Assessment of air separation technologies for the recovery of oxygen for use in hypersonic flight
by Nathan Jeremiah Binau

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Chemical Engineering
Montana State University

Abstract:
Various methods of air separation to recover large quantities of oxygen for use in hypersonic flight were investigated in this review. The specific separation processes that were considered included silver membranes, mixed conducting membranes, polymeric membranes, facilitated transport membranes, reversible chemical reactions, solid state adsorption, vapor-liquid equilibrium, and magnetic fields.

Despite the numerous commercial air separation technologies that exist, it was found that the volume and weight of the established, land-based air separation-systems prohibit their use in hypersonic flight.

The most promising hypersonic air separation method appears to be a vapor-liquid equilibrium system designed to operate on the principle of differential condensation and differential vaporization. The equipment to carryout the combined differential processes would require extensive engineering to make the system practical for hypersonic air separation.

One device in which differential condensation and differential vaporization may occur is a vortex tube. The vortex tube has been shown to separate high purity oxygen from air, but the oxygen recoveries were extremely low. Before the vortex tube could be useful in hypersonic air separation, its performance must be improved and a compression system must be developed to supply the tube with air at the required pressure level. If future experimental work could overcome these obstacles, the vortex tube has the potential to be successful in hypersonic air separation.

ASSESSMENT OF AIR SEPARATION TECHNOLOGIES FOR THE RECOVERY OF OXYGEN FOR USE IN HYPERSONIC FLIGHT

by

Nathan Jeremiah Binau

A thesis submitted in partial fulfillment
of the requirements for the degree

of

Master of Science

in

Chemical Engineering

MONTANA STATE UNIVERSITY-BOZEMAN
Bozeman, Montana

July 1997

APPROVAL

of a thesis submitted by

Nathan Jeremiah Binau

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citations, bibliographic style, and consistency, and is ready for submission to the College of Graduate Studies.

Dr. Frank P. McCandless — Frank P. McCandless (Signature) — 7-12-97 Date

Approved for the Department of Chemical Engineering

Dr. John T. Sears — John T. Sears (Signature) — 7-12-97 Date

Approved for the College of Graduate Studies

Dr. Robert L. Brown — R L Brown (Signature) — 7/18/97 Date

STATEMENT OF PERMISSION TO USE

In presenting this thesis in partial fulfillment of the requirements for a master's degree at Montana State University-Bozeman, I agree that the Library shall make it available to borrowers under rules of the Library.

If I have indicated my intention to copyright this thesis by including a copyright notice page, copying is allowable only for scholarly purposes, consistent with "fair use" as prescribed in the U.S. Copyright Law. Requests for permission for extended quotation from or reproduction of this thesis in whole or in parts may be granted only by the copyright holder.

Signature Nathan Jerrick Brian

Date 7/16/97

ACKNOWLEDGEMENTS

The author wishes to thank Dr. Phil McCandless for his support and guidance throughout this project. Thanks are also given to MSE Technology Applications for funding this project. Most importantly, the author would like to thank his wife, Heidi, for all her encouragement, support, and patience during the course of this research and the other requirements for the completion of the degree.

TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

TABLE OF CONTENTS--Continued

TABLE OF CONTENTS--Continued

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES--Continued

LIST OF FIGURES--Continued

LIST OF FIGURES--Continued

Figure Page

ABSTRACT

Various methods of air separation to recover large quantities of oxygen for use in hypersonic flight were investigated in this review. The specific separation processes that were considered included silver membranes, mixed conducting membranes, polymeric membranes, facilitated transport membranes, reversible chemical reactions, solid state adsorption, vapor-liquid equilibrium, and magnetic fields.

Despite the numerous commercial air separation technologies that exist, it was found that the volume and weight of the established, land-based air separation systems prohibit their use in hypersonic flight.

The most promising hypersonic air separation method appears to be a vapor-liquid equilibrium system designed to operate on the principle of differential condensation and differential vaporization. The equipment to carryout the combined differential processes would require extensive engineering to make the system practical for hypersonic air separation.

