MEMBRANE CONTACTORS FEATURING NON-WETTING PERFLUORINATED MEMBRANES FOR EFFICIENT GAS/DEGASIFICATION OF PROCESS FLUIDS

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INTRODUCTION

Compact Membrane Systems, Inc. (CMS) was founded in 1993 based on the acquisition of exclusive rights to certain Dupont patents and fluoropolymers with exceptional gas transport and chemical resistance properties. To date, most of CMS's business has been contract research.

CMS is a technology driven company with proprietary capabilities in coating and membrane formation and a growing patent portfolio. The performance of CMS membranes has been documented in a number of publications[1,2]. CMS's focus is the development and commercialization of membranes or thin films composed of highly fluorinated polymers. These membrane products are used in three high productivity applications: (1) gas separations for production of either oxygen or nitrogen enriched air, (2) introduction or removal of gases from liquids, and (3) separation and delivery of aggressive chemicals. CMS's product strategy is to develop and maintain coating and membrane manufacturing expertise in house, and to research and demonstrate product applications uniquely suited to our products. We are actively seeking collaborations with appropriate partners to develop and introduce products into the market.

In recent years, the chemical process industry has made impressive gains in efficiency through "process intensification" and application of green chemistry considerations. These efforts share a common theme in their search for any chemical engineering development that leads to a substantially smaller, cleaner, and more energy-efficient technology. Process intensification is "a strategy of developing systems of production with a lower equipment-size / production capacity ratio, lower energy consumption, lower waste production, and higher efficiency with respect to existing systems"[3]. Application of process intensification to chemical plants is designed to make them more compact, safer, more energy-efficient and cleaner[4].

Membrane contactors, devices in which hydrophobic membranes promote contact between phases, make important contributions to several useful process intensification methods: membrane reactors, absorbers, and degassers. They also find application in liquid/liquid extractions, scrubbing, stripping and other operations (listed below). In a membrane absorber or degasser, the membrane serves as a gas or vapor permeable barrier between the gas and liquid phases. With respect to traditional systems, they allow the independent variation of flow rates without flooding, foaming, entrainment or channeling, do not require separation after the process, and present higher surface area / volume ratios. We are actively developing applications for our membrane contactors since they offer improved performance and value over current unit operations, mainly absorption and gas stripping processes as performed by spray, tray bubble and packed towers, venturi injectors and wet scrubbers, distillation columns, and falling film/wetted wall reactors.

Membrane contactors provide up to two orders of magnitude more surface area per volume than conventional contactors. The 'specific' surface area (per unit volume) of various contactors range from ~0.033-0.33 [cm^2/cm^3] for free dispersion columns, ~0.33-3.3 [cm^2/cm^3] for packed and tray columns, ~1.6-5 [cm^2/cm^3] for mechanically agitated columns and ~16-66 [cm^2/cm^3] for membrane contactors[5]. Equipment volume reductions of up to 20x for gas absorption and up to 500x for liquid extraction have been reported[6]. Table 1 shows that mass transfer coefficients for CMS perfluorinated membrane contactors are superior to bubble contactors, and packed columns, and have the widest range of operational flexibility of any gas/liquid contactor[7].

Table 1. Operating Characteristics of Different Gas-Liquid Contactors

	Surface area / volume [cm^2/cm^3]	Mass Transfer Coefficient $k_l a$ [s^{-1}] x 10^{-2}	Gas / Liquid Volume Flow β [-]
Bubble Contactor	0.5 - 6	0.5-12	60% – 98%
Packed Column (Counter-Current)	0.1 – 3.5	0.04 - 7	2% - 25%
Venturi Injector	1.6 – 25	8 - 25	5% - 30%
Membrane Contactor	10 - 100	5 - ~50	1% - 99%

Table 2 lists desirable design and operation characteristics of membrane contactors that incorporate polymeric separation membranes.

