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Development of High-Performance Polymer Membranes for Hydrogen Separation and Purification in Petroleum Refineries in Nigeria

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ABSTRACT

This study on Development of High-Performance Polymer Membranes for Hydrogen Separation and Purification in Petroleum Refineries in Nigeria has been made to qualitatively understand membrane formation via the phase inversion method (immersion precipitation) and the effects of spinning and processing conditions on membrane morphology in order to develop hollow fiber membranes with good combination of permeability and selectivity for hydrogen recovery and purification. The trade-off of permeability and selectivity is the main hurdle faced by polymeric membranes. In this work, membranes with adequately high fluxes of the more permeable components (hydrogen and carbon monoxide, respectively) and sufficient selectivity have been developed. However, there is a significant improvement over current commercial membranes used for hydrogen separation and purification cost associated with the application of membrane technology. Consequently, the study provides a key approach to meet the increased demand of hydrogen (for hydrotreating, hydrocracking or hydrodesulfurization processes) considering the environmental regulations.

Keywords: *High-Performance Polymer Membranes, Hydrogen Separation and Purification, Petroleum Refineries, Hydrogen recovery, polyimide, polysulfone*

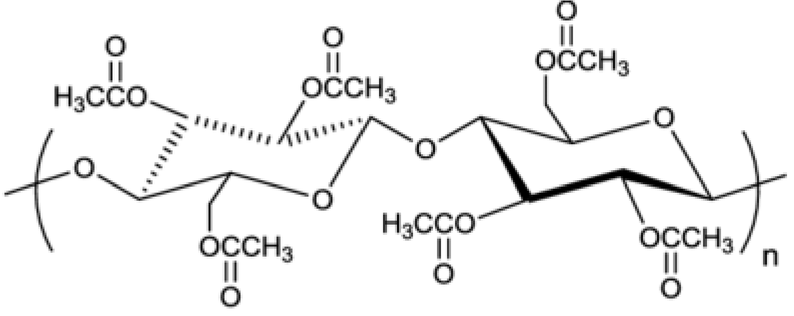
INTRODUCTION

The progress in membrane science and technology was accelerated during the 1980s by the development and refinement of synthetic polymeric membranes. Membrane gas separation emerged as a commercial process on a large scale during the 1980s (Abedini and Nezhadmoghadam, 2010). During this period, significant progress was made in virtually every aspect, including improvements in membrane formation processes, chemical and physical structures, configuration and applications (Pandey and Chauhan, 2001). Since the success of the membranes prepared by Loeb and Sourirajan in the early 1960, many studies have been carried out to understand the phenomena involved in the formation of solution-cast membranes (Loeb and Sourirajan, 1962). The majority of polymeric membranes since then have been prepared by controlled phase separation of polymer concentration. The concentrated phase solidifies shortly after phase separation and forms the membrane. Several kinetic aspects have been studied to interpret the morphologies. The thermodynamic approach by Strathmann et al., (1975, 1985); Wijmans**,** Kant, Mulder and Smolders (1985) provides a mechanistic view of membrane formation. The precipitation kinetics were related to the membrane properties and morphology by Reuvers (1987) who designates instantaneous and delayed demixing as a cause for porous and dense skin membranes, respectively. Phase separation of polymer solutions for porous membranes can be induced in several ways. They include (a) thermally induced phase separation (TIPS) (b) air casting of a polymer solution (c) precipitation from vapour phase and (d) immersion precipitation. Phase diagrams have been used to predict whether a solution of a certain polymer in a particular solvent is suitable for membrane formation or not. Binary phase diagrams – showing the phase boundaries as a function of temperature and composition – provide information on the thermally induced phase separation process. Thermal-isothermal phase diagrams are useful for the prediction of the phase transitions that could occur when phase separation is induced according to the air casting of a polymer solution, preparation from vapour phase and immersion precipitation (Pandey and Chauhan, 2001)**.** These phase diagrams provide information on the phase transitions, a polymer solution can undergo during the formation of a porous membrane. An equilibrium phase diagram provides a map for the different phase transitions that are favoured thermodynamically. The kinetics of the phase separation process determines whether the thermodynamically favoured transition will occur or not.

Over the last 30 years, polymer membrane has developed into a feasible industrial process for gas separations. During this time, several polymers (Figure 1) have been established as common gas separation membranes (Sanders *et al*, 2013). The majority of the commercially available membranes are produced by the so-called phase inversion process, starting from a polymer solution which is precipitated in a non-solvent coagulation bath (Broens et al., 1980). Many of the currently available commercial polymer membranes can be operated over a relatively wide temperature range (-20-150^{0}C) and can withstand pressure differences of up to 2000psig (Pinnau and Freeman, 1999)**.** According to Mulder (2000), most commercially available membranes are prepared by immersion precipitation: a polymer solution (polymer plus solvent) is cast on a suitable support and immersed in a coagulation bath containing a non-solvent. Broens *et al.* (1980) state that the resultant membranes prepared in this way have an asymmetric structure, that is to say, a very thin more or less dense skin is supported by a porous sublayer of the same material. Precipitation occurs because of the exchange of solvent and non-solvent. Synthetic membranes, according to Pinnau and Freeman (1999), have been used successfully in a wide variety of large-scale industrial applications. The membrane structure ultimately obtained results from a combination of mass transfer and phase separation (Mulder, 2000)**.** The technique of producing membranes by the phase inversion method has reached a high degree of reproducibility. This development has been sustained by the efforts to elucidate the mechanism of membrane formation (Broens et al., 1980). The rapid adoption of membrane in industry resulted from breakthrough developments in membrane materials, structures, and large scale production methods. To be useful in an industrial separation process, a membrane must exhibit at least the following characteristics (Pinnau and Freeman, 1999):

- High flux
- High selectivity (rejection).
- Mechanical stability.
- Tolerance to all feed stream components (fouling resistance).
- Tolerance to temperature variations.
- Manufacturing reproducibility
- Low manufacturing cost.
- Ability to be packaged into high surface area modules.

However, many membranes show a decline in separation performance (flux and/or selectivity) over time and must, therefore, be replaced on a regular basis. In particular, fouling, swelling or even degradation of the membrane limits the long term use of many current membrane types (Pinnau and Freeman, 1999). Membranes gas separation (MGS) has been introduced as a state of the art technology for gas vapor separations in the petroleum industry. In general, the techno-economical superiority of the method was demonstrated, especially at low to moderate scales of the current industrial plants, compared with the other related conventional methods such as absorption and cryogenic separations.



cellulose triacetate (CTA)

Figure 1: Structure of the three polymers are taken from Sanders et al, 2013

Despite decades of systematic efforts, it has proven elusive to synthesize polymers that combine the highly desirable properties of high permeability and high selectivity (Matteucci, Yampolskii, Freeman and Pinnau, 2006). From a qualitative viewpoint, the existence of permeability and selectivity trade-off relations is most easily understood from a free-volume view-point. The most typical way to significantly enhance the permeability of glassy polymers, such as those commonly considered as gas separation polymers, is to change the chemical structure by introducing packing-disrupting units into the polymer backbone, thereby increasing the free volume (Stern *et al*, 1989).

The idea of an “Upper bond” originally introduced by Robeson in 1991 is the carefully modulated balance between permeability and selectivity. This proposed upper bound provides insight into the maximum selectivity that is attainable for a given membrane permeability while using polymeric membranes for a given composition of gases in the H_2 feed stream.

Over the past 25 years, substantial progress had been achieved in developing polymeric membranes for hydrogen purification (Ockwig and Nenoff, 2007). However, much remains to be done before such membranes become a commercial reality. Advanced polymeric membranes with improved selectivity, diffusivity, H_2 fluxes and permeabilities are being developed. A wider range of operating conditions, specifically temperature and pressure, in addition to higher chemical resistance to hydrocarbons and other aggressive feed streams are all important properties. Cross-linkable polymers show promise in addressing some of these concerns; however, there is still a lot of research needed with those materials.

MATERIALS AND METHOD

The Department of Petroleum Chemistry, American University of Nigeria, Yola has an ongoing effort to produce novel and improve existing polymers for membranes. These polymer membranes are initially tested in the laboratory followed by pilot testing on slipstreams of actual gas plants and then installed in full-scale plants. The department of petroleum chemistry is developing both advanced spiral-wound and hollow fiber membranes including polysulfone and polyimide-based hollow-fiber membranes with enhanced permeability and selectivity for gas separation.

These advanced membranes have significantly higher selectivities than current commercial membranes, but have lower permeabilities. The permeability can be increased by adjusting operating conditions, such as temperature. The membranes are based on existing polymers that have been modified using different methods. The modification of these polymers and membrane processing conditions provide significantly higher selectivities at similar permeabilities to the resulting membranes. The objectives of this work are to:

i. Give more insight into membrane formation by immersion precipitation process using multi-component quench media.
ii. Develop some hollow fiber membranes with enhanced performance in terms of flux, selectivity and fouling resistance for application in hydrogen recovery and purification.
iii. Assess the effect of pre-treatment on membrane performance.

However, the preparation of membranes with high selectivity and high permeability is challenging due to the well-known trade-off between these two quantities. Membranes can be prepared from the polymer melt or from polymer solutions by different methods and techniques leading to membranes with the desired pore size, thickness and morphology and structure. The commercial polymers that have been reported and used widely are given in tables 1 and 2.

Table 1: Common polymers used for production of commercial membranes

Membrane material	**Membrane process**
Regeneration cellulose	Dialysis, ultrafiltration, microfiltration
Cellulose nitrate	Microfiltration
Cellulose acetate	Gas separation, reverse osmosis, dialysis, ultrafiltration, microfiltration
Polyamide	Reverse osmosis, nanofiltration, dialysis ultrafiltration, microfiltration
Polysulfone	Gas separation, ultrafiltration, microfiltration
Poly(ether sulfone)	Ultrafiltration, microfiltration
Polycarbonate	Gas separation, dialysis, ultrafiltration, microfiltration
Poly(ether imide)	Ultrafiltration, microfiltration
Poly(phenylene oxide)	Gas separation
Polyimide	Gas separation
Poly(vinylidene fluoride)	Ultrafiltration, microfiltration
Polytetrafluoroethylene	Microfiltration
Polypropylene	Microfiltration
Polyethylene	
Polyacrylonitrile	Dialysis, ultrafiltration, microfiltration
Poly(vinyl alcohol)	Pervaporation
Polydimethylsiloxane	Pervaporation, gas separation

Adopted from: Pinnau and Freeman, 1999

Table 2 (a): Polymers for Phase Inversion Membranes

Polymer	**Process**
Cellulose acetate	MF, UF, NF, RO, GS
Nitrocellulose	MF
Polysulfone	MF, UF, GS
Polyethersulfone	MF, UF
Polyacrylonitrile	MF, UF
Polyvinylidene fluoride	MF, UF
Polyimide	UF, GS
Aliphatic polyamide	MF, UF
Aromatic polyamide	NF, RO
Polyphenylene oxide	GS

MF = Microfiltration, UF = Ultrafiltration, NF = Nanofiltration, RO = reverse osmosis, GS = Gas Separation. ***Taken from: Mulder, 2000***

Table 2(b): Commercial Polymer Membrane Made by Phase Inversion

Membrane material	**Membrane Structure**	**Membrane Process**
Cellulose Acetate (CA)	Asymmetric	EP, MF, UF, RO, G.S
Cellulose Mixed esters	Asymmetric and Symmetric	MF, D
Polyacrylonitrile (PAN)	Asymmetric	UF
Polyamide (aromatic and aliphatic) (PA)	Symmetric and Asymmetric	MF, UF, RO, MC
Polyimide (PI)	Symmetric and Asymmetric	UF, RO, GS
Polypropylene (PP)	Symetric	MF, MD, MC
Polyethersulfone (PESU)	Symmetric and Asymmetric	UF, MF, GS, D
Polysulfone (PSU)	Symmetric and Asymmetric	UF, MF, GS, D
Sulfonated polysulfone (SPSU)	Symmetric and Asymmetric	UF, RO, NF
Polyvinylidenefluiride (PVDF)	Symmetric and Asymmetric	UF

D: Dialysis
EP: Electrophoresis
GS: Gas separation
MC: Membrane contactor
MD: Membrane distillation
MF: Microfiltration
NF: Nanofiltrations
RO: Reverse osmosis
UF: Ultrafiltration

Source: Strathmann, 2011

Selection of Commercially Relevant Polymers

For this research, three representatives of commercial polymers were modified and used. They are polysulphone, polyimide and cellulose acetate. Polysulphones are an important commercial membrane material for gas separations due to their excellent mechanical properties, a wide operation temperature range, fairly good chemical resistance and easy fabrication of membrane in a wide variety of configurations and modules.

Polyimide relevant to gas separation is BPDA-ODA, or Upilex$^{@}$ (Type R), which was developed by UBE industries by polymerizing biphenyl tetracarboxylic dianhydride (BPDA) and 4.4’-oxydianiline (ODA) (Figure 2) **(**Matteucci *et al*, 2006). Cellulose Acetate (CA) membranes are relatively inexpensive in part because cellulose (the raw material) is an abundant and renewable resource. The technology to produce membrane modules from cellulose acetate is also relatively well developed (Shell *et al*, 1989).

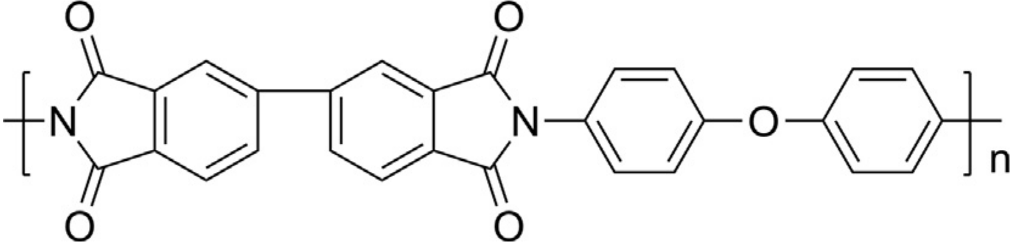


Figure 2: Chemical structure of BPDA-ODA polyimide
Source: Sanders ***et al*** (2013)

Membrane Material Modification

The development of high-performance membranes involves the selection of a suitable membrane material and the formation of this material into a desired membrane structure. However, it is often necessary to modify the membrane material of the structure to enhance the overall performance of the membrane. Figure 3 illustrates the chemical structures of several polysulfones. It also shows the basic repeat units of several commercially available polysulfones (Vitrex PES, Udel PSF and RadelR). According to Sanders *et al* (2013), a broad range of polysulfones can be prepared via nucleophilic aromatic (SNAr) polycondensation of an aromatic dihydroxy compound with a bis-(halophenyl) sulfone.

