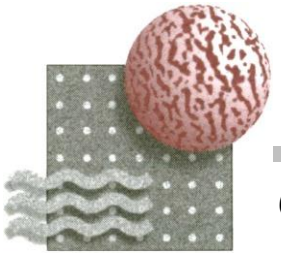
An Industrial Membrane System Suitable for Distributed Used Oil Re-refining

DE-SC0006185

Dr. Richard J. Ciora, Jr.,
Media and Process Technology Inc.
1155 William Pitt Way, Pittsburgh, PA 15238
412 292-4057, rciora@mediaandprocess.com

US DOE Advanced Manufacturing Office Program Review Meeting
Washington, D.C.
May 28 – 29, 2015

This presentation does not contain any proprietary, confidential, or otherwise restricted information.



Project Objectives

Ceramic membranes for large scale hydrocarbon liquid processing

Big Picture (Our mission)

Media and Process Technology Inc. (MPT) is the only US-based ceramic membrane manufacturer. MPT is developing low cost high performance ceramic membranes universally applicable to a wide range of separations at small to very large scales.

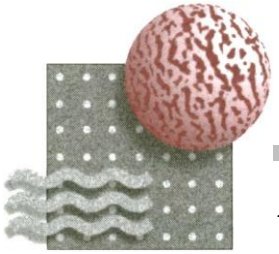
- Currently pursuing promising applications that require the unique features of ceramic membranes such as thermal and chemical stability, including waste oil re-refining, coal tar oil clean-up, and FCC slurry upgrading.

- In parallel, use these applications and know-how developed as a pathway to competing with lower cost polymeric membranes in a broad array of aqueous phase separations in large scale installations.

In this SBIR Project

Goal: Drive down the overall cost and complexity of the ceramic membrane based hybrid process concept we are developing for non-aqueous phase fluids operating at high temperature and pressure to make the technology more compatible with very large scale applications. Waste oil re-refining was selected by us as a first candidate due to its smaller scale.

Goal: Extend the hybrid process concept to several additional non-aqueous phase applications that had been feasibility demonstrated as part of our Phase I and Phase II activities. FCC slurry upgrading and coal tar oil clean-up are selected by us for Phase IIB to pursue.



Why is it difficult?

Barriers to large scale broad based ceramic membrane use

Barrier #1: Performance Stability and Long Term Reliability Barriers

Advantage: Ceramic membranes offer **material** stability far superior to polymeric membranes.

Problem: This is not an advantage if your **performance** stability is poor due to eg: irreversible fouling.

Problem Source: Ultrathin separating layer is susceptible to significant fouling due to (accidental) exposure to aggressive poisons.

Long term performance reliability is a key limitation of membrane technology. Ceramic membranes are not immune from this problem.

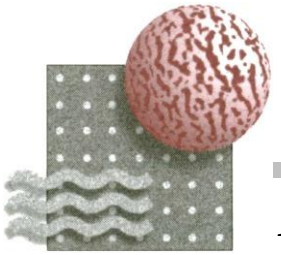
Barrier #2: Integrating a new membrane unit operation into an existing process

Advantage: *Ceramic membranes are ideal for hydrocarbon liquid processing.*

Problem: Generally **not a stand-alone** technology…integration with conventional technology is required.

Problem Source: Membranes are bulk separators (the 99% solution) but intrinsically inefficient in "fine" separations (the 99.99% solution).

It is necessary to develop the hybrid "process" that combines the membrane with the fine separation post treatment system as part of the commercial development and demonstration.



Project Tasks for Phase II & IIB

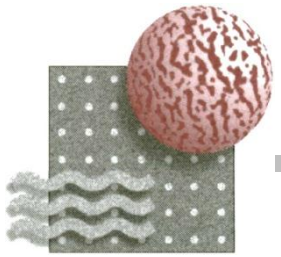
How to overcome the barriers and then promote our technology ?

- **Long Term Operation Stability of Full-Scale Industrial Membrane System**
  Continue the operation of the full-scale used oil re-refining semi-works to accrue long term performance stability at the production level based upon the industrial membrane system we have developed during Phase I&II.

- **Expand the Industrial Membrane System Applications**
  Begin field testing of additional processes identified and feasibility tested in Phase I including (i) upgrading of waste FCC slurry oil and (ii) upgrading of coal tar oils.

- **Upgrade the Industrial Membrane System (2nd Generation) for Mega-scale Applications**
  Scale-up the ceramic membrane element and module to deliver an order of magnitude increase in membrane area per module. This will reduce the cost and complexity of the system.

- **Upgrade the Hybrid System (2nd Generation) for Efficiency Improvements**
  Improve the productivity of the used oil re-refining process via the introduction of a chemical pretreatment of the used oil feedstock, and further explore its applicability in the two additional applications identified above.

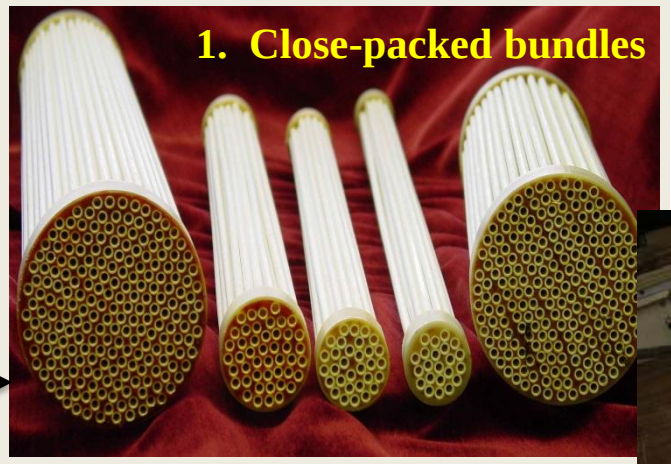


Background: MPT Ceramic Membrane

Multiple Tube Membrane Bundles – versatile, low cost

Ceramic Membrane Features
- Inorganic membranes, tubular format
- Ultra-thin film, nanoporous layers
- Flexible bundle packaging; many size and shape options
- Only US Manufacturer

Single tubes



Example: conventional micro- and ultrafiltration

Ex: porous heat exchangers & catalytic membrane reactors

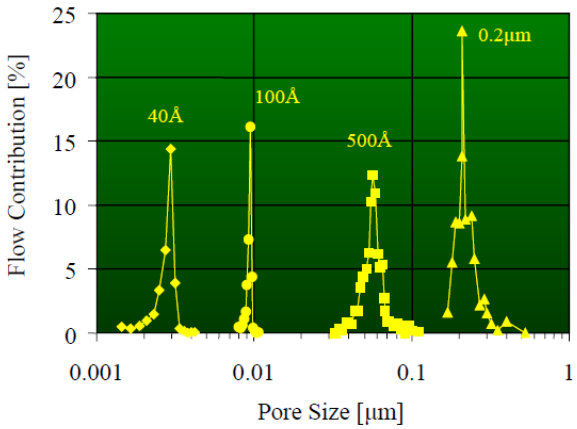
Ex: high pressure intermediate temperature gas separations

Our Core Expertise/Technology

#1: Packaging individual membrane tubes into commercially viable modules for field use.