Table 2. Operating Characteristics of Membrane Contactors (Compared to Conventional Gas-Liquid Contactors)

• independent pressure control of gas and liquid streams
• independent flow control of gas and liquid streams (may obviate typical column problems: flooding, weeping, priming, dumping, entrainment, and channeling)
• large turndown ratio; high flexibility with flow rates
• no physical mixing of phases (bubbleless gasification controls froth and foam)
• highly modular and scalable
• smaller size, weight; high surface area to contactor volume
• orientation and motion insensitive
• less energy intensive than conventional processes
• may support "green chemistry" and "process intensification" initiatives

A number of commercialized membrane contactor separation process have been described in the literature[8,9]. Most commercial separations involve aqueous solutions, although separation of organic fluids has increased with the development of improved, oleophobic membranes.

CMS now has several membrane contactor devices incorporating perfluorinated composite membranes that we anticipate will become commercially available in the very near future. In general, the most suitable applications for CMS membranes are those where larger molecules and compounds remain in the retentate, at or near the process operating parameters of the feed, while the smaller molecules permeate through the membrane.

Two different contactor designs are available: flat-sheet devices and hollow fiber devices. Flat sheet designs can include spiral wound and pleated pack configurations, and are most commonly used when pressure drop concerns dominate gas separation efficiency. Hollow fiber designs, which mimic shell-and-tube heat and fluid exchangers, offer much greater membrane surface areas per volume of contactor, and are better suited to higher pressure applications and where maximum separation efficiency is desired[10]. We have the capability to make modules with membrane surface areas ranging from one to 100 square feet.

Compact Membrane System's product focus is on applications/unit operations that cannot be performed by other existing commercial membrane contactors. In addition to the characteristics described above in Table 3, CMS membrane contactors[11] have the following unique or superior characteristics:

Table 3. Unique Characteristics of CMS Fluoropolymer Membrane Contactors

• Highest gas flux (permeance) of any nonporous/non-wetting gas transfer membranes[12].
• Nonporous, non-wetting surface compatible with low surface-tension 'wetting' fluids (alcohols, hydrocarbons, solvents, aqueous surfactant solutions, blood plasma) that would normally 'leak' through conventional hydrophobic microporous membranes (e.g. polysulfone, polypropylene, polyvinylidene fluoride, and expanded polytetrafluoroethylene).
• Chemically resistant to most aggressive gases or liquids

•	Bubbleless gasification/degasification, (low agitation and shear)
•	Very low levels of extractables (in all-fluoropolymer modules),
•	Low fouling / easy cleaning
•	The most stable high free-volume polymer

Suitable applications for gassing and degassing process fluids exist in dozens of industries and commercial areas, including:

- Water: potable, waste, process, boiler, ultrapure
- semiconductor & microelectronics
- food
- pollution control & environmental remediation
- petroleum hydrocarbons
- sterile humidification and dehumidification
- Feedstock and polymer chemical processes
- fine chemical
- pharmaceutical & bioreactors
- energy & power
- micro-gravity
- analytical

In this presentation, we have chosen to highlight four areas of application for CMS fluoropolymer membrane contactors. These membrane contactors outperform other non-porous membrane contactors for oxygenation, and are safer and more effective than sparging for certain flammable gases. They are more resistant than microporous membrane contactors to liquid wet-out and leakage in mixed aqueous solutions, surfactants and low surface tension liquids such as hydrocarbons, alcohols and solvents. Applications discussed below are: (1) oxygen feed to bioreactors, (2) biodenitrification of concentrated ion-exchange brines, (3) bubbleless ozonation of wastewater, and (4) degassing of low surface energy fluids and mineral oils.

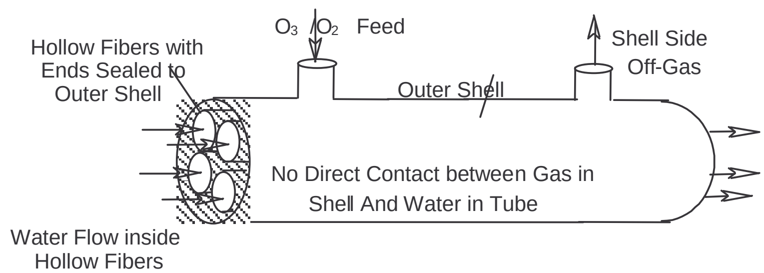
OZONATION OF WATER

Through a number of SBIR grants, Compact Membrane Systems (CMS) has successfully demonstrated the technical feasibility of applying our proprietary membrane technology to ozone dissolution into water for the purposes of disinfection of potable water, removal of organic compounds from waste waters, treatment of biofilms and for the provision of pyrogen-free water for medical and dialysis facilities[13]. Specifically through these studies, CMS has shown that devices based on this nonporous, fluoropolymer membrane can be employed to dissolve ozone in a bubble-free manner (i.e. at 100 % absorption efficiency) into water at flux rates that are commercially practical for numerous water disinfection and oxidative applications.

