OXYGEN FROM WATER

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Water to Breathe?
A new technology may make it possible...

A recently discovered technology facilitates the chemical breakdown of water into its elemental components, hydrogen and oxygen, by using a manganese-containing compound. The compound, chemical formula: $[H_2O(terpy)Mn(O)_2Mn(terpy)OH_2](NO_3)_3$ acts as a catalyst in a chemical reaction that produces hydrogen and oxygen gas from liquid water. The task assigned to our group was to develop a profitable process using this oxygen-evolving complex (OEC) to produce oxygen from water.

Several potential applications of this process were identified and research and economic analyses were conducted to determine which of these applications could warrant further attention. As a result of this analysis, applications for processes that require mass production of oxygen on an industrial-scale were eliminated. These processes would require plants comprised of costly equipment and very expensive chemicals that would make them economically inferior to current oxygen production methods. In the case of smaller-scale applications, especially those for use in space, this process is a more cost effective alternative than other competing technologies for the same environment.

After extensive research and analysis our group has developed a process that is tailored specifically to meet all the needs of the application that was determined to be most profitable. The following is our proposal for a process that will use the OEC with a series of reactors, hydrogen-oxygen separation equipment and solar power to provide life-supporting oxygen on manned Mars exploration missions.

Chemistry

In this process a catalyst discovered by a chemistry professor at Yale University is used[19]. An illustration of the dehydrated form of the catalyst can be seen in Fig. 1.

This process proceeds through three major reactions. The first of these major reactions is the production of oxygen and hydrogen along with the decomposition of the catalyst. It is illustrated by Eq. 1. In equation 1 the overall reaction for the oxygen production consumes two moles of catalyst, $C_{30}H_{26}Mn_2N_6O_4$, combined with 16 moles of water to produce two MnO_4^- ions, two Mn^{3+} ions, four $C_{15}H_{11}N_3$, or terpy, ligands, 8 moles of oxygen, and 17 moles of hydrogen.
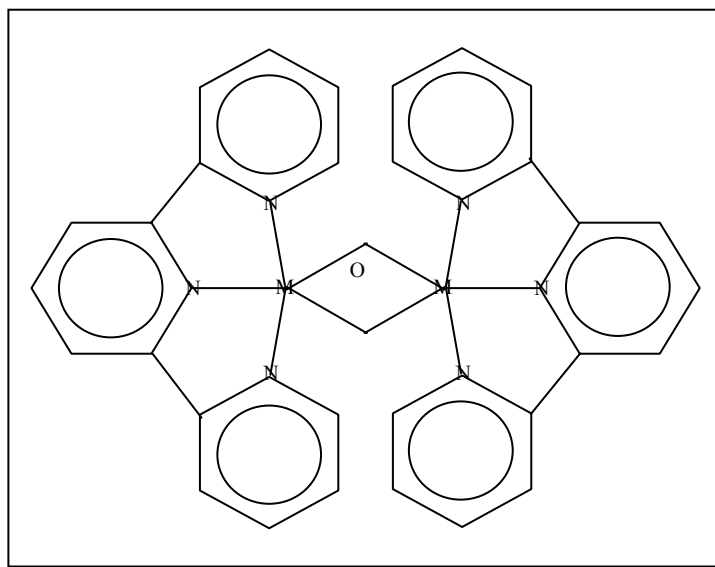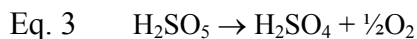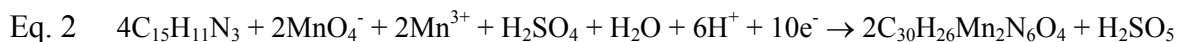
Figure 1: Illustration of the catalyst

The next major reaction is responsible for the rebuilding of the catalyst. It is illustrated by Eq. 2. This reaction also uses some of the hydrogen ions and electrons created by the primary reaction. It is important to note that this reaction is also the culmination of several individual redox reactions that have been left out for simplicity. In equation 2 the overall reaction for the regeneration of the catalyst uses the MnO_4^-, and Mn^{3+} ions along with the terpy ligands, hydrogen gas, and water to regenerate the catalyst and produce H_2SO_5. This reaction unfortunately presents a problem in that H_2SO_4 is converted to H_2SO_5 in order to sustain the catalyst. The third major reaction addresses this problem, and is illustrated by Eq. 3. In equation 3 the H_2SO_5 is oxidized back to H_2SO_4 in the presence of a heated MnO_2 catalyst. In the process, half a mole of O_2 gas is liberated for every one mole of H_2SO_5 converted.

