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HIGH TEMPERATURE CERAMIC MEMBRANE
REACTORS FOR COAL LIQUID UPGRADING

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I Introduction

Membrane reactors combine reaction and separation in a single unit operation, the membrane selectively removing one (or more) of the reacting or product species. These reactors have been most commonly used with reactions, whose yields are limited by thermodynamic equilibrium. This is because selectively removing one of the products through the membrane results in an increase in the conversion and yield, often beyond their corresponding equilibrium values. Membrane reactors have also been proposed and used for other applications; for increasing the selectivity and yield of enzymatic and catalytic reactions by influencing, through the membrane, the concentration of one or more of the various intermediate species; for selectively removing (or helping to keep at low concentrations) species, which otherwise would poison or deactivate the reaction; and for providing a controlled interface between two or more reactant species.

The membrane reactor concept dates back to the early 1950's. Most of the applications, however, have happened in the last couple of decades due to the significant developments that have occurred in membrane materials and modules. Most of the past applications are in the field of biotechnology [1-4], and these are typically low temperature applications ($<100^{\circ}\text{C}$). They make use of porous organic/polymeric membranes, but also of inorganic membranes like silica or alumina, for instances where enzyme or whole cell immobilization on such materials appears to offer some advantage. Most recent is the use of membrane reactors in high temperature applications, typically involving catalytic processes. These reactors use metal or inorganic membranes.

ACRONYM	DESCRIPTION
CMR	Catalytic Membrane Reactor
CNMR	Catalytic Nonpermselective Membrane Reactor
PBMR	Packed Bed Membrane Reactor
PBCMR	Packed Bed Catalytic Membrane Reactor
FBMR	Fluidized Bed Membrane Reactor
FBCMR	Fluidized Bed Catalytic Membrane Reactor

Membrane reactors are available in a number of different basic configurations (see Table 1 for easy reference): (i) The membrane is permselective for one (or more) of the reactants and/or products. It also acts as the sole catalyst for the reaction, either being catalytic by itself or by being impregnated with a catalyst. We will refer to this configuration as the "Catalytic Membrane Reactor", or "CMR". (ii) The membrane is catalytic and acts as the sole catalyst for the reaction. It is not permselective, however, but it simply provides for a well defined interface for two (or more) reactants flowing on opposite sides of the membrane. We will refer to this configuration as the "Catalytic Nonpermselective Membrane Reactor" or "CNMR". (iii) The membrane is permselective but not catalytic. The catalyst zone is a packed or fluidized bed of catalysts. We will refer to these two configurations as the packed (PBMR) or fluidized bed (FBMR) membrane reactors correspondingly. (iv) The membrane is catalytic and permselective. A packed or fluidized bed of catalysts also exists inside (or outside) the membrane. We will refer to these latter two configurations as the packed (PBCMR) or fluidized bed (FBCMR) catalytic membrane reactors.

For all these membrane reactor configurations, the CNMR being the sole exception, one can identify a feed and a permeate side of the membrane. For gas-phase reactions, often on the permeate side one applies vacuum or uses a sweep gas to increase the permeation of the reactant/product species of interest. The reactor can also be operated in a number of different feed/sweep flow configurations, such as cocurrent or countercurrent. Other membrane reactor configurations and operational modes also exist. It is possible for example to recycle part of the feed or permeate exit streams to increase conversion or to use membrane reactors in series or reactors with multiple feed ports. Hybrid membrane reactor systems have also been proposed, i.e. combinations of regular (like packed or fluidized bed reactors) and membrane reactors in series.

The first high temperature catalytic membrane reactors in operation used metallic (Pd, Pd alloy and Pd/Ag) membranes. These reactors were pioneered by Gryaznov and coworkers, who studied many (mostly vapor-phase) hydrogenation/dehydrogenation reactions, while testing various reactors containing flat foil, thin walled straight tube and spiral-type membranes [5,6]. Hydrogenation reactions studied involved the production of linalool from dehydrolinalool, the hydrogenation of cyclopentadiene to cyclopentene, naphthalene to tetralin,

furan to tetrahydrofuran, nitrobenzene to aniline and furfural to furfuryl alcohol [5-8]. The reactor used with all these reactions consisted of two chambers, separated by the flat metallic membrane, with H_2 being fed typically in one of the chambers and the other reactant in the other. For all hydrogenation reactions studied in a membrane reactor, Gryaznov and coworkers reported improvements in the yield. It is not entirely obvious why membrane reactors improve the yield of hydrogenation reactions. It is probably due to the fact that atomic hydrogen is an important intermediate for such reactions and the membrane helps to optimize its surface concentrations. Gryaznov and Slink'o [9] and Nagamoto and Inoue [10-12] have addressed this exact issue. For butadiene hydrogenation, for example, the significant improvements in yield observed in a membrane reactor, were attributed to butadiene inhibiting the dissociative chemisorption of H_2 in the absence of the membrane.

