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Towards commercialization: Challenges in scaling up lab scale membrane for field performance evaluation

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Abstract

Membrane technology is favorable for bulk CO_2 removal from natural gas due to several advantages such as simple operation, no chemical or moving parts, smaller footprint and weight over other technologies, and high reliability. It has led to massive fundamental research efforts in producing better membrane performance throughout the world. However, scaling up the lab scale membrane for field performance evaluation can be quite challenging. The challenges include consistency in membrane quality for large volume process, membrane module design and fabrication techniques, harsh operating conditions with field contaminants fluctuation, and process facilities requirement for offshore application. All the scale up challenges will need to be properly addressed diligently in order to ensure the membrane can be successfully applied as per the intended field specification.

Keywords: CO_2 removal, scale up, field performance evaluation, contaminants, robustness, durability.

INTRODUCTION

The increasing worldwide energy demand have directed the attention of oil and gas companies towards developing of high CO_2 gas fields (Ahmad *et al.*, 2012). CO_2 will need to be removed from contaminated natural gas to enhance its calorific value or energy content, to decrease the volume of gas been transported via pipeline, reduce corrosion issues, and prevent atmospheric pollution (Adewole *et al.*, 2013; Zhang *et al.*, 2013; Mushtaq *et al.*, 2013). Gas separation membrane technology competes with other types of separation technology namely absorption, adsorption, and cryogenic (Bernardo and Clarizia, 2013) for natural gas bulk CO_2 removal. Depending on the field development concept, membrane technology is being considered for the CO_2 percentage of more than 30% if the permeate is needed in the gas form for flaring, utilization, or conversion to valuable product. This application of membrane technology is due to its simplicity, reliability, modular, energy efficient, and compact module design (Sridhar *et al.*, 2014; Zhang *et al.*, 2013) which is crucial for offshore operation. For bigger flowrate, membrane will be suitable technology to be applied even for lower CO_2 content.

A number of large gas separation membrane systems have been installed on offshore platforms at CO_2 oilfield flood operations or where site specific factors particularly favor membranes (Baker, 2002). Gas separation membrane works on the principle that some gases are more soluble and pass more readily through polymeric membrane than other gases (Ahmad *et al.*, 2012). According to Lokhanwala *et al.* (2005) for absorption and adsorption, the high pressure towers including regeneration are expensive, large and require thick-walled heavy vessel. In natural gas dehydration, only a few hundred parts per million (ppm) of water must be removed, so this adsorption or absorption system are relatively compact and low in cost. However, for removal of CO_2 from natural gas that contain more than 10 % CO_2, large amount of sorbent need to be used in large tower. On top of that, it requires high maintenance cost for the cyclic process, high energy requirement, and incur some operational issues such as foaming, flooding, entrainment, weeping, overloading, corrosion, and sorbent degradation (Lokhandwala and Baker, 2005; Zhang *et al.*, 2013).

Cryogenic on the other hand, becomes very outstanding if the CO_2 percentage is high more than 50 % and the CO_2 product is produced in liquid form for cost-effective sequestration. The advantage of the CO_2 liquid product could offset its huge vessel and energy intensive operation which make this technology become attractive in order to reduce the greenhouse gas emission. By pumping and storing the highly concentrated bulk CO_2 deep underground in the depleted reservoir or aquifer, it makes the greenhouse gas emissions reduction more feasible (Zhang *et al.*, 2013).

There are three main aspects that are essential in determining the success of membrane technology application. The most important one is the membrane material selection, formulation, and fabrication improvement studies, followed by membrane module design, and finally the system design and engineering (Bernardo and Clarizia, 2013) which plays a vital role to come out with the compact process system scheme (Sridhar *et al.*, 2014). Excellent membrane material should posses good separation performance with reasonable high permeability, high durability and robustness, good mechanical strength, thermally and chemically stable, and cheaper production cost (Mohshi *et al.*, 2013; Mushtaq *et al.*, 2013).

