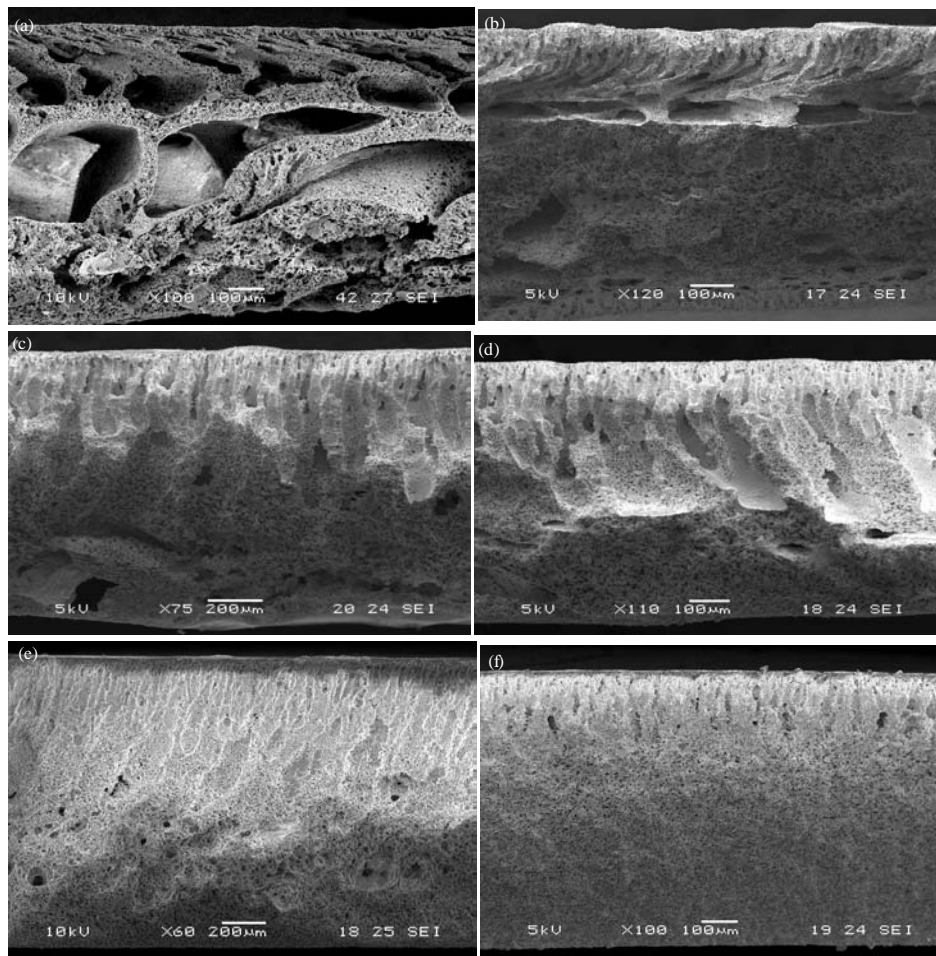


Fig. 4: SEM image of the kaolin membrane at sintering temperature 1400°C and different kaolin/PESf ratio (a) 1.0:1; (b) 1.5:1; (c) 2.0:1; (d) 2.5:1 and (e) 3.0:1; (f) 3.5:1

