Reduction of VOCs & Other GHG Emissions from Gas Streams using Membrane Technology

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VOC EMISSION

During storage, loading and transportation of crude oil, Volatile Organic Compounds (VOC) is emitted to the atmosphere. Evidently, the emission represents a loss of considerable monetary value. But the harmful consequences to the environment are supposed to be of greater importance.

Large VOC emission comes from offshore loading of shuttle tankers in the North Sea.

Floating production, storage and offloading units (FPSOs and FSOs) are also responsible for heavy VOC emission

- Typical carbon footprints for GAC based NMVOC scrubbers and Thermal Oxidizers operating at even low 200SCFM volumetric throughputs exceed 1,000 tons CO2 e and 300 tons CO2 e respectively due to large fossil fuel consumption.

- (Haley & Aldrich “Off-gas Treatment Carbon Footprint Calculator” Remediation Technology Symposium Oct. 2008)

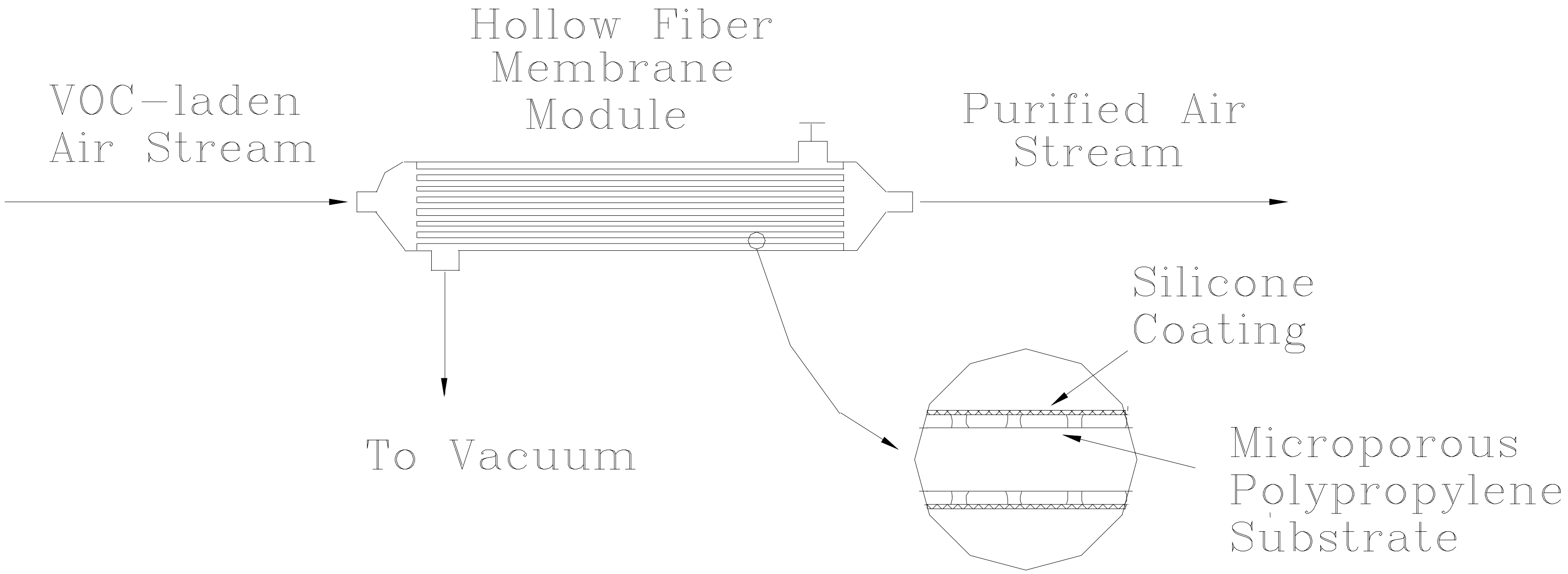
Types of Membrane Modules for Vapor Permeation

- Plate-and-frame module
  - contains a stack of round membrane envelopes around a central permeate tube

- Spiral-wound module
  - membrane is spirally wound, like a jelly roll, around the central collector tube

- Hollow fiber module
  - resembles a shell-and-tube heat exchanger

VOC Removal from N_2/Air at Atmospheric Pressure by Permeation through a Hollow Fiber Module



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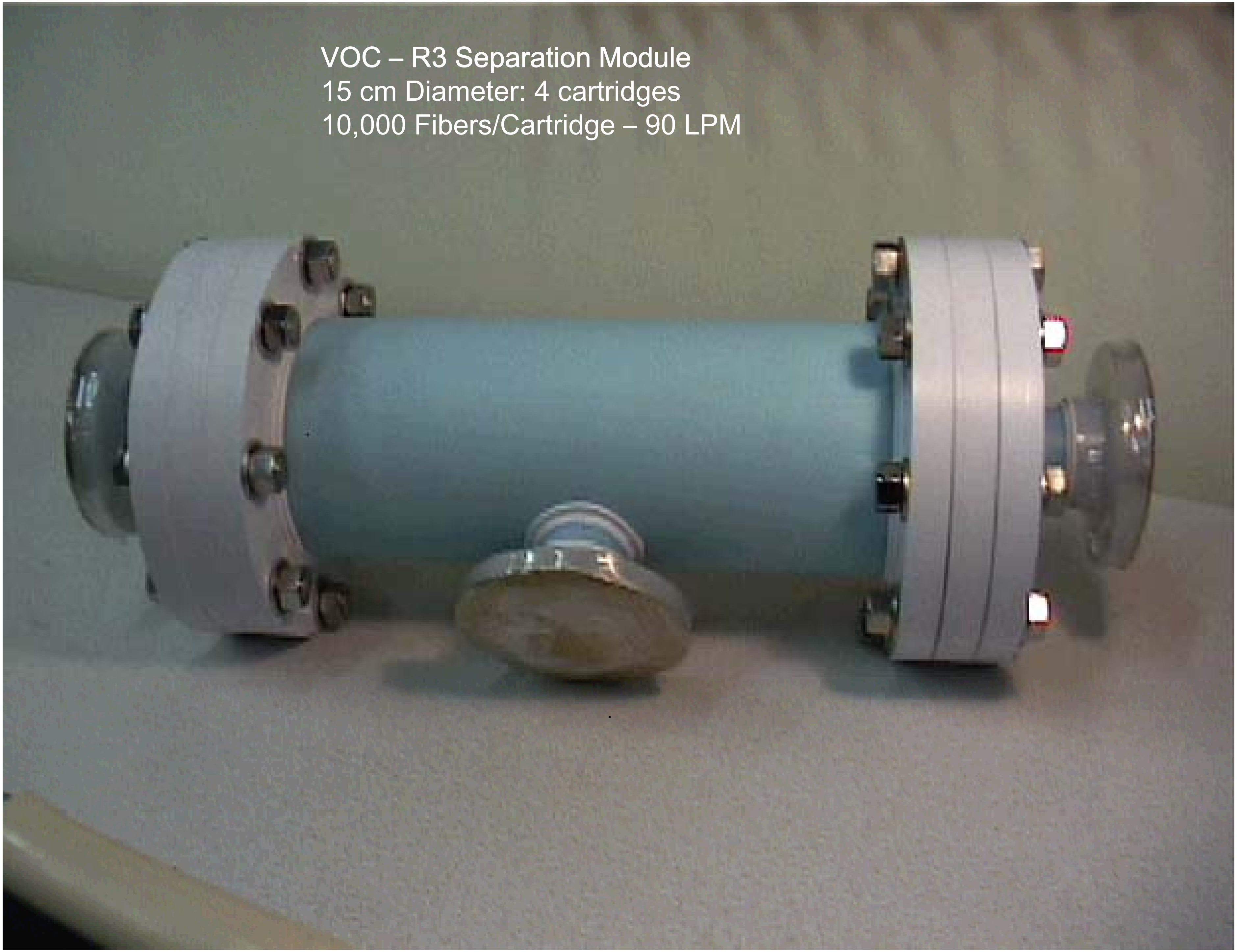
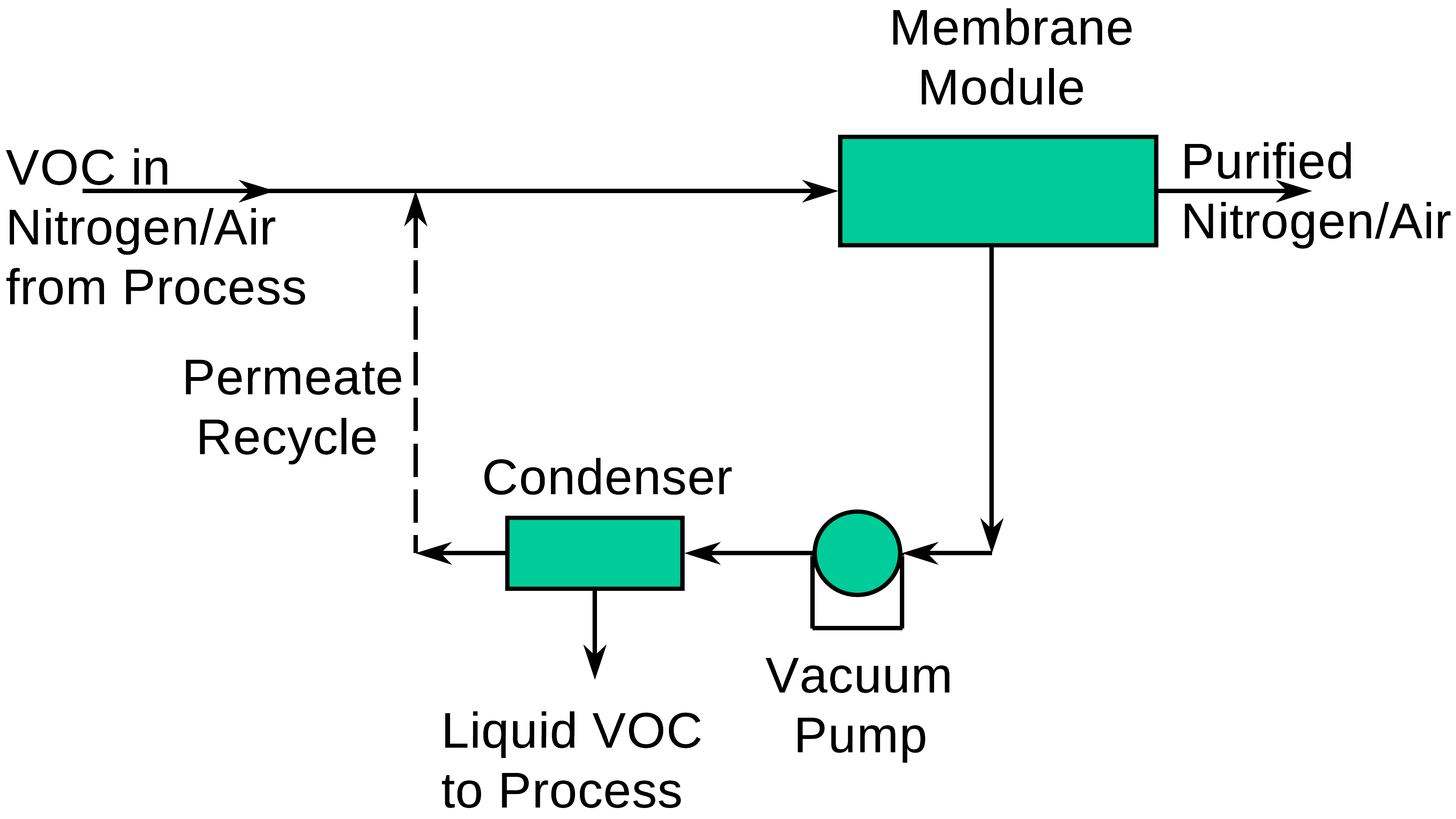
AMT/NJIT Hollow Fiber Membrane Processes