The primary aim of this review paper is to provide an overall understanding on the scale up complexity, challenges and the needs to explore furthermore than the basic fundamental at the single gas at low pressure stage. The emphasize should be more on the membrane fundamental behavior when exposed to multicomponents feed stream with multiple impurities at higher pressure.

MEMBRANE SCALE UP PROCESS

In the membrane development process, there are a lot of steps involved. The most important one is membrane material selection. It can be either glassy or rubbery type, organic, inorganic, or both, where the combination is called Mixed Matrix Membrane (MMM). MMM is characterized by dispersing the inorganic material into the continuous phase of polymeric material *et al.*, 2013). The commercial market for CO_2 separation is currently dominated by organic or polymeric membranes due to their relatively low manufacturing cost, processing ability, and well-documented research studies (Zhang *et al.*, 2013). In polymeric membrane formulation, concentration and ratio of polymer, solvent/s, non-solvent and additive will be determined and there are lots of literature on this key area of studies reported in the publication.

Next, the form of membrane need to be selected either dense, asymmetric, or composite where suitable fabrication method parameters either using spinning or casting need to be extensively defined. Manufacturing process of these types of membranes are different, where dense membrane production is using dry process, asymmetric is using wet process, and dry/wet process is used to produce ultrathin defect-free membrane. The new composite membrane is produced using other techniques like coating, dip-coating, or co-extrude spinning process to form dual-layer membrane (Julian and Wenten, 2012). The membrane form that is most commonly used for gas separation due to higher permeance rate is asymmetric membranes which composes of selective layer where the separation takes place and porous substrate as a support with minimal mass transfer resistance (Zhang *et al.*, 2013).

After the membrane has been formed, it needs to be weaved for hollow fibers, made in the form of envelope for spiral wound, and goes through post-treatment before it can be tested and characterized. Next, the fibers will be bundled to its optimum scale up size where study on epoxy formulation, curing conditions, machining techniques, and element design are required. Referring to Fig. 1, Computational Fluid Dynamic (CFD) simulation is conducted to ensure good flow distribution inside the membrane element and casing. From the study, optimized design will be finalized where the dead end area, non-homogeneous flow and flow concentration should be minimized by adding feed flow distributor, baffle and other internals design. Optimum flow pattern either cross flow, counter current, or co-current will also need to be analyzed (Ahmad *et al.*, 2013). Finally, process simulation on the pretreatment requirement and membrane arrangement are to be finalized in order to meet project techno-economic and product specification requirement for field testing. Different commercial process simulators are available to evaluate the operating conditions and optimize the design configurations which offer an easy and time saving way to examine an entire process. Among the important process parameters to be studied are flow rate, operating temperature, operating pressure, pressure ratio (between the feed and permeate pressure), composition, and stage cut (ratio of permeate to feed flowrate) (Ahmad *et al.*, 2012).

All gas separation membrane module types developed so far are mainly based on two general geometries, flat sheet in the form of plate and frame or spiral wound and tubular in the form of hollow fiber which the latter gives the highest surface area per unit volume with packing density of 10,000–30,000 m2/m3 (Sridhar *et al.*, 2014). For high pressure operation, the high performance spiral wound modules can compensate its low surface area and high cost, as compared to hollow fiber module. This makes both configurations become relevant for natural gas bulk CO_2 removal (Lokhandwala and Baker, 2005).

The processes described above comprise more than hundred parameters to be analyzed within the specific ranges of the target application. Therefore, it takes quite a long time for a new membrane invention to be applied successfully in the intended field application since it requires vast experience and skills to bring it to further steps.

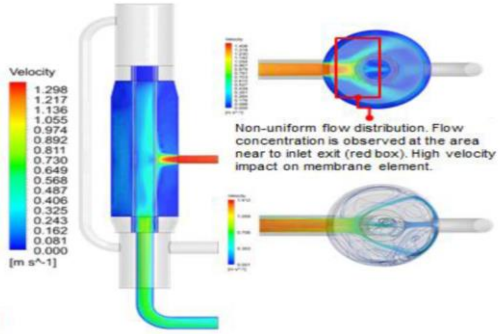

Fig. 1 Membrane element design hydrodynamic study.