Eq. 1 $\quad 2C_{30}H_{26}Mn_2N_6O_4 + 16H_2O \rightarrow 4C_{15}H_{11}N_3 + 2MnO_4^- + 2Mn^{3+} + 8O_2 + 17H_2 + 6H^+ + 10e^-$

Eq. 2 $\quad 4C_{15}H_{11}N_3 + 2MnO_4^- + 2Mn^{3+} + H_2SO_4 + H_2O + 6H^+ + 10e^- \rightarrow 2C_{30}H_{26}Mn_2N_6O_4 + H_2SO_5$

Eq. 3 $\quad H_2SO_5 \rightarrow H_2SO_4 + \frac{1}{2}O_2$

We have proposed to use this chemistry to design a process to beat the only competing technology, electrolysis, for Martian exploration oxygen production. Electrolysis proceeds through the splitting of water into hydrogen and oxygen through the use of an electrical current. It has the advantage of separating the two gases without additional equipment, but it is less efficient than our process. To design our oxygen production unit we initially relied on a near direct scale up from the chemistry proposed by the Yale chemist. This led to a design that was very large and not very efficient. It was based on two batch reactors that would carry out the oxygen production followed by the catalyst regeneration, and a third batch reactor to regenerate the sulfuric acid. Two reactors

were used to provide a near continuous production of oxygen. At this time the regeneration of the sulfuric acid was accomplished with the oxidation of NO to NO_2, which required an additional reactor to recover the oxygen and regenerate the NO along with a separator to separate NO_2 and O_2. Several safety concerns arose with the use of NO_2 and the fact that perfect separation was not possible which lead to NO_2 being released into the breathable atmosphere. The next iteration of the design saw a dramatic simplification by using an MnO_2 catalyst to regenerate the H_2SO_4 and liberate the oxygen. This design eliminated a reactor and a separator from the original design. We then found an article describing how compounds very similar to our own were insensitive to pH levels. This led to a decision to create a continuous system with oxygen production and regeneration happening at the same time. After communication with the Yale chemist as well as some chemists here at OU it was realized that this was feasible. These developments led to our final design with the oxygen production and catalyst regeneration occurring simultaneously in a CSTR while the sulfuric acid is regenerated in a PFTR. This final design provided us with the simplicity needed for reliability as well as continuous oxygen production. This latest iteration of the design is illustrated in the PFD below.
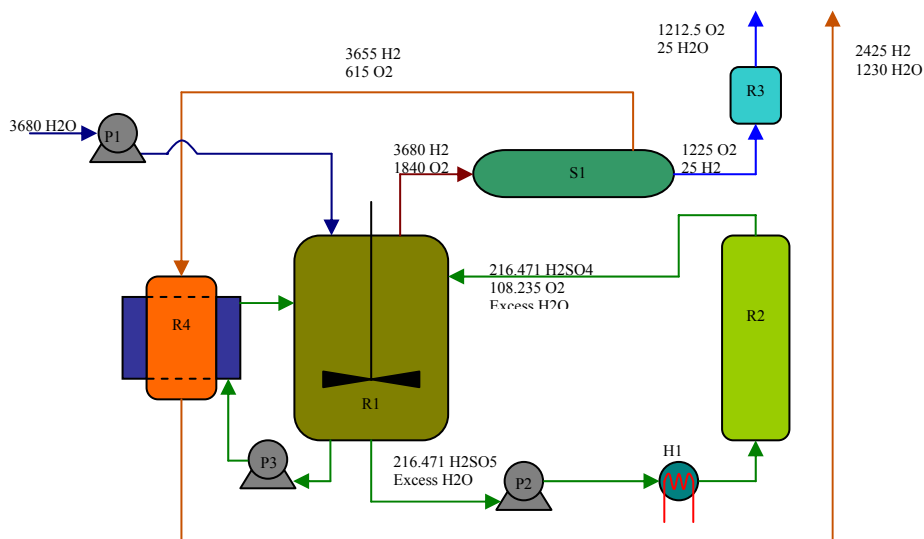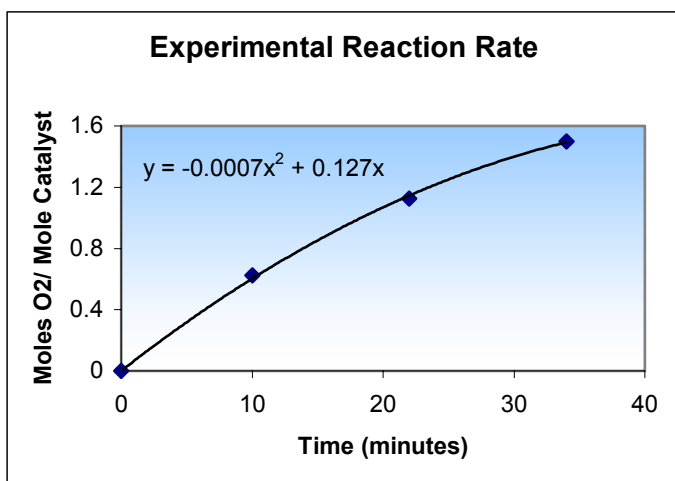