- Vapor Permeation
  - Two membranes:
    - ✓ Plasma polymerized silicone on porous PP fiber O.D. with feed gas through the fiber bore
    - Plasma polymerized silicone fibers containing VOC-selective absorbent in part of the pore inside the fiber



VOC – R3 Separation Module
15 cm Diameter: 4 cartridges
10,000 Fibers/Cartridge – 90 LPM


Membrane
Module
VOC in
Nitrogen/Air
from Process
Purified
Nitrogen/Air
Permeate
Recycle
Condenser
Vacuum
Pump
Liquid VOC
to Process

Advantages of Hollow Fiber-Based Membrane Systems

- Hollow fiber membranes are self supporting, commercial flat membranes must be supported in the modules

- Spirally wound modules are, per unit surface area, three times as expensive as hollow fiber membranes

- Hollow fiber membranes have two layers instead of three as in spirally wound modules

- Can achieve 10 times the surface area per module volume vis-à-vis spirally wound modules

- The process does not require a compressor, a vacuum pump alone is sufficient

Performs Work only on the Permeate Volume

- This technology does not require cooling the entire gas volume of the feed stream

- This technology does not require heating the whole gas stream as is Thermal Oxidation - Significant Reductions in Carbon Dioxide Emissions are possible by replacing what are essentially 24/7 Natural Gas burning incinerators

Versatility

- Removes in one continuous step any VOC or combination of VOC’s
- From waste gas/N2/air streams
- To the level of 90-98%
- Recovers VOC’s as condensed liquids

Simplified Operations

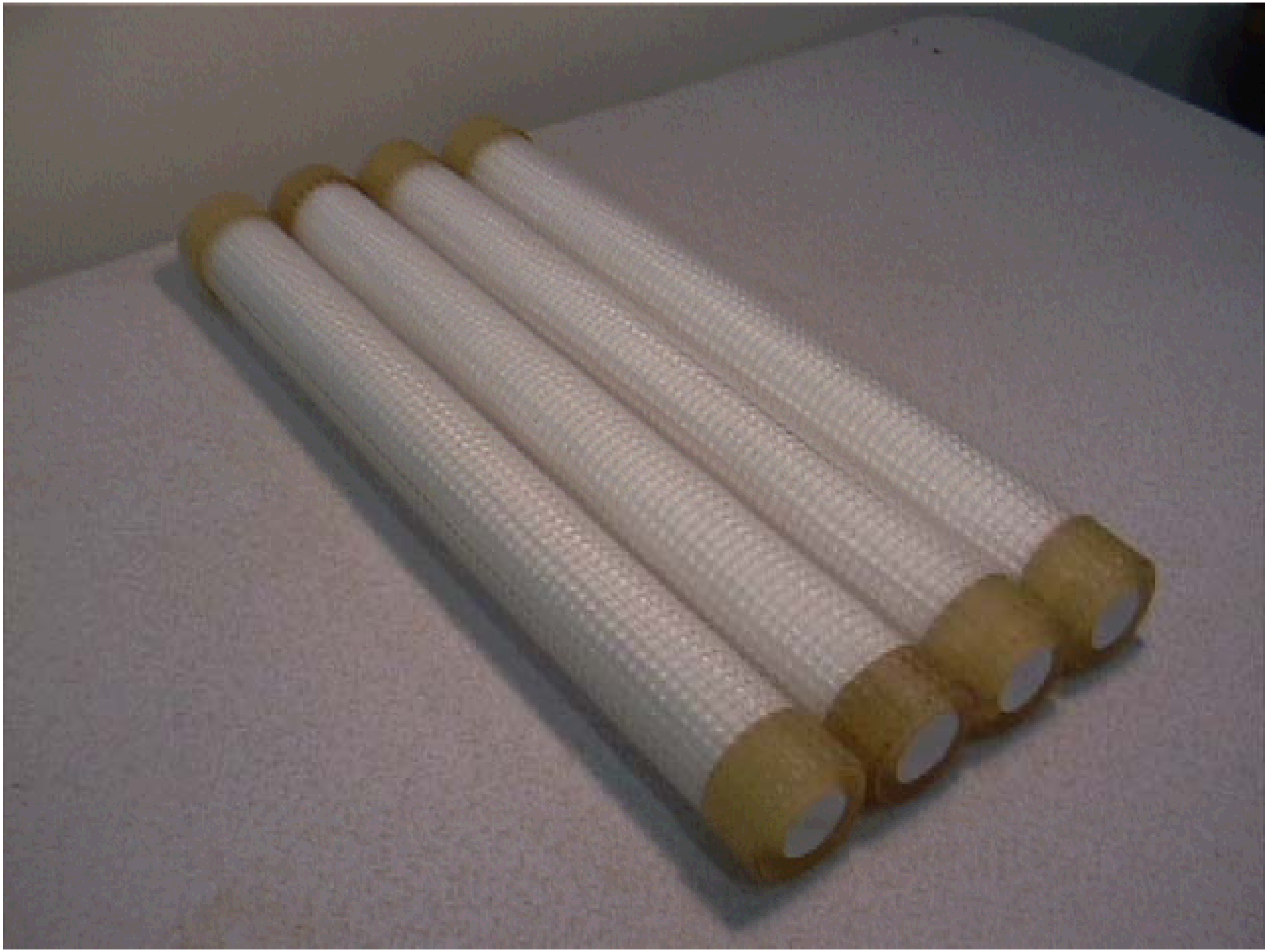
- This VOC Separation & Recovery Technology operates with electricity, blower, vacuum pump, condenser, and cooling water.

