



Membrane Separation Unit for Bio-Syngas (American Made Challenges H2 Shot Incubator Prize Voucher Program)

Cooperative Research and Development Final
Report

CRADA Number: CRD-22-23253

NREL Technical Contact: Mou Paul

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Technical Report
NREL/TP-5900-88380
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Cooperative Research and Development Final Report

Report Date: November 30, 2023

In accordance with requirements set forth in the terms of the CRADA agreement, this document is the CRADA final report, including a list of subject inventions, to be forwarded to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement: Green Fortress Engineering, Inc.

CRADA Number: CRD-22-23253

CRADA Title: Membrane Separation Unit for Bio-Syngas (American Made Challenges H2 Shot Incubator Prize Voucher Program)

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Sponsoring DOE Program Office(s):

Office of Energy Efficiency and Renewable Energy (EERE), Hydrogen and Fuel Cell Technologies Office

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	NREL Shared Resources a/k/a Government In-Kind
Year 1	\$50,000.00
Modification #1	\$0.00
TOTALS	\$50,000.00

Executive Summary of CRADA Work:

Evaluate membrane technologies synergistic with high-temperature hydrogen-rich syngas production from biomass to determine the type and integration thereof that is most cost-effective.

CRADA benefit to DOE, Participant, and US Taxpayer:

- Assists laboratory in achieving programmatic scope
- Uses the laboratory’s core competencies

Summary of Research Results:

Indirectly Heated Pyrolytic Gasification (I-HPG) is an all-electric, high-temperature, anoxic process that converts lignocellulosic and hydrocarbon feedstock into a tar-free syngas containing 45% hydrogen by molar volume. Within the Propose! Phase we engineered a solution to extract pure hydrogen for less than one dollar per kilogram. Because the I-HPG process is inherently self-perpetuating, generating surplus electricity, removal of a portion of the hydrogen gas allows this process to operate continuously for as long as feedstock is available. Our team identified a Membrane Separation Unit (MSU) technology, determined the proper scale of operations, and completed a techno-economic analysis. We have identified a straightforward pathway to experimental validation results in the Prove! Phase.

Of three MSU options explored with support from an NREL Senior Scientist, we selected supported silica sol-gel over porous alumina tubes as superior to Pd/Ag metal membranes or carbon mol-sieve technologies. The Center for Advanced Ceramic Technologies at Alfred University (NY) provided a letter of commitment to guide the fabrication of the MSU in the Prove! Phase. Three variants will be built and tested for selectivity and throughput to validate the pore diffusion modeling outlined herein.

The supported all-ceramic MSU, sized for a six-reactor I-HPG system, has been modeled from first principles assuming agricultural residue as feedstock (corn stover). Assuming a cost for feedstock gathering and handling of \$40 per dry ton, with a 35% efficient syngas-to-electricity genset, **the apparatus produces 99.5% pure hydrogen for 78 cents per kilogram.** Carbon emissions are net zero because all CO₂ effluent from the genset is carbon that was already in the atmosphere during the prior growing season. Exempting embedded carbon costs in the system manufacture, the marginal, new carbon emissions are 0.0 g-CO₂ eq/kgH₂. In case of a dry feedstock (< 20%), there is a carbon biochar excess, and the green hydrogen generation process becomes carbon negative.

The proposal work is based on literature review, calculations, modeling, and TEA analysis. If the project goes into next phase, experimental work will be done.

Purpose:

Low-cost “green” hydrogen from biomass can be achieved by gas separation from a patented method of thermochemical conversion called Indirectly Heated Pyrolytic Gasification (I-HPG). The traditional approach is a palladium-copper membrane, but this is expensive. The purpose of this project is to compare Pd-Cu membranes with two emerging technologies that are compatible with higher temperatures. The work will investigate the capacity, packaging, and integration with I-HPG for each of these three methods of membrane separation, and then derive the techno-economic analysis to down-select to the best choice. The figure below shows the Process & Instrumentation Diagram of the I-HPG system and indicates the range of sites where membrane separation units might be advantageously installed to produce a continuous slip stream of purified hydrogen gas.