Background: MPT Ceramic Membrane

Thin Film Deposition for Pore Size Control



Our Core Expertise/Technology

40Å to 100Å Pore Size Layer

500Å Pore Size Sublayer

0.2µm Pore Size Sublayer

#2: Our core expertise allows us to deposit a near perfect thin film on less-than desirable, but low cost porous tubular substrate.

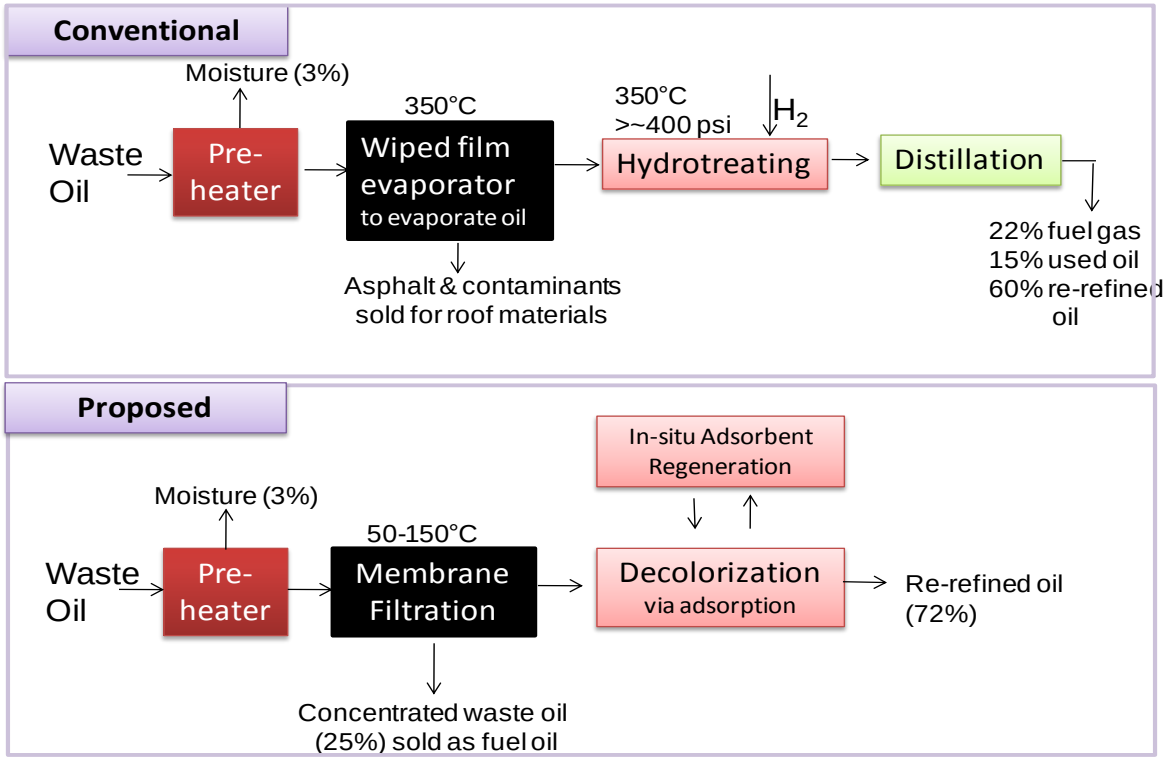
Technical Approach

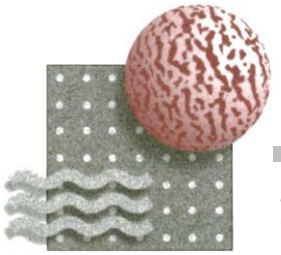
Used Oil Re-refining as the 1st Hydrocarbon Liquid Demonstration Process

Background on Used Oil Re-refining in the US

- *Used oil re-refining as a 1st Demonstration Application of the ceramic membrane hybrid process*
- *About 2 billion gallons/yr of waste oil generated in the US*
- *About 5 to 10% is re-refined today; balance is burned for energy recovery*
- *Current re-refining approach is to adapt conventional oil refining technology*

Comparison of Conventional versus Our Proposed Waste Oil Re-refining Process





Technical Approach

Technology Demonstration 1st Application: Used Oil Re-refining

Problems with Conventional Approach

- **Technically complex systems requiring highly skilled operators**
- **Centralized facilities are required; cannot be applied economically at scales below ~30MM GPY; less than 10 in operation in the US**
- **Waste oil sources broadly dispersed throughout the US; close to 500 collectors nationwide**

Solution Required

- **Simple technology economical at small scales to match the source distribution (bring the technology to the oil).**
- **Product quality must be essentially indistinguishable from virgin oil**

Media and Process Technology Approach

- **Low "tech" two stage process**
- **Simple to implement ceramic membrane filtration for bulk fluid clean-up**
- **Simple to implement adsorption technology for fine separation**
- **Limited technical skills required**
- **Modular and scalable; economical at scales as small as ca. 1MM GPY**

Results Snapshot

Stage 1: Ceramic Membrane for Ash/Metal Removal

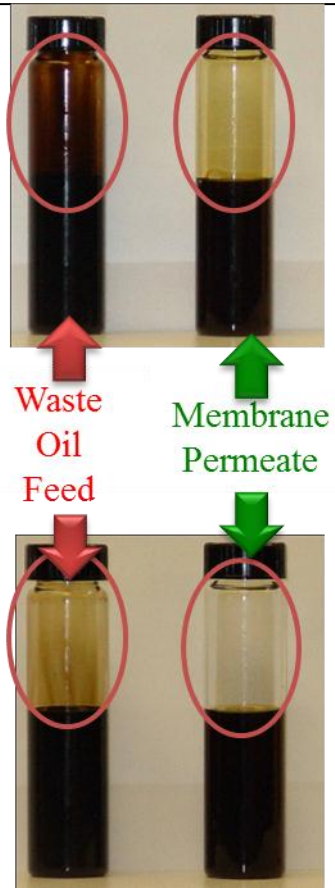
Ceramic Membranes for Used Oil Pretreatment

- ***Remove metals, ash, soot and suspended debris from the waste oil***
- ***Produce a microparticulate free product that does not "plug" the 2nd stage adsorbent; product is dark color but visually clear.***
- ***2nd Stage decolorization not possible without membrane pretreatment***

Typical Metal/Ash Removal from Used Crankcase Oils

Contaminant	Contaminant Concentration As Received [ppm]	Contaminant Concentration After Membrane [ppm]	Contaminant Removal Ratio [%]
Iron via ICP	205ppm	39ppm	81.0%
Chromium	5	2	60.0
Lead	67	12	82.1
Copper	202	18	90.1
Sodium	103	4	96.1
Magnesium	244	13	94.7
Calcium	726	15	97.9
Phosphorous	495	155	68.7
Zinc	860	165	80.8
Ash Content (ASTM D-482)	0.602wt%	0.097wt%	83.9

After 10 minutes of settling



After 16 hours of settling

The "Test"

Feed and membrane product generated in our re-refining process.

The samples were inverted and then left to stand for the times noted.

The cleanliness of the glass vial shows the permeate oil is dark but "clear". No haze and can visually see through the sample.