- Operational & maintenance expenses are minimal

- Recovered VOCs can be recycled or shipped for destruction off-site

Additional Benefits

- Handles VOC Levels from as small as 50-70 ppmv up to 10-20% concentration
- No Fire Hazards unlike Carbon regeneration from adsorption processes
- Note: Activated Carbons have difficulties with high conc, VOC’s as well as moisture at greater than 40-50% levels



Modeling Equations for HF Modules

$$\frac{d\left(Lx\right)}{dl} = \pi d_{lm}\left(\frac{Q_{im}\left(P_f x, P_p y\right)}{\delta_m}\right)\left(P_f x - P_p y\right) \tag{7}$$

$$\frac{Q_{im}}{\delta_m} = a\exp\left(bP_f x\right) \tag{8}$$

$$\left(\frac{\pi d_{lm} a P_f}{L}\right) l_f = \left[\ln x - \frac{\left(bP_f x\right)}{1.1!} + \frac{\left(bP_f x\right)^2}{2.2!} - \ldots..\right]_{x_W}^{x_f} \tag{9}$$

$$\frac{a}{\left(Q_{N_2} / \delta_m\right)} \ln\left\{1 - \frac{l_f}{l_f - L_f / [\pi d_{lm} P_f \left(Q_{N_2 m} / \delta_m\right)]}\right\} = \left[\ln x - \frac{\left(bP_f x\right)}{1.1!} + \frac{\left(bP_f x\right)^2}{2.2!} - \ldots\right]_{x_W}^{x_f} \tag{10}$$

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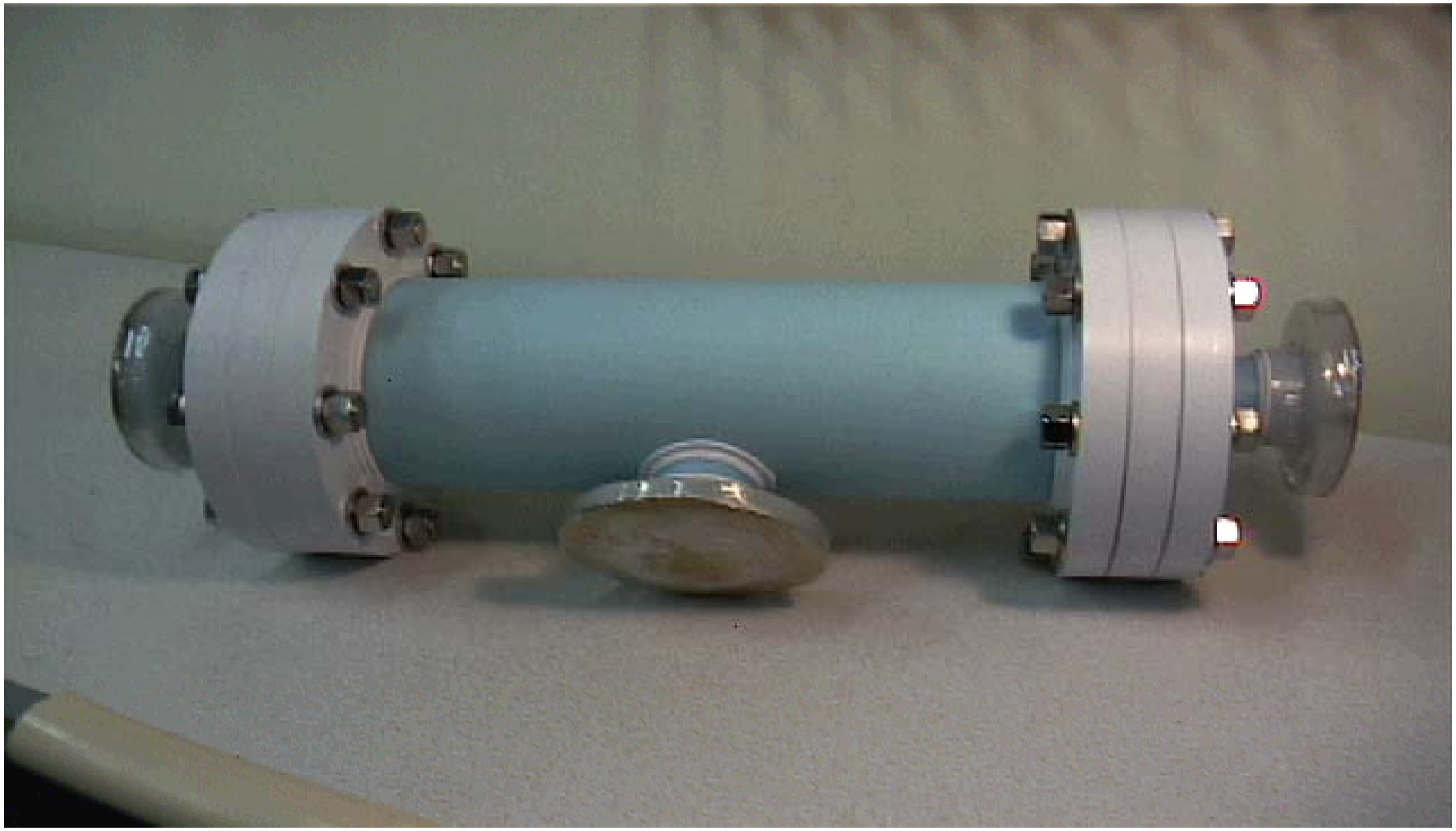
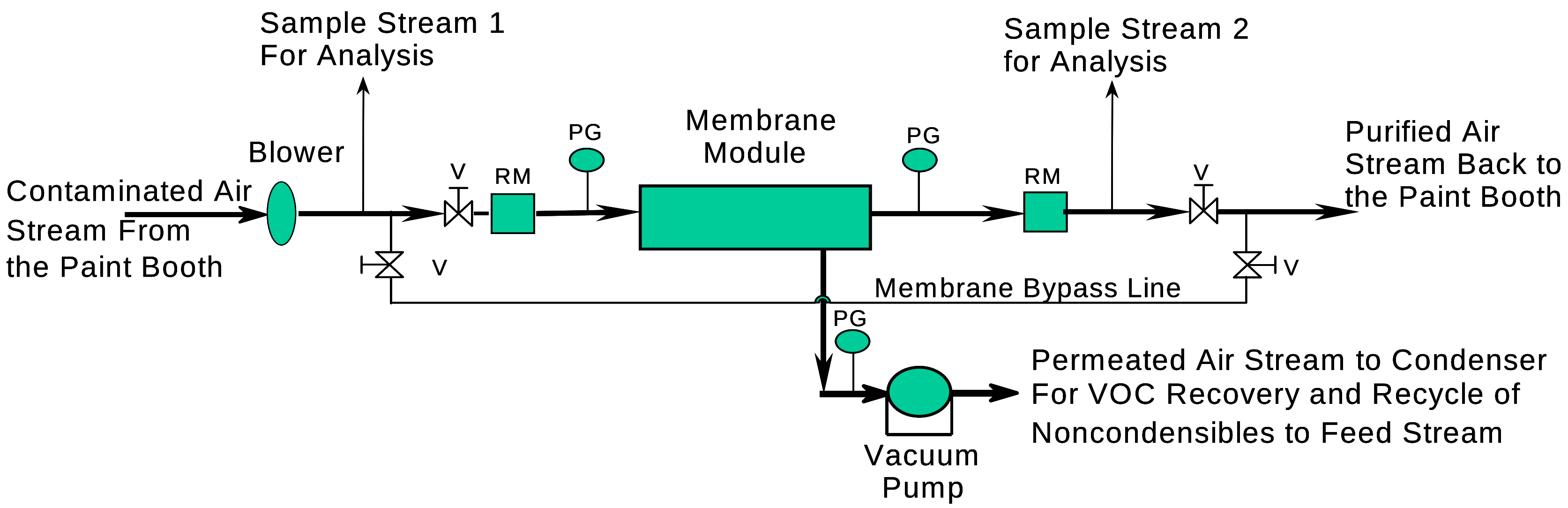
4 Cartridge Unit Tested at NASA Kennedy Space Center





PG: Pressure Gauge; RM: Rotameter; V: Valve

Figure 2. Experimental setup for VOC removal from a slipstream from the paint booth exhaust by hollow fiber vapor permeation membrane process.