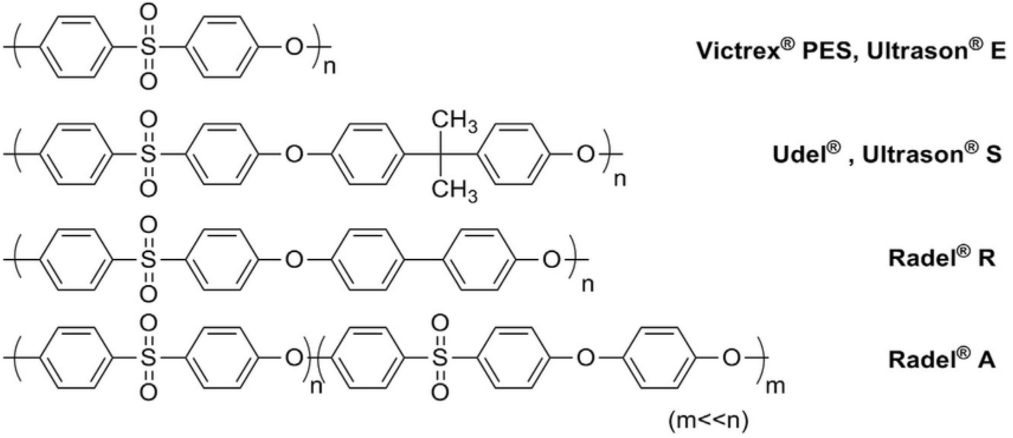


Figure 3: Chemical structures of several polysulfones.
Source: Sanders *et al* (2013)

Experimental Methods for Introducing Functional Groups

i. Polysulfone Carboxylic Acid Derivatives, DS = 0.85

This modification of polysulfone was carried out using the method reported by Guiver, Robertson, Yoshikawa and Tam (2000), with slight modifications. A 5 L 3-neck flask with a central resin kettle flange of internal diameter 10cm was used for the reaction. A mechanically stirred solution of polysulfone (177 g, 0.40 mol) in THF (2L) was lithiated to DS = 0.85 by addition of n-butyllithium (34 ml, 0.34 mol, 0.85 mol equivalents). A 0.5kg block of dry ice was freshly prepared from liquid CO_2 and thoroughly mixed into the solution with large rigid spatula. Extra blocks were mixed quickly, taking care to leave no unreached solution. The mixture was allowed to warm up overnight under inert atmosphere, then THF was drained off, and the solid was mixed in a Waring Blender with ethanol. The product was filtered, acidified with dilute HCl and finally washed to give the carboxylated polysulfone.

ii. Polyimide and Dicarboxylic acid complex formation

The experiment was conducted according to the methods developed by Smit (1991) and Beerlage (1994).

Membrane Modification by cross-linking

In another experiment, cross-linking was carried out using the method of Tin, Chung, Kawi and Guiver (2004). For the cross-linking modification, a 10% (w/v) of cross-linking reagent comprising of *p*-xylenediamine in methanol was prepared. The membrane modification was performed by immersing membrane films into the cross-linking reagent for specific durations (1 day or more). The films were then washed with fresh methanol immediately after removal from the reagent solution in order to wash away the residual solution on films, followed by drying naturally at room temperature. The above procedures were repeated by using pure methanol instead of the cross-linking reagent for methanol treatment (Tin, Chung, Kawi and Guiver, 2004). Cross-linking of polymers is often applied to improve the chemical stability and selectively of membranes for reverse osmosis, pervaporation and gas separation applications (Pinnau and Freeman, 2000).

The primary reason to cross-link a polymer is to decrease the plasticization of a polymer in order to derive a good-selectively. To develop high performance membranes, there arises a need to adjust membrane swelling while in contact with the feed mixture. To achieve this, the membrane must be cross-linked and the extent of cross-linking should be thoroughly controlled. Cross-linking can be executed in three ways. One is via chemical reaction by using a compound to connect two polymeric chains, the second by irradiation and third, is a physical cross-linking (Pandey and Chauhan, 2001). The use of cross-linkable polymers is another more recent methodology which has been used to improve the performance membranes. These cross-linking moieties have been shown to provide a selectivity improvement for H_2 much higher than the uncross-linked polymer membranes. The effect of cross-linking modification on selectivity was investigated at the preliminary stage of this work. The result suggested that the selectivity increased at a low cross-linking density but decreased at a high degree of cross-linking. Detailed examination reveals the swelling of polymer chains during cross-linking density us the possible reason resulting in the increment of selectivity. Therefore, it underlines the importance of the swelling effect on polyimide based membrane, where swelling by methanol emerged as an effective modification method of capabilities using the approach of chemical cross-linking modification. Fluorine containing polyimide was cross-linked according to the methods described by Hao, Rice and Stern (2008); Gigi *et al* (2016). However, in those works, the cross-linked fluorinated polyimide was evaluated for the separation of H_2S/CH_4 and CO_2/CH_4, while this current work is focused on hydrogen recovery.

Membrane Formation and Modification

Phase inversion is the most versatile technique with which to prepare polymeric membranes. The concept of phase inversion covers a range of different techniques such as precipitation by controlled evaporation, thermal precipitation from the vapour phase and immersion precipitation. The majority of phase inversion membranes are prepared by membrane precipitation and this is the process that is employed in this work.

Immersion precipitation membranes in their most simple form are prepared in the following way. A polymer solution consisting of a polymer (3) and a solvent (2) is cast as a thin film upon a support (e.g a glass plate) and then immersed in a nonsolvent (1) bath. The solvent diffuses into the coagulation bath (I_2) while the non-solvent will diffuse into the cast film (I_2). After a given period of time the exchange of solvent and non-solvent has proceeded so that the solution becomes thermodynamically unstable and demixing takes place. Finally, a solid polymeric film is obtained with an asymmetric structure. A schematic representation of the film-bath interface during immersion is shown in figure 4.

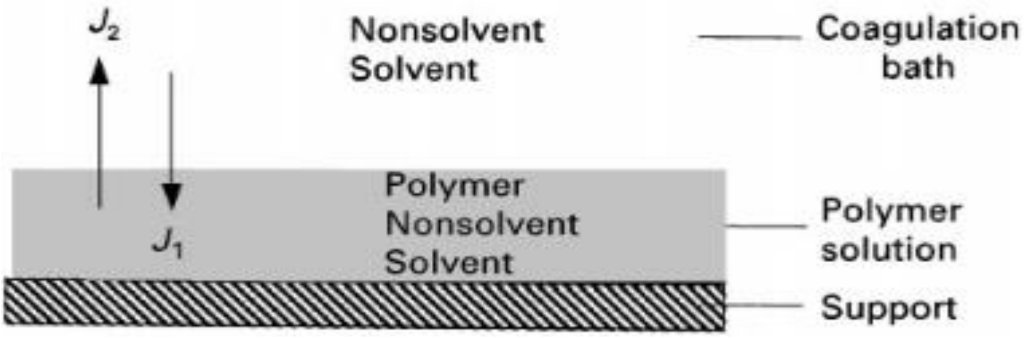


Figure 4: Schematic representation of a film-bath interface. Components: non-solvents, solvent and polymer. J_1 is the non-solvent flux and J_2 the solvent flux. Adopted from: Mulder, 2000

The formation of membranes made by the immersion precipitation method occurs a very short time scale, typically less than a few seconds. Different membrane structures can be obtained by careful control of the thermodynamic and kinetic variables involved in the immersed precipitation process. Some progress has been made in modeling the extremely complex thermodynamic and kinetic processes involved in the immersion precipitation process (Pinnau and Freeman 2000). However, the predictive capabilities of these models are limited, and thererfore, optimization of membranes made by immersion precipitation is still primarily based on empirically developed protocols. In this work, immersion precipitation method was adapted.

Most commercial membranes made by the immersion precipitation method are made from multi-component solutions containing polymer, solvent(s) and non-solvents or additives. In many cases, the porosity, pore size and skin layer thickness can be modified by the addition of non-solvents to the casting solution (e.g alcohols, carboxylic acids, surfactants etc), inorganic salts (e.g $LiNO_3$ or LiCl etc) or polymers (polyvinylpyrrollidone, polyethylene glycol among others) (Pinnau and Freeman, 2000). Even very small amounts of these solution additives can have a significant effect on the membrane structure, and hence, its separation performance. Examples of multi-component casting solutions and quench media use to prepare high performance membranes by the immersion precipitation process for a variety of applications are shown in Table 3. By varying one or more of these parameters the membrane structure can be changed to suit a particular application. The approaches in Table 3 were adopted in this work.

Membrane Morphology Evaluation

Based on the scanning electron microscopy [SEM] images, it was possible to determine the membrane pore sizes and distributions, using the image soft-ware. Membrane surface and across sectional-images were obtained using Quanta

600FEG Environmental Scanning Electron Microsoft [ESEM] operated in the secondary electron detection mode with a 10Kv accelerating voltage.

Table 3: Multi-Component casting or spinning solutions for production of membranes by the immersion precipitation process adopted in this work.

Polymer	Solvent	Non-solvent or Additives	Quench Medium	Application
22.2 wt% CA	66.7 wt% acetone	10.0 wt% water + 1.1 wt% $MgClO_4$	Water	RO
16.2 wt% PSF	79 wt% DMAc	4.8 wt% PVP	70.5 wt% IPA + 29.5 wt% water	UF
10.46 wt% PES	69.72 wt% DMF	19.82 wt% *t*-amyl alcohol	Water	MF
37 wt% PSF	36 wt% NMP	27 wt% proponic acid	Water	GS
18 wt% PI	82 wt% *p*-chlorophenol	-	35 wt% water + 65 wt% ethanol	GS

CA = Cellulose acetate, PSF = Polysulfone, PES = polyethersulfone; PI = polyimide; PVP = polyvinylpyrrolidone; DMAc = dimethylacetamide; MF = Dimethylformamide; NMP = N-methylpyrrolidone; ***Adopted from:*** Pinnau and Freeman, 2000

Membrane Modification Methods

Generally, the objectives for modification of pre-formed membranes are (i) Increasing flux and/or selectivity and (ii) increasing chemical resistance (solvent resistance, swelling, fouling resistance). Some of the most commonly practiced membrane modification methods are listed in table 4. This study employed the methods of solvent treatment, solvent exchange and chemical treatment (cross linking, fluorination and functionalization).

Table 4: Membrane Modification Methods

Modification	Goal	Application
Annealing • Heat treatment • Solvent	Eliminating of membrane defects Control of pore size	RO, GS, UF
Solvent exchange	Eliminating of membrane defects	GS, UF
Surface coating	Eliminating of membrane defects Improvement of fouling resistance	GS RO, NF, UF
Chemical treatment • Fluorination • Cross-linking • Pyrolysis	Improvement of flux and selectivity Improvement of chemical resistance Improvement of flux and selectivity	GS As selectivity, UF, GS RO, NF, UF

Adopted from: Pinnau and Freeman (2000)

Influence of parameters and preparation procedure on membranes structure and properties

As pointed out by Pinnau and Freeman (2000), the structure of membranes made by immersion precipitation can also be altered by using multi-component quench media. For example, the addition of a solvent to the quench medium results in an increase in the surface porosity and pore size of the membrane (Mulder, 1996). The formation of membranes made by the immersion precipitation process depends on a large number of material and process-specific parameters including:

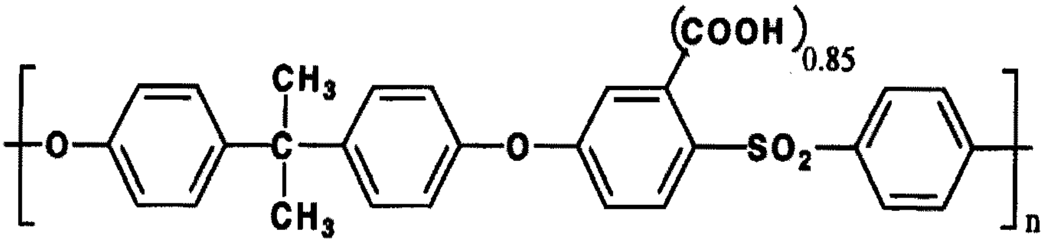
- Choice of the polymer (molecular weight, molecular weight distribution).
- Choice of the solvents
- Choice of additives.
- Composition of the casting solution.
- Temperature of the casting solution
- Choice of the quench medium
- Temperature of the casting atmosphere.
- Evaporation conditions
- Casting thickness
- Casting or spinning speed.
- Membrane support material (type of woven or non-woven)
- Drying conditions

Established theories on membrane formation from ternary systems can be extended to describe the effects of high or low molecular weight additives. The effect of addition of a carboxylic acid on the flux properties of polyimide membrane was studied. This study was limited to the effects of some of these parameters on membrane structure and properties for gas separation, especially the recovery of hydrogen.

Fabrication of Hollow Fiber Membranes by Phase Inversion Process

According to Chung (2008), the formation of modern hollow-fiber membranes consists of seven steps: (1) Dope preparation (2) Degas, (3) metering (4) spinning (5) evaporation (in the air gap region), (6) coagulation and (7) solvent exchange. Most commercially available hollow fibers are spun from a hot spinneret with an air gap distance and a moderate speed in order to increase the fiber production as well as to reduce fiber diameter (in order to increase fiber packing density per module). Mulder (1996), Chung and Kafchinski (1997), Freeman and Pinnau (1999), Sharpe *et al* (1999), Clausi and Koros (2000), Nunes and Peinemann (2001), Carruthers *et al.* (2003), Ho (2003) and Baker (2004) have studied the effects of dope concentration, internal and external coagulants' chemistry and spinning conditions on membrane formation and performance **(**Chung, 2008**)**. Often, the polymer dope concentration would be in the range of 30-35 wt% and small amounts of a water-soluble polymer (e.g poly (vinyl pyrrolidone) or poly (ethylene oxide) oligomers) could be added to optimize the porous structure (Chung, Teoh and Hu, 1997, Zhao and Yuan, 2006). To reduce macrovoid formation, water, alcohols or other additives are included in the original polymer dope, so that the dope is very close to the phase separation boundary before being cast or extruded (Chung, Teoh and Hu, 1997). For example, polysulfone hollow fibers can be spun from a dope containing 37% total solids (i.e polymer) dissolved in a mixture of 43 wt% propionic acid and 57 wt% *N*-methyl-2-pyrrolidone or 13 wt% formamide and 87 wt% formylpiperidine (Pinnau and Freeman 2000).

A typical hollow fiber bundle contains on the order of 10^5 hollow fibers which are tightly packed (packing fractions on the order of 50% are common) with both ends embedded in a thermosetting polymer epoxy (Kai and Duan, 2017). In this work, the use of membrane production facility of the Institute of Polymer Research, Geesthacht, Germany was facilitated by some workers (who choose to remain anonymous). Modified commercial polysulpone polyimide and cellulose acetate were used for the preparation of membranes with the structures shown below. Modifications of the commercial polymers as well as the processing conditions were done to improve the properties of the polymers and the performance of the resulting membranes in gas separation.



Carboxylated Polysulfone wth DS = 0.85 ***Taken from:*** Guiver et al., 2000.

The modified polysulphone (carboxylic acid derivative) was synthesized using the method reported by Guiver et al., 2000. The flourine – containing polyimide and cellulose acetate were obtained from the companies listed in table 5. Integrally-skinned asymmetric membranes were made by an immersion precipitation method. In this case, integrally-skinned asymmetric membranes were made form a binary solution containing a polymer (CA) and a solvent (acetone). Upon immersion of the cast solution into a liquid, which is a non-solvent for the polymer but miscible with the solvent, an asymmetric structure with either a porous or non-porous skin layer is formed. The structural gradient in integrally-skinned asymmetric membranes results from a very steep polymer concentration gradient in the nascent membrane at the onset of phase separation (Strathmann, 1985). During the development of integrally-skinned asymmetric cellulose acetate gas separation membranes it was found that water-wet membranes collapse and form an essentially dense film upon drying. Because water has a very high surface tension, it is often difficult to dry water-wet membranes without collapsing the membrane structure. An exchange of water with liquids having lower surface tension, such as alcohols or aliphatic hydrocarbons results in maintaining the original membrane structure upon drying (Chen, Mou, Wang, Matsuura and Wei, 2011). Typical solvent-exchange methods involve replacing water first with *iso*-propanol and then with *n*-hexane (Rowley and Slowig, 1971); Manos, 1978). Other methods of eliminating the collapse of finely porous membrane structures include freeze-drying and addition of structures to the water prior to drying of the wet membranes (Hayes, 1991).

