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10th International Congress on Membrane and Membrane Processes

Advances in gas and liquid separation plus latest innovations in membrane materials

Reviewed by Xavier (Xian-Yang) Quek
Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading, RG4 9NH, UK

Email: xavier.quek@matthey.com

1. Introduction

Jointly organised by the Aseanian Membrane Society, the European Membrane Society and the North American Membrane Society, the 10th International Congress on Membrane and Membrane Processes (ICOM) was held at Suzhou, China from 20th to 25th July 2014. ICOM is a highly regarded triennial conference in the membrane community, attracting scientists from around the world for scientific dissemination and discussion on membranes. The 10th ICOM attracted approximately 1300 delegates representing 39 countries. The programme consists of four plenary lectures, 86 keynote lectures, 424 oral presentations (split into nine parallel sessions) and 662 poster presentations. With such a vast selection of presentations, only selected highlights on themes related to gas separation, liquid separation, polymeric membranes, inorganic membranes and novel membrane processes and applications are discussed in this review.

Further information on the 10th ICOM can be found on the conference website (1).

2. Gas Separation

The following challenges in applying membranes to large scale separations were highlighted by William Koros (Georgia Institute of Technology, USA) in his plenary lecture:

- Gas fluxes (flow rate per unit area) across polymeric membranes are two orders of magnitude lower than liquid fluxes
- Trade-off relationship between flux and selectivity is much higher for gas than liquid separation
- Kinetic diameter differences between molecules in gas separation are much smaller than for liquid separation.

Plenary Lectures

William J. Koros (Georgia Institute of Technology, USA)	Membrane Technology Pathways to Low Energy Intensive Large Scale Gas Separations
Yiqun Fan (Nanjing University of Technology, China)	Inorganic Membranes for Sustainable Industry Processes
Tai-Shung Chung (National University of Singapore, Singapore)	Polymeric Membranes for Clean Water Production and Osmotic Power Generation
Matthias Wessling (Rheinisch Westfälische Technische Hochschule (RWTH) Aachen University, Germany)	Geometry Matters

This section on gas separation will cover carbon dioxide removal, paraffin/olefin separation and hydrocarbon separation.

2.1 Carbon Dioxide Separation

A key observation from this conference is that there has been an increase in the use of carbon molecular sieves and membrane contactors for CO_2 removal (in both natural gas purification and carbon capture). In addition, there were several lectures which emphasised the need for better understanding of the use of membranes in a process.

Under high CO_2 partial pressure and in the presence of hydrogen sulfide (H_2S) in the stream, polymeric membranes are known to swell, causing deteriorated separation performance. Koros showed in his plenary lecture that cross-linking of polymeric membranes is effective in stabilising the membranes and preventing swelling. However further improvements in membrane performance can only be achieved using membranes with molecular sieving abilities such as carbon molecular sieves (CMS). The performance of a CMS membrane was shown to exceed the present upper bound of Robeson's trade-off graph.

Membrane contactors, which combine the advantages of membrane technology and solvent absorption, are a promising technology for CO_2 removal. Shiguang Li (Gas Technology Institute (GTI), USA) presented on a pilot scale study for post-combustion CO_2 capture using poly(ether ether ketone) (PEEK) hollow fibre membrane contactors. The membrane contactor GTI is developing can be used in both the absorber and the desorber section. Laboratory testing has found that the performance of the PEEK membrane contactor is not affected by impurities such as oxygen or oxides of sulfur (SOx) and nitrogen (NOx). Initial pilot studies were carried out using a slip stream from Joliet power station and future tests will be conducted at the National Carbon Capture Centre.

Christophe Castel (Université de Lorraine, France) used a flue gas slip stream from one of Compagnie Parisienne de Chauffage Urbain (CPCU)'s power plants as a feed to their membrane contactor. Commercially available polytetrafluoroethylene (PTFE) hollow fibre membrane from PolyMem and 30% monoethanolamine (MEA) solution was used in their membrane contactor. Their pilot study is still at a very early phase in comparison to GTI's work.

