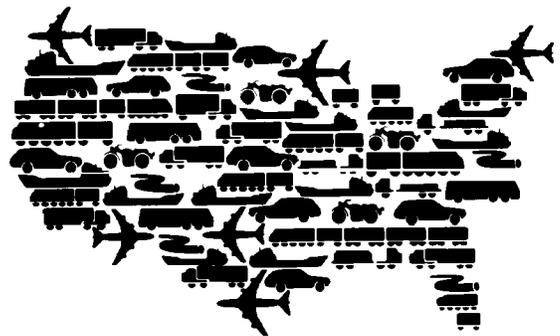

Membrane-Based Air Composition Control for Light-Duty Diesel Vehicles: A Benefit and Cost Assessment



**Center for Transportation Research
Argonne National Laboratory**

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A Benefit and Cost Assessment**

K. Stork and R. Poola
Center for Transportation Research
Energy Systems Division
Argonne National Laboratory

October 1998

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under contract W-31-109-Eng-38.

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Notation

Acronyms

| | |
|---------------------|--|
| CI | compression ignition |
| CIDI | compression-ignition, direct-injection |
| CMS | Compact Membrane Systems, Inc. |
| CO | carbon monoxide |
| CRADA | Cooperative Research and Development Agreement |
| DI | direct injection |
| DMAC | N,N-dimethyl acetamide |
| DOE | U.S. Department of Energy |
| EGR | exhaust-gas recirculation |
| FTP | Federal Test Procedure |
| HC | hydrocarbon |
| Hg | mercury |
| ID | inside diameter |
| IDI | indirect injection |
| LNC | lean-NO _x catalyst |
| MY | model year |
| N ₂ | nitrogen |
| NO, NO ₂ | constituents of NO _x |
| NO _x | nitrogen oxides |
| O ₂ | oxygen |
| OAAT | Office of Advanced Automotive Technology |
| OD | outside diameter |
| OH | hydroxide ion |
| PDD | perfluoro-2-2-dimethyl-1-3 dioxole |
| PM | particulate matter |
| PNGV | Partnership for a New Generation of Vehicles |
| SAE | Society for Automotive Engineers |
| SCR | selective catalytic reduction |
| SI | spark ignition |
| SO ₂ | sulfur dioxide |
| SRI | Stanford Research Institute |
| STP | standard temperature and pressure |
| TDC | top dead center |
| TDI | turbocharged direct injection |
| TFE | tetrafluoroethylene |



Units of Measure

| | |
|--------------------|--|
| μm | micrometer |
| \AA | angstrom |
| barrer | $\text{cm}^3 \text{ (STP)}/\text{cm}^2\text{-s-cm Hg} \times 10^{10}$ |
| cfm | cubic foot per minute |
| cm^2 | square centimeter |
| cm^3 | cubic centimeter |
| g/mi | gram per mile |
| gal | gallon |
| GPU | gas permeation unit(s) = $\text{cm}^3 \text{ (STP)}/\text{cm}^2\text{-s-cm Hg} \times 10^{10}$ |
| h | hour |
| hp | horsepower |
| in. | inch |
| kW/L | kilowatt per liter |
| L | liter |
| m^2 | square meter |
| mpg | mile per gallon |
| $^{\circ}\text{C}$ | degree Celsius |
| PM_{10} | particulate matter measuring 10 micrometers or less |
| $\text{PM}_{2.5}$ | particulate matter measuring 2.5 micrometers or less |
| psi | pound per square inch |
| psig | pound per square inch gauge |
| rpm | rotation per minute |
| s | second |
| scfm | standard cubic foot per minute |
| wt% | percentage by weight |

Summary

This report presents the methodologies and results of a study conducted by Argonne National Laboratory (Argonne) to assess the benefits and costs of several membrane-based technologies. The technologies evaluated will be used in automotive emissions-control and performance-enhancement systems incorporated into light-duty diesel vehicle engines. Such engines are among the technologies that are being considered to power vehicles developed under the government-industry Partnership for a New Generation of Vehicles (PNGV).

Emissions of nitrogen oxides (NO_x) from diesel engines have long been considered a barrier to use of diesels in urban areas. Recently, particulate matter (PM) emissions have also become an area of increased concern because of new regulations regarding emissions of particulate matter measuring 2.5 micrometers or less ($\text{PM}_{2.5}$). Particulates are of special concern for diesel engines in the PNGV program; the program has a research goal of 0.01 gram per mile (g/mi) of particulate matter emissions under the Federal Test Procedure (FTP) cycle. This extremely low level (one-fourth the level of the Tier II standard) could threaten the viability of using diesel engines as stand-alone powerplants or in hybrid-electric vehicles. The techniques analyzed in this study can reduce NO_x and particulate emissions and even increase the power density of the diesel engines used in light-duty diesel vehicles.

For nearly a decade, Argonne has been evaluating membrane-based methods to control the composition of air used in combustion. Membranes are the only practical method of modifying air composition for on-board use. The applicability of the technique depends strongly on both the technical and economic feasibility of implementing it on a vehicle. Over the past 10 years, significant technical advances have been made in the development of air-separation membranes. Researchers have developed and commercialized novel membrane materials that can efficiently separate air at the concentrations required for vehicle applications and have developed compact membrane modules that can be incorporated into vehicle design.

Previous analysis by Argonne and others has demonstrated the effectiveness of oxygen enrichment at reducing PM, smoke, hydrocarbon (HC), and carbon monoxide (CO) emissions while increasing engine power output. Under appropriate oxygen-enriched operating conditions, diesel engines have achieved a net increase of 10-20% in power density and a decrease of 30-60% in PM emissions. Nitrogen-enriched air can be used as an alternative to exhaust gas recirculation to control NO_x emissions and can also be used to generate a monatomic nitrogen plasma for exhaust post-treatment to reduce emissions of NO_x .

Argonne has recently identified an operating regime that can simultaneously reduce NO_x and PM while increasing power output when oxygen-enriched combustion air is used. This promising technique, which will be verified by additional experimental work at Argonne (using a range of engine sizes), will require the use of membranes similar to those analyzed in this study.



In this study, five membrane-based performance and emission control systems (hereafter, “cases”) are analyzed. The systems are optimized to achieve the following objectives: NO_x control, PM control, power-density enhancement, and optimized NO_x and PM control over a driving cycle. A final case is added to characterize a membrane system suitable for use with a new concept developed at Argonne to control PM emissions by injecting oxygen-enriched air directly into a cylinder during the expansion stroke.

The cost of the system developed for each case was estimated by means of a production process-based model developed for this study. The largest single cost, and the only area with significant potential for technical improvement and further cost reductions, is the membrane material itself. Other aspects of the systems — from auxiliary pumps to membrane casings and supports — are already produced in commercial quantities and cannot be expected to benefit from economies of scale. Improvements in membrane material coating processes using new materials, however, can be reasonably expected to reduce the cost of mass-produced systems. So a range of costs for mass-produced systems has been developed, with current membrane costs and reductions of up to one-third being assumed. These costs are presented in the following table.

| Case Number | Case Description | Projected Mass-Production Cost |
|-------------|--|--------------------------------|
| 1 | NO _x Control with Nitrogen Enrichment | \$75 – 110 |
| 2 | PM Control with Oxygen Enrichment | \$140 – 200 |
| 3 | Variable Air Composition for Minimum Driving-Cycle Emissions | \$190 – 265 |
| 4 | Power Enhancement with Oxygen Enrichment | \$180 – 260 |
| 5 | Late-Cycle Oxygen-Enriched Air Injection | \$100 – 120 |

Each case was compared with an alternative technology expected to provide similar benefits. The alternatives and their expected costs are listed in the following table.

| Case Number | Alternative Technology | Approximate Cost of Alternative |
|-------------|-------------------------------------|---|
| 1 | Lean NO _x Catalyst + EGR | \$300 |
| 2 | PM Trap + Fuel Additives | \$200 + \$0.02/gal |
| 3 | LNC, EGR + PM Trap | \$500 |
| 4 | Larger Engine or Turbocharging | ??? |
| 5 | PM Trap + Fuel Additives | (probably >10% engine cost) \$200 + \$0.02/gal |

Notes:

EGR = exhaust gas recirculation, LNC = lean-NO_x catalyst.

The results of our process-based systems cost analysis reveal that the costs of membrane-based performance and emission-control methods are competitive with those of expected alternative techniques.

Section 1

Introduction

Argonne National Laboratory's (Argonne's) Center for Transportation Research has been investigating oxygen- and nitrogen-enrichment technologies for emissions control and performance enhancement in internal combustion engines — particularly in diesel engines — for nearly a decade. To exploit the benefits of air-composition modification, a technology must be able to provide both oxygen (O₂)- and nitrogen (N₂)-enriched air in controlled amounts, at specified enrichment levels, and with good transient response. Furthermore, a self-contained, compact, and cost-effective system must be used to supply the required O₂-enriched or N₂-enriched air.

Membrane-based air separation is the only practical method available to effect the necessary separation. Alternative systems, while appropriate for some stationary applications (e.g., pressure-swing adsorption), are too energy-intensive and bulky for automotive systems. Over the past 10 years, significant advances in membrane science and technology have reduced the size and energy requirements of appropriate membrane systems to make them technically feasible for automotive applications.

Section 2 of this report presents the objectives of the study and the five cases developed to compare the costs and benefits of various membrane technologies. The cases for representative applications of membranes to diesel engines are based on a modern light-duty diesel engine. We designed the membrane systems to meet the demands of each case, and we compare each case to an alternative technology in terms of function and cost. Section 3 summarizes the benefits of air-composition control, and Section 4 describes the structure, operating principles, design, and application of various membrane technologies. Because the cost analysis was to be process-based, the membrane production process is also described. From this production process, a simple cost model is derived, and the costs of the resultant membrane systems are compared with those of competing technologies (Section 5).

Section 2

Objectives and Study Cases

The Compression-Ignition, Direct-Injection (CIDI) Engine Program Office of the U.S. Department of Energy's (DOE's) Office of Advanced Automotive Technology (OAAT) requested that Argonne perform a process-based cost analysis of a membrane system suitable for vehicle application. The purpose of the study was to quantify the current and potential future costs of various membrane systems, including auxiliary equipment, membrane manufacture, and system integration in a vehicle. This report documents the methods and results of our study.

Because this study was undertaken for the CIDI Program Office, its focus was on light-duty diesel engines — specifically, a 1.9-liter (L) Volkswagen turbocharged direct-injection (TDI) diesel engine with a peak power of 90 horsepower (hp). Such an engine, probably incorporated into a hybrid-electric vehicle, is a leading contender to power a high-mileage vehicle being developed as part of the Partnership for a New Generation of Vehicles (PNGV) program. Although the PNGV program vehicles might use a smaller engine, this production engine is modern and available, and specifications and some data on the engine have been published. The PNGV program goal is to produce a passenger vehicle with triple the fuel economy of a 1990 model year (MY) four-door sedan (to achieve approximately 80 miles per gallon [mpg]) with no sacrifice of safety, comfort, pollution control, or cost relative to the 1990 vehicle. Achieving this goal will require enormous advances in automotive engineering — a combination of technologies will almost certainly be required.

In order to present the cost of membrane systems in an appropriate context, we evaluated the benefits of air-composition control and compared the costs of the cases we developed with those of alternative systems expected to provide similar emissions or performance benefits. These competing technologies, and the membrane cases to which they correspond, are listed in Table 1.