Spinning dope preparation for the formation of Hollow Fiber membranes using the concept of critical concentration

Chung, Katchinski and Foley, 1992; Chung, Teoh and Hu, 1997); Wavy, *et al*. (2000) suggest that a higher polymer concentration can reduce the formation of defects in the skin layer of gas separation membranes (Clausi and Koros, 2000). Apparently, there is a critical concentration which exists. Above the critical concentration, relationship (that is, slope) of dope viscosity versus dope concentration is dramatically different from that below the critical concentration. This difference is mainly due to different degrees of polymer chain entanglement. The optimal concentration for asymmetric gas separation membrane may be obtained at a concentration equal to or slightly higher than the critical dope concentration (Chung, Teoh and Hu, 1997). However, the gas permeance, in most cases, may be reduced with an increase in dope concentration. The approach suggested by Li *et al* (2002) was adopted in this work.

The critical concentration for mixture in this study was determined using the figure 5. The theoretical background of the fabrication by dry–jet wet spinning of the hollow fiber is given here (Polyimide based hollow fibre) (Husk, Cassidy and Gebert, 1988; Tanaka, Kita, Okano and Okamoto, 1992).

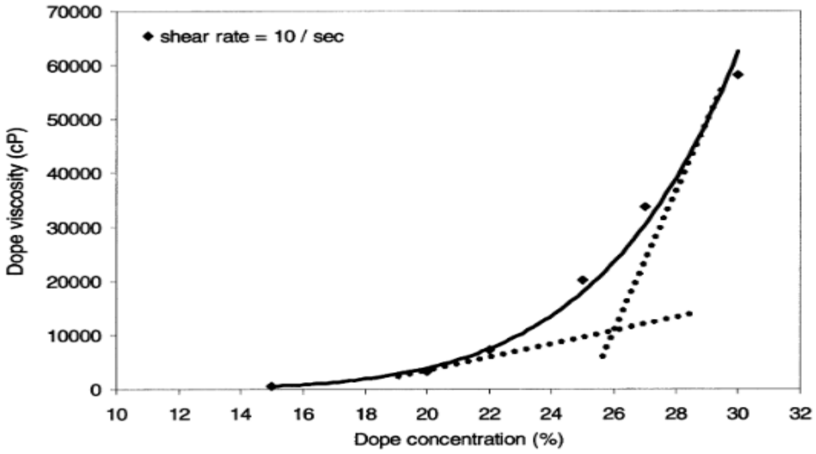


Figure 5: The critical concentration for mixture. **Adopted from:** Li et al (2002)

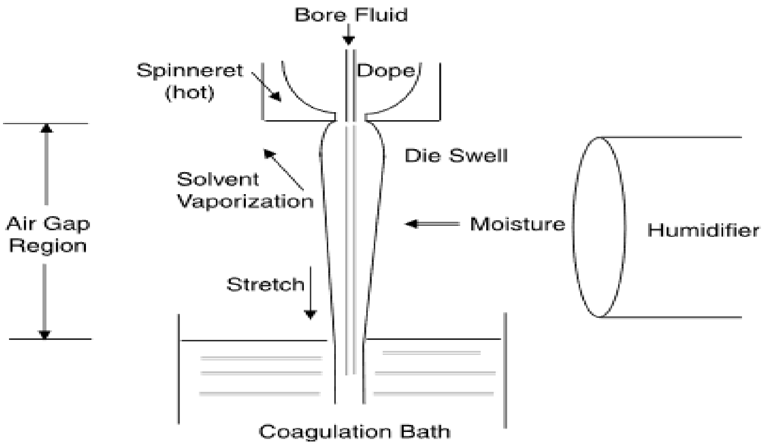


Figure 6: Schematic design of dry-jet wet-spinning of hollow-fiber membranes
Source: Tai-Shung Neal Chung (1999).

If the spinneret is hot, fraction of low-boiling dope solvents may evaporate and form the skin in figure 6: Humidity surrounding the fiber may affect the skin morphology because high humidity may induce early precipitation and increase the selective skin thickness (Chung, Katchinski and Foley, 1992). However, the effects of humidity on phase inversion and membrane performance depend on the duration of nascent fiber traveling through the air gap as if there is strong solvent evaporation occurring at the outer layer of nascent membranes. If the duration is very short or if there is a highly volatile solvent evaporation, the adsorption of water moisture upon the nascent hollow fiber may be diminished. Under these circumstances, the humidity effects on membrane separation performance may be negligible. The molecular sizes and solubility parameters of solvent and internal and external coagulants play important roles on membrane morphology (Kesting *et al*., 1990; Kesting and Fritzche, 1993). Large size solvents may have difficulties to leach out during the precipitation. The residual solvents may redissolve the skin and density the selective layer. The difference in solubility parameter between spinning solution and internal or external coagulation, according to Kesting (1985), Ho and Sirkar (1992), Chung, Katchinski and Foley (1992)**,** Chung, Kafchinski and Vora (1994), Matsuura (1994); Chung, Teoh and Hu (1997), affect the coagulation rate (Chung, 2008).

In addition, the ratio (*k*) of solvent outflow to coagulant influx determines the macroscopic membrane porosity (Yilmaz and McHugh, 1986, 1988; Matsuura, 1994), as illustrated in figure 7. Depending on the initial dope composition and *k* value, the precipitation path may occur via nuclei growth or spinodal decomposition. Because *k* is not a constant across the membrane thickness and *k* is also a function of temperature and dope viscosity, it becomes difficult to microscopically predict local membrane porosity. Therefore, figure 7 can only be used as a qualitative understanding of phase inversion.

In addition, the spinning dope suitable for fabricating hollow fibers generally has much greater viscosity and elasticity than that for flat membranes. To produce hollow fiber membranes for gas separation, Chung *et al.* (1992) have hypothesized that a dope exhibiting significant chain entanglement is one of the key requirements extrapolated from the viscosity versus polymer concentration relationship is recommended for the spinning solution (Chung, Teoh and Hu, 1997).

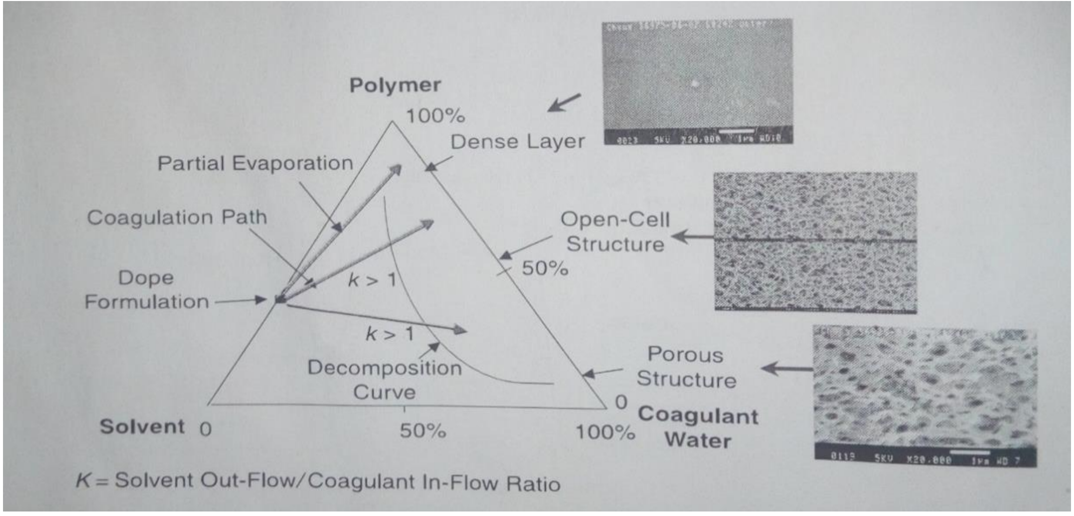


Figure 7: Relationships among dope composition, precipitation kinetics and membrane morphology

Below the critical concentration, the resultant hollow fibers may have too many defects and cannot be properly repaired by the silicone rubber coating (Henis and Tripodi, 1981). Above the critical concentration, the resultant hollow fibers may be a thick dense selectivity layer that reduces the permeance. As a rule of thumb, the optimal polymer concentration for gas separation hollow-fiber membranes may be located at or located at or 1-2 wt% above the critical concentration. According to (Chung, Teoh and Hu, 1997; Kapantaidakis *et al.*, 2002; Ren *et al.*, 2002; Barsema *et al.*, 2003; Liu *et al.*, 2005), this practice has been widely used and proved to be valid for gas separation and pervaporation membranes (Chung, 2008).

Rheological data suggest that high-viscosity non-Newtonian fluids behave differently from low-viscosity Newtonian fluids in the flow chamber of the spinneret. Non-Newtonian fluids memorize the shear and elongation stresses imposed on them, while Newtonian fluids do not. Furthermore, the hollow fiber spinning process is a dynamic process not an equilibrium process. Therefore, it may not be appropriate to predict the phase-inversion process by the traditional Flory-Huggins theory (Chung, 1997). Gravity force must sometimes be considered (Chung, Teoh and Hu, 1997). For a high-speed spinning process, the effects of spinning-line tension, convection and drag flow that occurred at the membrane surface in the coagulation bath should not be ignored. One must take these factors into consideration to develop hollow-fiber membranes with a desired structure and separation performance. Currently, there are many companies that produce and market polymeric membranes (table 5) below. However, some membranes having substantially higher permeabilities and selectivities than those listed in tables are being developed (Baker, 2002).

Table 5: Principal Gas Separation Markets, Producers and Membranes Systems

Company	**Principal markets/ estimated annual sales**	**Principal membrane material used**	**Module type**
Permea (Air Products)	Large gas companies	Polysulfone	
Medal (Air Liquid)	Nitrogen/air ($75million/year)	Polyimide/polyaramide	Hollow fiber
IMS (Praxair)	Hydrogen separation ($25million/year)	Polyimide	
Genome (MG)		Tetrabromo polycarbonate	
GMS (Kvaerner)	Mostly natural gas separations		
Separex (UOP)	Carbon dioxide/methane	Cellulose acetate	Spiral wound
Cynara (Natco)	($30million/year)		Hollow fiber
Aquilo		Polyphenylene oxide	
Parker-Hannifin		Polyimide	Hollow fiber

Ube	Vapor/gas separation, air dehydration, other ($20million/year)		
GKSS Licenses		Silicone rubber	Plate and frame spiral wund
MTR			

Source: Baker, 2002

Table 6: Gas membrane Applications and Suppliers

Gas separation	**Application**	**Suppliers**
O_2/N_2	Nitrogen generation, oxygen enrichment	A/G technology, Permea (Air products), Generon (Messer), IMS (Praxiar), Medal (Dupoint, Air Liquide), Aquilo (Parker Hannifin), Ube
H_2/Hydrocarbons	Refinery hydrogen recovery	Air products, Air Liquid, Praxiar
H_2/CO	Syngas ratio adjustment	Air products, Air Liquide, Praxiar
H_2/N_2	Ammonia purge gas	Air Products, Air Liquide, Praxiar
CO_2/Hydrocarbon	Acid gas treating, enhanced oil recovery, landfill gas upgrading	Kvaener (Grace Membrane System), Air Products, Ube
H_2S/Hydrocarbon	Sour gas treating	Kvaener (Grace Membrane System), Air Products, Ube
H_2O/Hydrocarbon	Natural gas dehydration	Kvaener, Air Products,
H_2O/Air	Air dehydration	Air Products, Ube
Hydrocarbon/air	Pollution control, hydrocarbon recovery	MTR, GMT, NKK
Hydrocarbons from process streams	Organic solvent recovery, monomer recovery	MTR, GMT, SIHI

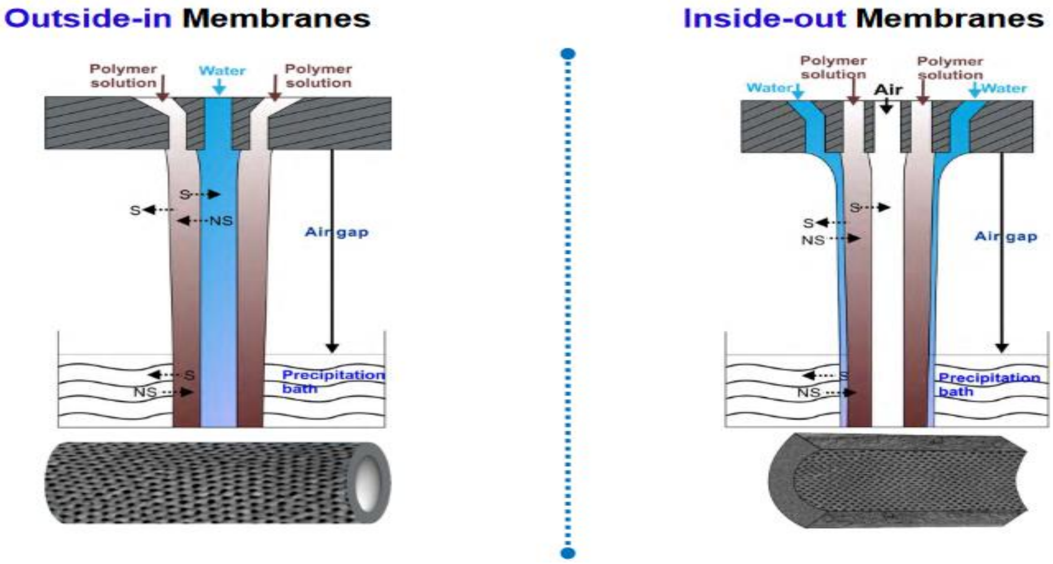


Figure 8: Fabrication of Isoporous Hollow Fiber Membranes. ***Adopted from:*** Volker, 2018

The fabrication of polymeric membranes commonly involves a phase inversion process, wherein a polymer solution is extruded through an annular die and contacted with a non-solvent (i.e water) (Volker, 2018). In order to assure pinhole-free hollow fibers, various coating and repair techniques can be employed (Henis and Tripodi, 1981). The diffusion of water into polymer solution causes phases separation by yielding polymer-rich phase and solvent-rich phase. The solvent-rich phase contains water, which can be extracted from the resultant porous hollow fiber membrane (Figure 8). If an air gap exists between the exit of the die and coagulation bath, thin dense skin layer of the order of 100nm or even the less will exist on the top of a porous and highly permeable polymer support (Volker, 2018). According to Henis and Tripodi (1981), after the hollow fibers are assembled into a cylindrical module with both ends of the fiber bundle encapsulated in a thermosetting polymer (for example, epoxy), the gas mixture to be separated can then be introduced on the outer area of the fiber bundle and in some cases; the gas mixture is introduced to the bore of the fibers.

