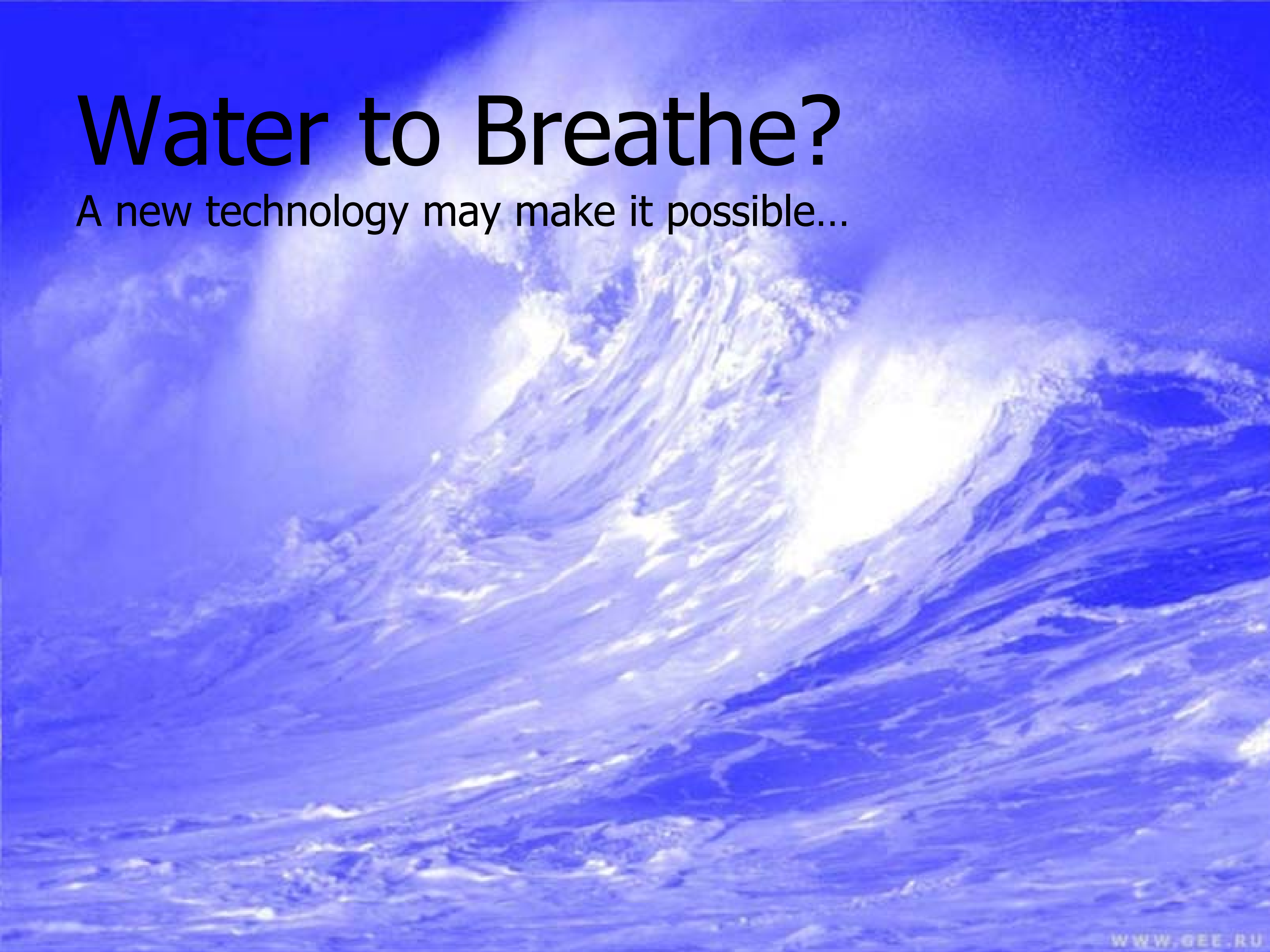
Water to Breathe?

A new technology may make it possible…



Oxygen From Water

Group 7

Anh Nguyen	Juste Tchandja
Dustin Duke	Justin Brown
Jorge Arias	Keith Orendorff

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New Technology

- A recently discovered technology uses the compound

  $[H_2O(terpy)Mn(O)_2Mn(terpy)OH_2](NO_3)_3$

  (oxygen evolving complex OEC)

  to catalyze the evolution of oxygen from water.

Project Objective

- To develop and design a profitable process that uses the OEC to produce oxygen from water.

Proposal

- We propose a process that will use the OEC with a series of multifunction reactors, a hydrogen oxygen separator and solar power to provide life-supporting oxygen on manned space exploration missions.

- As a basis for comparison we examine oxygen production to support a five man crew.

Space Exploration

- Currently, water electrolysis provides oxygen for the International Space Station and Mir.
- Also electrolysis is proposed for Mars exploration.
- Our task is to see if we can offer advantages over electrolysis.

Presentation Outline

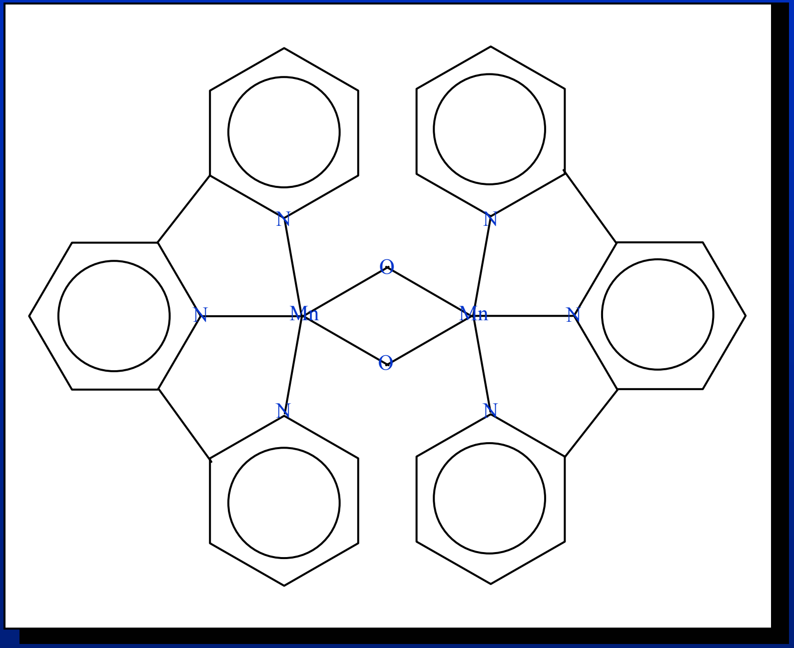
- How the Chemistry Works
- Process Design / Technical Details
- Mars Logistics
- Economic Justification
- Conclusion

Chemistry

- Process utilizes 2 sets of reactions.
  - Oxygen Production/Catalyst Regeneration
  - Sulfuric Acid Regeneration/O_2 Recovery
- 2 reactors involved
  - 1 CSTR and 1 PFTR
    - After several revisions to original design

Main Catalyst

- $C_{30}H_{22}Mn_2N_6O_2$
- In the process, the hydrated from is used.
- $C_{30}H_{26}Mn_2N_6O_4$
- This has an additional water molecule attached to the Mn atom.



Overview of Chemistry

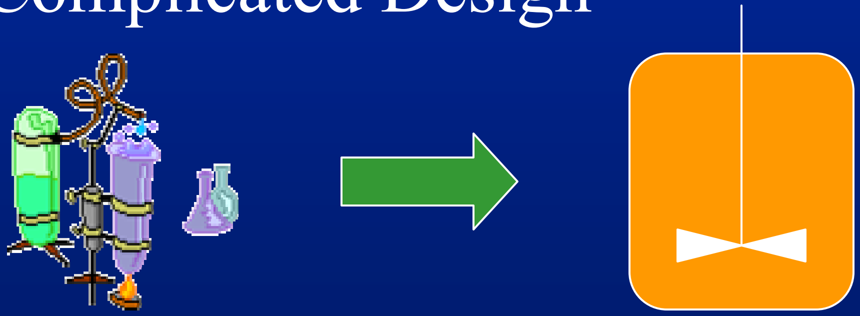
- Oxygen Production/Catalyst Regeneration

  $17H_2O + H_2SO_4 \rightarrow 17H_2 + 8O_2 + H_2SO_5$
- Sulfuric Acid Regeneration/O_2 Recovery

  $H_2SO_5 \rightarrow H_2SO_4 + \frac{1}{2}O_2$
- Overall
  - $17H_2O \rightarrow 17H_2 + 8.5O_2$
  - Daily: $2400H_2O \rightarrow 2400H_2 + 1200O_2$