The use of Pd membranes for dehydrogenation reactions dates back to the 1960s. Reactions studied include dehydrogenation of C_2H_6 to C_2H_4 [13], of cyclohexanediol to pyrocatechol [14] without phenol formation, isopropanol dehydrogenation [15] and the dehydrogenation or dehydrocyclization of alkanes to olefins, like for example 2-methylbutene-1 to isoprene, cyclohexane to benzene, heptane to benzene and methane and hydrodealkylation of toluene to benzene and CH_4 [16,17]. A Pd PBMR using a bed of $Pt/\gamma-Al_2O_3$ catalyst pellets was used by Itoh [18] for cyclohexane dehydrogenation to benzene and by Itoh *et al.* [19] and Zhao *et al.* [20] for oxidative cyclohexane dehydrogenation. A PBMR using a Pd-Ag alloy membrane and a zeolite catalyst has been proposed by Clayson and Howard for the dehydrocyclodimerization of alkanes to aromatics [21].

Pd membranes were the first to be used in catalytic membrane reactor applications because of their unique H_2 permselectivity. Pd alloy membranes containing 75% Pd, 25% Ag (Pd/25 Ag) have been commercialized for small scale on-site production of H_2 by reforming of CH_3OH or NH_3 and for purification of H_2 containing streams [22-24]. Large-scale applications have yet to materialize, however, due to a number of reasons, which include:

(i) Their prohibitively high cost. Current efforts in this area involve replacing the Pd membranes with other less costly materials such as Ti, Ta and V, which are also capable of permeating H_2 [25,26].

(ii) Their low H_2 permeability. Efforts in this area involve the development of composite

Pd/porous metal or Pd/ceramic membranes [27-36]. Such membranes were used by Uemiya and coworkers in a PBMR for the study of the water gas shift reaction [37,38], of methane steam reforming [39,40], and of the aromatization of propane [41]. Unfortunately these composite membranes have been found to be brittle and prone to pinhole formation and their commercialization in high temperature applications still remains questionable.

(iii) Pd membranes are prone to poisoning by sulfur, present in a number of petroleum and chemical feedstocks and to coking. This is the most serious of problems facing Pd membrane reactors. Sulfur or coke coverage of the surface of the Pd membranes results in an order of magnitude reduction in the H_2 permeation rates. Bend Research Inc. has reported on the use of Pt composite membranes [26] for the water-gas shift reaction. These membranes were proven resistant to H_2S poisoning.

Earlier applications of microporous inorganic membranes in membrane reactors involved the use of porous Vycor glass. Kameyama *et al.* [42-45], for example, used a porous glass PBMR containing a bed of MoS_2 catalyst pellets in the membrane shellside for H_2S decomposition. They reported conversions twice as high as the equilibrium. Shinji *et al.* [46] used a Vycor glass PBMR containing Pt/ γ - Al_2O_3 catalyst pellets to study cyclohexane dehydrogenation to benzene and also reported conversions over twice as high as the equilibrium conversion. A similar study was reported by Itoh *et al.* [47]. A Vycor glass membrane reactor was studied experimentally by Shindo *et al.* [48] and theoretically by Itoh *et al.* [49] for the decomposition of HI. The same reaction has been studied by Yeheskel *et al.* [50] in a Pd/Ag membrane reactor. A Vycor glass CMR and also PBMR were used by Sun and Khang for the study of cyclohexane dehydrogenation [51]. The membrane used in the CMR was Vycor glass impregnated with Pt. Conversions higher than the equilibrium were reported for both the PBMR and CMR.

With the exception of an earlier application by Kameyama and coworkers [42-45], who used a PBMR with a symmetric porous alumina membrane to study H_2S decomposition, all other reported applications of ceramic membranes in catalytic membrane reactors are more recent (less than four years old). Furneaux *et al.* [52] and Davidson and Salim [53] reported the use of anodic aluminas for C_2H_6 and cyclohexane dehydrogenation and for C_2H_4 hydrogenation and hydrogenolysis. It is hard to judge from their study the effect, if any, the

membrane reactor had on the yield of these reactions. Their work, nevertheless, brought forth some interesting ideas concerning the effect of metal deposition profiles in the membrane on the operation of CMRs. The use of CMRs with bifunctional catalytic membranes was also described for the first time in their paper [53]. A PBMR using an asymmetric hollow fiber alumina membrane was used by Okubo *et al.* for cyclohexane dehydrogenation [54]. The catalyst bed consisting of Pt/ γ -Al₂O₃ particles, was placed on the outside of the membrane. The use of a hybrid reactor system consisting of a packed bed reactor followed by a PBMR was also described in this paper. A similar concept has also been reported by Wu and Liu [55].

A PBMR containing an alumina membrane (Membralox[®]) was used by Wu *et al.*, for dehydrogenation of ethylbenzene to styrene [56]. The catalyst used was Fe₂O₃/ γ -Al₂O₃ promoted with K₂O and packed inside the membrane. A general improvement in conversion (~ 15%) was reported over the case with no membrane. More conservative gains in conversion have been recently reported by the same group. An alumina membrane PBMR has also been used by Moser *et al.* [57] to study the ethylbenzene dehydrogenation reaction. They reported conversions higher than the corresponding equilibrium conversions. A British patent by Bitter [58] claimed the use of an alumina membrane PBMR for several dehydrogenation reactions, including the propane to propylene reaction, for which significant improvements in yield were claimed. A CMR using an alumina membrane impregnated with Pt was used by Champagnie *et al.* [59,60] for ethane dehydrogenation with significant improvements in conversion. The same group reported the use of a PBMR and PBCMR for the same reaction also finding significant gains in conversion [61,62]. The use of a PBMR utilizing an alumina membrane for CH₄ steam reforming was also reported by the same group [61-63].