SCOPE OF STUDY

Membrane
Separation
Unit

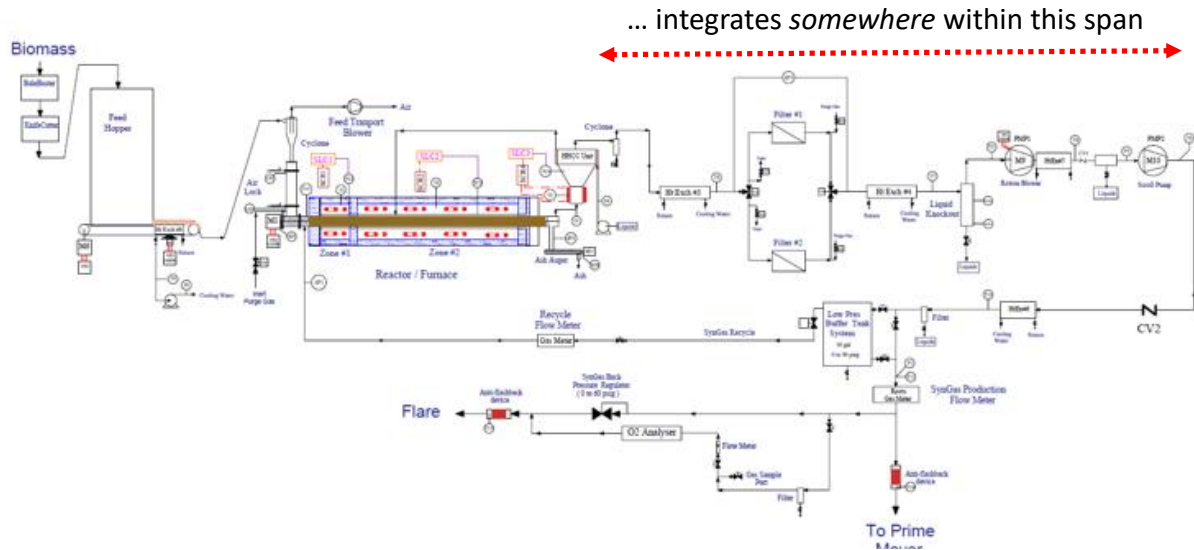


Figure 1. Process & Implementation Diagram of Indirectly-Heated Pyrolytic Gasification (I-HPG)

Statement of Work: Task Descriptions

Task 1

The Participant will provide P&ID diagrams, arrangement drawings, process modeling, experimental data, bill of material, and cost data on the base I-HPG system and establish the scale of production suitable for study.

Task 1 Results:

The participant provided all the necessary diagrams, drawing, modeling, and experimental data that were needed for the study. We had regular meetings where we discussed data and result and created a common folder where we could exchange the information.

Task 2

Contractor will evaluate and quantify flux versus purity for three MSU technologies: Pd-Cu, CMS, and BSCY (or similar).

Task 2 Results:

We have chosen the sol-gel doped SiO₂ on porous alumina tubes [Naito] as our membrane because of high hydrogen permeability, simple fabrication process, adequate selectivity and low cost. MSU designs are shown in figure 2, prepared by an engineering student at IUPUI.

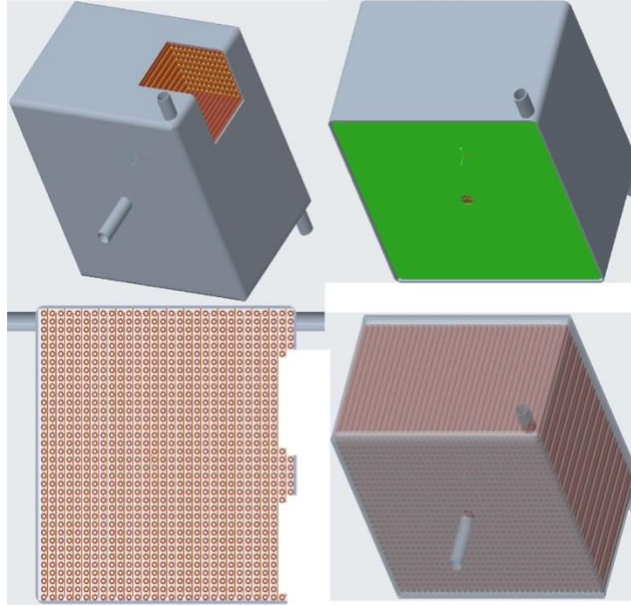


Figure 2. Four views of the Membrane Separation Unit design using microporous silica on hollow porous alumina fibers (red). TL notched view. TR hydrogen manifold in green. BL cross section of hollow fibers. BR translucent perspective.