For each case, costs were estimated at three volume levels of production corresponding to a total number of membrane modules that would require similar active membrane surface areas. Because of the different flow-rate and composition requirements of each case, the number of modules produced under constant scale assumptions for each case varied.

The main source for cost estimates for the competing technologies was a report entitled *Diesel Emission Control Options* (Environex, Inc., 1997), which contains a broad survey of current and developing control technologies.



Table 1 Membrane Cases and Competing Technologies

| Case Number | Case Description | Membrane Type | Competing Technology |
|--------------------|--|--|--|
| 1 | N ₂ -Enrichment for NO _x Control | N ₂ Membrane 100 cfm at 81% N ₂ | Lean NO _x Catalyst (+ Hydrocarbon Reductant) |
| 2 | O ₂ -Enrichment for PM Control | O ₂ Membrane 100 cfm at 23% O ₂ | Particulate Trap and Fuel Additives |
| 3 | Variable Air Composition for NO _x and PM Control | O ₂ /N ₂ Membrane 100 cfm at 23% O ₂ or 81% N ₂ | LNC + Particulate Trap |
| 4 | O ₂ for Increased Power Density | O ₂ Membrane 100 cfm at 25% O ₂ | Larger Engine or Turbocharging |
| 5 | Late-Cycle O ₂ Injection for In-Cylinder PM Control | O ₂ Membrane 10 cfm at 30% O ₂ | Particulate Trap and Fuel Additives |

Notes:

NO_x = nitrogen oxides, N₂ = nitrogen, cfm = cubic foot per minute, PM = particulate matter, O₂ = oxygen, and LNC = lean-NO_x catalyst.

Section 3

Benefits of Air Composition Control for Diesel Engines

Because of its high compression ratio and lean operation, the diesel engine has excellent thermal efficiency. Traditionally, however, diesel engines have not been considered clean engines, because of the emissions that result from their operation. In the United States, diesel penetration in the light-duty segment of the automotive market is negligible.

Its potential for high fuel economy has made the diesel engine one of several options considered to power the PNGV program vehicle. However, use of the diesel presents several significant challenges; the power density of diesel vehicles is insufficient to meet the 80-mpg goal of the program in a stand-alone configuration and — perhaps an even greater challenge — current diesel engines cannot meet the emissions goals of the program. It is uncertain whether even medium- and heavy-duty diesel engines, sold commercially in the United States, can meet PNGV emissions standards in the relatively near future. For the light-duty engines, engineers will encounter similar problems.

Much attention has been given to reducing NO_x emissions in diesels. Because of the well-known NO_x/PM trade-off, efforts to reduce NO_x have tended to increase particulate emissions. This is a problem even in heavy vehicles — one that will increase as PM standards are tightened. It is of particular concern to the PNGV program because the PM emission research goal (0.01 grams per mile [g/mi] PM₁₀) is 75% *lower* than the Tier II standard for light-duty vehicles not included in the PNGV program. So, the use of diesel engines in PNGV program vehicles poses a major challenge in reducing both NO_x and PM emissions. The authors believe that the membrane systems described in this study will go a long way toward solving the emissions and performance problems presented by using diesel engines in PNGV program vehicles.

Many in-cylinder and exhaust post-treatment techniques have been and are currently being investigated to reduce NO_x and PM emissions to acceptable levels. Altering the composition of air via membrane separation provides automotive engineers with a new design tool to solve difficult environmental problems. Membrane systems are now (or soon will be) available to provide O₂-enriched and N₂-enriched air from a single on-board module. This study addresses such critical issues as the cost, size, and power of such systems.

3.1 Oxygen Enrichment

Studies of the effects of O₂-enrichment on both direct-injection (DI) and indirect-injection (IDI) diesel engines have been carried out with the objective of reducing smoke, particulates, hydrocarbons (HC), and carbon monoxide (CO) emissions (Karim and Ward 1968; Ghajel et al. 1983; Watson et al. 1990; Virk et al. 1993). Most of these studies reveal significant reductions in exhaust emissions, with the exception of NO_x emissions.



With increased O₂ content in the combustion air, additional fuel is burned, thereby increasing the power output. Oxygen enrichment of combustion air allows ignition with minimum amounts of premixed fuel, because it reduces the ignition delay period (Iida et al. 1986). As a result, both the rate of pressure rise and the peak cylinder pressure are low. Oxygen-enriched combustion air also promotes combustion with alternative fuels, as well as low-grade and water-emulsified fuels (Sekar et al. 1990). With higher O₂ levels in the combustion air, the flame temperatures are higher, which increases in-cylinder formation of NO_x emissions. The reduction in the ignition delay period helps retard the injection timing (without adversely affecting power and particulate emissions) so that NO_x emissions can be reduced to a certain extent, but it is difficult to attain the baseline NO_x levels.

Figure 1a shows that the increase of particulate emissions caused by retarded injection timing is smaller when O₂-enriched intake air is used than when ambient intake air is used. Figure 1b shows an increase in cylinder power output with a disproportionately small increase in peak cylinder pressure. Both of these figures represent data from a 2.5-L, single-cylinder Caterpillar diesel truck engine (Sekar et al. 1990).

Despite the many benefits of O₂ enrichment, the accompanying increase in NO_x emissions hinders its widespread application. This problem can be addressed in a number of ways, including using a post-treatment device. Recent studies conducted at Argonne have identified an O₂-enriched operating regime (defined by the combination of various operating parameters) that can eliminate the increase in NO_x emissions, reduce PM emissions, and increase power output. If the results of the initial experiments can be confirmed for a variety of engines, this new approach may be used to attain the benefits of O₂-enrichment without increasing NO_x or reducing fuel economy or engine performance. At this time, the data from these studies cannot be published because they were collected under a Cooperative Research and Development Agreement (CRADA).

3.2 Nitrogen Enrichment

Nitrogen-enriched air from polymer membranes has been used for a number of years in such applications as food storage and inert blanketing of chemically sensitive products. Its application to combustion engines is technically new.

For In-Cylinder Combustion — A number of NO_x control methods are aimed at lowering in-cylinder combustion temperatures by increasing the specific heat capacity of the charge and/or by lowering the O₂ concentration. One such technique is exhaust-gas recirculation (EGR), in which part of the exhaust gas is mixed with the ambient intake air. This method, the most cost-effective way of reducing NO_x emissions from spark-ignition (SI) engines, is being considered by many investigators for use with compression-ignition (CI) engines (Dürnholz et al. 1992; Ladommatos et al. 1996; Psaras et al. 1997). However, its applicability for diesel engines is uncertain because of such drawbacks as increases in both particulates and smoke at higher engine loads, reduced engine durability (Nagai et al. 1983), and possible oil contamination caused by sulfur dioxide (SO₂) and soot particles in recirculated exhaust gas (Nagaki and Korematsu 1995).

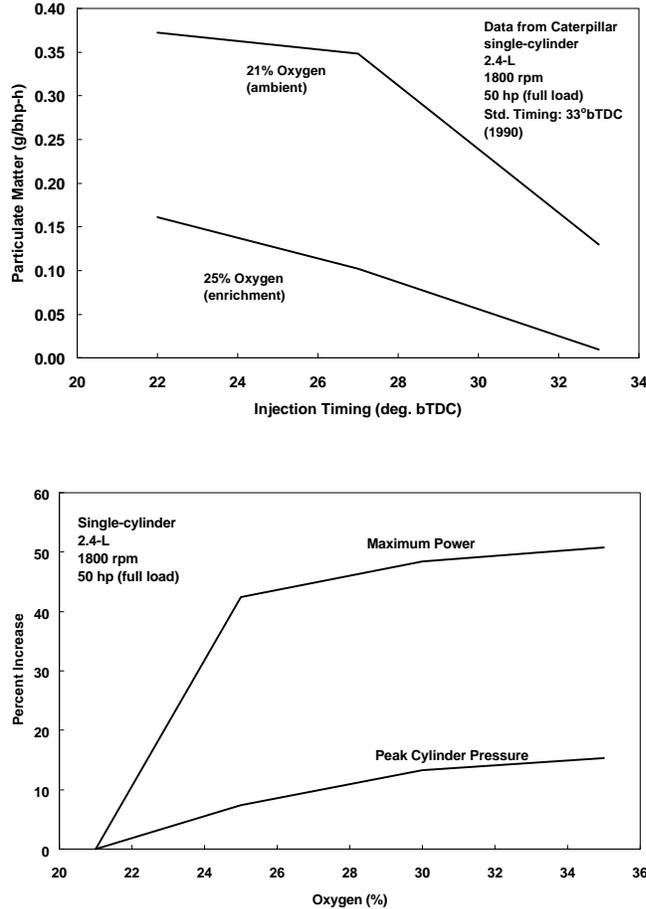


Figure 1 Benefits of O₂-Enriched Combustion for Diesel Engines (a: change in PM as function of injection timing; b: change in power with cylinder pressure)

In diesel engines, the NO_x reductions that can be achieved by using EGR vary with the amount of recirculated gases to be mixed with the ambient air, exhaust gas temperature and water content, fuel injection timing, and operating conditions. Arcoumanis et al. (1995) report that warm, uncooled, recirculated exhaust gases increase the temperature of the intake mixture, which speeds combustion and increases the formation of NO (the primary component of NO_x). Despite the simplicity of EGR, a heat exchanger would be necessary to cool the exhaust gases to further reduce NO_x emissions. However, cooled, dry, recirculated gases eliminate the water vapor, making the heat capacity lower than with the hot exhaust. Increasing the EGR rate would lead to lower NO_x emissions but increased soot, CO, and HC emissions. Also, because of unwanted species in the recirculated exhaust gases, it is difficult to obtain an optimal NO_x/PM trade-off without sacrificing performance and fuel economy.



Yu and Shahed (1981) maintain that local atomic O₂ concentration and local temperature during combustion are the primary variables that affect the formation of NO. Studies at Volkswagen AG (Röpke et al. 1995) and Imperial College (Arcoumanis et al. 1995) indicate that increasing the EGR rate by up to 30% would lower the intake O₂ concentration by about 4% (by volume) at an excess air factor of 1.5.

A similar decrease in the concentration of O₂ in the intake air can easily be achieved by using N₂-enriched air supplied by an air separation membrane. Used as a diluent, N₂-enriched air can be an effective way to lower the O₂ concentration, thereby lowering NO_x formation during combustion. The reductions in NO_x emissions achieved by adding N₂-enriched air would be similar to those obtained with EGR but without its deleterious effects. The advantages of using N₂-enriched intake air rather than EGR include elimination of the following problems: (1) unwanted exhaust species in the intake; (2) the need for a heat exchanger to cool the gases; (3) poor utilization of fresh air; and (4) oil contamination, piston ring failures, and wear. So, use of N₂-enriched intake air can be considered an effective alternative to EGR in reducing NO_x emissions from diesel engines.

Many investigators (Plee et al. 1981; Bowen et al. 1996; Li et al. 1997) have reported reductions in NO_x emissions from diesel engines by using N₂-enriched air. However, all these engine tests were conducted using bottled N₂, primarily to simulate EGR effects. The authors, for the first time, have conducted engine tests using an air separation membrane; the results were reported at the 1998 Society for Automotive Engineers (SAE) Congress (Callaghan et al. 1998).