Chemistry: In the Beginning

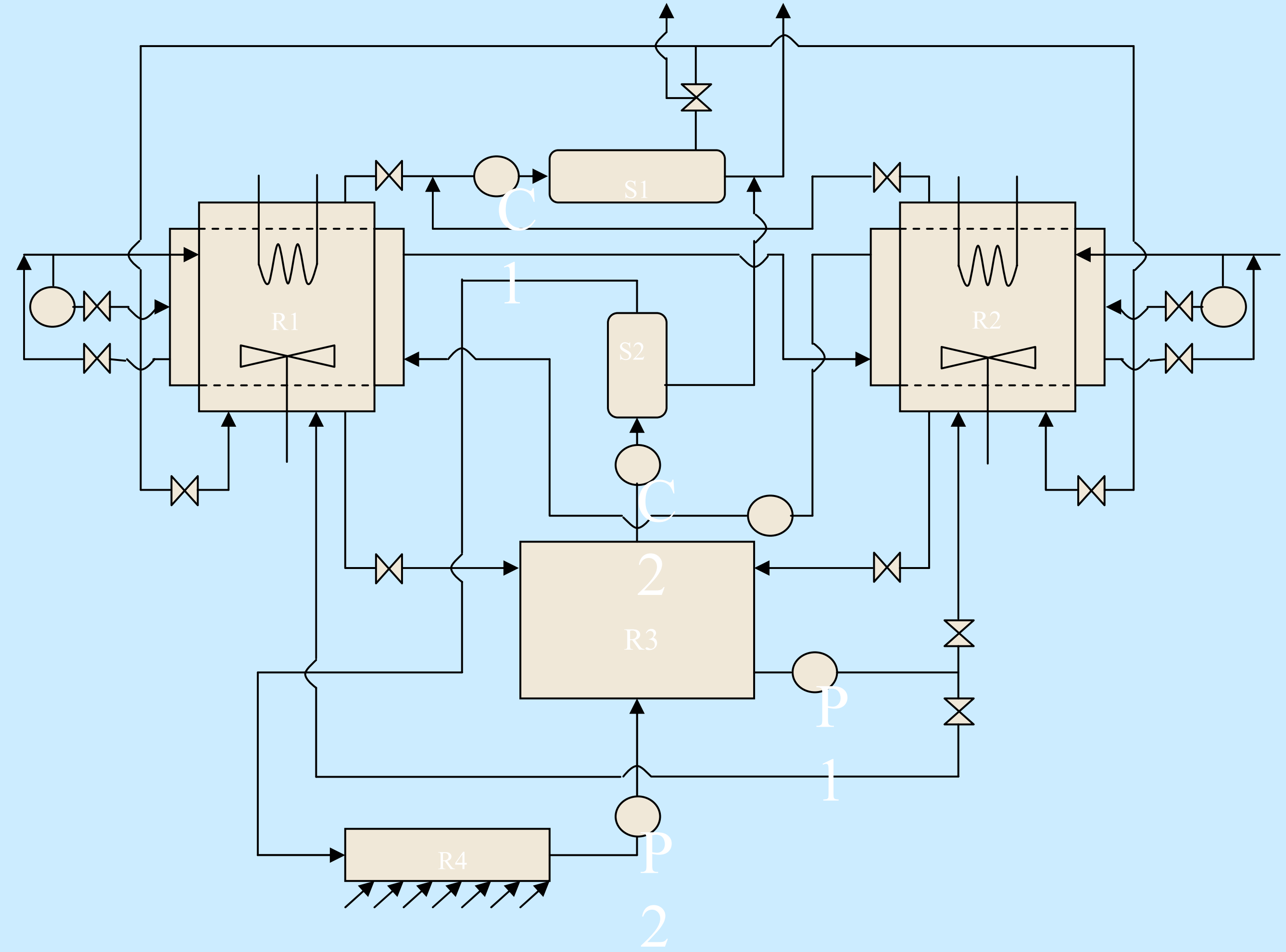
- Original Design was based on a direct scale up from the chemistry
  - Everything added to a beaker was poured into a batch reactor
  - Very Complicated Design



Problems: In the Beginning

- H_2SO_4 regenerated NO/NO_2 reaction
  - Air contamination
- Many reactors
  - Complicated PFD

The Beginning… ugly



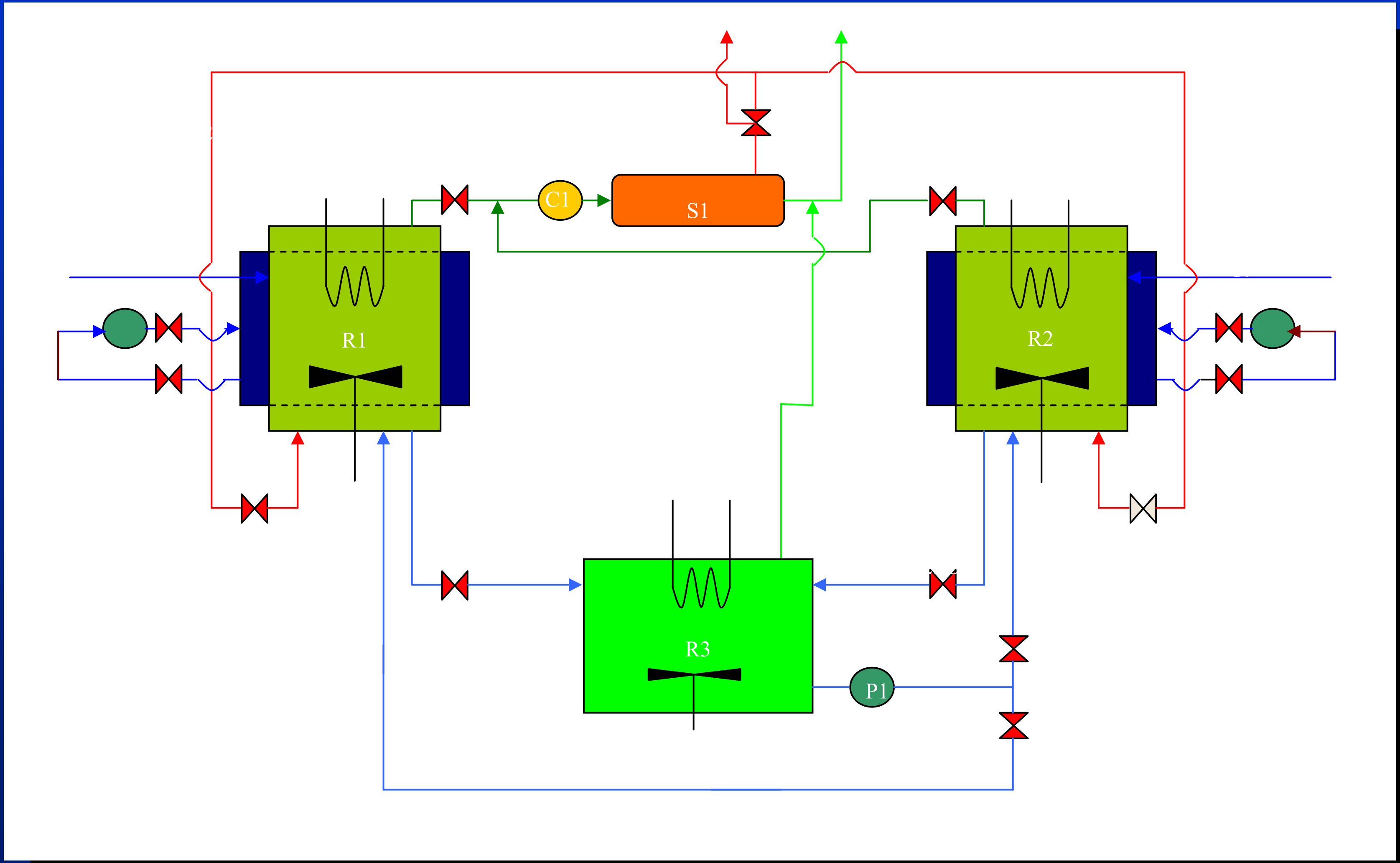
The Middle Ages

- We get wiser, eliminate NO/NO_2
  - Equipment Eliminated
    - 1 Reactor
    - 1 Separator
    - 2 Pumps
  - Healthier solution regenerates with MnO_2 catalyst
    - No new chemicals added