Preparation of Carboxylated Polysulphone Hollow Fiber

A hollow fiber was prepared from carboxylated polysulphone using the procedure described by King *et al.* (1982). The carboxylated polysulfone is admixed with dimethylacetamide to provide a dope containing about 27.5 weight percent polymer and the dope is coagulation spun into water at a temperature of about 4^0C through a spinnerette which is immersed in the water. The spinnerette has an outer orifice diameter of 0.0559 centimeters, inner pin of 0.0229 centimeters and an injection port of 0.0127 centimeters through which water is introduced. The dope is pumped and metered to the spinnerette at a rate of about 7.2 mill-liters per minute and is drawn from the spinnerette as a hollow fiber at a rate of about 33meters per minute. After the coagulation has substantially occurred, the hollow fiber is washed with water with water at room temperature. The hollow fiber is wound substantially without tension on a 12 inch (approximately 25.4 centimeters between inside heads) bobbin with a bobbin winder i.e the hollow fiber is fed through an axially traversing guide (which reverses at each end of the bobbin) and is collected on the surface of a rotating bobbin so that the hollow fiber is wound on the bobbin in sequential layers of helical coils. The bobbin is stored in an aqueous vat at room temperature during which time the fibers on the bundle shrink to impart crimps. Hollow fibers prepared by this procedure are assembled into a hollow fiber bundle (Danos and Heider, 1980).

A hank of dried hollow fibers containing about 20, 000 strands and being about 10 centimeters about 20, 000 strands and being about 10 centimeters in diameter (when tightly bound with tape) and slightly over 3 meters in length is severed at both ends to provide a hank slightly less than 3 meters in length. Plastic tape is wound around each of the hank to hold the end in tight circular configuration. An epoxy tube sheet is fabricated at one end of the hank by sealing the opening to the hollow fibers and then immersed the open end of the hank into a liquid epoxy resin and allowing the epoxy to cure (King *et al.*, 1982). Existing hydrogen permeable hollow-fiber membranes have the selectivities and fluxes required. The major problem is the low reliability of these membranes caused by fouling. Better design and pretreatment steps of the membranes developed in this work should resolve this problem.

Despite the progress that has been made in membrane science, fouling is still a serious problem in many membrane-based separation processes. The expression fouling covers all events during operation of a membrane unit, that lowers the membrane performance e.g permeate flux and is one of the major factors limiting the use of membranes in separation applications. Fouling is caused by undesired deposition of feed components on the membrane surface which is in the case of organic material favored by hydrophobic interactions (Van Der Waals) between the membrane material and the feed components (Zydney, 1996). Up to now only periodical cleaning methods such as back flushing with air or water or chemical cleaning are used to remove the fouling products from the membrane surface. Furthermore, special module designs have been introduced in the past which induce a turbulent flow above the membrane surface and which should reduce the deposition of feed components on the surface (Belfort, Brewster and Chung, 1993 and Belfort, 1997). In this work, a clear understanding of the effects of pretreatment on membrane properties aided in the development of improved membranes with better separation performance for high temperature processes and resistant to fouling.

Cartridge/Module construction

Module manufacturing procedures involve the method of winding and sealing the hollow fibres to form a membrane module or cartridge. Optimization of the cartridge manufacturing procedure involves selection, testing and optimizing of candidate epoxy resins to achieve the high pressure capability required of gas membranes in field tests (King et al., 1982).

Performance analysis of a single membrane permeator yields the extent separation attainable (concentrations of permeate and retentate streams), the required membrane area and the power or energy requirements for separations. Such an analysis depends on the following factors:

- Separation properties of the membranes (separation factor and permeance)
- Composition and flow rate of the feed stream.

- Operating temperature.
- Operating pressures on the feed and permeate sides of the membrane.
- Stage cut – fraction of the feed flow collected as permeate.
- Flow patterns on either side of the membrane, e.g countercurrent, co-current, cross-flow

Most of the cost of producing hollow-fibers is incurred in the fiber potting operation when fibers are mounted inside the module shell (Baker, 2000a, b).

Membrane Pre-Treatment

According to Clausi and Koros (2000), Chung *et al.* (2002), Ren *et al.* (2002), Cao *et al.,* 2004) as cited in Chung (2008) reported that the as-spun fibers have to go through solvent exchange post treatments in order to (1) remove residual solvents, (2) remove residual stress, (3) improve chain packing, and/or (4) eliminate defects. Conventional solvent exchange approaches are to immerse as-spun fibers in water, then in methanol, and/or then hexane. The hexane treatment is highly recommended because of its low surface tension, which may eliminate pore collapse during drying. Without proper solvent exchange, it has been reported that the apparent dense-selective layer thickness may increase from 730Å (after water, methanol and hexane treatments) to 4400 Å (after both water and methanol treatments) and 18,800 Å (only after water treatment) (Clausi and Koros, 2000).

Heat treatment has been considered as an effective method to (1) control pores size, (2) reduce pore sizes, and (3) remove membrane defects of as-spun hollow fibers since the birth of RO (Sourirajan and Matsuura, 1985). Its effects on microporous (Chung, 1996), gas separation (Chung *et al*., 2003), and pervaporation (Liu *et al*., 2005; Qiao and Chung, 2006; Chung *et al.*, 2006) membranes have been summarized elsewhere (Jianga, Chunga and Rajagopalan 2008).). Basically, heat treatment induces molecule relaxation and microscopically repackages the polymeric chains, which tend to perfect and densify the selective skins and minimize the surface defects (Widjojo, Li, Jiang and Chung, 2012)**.** Three different common membrane pre-treatments were selected. The procedures were adapted and applied to membrane samples prior to their use in gas separation as reported by (Albo, Wang and Tsuru, 2014).

Room Temperature – Oven (RTO): Membranes were washed several times in a pure-water, then dried at room temperature for 24 hours, and finally placed in an oven at 120^{0}C for 30 minutes.

Ethanol – Hexane **(EH)**: Membranes were washed several times in a pure-water bath, then immersed in ethanol for 5 minutes and afterwards soaked in a hexane bath for 1min. Finally, the solvent was evaporated at room temperature for 15 minutes.

Freeze Drying (FD): Membranes were washed several times in a pure-water bath, then immersed in 50, 75, 90, 95 and 100wt% *t*-butanol aqueous solutions for 15 minutes. Then, membrane samples were placed in pure *t*-butanol in freeze dried equipment under vacuum for 2 hours.

Gas Separation Experiment

Membrane samples ($2.21cm^2$) were tested in a stainless permeation cell at temperature that ranged from ambient (room temperature, 20 ± 3^0c) to 120^0c in an oven. A schematic drawing of the experimental apparatus appears in figure 9. The feed gas pressure was set at 2.5 bar and permeate was at atmospheric pressure. The flow rate of the permeating gas was measured using a bubble flow meter. The experiment was conducted according to the procedure of Albo, Wang and Tsuru (2014) with slight modification.

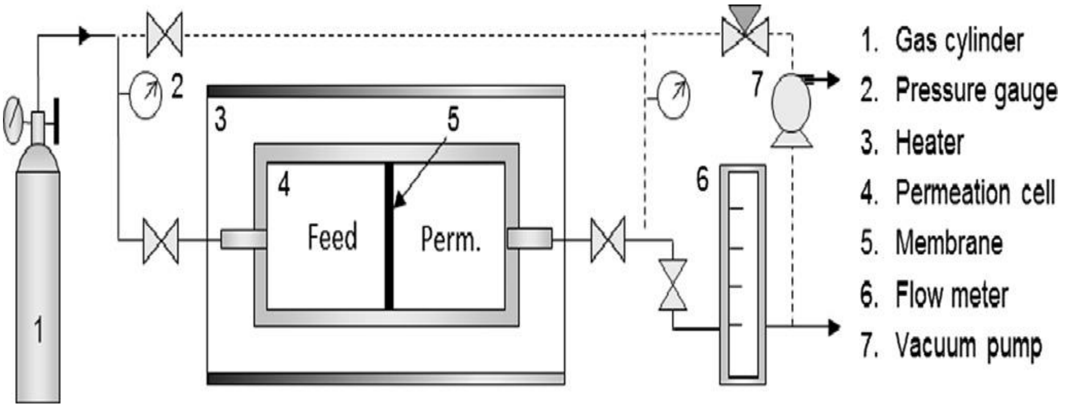


Figure 9: Schematic drawing of the gas experimental setup (5 minutes between different gas measurements in order to remove the gas from within the gas permeation equipment)

Gas permeances were calculated using the following equation;

$$P(i)=\frac{j(i)}{\Delta p} \quad [1]$$

Where P(i) is the permeance of *i* ($mol/(m^2sPa)$, J(*i*) is the permeate flux ($mol/(m^2s)$), and $\Delta p(i)$ is the partial pressure difference (Pa). The ability of the membrane to separate different gases, depending on the separating layer properties, was quantified by the membrane gas selectivity:

$$\alpha(i/j)=\frac{P(i)}{P(j)} \qquad [2]$$

Where a is the membrane selectivity for gas *I* relative to gas *j*.
It is generally recognized that the gas transport mechanism through polymeric membranes is controlled by the solution and diffusion processes of the permeating gases, where the temperature dependence of permeance is decided by the relative magnitude of two counteracting contributions: kinetic (diffusion) and equilibrium (sorption). The number of molecules with kinetic energy larger than the activation energy for permeation, E*p* is proportional to exp(-E_p/RT), assuming a Maxwellian velocity distribution of molecules. Therefore, the permeance P(*i*) for the activated diffusion mechanism can be expressed by an Arrhenius type relationship:

$$P(i)=C(i)\exp\left(\frac{-Ep(i)}{RT}\right) \qquad [3]$$

Where C(*i*) is a constant depending on the system and E*p*(*i*)(kj/mol) is the activation energy for the permeation of gas, *I*, which is the difference between the sorption energy and substantial activation for diffusion (Albo, Wang and Tsuru, 2014).

RESULTS AND DISCUSSION

Theoretical Background of the Formation of Phase Inversion membranes

It is shown in this section that two types of demixing process resulting in two different types of membrane morphology can be distinguished:

- Instantaneous liquid-liquid demixing, where the membrane is formed immediately;
- Delayed onset of liquid-liquid demixing, where the membrane takes some time to form (Mulder, 2000).

The formation of characteristic structures in phase-inversion membranes has been described by a model for diffusive mass transport in thin films of polymeric solutions and its effect on phase separation by liquid-liquid demixing (Smolders *et al*., 1992). The two types of demixing process will now be distinguished that lead to different types of membrane structure. These two different types of demixing process may be characterized by the instant when liquid-liquid demixing sets in. Figure 10 shows the composition path of polymer film schematically at the very instant of immersion in a non-solvent bath (at $t < 1$s). The composition path gives the concentration at any point in the film at a particular time. For any other time, another compositional path will exist.

When liquid-liquid demixing occurs instantaneously, membranes with a relatively porous top layer are obtained. This demixing mechanism results in the formation of a porous membrane (microfiltration/ultrafiltration type). However, when liquid-liquid demixing sets in after a finite period of time, membranes with a relatively dense top layer are obtained. This demixing process results in the formation of dense membranes used for gas separation/pervaporation.

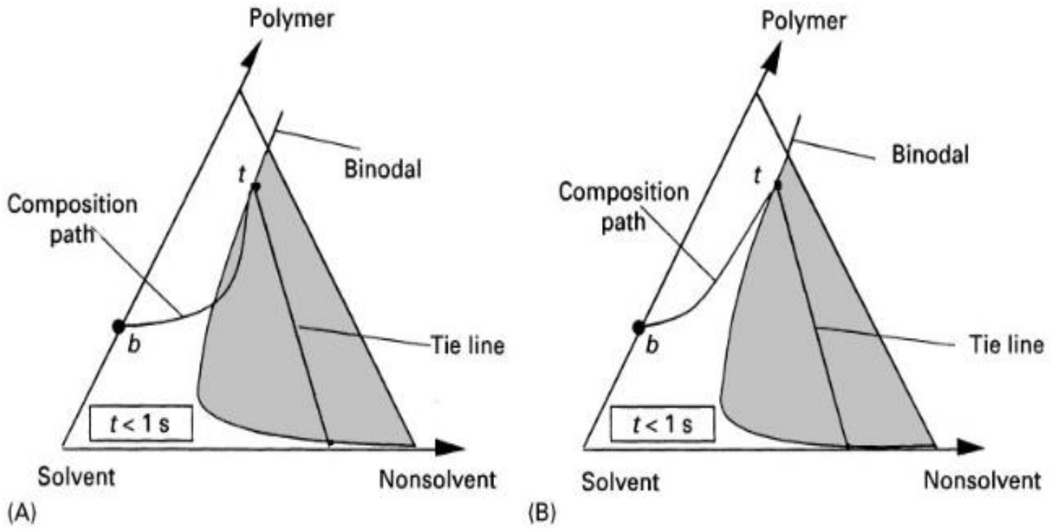


Figure 10: Schematic composition path of the cast film immediately after immersion; t is the top of the film and b is the bottom. Part (A) shows instantaneous liquid-liquid demixing whereas (B) shows the mechanism for the delayed onset of liquid-liquid demixing.
Adopted from: Mulder, 2000

Attempts to extend the time component model to more complex polymer systems, such as those required for hollow fiber preparations, have been undertaken. A number of other investigations of membrane formation have been reported (Machad, Habert and Borges**,** 1999). However, at this time, models capable of predicting membrane morphology and properties quantitatively are far from satisfactory.

Asymmetric membranes, on the other hand, are most commonly prepared by a wet phase inversion process. The phase inversion process involves the phase separation of a polymer solution in polymer rich and polymer lean phases. This separation is achieved by the immersion-precipitation technique. A homogeneous polymer solution is cast as a flat film, exposed to air for a specific time and then immersed in a quench medium, which is non-solvent for the membrane forming polymer. Phase inversion occurs by bringing the initially thermodynamically stable polymer solution to an unstable state by solvent/non-solvent exchange, involving a mass transfer process between components (Pandey and Chauhan, 2001).

The evaporation process for a typical ternary-casting system, consisting of polymer/solvent/nonsolvent used for the preparation of membranes made by dry/wet phase inversion, is described schematically in figure 11. The binodal curve deliminates the two-phase regions, namely the polymer-rich and polymer-lean. Their composition is given by the tie lines. The spinodal curve represents the line where all possible fluctuations in terms of phase separation occur and that lead to instability within the system. The region between the binodal and spinodal corresponds to a metastable composition where phase separation by nucleation and growth takes place. The point where the binodal and spinodal meet is referred to as the critical point, c. If the precipitation path crosses the binodal below the critical point, nucleation of a polymer-rich phase may initiate the phase separation process.

On the other hand, if the precipitation path crosses the binodal above the critical point, nucleation of the polymer-lean phases may occur. At higher, polymer concentrations, phenomena such as vitrification, gelation or crystallization can occur in the polymer solution, interrupting the polymer lean phase growth. These different regions in the phase diagrams indicate various separation mechanisms. However, in order to predict the morphologies that are developed, one must know how the polymer solutions, in contact with a non-solvent bath changes its composition with time. Reuvers *et al.* (1987) identify two different mechanisms occurring in phase separation of ternary systems by immersion-precipitation; instantaneous and delayed demixing. Instantaneous demixing occurs when phase separation begins, immediately after immersion. The precipitation path crosses the binodal and two distinct phases are formed. In this case, the instant of immersion is the onset of demixing in a barely stable casting solution. Delayed demixing can occur in the polymer solution when the precipitation path does not cross the binodal for a measurable period of time after the coming into contact with the non-solvent bath. Figure 11 (b) illustrates these two mechanisms and line 1-3 depicts the binodal line. When it crosses the line 1-2, instantaneous precipitation sets in. However, if the binodal line does not cross the line 1-2, the precipitation takes some time to begin (Pandey and Chauhan, 2001).