For Exhaust Post-Treatment — When excited nitrogen (N^{*}) atoms generated by an arc are supplied to exhaust gas containing NO, the extended Zeldovich reaction of N atoms with NO, O₂, and OH (hydroxide ion) takes place. Hilliard and Weinberg (1976) showed that NO decreases with time, on the basis of reactions of N with NO and O₂:



Morimune and Ejiri (1994) examined the influences of O₂, SO₂, carbon dioxide (CO₂), and water (H₂O) contained in the engine exhaust gas on the reduction of NO_x. They observed NO_x removal rates of 40–50% with an O₂ concentration of 3–5% and plasma power of 600 watts (W). Ng et al. (1995) reported on the effectiveness of monatomic nitrogen, induced by a pulsed plasma arc, in reducing NO and NO₂ (nitrogen dioxide, another constituent of NO_x) in the gas mixture (N₂+NO+NO₂+O₂). Figure 2 shows Argonne's pulsed plasma arc system.

The availability of pure nitrogen to generate monatomic nitrogen is critical for successful implementation of this technique in vehicular systems. Argonne is pursuing a method that uses N₂-enriched air generated by an air separation membrane, thereby eliminating the need for N₂ cylinders in the vehicle. The currently available polymer membranes can generate a purity of about 95% N₂ quite economically; achieving 99%+ purity is less cost-effective.

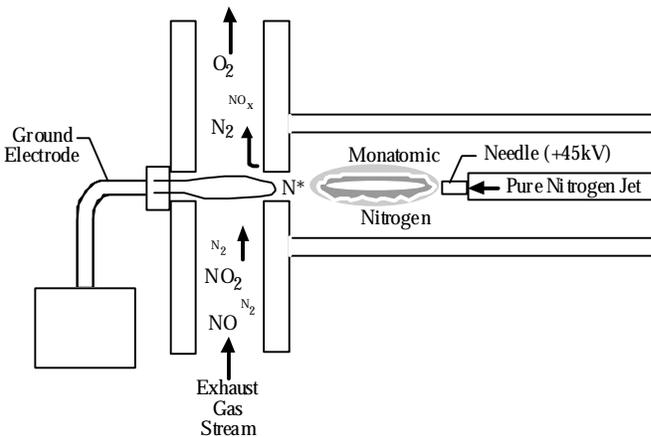


Figure 2 Argonne's Pulsed Plasma Arc System Generates Monatomic N₂ for NO_x Reduction

In addition to O₂ and N₂ enrichment, Argonne evaluated the following applications: variable-air composition and late-cycle O₂ injection. Both are conceptual, based on work performed by Argonne researchers over the past few years. Neither technique has been tested and no data are available to demonstrate their effectiveness, but they are promising extensions of the concept of modification of intake air.

3.3 Variable Air Composition

The usefulness of N₂- and O₂-enriched combustion can be combined by using both product streams of a membrane module selectively during engine operation to reduce NO_x under high-load conditions (with N₂ enrichment) and PM under all other conditions (with O₂ enrichment). The N₂-enriched stream could also be diverted for use in a nonthermal plasma after-treatment device, as described in Section 3.2.

Figure 3 shows the conceptual scheme of variable air composition with a membrane operating in vacuum mode. A bypass valve is provided downstream of the air filter to allow controlled ambient air to flow through the membrane. The O₂-enriched (permeate) or N₂-enriched (retentate) air is collected in a small plenum (optional) to regulate the air supply into the engine intake. By selective use of either permeate or retentate streams from the membrane, the composition of engine intake air can be varied. An electronic control unit can select the desired O₂ / N₂ ratio in the intake air and the duration of its operation to obtain the lowest exhaust emissions, on the basis of engine load and speed. If reformed air is not required, bypass valves can be manipulated to allow the air to pass directly from air filter to engine intake. Nitrogen-enriched air from the membrane can also be used for exhaust post-treatment devices (such as the pulsed plasma arc system developed by Argonne to generate monatomic nitrogen) to reduce NO_x emissions to very low levels.

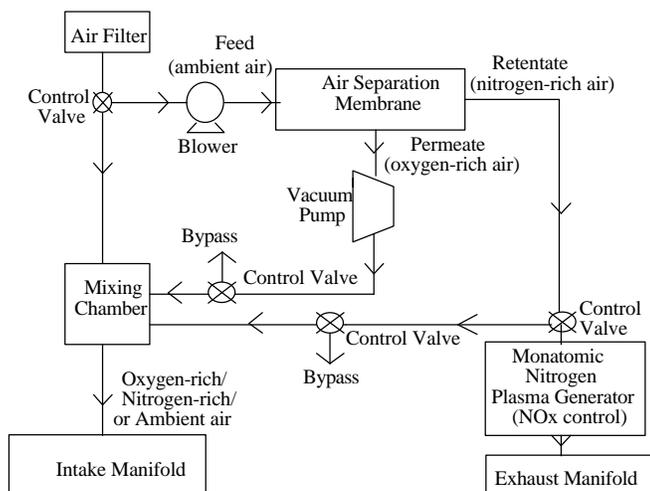


Figure 3 Conceptual Scheme of Variable Air Composition Supply System for Engine Applications

3.4 Late-Cycle Oxygen Injection

Soot and NO_x form during combustion under different conditions. By analyzing combustion, Argonne has developed a method to control PM without increasing NO_x . We call this method “late-cycle injection of O_2 -enriched air” and have applied for a patent for the technique.

During the later part of the expansion process, temperatures in the combustion chamber are generally below those that favor the formation of NO_x . Under these conditions, a small amount of O_2 -enriched air is injected directly into the cylinder to enhance combustion of soot. If the concept works, both NO_x and PM should be reduced relative to base levels.

In order to implement this concept, engineers would need to design an O_2 -enriched air injector as part of a cylinder and incorporate a small but powerful compressor to compress a small amount of air (approximately 10 cfm in the case of the Volkswagen TDI engine) to a high pressure (500–2,000 pounds per square inch [psi]). This new concept will require significant additional research if it is found to be promising.

Section 4

Membrane Systems: Operation and Design

The preceding discussions demonstrate that air separation membranes represent a key element in controlling vehicle combustion and emissions. It is important, then, to understand the mechanism of air separation and the conditions that influence its effectiveness so that membranes can be developed and optimized for specific applications. This section describes the basic operating principles of membranes and membrane geometry, performance characteristics, the production process, and membranes used for engine applications.

4.1 Basic Principle of Operation

Air delivered to engines can be enriched in O_2 or N_2 by selective permeation through nonporous, polymeric membranes via a well-known “solution-diffusion” mechanism (Winston Ho 1992). Air molecules dissolve into the membrane and then diffuse across it, as illustrated in Figure 4.

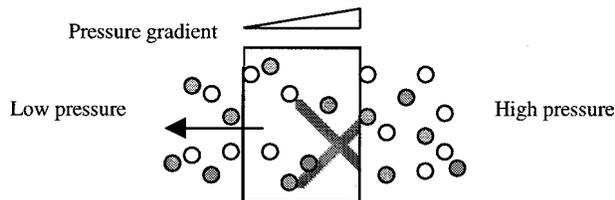


Figure 4 Basic Principle of Solution-Diffusion Membranes

The air, fed to the membrane device at elevated pressure, passes along one side of the membrane. The opposite side of the membrane is held at a lower pressure. The pressure differential and concentration gradient across the membrane provide the driving force for the dissolution and diffusion of O_2 and N_2 molecules across the membrane. Because the intrinsic rate of dissolution-diffusion of oxygen is greater than that of N_2 , oxygen diffuses more rapidly and becomes enriched in the low-pressure stream, called the permeate stream. The N_2 -enriched portion of the air that is swept out without crossing the membrane, the retentate, is necessary to effect separation.

4.2 Membrane Geometry

In general, membrane material is coated onto a porous support that provides mechanical strength and the ability to tolerate the pressure differentials imposed during operation (Henis and Tripodi 1980) The membrane geometry influences the manner in which the membrane is



packaged. Two geometries are commonly used: flat films and hollow fibers. Figure 5 shows flat-film and hollow-fiber membranes. Hollow fibers offer excellent packaging compared to flat films because hollow fibers are self-supporting. The inside and outside diameters of the fibers range from 100-500 μm and 500-1,000 μm , respectively. The membrane material, the ratio of the fiber's outside diameter (OD) and inside diameter (ID), and the detailed structure of the membrane determine the maximum external and internal pressures at which the membranes can operate.

Membranes are assembled into a cartridge in the final package (referred to as a membrane module or membrane separator) for operation.

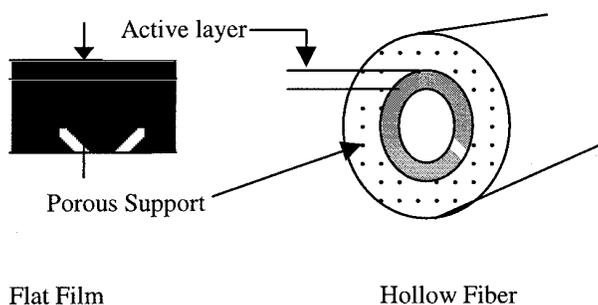


Figure 5 Geometries of Flat-Film and Hollow-Fiber Membranes

4.2.1 Cartridge Options

Whether the membrane is fabricated as a flat sheet or a hollow fiber, it must be incorporated into a “package” that is readily usable. A compact membrane cartridge design should have a high packaging density, because permeate flow per unit membrane area is inherently low. Flat-sheet, spiral-wound, and hollow-fiber geometries are the three membrane cartridge options available; each has its advantages and limitations.

Flat-sheet modules resemble plate-and-frame press filters. They are relatively easy to fabricate but provide the lowest surface area per unit volume. Spiral-wound cartridges consist of a number of leaves, each containing two flat sheets of membrane separated by porous support material. Spiral-wound cartridges are reasonably compact, and system designs incorporating spirals require a simple pressure vessel. However, air bypass around the cartridges caused by misalignment or failure within the pressure vessel may reduce the effectiveness of spiral-wound cartridges. Hollow-fiber cartridges consist of small hollow-fiber bundles sealed with an adhesive into header plates at opposite ends of the module — this design allows a large number of fibers in the cartridge. The packing density of the hollow-fiber cartridge is the highest by far, and the unit is simple to operate and maintain on clean air streams (Koros and Chern 1987) Typically, a hollow-fiber membrane module resembles a shell-and-tube geometry. Figure 6 illustrates the arrangement of a typical hollow-fiber membrane module (Baker et al. 1990).

