

# Smart Synthesis of Microporous Polymers by Flow Injection Method for CO<sub>2</sub> Capture to Reduce Environmental Pollution

Fadi Ibrahim

Department of Chemistry, Nano-Science Club of Saad bin-Alrabee Alansari School, Kuwait

## ARTICLE INFO

### Article history:

Received: 2 September 2017;

Received in revised form:

1 October 2017;

Accepted: 10 October 2017;

### Keywords

Polymeric Membrane,  
CO<sub>2</sub> capture,  
Hollow Fiber Membrane,  
Selectivity,  
Membrane Wetting;  
Environmental.

## ABSTRACT

Carbon dioxide is thought to be one of the contributing factors in the rise of global warming. Consequently the discovery for an efficient and economically valuable gas capturing system is highly in demand. Therefore there have been various recent developments in creating new, efficient and adaptable gas capturing materials. Microporous organic based materials received great research efforts in the field of environmental related applications such as gas storage and separations due to their permanent porosity, low density (i.e. composed of light weight elements) and remarkable physicochemical stability. Three anthracene microporous polymers (AMPs)<sup>1,2</sup> bridged by imide links were successfully prepared by conventional nucleophilic substitution reaction between different 9,10-dihydro-9,10-ethanoanthracenes and 2,3,5,6-tetrachlorophalonitrile (instead of fluoro-monomer)<sup>2</sup>. AMPs display a BET surface area in the range of 711-796 m<sup>2</sup> g<sup>-1</sup>, and adsorb reach to 1.70 wt. % H<sub>2</sub> at 1.09 bar/77 K. The enhanced microporosity, in comparison to other organic microporous polymers originates from the macromolecular shape of framework, as dictated by the anthracene units, which helps to reduce intermolecular contact between the extended planar struts of the rigid framework. The impressive hydrogen adsorption capture of these materials verified by Horvath-Kawazoe (HK) and NLDFT analyses of low-pressure nitrogen adsorption data, which expected to be use in transportation as a source of green chemistry. A novel synthesis method for AMPs was done by Flow Injection System (FIS). This method has the advantage over conventional synthesis method as saving time-solvent and lowering synthesis cost of. Optimizing conditions (sample & reagent volumes, 0.1 ml/min flow rate, with 0.5 m coil length and 0.5 mm i.d) were used for increasing percentage yield of the product.

© 2017 Elixir All rights reserved.

## Introduction

Since the industrial revolution took place in the middle 18th century, 321 billion tons of CO<sub>2</sub> has been released to the atmosphere and half of the CO<sub>2</sub> emission has taken place in the recent 30 years (1971 to 2002) [1,2]. There-fore, the increasingly intensive energy requirement, which comes mainly from the fossil fuel combustion, accounts for the significant atmospheric CO<sub>2</sub> increase and thus potentially the global climate change concerns.

While renewable energy will reduce the CO<sub>2</sub> emission in the long term, by switching the energy resource from the current fossil fuel based toward to emerging solar, biomass, wind and tides, CO<sub>2</sub> capture and sequestration from the large stationary coal/natural fired power plants, cement plants, oil refineries and steel plants, will reduce CO<sub>2</sub> emission in the intermediate time span. The easy operation, reliable performance (based mainly on physical phenomena) and easy scale up has made polymer membrane as favorite media to capture CO<sub>2</sub> from post combustion [3]. Historically, polymer membrane has been applied successfully in ammonia synthesis/purge, petrochemical/refinery and CO<sub>2</sub> separation on industrial scale in the recent 30 years. The latter mainly includes natural sweetening, CO<sub>2</sub> recovery from land

fill gas (biogas) and Enhanced Oil Recovery (EOR/natural gas processing) [4].

### Systematic Optimizations and Advantages of FIS

The replacement of traditional synthesis methods by (FIS) manufacturing process would be an environmental friendly one, which fulfils the developing economies. The FIS system has the advantage that overcome the traditional synthesis method, that are: 1- lower grate consuming of chemical, 2-reduce the long synthesis time, 3-reduce the high cost of synthesis, 4- it also reduce hazardous in nature and the high burden on the environment. Optimizing conditions (sample & reagent volumes, 0.01 ml/min flow rate, with 0.5 m coil length and 0.5 mm i.d) were used for increasing percentage yield of the product. AMPs was identified by using optical polarizing microscopy in conjunction with differential scanning calorimetry (DSC).