Scale up testing flow

After the membrane fabrication completed, the fiber will be first tested using single gas at low pressure in order to gauge the polymer performance potential. The measurement is being done in term of membrane ability to permeate a gas which is called permeability and the ability of membrane to separate two gases namely selectivity. The selectivity can be defined further in term of diffusion which is proportional to molecular size kinetic diameter and solubility or sorption which is proportional to gas condensability (Lokhandwala and Baker, 2005). Both these kinetic and thermodynamic parameters have been studied extensively by researchers in order to understand on the factors that might effect its values stability throughout the long term operation.

If single gas test, surpass the membrane performance target, next the fiber will be tested for pressure durability using static pressure test method. This testing will determine the highest pressure that can be applied to the newly fabricated fiber where it must be able to return to its original performance after the testing been reversed, as can be seen in Fig. 2. The lowest three (3) lines show that the membrane cannot return to its original performance while the highest line illustrates the ability of that membrane to return to its original performance after been subjected to high pressure testing.

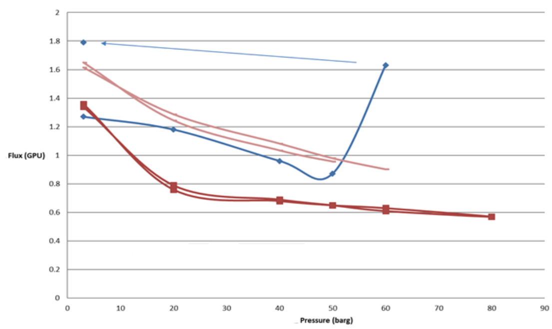

Fig. 2 Membrane static pressure test result.

In order to ensure that the membrane bundle can withstand the harsh operations at offshore, the membrane module is then subjected to cyclic process to simulate trips and unplanned shutdown where the membrane life can be determined. The test then proceeds with durability or aging test, which the membrane will be undergoing continuous 24 hours testing for certain defined duration until it reach plateau trending. If the membrane can pass all these series of testing and still maintain the required stable performance, it can be considered ready for the next scale up stage.

Membrane performance is important in term of its selectivity value which determines the product purity and hydrocarbon loss while permeance will determines the productivity which will relates to membrane area and footprint requirement. The trade off between permeability and selectivity in conventional membrane polymers was first evidence by Robeson in 1991 and then updated in 2008 illustrating the progress achieved by polymer science for the main gas separations (Bernardo and Clarizia, 2013). Among these two parameters, permeance is very important to be maintained at high value throughout the series of testing, since it will be very much affected during the operation through aging and compaction. The permeance number will have effect to the membrane productivity, membrane area required for a given separation, footprint, and cost. Selectivity is usually not much affected and will increase slightly for the aged membrane due to densification of the membrane layer. Hence, lots of effort need to be concentrated in increasing the membrane permeance value to the highest possible number. To obtain high permeation rates, the selective skin layer must be fabricated to be extremely thin around 0.1 micro meter and possibly of using new custom made synthesized polymer to form the thin skin of composite membrane (Baker, 2002).

At the same time, membrane characterization will also be conducted in order to understand the behavior or characteristic of the newly formulated membrane. Field Emission Scanning Electron Microscope (FESEM) image as shown in Fig. 3 will be used in order to understand the surface and cross-sectional morphology of the membrane, to study the microstructure at the skin and support layer, and to determine the membrane thickness (Bhargava *et al*., 2014). This explains why it posses the characteristics in term of permeance and selectivity. Other characterization methods that can be used are Thermo Gravimetric Analysis (TGA) to measure the amount and rate of change in the weight of material as a function of temperature, Differential Scanning Calorimetry (DSC) for determination of thermal behavior and glass transition temperature (Tg), Fourier Transform Infrared Radiation (FTIR) for determination of functional groups present in the substance, intermolecular interactions, and extent of modification induced, and Tensile Machine to assess tensile strength of the fiber produced (Bhargava *et al*., 2014) which can be correlate to its mechanical strength.