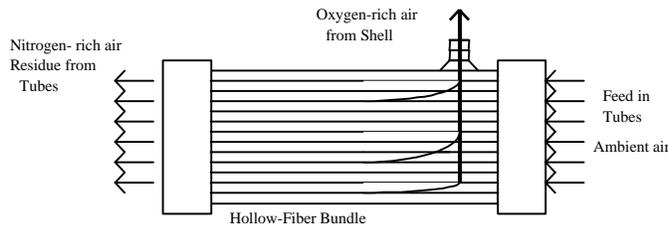
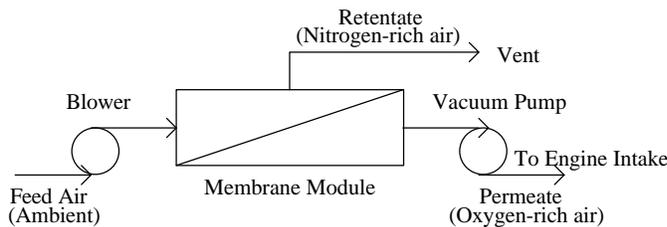


Figure 6 Schematic of a Counterflow Hollow-Fiber Membrane Module with Shell-and-Tube Geometry

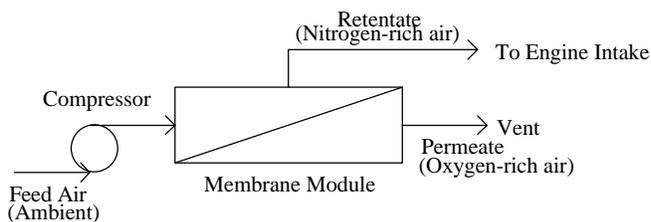
4.2.2 Operating Modes

Air separation membrane units can be operated in either vacuum or pressure mode, as illustrated in Figure 7. In the vacuum mode, the feed air is pressurized to only slightly above atmospheric pressure (1–3 pounds per square inch gauge [psig]), and a vacuum (5-20 inches of mercury [in. Hg]) is maintained on the permeate side of the membrane. The retentate is vented at atmospheric pressure. The vacuum mode is typically more energy-efficient than the pressure mode, primarily because a vacuum is applied only to the permeate (product stream).

In the pressure mode, the feed air is typically pressurized to several (1-5) atmospheres, while permeate is maintained at about atmospheric pressure. Higher driving forces are obtained in this mode because the differential pressures are higher than those of the vacuum mode, resulting in reduced membrane area requirements.



Membrane Operating on Vacuum Mode for Oxygen-Enriched Air



Membrane Operating on Pressure Mode for Nitrogen-Enriched Air

Figure 7 Air Separation Membrane Modes of Operation



For O₂-enriched air applications, the vacuum mode is more energy-efficient and so more suitable. However, because of the limited differential pressure, the vacuum mode requires a larger membrane area than the pressure mode.

For N₂-enriched air applications, the pressure mode is more suitable because the retentate can be obtained at conditions closer to feed conditions, allowing only flow loss in the tubes. The pressure mode is more energy-intensive when used for O₂-enriched air applications, because both permeate and retentate have to be compressed to higher pressures.

In certain applications, vacuum *and* pressure modes can be used in order to obtain the benefits of both. In such a “mixed mode” of operation, the feed air is pressurized, and a partial vacuum is maintained on the permeate side to increase both the pressure (feed-to-permeate) ratio and differential pressure (feed-to-retentate), and thus, the O₂ concentration. The oxygen-enriched permeate is then mixed with an ambient air stream to obtain the desired air flow and oxygen concentration.

The selection of a mode of operation depends on the economic trade-offs among membrane area costs, auxiliary equipment costs, input power requirements to maintain the required pressure or vacuum, and the compactness of the system.

4.3 Membrane Performance Characteristics

The performance of an air separator depends on the membrane’s intrinsic properties and on several other parameters, such as geometry (cartridge type, packaging density, and arrangement of separators), membrane polymer structure, skin thickness, geometry of the fibers, fiber dimensions, flow pattern, feed direction, and feed conditions. The selection of a membrane to achieve the desired O₂-enriched or N₂-enriched airflow is based on the power required to maintain the differential pressure across the membrane and the amount of space the separator occupies. The following sections briefly summarize the influence of certain key parameters on the performance of air separation membranes. More details can be found in Winston Ho (1992), Koros and Chern (1987), and Baker et al. (1990).

4.3.1 Intrinsic Properties

Membrane material is characterized by its permeability and selectivity, which are intrinsic for a given structure. The permeability, P_i , of a given gas is closely associated with Henry’s law for simple, noninteracting gases and for low concentrations. The permeability is calculated by using the following equation (Winston Ho 1992; Gollan and Kleper 1985; Ragland and Whipple 1989):

$$P_{ri} = S_i \times D_i \quad (2)$$

where P_{ri} is permeability of gas “i” in the membrane (cm³ (STP) cm/cm²-s-cm-Hg); S_i is the solubility of gas “i” in the membrane (cm³ (STP)/ cm³ cm-Hg); and D_i is the diffusivity of gas



“i” in the membrane (cm^2/s). (STP signifies “standard temperature and pressure.”) Fick’s law can be used to describe the overall permeability, a function of flow as well as of membrane composition, as follows:

$$N_i = \frac{P_{ri}A\Delta P}{\delta} \quad (3)$$

where N_i is the flow rate of gas “i” (cm^3 (STP)/s); A is membrane area (cm^2); δ is the membrane coating thickness (cm); and ΔP is the trans-membrane partial-pressure difference of gas “i” (cm of Hg).

Equation 3 indicates that the degree of separation between O_2 and N_2 depends on their relative permeabilities in the membrane material. This ratio of permeabilities is known as selectivity, or the separation factor. The separation factor (α) between O_2 and N_2 can be calculated as follows:

$$a = \frac{P_{r\text{O}_2}}{P_{r\text{N}_2}} \quad (4)$$

The larger the value of the separation factor, the more complete the separation. The stage cut (ϕ , or recovery) of an air separator is another important measure of performance; it is simply the permeate flow rate divided by the feed flow rate.

4.3.2 Polymer Structure

The effectiveness of polymeric solution-diffusion membranes for air separation depends on the chemistry of the polymers and its influence on the rate at which air molecules diffuse through the membrane. Rubbery and glassy polymers are the two classes of conventional materials used for air separation. A rubbery polymer is an amorphous polymeric material that is used at temperatures above its softening or glass transition temperature. These materials generally possess high permeability and low selectivity. A glassy polymer is an amorphous polymeric material that is used at temperatures below its softening or glass transition temperature. Because of the more restricted segmental motions in glassy polymers, these materials offer better selectivity than do rubbery polymers (at the cost of lower permeability).

As a result of growing interest in air separation membranes, a host of new materials (grouped as polycarbonates and polyimides) have been developed; these materials are specifically designed to enhance air permeability and selectivity. Table 2 lists the different membrane materials for O_2/N_2 separation. Membrane manufacturers are also vigorously pursuing development of newer materials that have superior properties for air separation. For example, perfluoro-2-2-dimethyl-1-3-dioxole (PDD) copolymerized with tetrafluoroethylene (TFE), under development at Compact Membrane Systems, Inc. (CMS), represents a new family of glassy membrane materials with high O_2 permeability and good selectivity for O_2/N_2 separation (Nemser and Roman 1991).



Table 2 Membrane Materials for Air Separation

| Polymer | Permeability (barrer ^a) | Selectivity |
|---|-------------------------------------|-------------|
| Rubbery polymers (e.g., silicon rubber, natural rubber, polychloroprene) | 600-900 | 2.0-2.5 |
| Glassy polymers (e.g., ethyl cellulose, cellulose acetate) | 1-20 | 4.0-8.0 |
| Polycarbonates | 1.0-4.0 | 5.0-7.0 |
| Poly(imides) | 1-400 | 3.0-7.0 |

Sources: Winston Ho 1992; Koros and Chern 1987; Brandup and Immergut 1975; Stern 1994.

^a barrer = cm³ (STP)-cm/cm²-s-cm Hg × 10¹⁰.

Dow Chemical Company has patented a series of halogenated polycarbonates and polyester carbonates that have high O₂/N₂ selectivities (Anand et al. 1989).

4.3.3 Skin Thickness of Membrane Coating

For compact modules, the skin thickness of a membrane coating on a porous support (hollow fibers) is critical. The rate of air transport across the membrane is inversely proportional to the skin thickness of the membrane (active) layer. For commercial membranes, skin thickness is typically on the order of 1,000–2,000 angstroms (Å); a thickness of 200–800 Å is attainable in more finely tuned membranes (Nemser 1997). Membrane material is applied to a porous support by spraying, immersion, or circulation of membrane material in a solvent (one that is not a solvent for the support material). Apart from the skin thickness, the morphology of the membrane across the entire thickness also influences the ultimate performance of the membrane.

4.3.4 Fiber Dimensions

Flow loss in the fiber bore can be significant if the bore diameter is small and the permeate flow rate is high. In hollow-fiber membrane systems, the fiber size is an important factor for packaging. Fiber sizes ranging from 50 to 2,000 μm are currently available. Larger fiber sizes offer less tube flow restriction, but their packaging density is lower than that of smaller-diameter fibers. There is a trade-off between the packaging density and pressure drop across the fibers. The internal and outside diameters of the fibers should be selected on the basis of the expected permeate flow rate per fiber, fabrication technology, and mechanical strength required.



In order to achieve higher flow rates through the membrane, membrane surface area ($A = \pi d l n$) needs to be increased. This area can be increased either by increasing the length (ℓ) or diameter (d) of the fiber or by increasing the number of fibers (n). However, the increase in pressure drop associated with longer length is higher than the increase that would be observed with a larger diameter, as the Hagen-Poiseuille flow equation demonstrates:

$$\Delta P = \frac{128 \mu \ell N}{d^2} \quad (5)$$

where “ μ ” is fluid viscosity and “ N ” is the flow rate. Therefore, the preferred practice to increase module flow output is to increase the fiber diameter and thus, the module diameter.

4.3.5 Flow Patterns

The performance of a membrane separator is affected by the relative directions of feed and permeate flow in the vicinity of the active layer of the membrane and/or the relative flow directions of the feed and permeate streams. The ideal flow patterns in a membrane are shown in Figure 8 (Winston Ho 1992). The feed and permeate streams may be directed cocurrently or countercurrently to one another. Crossflow permeation, with the permeate stream perpendicular to the membrane, is also possible. For co- and countercurrent permeation, the air in contact with the downstream side of the membrane consists of air that has just permeated through the membrane and permeate that is flowing past it. For cross-flow permeation, on the other hand, permeate that is in contact with the active layer consists entirely of air that has just passed through the membrane. Pan and Habgood (1974) reported that the countercurrent flow pattern is the best and that the cross-flow pattern is intermediate with respect to membrane area, enrichment, or stage cut. (Also, multiple permeate outlets make possible such hybrid flow patterns as the countercurrent-cocurrent flow depicted in Figure 8.)

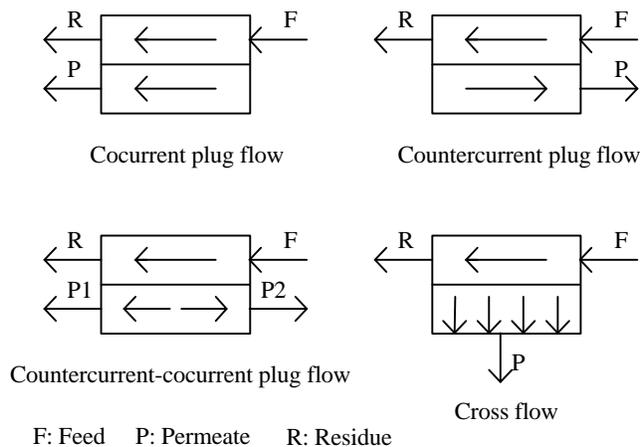


Figure 8 Ideal Flow Patterns in a Separator



4.3.6 Feed Direction

In shell-side feed separators, the feed (air) is brought into contact with the outer surface of the membrane fibers. Air permeates into the fiber and then flows down the fiber bore. From there, it passes through the tubesheet and out of the module. In tube-side feed separators (for example, see Figure 7), the feed is directed to the bore of the fibers. Two tubesheets are required — feed air is introduced through one, while nonpermeating air exits from the other. The choice between shell-side and tube-side feed in hollow-fiber modules is generally made on the basis of whether an O₂- or N₂-enriched stream is the desired product.