Membranes formed by instantaneous demixing have a porous top layer and are used in microfiltration and ultrafiltration processes. Membranes formed by delayed demixing have a dense skin and are appropriate for use in gas separation. However, the difference in terms of time between these two processes is barely matter of seconds (Pandey and Chauhan, 2001).

If an additive is used in the polymer solution, the phase diagram can be represented by a tetrahedron, in which the binodal and spinodal are zones/surfaces intercepting each other at the initial curve (figure 11). Due to the complexity in the three-dimensional representation, it is usual to consider the additive along with the polymer as a single component.

The above-mentioned strategies have been undertaken with a view to obtain both high permeability and selectivity. It is generally noticed that as the gas permeability increases, its selectivity decreases. This inverse relationship has been observed by Robeson (1992) that linear ‘upper bound’ exists in the inverse relationships between selectivity and permeability for binary gas mixtures of He, H_2, O_2, N_2, CH_4, CO_4, CO_2.

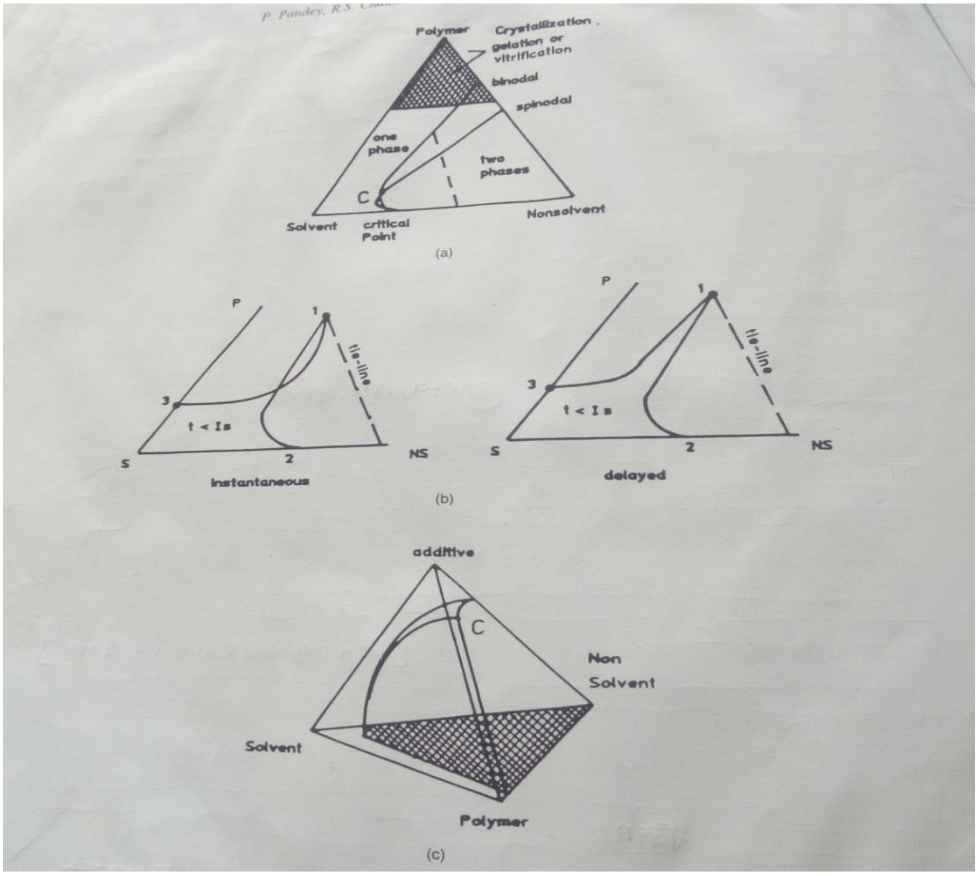


Figure 11: *(a) Schematic phase diagrams for ternary system consisting of polymers/solvent/non-solvent’. (b) Phase separation by instantaneous and delayed demixing of polymer solution in a ternary system. (c) Schematic phase diagram for quaternary system consisting of polymer/solvent/non-solvent additive, represented by a tetrahedron.*
Adopted from Machado, ***,*** *Habert and Borges (1999) and Pandey and Chauhan (2001).*

Cohen *et al. (*1979), Reuvers, Berg and Smolders (1987), Reuvers and Smolders (1987); Radovanovic, Thiel and Hwang (1992a,b) have conducted fundamental studies on membrane formation by immersion precipitation in ternary systems of polymer, solvent and non-solvent **(**Wienk *et al* 1996). The Phase separation of a polymer solution is induced by:

- Quenching the solution to a lower temperature
- Immersion of the solution in a bath of non-solvent
- Contacting the polymer solution with a vapor of the non-solvent.
- Evaporation of the solvent

For membrane formation, immersion precipitation is the most important and best studied process. Phase separation processes by evaporation or contact with a non-solvent vapour are closely related to the immersion precipitation process because they are also diffusion induced (Wienk *et al.*, 1996).

Upon immersion of a film of a polymer solution into a non-solvent or coagulation bath the non-solvent will diffuse into the polymer solution, whereas the solvent diffuses into the bath. The diffusion coefficient of the polymer is much lower and therefore the mobility of these polymeric molecules will reach only for smaller distances (Wienk, *et al*., 1996).

Membranes formed by instantaneous demixing generally show a highly porous substructure (with microvoids) and a finely porous, thin skin layer. Membranes formed by a delayed demixing mechanism show a porous (often closed-cell, macrovoid-free) substructure with dense, relatively thick skin layer. Which process takes place is mainly determined by the interaction between the solvent and the non-solvent, and by the non-solvent concentration in the bath (Yilmaz and McHugh, 1988; Wienk, *et al*., 1996).

From an evaluation of the origin of the difference in the onset of phase separation in ternary systems [Smolders, *et al* 1992]. It becomes clear that the tendency of mixing of the solvent-non-solvent pair plays a central role. Instantaneous demixing and macrovoids are found for solvent-nonsolvent pairs with a high mutual affinity (high positive values of $d\mu/\mathrm{dln}\varphi$), for the binary solution).

This is well exemplified by the curves in figure 12 which show delay times for 15 vol.% CA solutions in various solvents, immersed in coagulation baths which either consisted of pure water or contained increasing amounts of the solvents. The delay times were measured by light transmission experiments upon immersion 16(c). From THF as solvent to DMSO, the miscibility increases with water. Figure 12 also indicates that the delay time in pure water coagulation bath decreases going from THF as solvent to acetone. In case of dioxane, DMF or DMSO as solvent one has to add increasing amounts of these solvents to the coagulation bath, in order to enforce delayed demixing. It has been shown earlier (figure 12) that the transition from delayed to instantaneous onset of liquid-liquid demixing in these immersed films is situated in between a water-acetone volume ratio of 10/90 and 12 5/87.5 in the casting solution. Other phase separation types than liquid demixing i.e crystallization or aggregate formation (Smolders, *et al.*, 1992) can also occur in polymer solutions. It is clear from kinetic considerations of phase separation (Smolders *et al.*, 1992) that during the relatively fast membrane formation step, nucleation processes which need an ordering process (such as crystallization or aggregate formation) before taking place will not be operative. One can say that membrane morphology is determined by diffusion and liquid-liquid phase separation. In a secondary step formation of fibrillary or other structures in the polymer-rich phase might occur due to crystallization or aggregation phenomena. This can of course have an effect on the permeability of the dense top layer.

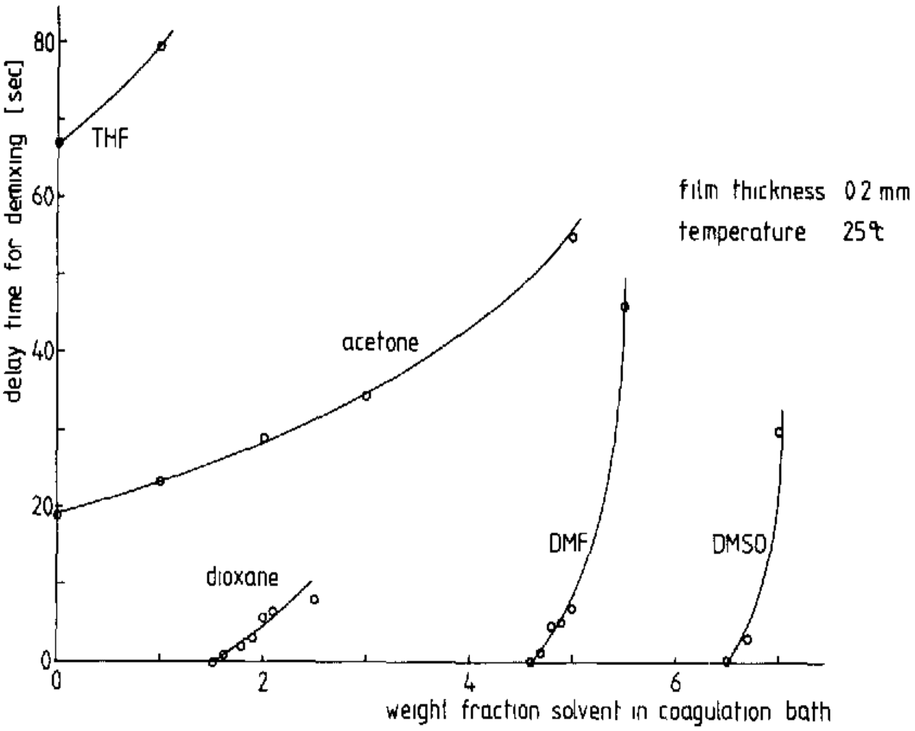


Figure 12: Experimental delay time for the onset of liquid-liquid demixing after immersion of a 15 vol% CA solution, prepared from the indicated solvent, into a coagulation bath with a varying initial solvent-water ratio.
Source: Smolders, Reuvers, Boom and Wienk, 1992.

According to Smolders et al. (1992), addition of solvent to the coagulation bath can yield delay of demixing. So, it is indeed clear that addition of extra amounts of water to the CA-acetone-water casting solution suppresses macrovoid formation. The occurrence of local delay of demixing is therefore also suppressed by nonsolvent addition.

Figure 13 gives some further evidence of the phase separation types, found in membrane forming system. The cloud point curves for polysulfone/DMF/water are given at 20⁰C and 40⁰C. Also, only a few percent of water in the solution are sufficient to introduce L-L separation here. There is no direct measurement on gelation yet, but it can be observed that a PSn solution in DMF, as used for membrane preparation, when stored at room temperature for some hours under exclusion of water gives a precipitate of PSn. Hence the usually employed PSn, solutions are on the verge of crystallization (or gelation). From other work (Broens et al., 1980). It is also known that PSn will crystallize from certain solvents.

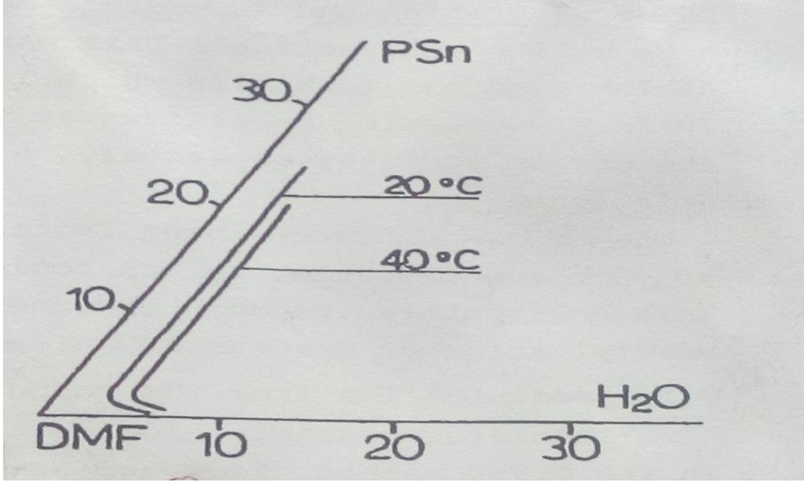


Figure 13: Ternary diagram of PSn/D.M. F./H_2O. Cloud point curves at 20^0C and 40^0C. **Source:** Broens *et al.*, 1980

An example of ternary phase diagram for polymer, solvents and coagulating non-solvent (typically water) is shown in figure 14. The path followed by the polymer during phase inversion is labelled "Coagulation path". Two-phase separation processes can occur, as noted in the literature (Sanders *et al.,* 2013). Spinodal decomposition will occur if the membrane formation path goes through the critical point or rapidly into the unstable region. Nucleation and growth can occur in the metastable region as well as the unstable region (Sanders *et al.*, 2013). The initial morphologies resulting from these processes are different and spinodal decomposition yields a more desired intertwined structure. As the phase separation process continues, the initial features of spinodal decomposition can become less recognizable due to structure coalescence. The thermodynamic interpretations of nucleation and growth versus spinodal decomposition and information directly related to membrane formation are available elsewhere (Sanders, et al., 2013).

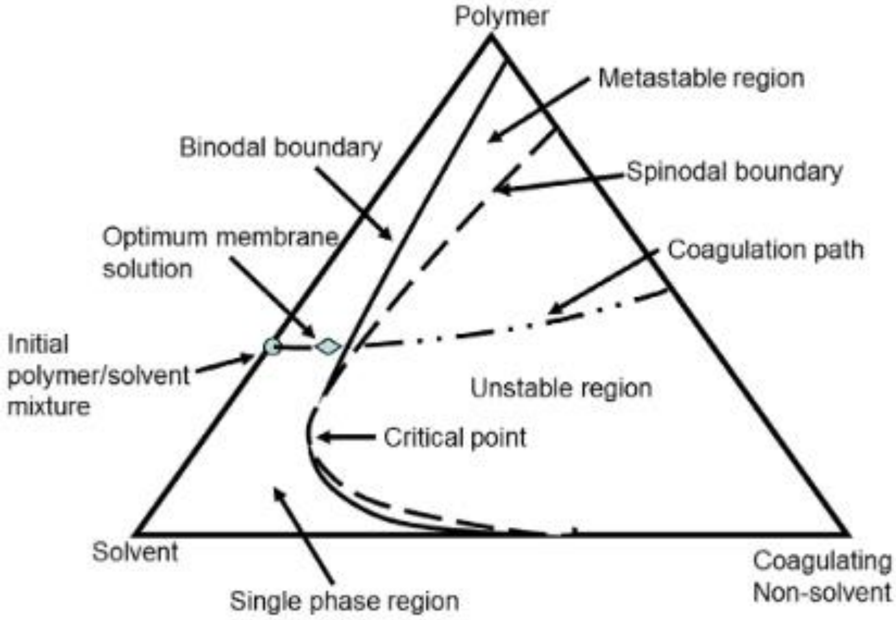


Figure 14: *Qualitative illustration of a phase diagram for a polymer/solvent/nonsolvent system. The path followed during formation of a phase inversion membrane is illustrated by the line labeled "Coagulation path".* ***Source:*** *Sanders et al., 2013.*

Influence of Various Parameters on Membrane Structure and Properties

Different factors have a major effect upon membrane structure. These are:

- Choice of polymer
- Choice of solvent and nonsolvent
- Composition of casting solution
- Composition of coagulation bath;
- Gelation, vitrification and crystallization behavior of the polymer.
- Location of the liquid-liquid demixing gap;
- Temperature of the casting solution and the coagulation bath; and
- Evaporation

By varying one or more of these parameters, which are not independent of each other, the membrane structure can be changed from very open porous form to a very dense nonporous variety (Mulder, 2000). Some examples are given in table 7 that clearly demonstrate the influence of various parameters on the membrane structure when the same system, DMAc/polysulfone (PSF), is employed in each case. To understand how it is possible to obtain such different structures with one and the same system, it is necessary to consider how each of the variables affects the phase inversion process. The ultimate structure arises through two mechanisms; (1) a diffusion processes involving solvent and nonsolvent occurring during membrane formation; and (2) demixing processes.