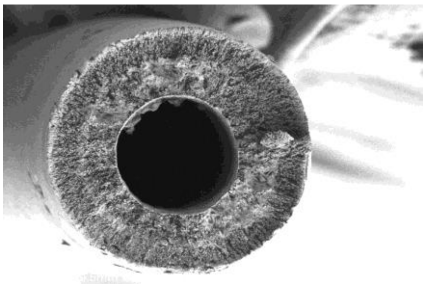

Fig. 3 FESEM image to check the membrane morphology.

SCALE UP CHALLENGES

The scale up challenges faced can be categorized into several development stages. As a start, the material screening criteria need to be defined properly such as the suitable polymer material for the target application, its performance, compatibility with other polymer for blending (if needed), compatibility with solvent and non-solvent for dilution, easiness to source the material, and screening cost. It is very useful to note that, permeability and selectivity are not the only criteria used to make commercial membrane, but to include the ability to form stable, thin, low cost membranes that can be packaged into high surface area modules (Baker, 2002).

In order to separate a particular component in a particular feed mixture, the polarity of one components must be close to the polarity of the membrane (Sridhar *et al.*, 2014). Polarity is one of the polymer properties that contribute considerably to the membrane separation performance specifically via diffusivity factor which is very dependent on the nature of the polymer.

The solvent chosen to dilute the polymer must be safe for mass manufacturing to avoid handling issues to the workers and lengthy waste management approval and procedure. In addition, cost element also need to be considered for the formulation studies that require exotic and expensive material. This will later makes the mass production becomes complex, time consuming, and requires high energy for its synthesis methodologies. On top of that, ease of processing, chemical and thermal resistance, pressure durability, mechanical strength, and many others (Sridhar *et al*., 2014) are the parameters that also need to be evaluated starting from the early stage.

During the spinning process, the membrane must be fabricated within less than 5 % deviation. This will create challenges if the manufacturing system is not fully automated with precision engineering where it must be handled by a very skillful worker. The uniformity of size and transport properties of the fibers in the bundle (Bernardo and Clarizia, 2013) is important to ensure no weak point exists in the membrane element which will cause defect and leak. After the membrane has been spun, it will undergo weaving, post-treatment, and drying process where the membrane structure will be fixed. The solvent post-treatment, chemical and thermal crosslinking also can be very challenging for the mass fiber production which will incur more time and cost to the production process.

Other than the normal low pressure single gas testing, scale up will require extensive testing as described in the previous section. Detail investigation in term of robustness of membrane during harsh operating conditions which will cause the membrane to have swelling, shrinkage, aging, plasticization, and compaction issues need to be understood. Plasticization in membrane gas separation processes is defined as pressure dependent phenomena caused by the dissolution of certain penetrants within the polymer matrix which disrupts the chain packing and enhance inter-segmental mobility of polymer chains (Adewole *et al.*, 2013). This causes the CO_2 permeability to increase as a function of pressure while the selectivity reduce, resultant from higher CH_4 permeance in the mixed gas experiment relative to the single gas experiment (Zhang *et al.*, 2013).

Membrane element fabrication is the next crucial step in order to ensure the weaved fibers is glued together surrounding the central core. Epoxy formulation, curing conditions, and machining techniques are among the area that need to be studied during scale up activities. In addition to that, membrane module element and casing design including its hydrodynamic studies are also important aspect to look at in order to ensure the success of the deployment stage.

FIELD CONTAMINANTS

Gas field contaminants from wells pose challenges to the membrane fiber material. Among the contaminants are CO_2, H_2S, N_2, H_2O, Hg, heavy hydrocarbon, and aromatics (Baker, 2002). Depending on the polymer material characteristic, it can be very much affected with certain contaminants and robust to the other. Other than the effect to the membrane polymer material, the presence of these impurities reduces the calorific value of natural gas, causes hydrate formations and corrosion issues (Adewole *et al.*, 2015).