4.3.7 Feed Conditions

Ragland and Whipple (1989) reported that raising the feed pressure results in a higher-purity permeate product when the separator is operated at the same fractional stage cut (recovery), although the extent of the increase diminishes at higher feed pressures. Undoubtedly, an increase in the feed pressure will lower the membrane area needed to obtain a given permeate recovery.

Temperature is also an important variable that directly affects the physical properties of the membrane, and hence its permeability and selectivity. The temperature limits for membranes are related to the glass transition temperature of the polymer. The permeability (product of the solubility and mobility coefficients) tends to be dominated by the diffusivity and increases with increasing temperature. On the other hand, the separation factor is moderated in its temperature dependence, because the temperature dependencies of the permeabilities of the N₂ and O₂ are rather similar.

The higher percentages of relative humidity in feed air do not appreciably affect the permeation, because water vapor readily permeates the membrane. In comparing the permeability coefficients of H₂O, N₂, and O₂ for several polymers, the permeability of H₂O is at least two orders of magnitude greater than those of either O₂ or N₂ (Brandup and Immergut 1975). However, membrane materials are susceptible to oil contamination. It is particularly important for engine applications to avoid placing wet-type air filters and/or oil-cooled pumping elements (blower/compressor/vacuum pump) upstream of the membrane.

The selection of a membrane to achieve the desired N₂- and O₂-enriched airflow is based on the power required to maintain a pressure differential across the membrane and the amount of space it occupies. The inherent trade-offs among membrane properties and design parameters suggest that a detailed evaluation should be conducted to select or design a membrane system suitable for a given application.

4.4 Description of Membrane Production Process

The membrane manufacturing process described here was adapted from a 1991 report by Stanford Research Institute (SRI) (Schwaar 1991) and a private 1992 DuPont study (Lopez 1991).



While other membrane production processes are available and have been described, the two studies used in this analysis had the advantages that both included cost analyses and the SRI study included material requirements for production of hollow-fiber membrane modules.

Conceptually, the process was broken down into five distinct subprocesses: hollow-fiber spinning, hollow-fiber drying, fiber-bundle potting, module assembly, and membrane coating. The first four are commercial processes employed for making membranes with uncoated fibers (for liquid-gas mixture, for example). The deposition of an ultra-thin layer of nonporous membrane material on the (porous) hollow-fiber substrate, along with the development of effective membrane materials, is the key to manufacturing the advanced membranes required for transportation applications. Figure 9 presents the process diagram for membrane production.

Hollow fibers are produced from a dope of polysulfone dissolved in N,N-dimethyl acetamide (DMAC) to a concentration of 27.5 wt%. The fibers are formed from the dope by extruding through spinnerets. A needle in the middle of the spinneret includes an annular opening through which the spinning dope passes. Water, used as a bore fluid, is directed down the annulus to make the spun fibers hollow. Immediately after extrusion, the fibers are immersed in a water bath to cool and coagulate. The fibers are collected on bobbins and wound separately from each spinneret (which are run 20 in parallel). This is a continuous process; the remaining process steps are completed in batches.

Fibers are collected into hanks consisting of up to 20,000 strands (depending on the desired module diameter) and hung to dry at ambient temperature and humidity.

After drying, an epoxy resin is applied to the ends of the hanks. This process, called potting, collects the hanks into stable fiber bundles. The potted ends are cut to expose the bore of the fibers, and the ends are trimmed with a razor to ensure a smooth face to the bundle and to ensure that the fiber bores are open. A small bit of the length of fiber (typically 1-2 in. per end) is rendered inactive by the application of the potting material.

Potted bundles are inserted into module containers along with O-ring seals at each end to separate the inside (bore) and outside of the fibers. The outside of the fibers is in contact with the space contained by the module casing, analogous to the shell in a shell-and-tube heat exchanger. After sealing the module casing, appropriate fittings are attached to route the air streams to and from the bore- or shell-side of the module, as appropriate.

At this point, the module contains only the porous, polysulfone substrate and possesses no gas-separation ability. The assembled module must still be coated with the active (i.e., non-porous) membrane material — in the cases considered in this study, that material is either CMS-3 or CMS-7.

The module coating is accomplished by dissolving the membrane material (CMS-3 or CMS-7) in an organic solvent (which is *not* a solvent for polysulfone or other materials used in

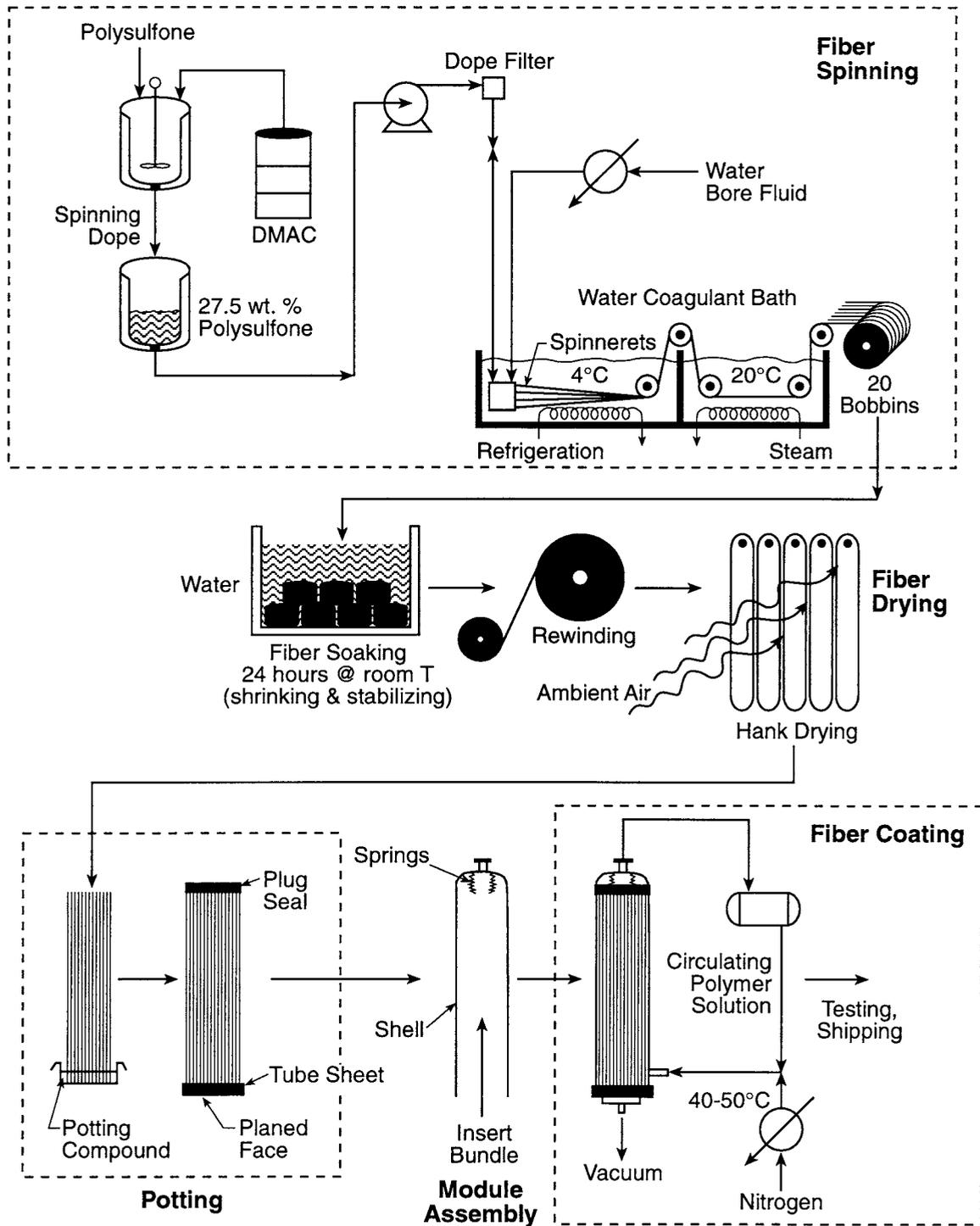


Figure 9 Process Flowchart for Membrane Production



the module construction, such as rubber for the O-rings) and circulating the solution through the fibers for a period of hours. Once the concentration of the coating solution ceases to change between the inlet and outlet of the module, coating is considered complete. The concentration of membrane material in the coating solution and the choice of solvent appear to be the primary factors that determine eventual membrane thickness.

After membranes have been coated, they are dried by pulling N₂ through the membrane for a period of up to 24 h. Then, after initial flow testing with N₂, pores and defects are repaired in a post-treatment operation. A pore-seeking compound (such as highly permeable silicone rubber), used in minuscule amounts as a “stop leak,” eliminates most Knudson and viscous flow by plugging any holes. Some small amount of active surface area is lost during the pore filling, but selectivity is greatly improved because even a few pores can ruin the separation ability of a membrane by allowing unrestricted mixing of feed gas with permeate through the pores.

4.5 Membranes for Engine Applications

The information provided in the preceding sections reveals the need for appropriate membrane intrinsic properties and coating thickness to obtain the smallest possible module size and lowest power demand for membrane engine applications. PDD-TFE copolymers were developed at CMS specifically for vehicular applications. Membrane material is coated by circulating the polymer in a solvent. Table 3 compares CMS membrane properties with those of conventional silicon rubber polymer.

Table 3 Comparison of CMS Polymers with Silicon Rubber

| Properties | PDD-1 /CMS-3 | PDD-2/CMS-7 | Silicon Rubber |
|------------------------------------|--------------|-------------|----------------|
| Permeability (barrer) ^a | | | |
| Oxygen | 290 | 1,980 | 500 |
| Nitrogen | 116 | 1,070 | 250 |
| Water vapor | 2000 | 4,500 | 5,000 |
| Selectivity | | | |
| O ₂ /N ₂ | 2.5 | 1.85 | 2.0 |
| Skin thickness (μm) | 0.1 | 0.1 | 1.0 |
| Oxygen flux (GPU) ^b | 1,800 | 9,000 | 500 |
| Upper use temperature (°C) | 160 | 240 | 130 |

^a barrer = cm³ (STP)-cm/cm²-s-cm Hg × 10¹⁰

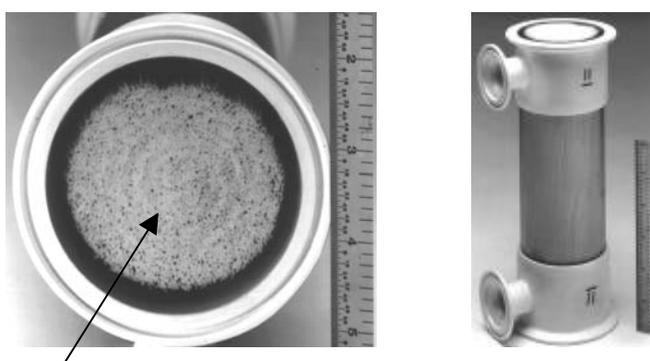
^b GPU (gas permeation unit) = cm³ (STP)/cm²-s-cm Hg × 10¹⁰

Of the two CMS polymers, CMS-7 appears to be more suitable for O₂-enrichment applications. Higher permeability at moderate selectivity provides higher permeate recovery (O₂-enriched airflow) with moderate O₂-enrichment level (about 26%), which is sufficient for current engine applications. CMS-3 is more appropriate for N₂-enriched air applications



because higher selectivity and lower permeability provide higher purity but lower percent recovery of permeate. Consequently, higher N₂-enriched airflow (retentate) can be obtained with moderate N₂ enrichment (about 83%).