A CNMR reactor was used by Sloot *et al.* [64] to study the Claus process for desulfurization of gases. A similar reactor concept was also used by Zaspalis *et al.* for the NO + NH₃ reaction in order to prevent NH₃ slip [65,66]. Other reactions studied by Zaspalis *et al.* include the dehydrogenation of methanol [65,67-69] and n-butane dehydrogenation [65,68]. The use of membrane reactors for multiphase reaction systems has been reported by Harold *et al.* [70,71]. The general idea here again is to use the membrane to create a well defined reactive surface. Omata *et al.* [72] have used an Al₂O₃ porous tube coated externally with

a dense MgO/PbO film in a CMR to study CH₄ oxidative coupling, with CH₄ fed in the shellside while O₂ was fed in the tubeside. A 2% conversion but with over 97% selectivity was reported. O₂ conducting nonporous ceramic or metal membranes have been utilized in membrane reactors since the early seventies. Early applications involved the use of ZrO₂ and Ca-stabilized ZrO₂ to decompose various O₂ containing compounds like NO, CO, CO₂ and H₂O with or without oxygen electrolytic pumping [72-77]. Yttria stabilized zirconias (YSZ) have been used by Vayenas, Stoukides and coworkers [78-82] and several other investigators (for a review see [82]) for increasing the yield of various partial oxidation reactions with the aid of electrochemical oxygen pumping, and by Gür and Huggins [83,84] to enhance the rate of CO and CO₂ methanation. Reactions studied by Vayenas, Stoukides and coworkers include ethylene and propylene epoxidation, NH₃ oxidation to co-generate NO and electric energy and oxidative dehydrogenation of ethylbenzene to styrene. YSZ based membrane reactors have also been used for oxidative CH₄ coupling [85,86] and various catalytic epoxidations [87]. A concept similar to electrochemical oxygen pumping has been tried with Pd membranes, where the imposed potential helps to facilitate H₂ permeation [88].

Besides ZrO₂ other oxygen conducting materials have also been tried. Dicosino *et al.* [89] report the use of bismuth oxides to carry out the oxidative dehydrodimerization of various allylic and benzylic compounds. A number of specialized materials have been tried for SO_x and NO_x and most recently H₂S decomposition [90]. Ag membranes, which also conduct O₂, have been used by Gryaznov and coworkers [91]. Oxygen anionic conductors are, of course, of greater interest in the area of solid oxide fuel cells (SOFCs), which are looked upon to date as means for replacing diesel engines for heat and power generation. SOFCs, in a general sense, represent a special group of catalytic membrane reactors (for a detailed review, see [82]).

The microporous ceramic membranes used in all membrane reactors studies so far can at best separate the various gases according to the Knudsen diffusion law, i.e. the permeabilities being inversely proportional to the square root of molecular weights. A number of efforts are currently under way for the development of membranes with molecular sieving properties. It is one of the primary goals of this project to develop such membranes with molecular sieving properties which are appropriate for coal liquid upgrading applications.

II The Research Project

This is the final report on the goals and research accomplishments of the project titled "High Temperature Ceramic Membrane Reactors for Coal Liquid Upgrading." This project was a collaborative research effort between the Department of Chemical Engineering at the University of Southern California, the Media and Process Technology Group of ALCOA (formerly the ALCOA Separations Technology Division) and the UNOCAL Corporation, which is a no-cost subcontractor to the project. The Principal Investigator of the project was Theodore T. Tsotsis, Professor of Chemical Engineering at the University of Southern California. The Principal Investigator of the Media and Process Technology Group team is Dr. Paul K. T. Liu and of the UNOCAL team is Dr. Ian A. Webster. The project was initiated on September 21, 1989 and terminated on November 20, 1992. The total budget was \$301,789.

During the project's performance, the USC research team was responsible for constructing and operating the membrane reactor apparatus and for testing various inorganic membranes for the upgrading of coal derived asphaltenes and coal model compounds. The USC effort involved the principal investigator of this project and two graduate research assistants. The Media and Process Technology Group team was responsible for the preparation of the inorganic membranes, for construction and testing of the ceramic membrane modules, and for measurement of their transport properties. Their research effort involved Dr. Paul K. T. Liu, who was the project manager of the research team, an engineer and a technician. UNOCAL's contribution was limited to overall technical assistance in catalyst preparation and the operation of the laboratory upgrading membrane reactor and in analytical back-up and expertise in oil analysis and materials characterization. UNOCAL was a no-cost contractor but was involved in all aspects of the project, as deemed appropriate in the technical capacity discussed above. The project's motivations and goals are described below.

A Project Motivation and Goals

The project's goal was to investigate the feasibility of applying catalytic membrane reactor technology to the upgrading of model and real coal derived liquids. As already discussed

the introduction, high temperature membrane reactors have attracted significant research interest recently due to the development of good quality microporous inorganic membranes. Such membranes were first produced in the early seventies but until recently had found no extensive industrial applications. This in part was due to problems with past production techniques resulting in membranes of poor quality in terms of pore size uniformity and material strength, a picture that is rapidly changing today.