Chemical and thermal resistance, hydrophobicity, hydrophilicity, plasticization resistance, glass transition temperature are among the membrane criteria investigated to ensure membrane robustness to field contaminants. According to Lokhanwala *et al.* (2005) all these contaminants including entrained oil mist, fine particles, CO_2 , BTEX (Benzene, Toluene, Ethylbenzene, Xylene) aromatics, and heavy hydrocarbon vapors can easily stick on the membrane surface and plasticize it which simultaneously degrade the membrane performance permanently. The absorbed contaminants will swell and dilate the polymer, hence cause reduction in polymer glass-transition temperature (T_g) and the mobility (size) term in the selectivity equation. BTEX aromatics concentrations of 200 to 1000 ppm can reduce the membrane performance by 30 to 50%. This is the reason why the performance of the membrane operating in real field is always found to be lower than commonly found in the literature that usually test using single gas at low pressure. High pressure natural gas that contain plasticizing gas components will in reality give lower membrane performance value during real application (Baker, 2002). This value is lower than the best upper bound materials found in the Robeson plot which used single gas at low pressure test data for comparison of permeability and selectivity data (Lokhandwala and Baker, 2005). Achieving good separation performance while maintaining good productivity for long term operation, plasticization and physical aging resistance, and conditioning remained as pivotal problems that need to be resolved for actual field application of membrane (Adewole *et al.*, 2013).

In order to overcome plasticization issues, high cost pre-treatment system will be designed in order to remove the feed gas contaminants such as using separator to remove liquid, adsorbent to remove water, heavy hydrocarbon and BTEX, cooler to remove heavy hydrocarbon, particle filter to remove dust together with particulate, and coalescing filter to remove mist. Some of the polymer material, cannot withstand the condensing liquid which will be present when the gas been permeated. Therefore, pre-feed heater will also be installed in order to avoid condensation to happen. Joule Thompson (JT) cooling happen in the membrane during the CO_2 removal, makes the residue temperature become lower. Heavy hydrocarbons which are retained and concentrated in the residue after the CO_2 been removed causes the phase envelope to shift to higher temperature (Lokhandwala and Baker, 2005). These two effects will make the gas reach the temperature where the hydrocarbon gas in residue reach their saturation values and condensation will occur. Temperature drop due to JT effect and pressure drop across the membrane cause the change in membrane permeance (Ahmad *et al.*, 2013) while condensation will affect the membrane material which will reduce the overall membrane performance.

On top of that, the glassy polymer have another issue which is compaction and physical aging which make the polymer chains to slowly relax into a preferred higher density hence lower permeability. Further research is needed in order to minimize the membrane compaction and aging issues during operation which will limit the membrane lifetime.

OFFSHORE APPLICATION DESIGN LIMITATION AND MEMBRANE ADVANTAGES

For offshore application, acid gas removal technology need to meet a few design criteria in order to be technically and economically attractive. First and foremost, the technology must be able to meet the pipeline product specification and have high hydrocarbon recovery or low hydrocarbon loss. Secondly, the technology should have smaller footprint as compared to the others where it require less space and weight which will give saving in term of platform structure cost. Next, the economic feasibility in term of capital and operational expenses to be further assessed in detail. The technology availability, simplicity, reliability, operability will also be considered during the selection process. In addition, the attractive technology is the one who require low energy consumption, less maintenance, no rotating equipment required, have minimal environment impact and can cater for wide range of feed gas pressure, compositions and flow rate fluctuation.

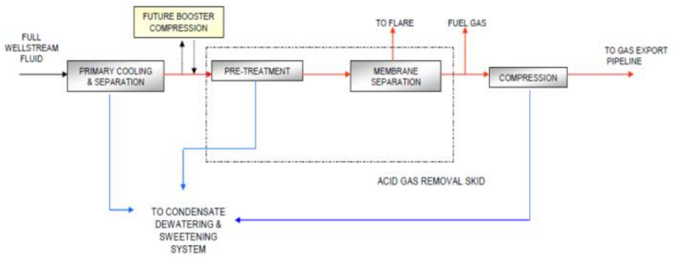

Fig. 4 Typical offshore process system.