Polymer membrane applied in gas separation falls mainly into three categories:

- 1) Physically selective membrane;
- 2) Hollow fiber membrane;
- 3) Facilitated transport. They have some common advantages and disadvantages. Compared to packed/tray columns, membrane operations are more flexible, economic, linear

scale up, predictable, compacted and higher mass transfer rate per volume [3,8]. performance, pressure, vacuum and dual/multi stages of membrane are exerted or simulated to reach the competitive performance and minimum cost of CO<sub>2</sub> capture [7,9-17].

## Results and Discussion

By following the concepts: rigidity and contorted molecular structure as a prerequisite for the synthesis of polymers with intrinsic microporosity (PIMs), a number of anthracene based polymers comprising imides-linkage moieties were prepared by using the dibenzodioxane-forming reaction as depicted in scheme 1.

Table 1 lists several significant parameters obtained from the isotherm analysis including Brunauer-Emmett-Teller (BET) surface area, micropore area, micropore volume and pore diameter based on Horvath-Kawazoe (HK). The BET surface areas of AMPs ranged from 836 to 1241 m<sup>2</sup>/g, with significant micropore area (786-1136 m<sup>2</sup>/g). The differences in the range surface areas might be due to the structural geometry variation of the monomers employed as well as their reactivity in the polycondensation reaction, which affect the resulting high-molecular-weight network structures. As the prepared microporous polymers, AMPs, are characterized by high surface area and an abundance of ultramicropores, it may potentially be suitable for the storage of small gases such as dihydrogen molecules.

**Table 1. Porous properties of PIM-OFPs.**

Polymers	SABET a (m <sup>2</sup> /g)	PVmicro (cm <sup>3</sup> /g)	HK median Pore width (nm)	CO <sub>2</sub> uptake (mmol/g) at 1 bar, 273/295 K	CO <sub>2</sub> uptake (wt.%, at 35 bar, 295/323 K)	Qst(CO <sub>2</sub> ) (kJmole <sup>-1</sup> )
AMP-5	786 (605)	0.25	0.60	2.93/1.92	39.03/28.42	29.23
AMP-6	1085 (892)	0.48	0.56	3.35/2.03	47.37/31.37	29.86
AMP-7	1136 (1108)	0.63	1.20	4.91/3.19	65.95/42.84	28.83

## Experimental

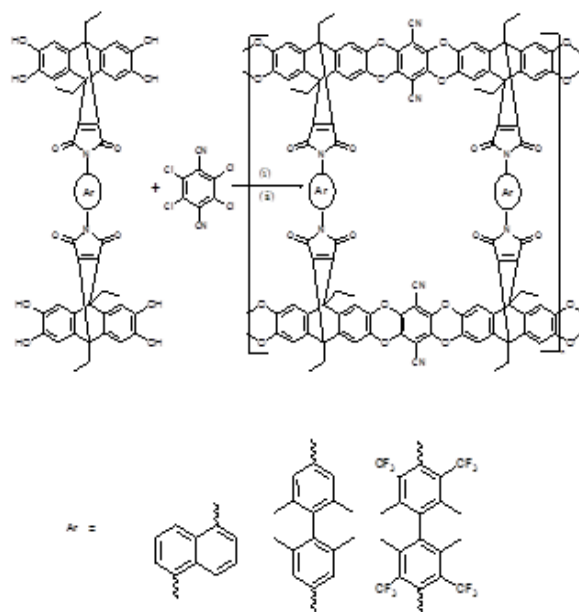
### Materials and Methods

All the chemicals were of reagent grade purity and used without further purification. The dry solvent Dimethylformamide (DMF) with water content less than 0.005% was purchased from Aldrich Co. The finely grounded anhydrous potassium carbonate was used after further drying at 200 °C. <sup>1</sup>H-NMR spectrum (400 MHz) of monomers were recorded on a Bruker DPX 400 spectrometer using CDCl<sub>3</sub> as the solvent and tetramethylsilane as the internal standard. Solid state <sup>13</sup>C-NMR measurement was carried out on a Bruker Avance 300 spectrometer equipped with a cross polarization magic angle spinning (CP/MAS) probe and a fully automated pneumatic unit for sample spinning. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. The micropore area was calculated using *t*-plot method. The pore size distributions were calculated from the adsorption isotherm using the Horvath-Kawazoe (H-K) and Nonlocal Density Functional (NLDFT) calculations. The heats of adsorption for H<sub>2</sub> was calculated using the ASAP 2020 software (Micromeritics, Norcross, GA).