Figure 2 Process Flow Diagram

Process Details
Continuous Reactors

The equipment for the continuous system consists of two continuous reactors, R1, and R2. It also uses a heat exchanger and a pump. R1 is where set 1 and set 2 reactions occur. R2 is where H_2SO_4 is regenerated. R1 is chosen as a CSTR and R2 is chosen as a PFTR. The heat exchanger is used to heat up liquid released by R1 to $90^{\circ}C$. The pump is used to pump the $90^{\circ}C$ liquid to R2. The outlet of R2 is recycled into R1 to keep regenerating the catalyst. Water is then continuously fed to R1 to produce the oxygen. Hydrogen formed from the set 1 reactions and oxygen formed from the set 1 and the set 3 reactions goes to the gas outlet of R1.

Figure 3 Reaction Data

Experimental Reaction Rate

$y = -0.0007x^2 + 0.127x$

(x-axis: Time (minutes); y-axis: Moles O2/ Mole Catalyst)

O_2 is continuously produced at a desired constant rate and catalyst is regenerated at a much faster rate. From the oxygen rate required, water feed flow rate and amount of catalyst deposited in R1 is calculated. The water feed flow rate is 2.71 mol/min or 2.93L/hr; and amount of catalyst needed is 6.5 kg or 4.04 L. Using 16L of water to wet the catalyst, the volume of R1 is 20L. Since the rate of the set 3 reactions is extremely high compared to the set 1 reactions, the volume of R2 could be less than 5 L. However, in order to maintain low acid concentrations the volume of R2 is required to be 10L. Catalyst MnO_2 is put into tubes inside the reactor. All products of the reactions (including O_2) go into R1. H_2SO_4 and water will be involved in set 1 and set 2 reactions, while O_2 is produced by the set 1 reactions. From Figure 3, the reaction rate for the main reaction was determined by taking the derivative of the resulting equation and evaluating it at 1 minute.

The heat required to raise the temperature of the liquid phase outlet of R1 to 90°C is 8.4 kW. The pressure being used to operate the system is 9atm. The temperature of R1 is kept at room temperature, while the temperature of R2 is maintained no greater than 90°C for safety concerns. The reactors must be glass-lined due to the presence of caustic H_2SO_4.

Hydrogen-Oxygen Separation System

In order to provide oxygen for life support, it is necessary to remove 100% of the hydrogen from the oxygen and hydrogen mixture of the main reactor effluent. Determining what separation technique is best for this specification is a dynamic function of the recovery of oxygen, and equipment volume, which can be an important issue to spacecraft designs.