Particular advantages of this technology are:

- Small volume of the membrane device.
- No need for a specified water depth (conventionally 16-20 ft) to achieve high absorption efficiency.
- Almost perfect mixing at the exit of the membrane module and hence no spatial variation in ozone residual.
- More precise control of O_3 dosage into the system via manipulation of feed gas.
- Chemical inertness of the fluoropolymer membranes.

Figure 1. CMS Membrane Ozonation Device



The performance of a CMS membrane contactor for ozone delivery was demonstrated in the laboratory by a 99.99% to 99.999% (4-5 log reduction) of bacterial loading (*E. coli, P. aeruginosa, S. typhimuirum and C. jejuni*) and coliphage using a CMS membrane module for injection of ozone. Removal efficiencies obtained during the treatment of synthetic wastewaters containing phenol, nitrobenzene, monochlorobenzene and humic acid were found to range between 25 to 80% depending on feed concentrations. Ongoing tests under continuous oxidative conditions show a stable composite membrane structure after six months exposure.

BIOREACTORS

Bioprocessing is a type of advanced manufacturing that involves chemical, physical and biological processes employing living organisms or their cellular components. Mammalian cells are chosen as hosts for protein expression, in particular, monoclonal antibody production. Hybridoma cells, recombinant chinese hamster ovary (CHO), and myeloma cells have been used for a number of industrially important therapeutic proteins. As the number of products produced in genetically engineered cells increases the need increases for better methods of culturing eukaryotic cells, which tend to be extremely fragile in some instances. Current improvements in bioreactors include enhancing the efficiencies of perfusion / waste removal, oxygenation of cell cultures, and cell harvesting. During scale-up however, the oxygen supply rate can severely affect product formation. Adequate oxygen supply is often necessary for energy production and formation of cellular constituents such as tyrosine and cholesterol. Since animal cells are more shear sensitive than bacterial cells, the use of membrane contactors to dissolve oxygen without forming bubbles will minimize cell damage since bursting bubbles are greatly reduced at the liquid- cell interface. Efficient membrane oxygenation for bioreactors has the potential to (1) increase the total yield of cell product by increasing the run length, (2) increase product concentration, reduce costs of synthesis and purification and increase yield, and (3) improve productivity by enabling larger batches or more bioreactors to be run simultaneously and improving product uniformity[14].

In general, an aqueous fermentation medium in equilibrium with air would not contain more than 7.0 x 10^{-3} kg /m^3 of dissolved oxygen at 100% saturation. This amount of oxygen is depleted within a few seconds by an active and concentrated cell culture. Nutrient consumption is negligible during that same interval. Thus, most aerobic cell cultures are oxygen limited. Conventional oxygen sparging supplies adequate oxygen for cell cultures up to approximately 2-5 x 10^7 cells /ml. To avoid foaming and cell damage, antifoam agents (typically surfactants) must typically be added to the bioreactor, and subsequently removed during downstream processing.

CMS membranes show particular resistance to wet out from surfactant solutions. CMS conducted bench tests of commercial contactors, circulating an aqueous solution of 5% Triton X-100 surfactant through the modules. Membrane contactors containing porous polypropylene hollow fibers wet out almost immediately; 120 milliliters of solution leaked through the membrane within one minute of exposure. Expanded polytetrafluoroethylene flat sheet membranes did little better; 12 milliliters of solution leaked through the membrane in less than eight minutes. In contrast, hollow fiber modules with CMS membranes applied to the outside of the fibers show no leakage even after overnight exposures to surfactant solution.