A series of prototype modules were developed, using both CMS-3 and CMS-7 materials with different coating thicknesses. In all the prototype modules, membrane area (1.7 m²) was kept constant, with an overall module size of 17.8 cm (7 in.) in length and 6.4 cm (2.5 in.) in diameter. The module was packed with a number of hollow fibers (5,630), each measuring 450 μm in ID and 720 μm in OD. Figure 10 shows a prototype module.



Hollow Fibers

Figure 10 Prototype Membrane Module

During prototype membrane development, the selectivity and flux of modules were obtained on the basis of single-gas tests (feeding first N₂ and then O₂ to arrive at the selectivity). Subsequent tests were conducted using air (also called “mixed gas”). These test results were reported at the 1998 SAE Congress and Exposition (Poola et al. 1998). Table 4 provides performance data for several prototype modules. From these data, and from additional modeling efforts, we were able to determine appropriate membrane module configurations for the study.

Limited information is available regarding the durability of membrane systems in automotive applications. Because of the sensitivity of membranes to oil contamination, good feed filtration is necessary; a generally well-protected membrane is required. In tests with ambient, unfiltered air, Nemser reports a *logarithmic* decline in membrane productivity (Nemser 1997). On this basis, the authors have assumed a 50,000-mile membrane service life.



Table 4 Performance of Prototype Modules Developed at CMS

| Membrane Module No. | Coating Thickness (μm) | O₂/N₂ Selectivity | N₂ Flux (GPU) |
|----------------------------|---|--|---------------------------------|
| CMS-7 | | | |
| 23 | 0.07 | 1.44 | 15,882 |
| 25 | 0.31 | 1.94 | 3,539 |
| 26 | 0.09 | 1.67 | 12,728 |
| 31 | 0.20 | 1.85 | 5,571 |
| 32 | 0.29 | 1.93 | 3,782 |
| 33 | 0.17 | 1.74 | 6,479 |
| 37 | 0.27 | 1.88 | 4,096 |
| 38 | 0.12 | 1.69 | 9,006 |
| 39 | 0.20 | 1.90 | 4,568 |
| 40 | 0.24 | 1.90 | 4,568 |
| CMS-3 | | | |
| A | 0.24 | 2.55 | 492 |
| B | 0.20 | 2.55 | 582 |
| C | 0.26 | 2.56 | 447 |
| D | 0.29 | 2.53 | 406 |

Section 5

Cost Analysis

A simple membrane cost model was developed on the basis of current membrane pricing at various production volumes and likely future improvements in the production process. By making thinner membrane coatings, manufacturers can reduce the mass of membrane material required per unit of membrane surface area. Because the cost of the membrane material represents approximately one-quarter of the total cost — overwhelmingly the largest single component of the total module cost — this reduction is important.

A thin membrane coating also is desirable because it would reduce the energy required for gas to flow through the membrane. The challenge is to create a nonporous skin of membrane that is also thin. Just a tiny portion of porous surface area can ruin the separation capability of a membrane by allowing feed-side gas to mix with the exit stream with little relative restriction. CMS has successfully coated its material as thin as 0.07 μm and has been making progress in producing even thinner coatings.

For our cost analysis, we used the membrane manufacturing process adapted from the 1991 report by SRI (Schwaar 1991) and the private 1992 DuPont cost study (Lopez 1991) (described in Section 4.4). The capital costs presented in those studies were simply increased to account for inflation. Material and labor costs, and other operating costs, were re-estimated for this study on the basis of a number of sources.

5.1 Membrane Production Cost

Table 5 presents the materials and production costs associated with the membrane production process described in Section 4.4. Capital costs were derived from the SRI study and increased to 1995 dollars to account for inflation; other costs were re-estimated on the basis of recent data (Schwaar 1991).

The key feature of the cost analysis is that the membrane material constitutes the largest variable cost — approximately 25% of the total cost of a module. This finding underscores the importance of reducing membrane thickness.

5.2 Cases Analyzed

Five separate cases were defined for the analysis. Each case was selected as a representative application of a membrane system in a diesel vehicle. For each case, the vehicle engine targeted was a 90-hp TDI diesel engine. This engine was selected because it is a modern production engine for which data are available, and it is typical of the type of engine that might be used to power a PNGV vehicle. The engine consumes 100.8 standard cubic feet



Table 5 Process-Based Cost of Membrane Manufacture ^{a,b}

| Variable | Amount Required | Cost | Cost per Year (\$) | Cost per Square Foot (\$) | Cost per Module (\$) |
|---|-------------------|----------------|--------------------|---------------------------|----------------------|
| Materials | | | | | |
| Polysulfone (for fiber supports) | 9,257 lb/yr | \$3.92/lb | 36,287 | 0.04 | 3.63 |
| Dimethyl acetamide solvent | 24,400 lb/yr | \$0.92/lb | 22,448 | 0.02 | 2.24 |
| Waste solvent disposal | 24,400 lb/yr | \$0.50/lb | 12,200 | 0.01 | 1.22 |
| Epon 826 resin | 0.7 lb/module | \$1.31/lb | 9,301 | 0.01 | 0.93 |
| Neopentyl glycol diglycidyl ether | 0.1 lb/module | \$1.10/lb | 880 | 0.00 | 0.09 |
| Aluminum powder | 0.5 lb/module | \$4.65/lb | 24,180 | 0.02 | 2.42 |
| Tubesheet curing agents | 0.1 lb/module | \$9.00/lb | 5,760 | 0.01 | 0.58 |
| Defect repair solution | 0.4 lb/module | \$1.50/lb | 6,000 | 0.01 | 0.06 |
| Membrane coating material | 10,000 modules/yr | \$36.00/module | 360,000 | 0.36 | 36.00 |
| Low-pressure shells (prefab, purchased) | 10,000 modules/yr | \$10.00/module | 100,000 | 0.10 | 10.00 |
| Operating Costs | | | | | |
| Utilities (steam, H ₂ O, N ₂ , refrigeration) | | | 20,000 | 0.02 | 2.00 |
| Maintenance labor and materials | | | 42,000 | 0.04 | 4.20 |
| Labor (2 operators at \$25/h, 2,000 h/yr) | | | 100,000 | 0.10 | 10.00 |
| Testing laboratory | | | 120,000 | 0.12 | 12.00 |
| Plant overhead (80% of total labor) | | | 115,400 | 0.12 | 11.54 |
| Depreciation, taxes, insurance | | | 84,000 | 0.08 | 8.40 |
| Total Operating Costs | | | 1,058,456 | 1.06 | 105.85 |
| Capital Recovery (5 yr at 10%) | | | 250,608 | 0.25 | 25.06 |
| Total Cost (capital and operating) | | | 1,309,064 | 1.31 | 130.91 |

^a Sources: Nemser 1997; Schwaar 1991; Lopez 1991.

^b The costs presented are based on the following assumptions: Hollow-fiber material used is polysulfone; hollow-fiber dimensions are 1,050 µm OD, 850 µm ID; annual plant capacity is 10,000 modules, 100 ft²/module; and the estimated capital cost for the plant is \$950,000 (in 1995 dollars).



per minute (scfm) of intake air at maximum power (i.e., engine speed of 4,000 rotations per minute [rpm]) and the specified maximum boost available from the turbocharger (i.e., 0.8 bar).

Membrane systems appropriate for each case were designed with the help of a DuPont computer model. This model — a multidimensional, mass- and momentum-transfer model — is used commercially by DuPont for membrane design. It is generic and is not biased in favor of a specific membrane material. Membrane properties are exogenous inputs. Argonne had access to the model through CMS.

The authors specified the membrane module characteristics sought, fixed case-dependent variables, and selected module sizes based on off-line calculations of approximate module geometry. The model was then run to produce an appropriate membrane and determine flows and pressures. The authors calculated the work requirement based on the expected duty cycle of the membrane (which, like the membrane itself, differed for each case) and sized the auxiliary equipment required for each case. We calculated the energy required to deliver the air stream of interest in each case as isentropic work times an efficiency factor (η). For pumps and compressors, η was assumed to be 0.7; for blowers, η was assumed to be 0.8.

After membrane systems were defined, the cost of each membrane module was estimated on the basis of process-based cost (in $\$/\text{ft}^2$), as described above. A current cost curve, based on the square-footage of membrane required, was developed from commercial data (Nemser 1997). The process-based analysis agreed well with the price-based curve, producing a point that lies quite near the curve at the production volume assumed for the process analysis (1,000,000 ft^2 membrane/year).

Future costs for the membrane systems were estimated on the basis of assumed reductions in membrane coating thickness (which reduces costs because less material is required to make a given surface area of pore-free membrane). Cost reductions of one-sixth and one-third of current costs were assumed. The three resulting cost curves are presented in Figure 11.

Historical reductions in the cost of membrane production have been significant. L'Air Liquide reported a decline in the cost of N_2 -enrichment membrane production from $\$/\text{ft}^2$ to $\$/\text{ft}^2$ between 1990 and 1996 (Roman 1996). Advances in fiber-spinning and processing technology allowed manufacturers to mass-produce modules and fabricate them while using less membrane material — which significantly reduced costs.

Advances in membrane production processes are the primary factors in reducing the cost of mass-produced membrane systems. Auxiliary equipment — filters, pumps, blowers, hoses, and (in some cases) a plenum — are already available in large quantities and are unlikely to benefit from economies of scale or from technology improvement. We have assumed that the auxiliary equipment is mature. The CMS membrane materials appear to have the potential to be coated in thinner layers, comparable to those achieved with commercial membrane materials. On the basis of this assumption, our future cost-reduction estimates of one-sixth and one-third for the membrane material are quite conservative.