Membrane reactors are today finding extensive applications for gas and vapor phase catalytic reactions (see discussion in the introduction and recent reviews by Armor [92], Hsieh [93] and Tsotsis *et al.* [94]). There have not been any published reports, however, of their use in high pressure and temperature liquid-phase applications.

The idea to apply membrane reactor technology to coal liquid upgrading has resulted from a series of experimental investigations by our group of petroleum and coal asphaltene transport through model membranes. Coal liquids contain polycyclic aromatic compounds, which not only present potential difficulties in upgrading, storage and coprocessing, but are also bioactive. Direct coal liquefaction is perceived today as a two-stage process, which involves a first stage of thermal (or catalytic) dissolution of coal, followed by a second stage, in which the resulting products of the first stage are catalytically upgraded.

Even in the presence of hydrogen, the oil products of the second stage are thought to equilibrate with the heavier (asphaltenic and preasphaltenic) components found in the feedstream. The possibility exists for this smaller molecular fraction to recondense with the unreacted heavy components and form even heavier undesirable components like char and coke. One way to diminish these regressive reactions is to selectively remove these smaller molecular weight fractions once they are formed and prior to recondensation. This can, at least in principle, be accomplished through the use of high temperature membrane reactors, using ceramic membranes which are permselective for the desired products of the coal liquid upgrading process. An additional incentive to do so is in order to eliminate the further hydrogenation and hydrocracking of liquid products to undesirable light gases.

B Knowledge Base To Be Developed

High temperature catalytic membrane reactors for coal liquid upgrading is a novel technology. To make it a reality requires the development of a new knowledge base addressing a variety of both fundamental and technical questions. These include:

1. Understanding the mechanism of membrane transport of coal liquid macromolecules. Transport under reactive conditions is of particular importance, especially under conditions for which the membrane porous structure changes as a result of metal/coke deposition. Coal liquids have a polydisperse character both in terms of M.W. distribution, and also in terms of their physicochemical and transport properties. This polydisperse nature introduces a degree of complexity in the mathematical description of transport and reaction of these compounds. Of relevance is the issue of membrane characterization. Techniques like BET and Mercury Porosimetry measure the accessible porosity, which is of importance during reaction. Not all of this accessible porosity, however, is of interest or importance during transport.
2. The development of thermally/hydrothermally/mechanically stable membranes with the desired transport/surface properties. The challenges to be faced here are significant and the research accomplishments in this area are the focal point of this report.
3. The development of a membrane characterization apparatus, and of membrane reactors that are capable of withstanding the pressures/temperatures typical of coal liquid upgrading. The experimental challenges to be faced here are significant and will be briefly discussed in this report. Of relevance are issues of modeling of the high pressure membrane reactor and of design and scale-up.
4. Catalytically impregnated membranes. Though not discussed in great detail in this report, there are significant obstacles to be overcome in this area. No universally accepted method for membrane impregnation currently exists. Should membranes be made catalytically active in the first place? No general answer to this question currently exists, for a complex reaction system like coal liquid upgrading, in which the catalytic membrane may be called upon to shoulder one or more of these functions.

These are some, but by no means all, of the important issues to be addressed in this area. In our project, our attention has been focused primarily on questions 1-3 above. An overview of our research accomplishments follows.

III Research Accomplishments

These are some of the highlights and accomplishments of our research studies:

1. We have studied in some depth the transport characteristics and mechanisms of model coal and petroleum liquid compounds and their hydrocracking products through microporous polymeric, anodic alumina and Sol-Gel membranes. Transport investigations of asphaltenes isolated from a variety of petroleum and coal liquids have also been carried out and detailed accounts can be found in recent reports (Sane *et al.* [95,96]). Statistical models of asphaltene transport have also been developed which account for the polydisperse nature of these compounds (Ravi Kumar *et al.* [97]).

A series of investigations has been carried out to understand transport and reaction of liquid macromolecules at the single pore level using anodic alumina membranes (Nourbakhsh *et al.* [98]) under conditions for which the pore structure is changing due to heteroatom deposition. Understanding reactive transport in evolving porous structures is, of course, of fundamental importance in the area of high pressure, high temperature coal liquid upgrading membrane reactors. The issues of inaccessible porosity and dead-end porosity, which do not contribute to transport, is of significance in the optimal design of membranes and membrane reactors, especially for evolving porous media. Anodic membranes, which have no hidden or dead-end porosity, are not well suited for such investigations. Experiments with Sol-Gel membranes are currently in progress.

A high pressure, high temperature pilot-plant scale unit for permeability measurements has been constructed at the Media and Process Technology Group at ALCOA, see Fig. 1. This is a versatile testing apparatus used in the membrane development effort (see below). It is equipped with a switchable liquid delivery system that can deliver 0-200 cc/min and 0-1 L/min, respectively. A two-heating zone furnace can independently

control the temperature up to 1000°F. A six-way valve and 10 cc sampling loops are available to collect the samples for feed, permeate and reject side.