Sizing for the MSU in fig. 2 is obtained by modeling porous flow as a function of pore size. Knudsen diffusion predicts a H₂:CO selectivity of 118:1 based on the formula below [Costa]. This does not change with temperature or pore size, where D_K is the Knudsen diffusivity, ϵ is the porosity, d_p is the pore diameter, τ is the tortuosity (taken as 1.0), and M is the molecular mass.

$$D_K = \frac{\epsilon d_p}{3\tau} \sqrt{\frac{8RT}{\pi M}}$$

The transition from Knudsen diffusion to the molecular sieving domain, where the physical size of the pore mouth precludes the larger species is not well-defined in the scientific literature. Our team developed a transition formula that modifies Knudsen diffusivity according to:

$$d_p' = \begin{cases} d_p * \left[1 - \left(\frac{md}{d_p} \right)^2 \right] & ; d_p > md \\ 0 & ; d_p \leq md \end{cases}$$

Where d_p' is the adjusted pore diameter in the Knudsen diffusivity, and depends on the ratio of the molecular diameter (md) and the nominal pore diameter d_p . The selectivity of H₂:CO using this new formula now includes a monotonic transition between regimes, and is plotted in figure 3. The region labelled “MOLSIV” is bracketed by the diameter of the CO molecule on the high end, and the diameter of the H₂ molecule on the low end. The selectivity is undefined (0) for pore mouth diameters smaller than the hydrogen gas molecule because such a membrane is impermeable. The target hydrogen purity of 99.5% is obtained at a pore size (d_p) of 0.474 nm. For cubic-packed spheres, this corresponds to a particle diameter of 1.15 nm, a value well within the range possible

with sol-gel deposition [Guizard]. Literature support for this new transition formula between Knudsen and molecular sieve regimes can be found in [Vaezi].

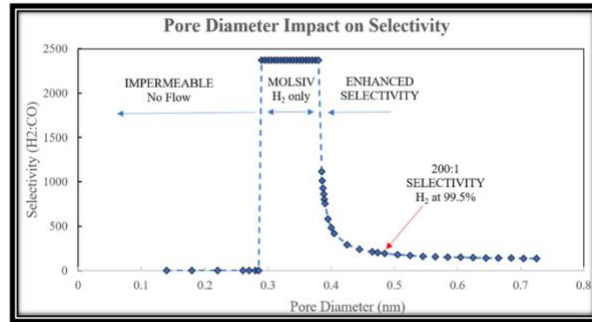


Figure 3. Selectivity of hydrogen to carbon monoxide as a function of pore diameter. Red arrow shows design target for 99.5% pure hydrogen permeate. The values marked “MOLSIV” are artificially capped for visual clarity, but are (theoretically) infinite in this region.

Flux is determined by area of the separation membrane and the pressure differential across it. Manufacturing defects in the membrane can be expected to decrease with membrane thickness. Figure 4 shows our calculations for the relationship. For techno-economic analysis, a thickness of 2.0 microns was used as a baseline.

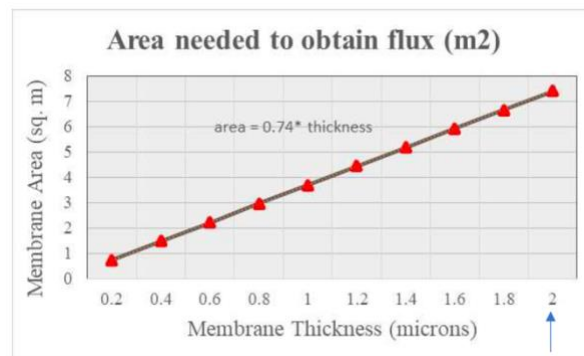


Figure 4. Hydrogen flux is inversely proportional to membrane thickness resulting in this trade space between thickness and membrane area to achieve desired flux.

Task 3

Participant will identify interface and volume requirements and constraints for integration of the MSU at various points in the gas flow, between reactor and delivery point.

Task 3 Results:

Participant identified the interface and volume information required for integration of the MSU in the system. Please refer to Figure 2 for four views of the Membrane Separation Unit design using microporous silica on hollow porous alumina fibers.