Still in the Dark

- Problem: Perpetual Acid Dilution
- Still complicated PFD

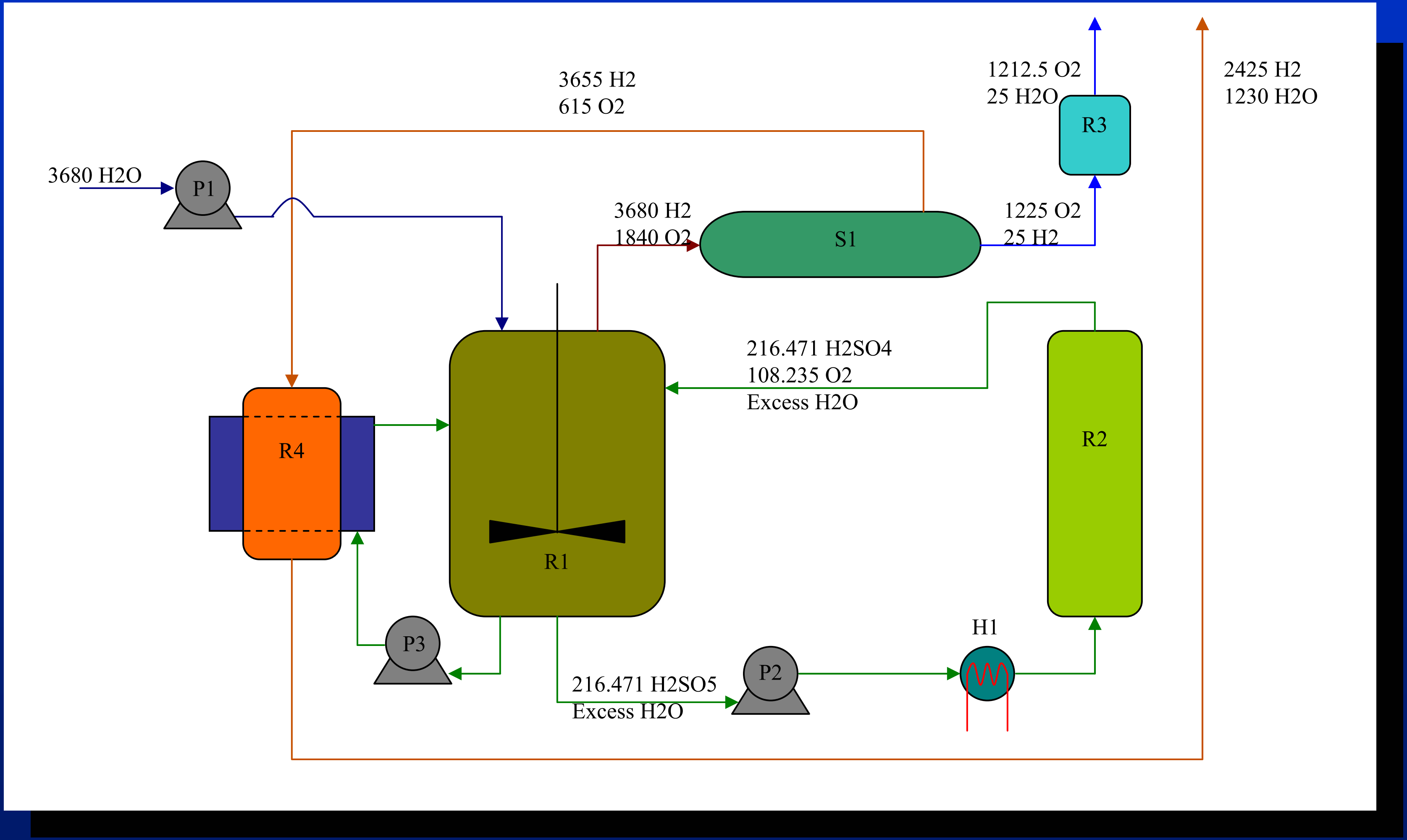
Not so Bright PFD



Chemistry Conquered: Bright Ideas

- Realize catalyst regeneration and O_2 production can occur simultaneously
  - Allows for continuous process
- Possible because
  - Catalyst not affected by pH
  - O_2 production is the Rate Limiting Step

PFD a Chemical Engineer can be Proud Of



Individual Reactions

- Oxygen Production/Catalyst Regeneration

$2C_{30}H_{26}Mn_2N_6O_4 + 16H_{2-}O \rightarrow 4C_{15}H_{11}N_3 + 2MnO_4{-}^{-} + 2Mn^{3+} + 8O_2 + 40H^+ + 44e^-$
$2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$
$7H_2SO_4 + 7H_2O \rightarrow 7H_2SO_5 + 14H^+ + 14e^-$
$34H^+ + 34e^- \rightarrow 17H_2$
$2Mn^{2+} + 2Mn^{3+} + 4C_{15}H_{11}N_3 + 6H_2SO_5 + 2H_2O + 4H^+ + 14e^- \rightarrow 2C_{30}H_{26}Mn_2N_6O_4 + 6H_2SO_4$

$17H_2O + H_2SO_4 \rightarrow 17H_2 + 8O_2 + H_2SO_5$

- Sulfuric Acid Regeneration/O_2 Recovery

$H_{2-}SO_5 + H_2O \rightarrow H_2SO_4 + H_2O_2$ (in the presence of MnO_2 catalyst)
$H_2O_2 \rightarrow H_2O + ½O_2$ (in the presence of MnO_2 catalyst)

$H_2SO_5 \rightarrow H_2SO_4 + ½O_2$

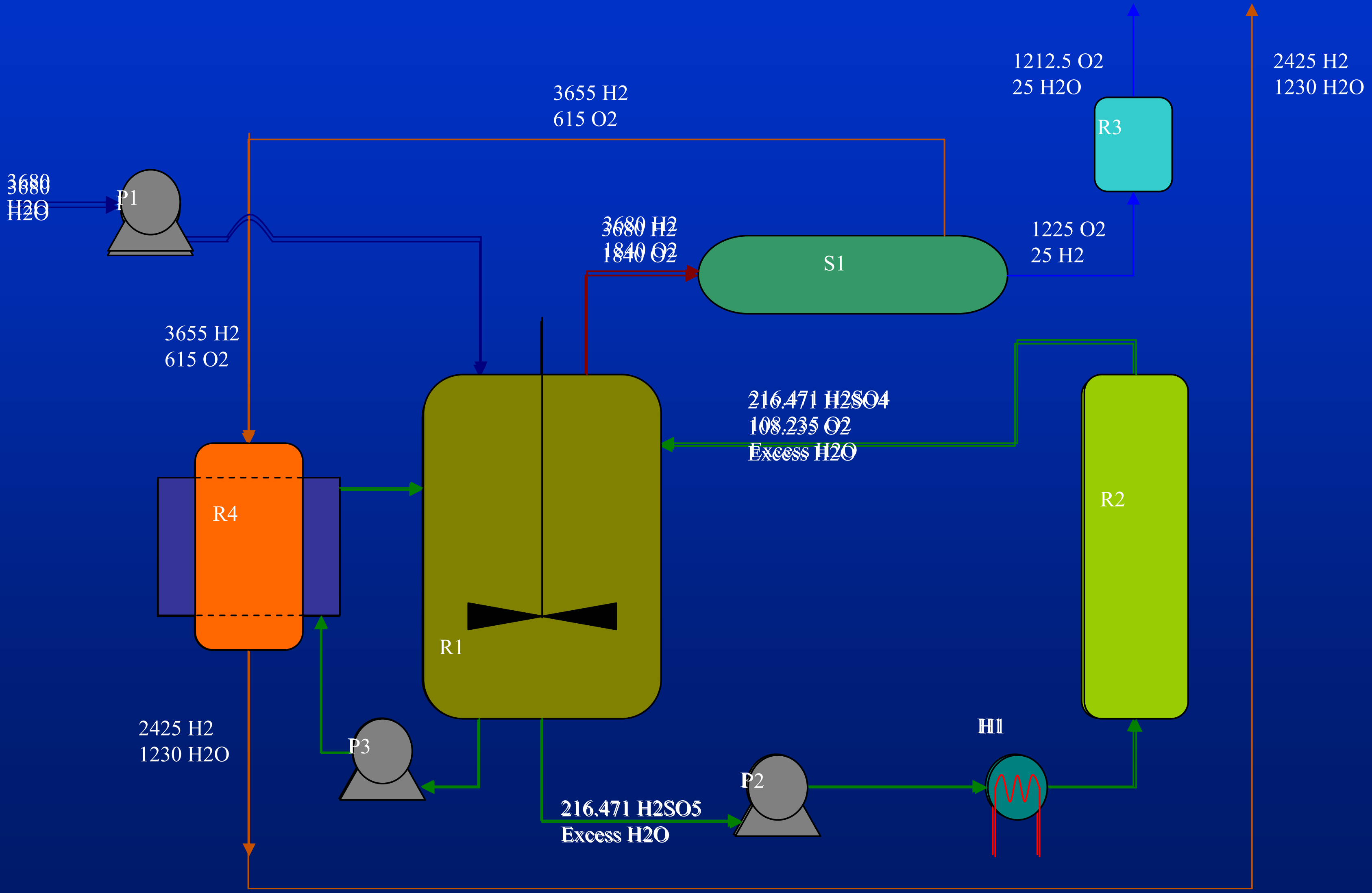
Theoretical Thermodynamics

- Reaction requires 285.8 kJ/mole H_2O
- Need 2400 moles H_2O per day
  - 685.920 MJ per day
  - 7.94 kW per day
  - Actual numbers are higher due to pumping, heat loss, etc…

Continuous System

- Advantages:
  - Simple operations
  - Smaller space occupied
  - Less catalyst required
  - Low equipment cost
  - Heat integration
  - Low operating cost
  - Keep the O_2 concentration constant