## Synthesis of AMPs

Microporous rigid polymers (AMPs) based on 9,10-dihydro-9,10-ethanoanthracenes monomers bridged by imide links was synthesized efficiently by the double aromatic nucleophilic substitution reaction as shown in Scheme 2. This nucleophilic substitution reaction apply dioxane,<sup>14</sup> forming reaction between the corresponding octahydroxy monomers and tetrachloro-terphthalonitrile (instead of tetrafluoro-terphthalonitrile)<sup>1</sup> in dry DMF and 100 °C and dried under vacuum. The anthracene based monomers(AMP[5-7]) were prepared in good yield by the straight forward one step imidisation reaction between corresponding anhydride and different amines in refluxing acetic acid. The proposed structure and purity of the obtained monomers were confirmed by routinely spectroscopic techniques as well as elemental analysis (See Supporting Information). The polymers AMP-[5-7]) were synthesized by the dibenzodioxane formation reaction between the tetrol, and tetra-chloroterephthalonitrile in dry DMF as illustrated in Figure 1.

The structures of all prepared AMPs were characterized by FT-IR, solid state <sup>13</sup>C NMR spectroscopy and elemental analysis. All materials retained its characteristic stretching bands related to the imide groups (C=O symmetric and asymmetric stretching in the range of 1722-1792). Moreover it is clear from the spectrum that the base catalyzed polymerization condition does not make any destruction in the imide units (See Supporting Information). The <sup>13</sup>C NMR spectra of the AMPs were fully consistent with their proposed structures (See Supporting Information). The signals originating from the hydroxyl groups of tetrol were disappeared, suggesting that the reaction was carried out completely through dibenzodioxane formation. The broad aromatic and aliphatic signals of AMPs were enough to confirm the formation of high molecular weight polymers.



**Figure 1: Synthetic pathway toward the polyamide network AMP(5-7)s. Reagent and conditions: (i) K<sub>2</sub>CO<sub>3</sub>, and DMF (ii) 100 °C for 48h.**

The network polymer was washed with a variety of organic solvents. The thermal properties were evaluated by TGA and DSC. The decomposition temperatures were also very high; where a 5-10 % initial loss around 400 °C, were observed, corresponding to the evaporation of the residual solvents

which has been identified as the entrapped solvents in the micropores used for processing the sample. The good thermal stability can be attributed to its double stranded structures. In DSC analysis no melting ( $T_m$ ) and glass transition ( $T_g$ ) was observed. Wide Angle X-ray Diffraction (WAXD) analysis of the AMPs was conducted to display no crystalline peaks and revealed that all the prepared materials were amorphous.

### Structure-property relationship

Different spacers have been employed in order to evaluate the structure feature on surface area. The anthracene groups as thermally and oxidatively stable, rigid moiety can improve physical properties such as enhanced thermal stability, increased chain stiffness, and decreased crystallinity.<sup>15</sup> However, for AMP-6 and 7 there is very highly restricted rotation about the imide bond linkages, giving rigidity to the polymer. In AMP-5, there is potentially more flexibility in the backbone, but the hexafluoroisopropylidene unit provides a kink in the chain and may be regarded as an additional site of contortion. The unique shape of the anthracene unit lead to a rigid network structure composed of nanoporous frameworks. The molecular structures of these PIM-polyimides have features of the spiro-center providing a site of contortion as well as having conventional imide linkages, this results a very highly restricted rotation about these bonds, giving rigidity to the polymer. The faces of the ribbonlike "struts" between the anthracenes are oriented nearly perpendicular to the plane of the macromolecular growth. This arrangement blocks face-to-face association between these planar struts, leading to greater IM. For the attainment of microporosity in network polymers, it appears that the requirement for the prevention of rotation about single bonds is unperturbed, presumably due to the network itself preventing structural rearrangement that could result in a collapse of the porous structure. Hence, the formation of rigid amorphous network polymers using anthracene monomer is compatible with obtaining highly microporous materials. Perhaps the clearest demonstration of IM is found for well defined rigid oligomers containing triptycenes as the concave unit. An interesting structure-property relationship is evident for these materials in that the longer the linear struts between the branch points, the lower is the porosity. And is likely related to a larger number of bonds with rotational freedom, which will reduce IM.<sup>10</sup>

### Nitrogen adsorption analysis

Nitrogen adsorption measurements of AMPs were measured, for example, the BET surface area of AMPs is relatively high, which is higher than the Trip-PIM<sup>16</sup> but less than the HCPs<sup>17</sup> as shown in Figure 2.