Membrane separation processes have several advantages over PSA (Pressure Swing Adsorption) separation processes and cryogenic distillation processes for this design. The design flowrate is low which is adequate for a membrane separation. Membranes occupy much smaller volume and weight significantly less than other types of equipment, **Table 1**, which saves precious volume and weight in the spacecraft design. Other advantages of the membrane separation process over other methods are that there are no moving parts, and there is instantaneous start-up.

Separation Process	Favored by Flowrates	Equipment
Cryogenically distillation	High	Compressor Heat exchanger Expander Distillation Column Condenser
PSA (Pressure Swing Adsorption)	Medium	Two adsorbers Compressor
Membrane	Low	Compressor Membrane

Table 1 Equipment Comparison

This system features a reactor containing a platinum catalyst to achieve 100% purification of the oxygen rich stream. The oxygen within the hydrogen rich permeate stream may be burned in order to melt the ice and distill the water from the Mars' poles. The Mars' pole water contains minerals and impurities that could build up and at some point foul the catalyst and clog the reactor.

Next, the membrane process will be analyzed to achieve the most optimal arrangement. This allows the most oxygen recovery feasible to be chosen for implementation into the design of the so-called oxygen from water technology.

Membrane Separation Process

Pressurization and separation through a membrane are the basic operations in a membrane process. These units are to be optimized to recover as much oxygen as possible.

Several different membrane arrangements were considered; one with the compressor before and the other one after the membrane. Other arrangements include splitting the feed stream into the same number of membranes to achieve the same composition at the entrance. Also, It was considered to send the hydrogen and oxygen permeate (waste) to another membrane in order to achieve further recovery of oxygen.

After taking these options into consideration the one with the compressor before the membrane was selected since with this arrangement a pressure ratio higher than one was obtained. This is important because the hydrogen permeate through the membrane is higher at pressure ratio higher than one. This implies that with this arrangement it is easier to get a high purity of oxygen.

The process was optimized by running simulations on a excel program. This program was designed to optimize nitrogen – oxygen separation membranes. Consequently this excel-based program was altered to solve the hydrogen – oxygen separation membranes and to include the catalyst performance to complete the purification of oxygen. It makes use of the solver function to maximize the recovery of oxygen.
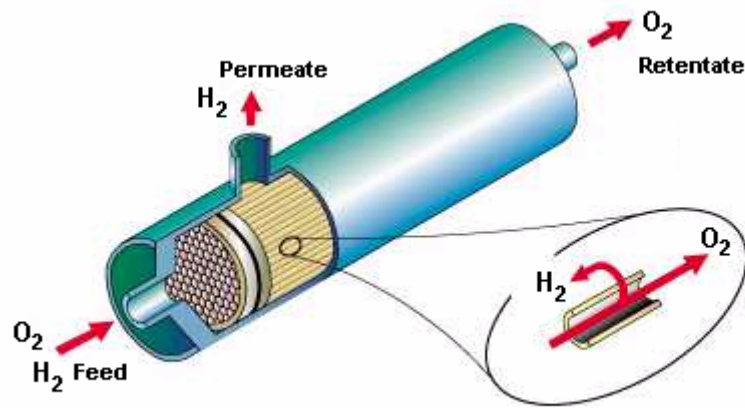
Figure 4 Membrane unit

Stream	Flowrate (gmol/h)	Pressure atm	Composition (Mole Fractions)	
			O_2	H_2
Feed	230.77	9	0.34	0.66
Retentate	51.18	9	0.98	0.02
Permeate	179.59	1	0.25	0.75

Table 2 Membrane Unit Mass Balance

A hollow fiber separator is to be optimized. The parameters that were varied to optimize the system, included selectivity, feed/permeate pressure ratio and both recovery of hydrogen and oxygen. After running every single arrangement, it was obtained that the most optimal arrangement is the one with one membrane, has a pressure ratio equal to 9, recovery of oxygen of 65% with a purity of 98%, **Table 2**.

Reactor 3

The membrane separator used to separate the mixture of oxygen and hydrogen gas evolved from the main reactor is capable of producing an oxygen-rich stream with a maximum of approximately 98% purity. Consequently, the remaining hydrogen must be removed from the oxygen stream in order to prevent build up of hydrogen gas inside the life-support area. To perform the task of removing the hydrogen, a 0.5 L plug flow reactor with a fixed-bed 0.5% platinum catalyst will be used (Reactor 3). The reaction $2H_2 + O_2 \rightarrow 2H_2O$ will occur in the reactor and remove 100% of the hydrogen from the oxygen stream. This reactor will cost approximately $700.