Results Snapshot

Stage 2: Adsorbent Polishing. Finished Oil Quality

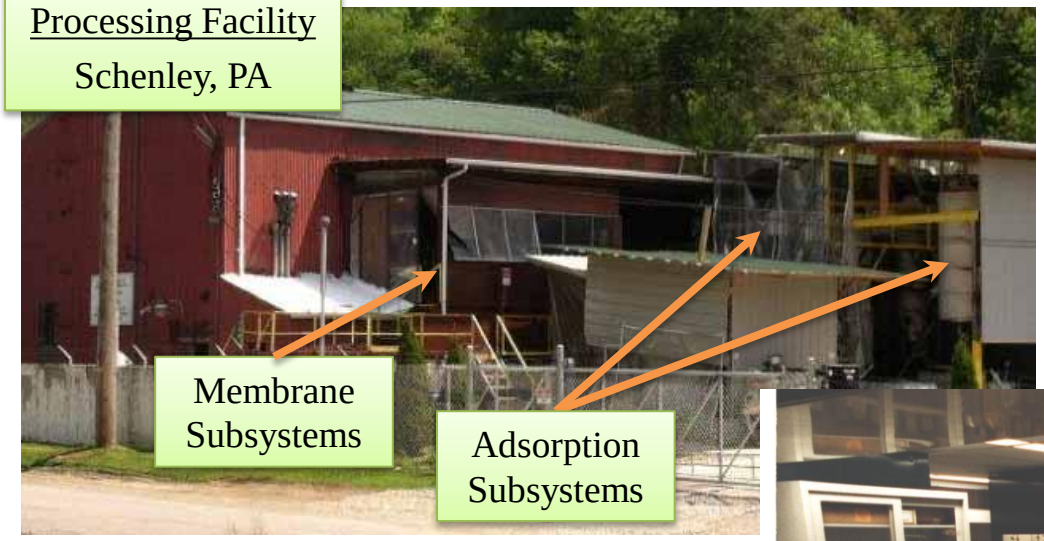
Finished Oil Quality: MPT versus Virgin Base Oil

Parameter		Method	MPT	SN-150
Kinematic Viscosity	@40˚C [cSt]	D445, ASTM	26.9	30.9
	@100˚C [cSt]	D445, ASTM	5.0	5.3
VI [-]		D2270, ASTM	110	107
Color [-]		D1500, ASTM	<0.5	<0.5
Appearance [-]:			C+B	C+B
Flash Point [˚C]:		D92, ASTM	210	210
Total Acid Number [mg KOH/g]:		D664, ASTM	<0.05	<0.05
Pour Point [˚C]		D5950, ASTM	<-15	-15
NOACK Volatility [wt%]		D2887, ASTM	13	14
Metals Content:				
Iron [ppm]:		ICP	<1	all <1
Copper		ICP	<1	
Tin		ICP	<1	
Silicon		ICP	2	
Boron		ICP	<1	
Calcium		ICP	<1	
Barium		ICP	<1	
Phosphorous		ICP	4	
Zinc		ICP	<1	
Potassium		ICP	<1	

MPT Re-refined Oil
Clear and water white

MPT Facilities

Semi-works Used Oil Processing and Support Laboratory



Used Oil Processing Facility (Schenley, PA)

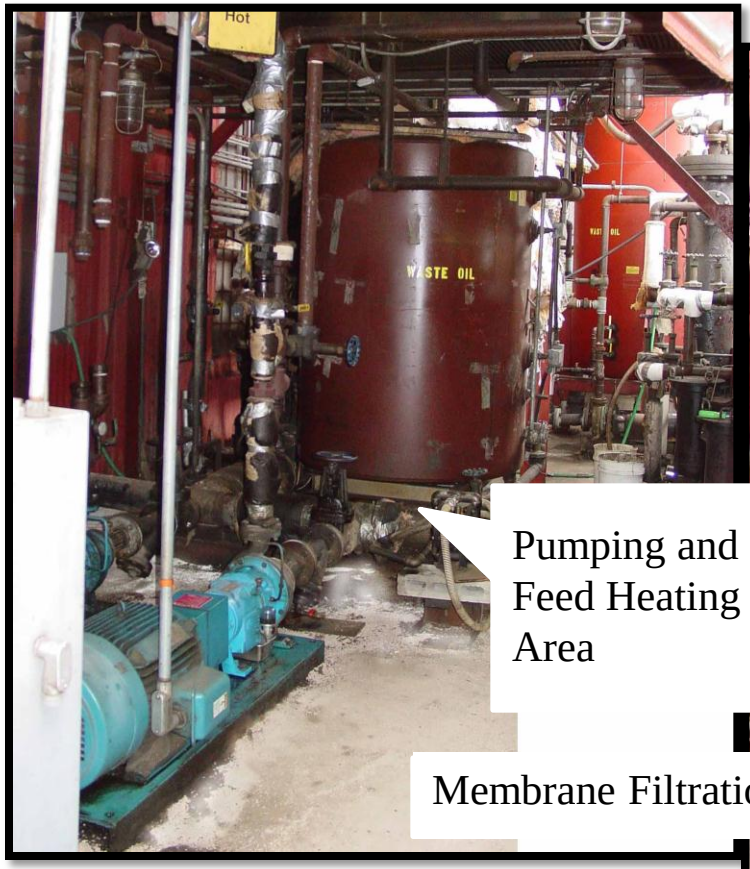
- PA Permitted Used Oil Processing Facility
- Semi-works used oil re-refining demonstration, fully operational
- Potential to produce several million gallons per year of re-refined oil

Laboratory Support Facility (Pittsburgh, PA)

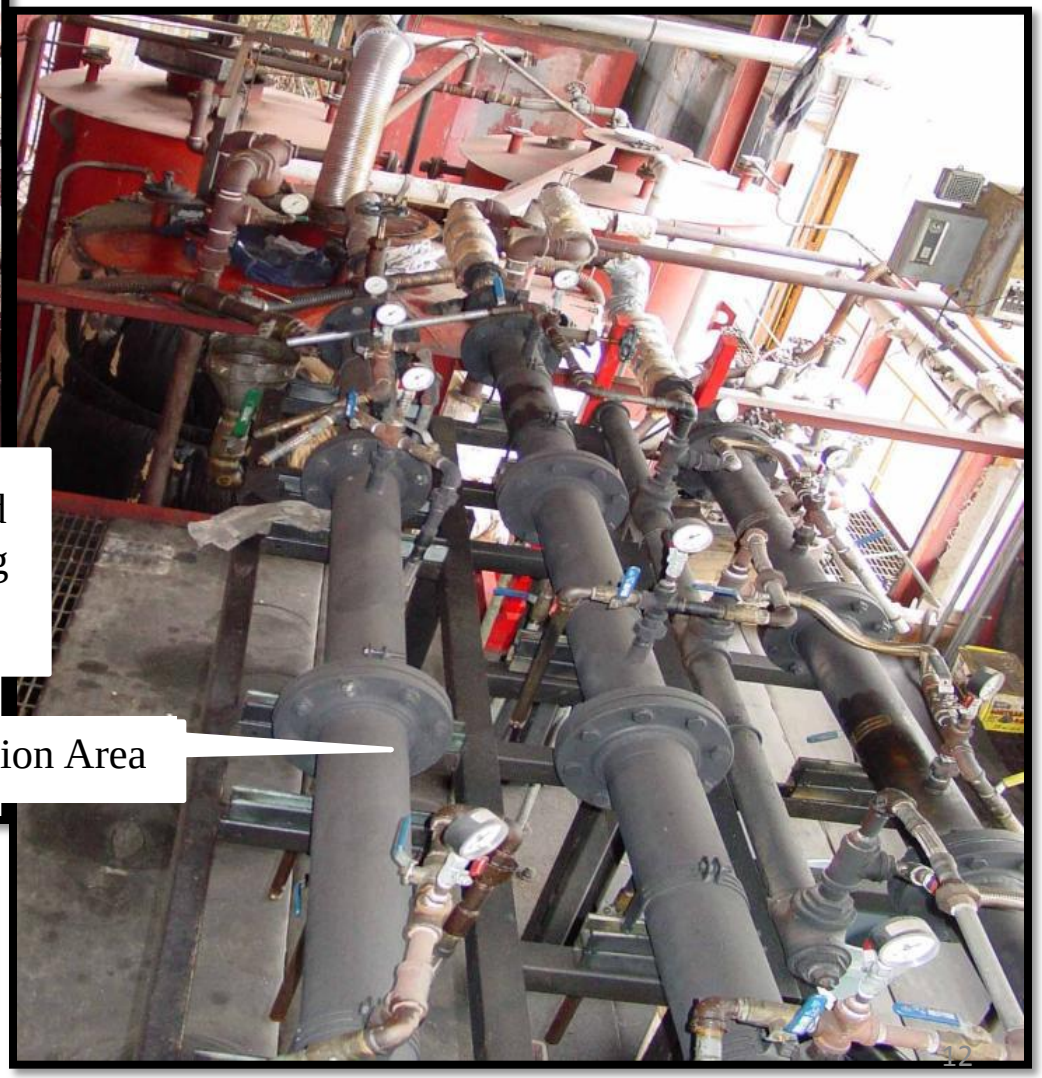
- Full range of membrane preparation, characterization, and testing capability
- Full range of used and finished oil characterization capability