Task 4

Contractor and Participant will jointly determine where to integrate each MSU technology within the I-HPG system, and determine the requirements for power, sensors, controls, and packaging (including maintenance or consumables access), taking advantage of high temperature wherever possible.

Task 4 Results:

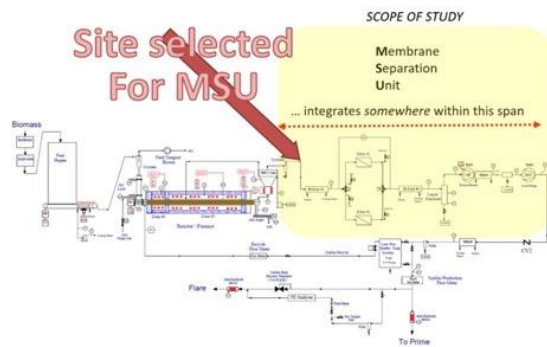


Figure 5. Task 4 of the GFE-NREL CRADA is to select where to integrate the MSU within the I-HPG thermochemical conversion system. Large red arrow indicates the MSU to be installed immediately downstream of the particulate cyclone that follows the afterburner.

Task 5

Participant will develop the TEA framework and identify the specific metrics or costs needed to complete the TEA for the I-HPG that includes a MSU with hydrogen delivered to a suitable end-use or storage facility.

Task 5 Results:

A TEA framework was developed by identifying the metrics and cost needed for the I-HPG with the MSU unit.

Techno-economic analysis assumed the following:

- a) Membrane thickness of 2.0 microns with pore size 0.474 nm
- b) Biomass conversion is all electric and electricity costs for cold start is \$0.1 USD/kWh
- c) A SOFC prime mover converts retentate gas to electricity with efficiency of 70%
- d) The I-HPG gasifier has 6 parallel tubes with 21 tons/day throughput
- e) Feedstock is lignocellulosic (non-food) biomass with 20% moisture
- f) Base CAPEX cost of I-HPG "Six Banger" is \$1.6M

Feedstock costs varied between \$30 and \$80 per ton dry weight delivered to the apparatus. This range assumes agricultural residues (“crop waste”) such as corn stover (stalks, husks, cobs, and leaves), but may also include wood chips or “energy crops” such as *Miscanthus*. Furthermore, these values include labor and equipment usage on-site, and do not envision transport costs by road or rail.

Task 6

Contractor will obtain or develop the financial supporting information on the MSU media, packaging, integration, operations, and maintenance, as will be needed to complete the TEA

Task 6 Results:

In addition to the metrics listed from a to f in task 5, TEA analysis also included the cost of the MSU media which was a ceramic MSU unit.

g) Ceramic MSU cost yielding 185 kg/day hydrogen has a production cost of \$22,956

- a) Integration point is immediately downstream of sintered metal filters
- b) Note that TEA performed on Pd-alloy MSU gave a production cost of \$537k

Figure 6 shows the result, with the baseline feedstock cost of \$40/MT highlighted.

A steady stream of “green” hydrogen is produced at 99.5% purity for \$0.78/kg. Emissions of new carbon are zero (0.0) because the retentate used to self-power the device derived its carbon from extant CO₂ in the atmosphere during the just-completed growing season. This is the definition of carbon neutrality.

Note that for feedstock moisture content below 20% (ref. assumption e. above) there is an excess of pure carbon biochar. Biochar can be tilled into soil to improve productivity, and also sequesters that carbon for millennia. Excess heat from I-HPG can be used to dry incoming feedstock if desired. Operated in this way, our green hydrogen is carbon negative.

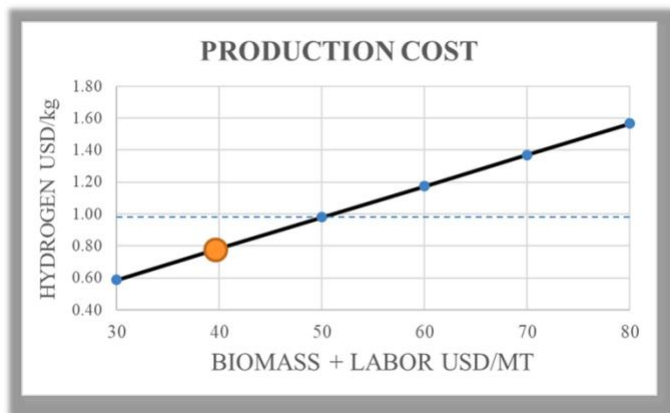


Figure 6. Techno-economic analysis result for “Six-Banger” I-HPG reactor with MSU sized for syngas throughput showing hydrogen cost versus biomass cost. Orange dot shows 0.78 USD/kg for biomass collection with handling cost of 40 USD per dry ton.