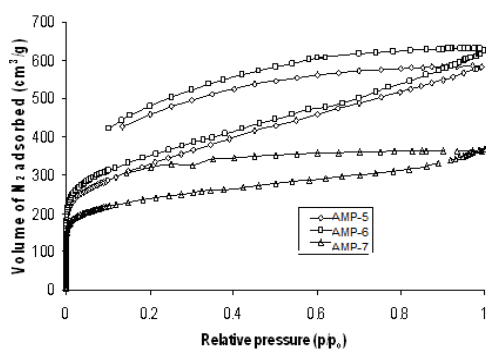


Figure 2: Nitrogen adsorption/desorption isotherm at 77 K for AMPs.

Table 1: <sup>a</sup>BET surface area of AMP (5-7)s calculated from nitrogen adsorption isotherm. The number in the parenthesis is the micropore surface area calculated using the *t*-plot analysis.  $PV_{micro}$  is the micropore volume. <sup>b</sup>Surface area calculated from the  $H_2$  adsorption isotherm using Langmuir equation at 77 K and 87 K. increase gradually with pressure increase. The isotherms are fully reversible and exhibit a sharp rise at low pressure region which is consistent with the physisorption of hydrogen on a microporous material. All the prepared AMPs show similar behaviors in their isotherm with a significant uptake at two different temperatures (Table 1). The adsorption/desorption isotherms clearly exhibit pronounced hysteresis up to low partial pressure, which is typically observed for microporous materials. Nitrogen uptake increases in the sequence AMP-5 < AMP-6 < AMP-7, this is reflected in the results of analysis by the (BET) method, which gave apparent surface areas of 750, 711, and 796  $m^2/g$  respectively

### Hydrogen adsorption

The main task is finding the potential of the prepared materials in storing considerable amount of hydrogen. For example, the hydrogen storage quantities for AMP-5 in a pressure range 0-100 bar (as shown in Figure 3).

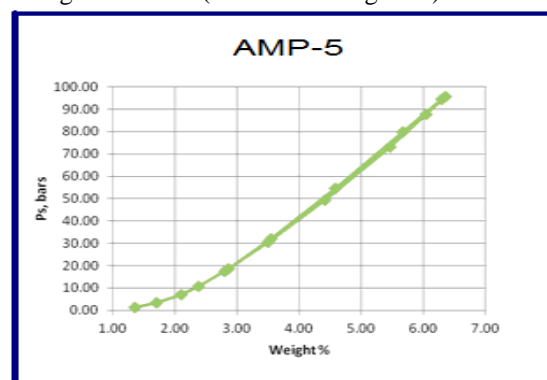
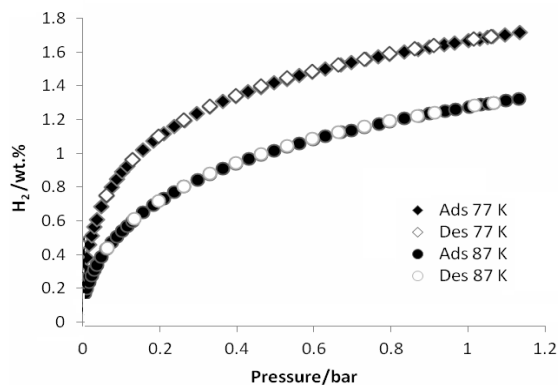


Figure 3. High pressure  $H_2$  adsorption capacity of AMP-5 (0-100 bar).