Emphasis on understanding membrane processes was reflected by a significant number of presentations dedicated to engineering studies on membrane processes.

A series of presentations by Membrane Technology and Research, Inc (MTR) on post-combustion carbon capture demonstrated the importance of understanding the processes in order to better utilise the membranes. Richard Baker (MTR, USA) emphasised the importance of pressure ratio. Through their studies, the typical economical pressure ratio range is about 5 to 10. Pingjiao Hao (MTR, USA) showed that combining a conventional CO_2 separation membrane with a gas/gas membrane contactor (**Figure 1(a)**) (2) is more effective for carbon capture than a standalone membrane unit. Xiaotong Wei (MTR, USA) showed that carbon capture from a natural gas power plant is more complex than from a coal power plant (**Figure 1(b)**) (3). This is due to significantly lower CO_2 concentration in the flue gas being emitted from a natural gas plant.

Numerous other presentations have also emphasised the importance of using process engineering tools to understand membrane processes at very different scales. Eric Favre (Université de Lorraine, France) used process engineering tools to design membrane processes and evaluate their economic benefits in carbon capture. Maria Grätz (Helmholtz-Zentrum Geesthacht, Germany) used simulations to investigate the effects of various process parameters for pre-combustion carbon capture using membranes. Iran Chary-Prada (Saudi Aramco, Saudi Arabia) investigated the configurations and economics for two- and three-stage membrane processes used for bulk acid gas removal from natural gas.

2.2 Paraffin/Olefin Separation

Separation of paraffin/olefin mixtures is one of the most challenging processes due to the small differences in the kinetic diameter. Several reports demonstrated promising progress in the separation of paraffin/olefin mixtures using inorganic membranes and facilitated transport membranes.

William Koros showed that polymer derived CMS membranes are effective for paraffin/olefin separation. The membrane was proposed to be used for debottlenecking of existing distillation processes. Thinner CMS selective layers can increase the flux of propylene through the membrane. Jerry Lin (Arizona State University, USA) has shown that thinner CMS membranes were prepared by coating the surface of α-Al_2O_3 support with γ-Al_2O_3. The smaller pores of γ-Al_2O_3 allow a thinner defect-free CMS layer to be prepared.

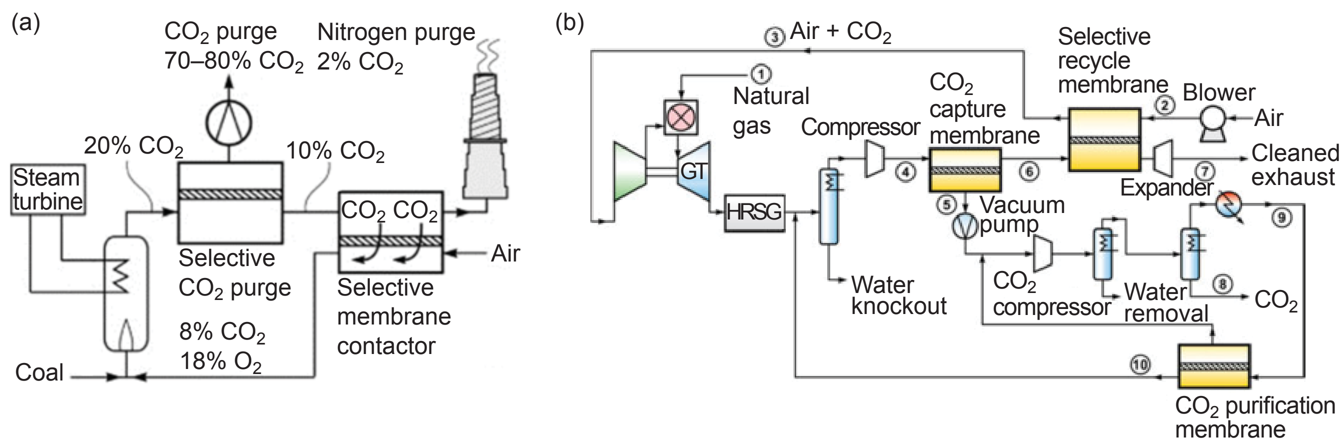

Fig. 1. Block flow diagram of MTR's proposed post-combustion carbon capture in: (a) an integrated gasification combined cycle power plant (Reprinted with permission from (2). Copyright 2014 Elsevier); and (b) a natural gas combined cycle power plant (Reprinted with permission from (3). Copyright 2013 American Chemical Society)