Continuous Design PFD



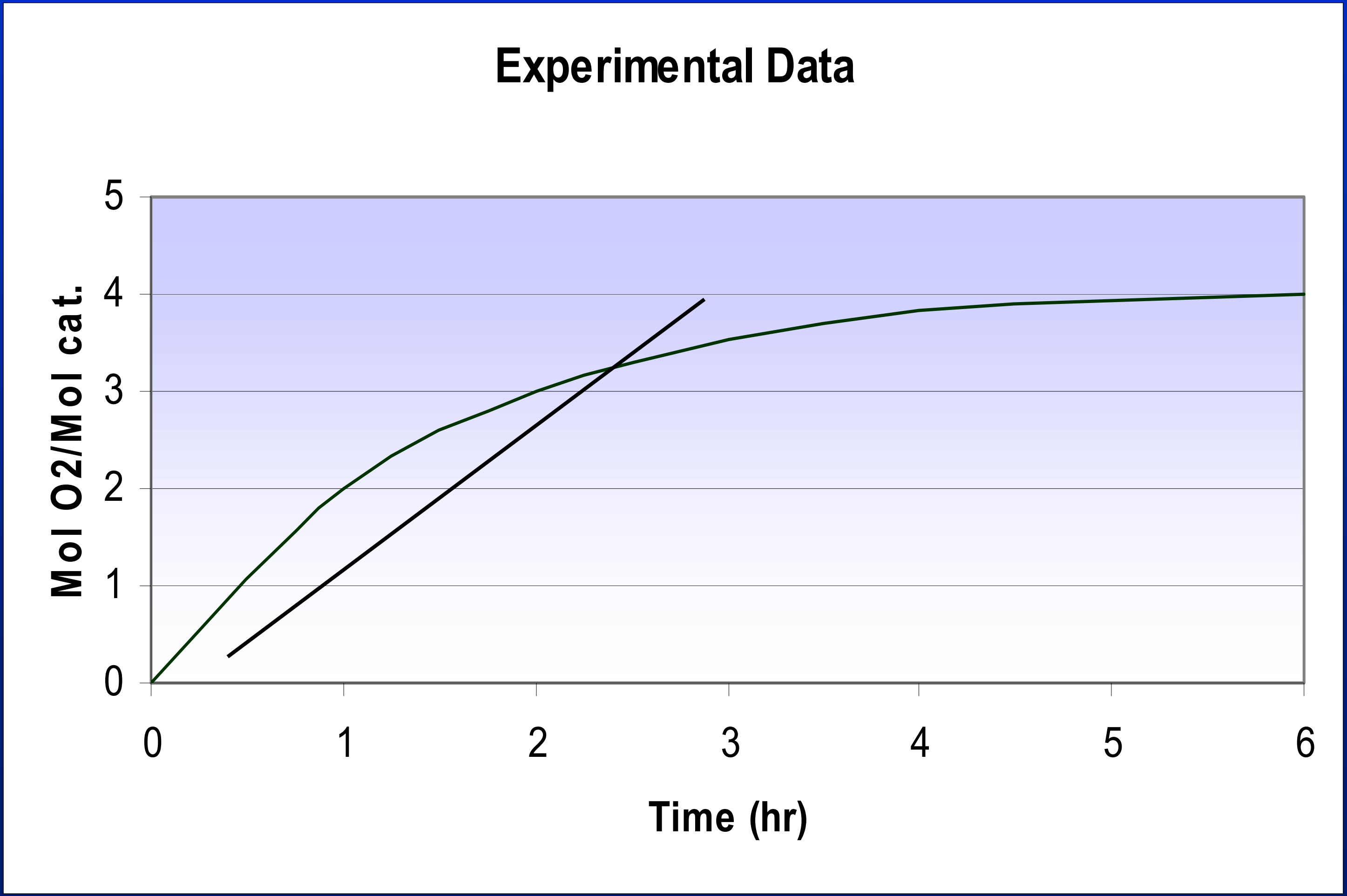
Continuous System (cont.)

- Require two reactors
- Total reactor volume 30 L
- Reactor costs $15,500 (Including heat exchanger)

Continuous System (cont.)

- CSTR:
  - Produce O_2
  - Regenerate catalyst
  - Condition:
    - Pressure: 9 atm
    - Temperature: 25^{o}C

Continuous System (cont.)



Continuous System (cont.)

- CSTR:
  - Volume: 20L
  - Energy required: 8.4kW
  - Catalyst used: 10.1 moles
  - Feed water flow rate: 2.8L/hr
  - Sulfuric acid 0.57M, flow rate: 111L/hr

Continuous System (cont.)

- PFTR
  - Regenerate sulfuric acid
  - Enthalpy change: -0.27kW
  - Catalyst: MnO_2
  - Condition:
    - Pressure: 9 atm
    - Temperature: between 50 and 100^{o}C

Continuous System (cont.)

- PFTR:
  - Volume: 10L
  - ID = 15cm
  - Length 56cm
  - Feed flow rate: 111L/hr
  - Catalyst lined reactor tubes

Hydrogen Oxygen Separation

Definition of the problem

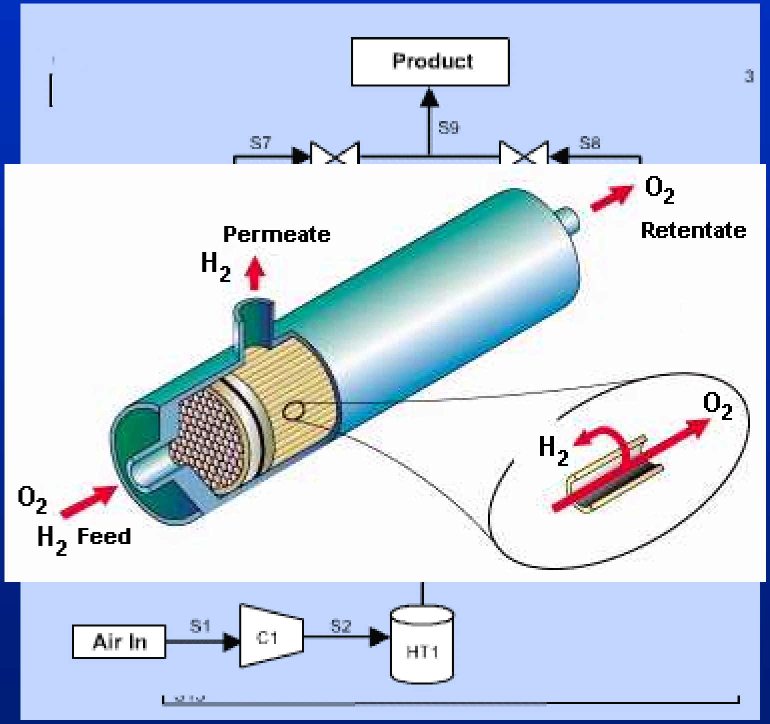
Design a particular process that can meet the requirements.