The Langmuir isotherm theory assumes monolayer coverage of adsorbate over a homogenous adsorbent surface of equal energy. The isosteric heat of adsorption, ( $Q_{st}$ ), for dihydrogen molecules on all samples was calculated from the adsorption isotherms at 77 and 87 K as shown in Figure 4. The chemical nature of the accessible surfaces and morphology of the pores have thus to be tuned to enable a high adsorption enthalpy. It has been already known that microstructure had a deep impact on hydrogen uptake which is further influenced by the geometry of the building units. So materials containing high electron rich sites were found to increase the hydrogen adsorption enthalpy. The combination of microporosity and chemical functionality of these AMPs are very promising for applications in the air purification, or separation. As compared to MOFs and similar metal containing porous structures, the concept of preparing hydrothermally stable AMPs having organic spacers along with predefined functionality allows them to extend in many adsorption applications. In order to attain good storage capacity, it will be necessary to design materials with greater accessible surface area and microporosity. The hydrogen adsorption isotherm measured at 77 K and 87 K and the calculations involve the Langmuir equation and *t*-plot analysis. This methodology avoids the problem of over counting the nanopores that is associated with the specific surface area measured by nitrogen adsorption. Figure 4 shows the hydrogen adsorption/desorption isotherms of AMP-6.



**Figure 4.** Adsorption/desorption isotherms at 77 and 87 K for AMP-6.

In addition, the adsorption is completely reversible and there is no significant hysteresis which can be correlated with the physisorption of hydrogen on a microporous material. The repeatability of the hydrogen adsorption was also checked and found to be constant even after the repeated cycles. The shape of the isotherm indicates that adsorption has not reached saturation and further significant hydrogen uptake could occur at higher pressures. The framework OFP-6 afforded a hydrogen storage capacity of 1.70 wt% at 1 bar and 87 K, which is comparable with the other reported microporous polymers. However, at 77 bars AMP-7 adsorbs nearly 1.55 wt% by weight of material.

#### Synthesis of AMP-7

To a solution of octahydroxy-anthracene (0.2 g, 0.21 mmol) and 2,3,5,6-tetrachlorophalonitrile (0.08 g, 0.43 mmol) in dry DMF (40 ml),  $K_2CO_3$  (0.35 g, 2.52 mmol) was added and heated to 100 °C for 48 h. Then, the reaction mixture was allowed to cool and precipitated in acidified water. The precipitate was filtered off and washed with deionised water and then with methanol. The purification was done by washed repeatedly with THF and methanol. The resulting AMP-7 is brown solid and dried in vacuum at 80 °C for 12 hrs (yield 80 %).

Yield 85%; m.p. > 300 °C; MS (EI): m/z (%) 1851(M<sup>+</sup>). IR/cm<sup>-1</sup> (KBr): 1788 (asym C=O, str), 1722 (sym C=O, str), 1366 (C-N, str), 744 (imide ring deformation). <sup>13</sup>C NMR (100 MHz): 169.7, 148.7, 145.3, 142.8, 141.5, 139.5, 138.2, 128.8, 121.6, 123.8, 115.8, 115.2, 104.6, 109.2, 55.8, 55.5, 42.9, 39.6, 15.5, 10.3, 8.6. CHN Calculated for C<sub>105</sub>H<sub>80</sub>F<sub>6</sub>N<sub>10</sub>O<sub>16</sub> (1851): C 68.02; H, 4.32; N, 7.56. Found: C, 67.70; H, 4.21, N, 7.22. BET surface area = 796 m<sup>2</sup>/g; total pore volume = 0.51 cm<sup>3</sup>/g.

#### Acknowledgments

I'm grateful for the facilities from Ministry of Education, Chemistry department Nano-Science club of Saad bin-Alrabee Alansari School and student, Dr.Nawaf El Dehany, Sabah Al-Ahmad Center for Giftedness and Creativity " Dr.Mohamed Rabie Alenezi, and ANALAB, College of Graduate Studies in Kuwait University,

#### Conclusions

In summary a series of imide-linked organic framework polymers with intrinsic microporosity Anthracene-based microporous polymers (AMPs), have been synthesized by the conventional dioxane forming reaction in flow injection method. These prepared AMPs exhibit high carbon dioxide uptake capacity at ambient and high pressure, which can be explained by the high concentration of narrowly distributed and fine-tuned micropores along with the better interaction with accessible surfaces featured by imide functionality,

leading to higher isosteric heat of adsorption (Q<sub>st</sub> : CO<sub>2</sub> 28-30 kJ/mol). The promising porous properties of AMPs may thus provide an outline for the design of more novel porous materials with improved gas storage capacity and applicable Q<sub>st</sub> based on the structural features of the prepared monomers in this work.