System Snapshot. Used Oil Re-refining

Stage 1: Ceramic Membrane Filtration



Pumping and Feed Heating Area



Membrane Filtration Area

Aggressive operating conditions:
130 to 150°C; 30 to 100 psig.

System Snapshot. Used Oil Re-refining

Stage 2: Adsorption for Final Polishing

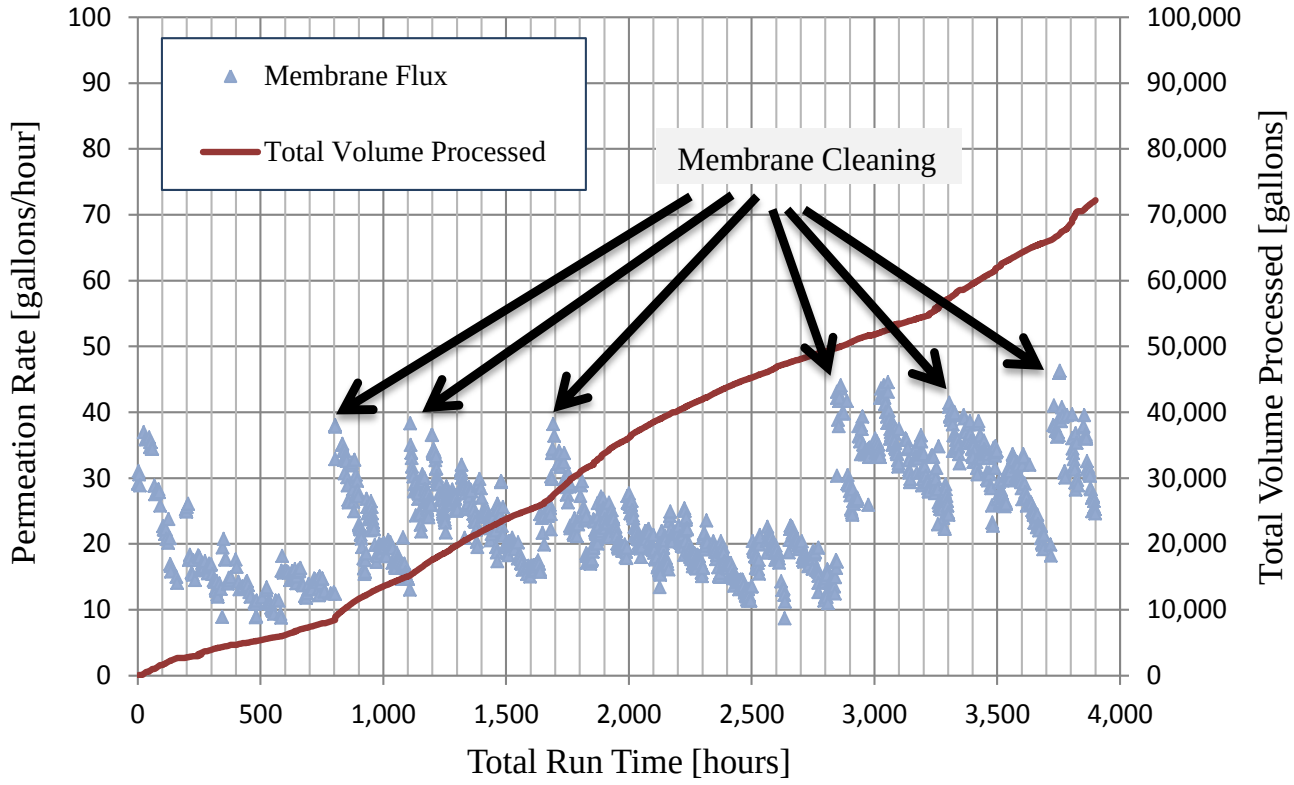
8x 24" and 1x 36" Diameter by 10' Length Adsorbers

Summary of Results

Used Motor Oil Processing: Long Term Membrane Performance

Media and Process Technology Approach

- **Over 4,000 hours of waste oil processing in over 12 months of testing.**
- **Over 70,000 gallons of used oil processed**
- **Permeation rate is "stable" and reproducible with periodic cleaning**



Summary of Results

Used Motor Oil Processing: Membrane Cleaning

Our Used Oil Fouled Membrane Cleaning Approach

- **Simple and reproducible cleaning method**
- **Can be implemented as a clean-in-place operation**
- **Developed and patented; green and environmentally friendly**
- **Cleaning method is superior to a wide array of possible solvent based cleaners**

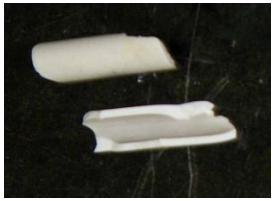
Wide Array of Solvents Do Not Work

Hexane	**No effect**
Mineral Spirits	Very modest
Acetone	No effect
MEK	Very modest
Methanol/Ethanol	No effect
Toluene	Very modest
Lacquer Thinner	Modest
Methylene Chloride	Very modest
10% NaOH	No effect