Feed flowrate = 1200 mol O_2/day

Purity = 100%

Less is more

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



Membrane

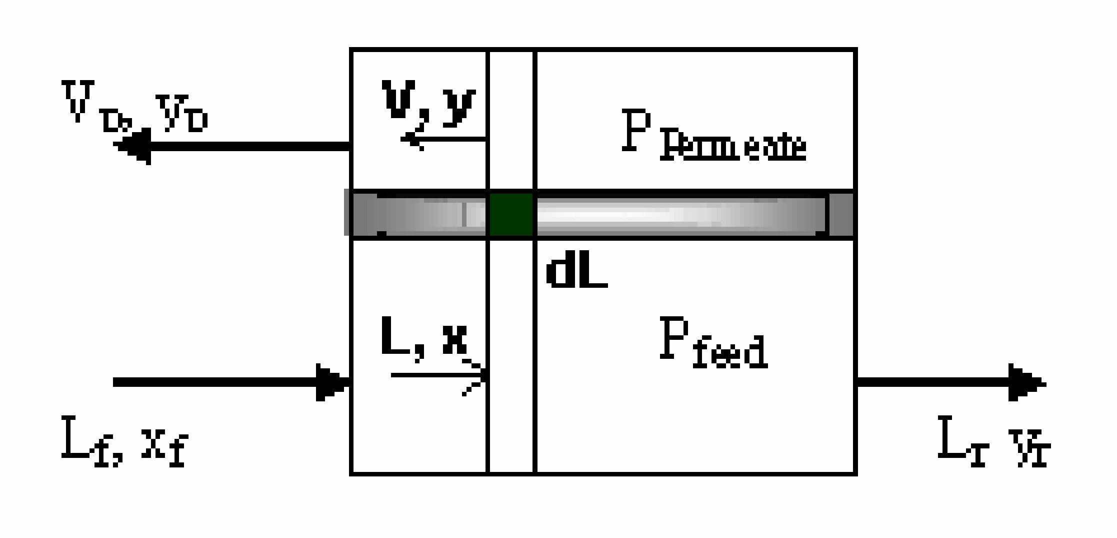
Goal: Maximum recovery of Oxygen

Topological Optimization

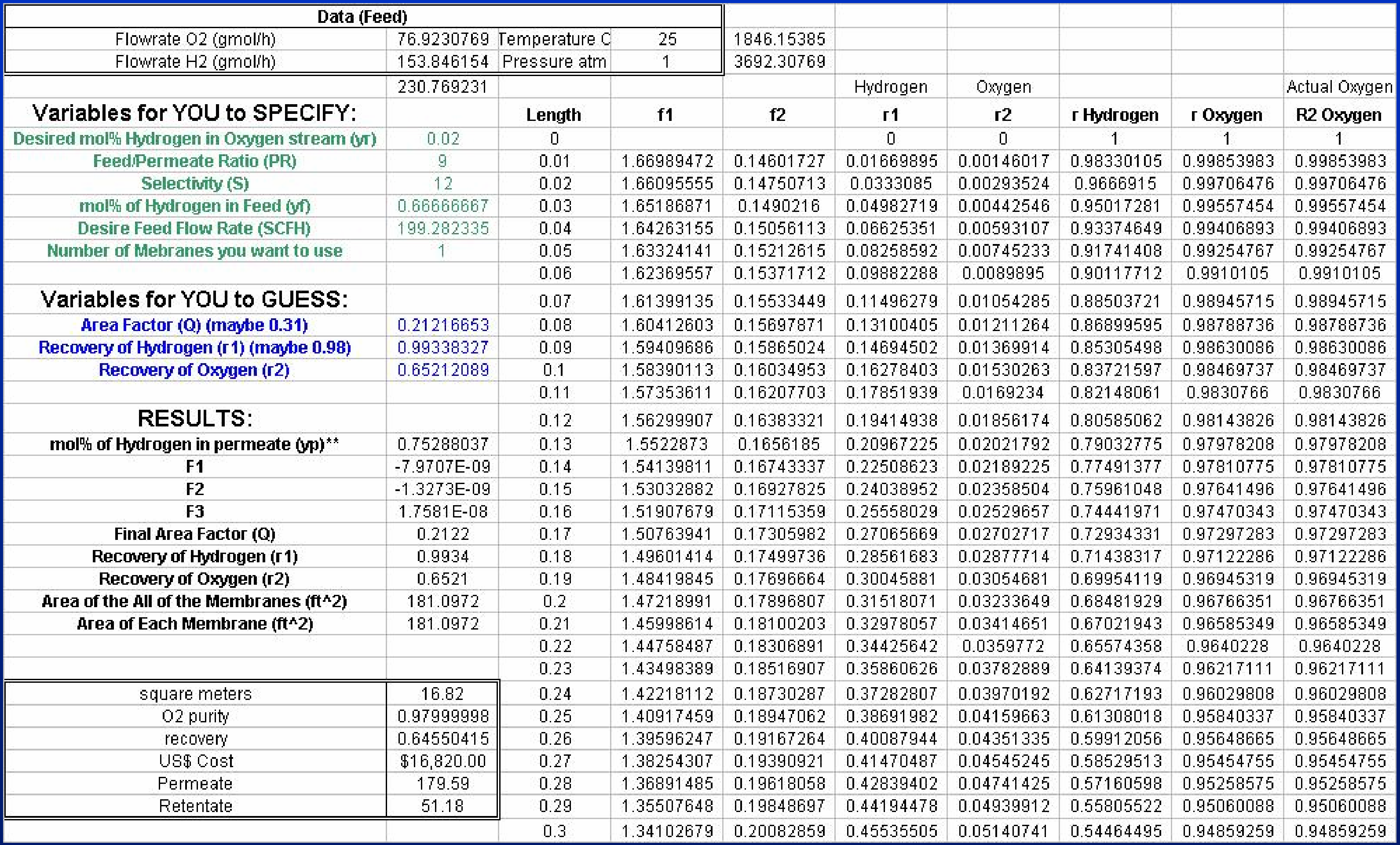
Several different flowsheets were considered

Optimization includes: Feed/permeate pressure ratio, Number of membrane units and recovery of hydrogen.

Excel Based Program



Spreadsheet



Data (Feed)									
Flowrate O2 (gmol/h)	76.9230769	Temperature C	25	1846.15385					
Flowrate H2 (gmol/h)	153.846154	Pressure atm	1	3692.30769					
	230.769231				Hydrogen	Oxygen			Actual Oxygen
Variables for YOU to SPECIFY:		**Length**	**f1**	**f2**	**r1**	**r2**	**r Hydrogen**	**r Oxygen**	**R2 Oxygen**
Desired mol% Hydrogen in Oxygen stream (yr)	0.02	0			0	0	1	1	1
Feed/Permeate Ratio (PR)	9	0.01	1.66989472	0.14601727	0.01669895	0.00146017	0.98330105	0.99853983	0.99853983
Selectivity (S)	12	0.02	1.66095555	0.14750713	0.0333085	0.00293524	0.9666915	0.99706476	0.99706476
mol% of Hydrogen in Feed (yf)	0.66666667	0.03	1.65186871	0.1490216	0.04982719	0.00442546	0.95017281	0.99557454	0.99557454
Desire Feed Flow Rate (SCFH)	199.282335	0.04	1.64263155	0.15056113	0.06625351	0.00593107	0.93374649	0.99406893	0.99406893
Number of Mebranes you want to use	1	0.05	1.63324141	0.15212615	0.08258592	0.00745233	0.91741408	0.99254767	0.99254767
		0.06	1.62369557	0.15371712	0.09882288	0.0089895	0.90117712	0.9910105	0.9910105
Variables for YOU to GUESS:		0.07	1.61399135	0.15533449	0.11496279	0.01054285	0.88503721	0.98945715	0.98945715
Area Factor (Q) (maybe 0.31)	0.21216653	0.08	1.60412603	0.15697871	0.13100405	0.01211264	0.86899595	0.98788736	0.98788736
Recovery of Hydrogen (r1) (maybe 0.98)	0.99338327	0.09	1.59409686	0.15865024	0.14694502	0.01369914	0.85305498	0.98630086	0.98630086
Recovery of Oxygen (r2)	0.65212089	0.1	1.58390113	0.16034953	0.16278403	0.01530263	0.83721597	0.98469737	0.98469737
		0.11	1.57353611	0.16207703	0.17851939	0.0169234	0.82148061	0.9830766	0.9830766
RESULTS:		0.12	1.56299907	0.16383321	0.19414938	0.01856174	0.80585062	0.98143826	0.98143826
mol% of Hydrogen in permeate (yp)**	0.75288037	0.13	1.5522873	0.1656185	0.20967225	0.02021792	0.79032775	0.97978208	0.97978208
F1	-7.9707E-09	0.14	1.54139811	0.16743337	0.22508623	0.02189225	0.77491377	0.97810775	0.97810775
F2	-1.3273E-09	0.15	1.53032882	0.16927825	0.24038952	0.02358504	0.75961048	0.97641496	0.97641496
F3	1.7581E-08	0.16	1.51907679	0.17115359	0.25558029	0.02529657	0.74441971	0.97470343	0.97470343
Final Area Factor (Q)	0.2122	0.17	1.50763941	0.17305982	0.27065669	0.02702717	0.72934331	0.97297283	0.97297283
Recovery of Hydrogen (r1)	0.9934	0.18	1.49601414	0.17499736	0.28561683	0.02877714	0.71438317	0.97122286	0.97122286
Recovery of Oxygen (r2)	0.6521	0.19	1.48419845	0.17696664	0.30045881	0.03054681	0.69954119	0.96945319	0.96945319
Area of the All of the Membranes (ft^2)	181.0972	0.2	1.47218991	0.17896807	0.31518071	0.03233649	0.68481929	0.96766351	0.96766351
Area of Each Membrane (ft^2)	181.0972	0.21	1.45998614	0.18100203	0.32978057	0.03414651	0.67021943	0.96585349	0.96585349
		0.22	1.44758487	0.18306891	0.34425642	0.0359772	0.65574358	0.9640228	0.9640228
		0.23	1.43498389	0.18516907	0.35860626	0.03782889	0.64139374	0.96217111	0.96217111
square meters	16.82	0.24	1.42218112	0.18730287	0.37282807	0.03970192	0.62717193	0.96029808	0.96029808
O2 purity	0.97999998	0.25	1.40917459	0.18947062	0.38691982	0.04159663	0.61308018	0.95840337	0.95840337
recovery	0.64550415	0.26	1.39596247	0.19167264	0.40087944	0.04351335	0.59912056	0.95648665	0.95648665
US$ Cost	$16,820.00	0.27	1.38254307	0.19390921	0.41470487	0.04545245	0.58529513	0.95454755	0.95454755
Permeate	179.59	0.28	1.36891485	0.19618058	0.42839402	0.04741425	0.57160598	0.95258575	0.95258575
Retentate	51.18	0.29	1.35507648	0.19848697	0.44194478	0.04939912	0.55805522	0.95060088	0.95060088
		0.3	1.34102679	0.20082859	0.45535505	0.05140741	0.54464495	0.94859259	0.94859259

Optimization Equations

Pressure Ratio = PR = $\frac{P_{Feed}}{P_{Permeate}}$

$$y_p = \frac{R_{1G}}{\left[R_{1G} + \left(1 - y_f\right)/\, y_p \cdot R_{2G}\right]}$$

Recovery of Hydrogen = r_1 = $\frac{Q \cdot \left(y_r \cdot PR - y_p\right)}{y_f}$

Recovery of Oxygen = r_2 = $\frac{Q \cdot \left(PR \cdot \left(1 - y_r\right) \cdot \left(1 - y_p\right)\right)}{S \cdot \left(1 - y_f\right)}$

$$y_r = \frac{\left(1 - r_1\right)}{\left[\left(1 - r_1\right) + \left(1 - y_f\right)/\, y_p \cdot \left(1 - r_2\right)\right]}$$