Task 7

Participant and Contractor will jointly develop decision metrics and obtain numeric values for each regarding the options for the three MSU technologies integrated with the I-HPG system. Participant and Contractor will jointly develop a ranking and decision-making process to down-select MSU technologies into a 1st and 2nd choice.

Task 7 Results:

We conducted a literature survey on the three different MSU technologies and jointly ranked them based on performance criteria. Below is the summary of our findings.

Membranes for hydrogen separation should have the following characteristics: high selectivity towards hydrogen, high hydrogen permeance, high thermal, mechanical and chemical stability, and low cost. Hydrogen separation membranes may be classified into the following categories: polymeric, porous, dense metal and proton conducting membranes. Table 1 shows a comparison between these different types of membranes [Gallucci].

Table 1
Comparison of membrane types for hydrogen separation (Kluiters, 2004; Liu et al., 2010)

Membrane type	Polymeric	Microporous ceramic	Porous carbon	Dense metallic	Proton conducting dense ceramic
Materials	Polymers: polyimide, cellulose acetate, polysulfone, etc.	Silica, alumina, zirconia, titania, zeolites, metal-organic frameworks (MOF)	Carbon	Palladium alloys	Perovskites (mainly SrCeO _{3-δ} , BaCeO _{3-δ})
Temperature (°C)	< 100	200–600	500–900	300–700	600–900
H ₂ selectivity	Low	5–139	4–20	> 1000	> 1000
H ₂ flux (10 ⁻³ mol m ⁻² s ⁻¹) at ΔP=1 bar	Low	60–300	10–200	60–300	6–80
Transport mechanism	Solution-diffusion	Molecular sieving	Surface diffusion, molecular sieving	Solution-diffusion	Solution-diffusion
Stability issues	Swelling, compaction, mechanical strength	Stability in H ₂ O	Brittle, oxidizing	Phase transition (causes embrittlement)	Stability in CO ₂
Poisoning issues	HCl, SO _x , CO		Strong adsorbing vapors, organics	H ₂ S, HCl, CO	H ₂ S
Cost	Low	Low	Low	Moderate	Low

Out of these different membrane types, our project aims to compare between dense metallic, carbon molecular sieve (CMS), and microporous ceramic membranes.

Dense metallic membranes are attractive candidates for separating hydrogen from a mixture because of their unique ability to produce high purity hydrogen using a single separation step, with low energy penalty, based on a solution-diffusion mechanism. Dense membranes made from palladium or palladium alloys [Habib, Conde] have been investigated thoroughly for hydrogen transport and separation. One limitation of these membranes is low hydrogen permeance resulting from the lack of physical porosity. Another major drawback of palladium-based membranes is the susceptibility to poisoning such as sulfur poisoning produced by H₂S, and also CO poisoning. For our proposal, CO poisoning can be detrimental as our feed composition consists of 45% CO. Moreover, even though Pd based technology had been commercially available since the early 1960's, they are expensive and are limited to operating temperatures below ≈600°C. Based on these drawbacks, dense metallic membranes were not selected for our proposal.

Inorganic microporous membranes including silica, zeolites, carbon molecular sieve (CMS) and graphene/graphene oxide membranes have been intensively investigated for hydrogen separation because of their thermal and chemical stability advantages [Meulenberg, Meha, Koros, Linfeng, Khalid, Cristina, Jeeban, Nirikazu, Alkudhiri].

Carbon molecular sieve (CMS) membranes have emerged as an exciting new class of materials that has angstrom-scale pores but very high gas permeability thus combining high gas permeability with high selectivity [Jones] and has demonstrated good technical readiness [Touma]. In addition to its outstanding selectivity and permeability, the stability of CMS membranes in harsh environments (e.g., high temperatures, chemicals) often cause problems with polymeric membranes [Rezazakemi] and makes it a promising membrane candidate [Parsley]. Depending on the polymer precursor, pyrolysis conditions and membrane form, a range of hydrogen permeabilities and selectivity values of different gas mixtures have been reported [Briceño], though it is rare to find out CMS membrane selectivity for a H₂:CO mixture. However, it is challenging to develop ultrathin and defect-free CMS membranes with pore sizes suitable to separate H₂-CO gas pairs. Based on these shortcomings, CMS membranes were not selected for our proposal.