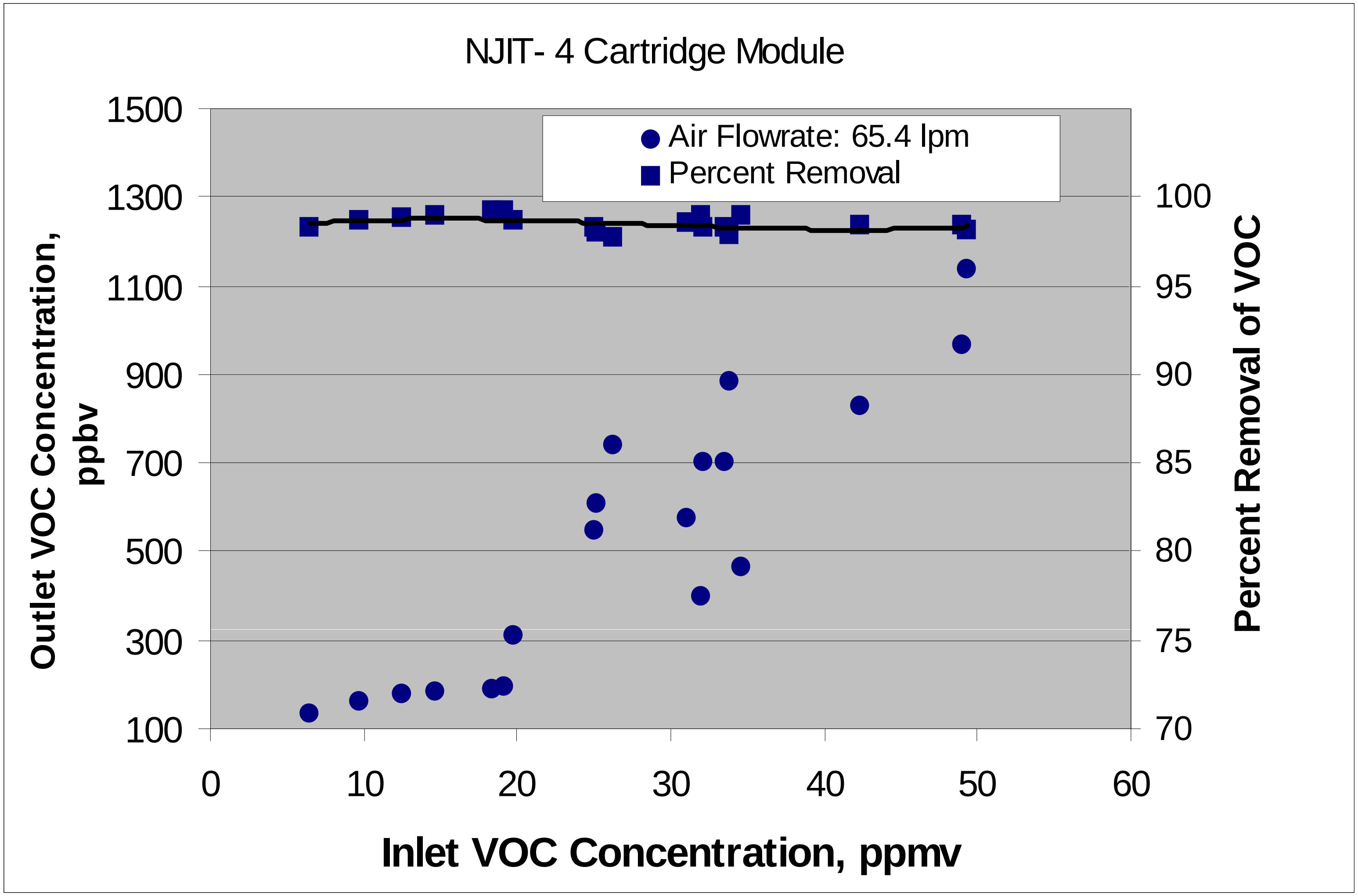


Figure 4. VOC removal performance of NJIT-4 cartridge membrane module from a paint booth exhaust stream at feed flow rate of 65.4 lpm (permeate pressure: 2.8 cm Hg)

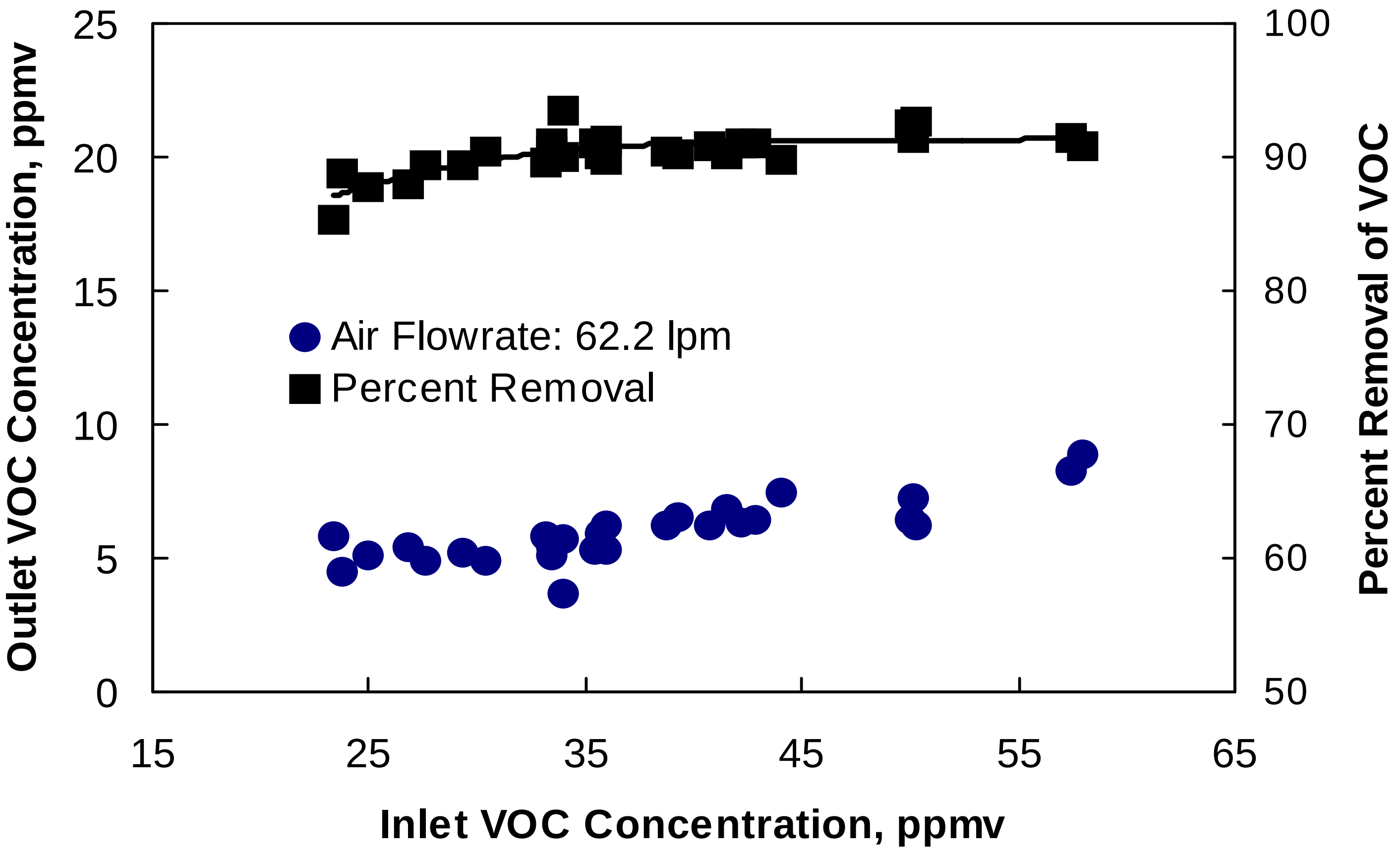


Figure 7. VOC removal performance data from 2 cartridge set of NJIT-4 cartridge membrane module from a paint booth exhaust stream (permeate pressure: 2.8 cm Hg)

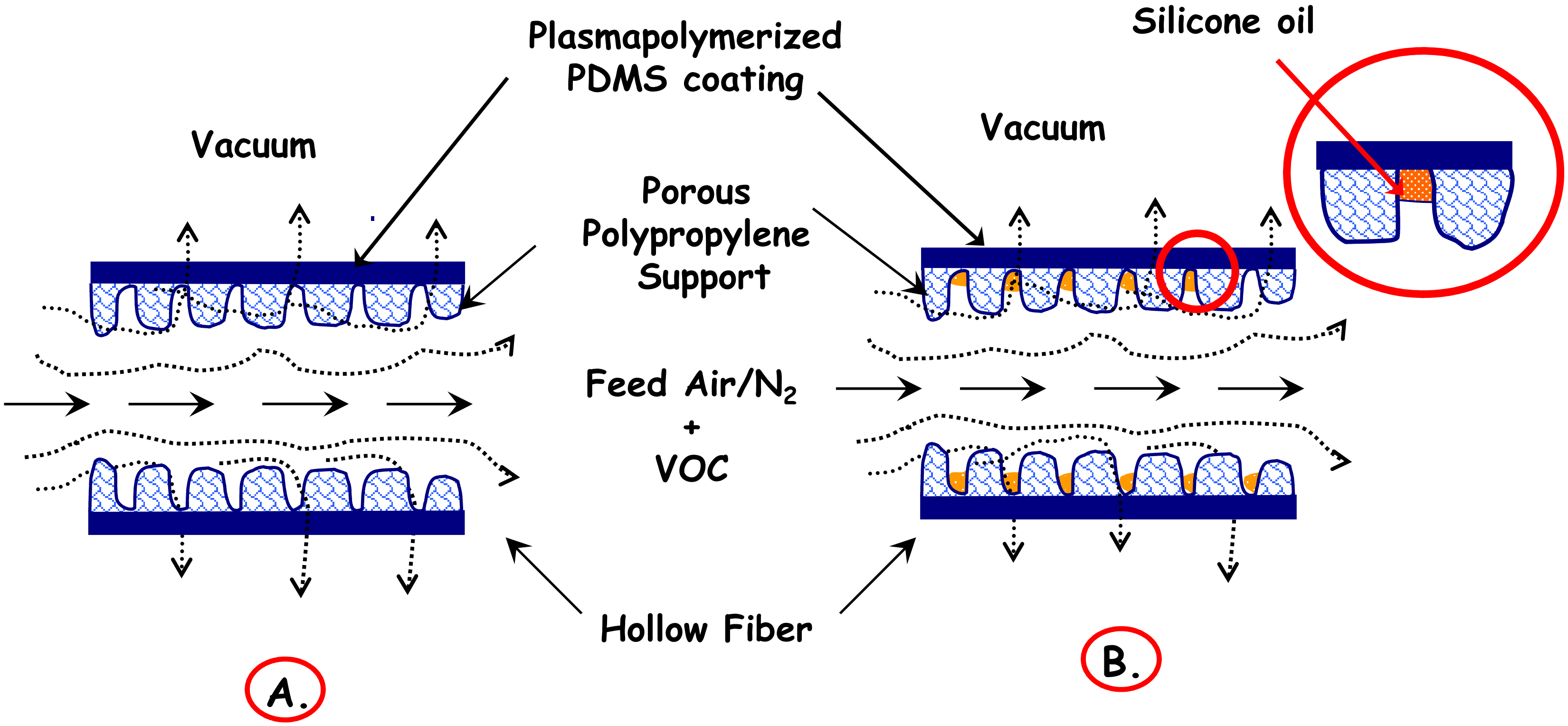


Figure 1. Vapor permeation configuration using hollow fibers having a rubbery VOC-selective coating:
A. Basic configuration with VOC-containing feed in fiber bore,
vacuum on shell side and silicone coating on the outside surface;
B. A thin layer of silicone oil in the pore next to the coating of configuration A.