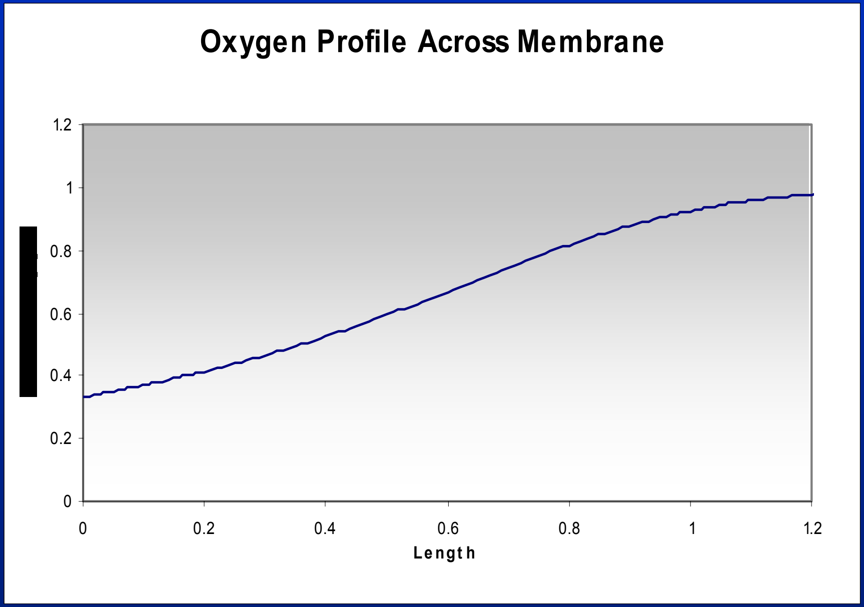
$$y_p = \frac{R_{1G} - r_1}{\left[\left(R_{1G} - r_1\right) + \left(\left(1 - y_f\right)/\, y_p \cdot R_{2G} - r_2\right)\right]}$$

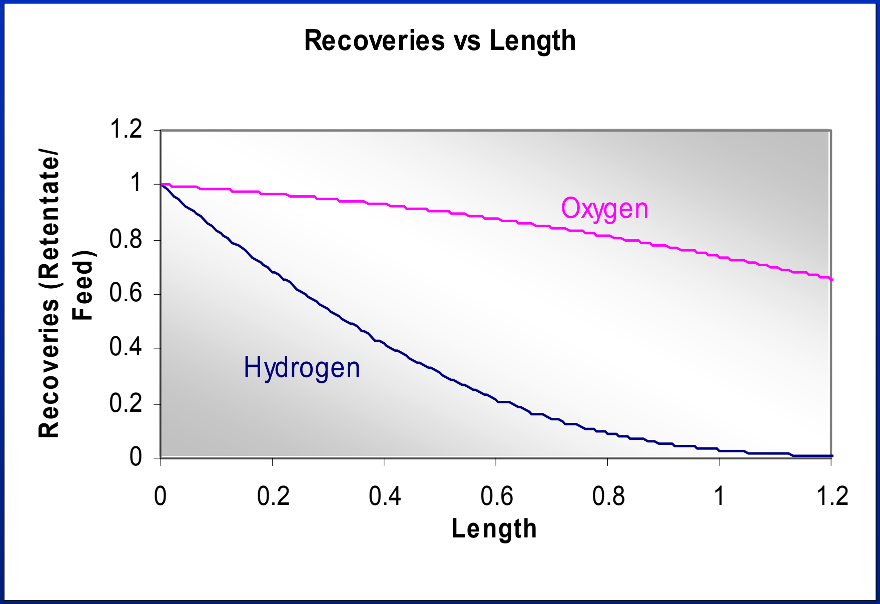
Engineering Ideas

Optimized Flowsheets

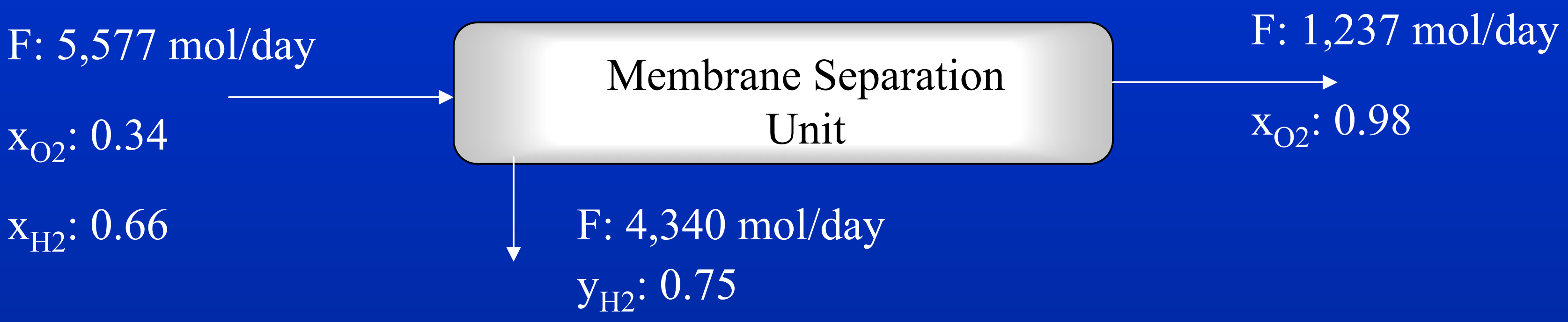
	Without Reactor	**Featuring a Reactor**
Oxygen Concentration	98%	100%
Recovery of Oxygen	62%	64%
Membrane Units	2	1

Results


Oxygen Profile Across Membrane
[redacted]
1.2
1
0.8
0.6
0.4
0.2
0
0
0.2
0.4
0.6
0.8
1
1.2
Length


Recoveries vs Length
Recoveries (Retentate/ Feed)
1.2
1
0.8
0.6
0.4
0.2
0
Oxygen
Hydrogen
0
0.2
0.4
0.6
0.8
1
1.2
Length

Optimized Membrane



F: 5,577 mol/day

x_{O2}: 0.34

x_{H2}: 0.66

Membrane Separation Unit

F: 1,237 mol/day

x_{O2}: 0.98

F: 4,340 mol/day

y_{H2}: 0.75

- Recovery of Oxygen: 65 %
- Pressure Ratio: 9
- PRISM® hollow fiber membrane
- Membrane Area: 17 m^2
- Estimated cost: $17,000

Reactor 3

1,237 mol/day

y_{O2}: 0.98

y_{H2}: 0.02

PFTR

1,200 mol O_2/day

25 mol H_2O/day

$$2H_2 + O_2 \rightarrow 2H_2O$$

- Complete purification of Oxygen
- Catalyst: a fixed-bed 0.5% Platinum
- Volume: 0.5 L
- Estimated cost: $700

Reactor 4

4250 mol/day

y_{O2}: 0.15

y_{H2}: 0.85

PFTR

2,400 mol H_2/day

1300 mol H_2O/day

$$2H_2 + O_2 \rightarrow 2H_2O$$

- Complete purification of Hydrogen
- Catalyst: a fixed-bed 0.5% Platinum
- Volume: 2.7 L
- Estimated cost based on Pt cost: $3800

Cost Breakdown

Table 1: Price Breakdown 1200 mole per Day Ex.

Unit	**Quantity**	**Price / Unit**	**Total Cost**
Reactor 1	1	$10,100	$10,100
Reactor 2	1	$3,800	$3,800
Heat exchanger	1	$500	$500
Reactor 3	1	$700	$700
Reactor 4	1	$3,700	$3,700
H_2-O_2 Separator	1	$17,000	$17,000
Water Pump	1	$3,600	$3,600
Liquid Pumps	3	$160	$480
Catalyst	10.1 mol	$25,200 / mol	$254,500
Total Unit Cost	**	**	**$294,220**

Water in Mars

- Where can we find water in Mars?
  - North pole: 75% of top 3 ft of soil is ice
  - Subsurface as liquid

- How much water is on Mars?
  - 0.03% of mars weight

What to do with H_2 produced?

- Vent H_2 gas to the Martian atmosphere
- Future Options:
  - Produce more water from CO_2

    $$4H_2 + CO_2 \leftrightarrow 2H_2O + CH_4$$

  - Methane can be liquefied and used for space vehicle propulsion

Power Supply

- Total system energy requirements 9.2 kW
- Mars may receive 44% less solar radiation than Earth
- Solar panel area needed: 1880 ft^2
- 139 panels cost $83, 400

Battery Power Supply

- Rechargeable batteries ensure constant power supply.
- Design for emergency 1 day power supply

Battery

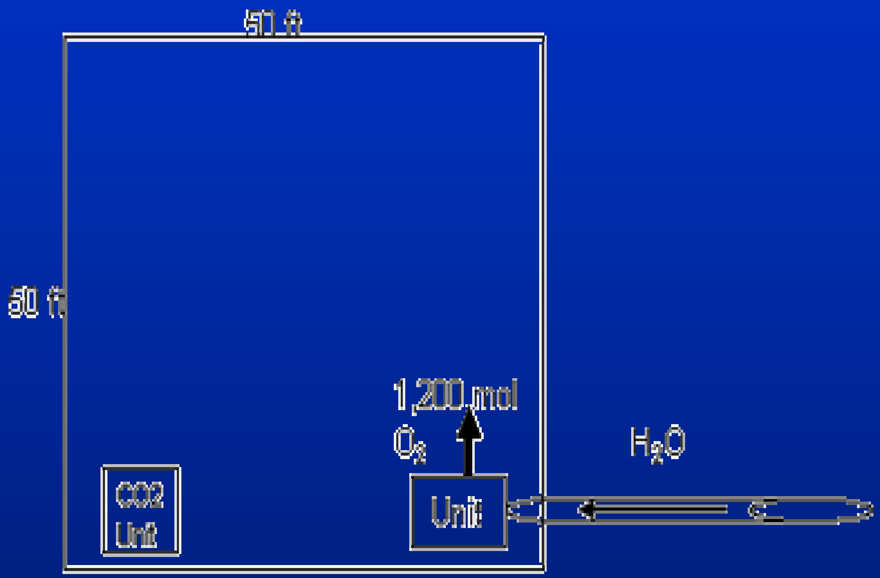
- Characteristic:
  - 12 V/ 446 AH at 100 hr rate
  - Weight: 272 grams
  - Operating conditions: - 40 C to 60 C
  - Cost is $813 per battery
  - Each battery delivers 53.5 Watts