Membrane "Chip" Cleaning

Fouled Membrane

Cleaned Membrane



Membrane Bundle Cleaning

Before and After Patented MPT Cleaning Method

Summary of Results

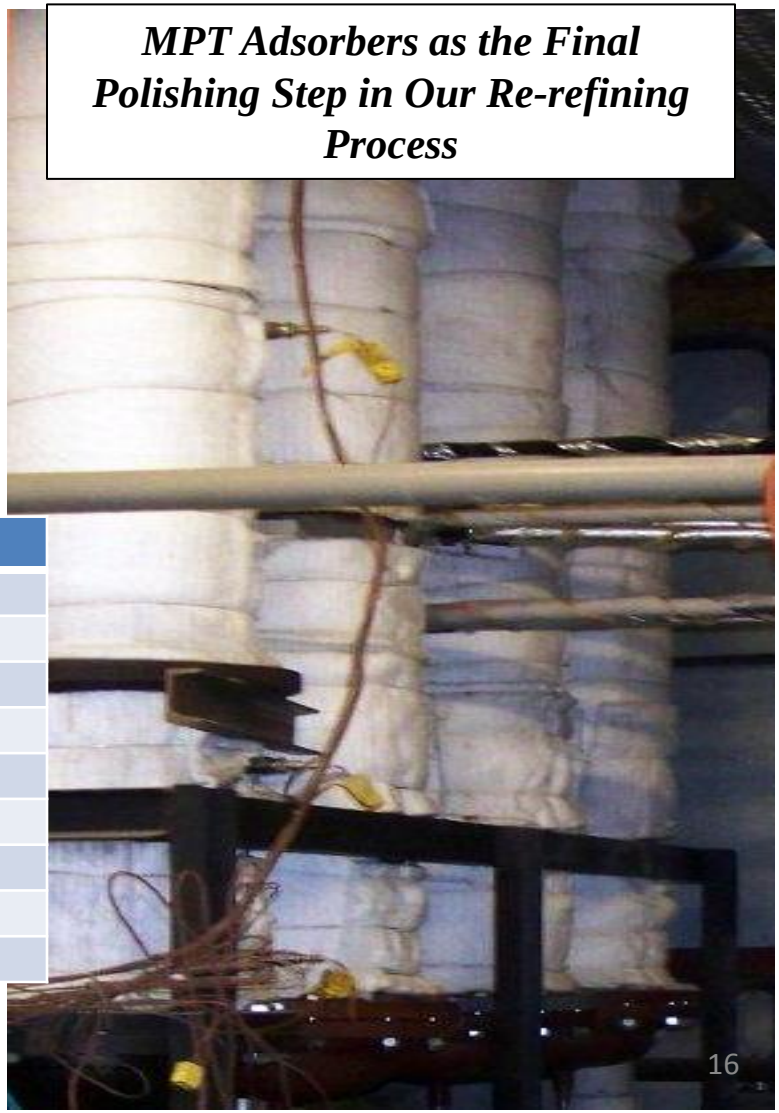
Used Motor Oil Processing: Long Term Adsorber Performance

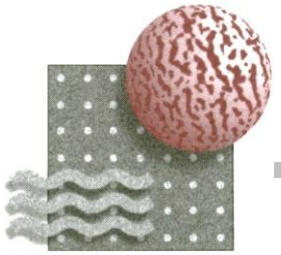
Demonstrated Used Oil Decolorization via Adsorption

- ***Adsorbers demonstrated to be highly effective at color removal from the membrane permeate.***
- ***Nine columns currently in place***
- ***Hybrid process economics requires re-use of the adsorbent.***
- ***Thermal regeneration demonstrated to be very effective.***
- ***Operational mode: two regenerating and seven in operation.***
- ***Minimum of ~10 regenerations necessary for economical operation***
- ***Up to 28 regenerations demonstrated with minimal loss in performance***

Adsorber #	Regenerations
1 (24”)	28
2	25
3	22
4	23
5	21
6	21
7	22
8	23
9 (36”)	15

MPT Adsorbers as the Final Polishing Step in Our Re-refining Process





Process Economic Targets and Results

Used Motor Oil Re-refining

Summary of the major operating cost contributors for re refining based upon the Phase I estimates and the updated results from the Phase II semi works operation (excluding labor contributions).		
	Phase I "Target"	Phase II Results
Membrane Yield [%]	75%	73 to 78%+
Decolorization Yield [%]	80%	83 to 85%
Overall Process Yield [%]	60%	61 to 66.3%
Membrane Subsystem	$/gal finished base oil	$/gal finished base oil
Main Process Heater	0.088	0.14
Main Process Heaters	0.032	0.037
Decolorization Subsystem		
Adsorbent Replacement	0.18	<0.10
Heaters/Air Consumption	0.03	0.021
Operating Cost Summary	Phase I	Phase II Semi-works
Subsystem Costs	0.33	<$0.30
Labor Cost at 2MM GPY	0.19	0.19
Yield Improvement	NA	~0.01 to 0.05 improvement versus Phase I

Overall Technical Accomplishments – Phase II

Objective #1. Demonstrate the used oil re-refining process at the semi-works scale

We have successfully completed construction (Task 1) and shakedown testing of our semi-works scale used oil re-refining facility (Subtask 2a). As currently configured, it is possible to produce at this facility approximately 6,000 gallons per week of finished membrane treated oil (permeate) from waste crankcase oil using a nine membrane system. Further, we can produce approximately 1,600 to 2,000 gallons per week of finished high quality base oil from membrane permeate in our decolorization subsystem with our eight pilot scale adsorbers. These two subsystems have been in operation for over nine months as part of our Phase II program.

Objective #2: Economic Analysis and Business Development

For our target baseline 2MM gallon per year of finished re-refined base oil, we project operating costs of $0.49 per gallon (including operating labor) and net revenues of $0.89 per gallon for the current market prices of $3.00 per gallon for the finished product and $1.60 per gallons for delivered on-spec waste oil. Overall system cost is ca. $1.75MM. For a 2MM gallon per year facility, capital payback is just over one year.

Objective #3: Expand the Developed Industrial Membrane System in Other Hydrocarbon Processing

We have successfully demonstrated the technical feasibility of our ceramic membrane technology in the upgrading FCC slurry to a hydrocracker feedstock quality and in the filtering of coal tar oils to prevent downstream plugging of the downstream hydroprocessing systems.

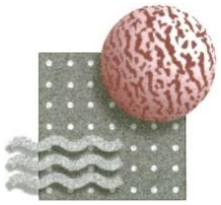
Bottom Line

We have overcome the two barriers (described in Slide #3) which limit the membrane process for industrial applications:

- ❑ **long term operation stability**
- ❑ **its integration into existing industrial processes.**