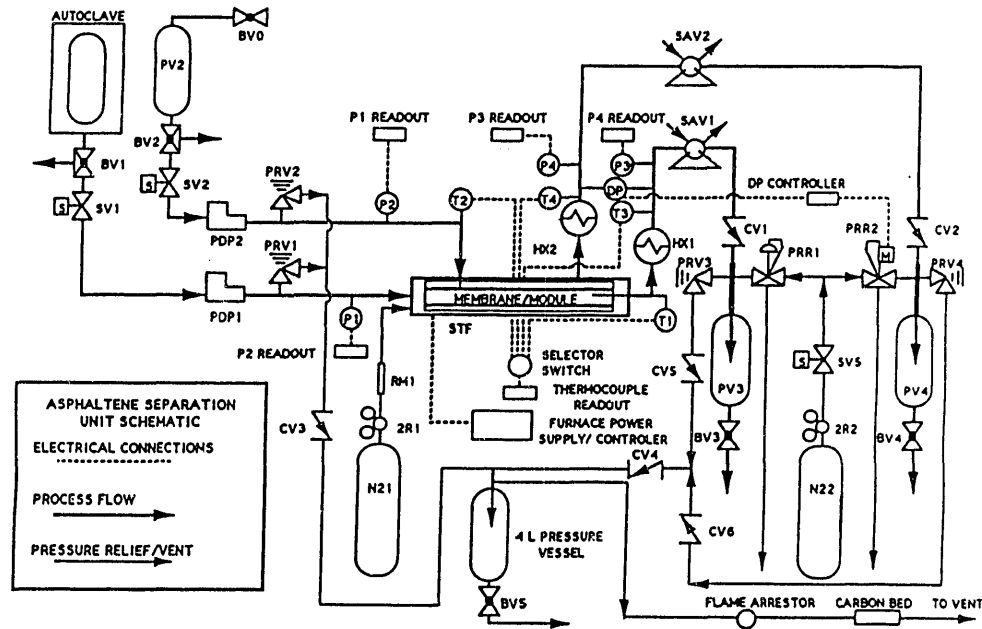


Figure 1: Schematic of Coal Liquid Separations Unit.

The diffusivity experiments using flat, disk type membranes have been carried out at USC in the diffusivity apparatus described in detail in several reports (Sane *et al.* [95,96]). Diffusivity/permeability measurements of cylindrical membranes are being carried out in situ in the high pressure/temperature membrane reactor, see Fig. 2 and discussion to follow.

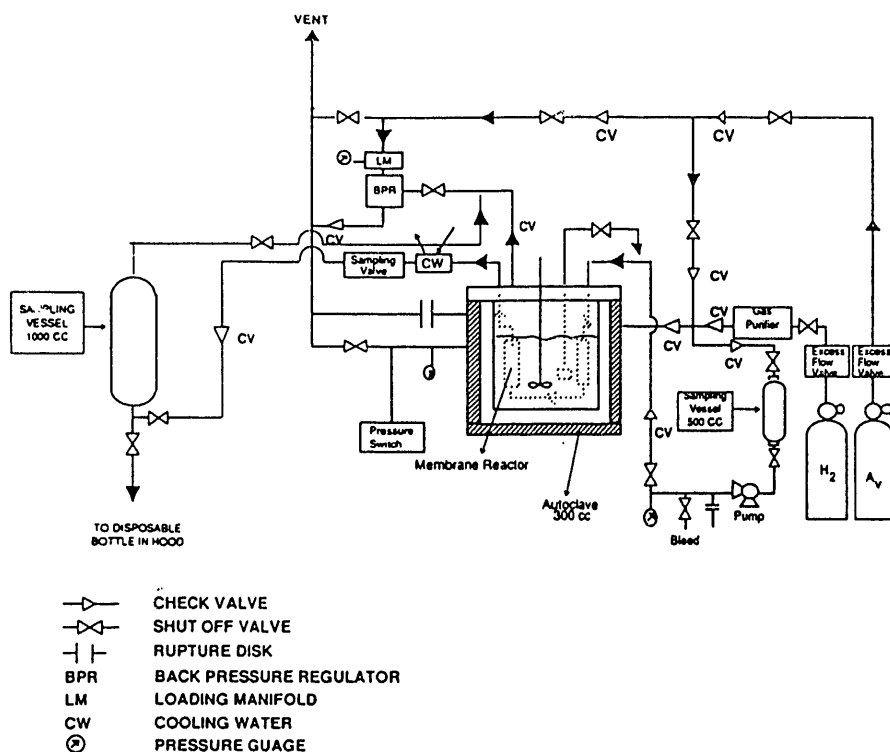
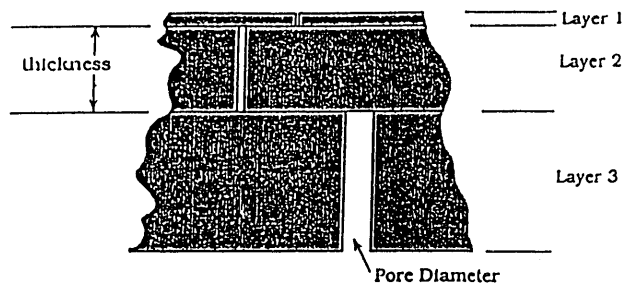


Figure 2: Batch-Continuous Membrane Reactor System.