All of the above requirement, can be fulfilled by polymeric membrane technology since it is light, relatively cheap and can have high turndown ratio. Long membrane lifespan which means less replacement needed and minimal maintenance requirement will leads to low opex for this technology. One more extra bonus point for membrane technology will be its ability to co-remove CO_2, N_2 and H_2S gases where this can contribute to cost and space saving for the overall platform design.

Membrane system can be design in a few steps in order to meet the product specification as per the pipeline requirement. Additionally, the membrane can be designed to meet flare requirement by using single stage design or to minimize hydrocarbon loss by using dual stage design with additional cost and footprint of compressor. For onshore process, dual stage design can be very attractive however for offshore process the advantage of recovering the hydrocarbon cannot be offset by the additional cost, power and footprint required by the big compressor addition. Fig. 4 shows a typical offshore process where the full wellstream fluid from the reservoir will flow through the primary cooling and separation before it is passed to pre-treatment, membrane separation, and compression for sales gas to be exported via pipeline. In this case, acid gas removal skid consists of pre-treatment and single stage membrane separation system only.

Detailed comparison study will need to be done in order to analyze the advantages of high operating pressure application. While riding the energy saving from wells pressure, the analysis in term of the need to have high rating pipe and equipment, higher booster compressor requirement while reducing export compressor pressure will need to be investigated properly. According to Adewole *et al*. (2013), increased pressure means that the average CO_2 concentration would be higher throughout the membrane, which in turn increases the chances of plasticization which affect the membrane performance and long term stability. This means that the membrane process design cannot be model by assuming constant membrane performance. The permeability coefficient of gases at higher feed pressure usually deviates from dual mode sorption model due to plasticization of polymer chains (Adewole *et al.*, 2015). Membrane with higher plasticization pressure is needed since its can maintain the selectivity better on high CO_2 feed concentration or on high operation pressure application (Julian and Wenten, 2012).

CONCLUSION

Tremendous focus on the membrane material development using single or binary gas testing have been done. Several approaches have been suggested and investigated such as invention of new membrane material such as graphene oxide and Polymer of Intrinsic Microporosity, PIM-1 (Ho and Li, 2016), thermal treatment, polymer blending and modification, copolymer, grafting, cross-linking, mixed matrix membrane, inorganic membrane, novel manufacturing or spinning techniques, and many others (Adewole *et al.*, 2013; Julian and Wenten, 2012; Mushtaq *et al.*, 2013). New material that is needed to be synthesized with complex methodology will incur high cost and complexity. In the other hands, mixed matrix and inorganic membrane still have some fundamental issues that need to be solved to enable mass production of defect free membrane that can be commercialized at cheaper cost. Although MMM has proven an enhancement of selectivity, it was noticed that most of them have poor adhesion between organic matrix and inorganic particles (Mohshim *et al.*, 2013; Mushtaq *et al.*, 2013). Hence, the industry is mainly focusing on the polymeric membrane studies. However, scale up fundamental knowledge and issues are still not fully understood for a complex mixture consist of multicomponents with contaminants at high pressure. This knowledge is very crucial for the scale up of membrane technology which can help to expedite the deployment and commercialization of numerous new polymer membrane invented in the literature. Understanding of the real field application conditions and limitations are needed to ensure the numerous academia studies can be exploited for real field application. Contaminants at field which have severe effects to the membrane performance need to be evaluated in the effort to develop more robust membrane that can reduce the intensive pre-treatment requirements. In addition, the membrane that been newly formulated also need to have stable long term high permeability in the presence of complex and aggressive feed without compromising its selectivity throughout the membrane life (Adewole *et al.*, 2013; Zhang *et al.*, 2013; Julian and Wenten, 2012). Last but not least, study on element and module hydrodynamic study need to be intensify since it is one of the area that is not fully understood on its contribution to the membrane performance, robustness, and durability.

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