Environmental Market: VOC/Air Treatment

Hollow Fiber Membrane Module Systems

NASA SKID VOC MEMBRANE UNITS

12 Cartridges per Housing

Each Can Treat (255 LPM)

Skid Scaled for 30CFM (850LPM)

Add Metered Vent Stack

System Feed Inlet: **A slipstream of contaminated air is drawn through a blower (Pacific Blower PB-200, relief valve PB20002, vacuum filter PB11002) to the inlet manifold feeding the inlet gas through five 10-inch diameter membrane modules**

Moderately high vacuum was maintained on the other side of the membranes by a vacuum pump (Travaini Liquid Ring Vacuum pump, Model TRMB40-110/RX).

SKID FRAMING

ADD ELECTRICAL PANELS

Completed VOC Removal & Recovery System
Hollow Fiber Membrane Based
(600,000 Hollow Fibers)


NASA
National Aeronautics and
Space Administration
Goddard Space Flight Center
Wallops Flight Facility
+ 72°F

Results and discussion based on three stages of field testing

- The test skid had five large membrane modules each containing 12 cartridges.

- During our first field testing, data were collected using either all 5 modules, or 4 modules or 1 module at any time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HEARING PROTECTION REQUIRED
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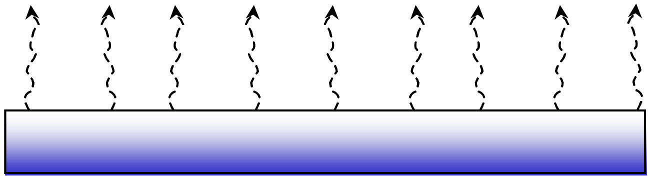
Thin ILM preparation



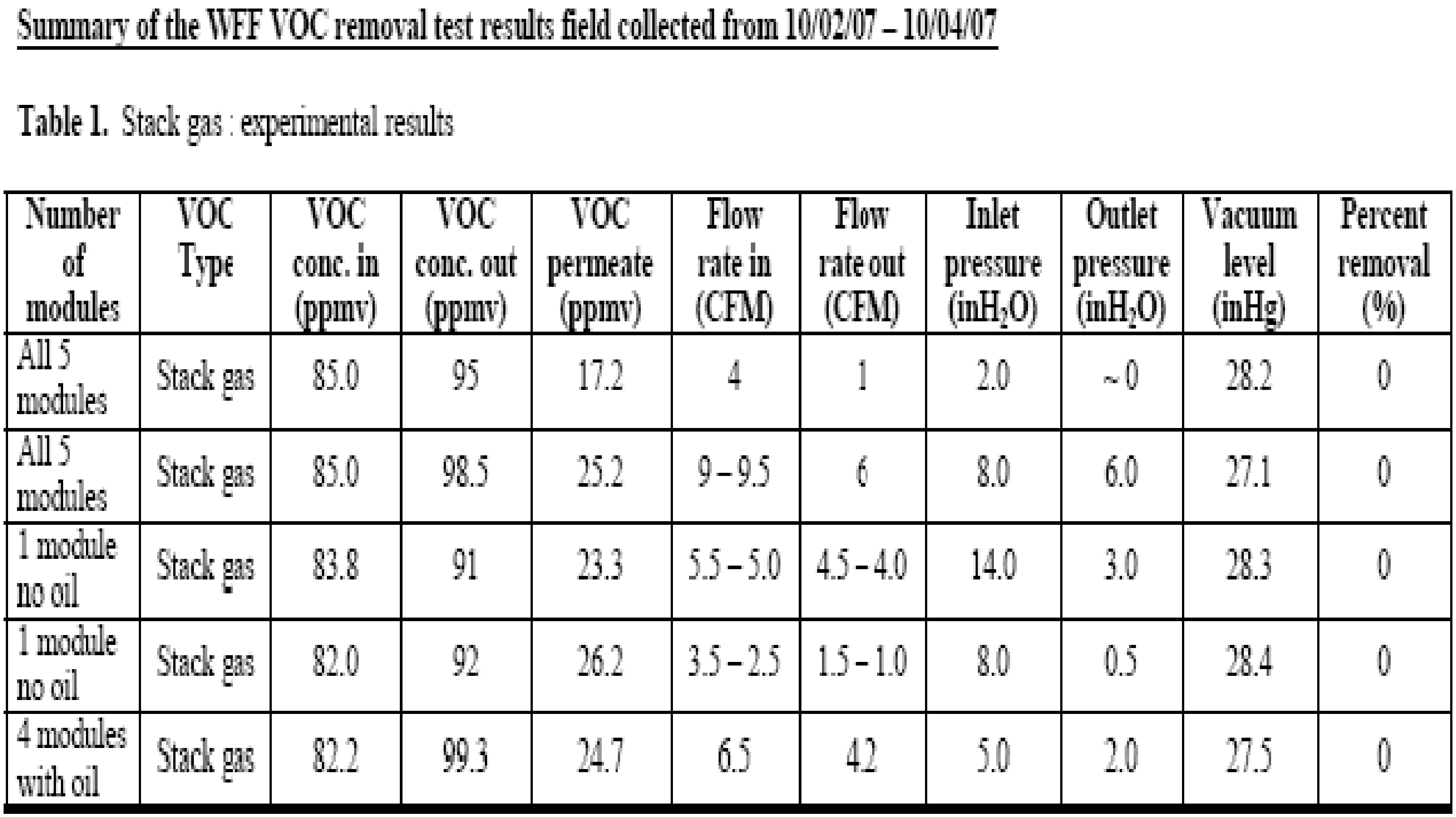
Partial evaporation of pure or mixed solvents

- Solvent being studied: silicone oil
- Preparation of thin ILM:
  - wet pores with hexane containing 30% silicone oil
  - pull vacuum from shell side to remove hexane and pass N_2 on tube side

Initial Stack Gas Results: almost no VOC removal was observed on Stack GasFeed when coated membrane ***with fully filled liquid membrane in the micropores was used.***

Note: This is at modest Vacuum Levels & with below 100 ppmv VOC Feed Concentrations.

WFF VOC STREAM below 100ppm



Summary of the WFF VOC removal test results field collected from 10/02/07 – 10/04/07

Table 1. Stack gas : experimental results

Number of modules	VOC Type	VOC conc. in (ppmv)	VOC conc. out (ppmv)	VOC permeate (ppmv)	Flow rate in (CFM)	Flow rate out (CFM)	Inlet pressure (inH_2O)	Outlet pressure (inH_2O)	Vacuum level (inHg)	Percent removal (%)
All 5 modules	Stack gas	85.0	95	17.2	4	1	2.0	~ 0	28.2	0
All 5 modules	Stack gas	85.0	98.5	25.2	9 – 9.5	6	8.0	6.0	27.1	0
1 module no oil	Stack gas	83.8	91	23.3	5.5 – 5.0	4.5 – 4.0	14.0	3.0	28.3	0
1 module no oil	Stack gas	82.0	92	26.2	3.5 – 2.5	1.5 – 1.0	8.0	0.5	28.4	0
4 modules with oil	Stack gas	82.2	99.3	24.7	6.5	4.2	5.0	2.0	27.5	0

Initial Testing Modules 1, 2, 3 and 4 (with thick liquid membrane)

- For inlet acetone concentration of 1,200-1,500 ppmv and a flow rate of 10 CFM, 81% removal rate was achieved (Table 12).

- As the inlet gas flow rate was increased to 16 CFM removal rate dropped to 59% and for 21 CFM the removal rate was 42% while the vacuum level was maintained at 26.9-27.0 inHg.