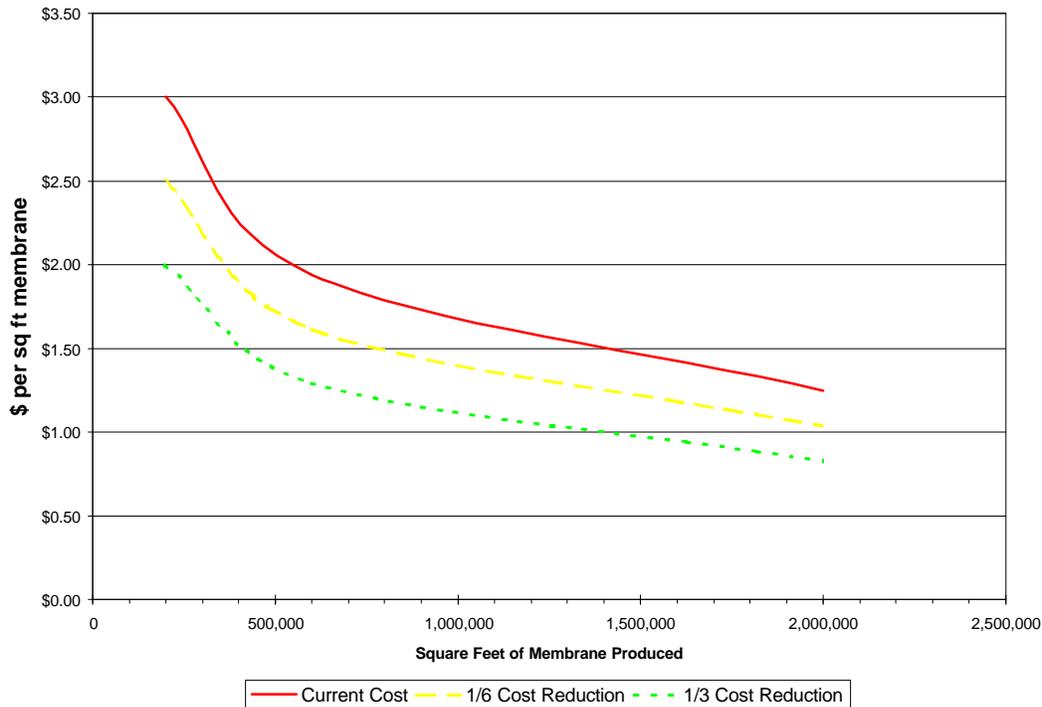


Figure 11 Current and Projected Membrane Cost as a Function of Surface Area Manufactured

During the decade in which Argonne has been evaluating O₂-enrichment membranes, the productivity of membranes has increased markedly. Figure 12 illustrates this trend by showing module volume per unit flow rate of tested O₂-enrichment membranes since 1989. By 1999, we project 1.5 in.³/scfm will be achieved.

5.3 Evaluation of the Cases

The cases defined in Table 1 were selected to address specific emissions problems or performance issues that affect light-duty CIDI engines. Figures 13-17 and Tables 6-10 summarize the results for each of the cases. The figures present cost curves for the systems in each case, developed at the three potential membrane price levels. The tables summarize the characteristics of the membrane for each case and those of the competing technology.

The expected duty cycle for the membrane system in each case differed, depending on the application of the system. For lack of a definitive driving cycle, portions of the FTP were used to estimate the amount of time each module would typically be operating. Use of the FTP affected the parasitic load (or power benefit) of the system as an operating cost (or benefit).

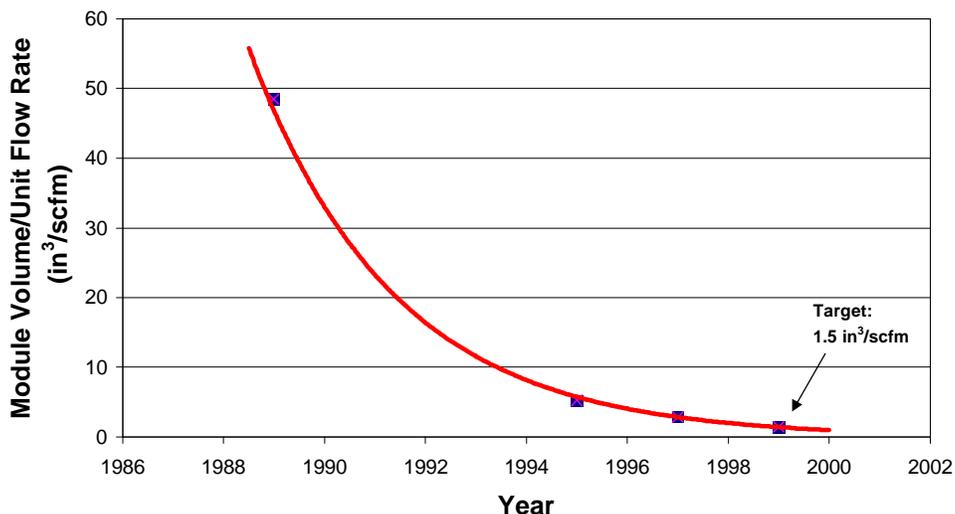


Figure 12 Membrane Size vs. Time

5.3.1 NO_x Control Case

The NO_x control case (using N₂-enriched air in the intake on demand) is the simplest of the cases analyzed. Minimal auxiliary equipment is required because operation is in pressure mode and driving force is provided by the turbocharger. Thus, in this case, the auxiliary equipment was limited to fittings, tubing, and valves. This system was compared to an advanced lean-NO_x catalyst (which as yet does not exist) along with EGR (which, as noted above, introduces hot gas and deleterious material into the cylinders if unfiltered — N₂-enriched air does not). Table 6 summarizes the results of the NO_x control case, and Figure 13 presents the resulting cost curve for the system.

Table 6 Results: NO_x Control Case

| Membrane System | Competing Technology |
|--|---|
| 100 cfm of 81% N ₂ -Enriched Air • Cost: \$75 – 110 • Parasitic power: 2.2 hp while in use • Fuel economy: Negligible penalty; expected to be used ~25% of the time, on the basis of accelerations and high load portions of FTP | Lean-NO _x Catalyst, SCR ^a Type + EGR • Cost: ~\$300 + maintenance • Parasitic power: added backpressure and electricity for catalyst lightoff • Fuel economy: penalty for use of diesel fuel as reductant; requires premium fuel |

^a SCR = selective catalytic reduction.

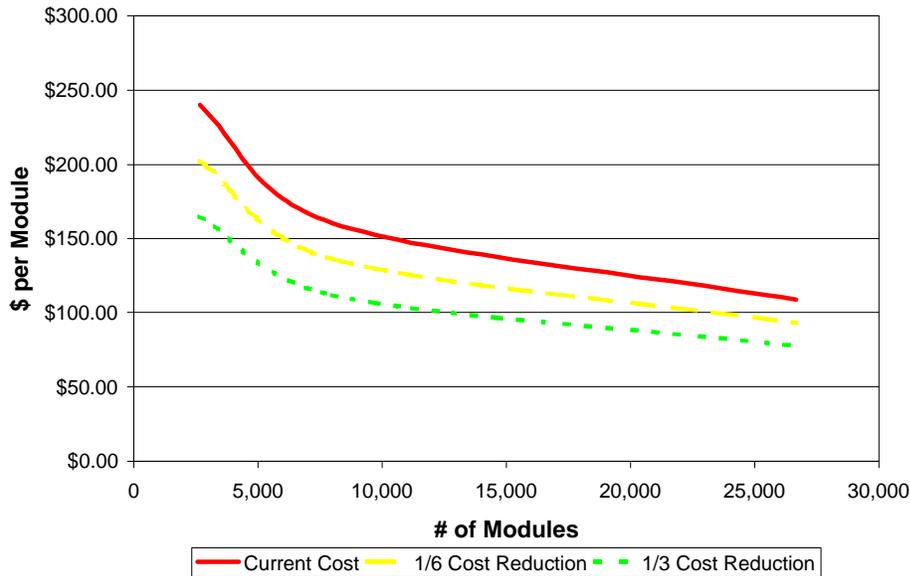


Figure 13 N₂-Enrichment Module Cost Curves

The per-module system cost of 10,000 N₂-enrichment modules would be approximately \$160 for the current-price case, \$130 for the 1/6 cost-reduction case, and \$110 for the 1/3 cost-reduction case.

5.3.2 PM Control Case

The PM control case uses O₂-enriched air to help reduce PM emissions for diesels and may allow the diesel to meet the PNGV research goal of 0.01 g/mi PM — a level of control not achievable with any current technology. For vacuum-mode operation, which is necessary in this case, a vacuum pump is required. A particulate trap could be designed to control PM to this level but would cause significant backpressure and probably durability problems. Table 7 and Figure 14 present the results and cost curves, respectively, for the PM control case.

Table 7 Results: PM Control Case

| Membrane System | Competing Technology |
|--|---|
| 100 cfm of 23% O ₂ -Enriched Air <ul style="list-style-type: none"> • Cost: \$149 – 200 • Parasitic power: 6.4 hp while in use • Power regained by increase in engine power • Fuel economy: Possible improvement • Used under high-PM conditions (~10% of the time under the FTP) | Particulate Trap with Fuel Additives <ul style="list-style-type: none"> • Cost: ~\$200 + \$0.02/gal for additives • Parasitic power: Significant increase caused by backpressure increase and trap regeneration • Fuel economy: unknown penalty • Traps generally have durability problems |

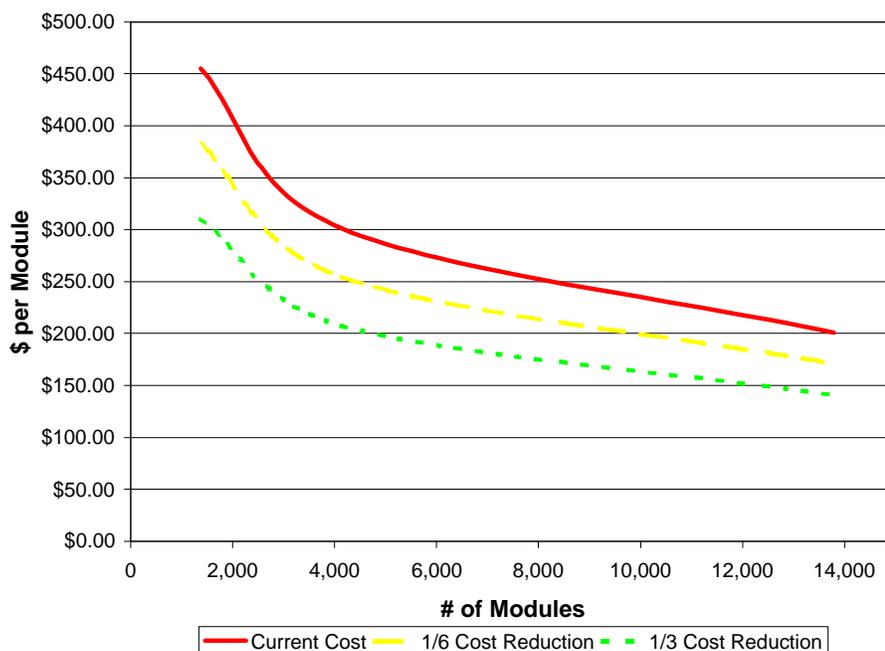


Figure 14 O₂-Enrichment Module Cost Curves

The per-module system cost of 10,000 O₂-enrichment modules would be approximately \$240 for the current-price case, \$205 for the 1/6 cost-reduction case, and \$160 for the 1/3 cost-reduction case.

5.3.3 Variable Air Composition Case

The variable air composition case combines elements of both the PM and NO_x control cases. This case has the greatest potential to allow the CIDI engine to meet *both* the NO_x and particulate standards by virtue of controlled introduction of N₂-enriched or O₂-enriched air into the cylinder as required by the driving cycle (determined by the speed and load of the engine). This case is also the most complicated system, as indicated in Figure 3. We do not, at this point, have sufficient data on the transient response of the membrane to make a quantitative assessment of the system's effectiveness. The variable air composition system is compared to a combination of a lean NO_x catalyst and a particulate trap — simply combining the technologies of the first two cases. Table 8 and Figure 15 present the results and cost curves, respectively, for the variable air composition case.