Reactor 4

As a result of the separation inefficiencies, almost 35% of the oxygen produced will be contained in the hydrogen rich waste stream. Another almost identical reactor to R3 will be used to combust this oxygen with the hydrogen waste and then exchange heat with the contents of Reactor 1. In this manner most of the energy that would otherwise be wasted can be recovered and used to provide heat necessary for Reactor 1. This reactor will be approx. 2.7L, containing the same Pt catalyst as R3, and will operate at 9 atm and approximately 200 $^{\circ}$C.

Creating a Breathable Atmosphere

One major consideration for utilizing this technology on Mars is establishing a breathable atmosphere with the oxygen generated. This entails supplying the environment with nitrogen, removing carbon dioxide, and removing excess water vapor to maintain a desired humidity. Liquid nitrogen can be used and would be transported in tanks from earth. The carbon dioxide and water vapor will be removed from the tent using a silica gel column along with a column containing the molecular sieve 13X. The silica gel is used to adsorb the water vapor while the molecular sieve 13X will be used to adsorb the carbon dioxide.

Economic Comparison

In order to determine which applications could represent economically viable possibilities for the OEC technology our group examined a variety of processes that ranged from small-scale to industrial-scale production. Economic analysis indicated that only small-scale applications such as life-support for space exploration would be profitable.

First, large industrial-scale oxygen production applications were researched in order to determine whether or not they could present an economically viable project. Applications such as production for steel-making industries, paper manufacturing, sewage treatment or any other process that requires mass production of oxygen in an industrial-scale were eliminated as project possibilities. Initial estimates indicated that the cost of the catalyst alone for the oxygen from water process would be approximately three times more than entire plant cost for the competing methods.

Instead the decision was made to focus on smaller-scale applications, those where the seemingly high capital costs of this method of oxygen production could be kept small in comparison with the value of the product. Specifically, this technology would be very useful for life-support systems where the need for oxygen is critical. Such applications would include home health care and space and Mars exploration missions.

Space Station

The prospect for an oxygen-producing unit for a space station is promising since, for example, Mir (which currently uses electrolysis as its primary oxygen source) has had serious problems with its oxygen supplying equipment. While electrolysis is not the only source of oxygen on the space station, it is the only one that is sustainable.

Table 1: Electrolysis and OEC process cost comparison.

Cost Comparison		
	Oxygen from Water	Electrolysis
Energy Required	9.2 kW	12.7 kW
Basic Equipment Cost	$295,000	$720,000
Solar Panel and Battery Costs	$394,000	$555,000
Total Costs	$689,000	$1,275,000

The equipment necessary for the OEC process and that used for electrolysis is comparable in size. The cost however is not quite as close. For example, an electrolysis unit that would produce 1200 mol O_2 per day (enough for a five-man crew) would cost nearly $1,275,000 compared to $689,000 for an OEC unit. For either process, costs associated with supplying energy make up the largest fraction of the total price. The oxygen

from water process gains a significant advantage here because electrolysis uses 38% more energy.

<u>Mars Exploration</u>

For a Mars exploration expedition the comparison is nearly the same as that for the space station. A sustainable oxygen source is absolutely necessary since traveling to Mars would take a few years for the round trip. In this case the only other competing technology is electrolysis. Again the comparison here between the oxygen from water process and electrolysis is cost and energy usage. On a trip of this nature, where storage space and efficiency are absolutely critical, the oxygen from water process presents a great advantage over electrolysis simply because electrolysis requires 38% more energy and therefore needs a much larger area of solar panels to provide power. This is an advantage in addition to the cost savings represented by using fewer solar panels.

Conclusion

In conclusion, through the use of a newly discovered catalyst along with some carefully orchestrated engineering designs and clever chemical reactions it is possible to revolutionize the space industry by eradicating the impeding dilemma of oxygen production in alien environments sans suitable life sustaining atmospheres.