AMPs display a BET surface area reach to 796 m<sup>2</sup> g<sup>-1</sup>, and reversibly adsorb reach to 1.70 wt. % H<sub>2</sub> at 1.13 bar 77 K. The isosteric heat of adsorption about 7.4 kJ/mole. The enhanced microporosity, in comparison to other organic microporous polymers, originates from the macromolecular shape of the framework, as dictated by the triptycene units.

#### References

- 1- Saad Makhseed and Jacob Samuel J. Mater. Chem. A, 2013,1, 13004-13010
- 2-Fadi Ibrahim. Elixir Nanocomposite Materials, 62, 2013,17542-17548.
- 3-J.-L. Li and B.-H. Chen, "Review of CO<sub>2</sub> Absorption Using Chemical Solvents in Hollow Fiber Membrane Contactors," Separation and Purification Technology, Vol. 41, No. 2, 2005, pp. 109-122.
- 4-D. R. Paul and Y. P. Yampol'skii, "Polymeric Gas Separation Membranes", CRC Press, Boca Raton, 1994.
- 5-C. A. Hendricks, K. Blok and W. C. Turkenburg, "The Recovery of Carbon Dioxide from Power Plants," In: P. A. Okken, R. J. Swart and S. Zwerver, Eds., Climate and Energy, Kluwer Academic Publishers, Dordrecht, 1989.
- 6-J. P. Van Der Sluijs, C. A. Hendricks and K. Blok, "Feasibility of Polymer Membranes for Carbon Dioxide Recovery from Flue Gases," Energy Conversion and Management, Vol. 33, No. 5-8, 1992, pp. 429-436.
- 7-T. C. Merkel, H. Q. Lin, X. T. Wei and R. Baker, "Power Plant Post-Combustion Carbon Dioxide Capture: An Opportunity for Membranes," Journal of Membrane Science, Vol. 359, No. 1-2, 2010, pp.
- 8-Gh. Bakeri, A. F. Ismail, M. Shariaty-Niassar and T. Matsuura, "Effect of Polymer Concentration on the Structure and Performance of Polyetherimide Hollow Fiber Membranes," Journal of Membrane Science, Vol. 363, No. 1-2, 2010, pp. 103-111.
- 9-E. Favre, "Membrane Processes and Post Combustion Carbon Dioxide Capture: Challenges and Prospects," Chemical Engineering Journal, Vol. 171, No. 3, 2011, pp. 782-793.
- 10-R. Khalilpour, A. Abbas, Z. P. Lai and I. Pinnau, "Modeling and Parametric Analysis of Hollow Fibre Membrane System for Carbon Capture from Multicomponent Flue Gas," Processing System Engineering, Vol. 58, No. 5, 2011, pp. 1550-1561.
- 11-A. Brunetti, F. Scura, G. Barbieri and E. Drioli, "Membrane Technologies for CO<sub>2</sub> Separation," Journal of Membrane Science, Vol. 359, No. 1-2, 2010, pp. 115-125.
- 12-M. T. Ho, G. W. Allison and D. E. Wiley, "Reducing the Cost of CO<sub>2</sub> from Flue Gas Using Pressure Swing Adsorption," Industrial Engineering Chemical Research, Vol. 47, No. 5, 2008, pp. 1562-1568.
- 13-M. T. Ho, G. W. Allison and D. E. Wiley, "Reducing the Cost of CO<sub>2</sub> from Flue Gas Using Pressure Swing Adsorption," Industrial Engineering Chemical Research, Vol. 47, No. 5, 2008, pp. 4883-4890.
- 14-J. Kotowicz, T. Chmielniak and K. Janusz-Szymanska, "The Influence of Membrane CO<sub>2</sub> Separation on the Efficiency of a Coal-Fired Power Plant," Energy, Vol. 35, No. 2, 2010, pp. 841-850.