Due to their molecular sieving ability, zeolite membranes have also been investigated in paraffin/olefin separation. Masahiko Matsukata (Waseda University, Japan) showed that in a propane-rich stream, the propylene permeance and separation factor for zeolite membranes are better than the values reported for CMS. However membrane performance is strongly influenced by the feed composition.

Facilitated olefin transport membranes incorporate a reactive carrier (Ag^+) in the membrane for separation. The major technological hurdle for commercialising facilitated transport membranes is the stability of the Ag^+ carrier. Yong Soo Kang (Hanyang University, Korea) investigated membranes using Ag nanoparticles with positively induced charge, as a stable reactive carrier. An electron acceptor ligand is coordinated to the Ag nanoparticles to induce a positive change on the particles. These positively charged Ag nanoparticles, which are embedded into a polymeric matrix, show long term stability in olefin/paraffin separation.

2.3 Hydrocarbon Separation

Yuri Yampolskii (Russian Academy of Sciences) reviewed the membranes used for C_{2+} removal from natural gas. Rubbery membranes are commonly used in this application, where the current state-of-the-art membranes are polyacetylene type polymers. A recent development is a novel norbornene polymer membrane with a flexible Si-O group. Although selectivity of these novel membranes is lower than polyacetylene type membranes, the permeance is much higher. Despite high separation factors being observed for C_4/C_1 separation, the C_n/C_{n-1} separation factors for these membranes are very low (**Figure 2**) (4).

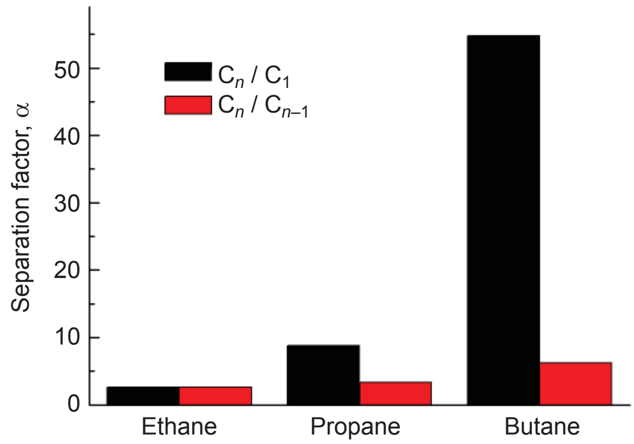

Fig. 2. Highest C_4/C_1 membrane separation, plotted from data reported in (4)

3. Liquid Separation

This section on liquid separation will discuss advancement in membranes for pervaporation, organic solvent nanofiltration and waste water treatment.

3.1 Pervaporation/Vapour Permeation Membranes

Pervaporation was first commercialised by GFT in the 1980s based on cross-linked poly(vinyl alcohol) (PVA) composite membranes. Wilfredo Yave (Sulzer Chemtech, Switzerland) presented the recent improvements made to the PREVAP™ membrane, which is a PVA composite membrane. The membrane was modified to improve its separation performance, stability and also lifetime. The major improvement made was to have multiple selective layers instead of a single layer as used in their previous generation of membranes.

Inorganic membranes have been investigated and used in pervaporation to avoid swelling which is often encountered by polymeric membranes. The plenary lecture by Yiqun Fan (Nanjing University of Technology; and Jiuwu Hi-Tech, China) discussed the use of polydimethylsiloxane (PDMS) supported on ceramic for pervaporation. The purpose of using a ceramic support is to constrain the swelling of the PDMS. Another pervaporation membrane supplied by Jiuwu Hi-Tech is a hydrophilic NaA zeolite membrane.