One device in which differential condensation and differential vaporization may occur is a vortex tube. The vortex tube has been shown to separate high purity oxygen from air, but the oxygen recoveries were extremely low. Before the vortex tube could be useful in hypersonic air separation, its performance must be improved and a compression system must be developed to supply the tube with air at the required pressure level. If future experimental work could overcome these obstacles, the vortex tube has the potential to be successful in hypersonic air separation.

CHAPTER 1

INTRODUCTION

Traditional propulsion systems for hypersonic flight utilize onboard supplies of liquid hydrogen and oxygen for fuel. The liquid oxygen is obtained from a land-based air separation facility such as a cryogenic distillation plant. In order to eliminate the need for onboard oxygen storage on takeoff, it is desirable to develop a launch vehicle that is not only capable of takeoff using airbreathing engines but is also able to collect, separate, and store oxygen for later use in flight.

The goal of the current project is to screen available air separation technologies for possible use in hypersonic flight. Based on this objective, four main tasks were developed for the successful completion of the project. These tasks are as follows:

1) Define the technology requirements and performance evaluation criteria;
2) Identify feasible candidate technologies for detailed evaluation;
3) Evaluate the potential performance of the feasible technologies; and
4) Prepare a report on the findings.

Project task 1 was completed on August 14, 1996 in a project kickoff meeting involving representatives from NASA, MSE Technologies, and Montana State University. The following list of project requirements was developed in this meeting:

1) The feed rate to the separation system must be 100 pounds per second;

2) The purity of the oxygen product must be at least 90% (molar) and the oxygen recovery must be at least 50% (molar);

3) The mass of the system divided by the inlet air mass flowrate cannot exceed 10 lbs/(lbs/s) (1,000 pounds) and the volume of the system divided by the inlet air mass flowrate cannot exceed 0.5 ft^3/(lbs/s) (50 ft^3);

4) The feed air will be supplied dry and carbon dioxide free at a pressure of 10 psia and a temperature of 100 K. If different feed conditions are required, the process must deal with impurities (such as carbon dioxide and water) in the feed stream;

5) The minimum pressure of the oxygen product is 8 psia; and

6) Liquid hydrogen at 25 R and 20 psia is available for use as a refrigerant.

Project tasks 2, 3, and 4 are addressed in the subsequent chapters of this review. The format of these chapters will include a discussion on the theory of the separation technology, an evaluation of the technology's applicability to air separation in hypersonic flight, and a recommendation as to whether or not the technology should be included in further research or laboratory testing.

In the evaluation of all the separation technologies included in this review, the composition of the feed air was assumed to be 79% nitrogen and 21% oxygen. The actual composition (volume) of dry air at sea level is 78.08% nitrogen, 20.95% oxygen, and 0.93% argon with the remaining balance containing carbon dioxide, helium, krypton, and other rare gases (Lide 1993, 14-12). Although the 79% nitrogen and 21% oxygen feed air composition is reasonable for an initial screening of separation technologies, the actual composition must be considered in any calculation requiring extremely accurate results.

CHAPTER 2

SILVER MEMBRANES

Summary of the Technology

Many researchers have verified that the permeation of gases through dense metal membranes can be modeled with a solution to Fick's Law. This relationship, which is known as Sieverts law (Eichenauer and Müller 1962, 324), is given as:

$$\frac{M_i}{A} = \frac{q_i}{l}(p_{i,h}^{0.5} - p_{i,l}^{0.5}) \tag{2.1}$$

In this equation, M_i is the permeation rate of the species of interest through the membrane, A is the membrane area, q_i is the permeability of the gas species through the membrane, l is the membrane thickness, and $P_{i,h}$ and $P_{i,l}$ are the partial pressures of the permeating species on the high and low pressure sides of the membrane (Hwang and Kammermeyer 1975, 92). This relationship is very similar to the governing equation for the diffusion of gases through polymeric membranes, the only difference being that the permeation rate through metals is governed by the difference in the square root of the permeating species' partial pressure instead of the partial pressure itself.