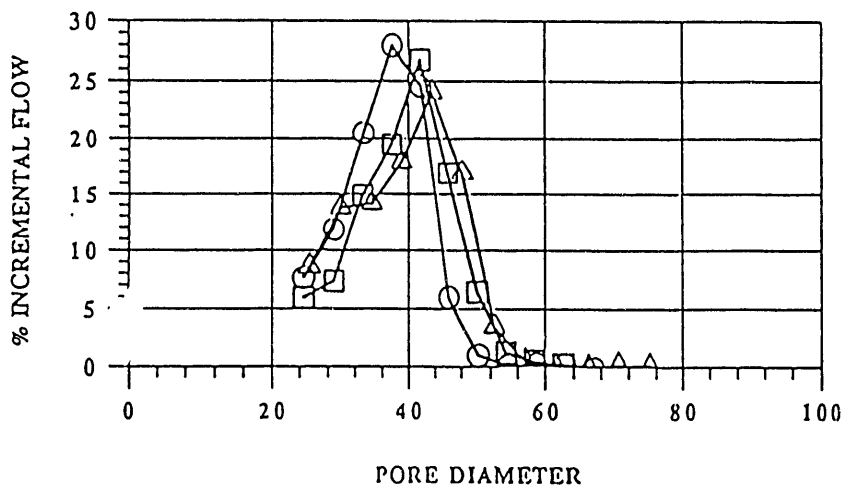
2. Our study used state-of-the-art ceramic membranes available from ALCOA Separations Division (currently U.S. Filter). It is a multiple layer (see Fig. 3 for a schematic), composite, asymmetric membrane with $\gamma\text{-Al}_2\text{O}_3$ as an effective top layer. The smallest pore available without any further modification is 40\AA with a $3\text{-}5\ \mu$ top layer thickness. These membranes can be produced reproducibly and with a very narrow pore size distribution, see Fig. 4. They are also mechanically stable at pressures greater than 1800 psi and thermally stable in N_2 at 640°C . For example, Fig. 5 shows the pore size of a fresh and a thermally treated (over 100 hr) membrane. The change in pore size distribution is insignificant and is within the uncertainty of the instrument.

An extensive testing of the membranes under realistic upgrading experiments with coal asphaltens was carried out in the membrane reactor of Fig. 2. Though some plugging of the pore structure occurs (typical experimental run lasts 3 days), we were able to recover the full membrane permeability after decoking of the membrane structure. The



Layer 1: Pore diameter = 40 Å; thickness = 5 μm; porosity = 50%
 Layer 2: Pore diameter = 0.2 μm; thickness = 30 μm; porosity = 35%
 Layer 3: Pore diameter = 0.8 μm; thickness = 50 μm; porosity = 40%
 Support: Pore diameter = 10-15 μm; thickness = 1.5-2.0 mm; porosity = 40-45%

Figure 3: Schematic of Microporous Multiple Layer Asymmetric Ceramic Membrane.



⊖ E12462 D=36.9 Å ⊞ E12269 D=39.6 Å ⊠ E12458 D=39.9 Å

Figure 4: Pore Size Distribution Analysis of 40Å Ceramic Membranes.

membranes are also able to withstand up to 500 psi of transmembrane pressure at 2000 psi total pressure of H₂, 400°C and in a 15% coal asphaltene solution in tetralin for up to a week with no visible deterioration of their mechanical/thermal properties.

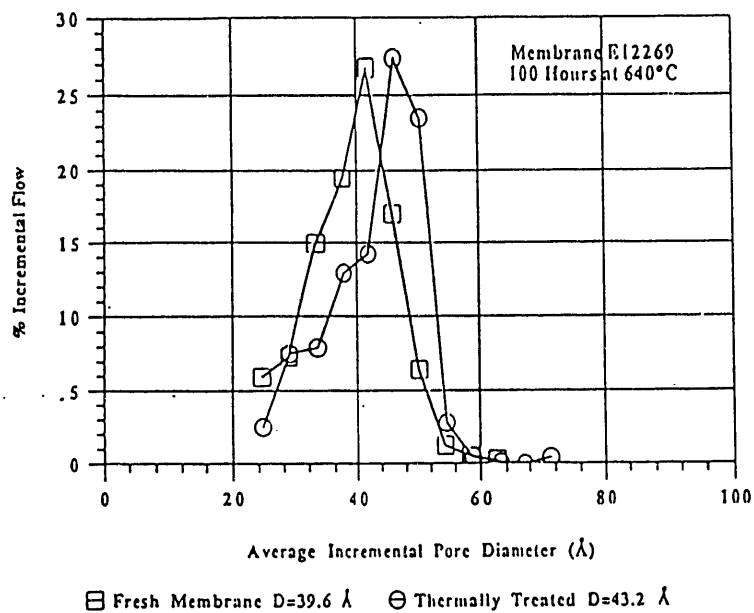


Figure 5: Pore Size Distribution with Thermal Treatment.