Table 8 Results: Variable Air Composition Case

| Membrane System | Competing Technology |
|---|---|
| 100 cfm of 23% O ₂ - or 81% N ₂ -Enriched Air • Cost: \$190 – 265 • Parasitic power: 6.4 hp while in use • Fuel economy: depends on duty cycle | Lean-NO _x Catalyst, EGR & Particulate Trap • Cost: ~\$500 + maintenance + fuel additive cost • Parasitic power: significant primarily because of backpressure and trap regeneration • Fuel economy: unknown penalty |

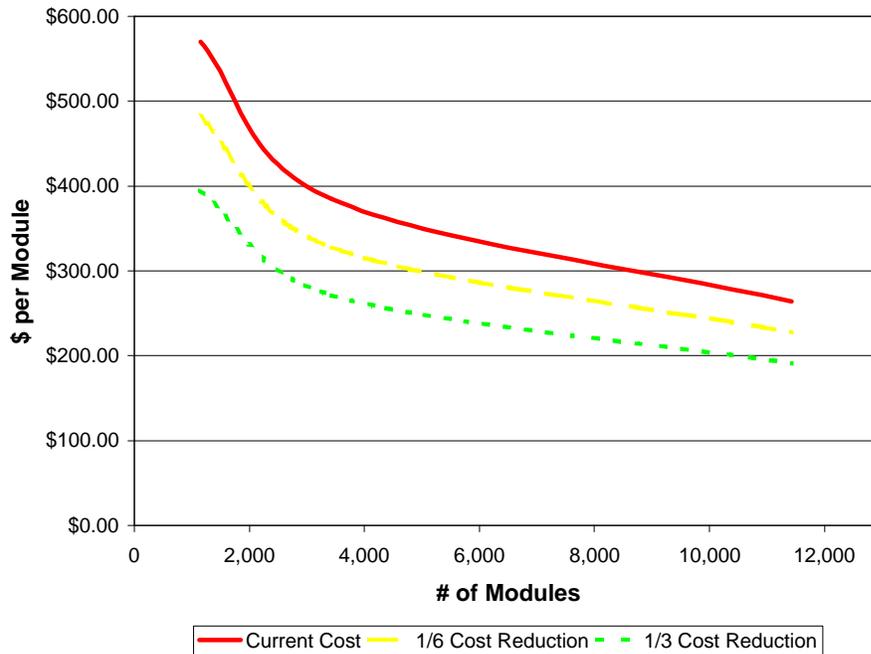


Figure 15 Variable Air Module Cost Curves

The per-module system cost of 10,000 variable air-composition modules would be approximately \$290 for the current-price case, \$250 for the 1/6 cost-reduction case, and \$215 for the 1/3 cost-reduction case.

5.3.4 Power-Enhancement Case

The power-enhancement case is a variation of the PM control case; 25% O₂ rather than 23% O₂ is used in this case. While there would be a net increase in specific power for the PM control case, it would be moderate relative to the power-enhancement case. Earlier Argonne studies indicate a net increase of 10-20% in engine power output for the power-enhancement case (Sekar et al. 1990; Poola et al. 1996). This estimate is net in the sense that power to operate the membrane system has been deducted from the total (gross) engine power output. As



an O₂-enrichment case, vacuum-mode operation is anticipated and a suitable vacuum pump would be required. Table 9 and Figure 16 present the results and cost curves, respectively, for the power-enhancement case.

Table 9 Results: Power-Enhancement Case

| Membrane System | Competing Technology |
|--|--|
| <ul style="list-style-type: none">100 cfm of 25% O₂-Enriched Air• Cost: \$180 – 270• Parasitic power: 7.7 hp (more than offset by net power increase)• Increase in <i>net</i> power by 10-20%, as needed | <ul style="list-style-type: none">Larger Engine or Turbocharger• Cost: cost of a larger engine or turbocharger• Parasitic power: N/A• Specific weight target (>45 kW/L) is difficult to attain |

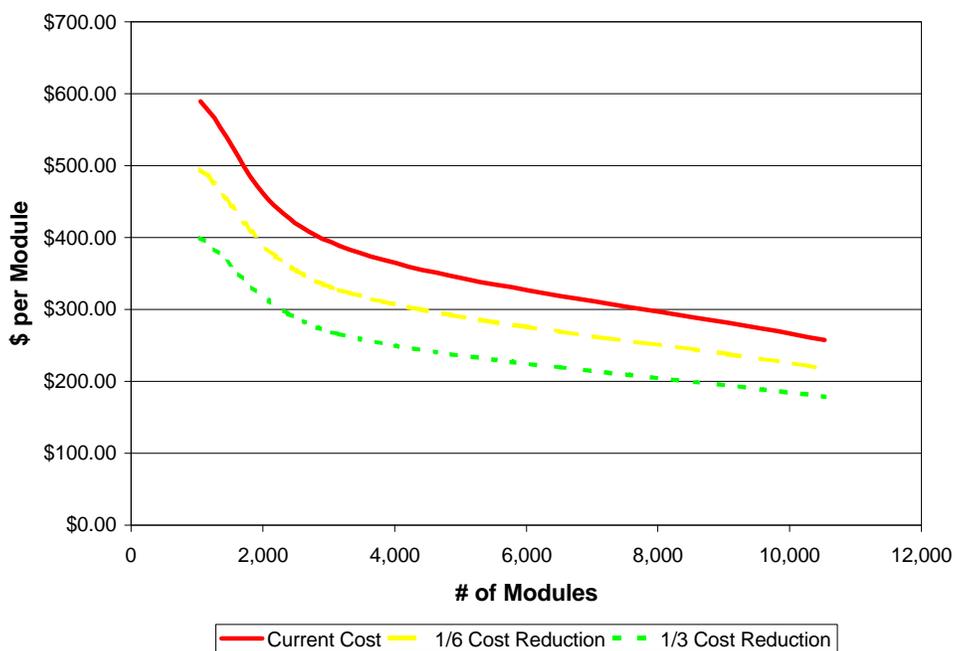


Figure 16 Power-Enhancement O₂ Module Cost Curves

The per-module system cost of 10,000 power-enhancement modules would be approximately \$280 for the current-price case, \$240 for the 1/6 cost-reduction case, and \$190 for the 1/3 cost-reduction case.



5.3.5 Late-Cycle O₂ Injection Case

The final case is a membrane system appropriate for use with Argonne's concept of late-cycle O₂ injection, described in Section 2. The flow requirements for this application are quite low (10 scfm), but the O₂ level desired is relatively high (30% O₂). After the generation of the O₂-enriched permeate in this case, the stream would be highly pressurized to allow it to be injected directly into the cylinder, after top dead center (TDC), to help oxidize particulates.

This case, the least developed of those evaluated, is derived from a concept that is untested, although Argonne has applied for a patent. Auxiliary equipment includes a compressor to generate high-pressure feed plus modifications to the engine to allow injection of O₂-enriched air into the cylinder. Costs estimated here *do not* include engine modifications. Table 10 and Figure 17 present the results and cost curves, respectively, for the late-cycle O₂ injection case.

Table 10 Results: Late-Cycle O₂ Injection Case

| Membrane System | Competing Technology |
|---|--|
| 10 cfm of 30% O ₂ -Enriched Air | Particulate Trap + Fuel Additives |
| <ul style="list-style-type: none">• Cost: \$100 – \$120• Parasitic power: 5.0 hp while operating• Fuel economy: unknown effect• Potential for in-cylinder PM control | <ul style="list-style-type: none">• Cost: ~\$200 + \$0.02/gal for additives• Parasitic power: significant increase caused by backpressure increase and trap regeneration• Fuel economy: unknown penalty• Traps generally have durability problems |

The per-module system cost of 10,000 late-cycle O₂-injection modules would be approximately \$120 for the current-price case, \$110 for the 1/6 cost-reduction case, and \$105 for the 1/3 cost-reduction case (not including the cost to modify the engine to allow injection of air directly to the cylinder).

5.4 Conclusions

The membrane systems analyzed compete well with the alternative technologies. Most of these alternatives, at this point, do not exist in the market and therefore are on relatively equal footing with developmental membrane systems. Table 11 summarizes the cases analyzed in terms of cost, size (diameter \times length), power requirements, and benefits of each case.

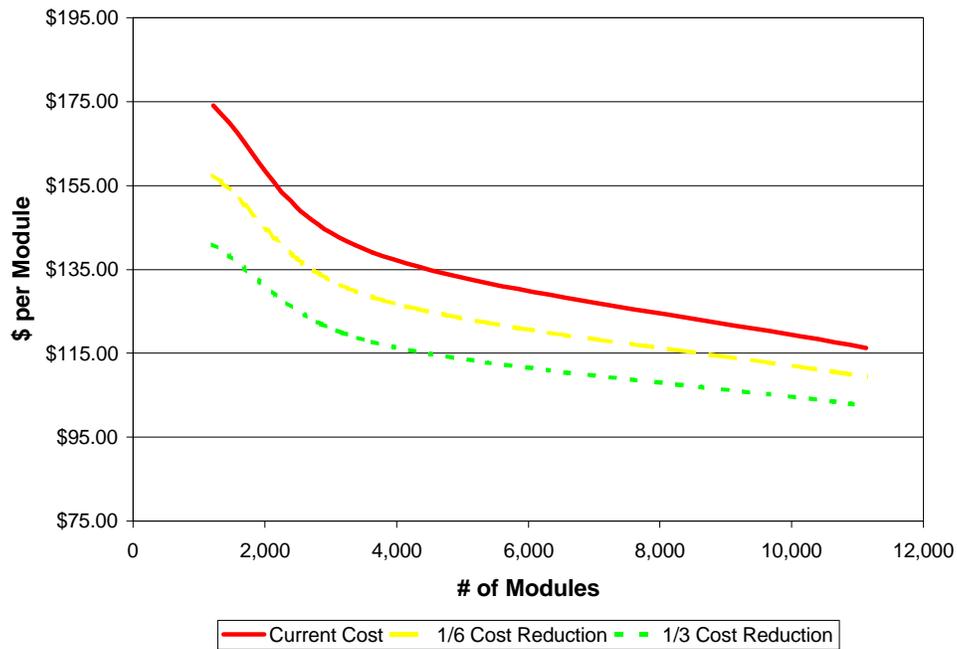


Figure 17 Late-Cycle O₂ Injection Module Cost Curves

Table 11 Summary of Cases

| Case (module size) | Current Prototype Cost (\$/module) | Future, Mass- Produced Cost (\$/module) | Power Required (hp) | Potential Benefit |
|---|---------------------------------------|---|---------------------------|---|
| NO _x Control (13 in. × 5 in.) | 240 | 75–110 | 2.2 ^a | Less expensive than NO _x catalyst |
| PM Control (18 in. × 8 in.) | 455 | 140–200 | 6.4 | Reach PNGV target of 0.01 g/mi PM |
| Variable Air (15 in. × 8 in.) | 570 | 190–265 | 5.8 | Low duty-cycle emissions of PM and NO _x |
| Power Enhancement (18 in. × 9 in.) | 590 | 180–260 | 7.7 | 10 – 20% net power increase on demand |
| Late-Cycle O ₂ (12 in. × 4 in.) | 175 | 100–120 | 5.0 | Control of PM to 0.01 g/mi |

^a Additional power is required for the N₂-product membrane. Power can be recovered from the engine in other cases (depending on duty cycle).

Section 6

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