It is widely known that elemental silver is nearly 100% selective for the permeability of oxygen over nitrogen (Mullhaupt 1967, 1). The permeability of atomic oxygen through metallic silver is given by the product of oxygen's diffusivity and solubility

which is a strong function of temperature (Gryaznov, Gul'yanova, and Kanizius 1973, 1517). Equations 2.2 and 2.3 have been developed to describe the diffusivity and solubility of atomic oxygen in solid silver over the temperature range of 750 to 950 °C (Ramanarayanan and Rapp 1972, 3239).

$$D_O(Ag) = 0.0049 \cdot e^{\frac{-11600}{RT}} \text{ (cm}^2\text{/s)} \tag{2.2}$$

$$N_O^s(Ag) = 7.2 \cdot e^{\frac{-11500}{RT}} \text{ (at. pct.)} \tag{2.3}$$

Using these equations, the diffusivity of oxygen in silver at 900 °C is calculated to be 3.38×10^{-5} cm^2/s and the solubility of oxygen in silver is equal to 0.052 mole percent. The oxygen permeability through silver is therefore equal to 1.91×10^{-5} cm^3-cm/cm^2-s-atm$^{0.5}$. Similar calculations were made using data contained in other references and the results are shown in Table 1.

Table 1. Comparison of various literature values of the permeability of oxygen through silver at 900 °C.

Reference	Oxygen Permeability (cm^3-cm/cm^2-s-atm$^{0.5}$)
Ramanarayanan and Rapp 1972, 3239	1.9×10^{-5}
Hwang and Kammermeyer 1975, 94	1.0×10^{-5}
Ramanarayanan and Rapp 1972, 3245	1.5×10^{-5}

Equation 2.1 indicates that the permeation rate of oxygen through silver is a linear function of the film thickness. Consequently, it is desirable to use a very thin film in the design of silver membranes. Since thin silver films are very delicate, a composite membrane must be used in which silver is deposited on a porous inorganic support

capable of withstanding high temperatures and pressures. Porous alumina is a commonly used support material (Hsieh 1996, 149).

Use of Silver Membranes in Hypersonic Air Separation

As was previously stated, the rate that oxygen permeates through silver is a strong function of temperature. The higher the membrane's temperature, the greater the rate of oxygen permeation. Equation 2.1 shows that the permeation rate will also be governed by the pressure of both the feed and product streams. Since the outlet stream from the feed gas conditioning unit will have both a low pressure (10 psia) and low temperature (100 K), it would be necessary to compress and heat the air prior to introduction into a silver membrane.

A convenient way to obtain compressed air at a high temperature would be to utilize the stagnation pressure that could be generated if the inlet air was brought to rest isoentropically. The equation that can be used to estimate the stagnation pressure of a supersonic gas stream is presented as equation 2.4 (McCabe, Smith, and Harriott 1993, 151).

$$p_s = p_o\left(1+\frac{\gamma-1}{2}N_{Ma,o}^2\right)^{\frac{1}{1-\frac{1}{\gamma}}} \tag{2.4}$$

In this equation, p_s is the stagnation pressure, p_o is the pressure in the undisturbed fluid, γ is the ratio of specific heat capacities, and $N_{Ma,o}$ is the Mach number of the approaching fluid. Since the stagnation process was assumed to be isoentropic, it is by definition adiabatic. Because adiabatic processes have no heat transfer, the temperature of the gas

will dramatically increase during the stagnation process. The temperature of the gas after compression can be predicted by equation 2.5 (McCabe, Smith, and Harriot 1993, 151).

$$T_s = T_o\left(1+\frac{\gamma-1}{2}N_{Ma,o}^2\right) \tag{2.5}$$

In equation 2.5, T_s is the stagnation temperature and T_o is the temperature in the undisturbed fluid. When the ratio of the specific heat capacities is assumed to be constant and published atmospheric temperature and pressure data as a function of altitude (Lide 1993, 14-13 to 14-14) are used to describe the pressure and temperature of the undisturbed fluid, equations 2.4 and 2.5 can be used to compute the stagnation pressure and temperature of a supersonic gas stream as a function of Mach number. The results of the calculations are shown in Figures 1 and 2.