The 40Å membrane exhibits a molecular weight cut-off of 10,000 based upon 90% of rejection of dextran. It also demonstrated some rejection (27%) of dextran 6,000, but it shows a rather poor rejection for smaller compounds, such as 6% for vitamin B-12 (molecular weight 1,355). A program was therefore undertaken to develop membranes with small pore diameters ranging from < 40 to ~ 6Å through modification of existing alumina membranes by chemical vapor deposition. Modified membranes down to 15Å in diameter have been characterized by a pore size distribution analysis. They have been shown to have a sharp pore size distribution, as presented in Fig. 6. Their rejection of dextran is higher (40-100%), but their rejection of vitamin B-12 is still small (< 20%).

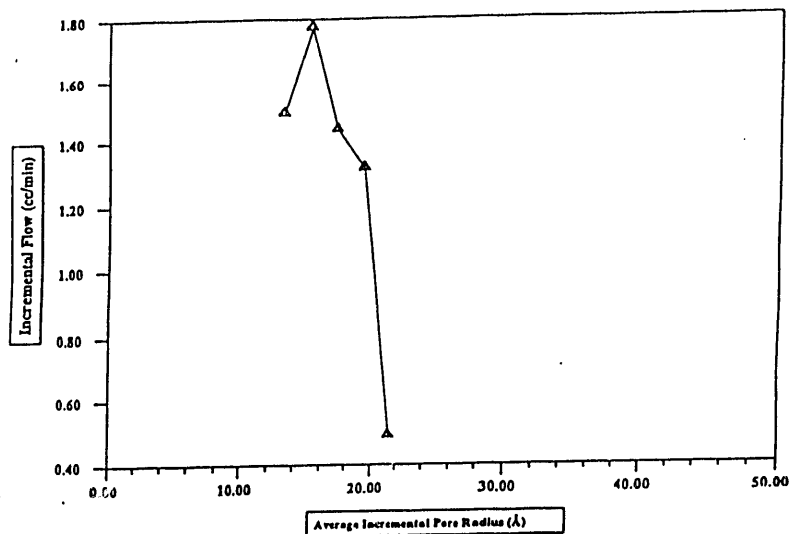


Figure 6: Pore Size Distribution of Modified Membrane with Average Pore Diameter of 28Å.

A series of modified membranes with pore sizes less than 15Å was also recently obtained through a progressive control of the operating parameters in chemical vapor deposition. Unfortunately, these membranes cannot be characterized by the pore size distribution analyzer due to the fact that the Kelvin equation is no longer valid at this range, i.e. $\leq 15\text{Å}$. However, the pore size of these membranes was deciphered from gas and liquid separations with selected probe compounds. These membranes demonstrated Knudsen diffusion for H_2/N_2 . Table 1 shows the characteristics of four such membranes in terms of N_2 /neopentane selectivity and pyrene/hexane rejection. For the membrane with the smallest pore size (AS064) a N_2 /neopentane selectivity of 28.7 was observed. Since neopentane still penetrates through, however, (neopentane has a kinetic diameter of 6.2Å), the average pore size of such membranes must be larger than 6Å. These membranes show progressively higher rejection of vitamin B-12 (up to complete 100% rejection). They also show progressive improvement in pyrene rejection from 10 to 78%, which correlates well with separation of nitrogen from neopentane as shown in Table 1. The AS064 membrane was also tested for the separation of diphenylmethane from hexane. Since the molecular dimension of diphenylmethane is

less than pyrene's, it is anticipated that the rejection ratio for this mixture would be lower. Our experimental results supported this, 30 vs. 78% for diphenylmethane vs. pyrene in hexane. Further, these membranes show no separation between hexane and hexadecane. It is anticipated that these modified membranes can selectively remove compounds from coal liquefaction and improve the upgrading efficiency.

Samples	Pyrene/Hexane Rejection*	N ₂ /Neopentane Selectivity
Alumina (40Å)	0%	1.6 (ca)
AS033 (<15Å)	30%	2.5
AS038 (<15Å)	33%	15.3
AS025 (<15Å)	76%	24.4
AS064 (<15Å)	78%	28.7

Table 1: Separation of Pyrene/Hexane and N₂/Neopentane with Existing and Modified Membranes.

A number of carbon (monolayer) coated alumina membranes were prepared. Carbon-coated alumina membranes are of interest since carbons have been proposed as novel supports for petroleum/coal liquid upgrading. The methodology of thin film coating of carbon onto ceramic membranes has been established. It results in uniform carbon coatings which adhere strongly to the ceramic surface so that delamination does not take place during permeation/reaction. Once the proper pore size of the membranes is determined, we will fabricate the carbon-coated membrane with desirable pore size for catalytic study. Work in this area is continuing. In summary, we have prepared and characterized a number of modified inorganic membranes. These membranes show good rejection of selected coal liquid compounds. More studies are needed of the separation characteristics of these membranes under reactive, high temperature and

pressure upgrading conditions.