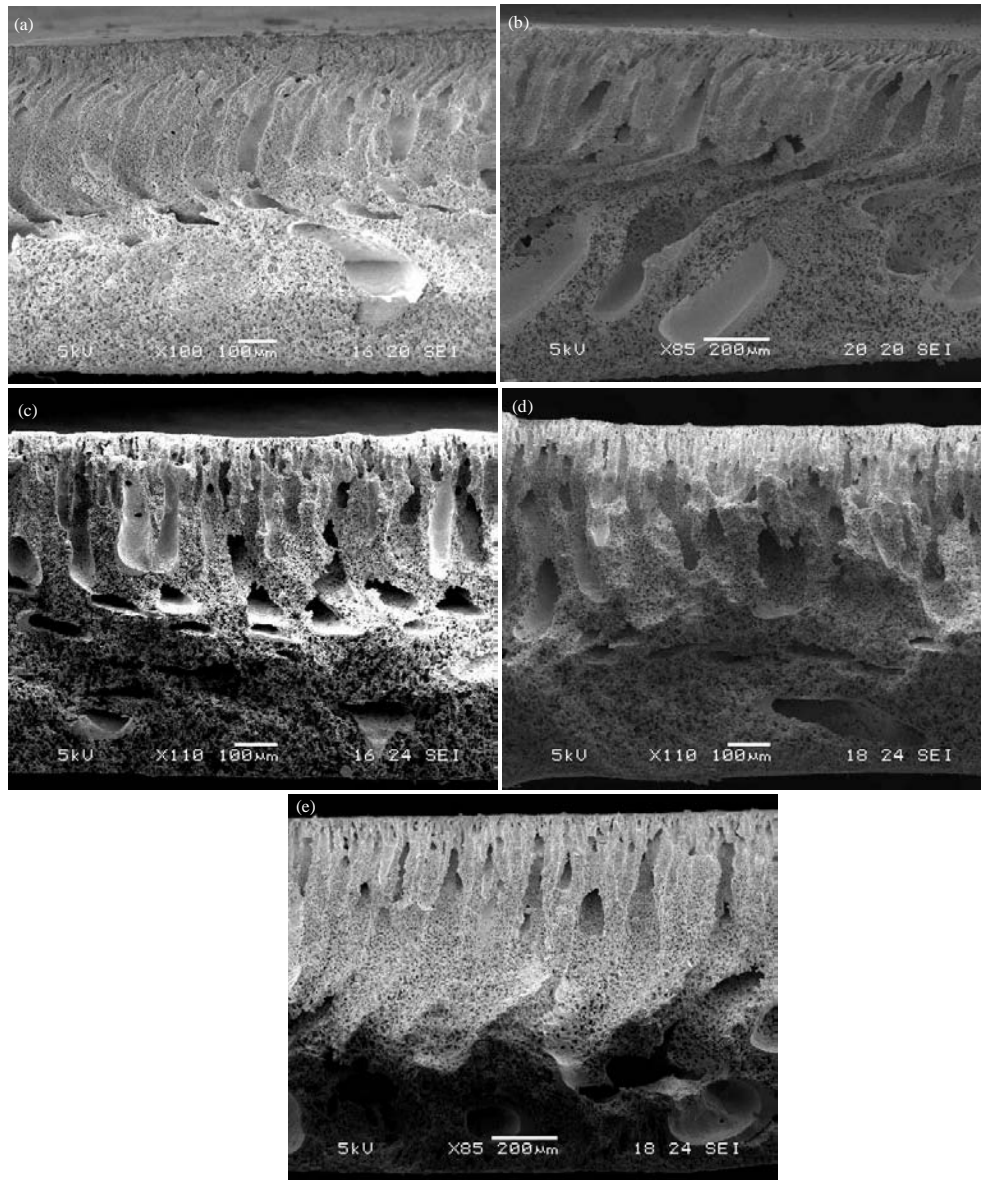


Fig. 5: SEM image of the kaolin membrane at kaolin/PESf ratio 2.5:1 and different sintering temperature (a) 1100°C; (b) 1200°C; (c) 1300°C; (d) 1400°C and (e) 1500°C

increase the sintering temperature will decrease the pore size of the flat sheet membrane.

Experimental results show that it is difficult to form a flat sheet kaolin membrane support if the kaolin/PESf ratio is lower than 2.5:1 and <1300°C sintering temperature which will produce a porous membrane. It is also showed that the membrane with insufficient

mechanical strength was produced when using kaolin/PESf ratio of <2.5:1.

Therefore, it can be said that sintering temperature and solid loading played an important role to create the asymmetric structure. The membranes sintered at higher temperature (>1300°C) were exhibit sufficient mechanically strength than the ones sintered at lower temperature

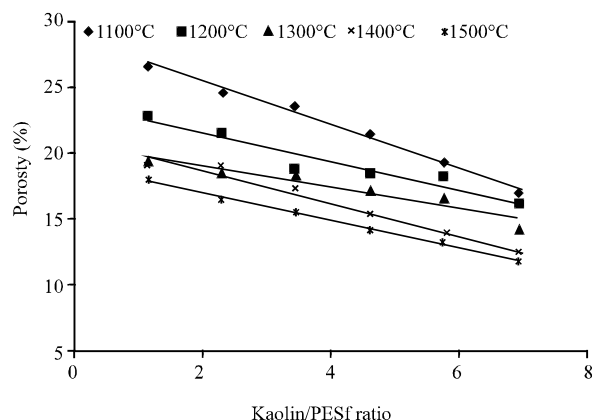


Fig. 6: Effect of kaolin/PESf ratio and sintering temperature on the membrane pore size: 1100°C, = 1200°C, = 1300°C, x = 1400°C and K = 1500°C

(<1300°C). This result was also obtained and inline by the work done by several authors (Liu *et al.*, 2001; Koonaphaddeert and Li, 2007).