AIR STREAM WITH ACETONE

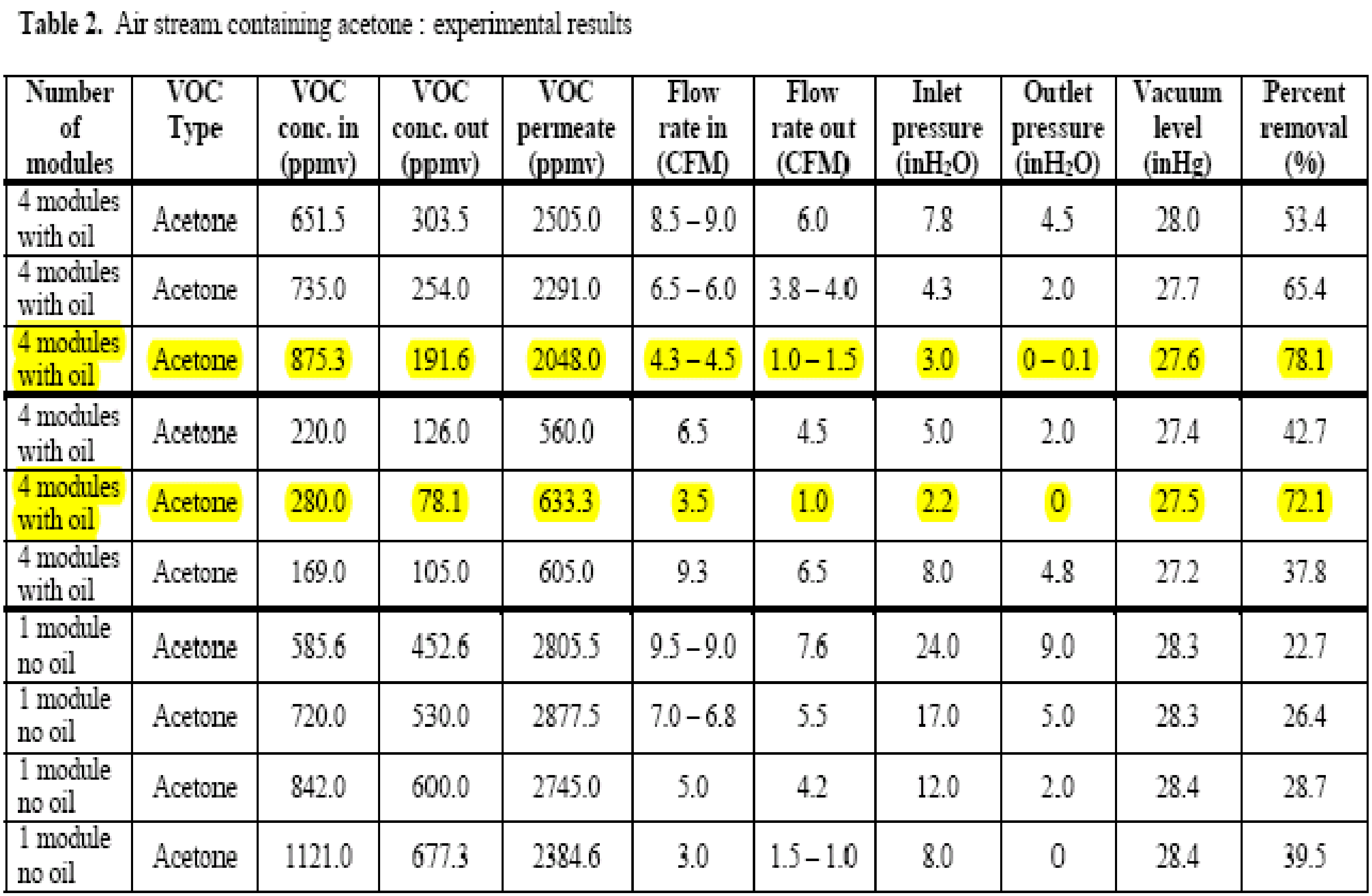


Table 2. Air stream containing acetone : experimental results

Number of modules	VOC Type	VOC conc. in (ppmv)	VOC conc. out (ppmv)	VOC permeate (ppmv)	Flow rate in (CFM)	Flow rate out (CFM)	Inlet pressure (inH_2O)	Outlet pressure (inH_2O)	Vacuum level (inHg)	Percent removal (%)
4 modules with oil	Acetone	651.5	303.5	2505.0	8.5 – 9.0	6.0	7.8	4.5	28.0	53.4
4 modules with oil	Acetone	735.0	254.0	2291.0	6.5 – 6.0	3.8 – 4.0	4.3	2.0	27.7	65.4
4 modules with oil	Acetone	875.3	191.6	2048.0	4.3 – 4.5	1.0 – 1.5	3.0	0 – 0.1	27.6	78.1
4 modules with oil	Acetone	220.0	126.0	560.0	6.5	4.5	5.0	2.0	27.4	42.7
4 modules with oil	Acetone	280.0	78.1	633.3	3.5	1.0	2.2	0	27.5	72.1
4 modules with oil	Acetone	169.0	105.0	605.0	9.3	6.5	8.0	4.8	27.2	37.8
1 module no oil	Acetone	585.6	452.6	2805.5	9.5 – 9.0	7.6	24.0	9.0	28.3	22.7
1 module no oil	Acetone	720.0	530.0	2877.5	7.0 – 6.8	5.5	17.0	5.0	28.3	26.4
1 module no oil	Acetone	842.0	600.0	2745.0	5.0	4.2	12.0	2.0	28.4	28.7
1 module no oil	Acetone	1121.0	677.3	2384.6	3.0	1.5 – 1.0	8.0	0	28.4	39.5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AIR STEAM WITH TOLUENE