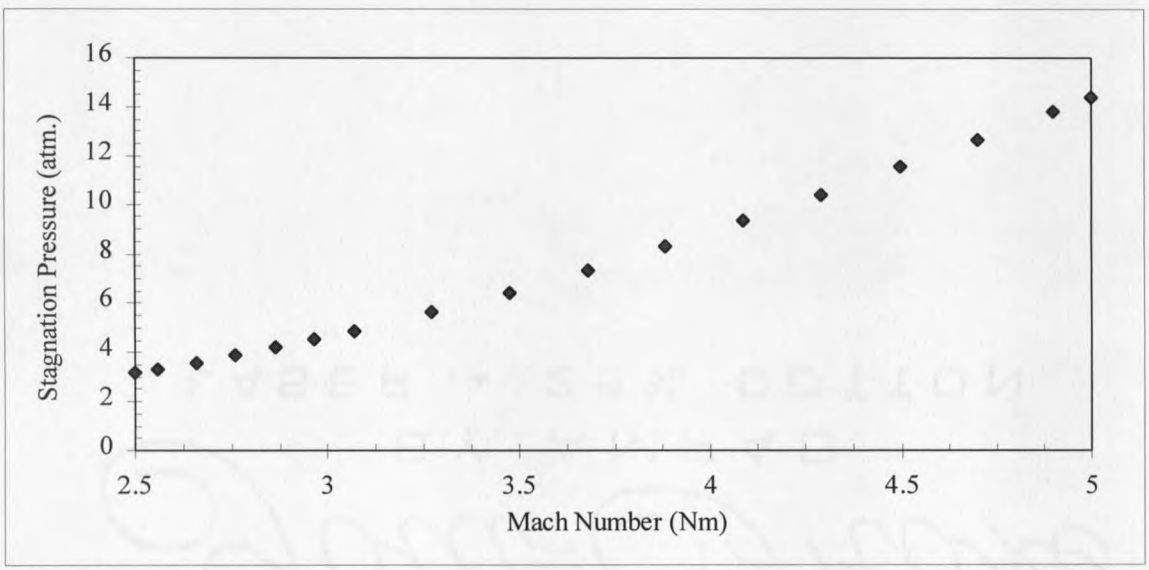

Figure 1. Stagnation pressure as a function of Mach number in uniform acceleration from Mach 2.5 to 5.0 at an initial elevation of 40,000 feet to a final elevation of 80,000 feet.