Masahiko Matsukata (Waseda University, Japan) shared his work on zeolite membranes for pervaporation in isopropyl alcohol (IPA) dehydration. Y-type zeolite and SSZ-13 tubular membranes were developed and tested on a bench-scale rig located next to an IPA production plant as shown in **Figure 3**. The product stream from the plant was used as a feed for the test.

Process engineering tools are essential to evaluate the benefits of using a membrane for separation. Masahiko Matsukata evaluated the process design and economic benefits for his studies on IPA dehydration using zeolite membranes as presented above. Three different methods of implementing membranes in an IPA dehydration process were considered. Results show that co-production of IPA with a membrane would yield a higher energy saving compared to the other methods.

Ivy Huang (MTR, USA) looked at applying pervaporation membranes to ethanol dehydration from a process engineering viewpoint. Various configurations were investigated to use membranes together with other unit operations. Heat integration within the membrane process and with other separation units was identified to be the key to reduce operating cost. Debottlenecking has been identified as a possible opportunity to implement membranes in bioethanol separation.

3.2 Organic Solvent Nanofiltration

Andrew Livingston (Imperial College, UK) presented on the use of membrane separation in organic liquids. The main challenges in organic solvent nanofiltration are to increase the stability of the membrane (chemical, thermal and operational), increase permeance and to obtain more precise separation. Stability can be enhanced by performing cross-linking or using polymers which are inherently stable in organics. A recent development is to prepare thin film composite membranes by interfacial polymerisation, followed by post-treatment to remove oligomers. This membrane was found to have higher flux and better molecular weight cut off rejection.

Cheryl Tanardi (University of Twente, Netherlands) presented on the use of polymer grafted ceramic membranes for organic solvent nanofiltration. A layer of γ-Al_2O_3 was coated on the α-Al_2O_3 support to provide more functional groups for grafting PDMS on to the support.

Ludmila Peeva (Imperial College) demonstrated the use of organic solvent nanofiltration in a continuous catalytic Heck coupling reaction, where a homogeneous catalyst is used. Different materials were investigated and PEEK was identified as the most suitable material.

Fig. 3. JX-Nippon Oil and Energy's IPA production plant and the bench-scale zeolite membrane located beside the plant (Image courtesy of Masahiko Matsukata, Waseda University, Japan (5))

The use of a membrane reactor resulted in a lower concentration of catalyst contamination in the product.

3.3 Waste Water Treatment

The plenary lecture by Neal Chung (National University of Singapore) was on the use of membranes for clean water production. Nanofiltration for heavy metal ion removal was achieved by using a dual charge membrane. This membrane comprises of a selective layer and support with opposite charges. A similar concept was used to synthesise a membrane with both hydrophobic and hydrophilic properties for membrane distillation, where the membrane flux was increased. A dual skin membrane with a selective layer for forward osmosis (FO) on one side and nanofiltration on the other side of a support was used for shale gas waste water treatment. The nanofiltration prevents fouling of the membrane due to the substrate becoming clogged by stabilised emulsified oil droplets. The advantages of using a combination of FO and reverse osmosis (RO) for desalination were also discussed.

Thomas Schiestel (Fraunhofer Institute for Interfacial Engineering and Biotechnology IGB, Germany) presented on the use of composite adsorber membranes. Polymers coordinated on hydrogel particles, which can adsorb neodymium, silver, copper and lead ions, were embedded in a microfiltration membrane. Stability of the membrane in five adsorption-desorption cycles was demonstrated.

4. Polymeric and Hybrid Membranes

4.1 Transport Properties

In the final plenary lecture of ICOM 2014, Matthias Wessling (RWTH Aachen University, Germany) showed the importance of membrane geometry for both the transport properties and the membrane performance. By introducing nanometre thick dots and striped structures to the surface of an electrodialysis membrane, concentration polarisation can be minimised. Another example shows the use of twisted finned hollow fibres in a membrane bioreactor, which improves the secondary flow and minimises the build-up of particles on the surface. When twisted spacers are used in ultrafiltration (UF), higher yield flux and also sharper molecular weight cut-off was obtained.