Cellex Biosciences and CMS compared the performance of a CMS membrane contactor and a spiral-wound silicone sheet membrane oxygenator in their AcuSyst hollow fiber bioreactor. They reported higher oxygen transfer rates with CMS membranes than with silicone membranes for a given oxygen partial pressure driving force and aqueous flow rate. Volumetric mass transfer coefficients were shown to be 25% to 50% higher for the CMS membrane contactor than for the silicone membrane devices when operated in an identical manner. This in turn could sustain additional hollow fiber bioreactors, with the same membrane oxygenator, leading to larger and more uniform batches of product.

BIODENITRIFICATION

Nitrates present in drinking water pose considerable health problems especially to infants in the form of methemoglobimia (blue baby syndrome) and as a potential carcinogen when they form nitrosoamines. The Maximum Contaminant Level (MCL) set by the U.S. EPA for nitrate in drinking water is 10 mg NO_3^--N/L. An estimated 1.2 percent of community wells and 2.4 percent of rural wells exceeded the nitrate MCL.

Nitrate is a stable and highly soluble anion that is difficult to remove by conventional water treatment technologies such as lime softening and filtration. Ion exchange is considered to be the process of choice, especially for smaller water treatment facilities, because of its simplicity, robustness, effectiveness, and perceived low operational costs[15].

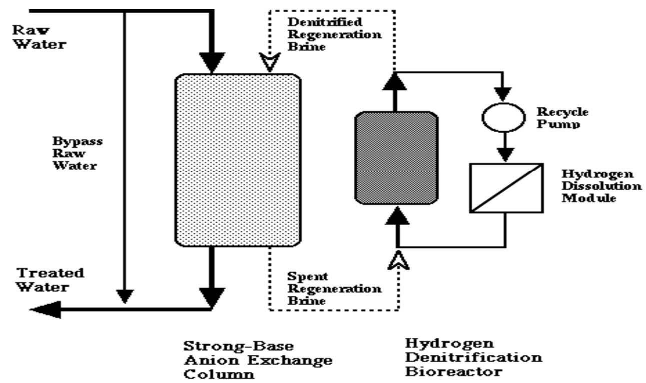
The ion exchange process uses a packed bed of anion resin in the chloride form. Nitrate, sulfate, and other freshwater anions are exchanged with chloride on the strong-base anion resin. The nitrate-free effluent is blended with untreated bypass water to produce water with an acceptable nitrate concentration. Prior to nitrate breakthrough, the ion exchange column is regenerated with a 0.5 to 2.0 N sodium chloride (NaCl) solution. The spent regeneration brine contains elevated concentrations of nitrate, sulfate, and NaCl. In many locations, the spent brine is defined as and must be disposed of as a hazardous waste. Estimated disposal costs range from $1.30 to $4.36 per gallon of brine (per volume basis for Upper Midwest) not including the cost of appropriate containers. This results in an operating cost that can approach $2.32 per 1000 gallons, assuming a brine generation rate of 1.4 gallons per 1000 gallons, an operating cost for nitrate removal by ion exchange of $0.50 per 1000 gallons, and a brine disposal cost of $1.30 per gallon. Brine disposal therefore can account for about 78% of the total operating costs for ion exchange if disposal as a hazardous waste disposal is required.

Several studies have demonstrated the viability of biological denitrification to regenerate ion exchange brines[16]. Methanol is frequently used as an added electron donor, however ethanol and acetic acid are used in drinking water treatment due to their lower cost and reduced toxicity[17,18]. Inorganic compounds may also be used as electron donors and these include hydrogen gas and various forms of reduced sulfur.

As an electron donor, hydrogen has the lowest chemical cost per pound of nitrate removal and also results in lower biomass generation potential (true yield) than the organic substrates used for biological denitrification. Hydrogen costs only $0.84/pound, compared to ethanol at $2.06/pound, methanol at $9.39/pound and acetic acid at $13.24/pound. The lower true yield for hydrogen is a great advantage for regeneration of brines, because less biomass must be wasted from the system, less backwashing of the fixed-bed bioreactor is required to remove excess biomass, and less biomass decomposition products (humic compounds and other recalcitrant organic compounds) will contact the anion exchange resins. The reduced contact between recalcitrant anionic organic compounds and the anion exchange resins reduces the potential for fouling the resins.