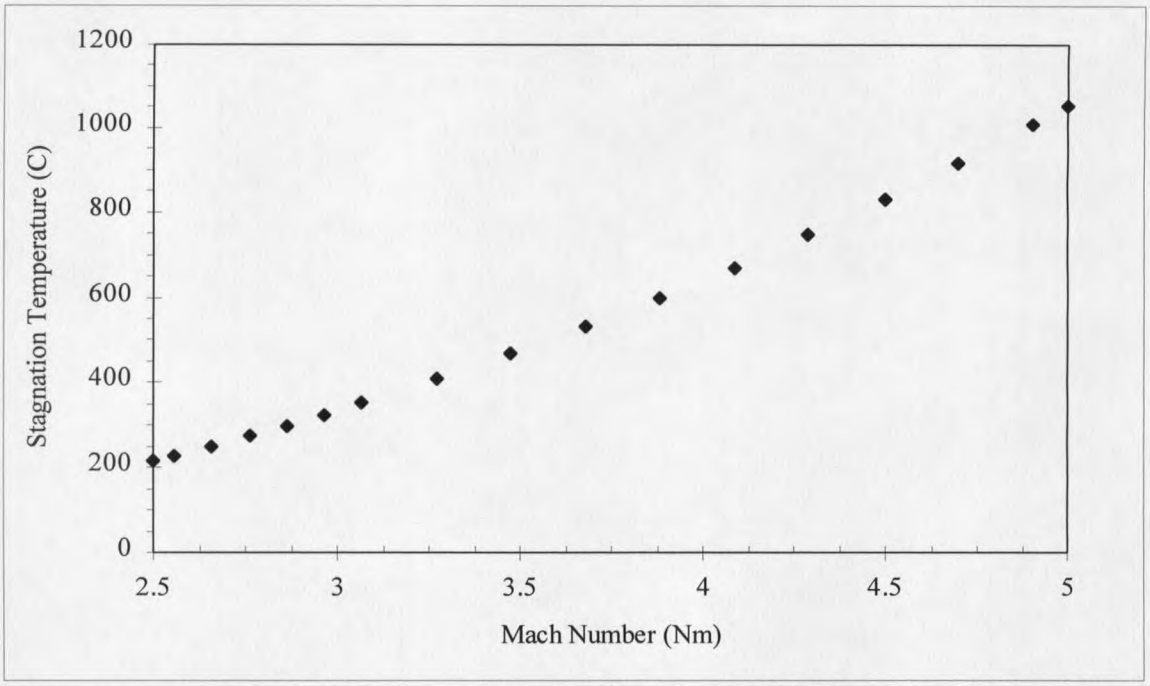

Figure 2. Stagnation temperature as a function of Mach number in uniform acceleration from Mach 2.5 to 5.0 at an initial elevation of 40,000 feet to a final elevation of 80,000 feet.

The data contained in these plots shows that the expected stagnation pressure will range from approximately 3.2 to 14.4 atmospheres and the stagnation temperature will range from approximately 210 to 1050 °C in uniform acceleration from Mach 2.5 to 5.0 at an initial elevation of 40,000 feet to a final elevation of 80,000 feet.

Calculation of the Required Membrane Area

In order to calculate the membrane area required to recover 50% of the oxygen from an inlet air stream of 100 lbs/s, the following assumptions were made regarding the operating conditions of the membrane module.

1) The membrane has a silver film thickness of 0.5 μm;

2) The permeability of oxygen through the silver film is accurately described by the product of oxygen diffusivity and solubility predicted by equations 2.2 and 2.3, respectively;

3) There is no pressure drop in the feed or product streams and no mixing occurs in the feed stream; and

4) Oxygen diffusion through the porous media on which the silver is supported is very fast compared to the rate in which oxygen diffuses through the silver.

The required membrane area was calculated using a modified version of equation 2.1 which relates the incremental oxygen permeation rate to an incremental membrane area. This equation, which originally was derived for polymeric membranes (Saltonstall 1987, 186), was modified to reflect the permeation process through metallic membranes. After modification, the equation (given as equation 2.6) was incorporated into a MATLAB® program which calculates the membrane area as a function of the amount of feed gas that has permeated the membrane. Since equation 2.6 is an ordinary differential equation (ODE), it can be easily solved with MATLAB's® ODE 45 integrator. A copy of the program has been included as Appendix A.

$$\frac{dM_i}{dA} = \frac{q_i}{l}\left(p_{i,h}^{0.5} - p_{i,l}^{0.5}\right) \tag{2.6}$$

Using this program, a study was completed in which the required membrane area was calculated as a function of the feed pressure, product pressure, and membrane operating temperature. The results of this study have been summarized in Figures 3 through 5.