4.2 Membrane Materials

Zhenjie He (MTR) presented on MTR's development on perfluoropolymer composite membranes. Surface fluorination of polyimide membranes improves the membrane permeability and selectivity. However the performance of these surface fluorinated membranes decays during storage. MTR have recently developed a new perfluoropolymer membrane from fluorinated polymers commonly used in optical fibres. Compared to their existing membrane, these new membranes exhibit three times higher selectivity with comparable flux.

Mathias Ulbricht (Universität Duisburg-Essen, Germany) discussed the different methods to tailor the surface properties of polymeric membranes. One method is to synthesise the membrane from functionalised polymers or blend established membrane polymer materials with functionalised copolymers. Another method to introduce functionality into membranes is *via* post-synthesis functionalisation. This can be achieved by using ultraviolet (UV) radiation or using a copolymer with an attached macro-initiator.

Peter Budd (University of Manchester, UK) summarised the development of polymers of intrinsic microporosity (PIM) membranes. Many new PIMs have been developed but PIM-1 is still the most widely studied material. Chemical modification of the polymer precursor to introduce amines to PIMs was shown to be effective in increasing the CO_2 adsorption. UV and thermal treatment of PIM membranes is able to increase the selectivity while maintaining the flux. PIMs are also widely investigated in mixed matrix membranes (MMMs). It was found that the different forms of CC3 introduced into PIM-1 caused minor changes in free volume but resulted in significant change in gas permeation.

Cher Hon Lau (Commonwealth Scientific and Industrial Research Organisation (CSIRO), Australia) used MMMs as a means to improve the stability of super glassy polymeric membranes. By incorporating porous aromatic frameworks (PAF-1) into polytrimethylsilylpropyne (PTMSP), membrane ageing was prevented.

5. Inorganic Membranes

Inorganic membranes were shown to exhibit better separation rates, withstand higher temperatures and pressures and also display better resistance towards chemicals and moisture compared to polymeric membranes. However, inorganic membranes are expensive, difficult to process and prone to the formation of non-selective defects.

The higher cost of manufacturing inorganic membranes was addressed by Yiqun Fan (Nanjing University of Technology, China). Some of the methods used to reduce costs include co-sintering, hot compressive sintering and the use of more environmentally benign precursors.

In order to avoid the formation of non-selective defects in inorganic membranes, Aisheng Huang (Ningbo Institute of Material Technology and Engineering, China) used polydopamine (PDA) functionalised supports to synthesise zeolites and metal-organic framework (MOF) membranes. The adhesive property of PDA on the support favours nucleation and growth of uniform zeolites and MOFs on the support. Seeding of the parent zeolite or MOF on the support was not required. ZIF-8, ZIF-90 and LTA type zeolite membranes were synthesised using this method.

Miao Yu (University of South Carolina, USA) gave an overview on graphene and graphene oxide membranes. Graphene membranes show potential applications in both liquid and gas separation. A graphene membrane supported on polyamide was shown to prevent irreversible membrane fouling and also exhibit higher flux than polyamide membranes for oil/water separation. In gas separation, graphene membranes perform better in H_2/CO_2 separation compared to polymeric and zeolite membranes. One of the main challenges ahead for graphene membranes is to control the porosity. The stability of graphene membranes under real gas conditions is also poorly understood.

6. Novel Membrane Processes and Applications

6.1 Novel Membranes

One class of membrane which is considerably different from other membranes reported at ICOM 2014 are stimuli-responsive membranes, which have the ability to respond to a change in the environment. Liang-Yin Chu (Sichuan University, China) gave a general overview on this type of membrane, which contains an artificial smart gate where the presence of an external influence can open or close the pores of the material. The smart gate can be introduced before, during or after membrane synthesis. These membranes can be made to respond to temperature, pH, light, electric field, magnetic field, ions, chemical species and biological species. Membranes can also be designed to respond to more than one type of stimuli; dual, triple and quadruple stimuli responsive membranes have been reported.