CMS has been investigating the use of hydrogen gas to biologically reduce nitrate from ion exchange brines. Figure 2 shows a schematic of the process. Biological treatment of the ion exchange regenerated brine converts the nitrate to nitrogen gas (which leaves the brine) and results in reduced operating costs by allowing the reuse of the denitrified brine and lower disposal costs. The biological removal of nitrate from spent ion exchange brines is an example of a biological process costing substantially less than the traditional physical/chemical process. The disposal of the brine as a hazardous waste has a minimum cost of $1.82 per 1000 gallons of delivered water, based on the stoichiometric conversions and H_2 costs. Thus, in terms of operating costs, the conversion of hazardous waste disposal via biological treatment and reuse of the ion exchange brine will save the water utility money.

Figure 2. Schematic diagram of the combination ion exchange/hydrogen bioreactor process for removing nitrate from drinking water.



The use of H_2 requires considerable investment in safety, and H_2 recovery, equipment to be economically justifiable. Membrane contactors, however, offer the flexibility of dissolution of H_2 without forming bubbles and the added control of maintaining a fixed contact area between the gas and liquid phases, thereby allowing precise metering of H_2 for the purposes of biological denitrification. This allows for a safer and a more economical operation along with all the advantages of membrane contactors as outlined earlier. In addition, CMS membrane contactors improve on the existing membrane contactors by (1) allowing long term operation without wet out of the microporous substrate as a result of liquid infiltration and (2) the perfluoropolymer nature of the surface should make it easier to slough off any attached biofilm. Recently, a Phase II SBIR was granted to CMS by the National Science Foundation to demonstrate denitrification at feed concentrations present in concentrated ion exchange brine.

DEGASSING OF OILS AND OTHER NON-AQUEOUS FLUIDS

Removal of gases from low surface tension liquids is uniquely suited to oleophobic fluoropolymer membranes. Certain industrial applications require degassing of oils. Daimler Chrysler was recently granted a patent in Europe to both dehydrate and degas hydraulic fluids via pervaporation through membranes[19]. In another application, electrical and thermal stresses can degrade dielectric oil contained in electrical current transformers to a range of 'fault gases', including hydrogen, light alkane, alkene and alkyne hydrocarbons, carbon monoxide and carbon dioxide[20]. Air may be present as well. Early monitoring and detection of these gases in dielectric oil[21] can result in early detection of developing faults, preventing catastrophic failure of critical power system components[22], especially large power transformers.

Certain polymer production processes also require deoxygenated process streams to avoid poisoning of catalysts. Propylene, hexene, octene, butene, benzene and styrene are all examples of monomers requiring degassing to ≤1 ppm prior to polymerization. In particular, deoxygenation is required to avoid poisoning of downstream catalysts and corrosion of process equipment and piping. The typical degassing process now is energy intensive, and involves heating the stream and flowing it through a column to degas it, then cooling it again prior to use. In recent months, we have had inquiries to degas all of the monomers listed above. Arrangements are currently being made to conduct feasibility demonstrations for some of these fluids.

Chemical and temperature incompatibilities, swelling or 'wet out' will severely limit the use of either conventional contactor porous hollow fibers (e.g. polypropylene and polysulfone), or flat sheets (e.g. expanded polytetrafluoroethylene, polydimethyl siloxane and silicones) with most oils. CMS fluoropolymer membrane modules have been demonstrated to degas napthenic lubricating oil at temperatures as high as 60 °C without leakage or wet out. Microporous polymers, including polypropylene and polytetrafluoroethylene membranes, will leak oils.

CONCLUSION

Membrane contactors offer a viable technology in the development of intensive chemical and biological processes for gasification and degasification. The processes discussed here are meant to be suggestive of other possibilities for development. CMS is actively seeking business partners to develop commercial products in these and other application areas. Please contact the authors for a more detailed presentation record containing performance data, or to discuss feasibility of other applications.

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