Table 7: Influence of preparation procedure on membrane structure

Evaporation PSf/DMAc = pervaporation separation
Precipitation of 15% PSf/DMAc/THF in water = gas separation
Precipitation of 35% PSf/DMAc in water = pervaporation/gas separation
Precipitation of 15% PSf/DMAc in water = ultrafiltration
Precipitation of 15% PSf/DMAc in water/DMAc = microfiltration

Even more often than a second polymer, low molecular weight additives are used to improve the morphology and performance of membranes. Kesting *et al.* (1985, 1990, 1993) also described an effect of the addition of a carboxylic acid (non-solvent for the polymer) on flux properties (hence the skin thickness) of gas separation membranes. They described the association of the additive with the solvent used (DMF, NMP) (N-methyl pyrolidone).

Wienk *et al*. (1996) used a number of dicarboxylic acids as additives in polyimide/dimethylformamide solutions for the preparation of ultrafiltration membranes. It was found that some of the dicarboxylic acids reduce the number of pores in the top layer and suppress the formation of macrovoids; the best results were obtained using oxalic acid.

Effective dicarboxylic acid molecules are able to form with their two –OH groups a bridge-complex on the imide carbonyl and nitrogen (figure 15). As was shown by Smit (1991) the imide nitrogen atom is a flexible link or “pivot point” of the polyimide chain. The complex formation thereby causes a decrease in polymer chain flexibility due to steric hindrance at the pivot point. Therefore, the result of complex formation may well be a change in the polymer properties, as was also indicated by a visible increase in polymer solution viscosity upon addition of an effective dicarboxylic acid. Thus the dicarboxylic acid causes temporarily a decrease of polymer chain mobility. The stability of the acid polymer complex is higher in case the interaction between acid and non-solvent is lower i.e when the solubility of the dicarboxylic acid in the coagulation bath is lower.

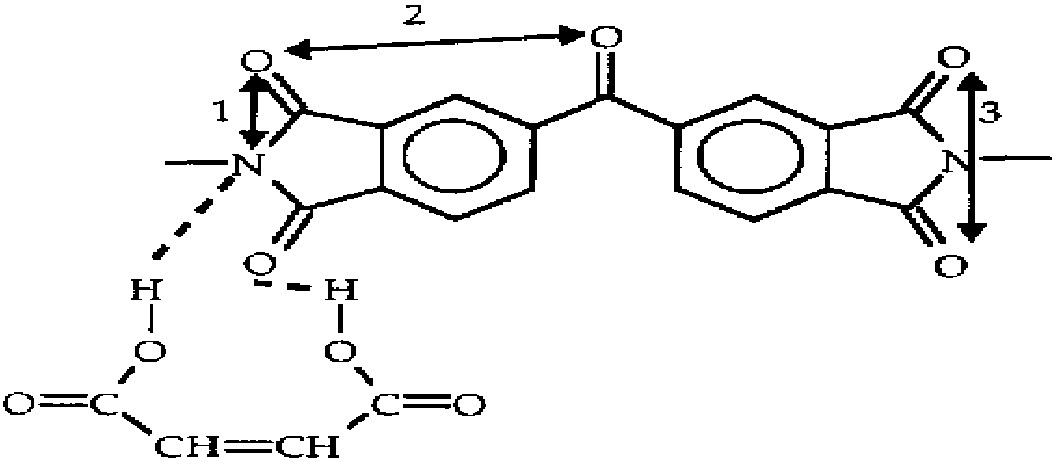


Figure 15: Schematic drawing of the complex formation of maleic acid and polyimide. The complex formation results in decreased flexibility of the polyimide chain since the imide nitrogen atom serves as a pivot-point i.e a flexible link. ***Adopted from:*** Wienk *et al*. (1996)

The observations made in this work are in conceptual agreement with the earlier proposed mechanism and results on the effects of important variables on the structure and properties of membranes (Broens et al., 1980).

Membrane Fabrication Process

Today, virtually all gas separation membranes are made by processes based on the concept of phase inversion because it is the only commercially viable way known for making thin (i.e of the order of 100nm or less), defect-free membranes at large enough surface areas to be useful for practical applications. The phase inversion process, invented by Loeb and Sourirajan [1962] to make cellulose acetate desalination membranes can be used to produce asymmetric membranes with very thin; dense films on a porous substrate and provided a practical route to prepared high flux membranes. This process remains the primary method by which commercial gas separation membranes are prepared and has allowed membranes to be prepared in sufficiently large area to process, for example from 50 to 700million standard cubic feet of natural gas per day in some locations (Xiao et al., 2009). To prepare membranes via phase inversion, a water –insoluble polymer is dissolved in a water miscible, high boiling solvent or mixtures; the resulting solution is often referred to as a polymer dope.

For most cases, macrovoids in asymmetric hollow fibers may be undesirable because they are the weak mechanical points that usually result in membrane failure at high pressures. The origins of macrovoids formation in the cross section of phases-inversion membranes have been often studied. According to Broens et al. (1980), Reuvers et al. (1987), Yao et al. (1988), Smolders et al. (1992), it originates from thermodynamic aspects of chemical potential gradient (Chung, 2008). Matz (1972); Strathmann et al. (1975), Strathmann and Kock (1977), Chung and Kafchinski (1997), Wang (2004a); consider it starts from local surface instability and material and stress imbalance, which induce solvent intrusion and capillary flow (Widjojo and Chung, 2006).

Several studies have indicate ways to reduce macrovoids or modify the phases-inversion conditions to yield a sponge like structure using high polymer concentration solutions (Kesting et al., 1990; Kesting and Fritzsche, 1993), using high viscosity spinning solutions (Chung et al., 1994), (3) spinning at high shear rates (Ren et al., 2002), the induction of delayed demixing (Kim et al., 2001) or gelation (Lin et al., 2002), the addition of surfactants (Tsai et al., 2001), the addition of high-viscosity components (Li et al., 2002) or the reduction of air gap distance and flow channel thickness in the spinneret (Widjojo and Chung, 2006).

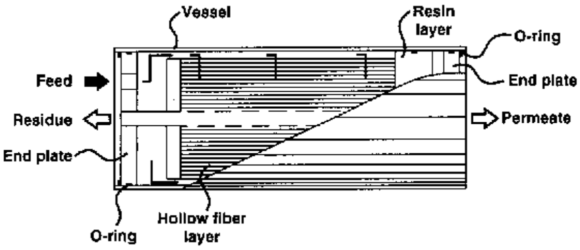
Membrane Modules Prepared by the Phase Inversion Process

Most of today’s gas separation membranes are formed into hollow-fiber modules, with perhaps fewer than 20% being formed into spiral wound modules. Schematics of these modules type is employed for particular applications are shown in figure 16.

Effects of Air Gap on Hollow-Fiber Membranes

Many scientists have used the Flory-Huggins equations, derived in 1942, to study the phase-inversion process during the formation of asymmetric flat membranes. However, the Flory-Huggins equations of solutions may not be fully capable of describing the Gibbs free energy for the state of as-spun hollow-fiber solutions (nascent fibers) spun non-isothermally with tension (Chung, 1997). At least two additional terms have to be included in this equation if the fiber is spun isothermally; one is the work, done by the external stresses to the as-spun nascent fiber and the other is an extra entropy change, $\Delta S^{EXTRA}/\mathrm{RT}$, induced by these stresses (Chung, 2001). Experimental results suggest that the effectiveness of external stresses (work) on the phase stability of a spinning solution depends on the chemistry of coagulants. The wet-spun hollow fiber has a tight external surface morphology, while the dry-jet wet-spun fiber with a long air gap may have a three-dimensional open-cell structure.

High-Pressure, Shell-Side Feed Hollow Fibers



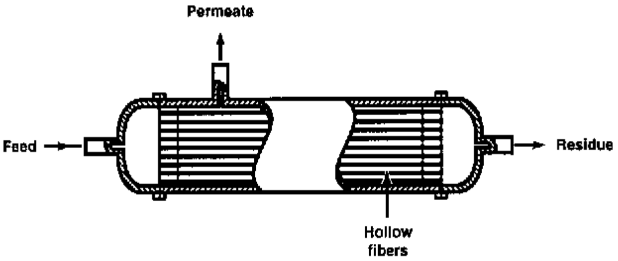
Features

- Cross-flow
- Feed gas need very good pretreatment
- Good feed flow distribution
- Used by Medal, Cynara, others

Typical applications

- H_2 recovery in refineries
- CO_2 removal from natural gas

Low-Pressure, Bore-side Feed Hollow Fibers



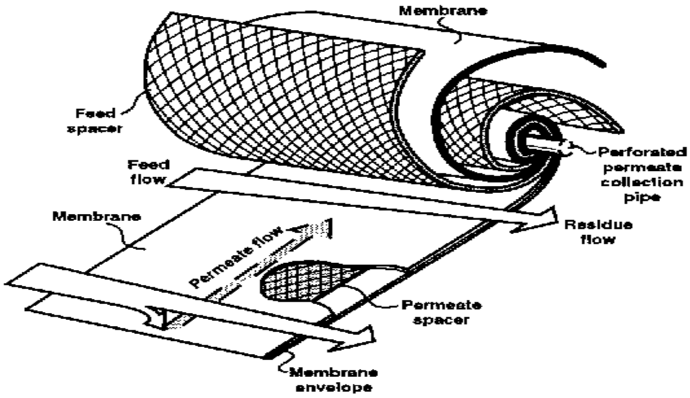
Features

- Counter-flow
- Fouling not usually a problem
- Used by medal, air products, others

Typical applications

- Nitrogen from air
- Dehydration of air

Spiral-Wound Modules



Features

- Cross-flow
- Fouling not usually a problem
- Wide range of membrane can be used
- Used by separex, MTR

Typical applications

- CO_2 removal from natural gas
- Vapor/gas separations

Figure 16: Principal Gas Separation Membrane Module Configurations
Adopted from: Baker, 2002.

Membranes Performance Evaluation

During this work, an extensive search was conducted for published literature which highlights the development of various gas separation technologies that are useful to evaluate their future research possibilities. Since the advent of commercial membrane gas separation systems, structure-property data on polymeric membranes has significantly increased in the literature, it became apparent that balance (tradeoff relationship) existed between selectivity and permeability (Sanders *et al.*, 2013).

The membrane performance was evaluated by measuring the permeability and selectivity of gases. The permeability is the product of absorption and diffusion coefficient a follows:

$P=K_iP_i$ [4]

Where K*i* is the sorption coefficient and D*i* is the diffusion coefficient. The unit of permeability is Barrer that equals 10^{-10} (cm3/cm-s-cmHg). Experimentally, the permeability can be calculated based on the flux.

$P=J\frac{\Delta l}{\Delta P}$ [5]

Where J is the flux (volume flux rate per unit area), Δl is the membrane thickness, and ΔP is the pressure difference across the membrane. On the other hand, selectivity (αij) refers to permeability ratio of two *j*.

$\frac{Pi}{Pj}$ [6]

Ficks Law, shown below, is widely used to approximate the solution-diffusion process:

$J = \frac{\mathrm{k\ x\ D\ x}\ \Delta p}{\ell}$ [7]

J	is the membrane flux of hydrogen, that is, the molar flow hydrogen through the membrane per unit area of membrane.
k	is the solution of hydrogen in the membrane
D	is the diffusion coefficient of hydrogen through the membrane
ΔP	is the partial pressure difference of hydrogen between the feed (high pressure) and permeate (low pressure) side of the membrane.
ℓ	is the membrane thickness.

Several key factors in membrane transport performance include flux, permeability, and selectivity. The flux is governed by a choice (permeability) and its effective thickness. The selectivity is also determined by the choice of polymer and the ability to achieve “pinhole-free” membranes. As thickness is a process fabrication parameter, the permeability and selectivity of the polymer are key material properties for polymer studies. A considerable number of structures – property studies have identified polymer structural components that yield high permeability, and many of these studies have defined structural characteristic desirable for gas separation (Sanders *et al*., 2013).

It is well established that the chemical structure coupled with subtle physical properties of the membrane material influence the permeability and selectivity (Pandey and Chauhan, 2001]. Many studies on polyimides gas separation membranes indicate that the separation properties can be tailored by using different dianhydride and diamine monomers. Structure/property studies (Kim *et al*, 1988; Stern *et al*, 1989) show that restricting both chain mobility and chain packing can simultaneously increase permeability and selectivity in polyimide (Sanders *et al*, 2013). In particular, polyimides with a hexafluoro substituted carbon (-C(CF_3)$_2$-) in the polyimide backbone have been the object of much research, as they tend to be considerably more gas selective (Sanders *et al.*, 2013). Fluorinated polyimides are made using 2, 2-bis (3, 4-dicarboxyphenyl) hexafluoropropanedianhydride (6FDA), and the permeability can be boosted to 456 barrer no (i) (Liu *et al.*, 2001; Sanders, Smith, Guo and Robeson, 2013)**.**

It has also been established that the presence of –C(CF_3)$_2$- groups in diahydride as well as diamine moieties exhibit both high selectivity and permeability. This is attributed to increased chain stiffness, resulting due to the bulky groups, which inhibit intra-segmental mobility, thereby resulting in enhanced selectivity. Furthermore, these groups inhibit chain packing due to their size, which serve as “molecular spacers” thereby increasing the permeability (Sridhar *et al*., 2007a, b).

Chain stiffness influences intra-segmental (rotational) mobility, whereas packing density influences inter-segmental spacing. A “trade-off” should be found to inhibit chain mobility, to achieve higher selectivity’s by molecular sieve mechanism and to achieve higher permeabilities due to an increase in free volume.

Preliminary studies have paved the road to membrane preparation and modification techniques to obtain reasonable selectivity and permeability. Permeabilities and selectivities for acid gas in different polymeric membranes are listed in table 8. From these data, it can be noted that the membranes prepared in this work have better performance than the commercial membrane.