6.2 Novel Membrane Processes

One of the novel membrane processes reported at ICOM is the cyclic pressure-vacuum swing permeation process described by Xianshe Feng (University of Waterloo, Canada). This process, as shown in **Figure 4** (6), is a non-steady state process which makes use of transient conditions to maintain high permeance through the membrane. This process uses a single pump to pressurise the feed and also to extract vacuum for permeate removal. The process switches between three modes, namely: (a) feed pressurisation, (b) permeate evacuation and (c) retentate venting. This process would be an advantage for a feed with low pressure.

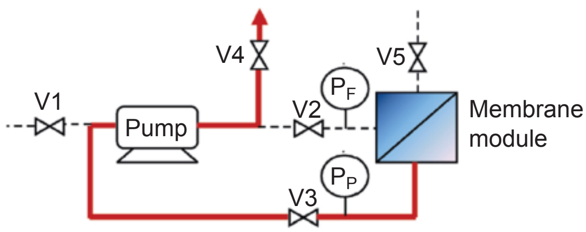

Fig. 4. Pressure-vacuum swing permeation process as reported in (6). Red line shows the path for permeate evacuation (Reprinted with permission from (6). Copyright 2014 Elsevier)

6.3 Novel Applications

This section summarises the use of membranes in less commonly discussed applications presented at ICOM2014 such as biorefinery, pharmaceutical and biopharmaceutical uses.

Mathias Wessling (RWTH Aachen University, Germany) proposed several areas where nanofiltration can be utilised in a biorefinery. One such use is for the recovery of oxalic acid. Oxalic acid is used to disintegrate lignocellulose to its individual fractions (lignin, hemi-cellulose and cellulose). Separation occurs *via* molecular weight-cut off and charge exclusion. Another use of nanofiltration in a biorefinery is to aid downstream recovery of itaconic acid, which is an important intermediate. Nanofiltration is used to concentrate the feed from the fermenter and itaconic acid can be recovered by crystallisation.

Andrew Livingston (Imperial College) demonstrated the use of organic solvent nanofiltration in liquid phase peptide synthesis for pharmaceutical applications. This permits the use of lower amino acid excess in each sequential coupling step, while allowing ease of separation. The membrane is used to remove unreacted amino acid and solvent between each step. This synthesis method can also be used to synthesise mono-dispersed heterobifunctional polyethylene glycol (PEG).

Dieter Melzner (Sartorius-Stedim Biotech GmbH, Germany) presented on the use of membranes for virus separation. Separation is *via* size exclusion and/or adsorptive mechanisms. Membrane chromatography is also used in virus processing, which can operate in two modes: (i) bind and elute mode, used to purify virus particles; and (ii) polishing mode, used to adsorb impurities while allowing the virus product to flow through.

7. Conclusion

The study and understanding of membranes and membrane processes continues to be an essential part of research to develop better fundamental understanding and allow possible industrial exploitation. This review covers emerging areas in gas separation and liquid separation and also recent innovations in membrane materials. Novel membrane processes and applications were also briefly discussed. However this review only represents a small portion of the work presented at ICOM 2014.

In general, there was a good mix of talks focusing on both new membrane material development and applications of membranes in processes. However, more attendees were observed in the material talks especially those on novel membrane materials such as graphene. Despite the massive scale and number of attendees, ICOM 2014 was very well organised with plenty of opportunities to network. The next ICOM will be held in San Francisco, USA, in 2017.

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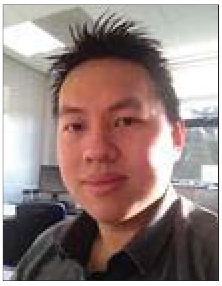

Xavier (Xian-Yang) Quek graduated with a BEng in Chemical Engineering from Nanyang Technological University, Singapore, and a PhD in heterogeneous catalysis from Eindhoven University of Technology, the Netherlands. In 2013, he joined the Low Carbon Technology group at Johnson Matthey Technology Centre, Sonning Common, UK. His current research focuses on the use of Pd and Pd-alloy membranes for pre-combustion carbon capture. He also has a wider interest in membranes and the use of membranes in various processes.