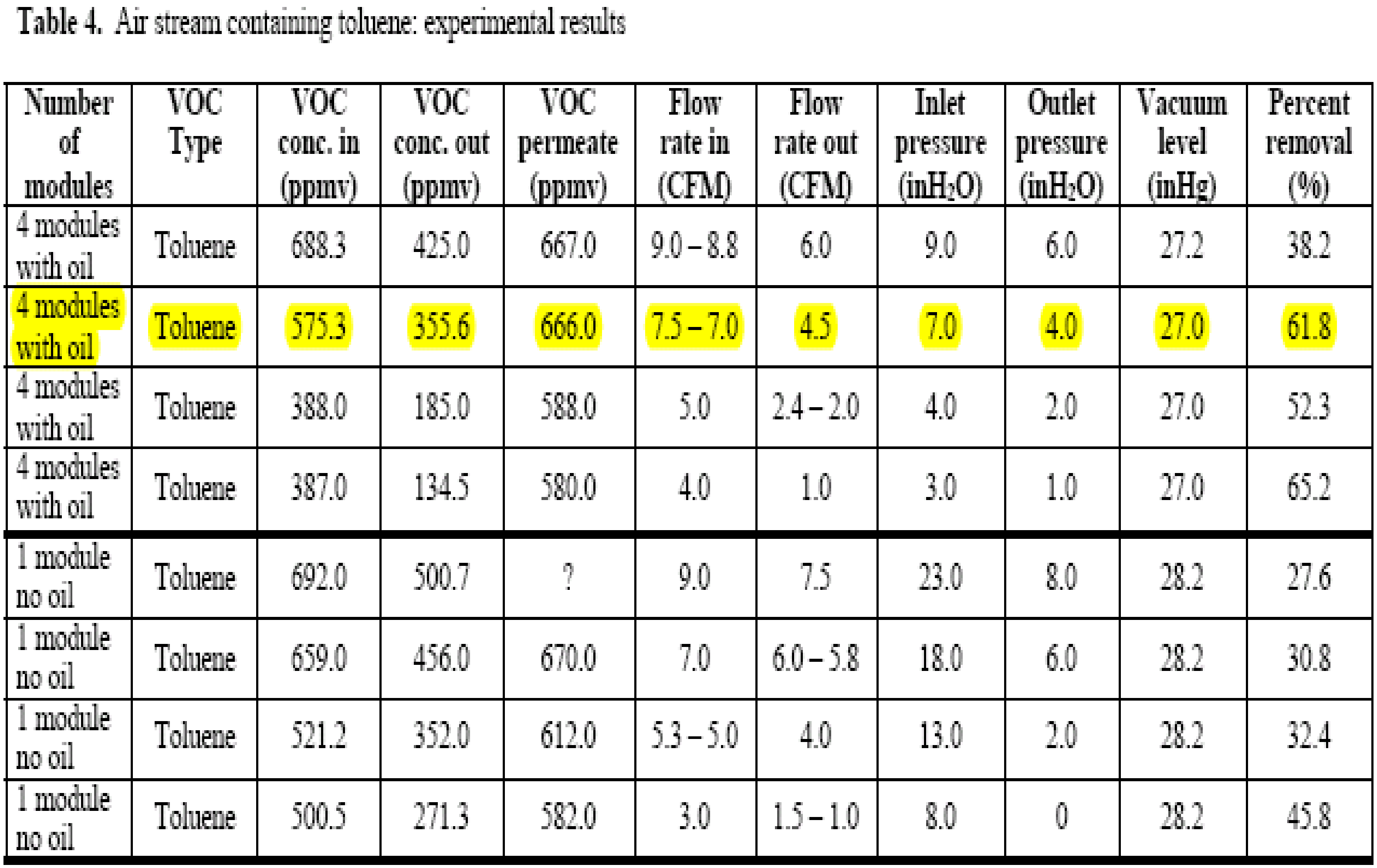

Table 4. Air stream containing toluene: experimental results

Number of modules	VOC Type	VOC conc. in (ppmv)	VOC conc. out (ppmv)	VOC permeate (ppmv)	Flow rate in (CFM)	Flow rate out (CFM)	Inlet pressure (inH$_2$O)	Outlet pressure (inH$_2$O)	Vacuum level (inHg)	Percent removal (%)
4 modules with oil	Toluene	688.3	425.0	667.0	9.0 – 8.8	6.0	9.0	6.0	27.2	38.2
4 modules with oil	Toluene	575.3	355.6	666.0	7.5 – 7.0	4.5	7.0	4.0	27.0	61.8
4 modules with oil	Toluene	388.0	185.0	588.0	5.0	2.4 – 2.0	4.0	2.0	27.0	52.3
4 modules with oil	Toluene	387.0	134.5	580.0	4.0	1.0	3.0	1.0	27.0	65.2
1 module no oil	Toluene	692.0	500.7	?	9.0	7.5	23.0	8.0	28.2	27.6
1 module no oil	Toluene	659.0	456.0	670.0	7.0	6.0 – 5.8	18.0	6.0	28.2	30.8
1 module no oil	Toluene	521.2	352.0	612.0	5.3 – 5.0	4.0	13.0	2.0	28.2	32.4
1 module no oil	Toluene	500.5	271.3	582.0	3.0	1.5 – 1.0	8.0	0	28.2	45.8

Second Trials

- When a thinner liquid-membrane was tested for VOC removal from the stack gas, significant removal of VOCs from the stack gas was observed, compared to the results obtained in tests carried out in late 2007


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AIR STREAM WITH MEK

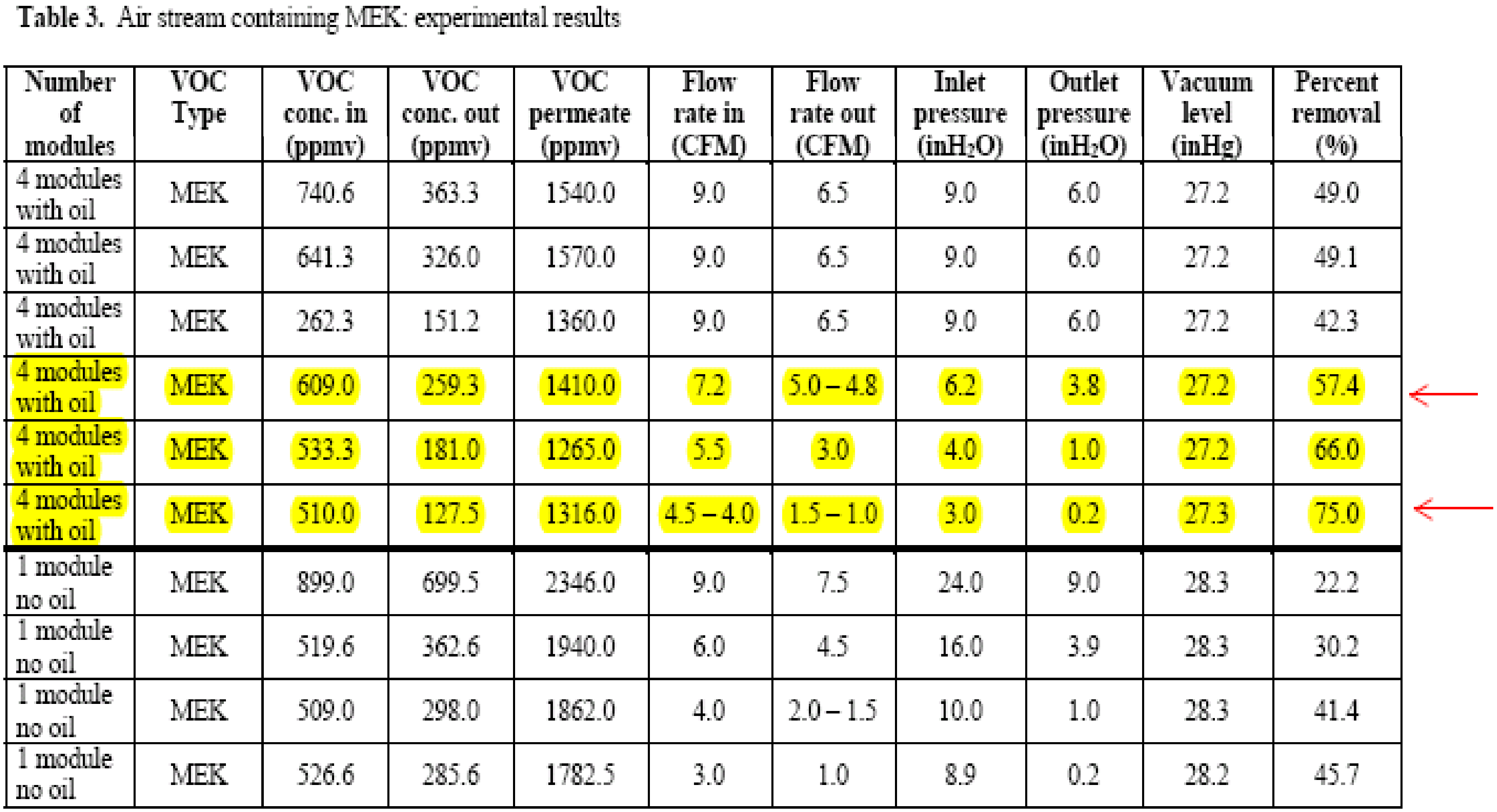


Table 3. Air stream containing MEK: experimental results

Number of modules	VOC Type	VOC conc. in (ppmv)	VOC conc. out (ppmv)	VOC permeate (ppmv)	Flow rate in (CFM)	Flow rate out (CFM)	Inlet pressure (inH_2O)	Outlet pressure (inH_2O)	Vacuum level (inHg)	Percent removal (%)
4 modules with oil	MEK	740.6	363.3	1540.0	9.0	6.5	9.0	6.0	27.2	49.0
4 modules with oil	MEK	641.3	326.0	1570.0	9.0	6.5	9.0	6.0	27.2	49.1
4 modules with oil	MEK	262.3	151.2	1360.0	9.0	6.5	9.0	6.0	27.2	42.3
4 modules with oil	MEK	609.0	259.3	1410.0	7.2	5.0 – 4.8	6.2	3.8	27.2	57.4
4 modules with oil	MEK	533.3	181.0	1265.0	5.5	3.0	4.0	1.0	27.2	66.0
4 modules with oil	MEK	510.0	127.5	1316.0	4.5 – 4.0	1.5 – 1.0	3.0	0.2	27.3	75.0
1 module no oil	MEK	899.0	699.5	2346.0	9.0	7.5	24.0	9.0	28.3	22.2
1 module no oil	MEK	519.6	362.6	1940.0	6.0	4.5	16.0	3.9	28.3	30.2
1 module no oil	MEK	509.0	298.0	1862.0	4.0	2.0 – 1.5	10.0	1.0	28.3	41.4
1 module no oil	MEK	526.6	285.6	1782.5	3.0	1.0	8.9	0.2	28.2	45.7

Third Phase of Field Trials -2008

- Based on the field testing of the system in August, 2007, and October, 2007
- Personnel from Chembrane, AMT and NJIT went back to Wallops Inland Flight Facility (WFF), VA, in May, 2008 to test further modifications to the membrane cartridges.

Third Trial Stack Gas Results

- When the thickness of the ILM composite membrane of silicone oil was controlled the coated polymer layer was adequately swollen.

- This swollen silicone-fluorine polymerized layer and the thin immobilized liquid membrane provide a lower mass transfer resistance to pentanes and hexanes.