Table 8: Result of Comparative Study of Permeability and Selectivity of Membranes

Material	**PH_2 (Barrer)**	**H_2/CO**	**$\propto H_2/CH_4$**	**$\propto H_2/N_2$**
Carboxylated polysulphone	31	115.0	157.6	50.8
Fluorinated cross-linked polyimide	66.2	142.2	163.4	70.2
Integrally skinned symmetric cellulose acetate	29	87.6	104.3	44.7

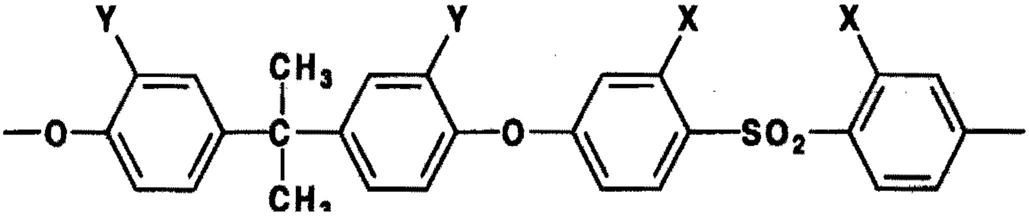
Source: Experiment of this work

Comparison of the three membranes in table 8 shows that the use of fluorinated cross-linked polyimide membrane gives the best result. Consequently, the separation performance of the polyimide membrane was optimized by different pre-treatments and permeation temperatures. The gas transport properties improve when the membranes were pre-treated with ethanol-hexane and freeze-drying, respectively compared to samples dried at room temperature and oven. As permeability values did not correlate for freeze-drying and room-temperature-oven treatments, but there was correlation for the ethanol-hexane pre-treatment procedure. This was mainly attributed to the avoidance of the pore shrinkage during the ethanol-hexane procedure, as well as the removal of plugging compounds from within membrane structure during alcohol immersion. This observation is consistent with the work reported by Albo, Wang and Tsuru, 2014.

Gas separation membranes are highly material dependent and significantly changes in solubility, fractional free volume, and chain rigidity are possible through appropriate choice and site of functional group (Guiver, *et al*, 2000). Polysulfone has overall thermal and chemical stability combined with good mechanical and membrane making qualities. It is a stable platform for functional group attachment and a good candidate material having tailored properties. This research work examined the usefulness of polysulfone functionalization, as an approach to modification.

This modification procedure was based on directed lithiation, taking advantage of the strong ortho-directing power of the sulfone group in the polysulfone backbone. Lithiation route is a convenient way to produce an homologous series of functional groups having incremental changes structure and is therefore a potentially useful tool in studying structure-property relationship in gas separation membranes (Guiver *et al*., 2000).

The structure of modified polyfulfones is indicated by the general structure shown below.



In this work, carboxylated polysulfone (CPSf) was formed readily by reaction of carbon dioxide with lithiated polysulfone according to the procedure reported by Guiver *et al.*, (2000).

Gas separation membrane was made from the carboxylated polysulfone. Membrane formation behavior and pore size range is quite different from PSf, suggesting that carbonyl groups significantly alter the kinetics of the phase transition. Certainly, the polymer precipitation points of CPSf in different solvent-water systems are quite different from PSf. This approach is to incorporate functional group having a chemical interaction with one of the feed gases, thereby increasing the permeability and selectivity. There are also groups that have particular steric shapes and that are sited around flexible chain linkages having a potential to bring about a simultaneous increase in selectivity and permeability by increasing chain rigidity and decreased chain packing. This explanation helps to understand why the membranes based on carboxylated polysulfone has a better performance than the unmodified polysulfone (see and compare results in table 8 and 11).

Hydrogen Recovery

Hydrogen is a key element for many processes in the refinery such as hydrocracking and hydrotreating. In hydrocracking, hydrogen is used to convert large hydrocarbons into smaller ones in presence of a catalyst while in hydrotreating; hydrogen is used to remove sulfide compounds in the form of hydrogen sulfide (Klerk, 2011). Furthermore, hydrogen is a feedstock for many industries like ammonia synthesis and methanol production (Fahim *et al.*, 2009).

Hydrogen is produced in the refinery by steam-methane reforming (SMR) where methane reacts with water to produce hydrogen and carbon monoxide. The produced gas is called syngas, and hydrogen yield can be further increased by the reaction of carbon monoxide with water to form hydrogen and carbon dioxide (Padro and Lau, 2007). In petroleum industry, hydrogen separation can be practiced in the following processes;

i. To recover some hydrogen during natural gas production
ii. To adjust hydrogen to carbon monoxide ratio (H_2/CO) in syngas,
iii. To recycle part of hydrogen from hydrocracker and hydrotreatment tail gases,
iv. To separate hydrogen from nitrogen in ammonia plant and
v. To purify hydrogen so it can be used as a feestock for other industries **(**Aitani, 1996; Kluiters, 2004; Alqaheem, Alomir, Vinoba and Perez*,* 2017). Content of hydrogen in refinery off-gas is given in table 9.

Table 9: Hydrogen composition in refinery off-gases

Process	Hydrogen content (vol%)
Catalytic reforming	40-85
Thermal hydrodealkylation	50-75
Hydrocracking	40-60
Hydrotreating	25-35
Catalytic cracking	10-30

Source: Alqaheem *et al.*, 2017

In a comparison of three separation technologies (membrane, PSA, cryogenic distillation) applied for H_2 recovery from refinery off-gas, Spillman (1989a, b) reported that the use of membranes represents the best choice. An evaluation of these processes is provided in terms of sustainability indexes. Comparison between the three technologies is given in table 10. As indicated, the membrane has a better capability to treat a wider range of hydrogen from 30 to 90 mol%.

Table 10: Comparison between current technologies for hydrogen recovery

Category	**Cryogenic distillation**	**PSA**	**Membrane**
Feed composition (H_2 mol%)	30-75	75-90	30-90
Product purity (H_2 mol%)	90-98	>99	90-98
Product volume (NM_3/h)	>10,000	1000-10,000	<30,000
Reliability (%)	Poor	95	100
Turndown (%)	10	30	30-50

Source: Alqaheem ***et al., 2017***

Table 11: Hydrogen permeability and selectivity of various membrane materials

Material	PH_2(Barrer)	$\alpha H_2/CH_4$	αH_2/CH	αH_2/t	T(^{0}C)	P(bar)
Polyimide (matrimid 5218)	2.5	7	11	17	30	2
Polysulfone	14	56	40-56	56	35	-
Polyethylene	17	2.2	-	4.1	30	2
Polystyrene	24	30	-	40	30	2
Cellulose acetate	24	67	30-40	73	25	-
Polyetherimide	26	51	39	71	23	0.3-0.8
Polyimide (BPDA-based)	50	125	50	83	60	-
Dimethyl silicone rubber	65	0.8	0.7	2.2	25	1
Poly (2,6-dimethylphenylene oxide)	80	30	-	31	22	-
Polydimethylsiloxane (PDMS)	1500	1	-	2.5	35	1-15

Source: Alqaheem *et al.*, 2017

Hydrogen is often highly permeable in polymers and typically is much more permeable than other gases, such as nitrogen, methane, and carbon monoxide, leading to high selectivity for hydrogen in gas mixtures for many polymers. As a result, hydrogen separation from mixtures with other gases was an initial target for membrane separation (Fleming and Koros, 1986].

Monosanto was the first company in this market, offering a polysulfone hollow fiber system marketed as Prism® membranes around (Lonsdale, 1982). Other hydrogen separations involve adjusting molar ratios of syngas (H_2/CO) and hydrogen recovery in refinery hydrotreaters (H_2/CH_4). Syngas is a mixture of H_2 and CO produced from steam reforming of natural gas, oxidation of heavy oils, or gasification of coal or coke (Scott, 1995). Depending on the method used to produce syngas, H_2/CO ratios will vary between 1 and 5 (Bernardo *et al.*, 2009; Liu K, 2010), and this ratio must be adjusted for specific synthesis applications. Because H_2 can easily be separated from CO with gas separation membranes, this application was early target for membrane-based separations Prism® membranes introduced by Monsanto were first installed in 1977 for syngas ratio adjustment, and other companies now offer a range of gas separation membranes for these applications (Sanders *et al*., 2013).

Refinery off gas purification is another hydrogen-based commercial membrane application. Petroleum crude feedstocks contain many different molecular weight products that must be separated before use. The heavier fraction of these products is often cracked, i.e broken into smaller components, through a catalytic process known as hydrocracking. This process relies on injecting hydrogen into the cracker to improve several aspects of the reaction chemistry. For example, hydrogen often reacts with polycyclic aromatic compounds that are generally inert to other cracking processes. Furthermore, hydrogen helps eliminate unsaturated hydrocarbons and reduces the formation of tar and coke (Sanders et al., 2013). Increasing the purity of hydrogen used in a hydrocracker can increase the life of the cracker catalyst and increase the production of higher paraffinic compounds (Posey, 1983). It is highly desirable to recycle H_2 from the hydrocracker products to the hydrocracker feed. Polymer membranes are used in the recycle loop to achieve this separation. Being a high-throughput process, membranes with H_2/CH_4 selectivities of approximately 20-25 and very high permeabilities are suitable for this application. Such selectiveness is readily obtained with many glassy polymers having H_2/CH_4 selectivities above 100, though the higher selectivity is often accompanied by lower permeability (Sanders *et al.*, 2013). Like with many other hydrogen separations, Prism® membranes are often used for refinery off gas purification (Baker, 2004).

While DuPont's hollow fibers were ground breaking, their low permeance was not efficient or productive enough to provide economically sustainable gas separation, according to Ockwig and Nenoff (2007), their performance shortfall was addressed by Monsanto when asymmetric polysulfone purge gases were developed**.** The next advance was introduced by Separex in the form of spiralwund cellulose acetate membranes (Separax) for H_2 and natural separation**.** As the transport properties of polymeric H_2 separation membranes evolved (table 12), they became more commonly utilized on commercial scales for various recovery processes that eventually included H_2 reclamation from recycled refinery gas (Ockwig and Nenoff, 2007).

Table 12: Hydrogen Separation Ability of First-Generation, Commercial Membranes for Gas Separations

Membrane material(s)	**Developer**	**H_2/N_2**	**H_2/CO**	**H_2/CH_4**
Polysulfone	Monsanto	39	23	24
Polyimide	Ube	35.4	30	
Cellulose acetate	Separax	33	21	26

Source: Ockwig and Nenoff, 2007

The first application of gas separation membranes was for hydrogen removal. It was developed in 1970s by Monsanto (Air Products) to recover hydrogen from purge gas in ammonia plant (Tarasov and Lototskii 2006; Ockwig and Nenoff 2007; Drioli, Barbieri and Peter 2011). The spiral wound membrane was based on polysulfone and it has a permeability of 17 Barrer (Alqaheem *et al.*, 2017). Cellulose acetate membranes were introduced then by Separax and they showed a better permeability and stability; therefore, they were employed for removal of hydrogen from natural gas (Schell and Houston, 1982). The permeability was greatly improved from 14 to 24 Barrer when cellulose acetate was used instead of polysulfone. For adjustment of H_2/CO ratio in syngas, polyimide (made by UBE) gave a better permeation of 50 Barrer with superior selectivity of H_2/CH_4, (125), H_2/CO (50), and H_2/N_2 (83) (Baker, 2012). Mivechian and Pakizeh (2013) evaluate the feasibility of using a membrane system to separate hydrogen from refinery off-gas containing 72mol% hydrogen with light hydrocarbons (C_1-C_6) based on polyimide. The study shows a better recovery of 95% compared to 79% using PSA. The membrane also achieved a hydrogen purity of 98.3%.

In this work, a hollow fiber membrane from fluorinated cross-linked polyimide was evaluated for hydrogen recovery, hydrogen upgrading, inert by product rejection and off-gas upgrading. When the feed gas enters the separator, the fast gas (hydrogen) permeates the membrane wall more quickly than the heavier compounds and exits the bore side of the hollow fiber membrane bundle. This purified stream is returned to the hydroprocessor along with makeup hydrogen. In refinery operations, high value hydrogen is required to perform hydroprocessing. High pressure off-gas is produced from the hydroprocessor (rich in hydrogen but also containing “inerts” such as methane and heavier hydrocarbon compounds). By rejecting the “inerts” the hydrogen stream can be recycled to the hydroprocessor with a smaller makeup volume of hydrogen required to perform the hydroprocessing. The results are given in table 13 below.

Table 13: Evaluation of hollow fiber membrane

Feed gas composition	Permeate
H_2 (86 mole%)	H_2 (98 mole%)
CH_4 (9 mole%)	CH_4 (1 mole%)
C_3 (4 mole%)	$C_3 < 1$ mole%
C_2 (1 mole%)	$C_2 < 1$ mole%

Source: This work

The results show that with this hollow fiber membrane based on fluorinated cross-linked polyimide, purge gas stream from hydroprocessing can be upgraded to hydrogen purities of 94 to 98 mol% at recoveries of 86 to 97%. Even catalytic cracker off-gas streams containing 20-30 mole % hydrogen can be upgraded to 80 to 95 mole % purity (with a single stage separation) or up to 98 mol% with a two stage system. Typical oil refinery systems produce hydrogen with purities between 90 to 98 mol%. Product gas purity is dependent upon feed composition, available differential partial pressure and required hydrogen recovery level. The hydrogen-rich stream is returned at nearly the same pressure as the feed gas for use as fuel gas. These results suggest that this membrane system be optimised for possible integration into a refinery flow sheet for hydrogen recovery, inert byproduct rejection, and plant debottlenecking. In principle, recovering hydrogen from the inert purge gas is an easy application for membranes. A simplified flow scheme for the treatment of a purge stream is shown in figure 18. The feed gas, off-gas from a separator with a dew point of 31^{0}C, contains 75% hydrogen; 22% methane, ethane and propane and 3% C_{4+} hydrocarbons. As hydrogen is removed through the membrane, the remaining gas becomes enriched in hydrocarbons, and the dew point increases to 64^{0}C (Baker, 2002). To avoid condensation of hydrocarbons on the membrane, the gas must therefore, be heated to at least 64^{0}C. In practice, to provide a safety margin and to minimize plasticization of the membrane, the gas must be heated.

As hydrogen is removed from the pressurized feed, the gas becomes enriched in condensable hydrocarbons and its dew point increases to 15-20^{0}C above the expected residue gas dew point. Thus, the example illustrated in figure 18 implies that the gas must be heated to above 80^{0}C, at which temperature membrane and module performance can be adversely affected (Baker, 2002). Even heating the gas does not provide absolute membrane protection. Variations in gas composition are common in refinery applications, for example, when the source is a catalytic process from which off-gas content changes as the catalyst activity changes**.** In cognizance with Baker's, more sudden changes occur when the feedstock to the upstream unit changes. The hydrocracker typically handles multiple streams from diverse sources: feed quality changes can be rapid and substantial as one or more streams are added or subtracted. The process parameters, such as pressure and temperature, deviate from the normal operating range as a result of plant upsets or deliberate plant operator action to optimize a particular product. Any of these changes can bring the gas close to its dew point and cause membrane failure (Baker, 2002).