Hydrophobic DDR-type zeolites display excellent hydrothermal stability but suffer from narrow selectivity for smallest gas molecules as the pore size is about 0.4 nm. Additionally, they are prone to defects and hence difficult to scale up for industrial application. In contrast, graphene-based membranes show excellent selectivity for hydrogen separation, but have low H₂ permeance (10⁻⁹ to 10⁻⁸ mol m⁻² s⁻¹ Pa⁻¹) to become commercially attractive [Van Gestel, Ibrahim]. Moreover, the synthesis procedure is complex and membrane material is costly.

Silica membranes are the most attractive material among different microporous membranes as they can be easily fabricated as ultra-microporous thin layers compared to other metal oxides such as alumina, zirconia or titania. Silica, formed of irregular Si–O–Si rings has an effective size of about 0.3 nm. This is suitable for separation of H₂ (0.29 nm) through molecular sieving mechanism. Sol-gel [Tsuru 2008, Tsuru 2011] and chemical vapor deposition (CVD) [Nagano 2018] are the most widely used technologies for fabrication of silica layers on porous substrates. The CVD technique can produce highly selective silica membranes with pore diameters less than 1 nm, but have relatively low H₂ permeability and require substantial capital and complicated fabrication process. In contrast, sol-gel process produces membranes with higher H₂ permeability. Even though the selectivity can be lower compared to CVD derived membranes, there is opportunity to explore and control the pore sizes through much easier and less complicated sol-gel process. One of the limitations of this membrane, is its poor hydrothermal stability [Nagano 2014]. Different approaches such as doping of silica with inorganic oxides [Kanezashi 2006] (e.g., alumina, zirconia, or titania) and hybrid inorganic organic silica membranes [Duke, Kanezashi 2009] have shown promise to improve the hydrothermal stability.

We have chosen the sol-gel doped SiO₂ on porous alumina tubes [Naito] as our membrane because of high hydrogen permeability, simple fabrication process, adequate selectivity and low cost.

A safe and effective laboratory-scale demonstration with the ceramic based MSU will include the following steps:

1. Procure a syngas mixture from an industrial gas supplier such as Linde that replicates gas analysis composition analyzed previously from Argonne National Laboratory. In addition to the 45% hydrogen and 45% carbon monoxide, the remainder gas will be 5% CO₂ and 5% N₂. Gas cylinders will be secured in Schubert's chemistry lab (ET 116) on the IUPUI campus (Indianapolis). This lab includes hydrogen gas (with dedicated wall-mounted sensor), and chemicals such as HF, HNO₃, HCl plus solvents, and includes high temperature processing equipment (750 C). The most recent audit by campus Environmental Health and Safety resulted in an A+ safety rating ('no issues identified').
2. Prototype MSUs prepared by Albert University's Center for Advanced Ceramic Technology will be installed inside an explosion-proof box placed within a 4-foot fume hood in the ET 116 lab and heated to the process temperature, then fed with the syngas mixture at a regulated pressure. Prior work in this same fume hood has included hydrogen at 8 bar.
3. A gas sampling apparatus will be pre-filled with helium gas, then affixed to the permeate port of the MSU and operated for a sufficient time to reach steady state. A mass flow meter will measure the flux of permeate. The gas will be captured and tested to determine the selectivity. This will be repeated three times per MSU sample (for error estimation), with three MSU pore sizes, for a minimum of nine test runs.

Task 8

The Contractor will prepare a CRADA Final Report: Preparation and submission in accordance with the terms of this agreement.

Task 8 Results:

This report serves to meet the requirement for the CRADA Final Report with preparation and submission in accordance with the agreement's Article X.

Task 9

Other work at the direction of the Participant, consistent with the scope and subject to the availability of funds may include:

- *The Contractor may perform testing on the two emerging MSU technologies listed above in order to provide greater accuracy to **Task 2** above.*

It was agreed between the participant and the contractor that this was a stretched goal and was contingent on receiving more funds. We haven't received any extra funds, and this task was not performed.

Subject Inventions Listing: None

ROI #: None