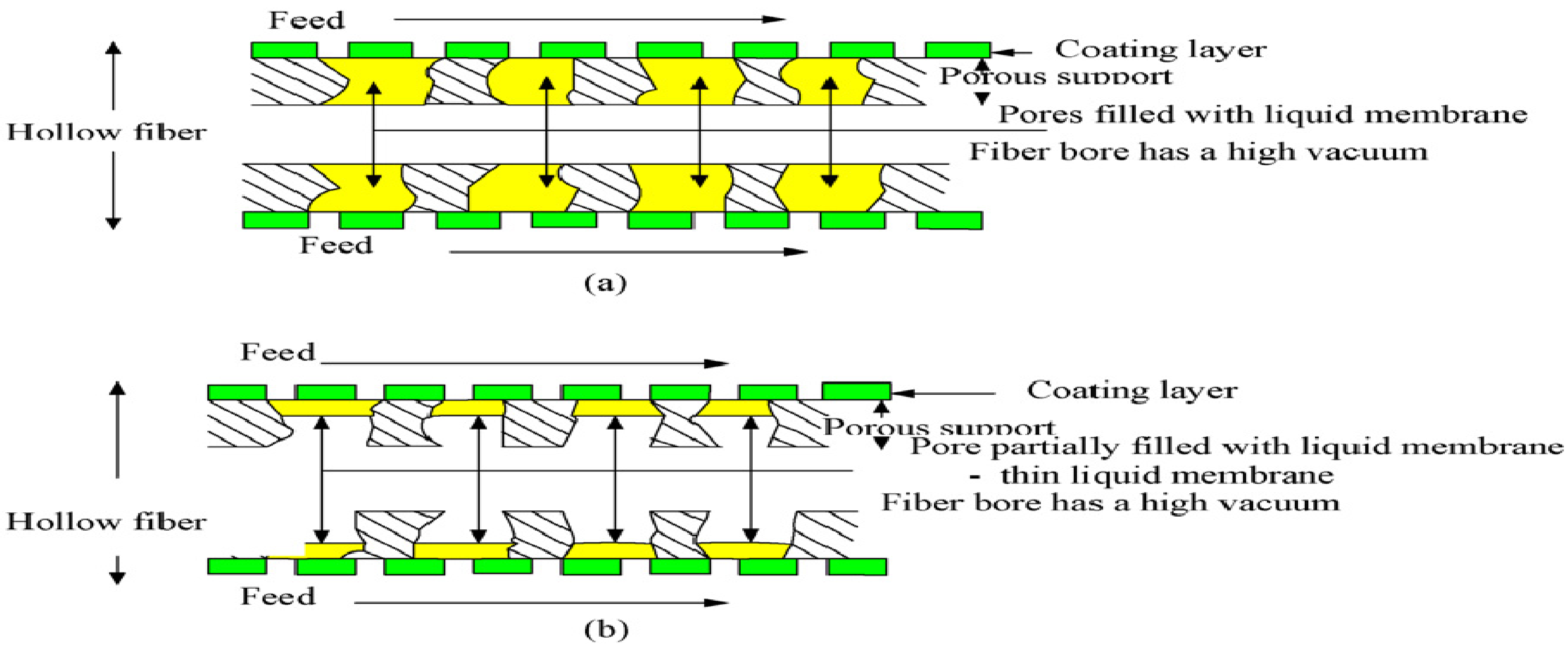
- Therefore, a significant removal of VOCs (mainly pentanes and hexanes) from the stack gas was observed.

Controlled Dual Layer ILM Membrane Composite

- **Third trials utilized special membrane modules**

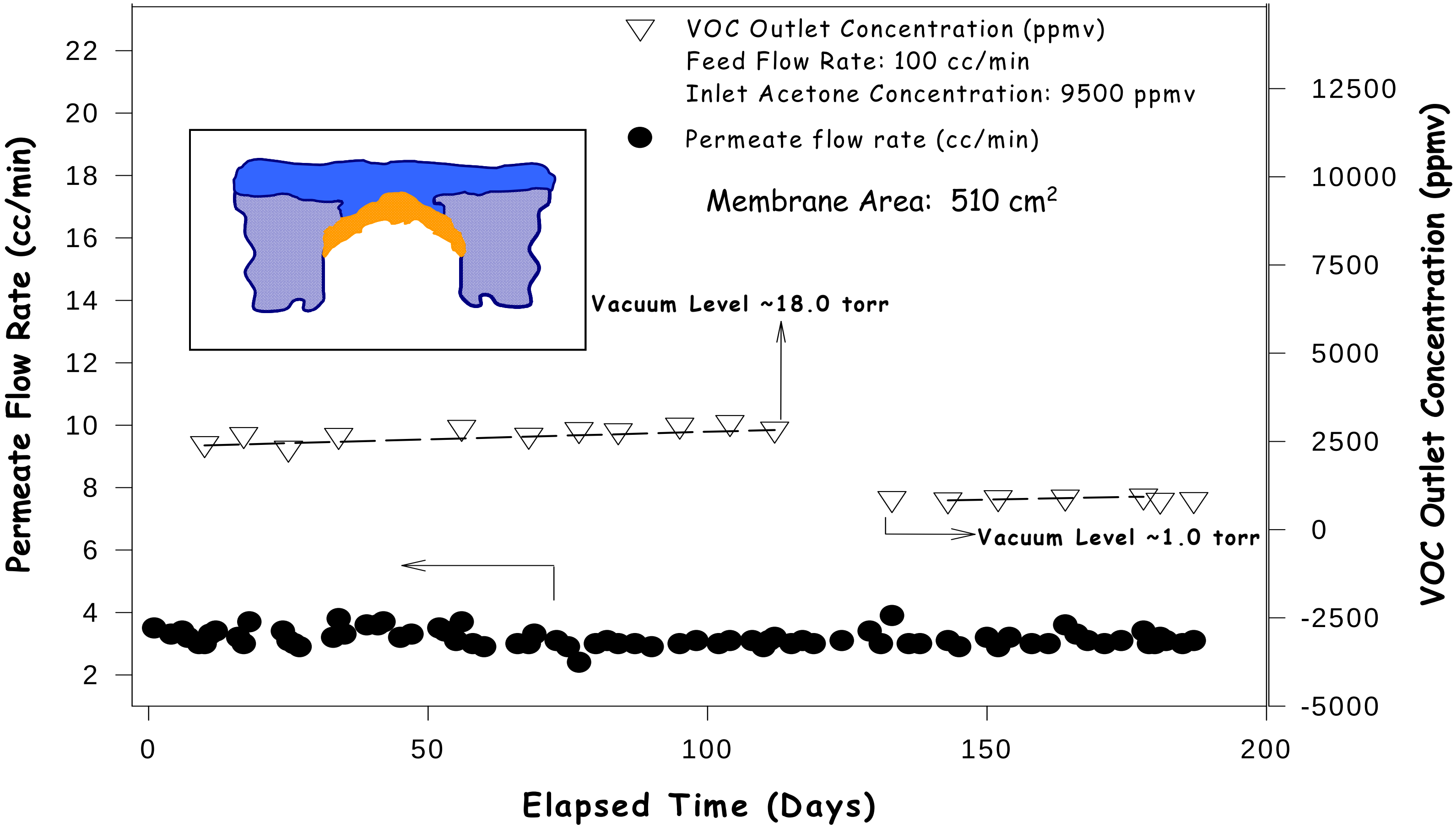
- **With more controlled liquid-membrane-thickness immobilized in the micropores of the porous hollow fiber having a controlled thinner & less crosslinked ultrathin-coating resulting from plasma-polymerization.**

- ***This novel coating technology combines advantages of AMT's plasma polymerized nanopore coated hollow fibers with highly selective nonvolatile mobile liquid absorbents.***



- **Fig. 1.** Liquid membrane immobilized in porous hydrophobic hollow fiber membranes; the fiber has a nanoporous coating on the outside surface: (a) fiber with coating and substrate pores completely filled by liquid membrane and (b) same as in (a) except liquid membrane covers only part of the substrate pore length—thin LM

Simulation Results for Acetone



Positive Effects on Higher Solubility VOC’s

- VOCs having a higher ability to swell the Plasma Polymer Coated Layer have even higher solubility in the Silicone Oil Layer.
- Acetone, MEK and Toluene, showed significantly improved mass transfer rates as well in these modified Controlled Dual Layer ILM Composites.

CO2 GHG Emissions from Biorefineries

CO2 GHG Emissions from Biorefineries

- Half of the total CO2 emissions arise from DDGS dryers. Thermal Oxidizers at a typical Biorefinery consume more than 250 MMBtu/hr in heat inputs and have the potential to emit more than 100 tons per year of VOCs etc.

- The reporting requirements for UNFCCC includes indirect GHG such as CO, NOx, NMVOCs, and SO2. These gases may undergo photochemical reactions in the atmosphere to form compounds that are Greenhouse Gases or prolong the lifetime of other GHGs.

Increased emphasis on Life Cycle Analysis (LCA)

Analysis of *Carbon footprints* related to Bioprocesses show needed improvements for *direct GHG Emissions* reduction technologies,

as well as, to mitigate *indirect GHG Emissions* produced by conventional NMVOC Control Technologies such as Thermal Oxidizers and Granular Activated Carbons.

OTHER BIO APPLICATIONS

- H2S & CO2 & NMVOCs associated with *LANDFILL* gases and *BIOGASES* offer clear targets for use of this type of advanced membrane based liquid absorbent system.

BIOFUEL MEMBRANES
EUROPE BIOGAS PIPELINES

Membranes/Modules for Biogas Upgrading

Volumetric Treatment Capacity

- Capacity can easily be varied from small streams around 2-10 scfm up to 500-750 scfm

- Larger capacity systems being designed to utilize hybrid membrane oil stripping based module systems

Concluding remarks and recommendations

The objective of the current project was several fold:

- To carry out large-scale demonstrations of removal of solvent vapors present in stack gas exhaust air streams under real operating conditions using a novel hollow fiber membrane based technology
- and to test the performance of large scale commercial hollow fiber modules.

A pilot-scale membrane VOC Skid was successfully field demonstrated

- The Skid was built at AMT Inc. and transported to the NASA Wallops Island Flight facility (Wallops Island, VA) for separation of volatile organic compounds (VOCs) from air.
- Highest percent removal for VOCs from the stack gas was 67%.
- Very high VOC removal (~96%) was obtained while testing the system with artificially introduced Acetone and MEK.

Environmental Market: VOC/Air Treatment

Hollow Fiber Membrane Module Systems