Effect of kaolin/PESf ratio and sintering temperature on porosity: It has been shown that higher kaolin content in the dope solution produce a denser membrane with a lower porosity. Similar result was obtained by Liu *et al.* (2003).

Figure 6 shows the porosity of the flat sheet kaolin membrane with different kaolin/PESf ratio and sintering temperature. Decrease in membrane porosity was supported by SEM micrograph. The porosity of the membrane obtained in this study decrease from 26 to 11% when the membrane was sintered at temperature 1100 to 1500°C.

Tan *et al.* (2001) indicated that decrease in membrane porosity was due to the formation of closed pores, shrinkage and pore blockage of the membrane microstructure. In addition, the occurrence of fusion and bonding at high temperature also decrease the membrane porosity. According to Yang *et al.* (2008) the sintering temperature should be controlled to give high porosity of kaolin membrane produced.

CONCLUSION

Asymmetric kaolin membrane support had been prepared by phase inversion and sintering technique. In this study viscosity of the dope solution increased exponentially when the kaolin/PESf ratio increased. The experimental results obtained from the SEM study indicated both of the pore size and porosity of the prepared membrane decreased from 20 to 8 μm and 26 to 11%, respectively if kaolin/PESf ratio and sintering

temperature is increased. Porous kaolin support was successfully produced for kaolin/PESf ratio 2.5:1 to 3.5:1 and sintering temperature 1300°C to 1500°C. Porosity of the kaolin membrane greater than 20% can be produced when the kaolin/PESf ratio 1.0:1 to 2.5:1 and sintering temperature 1100°C and 1200°C.

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REFERENCES

- Hsieh, H.P., 1996. Inorganic Membranes for Separation and Reaction. Elsevier, Netherlands, ISBN: 0444816771, pp: 591.
- Jong, J.D., N.E. Benes, G.H. Koops and M. Wessling, 2004. Towards single step production of multi-layer inorganic hollow fibers. *J. Membrane Sci.*, 239: 265-269.
- Khider, K., D.E. Akretche and A. Larbot, 2004. Purification of water effluent from a milk factory by ultrafiltration using Algerian clay support. *Desalination*, 167: 147-151.
- Kingsbury, B.F.K., Z. Wu and K. Li, 2010. A morphological study of ceramic hollow fibre membranes: A perspective on multifunctional catalytic membrane reactors. *Catal. Today*, 156: 306-315.
- Koonaphaddeert, S. and K. Li, 2007. Preparation and characterization of hydrophobic ceramic hollow fibre membrane. *J. Membrane Sci.*, 291: 70-76.
- Li, K., 2007. Ceramic Membrane for Separation and Reaction. John Wiley and Sons Ltd., Chichester, England.
- Li, K., X. Tan and Y. Liu, 2006. Single-step fabrication of ceramic hollow fibers for oxygen permeation. *J. Membrane Sci.*, 272: 1-5.
- Liu, S., X. Tan, K. Li and R. Hughes, 2001. Preparation and characterisation of srce0.95yb0.05o2.975 hollow fibre membranes. *J. Membrane Sci.*, 193: 249-260.
- Liu, S., K. Li and R. Hughes, 2003. Preparation of porous aluminium oxide (Al₂O₃) hollow fibre membranes by a combined phase-inversion and sintering method. *Ceram. Int.*, 29: 875-881.
- Liu, Y. and K. Li, 2005. Preparation of srce0.95yb0.05o3-α hollow fibre membranes: Study on sintering processes. *J. Membrane Sci.*, 249: 47-54.
- Mohammadi, T. and A. Pak, 2003. Effect of calcination temperature of kaolin as a support for zeolite membranes. *Sep. Purif. Technol.*, 30: 241-249.

- Nandi, B.K., R. Uppaluri and M.K. Purkait, 2008. Preparation and characterization of low cost ceramic membranes for micro-filtration applications. *Applied Clay Sci.*, 42: 102-110.
- Phelps, G.W. and J.B. Jr. Wachtman, 2005. *Ceramics, General Survey*. Wiley-VCH, Weinheim.
- Tan, X., S. Liu and K. Li, 2001. Preparation and characterization of inorganic hollow fiber membranes. *J. Membrane Sci.*, 188: 87-95.
- Yang, N., X. Tan and Z. Ma, 2008. A phase inversion/sintering process to fabricate nickel/yttria-stabilized zirconia hollow fibers as the anode support for micro-tubular solid oxide fuel cells. *J. Power Sources*, 183: 14-19.
- Zheng, Q.Z., P. Wang, Y.N. Yang and D.J. Cui, 2006. The relationship between porosity and kinetics parameter of membrane formation in PSF ultrafiltration membrane. *J. Membrane Sci.*, 286: 7-11.