Power Requirements

- The system requires 9.2 kW
- We will need 172 batteries to provide 9.2 kW
- Total cost of $140,000

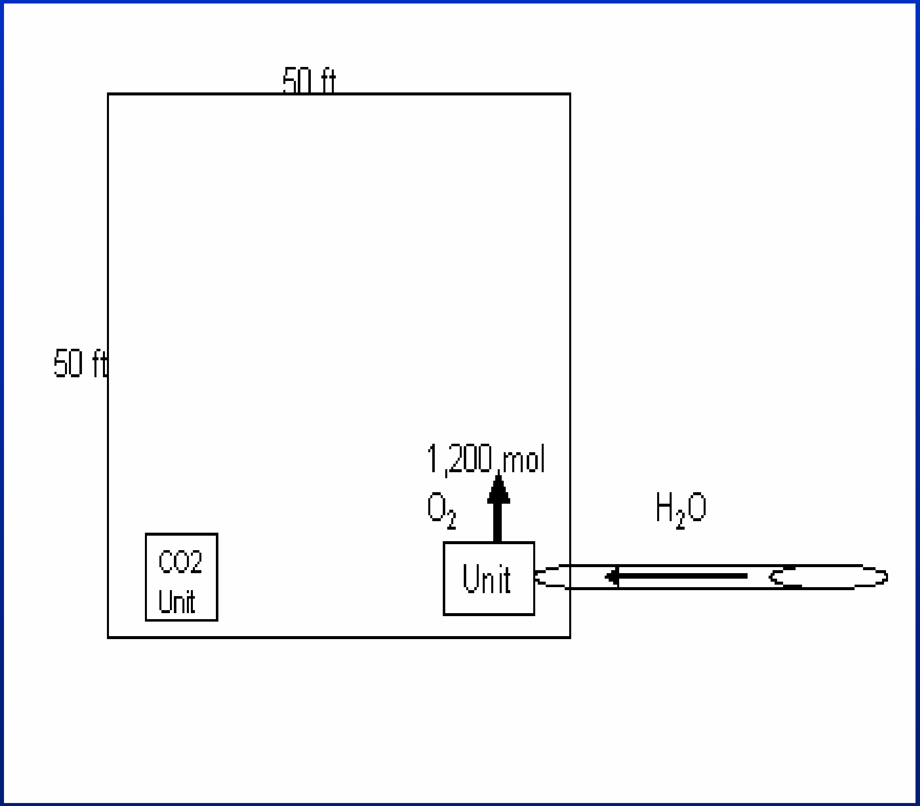
Establishing an Atmosphere in Tent on Mars

- Tent Size
- Tent Volume = 25,000 ft^3
- 79% N_2 & 21% O_2 needed
- CO_2 & H_2O vapor removed



Establishing an Atmosphere in Tent on Mars

- O_2 Produced by unit per day
- Amount of O_2 5 men need per day
- Air Needed in Tent = 25,000 ft^3 = 19,750 ft^3 N_2 & 5,250 ft^3 O_2
- Time Needed to Fill Tent with O_2 = 5.5 days

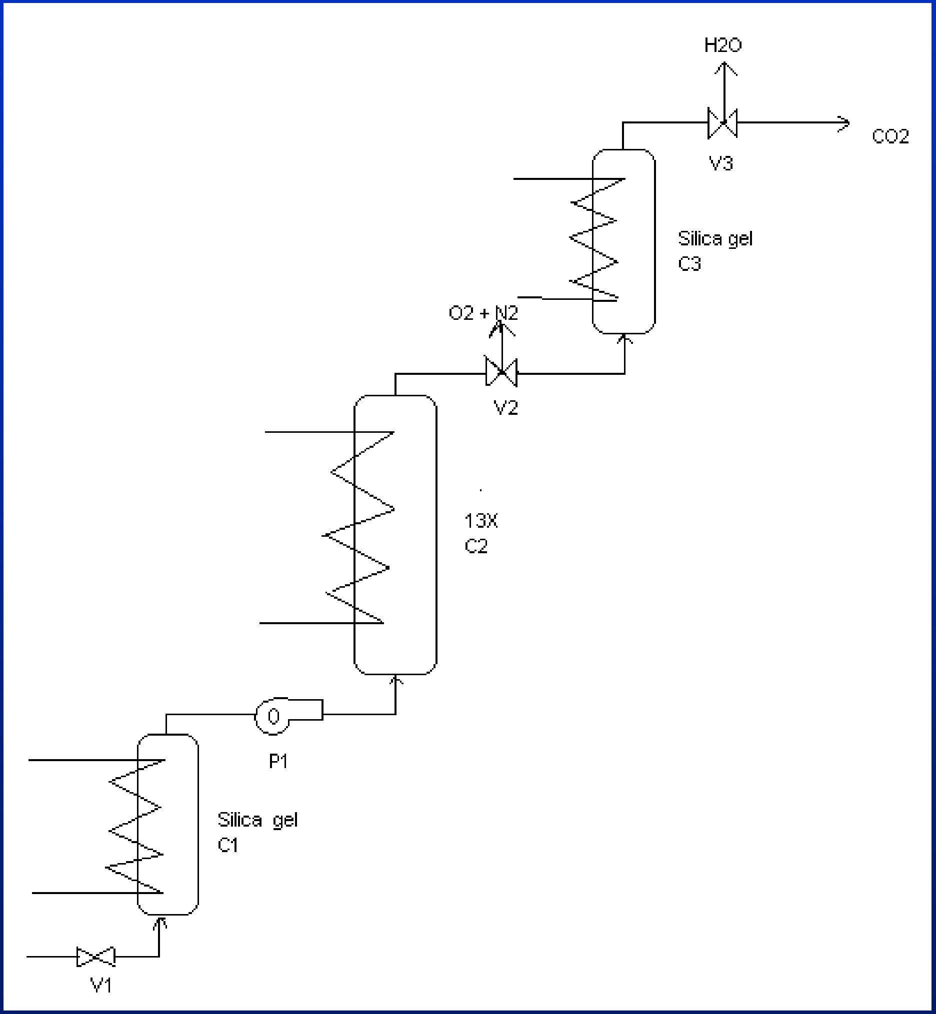


Establishing an Atmosphere in Tent on Mars

- N_2 needed
  - 2 x 800 L Liquid N_2
- CO_2 & H_2O removed
  - 1 person = 234 moles / day
  - 5 man team = 27,000 L of each / day
- Silica gel - Molecular Sieve System

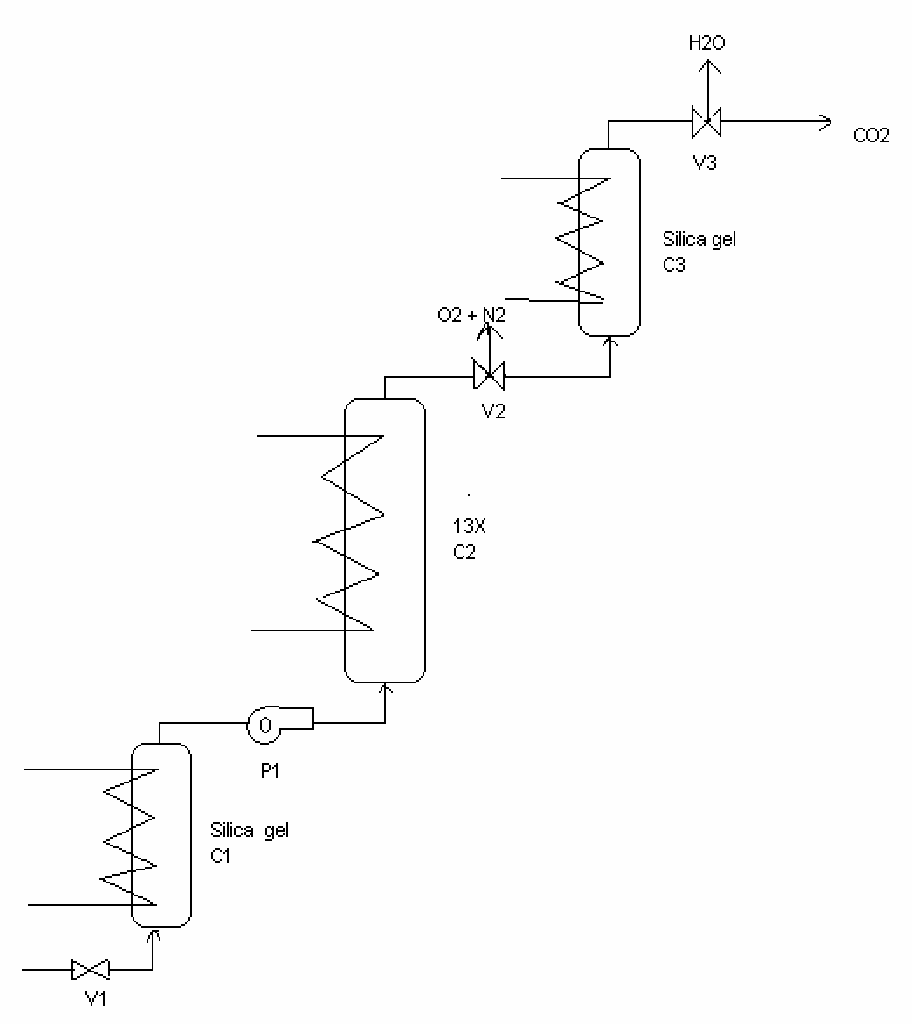
Establishing an Atmosphere in Tent on Mars