- 15-L. Zhao, E. Riensche, R. Menzer, L. Blum and D. Stolten, "A Parametric Study of CO<sub>2</sub>/N<sub>2</sub> Gas Separation Mem-brane Process for Post-Combustion Capture," *Journal of Membrane Science*, Vol. 325, No. 1, 2008, pp. 284-294.
- 16-K. Okabe, H. Mano and Y. Fujioka, "Separation and Recovery of Carbon Dioxide by a Membrane Flash Proc-ess," *International Journal of Greenhouse Gas Control*, Vol. 1, No. 1, 2009, pp. 1281-1288.
- 17-R. Wang, H. Y. Zhang, P. H. M. Feron and D. T. Liang, "Influence of Membrane Wetting on CO<sub>2</sub> Capture in Micro-porous Hollow Fiber Membrane Contactors," *Separation and Purification Technology*, Vol. 46, No. 1-2, 2005, 33-40.
- 18-J. Zou and W. S. W. Ho, "CO<sub>2</sub>-Selective Polymeric Membranes Containing Amines in Crosslinked Poly(Vinyl Alcohol)," *Journal of Membrane Science*, Vol. 286, No. 1-2, 2006, pp. 310-321.
- 19-X. Z. He and M.-B. Hägg, "Hollow Fiber Carbon Membranes: Investigations for CO<sub>2</sub> Capture," *Journal of Membrane Science*, Vol. 2006, pp. 310-321.
- 20-H.-Y. Zhang, R. Wang, D. T. Liang and J. H. Tay, "Modeling and Experimental Study of CO<sub>2</sub> Absorption in A Hollow Fiber Membrane Contactor," *Journal of Membrane Science*, Vol. 279, No. 1-2, 2006, pp. 301-310.
- 21-A. Gabelman and S.-T. Hwang, "Hollow Fiber Membrane Contactors," *Journal of Membrane Science*, Vol. 159, No. 1-2, 1999, pp.
- 22-M. Mavroudi, S. P. Kaldis and G. P. Sakellariopoulos, "Reduction of CO<sub>2</sub> Emissions by a Membrane Contacting Process," *Fuel*, Vol. 82, No. 15-17, 2003, pp. 2153-2159.
- 23-D. Shekhawat, D. R. Luebke and H. W. Pennline, "A Review of Carbon Dioxide Selective Membranes—A Topical Report," National Energy Technology Laboratory, United States Department of Energy, 2003.
- 24-R. Bounaceur, N. Lape, D. Roizard, C. Vallieres and E. Favre, "Membrane Processes for Post-Combustion Carbon Dioxidecapture: A Parametric Study," *Energy*, Vol. 31, No. 14, 2006, pp. 2556-2570.
- 25-E. Favre, "Carbon Dioxide Recovery from Post-Combustion Processes: Can Gas Permeation Membranes Compete with Absorption?" *Journal of Membrane Science*, Vol. 294, No. 1-2, 2007, pp. 50-59.
- 26-C. E. Powell and G. G. Qiao, "Polymeric CO<sub>2</sub>/N<sub>2</sub> Gas Separation Membrane for the Capture of Carbon Dioxide from Power Plant Flue Gases," *Journal of Membrane Science*, Vol. 279, No. 1-2, 2006, pp. 1-49.
- 27-S.-P. Yan, M.-X. Fang, W.-F. Zhang, S.-Y. Wang, Z.-K. Xu, Z.-Y. Luo and K.-F. Cen, "Experimental Study on the Separation of CO<sub>2</sub> from Flue Gas Using Hollow Fiber Membrane Contactors without Wetting," *Fuel Processing Technology*, Vol. 88, No. 5, 2007, pp. 501-511.
- 28-A. Mansourizadeh and A. F. Ismail, "A Developed Asymmetric PVDF Hollow Fiber Membrane Structure for CO<sub>2</sub> Absorption," *International Journal of Greenhouse Gas Control*, Vol. 5, No. 2, 2010, pp. 374-380.
- 29-U. E. Aronu, H. F. Svendsen and K. AndersHoff, "Investigation of Amine Amino Acid Salts for Carbon Dioxide Absorption," *International Journal of Greenhouse Gas Control*, Vol. 4, No. 5, 2010, pp. 771-775.
- 30-J. Kittel, R. Idem, D. Gelowitz, P. Tontiwachwuthikul, G. Parrain and A. Bonneau, "Corrosion in MEA Units for CO<sub>2</sub> Capture: Pilot Plant Studies," *Energy Procedia*, Vol. 1, No. 1, 2009, pp. 791-797.