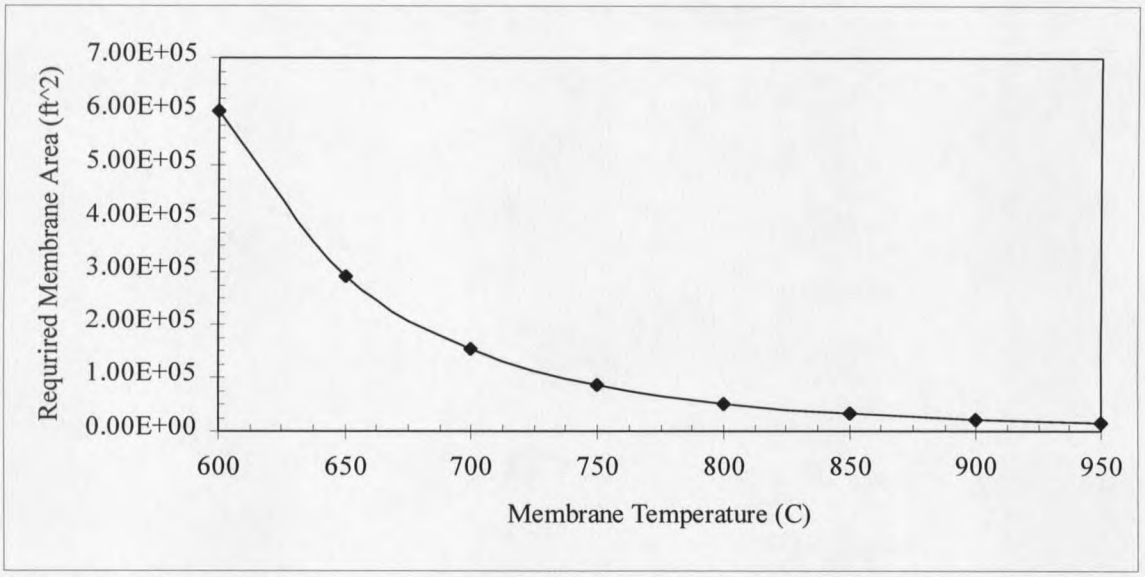

Figure 3. Required silver membrane area as a function of feed temperature (feed rate=100 lbs/s, oxygen recovery=50%, feed and product pressures of 10 atm. and 8 psia, and silver film thickness of 0.5 μm).

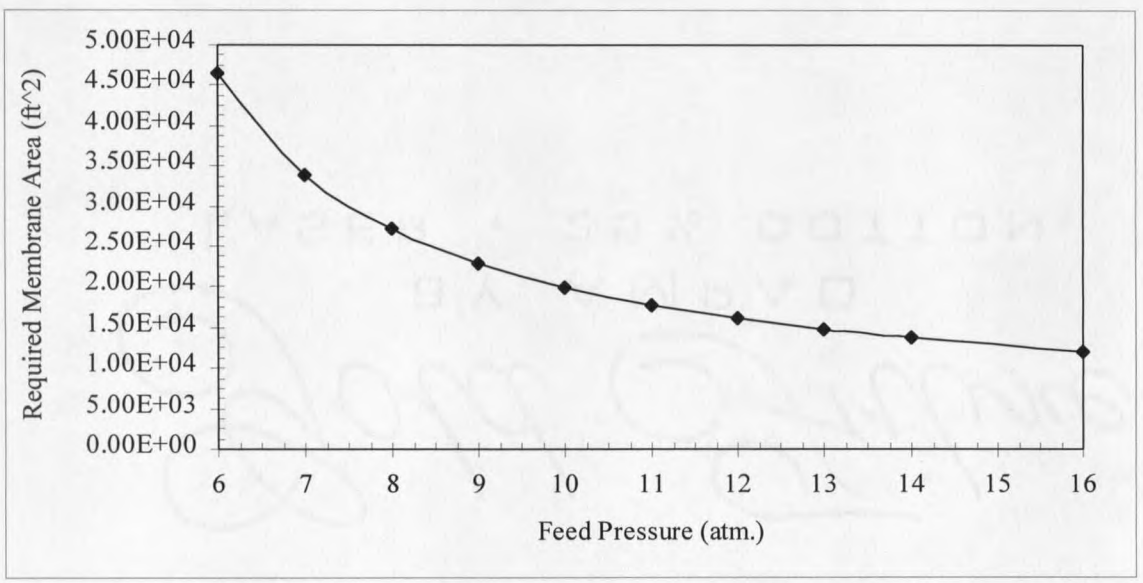

Figure 4. Required silver membrane area as a function of feed pressure (feed rate=100 lbs/s, oxygen recovery=50%, feed temperature of 900 °C, product pressure of 8 psia, and silver film thickness of 0.5 μm).