- Two Systems Used
  - 1 Adsorbing & 1 Desorbing
- Columns will regenerate 4 Times / day
- Regenerate by Heating Columns to 300 °C



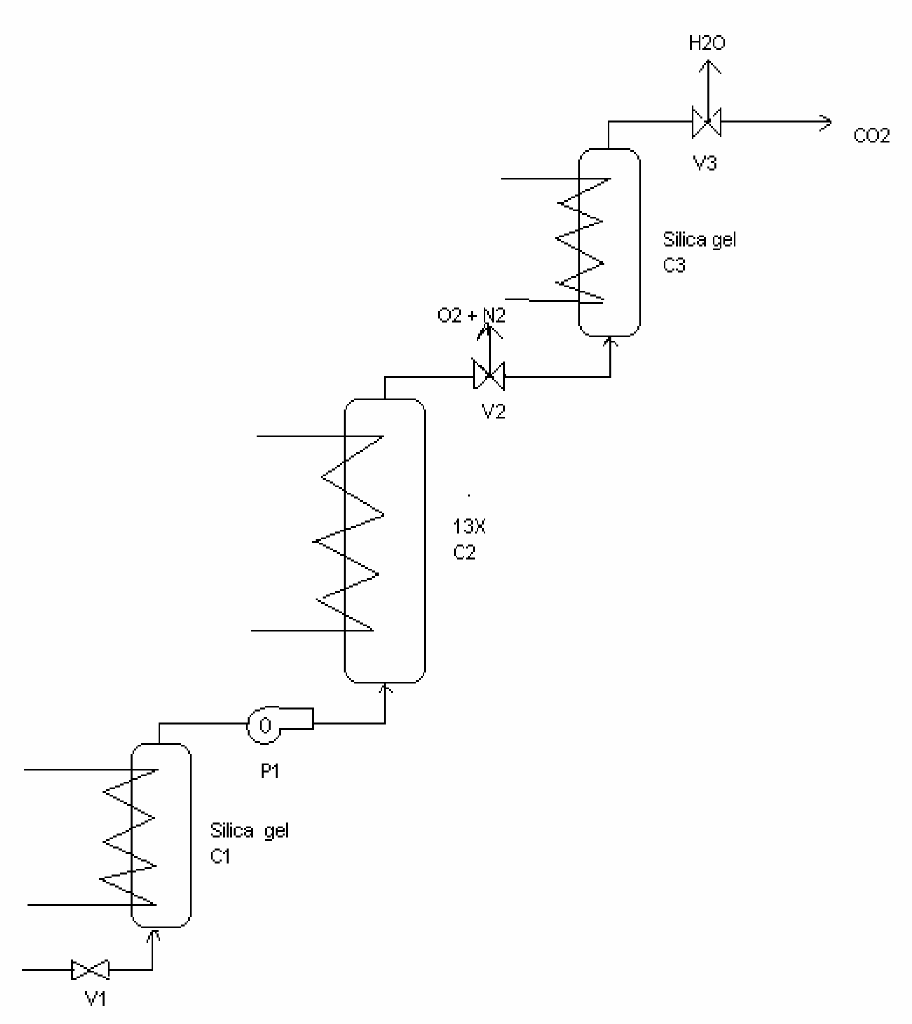
Establishing an Atmosphere in Tent on Mars

- H_2O Vapor Removed
  - Want 30% Humidity
  - Need 7,500 ft^3
  - If 27,000 ft^3 H_2O removed, Air should stay at 30% Humidity
  - Silica Gel Adsorbs 6,750 L H_2O / time
  - 0.481 L / Column
  - Need 4 L Silica Gel
  - Column = 1 ft high & 1.8 in diameter
  - Silica Gel cost =$643.



Establishing an Atmosphere in Tent on Mars

- CO_2 Removed
  - 27,000 ft^3 / day
  - Molecular Sieve 13X Adsorbs 6,750 L CO_2 / cycle
  - 65.3 L / column
  - 262 L Molecular Sieve 13X
  - Column = 4 ft high & 10.3 in diameter
  - 13X Cost = $70,100



Economics

- Identified Possible Applications for the Process
  - Steel-making Industry
  - Paper Manufacturing
  - Sewage Treatment
  - Medical Use
  - Life Support Applications

Economics

- Industrial Scale Applications
  - Typical Plant produces 2000 tons O_2 per day
  - For Our Process:

(56 mil. mol O_2 / day)(1 mol cat. / 182.4 mol O_2 day)

= 307,000 mol cat.

At catalyst cost of \$25,200 / mol cat.

Total catalyst cost would be \$7.7 billion!

Compared to less than \$200 million for a Cryogenic Plant

Economics

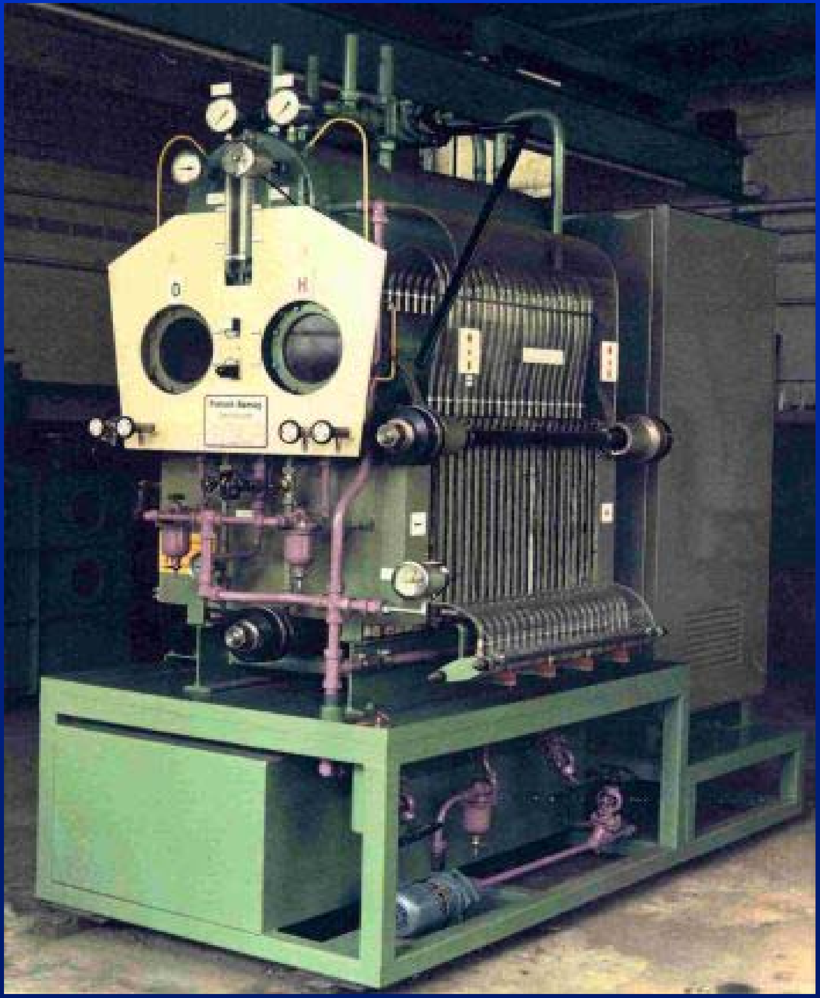
- Small Scale Applications
  - Laboratory
  - Home Medical Use
  - Space Station
  - Mars Exploration

On Earth

- For laboratory or home use, compressed oxygen costs less than $0.30 per 100 scf.
- Comparable Oxygen from Water unit = no less than $50,000
- Not worthwhile when maintenance and energy costs are included.

In Space

- To provide a 5 man crew with oxygen:
  - Electrolysis requires 12.7 kW
  - OFW only needs 9.2 kW



Comparison

- Thermodynamic Efficiency: $\dfrac{\Delta H_{RXN}\ H_2O}{\text{Energy Required}}$

- $\Delta H_{RXN}\ H_2O = 686$ MJ

- TE electrolysis = 686 MJ / 1080 MJ = 63.5 %

- TE OFW = 686 MJ / 795 MJ = 86 %

Comparison

- Electrolysis total cost $1,275,000
  - Electrolysis equipment cost approx. $720,000
  - Additional cost for power supply $555,000
  - Power supply is 44% total cost

- OFW total cost $689,000
  - OFW unit cost $295,000
  - Power supply costs $394,000
  - Power supply is 57% total cost

Comparison

- Advantages of OFW over electrolysis:
  - – For electrolysis, 38% more energy means 38% more solar panel area required
  - – Potentially much less than 1/2 of the cost of electrolysis

Uncertainties

- Experimentation to test catalyst useful life
- Continuous reaction efficiency
- Reactor scale-up

Conclusions

- Water can be used for O_2 production
- Eventually plants will be used
- Waste H_2 stream has many possibilities
- Infinite space exploration potential
- Nifty thinking on our part