Emerging Application Results

- **Fluid Catalytic Cracker Slurry Upgrading**
- **Coal Tar Liquids Upgrading**



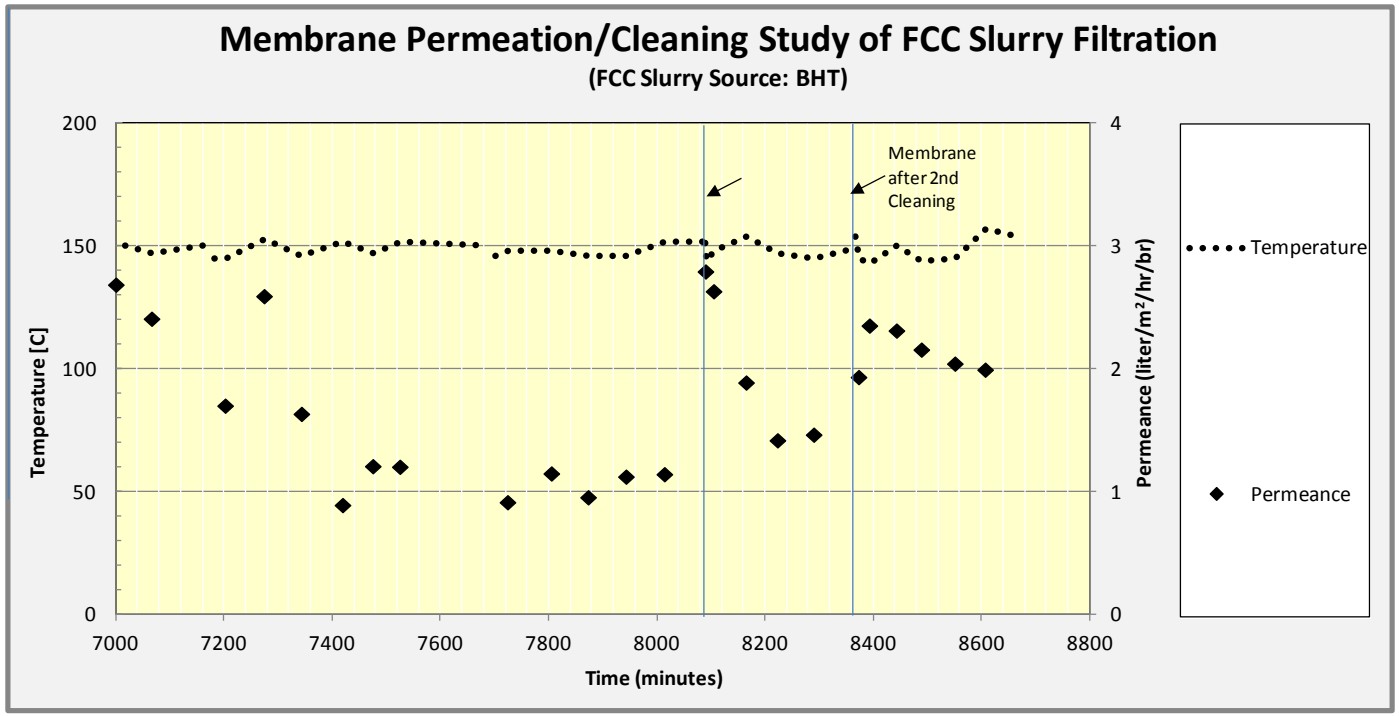
Media and Process Technology Inc. (M&P)
1155 William Pitt Way
Pittsburgh, PA 15238 - 1678

Upgrading FCC Slurry Oils

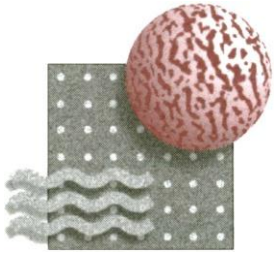
Membrane Performance and Stability

Upgrading Fluid Catalytic Cracker (FCC) Slurry Oils

- Convert low value FCC slurries to high value fuel
- Remove metal, ash, and microparticulates
- Pretreatment to downstream hydroprocessing
- High viscosity liquid requires very high processing temperatures, ideal for ceramic membranes
- Metal based membranes have failed…poor pore size control yields rapid irreversible fouling.



The viscous FCC slurry was filtered effectively through the MPT ceramic membrane at a high temperature. Further, the membrane was cleaned effectively to demonstrate the original permeate flux restoration in this preliminary study.



Upgrading FCC Slurry Oils

Membrane Product Quality

Upgrading Fluid Catalytic Cracker (FCC) Slurry Oils

- Nearly complete removal of solids debris
- Nearly complete removal of metals and ash
- Product is suitable for hydroprocessing to fuel

Contaminants Removal and Other Characteristics

Contaminants	Before	After	% removal
Total Metals (mg/kg)	385.51	0.8	100
Mechanical Debris， %(w)	0.213	0.008	96
Solid content， %(w)	0.30	<0.02	>93
Carbon Residue， %(w)	8.41	9.10	-
100 viscosity， mm ^{2}/s	27.46	30.30	-
80 viscosity， mm ^{2}/s	76.36	86.32	-

Contaminants Removal

Contaminants	Before	After	% removal
Fe， mg/kg	14.3	0.4	97
Ni， mg/kg	7.7	0.2	97
Cu， mg/kg	<0.1	<0.1	-
V， mg/kg	5.6	0.2	96
Na， mg/kg	5.1	1	80
Ca， mg/kg	35.9	6.2	83
Mg， mg/kg	1.5	0.2	87
Pb， mg/kg	<0.1	<0.1	-
Al， mg/kg	382	0.6	100
K， mg/kg	2.7	<0.1	100
S， %	0.53	0.52	2
N， %	0.28	0.28	0