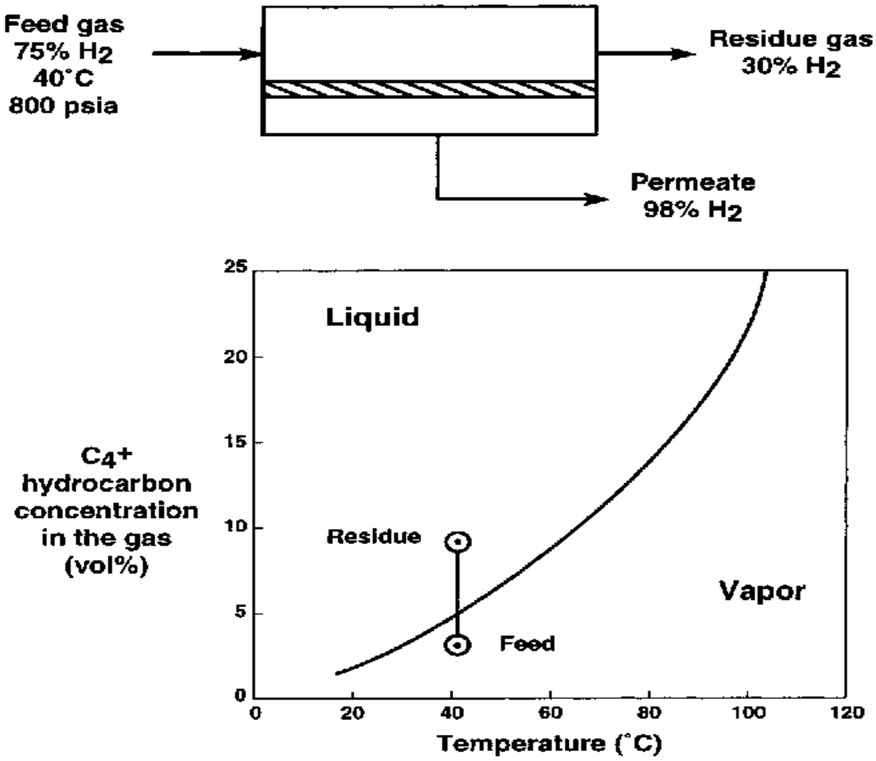


Figure 18: Illustration of the hydrocarbon condensation problem on the residue side of a hydrogen-permeable membrane**.** ***Source:*** Baker, 2002.

Membrane module development and integrated performance testing

In this research work, module development started with the construction and performance testing of small laboratory scale units. Extensive experimental development led to be production of hollow fiber substrates from different polymer materials with different pressure ratings and separation properties. This report covers one of these membranes (a polyimide hollow fiber) capable of operation at intermediate pressure up to 700psig. During membrane formation prototype modules are constructed and continuously undergo detailed performance testing.

Module development includes the modeling of flow dynamics through and around the fibers in the membrane module and construction of modules from fibers. Finally, result will be evaluated on both technical and economic grounds to assess the commercial potential of the membrane for gas separation. Membrane manufacture involves spinning and coating of hollow fibers, wnding and potting the fibers to form cartidges and quality control of the cartridges as they are produced. When membranes are intended for commercial applications it is important to determine their resistance to contaminants in the feed stream.

Extensive testing facilities made it possible to measure the permeability of membranes for various gas components as shown in table 13. Separation and permeation performance can be measured at different temperatures and pressures. The feed is either pure or mixed gas and feeds are in flow-through or dead-end mode arrangements with provision for an inert sweep gas on the permeate side.

Facilities exist for membrane modules ranging in size from a few fibers, to large commercial size cartridges. During the membrane development stages, hollow fibers are tested in small modules (8 fibers) or mild-sized modules (80 fibers). There was, however, no facility for performing field tests on commercial sized cartridges.

The module production methodology was subsequently used in the construction of the prototype modules that are to be used in the field tests in Phase II of this project, according to the prototype illustration of Bollinger *et al.* (1984) and Henis (1994).

Membrane Hydrogen Recovery

A typical application, illustrated in figure 19, is the recovery and reuse of hydrogen from an oil hydrocracker purge gas. Hydrocrackers are used in refineries to break down high-molecular-weight components to remove impurities, and to hydrogenate aromatics. Ideally, heavy oil is cracked to C_{5+} hydrocarbons, but inevitably some methane, ethane and propane are produced as byproducts of the reaction. The oil/gas mixture from the hydrocracker is sent to a lower-pressure separator from which the C_{5+} product is removed. Unreacted hydrogen is recirculated back to the reactor. Methane, ethane and propane accumulate in the recycle stream and must be removed as an inert purge. Typically, 3-4 mol of hydrogen are lost with every mol of light hydrocarbon purged from the reactor.

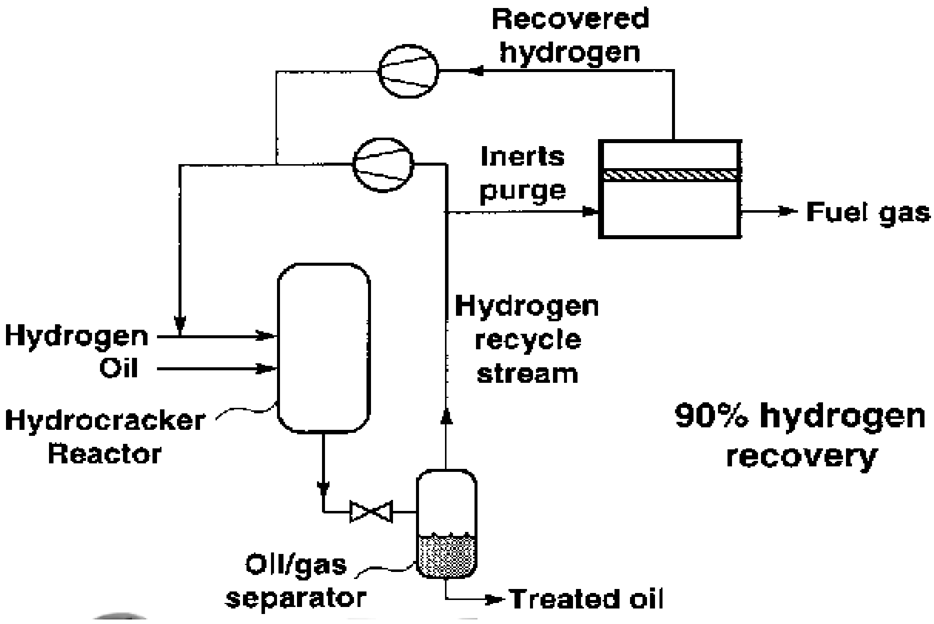


Figure 19: Use of hydrogen-permeable membranes to recover and recycle hydrogen from hydrotreater purge gas streams. ***Adopted from:*** Baker, 2002

Solution-Diffusion Mechanism of Gas Separation

Polymer membranes used for separation processes operate according to the solution diffusion mechanism. According to this mechanism, the rate of diffusion through the polymer membrane is governed by Fick's law of diffusion. For simple gases, it can be shown that Fick's Law leads to the expression

$$J = \frac{Dk\Delta p}{l} \qquad [8]$$

Where J is the membrane flux (cm^3(STP)/cm^{2}s), k is the Henry's sorption coefficient linking the concentration of gas in the membrane material to the pressure of the adjacent gas (cm^3(STP)/cmHg), Δp is the partial pressure difference across the membrane, l is the membrane thickness (cm), and D is the permaneant diffusion coefficient (cm^{-2} s^{-1}), a membrane of the permeant's mobility in the membrane. This expression can be further simplified to

$$J = \frac{P\Delta p}{l} \qquad [9]$$

Where P is the permeability, equal to the product Dk, and is a measure of the rate at which a particular gas moves through the membrane of a standard thickness (1 cm) under a standard driving pressure (1 cm Hg). The permeability unit, 1 x 10^{-10}cm^3 (STP)cm/cm^{2}s cm Hg, is called a Barrer, after R.M. Barrer, a pioneer in membrane permeation studies.

A measure of the ability of a membrane to separate two gases (1) and (2) is the ratio of their permeabilities called the membrane selectivity, ∝;

$$\propto_{1,2}=\frac{P1}{P2}=\frac{D1}{D2}\text{X}\frac{k1}{k2} \qquad [10]$$

The factors that determine membrane permeability can best be understood by considering the component terms *D* and *k.* For simple gases, the diffusion coefficient tends to decrease with increasing permeant diameter, because large molecules interact with more segments of the polymer chains and are thus less mobile. In glassy, rigid polymers such as polysulfone or polyimides, permeant diffusion coefficients are most important. Therefore, these polymers preferentially allow the small, non-condensable gases, hydrogen, nitrogen and methane to permeate over the large, condensable gases such as propane and butane. The mechanism for gas separation is independent of membrane configuration and is based on the principle that certain gases permeate more rapidly than others (figure 20).

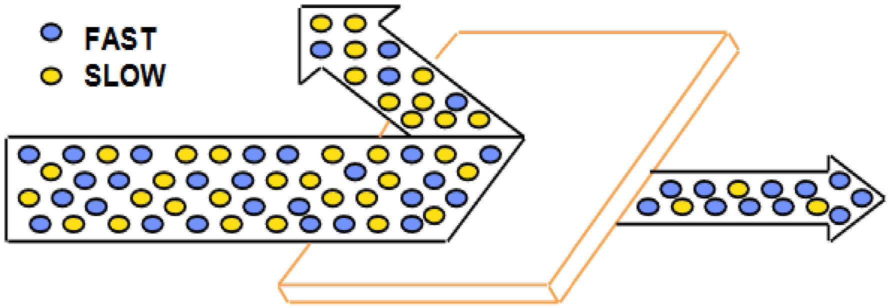


Figure 20: Thin semi-permeable Barriers that Selectively Separate Some Compounds from Others.
Taken from: William and UOP (1999)

While permeability is a measure of the rate at which gases pass through the membrane, selectivity refers to the relative rates of permeation among gas components. The permeation rate for a given gas component through a given membrane is determined by the molecule’s size. Selectivity allows a gas mixture of two or more components of varying permeability, to be separated into two streams, one enriched in the more permeable components and the other enriched in the less permeable components. Figure 21 shows the relative permeability of the components most common in a natural gas stream for glassy-type membrane. Membrane based gas separation process depends on the gas components, membrane material and the process conditions.

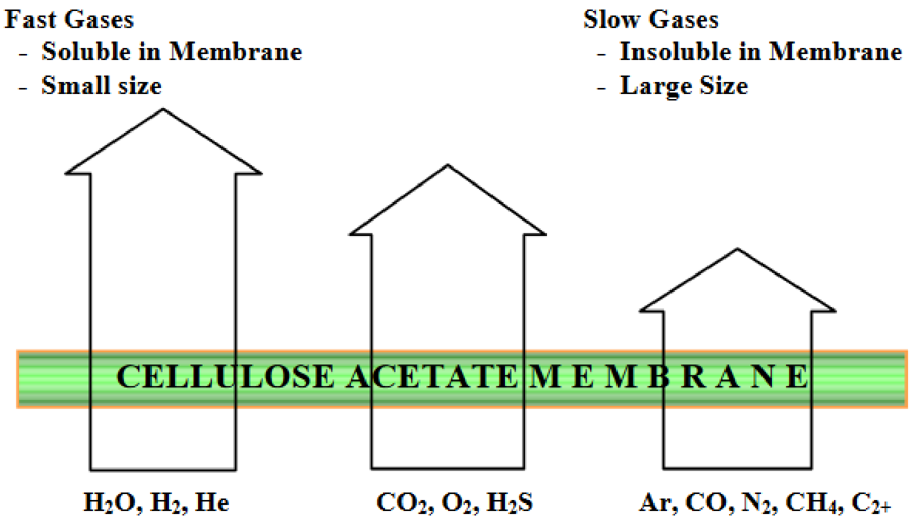


Figure 21: Relative Solubility of Some Typical Gas Components
Taken from: William and UOP (1999)

The solution diffusion model is widely accepted as the transport model for polymer membranes. The flux is based on Fick's Law and describe as

$$Ji = \frac{Pi}{l}(p_i x_i - p_p y_i) \qquad [11]$$

Where P_i is the permeability of gas component *i*, *l* is the membrane thickness, p_i and p_p are pressure on feed and permeate side x*i* and y*i* are the fractions of components *i* in feed and permeate stream. The above expression can be re-written as,

$$Ji = \frac{Di}{l}(c_{i,f} - p_p y_i) \qquad [12]$$

Where D*i* is the Fick's diffusion coefficient and $c_{i,f}$ and $c_{i,p}$ the concentration of component *i* on the feed and permeate side of the membranes.

CONCLUSION AND RECOMMENDATIONS

Phase inversion is one of the most important processes to prepare asymmetric hollow-fiber membranes. The resultant membranes have a dense skin layer that is integrally bonded in series with a thick porous substructure. The skin and the substructure are composed of the same material. The skin layer, which contains the effective separating layer, is one of the key elements in determining membrane flux and separation factor permeance and selectivity for gas separation.

In this report, a description of the membrane formation mechanism based on theoretical and experimental knowledge of phase separation phenomena in concentrated polymer solutions is given. It has been demonstrated that different types of phase separation are responsible for the build-up of the dense skin layer and the porous supporting layer in asymmetric membranes of several materials: cellulose acetate, polysulfone, and polyimide.

Structural characteristics in membrane formed by diffusion induced phase separation processes have been discussed. Established theories on membrane formation from ternary systems can be extended to describe the effects of high or low molecular weight additives. Membranes formation studies suggested that the processing conditions during the preparation of membranes appear to affect their gas transport properties.

Even though there might be some challenges to overcome, the development of suitable membranes and the possibility of up-scaling the membranes, keeping in mind that the structure-property relationships of the materials, the membrane formation techniques and modular configurations that yield not only high permeabilities, but also moderately good selectivities should be given considerable attention. Flux and selectivity (rejection) determine the selective mass transport properties of a membrane. The higher the flux of a membrane at a given driving force, the lower is the membrane area required for a given feed flow rate, and therefore, the lower are the capital costs of a membrane system. The selectivity determines the extents of separation. Membranes with higher selectivity are desirable because a higher product purity can be achieved in a separation process. Within the framework of this work, it can be concluded that membranes fabricated from fluorinated cross-linked polyimide and carboxylated polysulphone compete well with membranes manufactured by the world leading companies for hydrogen permeable membranes, such as Air products, and UBE. PRISM membrane (based on polysulfone and developed by Air Products) is able to recover 90 to 98 mol% of hydrogen from purge gas in ammonia plant. The membrane can also upgrade hydrocracker off-gas stream containing 20-30 mol% hydrogen to 70-90 mol% in a single stage or to 95% mol% by two stages as reported in literature. On the other hand, the membranes developed in this work showed better permeability and selectivity in addition to higher resistance to fouling, which was improved by pre-treatment processes (Bitter, 1984). The lower selectivitiess reported for the commercial membranes could be ascribed either to membrane defects or to the presence of fouling agents. The membrane fabricated from fluorinated cross-linked polyimide showed more favourable permeability/selectivity combinations than current commercial membranes used for hydrogen recovery. The industrial importance of this research is based on the fact that the recovery of hydrogen in refineries will become a significant growth area in the next decade become.

Hydrogen is in short supply in almost all refineries. H_2 recovery from refinery streams is an emerging field for membrane separation hydrogen in the petroleum industry; it is a key approach to meet the increased demand of hydrogen (for hydrotreating, hydrocracking or hydrodesulfuriization processes) owing to new environmental regulations. An example is the H_2 recovery from high pressure purge gas of hydrotreater.

The findings of this work are recommended for application in the Nigerian petroleum refineries. Process optimization and economics are the most important aspects to consider when studying membrane-based gas separation. This is because they are related to the implementation of membranes on an industrial scale. Therefore, for the acceleration of the commercialization of these findings, considerable amount of development activities, both academic and industrial, are essential. Academicians can support the development of demonstration projects that showcase the membrane-based separation technology, validate product reliability and output, to provide data necessary for commercialization. Industry, on the other hand, can engage in standardizing the module configuration and increasing production volumes, which can result in the reduction of production costs.

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