3. A high pressure/temperature membrane reactor system for coal liquid upgrading has been constructed and is shown in Fig. 2. The heart of the experimental system is a high pressure autoclave, which in its interior can accommodate one or several high temperature ceramic membranes, placed vertically. The tubular membranes are aligned using bellows and are effectively sealed using graphite packings and Swagelok fittings. One side of these membranes is exposed to the contents of the autoclave, while the other side, through an independent flow system, is exposed to flowing pure solvent. The pressure in the interior and the exterior of the membrane can be independently adjusted and controlled. The pressure, both inside and outside the membranes, is maintained using back pressure regulators. In addition to the concentration gradient across the membrane, one can maintain a pressure gradient using a differential pressure gauge. The flow rate in the interior of the membrane can be independently controlled using an HPLC pump.

In situ diffusivity/permeability measurements, testing of the membranes' mechanical, thermal/hydrothermal stability and upgrading experiments have been performed in this reactor. The membrane reactor experiments are initiated by placing the model and real liquids (asphaltenes) in the autoclave space exterior to the membrane, pressurizing the exterior and interior membrane volume and initiating the flow of solvent. One has the option of running the experiments in a batch (exterior), continuous (interior) or batch-batch mode. The option also exists for loading catalyst in the exterior volume either in a pellet or a slurry form, or using metal impregnated membranes.

For petroleum liquids using the 40Å standard Membralox™ alumina membranes, improvements both in conversion and selectivity were observed. A series of experiments, for example, was performed for upgrading Fondo asphaltenes in a tetralin solvent both in the absence and presence of the membrane in the temperature range of 350°C-400°C and 1500 psig of H₂. Asphaltenes were separated from each sample by solvent (heptane) extraction and filtration. The solid residue (asphaltenes) is dissolved in xylenes and is analyzed by using GPC, XRF and NMR. The filtrate (maltenes) is evaporated

to remove most of the heptanes and is analyzed by GC and XRF.

Experiments were run without the membrane and catalyst, only with the membrane, with the catalyst (a UNOCAL proprietary Ni-Mo/ γ -Al₂O₃ catalyst in a slurry form) but without the membrane, and with both the membrane and catalyst present. Modest, by gas (vapor)-phase membrane reactor standards, but yet experimentally significant, improvements in conversion were observed. At 350°C, for example, in a batch-continuous type experiment after 20 hours reaction time for the experiment with the catalyst but without the membrane, the asphaltene conversion was 22%; with the membrane present, the asphaltene conversion was over 35%.

Similar experiments with the 40Å membranes were run with asphaltenes isolated from two coal liquids. Unfortunately, the results were inconclusive. We attribute this to the smaller cluster size of the coal asphaltene molecules as compared to the petroleum asphaltenes. We believe that for significant improvements in conversion to be attained for coal asphaltene hydrocracking, the recently developed membranes with pore sizes in the range of 6-15Å must be used. These membranes show reasonable rejection characteristics for compounds with molecular weights in the M.W. range of coal asphaltene clusters. With such membranes, we also believe that the conversion and selectivity for the hydrocracking of petroleum asphaltenes will also significantly improve. Membrane reactor experiments with the CVD modified membranes are planned in the near future. The primary focus of these experimental studies was to prove that the membrane reactor concept works for processing of these coal model compounds. Once accomplished, a number of other questions and issues will be addressed in detail to establish the optimal operating conditions and policies during coal liquid upgrading in a membrane reactor, namely:

- (i) Investigate the effect of various reactor parameters, such as temperature, overall pressure, partial hydrogen pressure gradient across the membrane (while maintaining equal total pressure on either side of the membrane), solvent type, and feedstock tube and cell side liquid space velocities.

- (ii) Investigate the effect of various membrane parameters such as pore size, thickness, overall metal loading, and various metal distributions along the membrane.
4. Relatively less attention has been paid to impregnating the membranes with upgrading metal catalysts, since the early stages of this project have been devoted to the development and complete characterization of permselective membranes and the construction and testing of the high temperature/pressure permeability and membrane reactor systems. This is a topic of considerable interest, however, since metal impregnation not only affects the catalytic properties, but also the transport characteristics since the pore structure and surface properties change. We have initiated an effort in this area recently, studying how metal impregnation affects the porous structure of the membranes.

The ceramic membranes are rendered catalytic, by impregnating with Mo promoted with Co or Ni. Typically, extra-pore MoO_3 represents less than 0.1% of the total metal content in the membrane and its effect is rather insignificant. When the need arises, however, it is removed by direct chemical dissolution. The transport characteristics of the resulting catalytic ceramic membranes are measured by techniques such as Ar permeability, diffusion of small molecules across the membrane, and the model compound molecules themselves (performed at USC and at the Media and Process Technology Group) as well as by direct SEM and HREM microscopic observations (performed at UNOCAL). The overall metal content is studied by using atomic absorption spectroscopy (at USC) and the intra-membrane metal distributions are studied qualitatively by SEM/EDAX, and quantitatively by electron microprobe analysis (at UNOCAL).

IV Conclusions

We have presented here a brief overview of our research accomplishments in the area of high temperature/pressure catalytic membrane reactors. Our main effort during this project has been in developing permselective inorganic membranes which are resistant to the harsh conditions found in coal liquid upgrading. We have also devoted considerable effort in the

development and testing of high temperature and pressure permeability measurement and membrane reactor systems. We are now ready to embark toward the second stage of our project, aimed at making catalytic upgrading membrane reactor technology a reality.

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