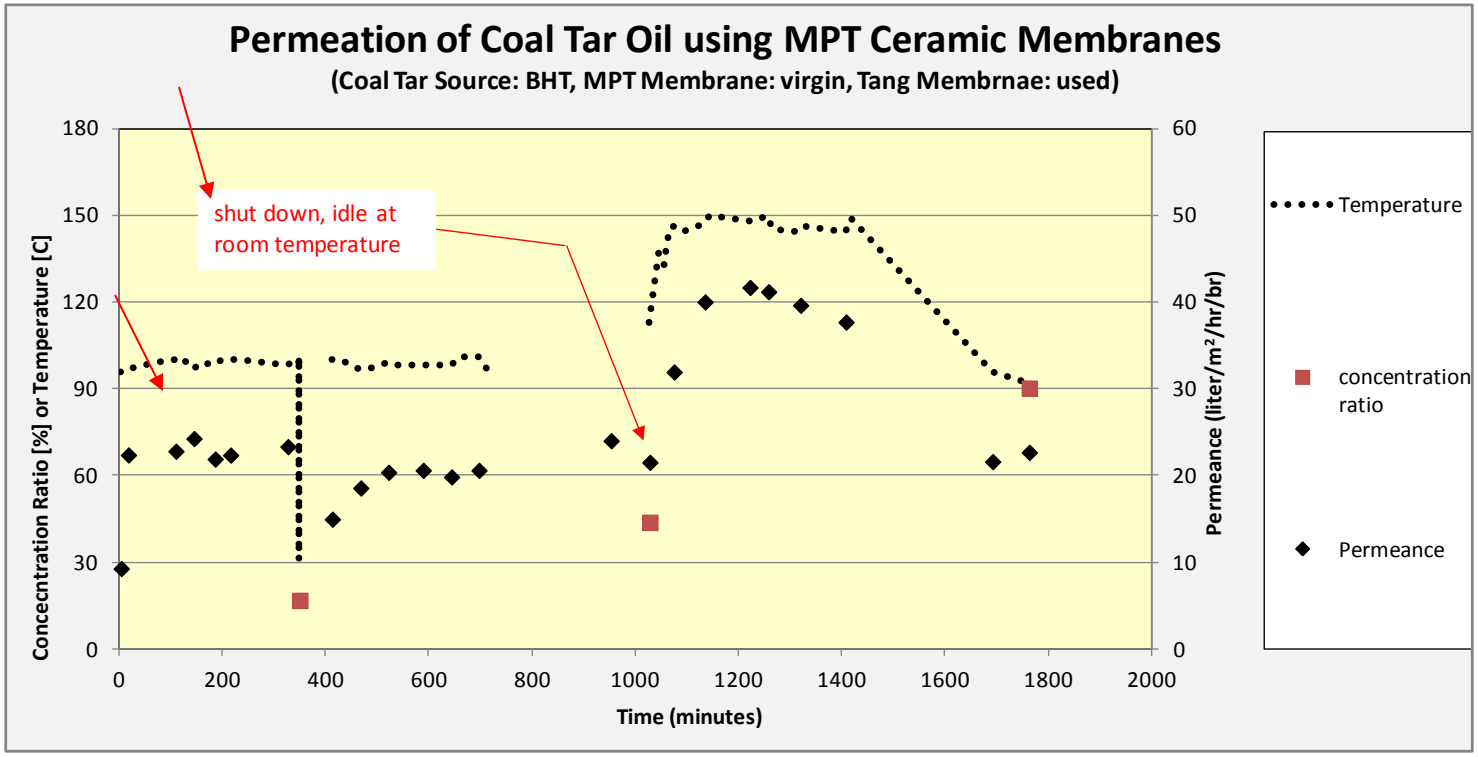
Upgrading Coal Tar Liquid

Membrane Performance and Stability

Upgrading Coal Tar Liquids

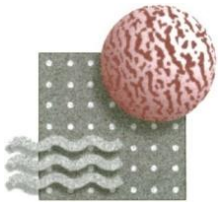
- Coal tar oil was effectively filtered at high temperature.
- Good permeate flux stability demonstrated in lab.
- Remove metal, ash, and microparticulates
- Pretreatment to downstream hydroprocessing

Contaminants	Before	After	Removal [%]
Total Metal (ppm)	62.59	10.9	83
Mechanical Impurities (wt%)	0.061	<0.005	>92
Ash (wt%)	0.034	0.007	79



Solid and mechanical impurities are nearly completely removed.

Commercialization Strategy



Media and Process Technology Inc. (M&P)
1155 William Pitt Way
Pittsburgh, PA 15238 - 1678

Business Partnerships for Commercialization of the Oil Phase Ceramic Membrane Filtration System

Media and Process Tech Inc (MPT)

Phase II Commercialization Partners

Pathway #1
1st Regional Re-refining Center - ComA

ComA is a waste oil collector in the East Coast. ComA will provide facility, and capital while MPT will provide the membranes. As a step one, during Phase II, ComA has provided the feedstock and buyback of the products before its own facility is completed.

Pathway #2
2nd Regional Re-refining Center - ComB

ComB is a waste oil collector in the West Coast. MPT will retrofit its existing facility with our membrane and decolorization technology.

An international ceramic company has committed funding and ceramic production know-how to expand and upgrade our existing ceramic membrane manufacturing facility to support the anticipated increasing demand from the Pathway #1, 2, 3 &4 activities.

Pathway #3
FCC Slurry Upgrading

Pathway #4
Coal Oil Clean-up

A Beijing based refinery engineering company has signed an JV agreement with us to provide the funding and commercialization resources for field test and commercialization of our industrial membrane systems for these two applications.

Commercialization Accomplishments – Phase II

- ***Phase III Commercialization Partner – A Waste Oil Recycle Company (ComA) as Our 1st Regional Operation***

  We have completed the design, construction and test run of a semi-works facility for waste motor oil re-refining based upon the developed industrial ceramic membrane system. Thus far, we have completed a nine month around-the-clock test run, producing 150,000 gallons on-spec products, which were sold to ComA as our Phase III commercialization partner, ComA has begun the planning of its regional re-refining center at its waste oil collection facility.

- ***Phase III Commercialization Partner – A Waste Oil Recycle Company (ComB) as Our 2nd Regional Operation***

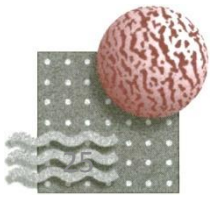
  We have been working with ComB for the 2nd recycle center to retrofit its existing re-refining operation. We anticipate the completion of the facility and beginning the generation of profit from this facility during Phase IIB.

- ***Phase III Commercialization Partner – A Joint Venture Agreement with An Engineering Company familiar with the Petrochemical and Refining Industry in China***

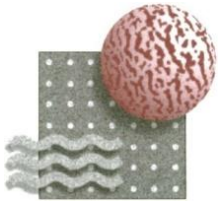
  We have demonstrated the technical and commercial viability for two additional applications based upon our industrial membrane system, including upgrading the refinery fluid catalytic cracking (FCC) slurry oil to become hydrocracking feedstock as opposed to the current use of low quality fuel blend (Pathway #2), and removing solid residue from coal oil produced via liquefaction (Pathway #3). We have established a joint venture agreement with this company to pursue the commercial development for these two and other applications based upon our ceramic membranes. The JV partner has committed the financial and other resources required to commercialize the technology in China.

- ***Phase II Commercialization Partner - An International Ceramic Company as a Membrane Production Partner***

  An internationally well-know high-tech ceramic company has made the commitment to become our manufacturing partner. A total of $1 million investment has been committed thus far to assist us in ceramic membrane manufacturing.

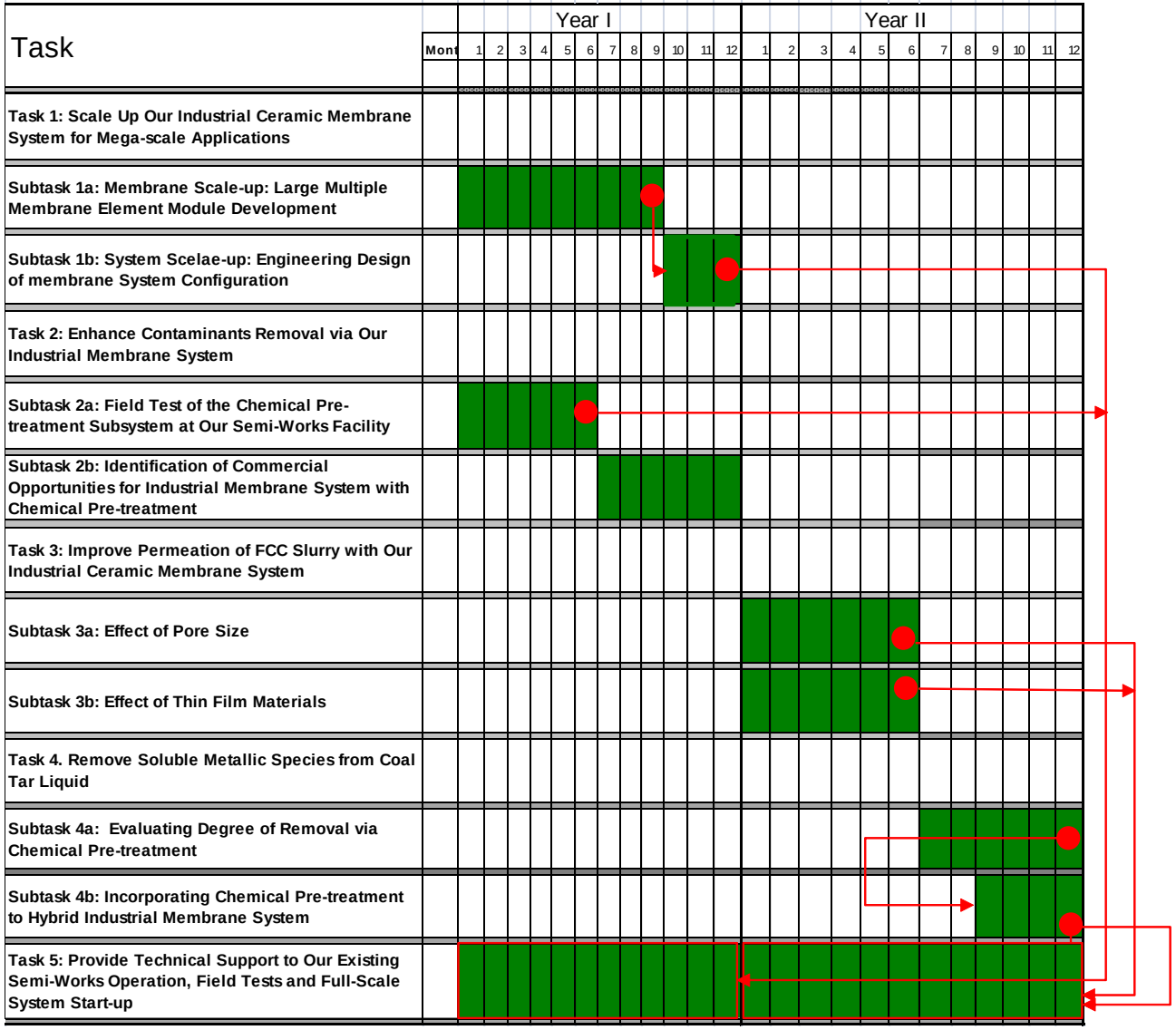


Project Management and Budget

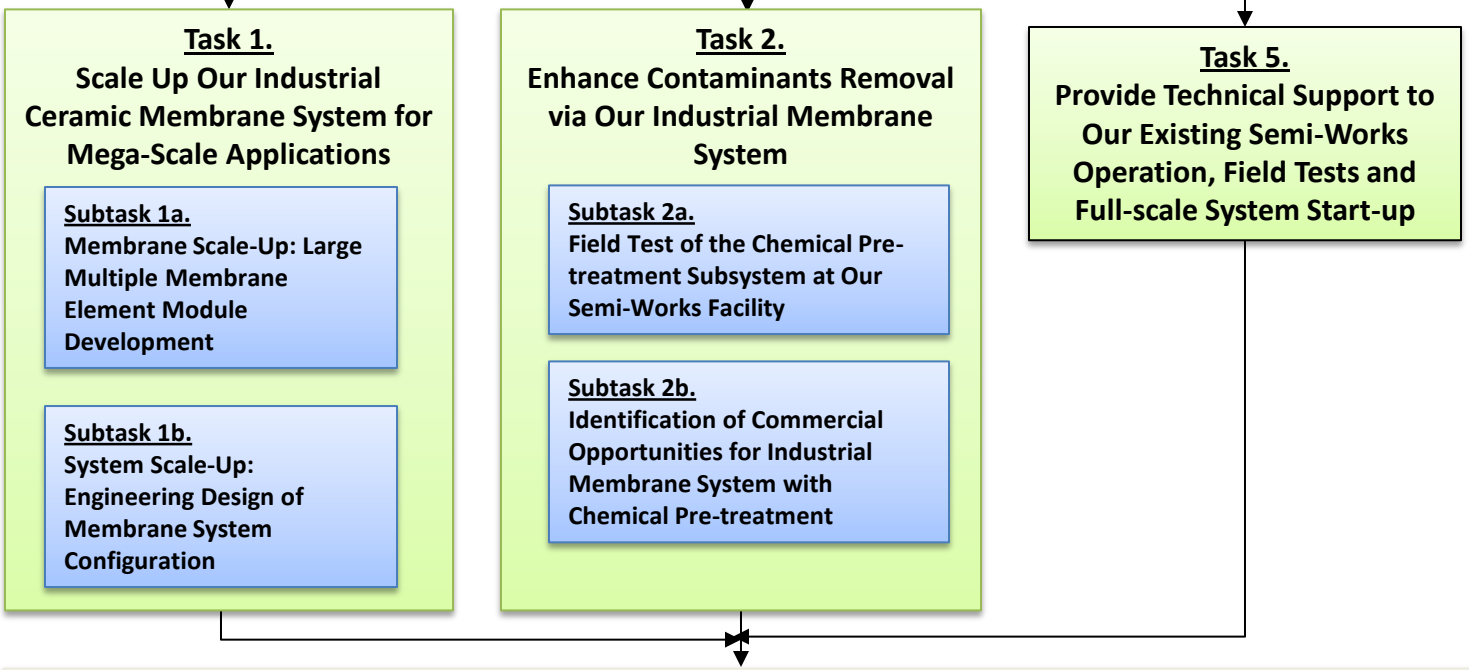


Media and Process Technology Inc. (M&P)
1155 William Pitt Way
Pittsburgh, PA 15238 - 1678

Task Schedule for Proposed Phase IIB



Flow Diagram of Work Plan for Phase IIB (1-12 months)



Deliverables

1. Complete design, construction and testing of (i) high surface area/module ceramic membrane element, and (ii) multiple element module design with built-in permeation channels.
2. Completion of the membrane system design based upon the large multiple membrane element module developed from Task 1.a
3. Development and verification of the chemical subsystem for its integration into our industrial membrane system.
4. Identifying commercial opportunities for our industrial membrane system with the chemical pre-treatment.
5. Maintaining operation of the semi-works used oil re-refining continuously for 12 months.
6. Providing technical support required for ComA to complete the design and construction of the testing systems for FCC slurry upgrading and coal tar oil clean-up.

Flow Diagram of Work Plan for Phase IIB (13-24 months)

Task 3.
Improve Permeation of FCC Slurry with Our Industrial Ceramic Membrane System

- **Subtask 3a.** Effect of Pore Size
- **Subtask 3b.** Effect of Thin Film Materials

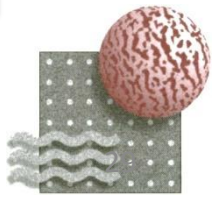
Task 4.
Remove Soluble Metallic Species from Coal Tar Liquid

- **Subtask 4a.** Evaluating Degree of Removal via Chemical Pretreatment
- **Subtask 4b.** Incorporating Chemical Pre-treatment to Hybrid Industrial Membrane System

Task 5.
Provide Technical Support to Our Existing Semi-Works Operation, Field Tests and Full-scale System Start-up

Deliverables

1. Determination of pore size and thin film materials for incorporating into our industrial membrane system for FCC slurry upgrading
2. Achieving >95% removal of soluble metallic specifies present in coal tar liquid.
3. Incorporating the chemical pretreatment into a hybrid industrial membrane system for coal tar oil clean-up
4. Maintaining operation of the semi-works used oil re-refining continuously for 12 months.
5. Providing technical support required for ComA to conduct field testing for FCC slurry upgrading and coal tar oil clean-up.



Project Budget and Duration for DE-SC0006185

SBIR Phase	Funding	Begin	End
I	$115,000	6/17/2011	1/16/2012
II	$1,000,000	8/17/2012	8/16/2015
IIB	$1,000,000	8/17/2015	8/16/2017