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DISCLAIMER

ABSTRACT

Gas Technology Institute is developing a novel concept of membrane gasifier for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal synthesis gases. The objective of this project is to determine the technical and economic feasibility of this concept by screening, testing and identifying the potential candidate membranes under high temperature, high pressure, and harsh environments of the coal gasification conditions. The best performing membranes will be selected for preliminary reactor design and cost estimates.

To evaluate the candidate membrane performance under the gasification conditions, a high temperature/high pressure hydrogen permeation unit will be constructed in this project. During this reporting period, the design of this unit was completed. The unit will be capable of operating at temperatures up to 1100^{o}C and pressures to 60 atm for evaluation of ceramic membranes such as mixed ionic conducting membrane. The membranes to be tested will be in disc form with a diameter of about 3 cm. By operating at higher temperatures and higher hydrogen partial pressures, we expect to demonstrate commercially relevant hydrogen flux, 10~50 cc/min/cm^{2}, from the membranes made of the perovskite type of ceramic material. The construction of the unit is planned to be completed by the end of the next reporting period.

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INTRODUCTION

The objective of this project is to develop a novel membrane reactor for high efficiency, clean and low cost production of hydrogen from coal. The concept incorporates a hydrogen-selective membrane within a gasification reactor for direct extraction of hydrogen from coal synthesis gases. This concept has the potential of significantly increasing the thermal efficiency of producing hydrogen and simplifying the processing steps thus reducing the cost of hydrogen production from coal. The specific objective of the project is to determine the technical and economic feasibility of using the membrane reactor to produce hydrogen from coal. GTI and our project team (University of Cincinnati, University of Florida and American Electric Power (AEP)) have identified and will evaluate potential membranes (ceramic and metal) suitable for high temperature, high pressure, and harsh coal gas environments. The best performing membranes will be selected for preliminary reactor design and cost estimates. The overall economics of hydrogen production from this new process will be assessed and compared with other hydrogen production technologies from coal.

Our approach to the membrane material screening and testing is to first identify the materials that have good thermal stability under the condition of the gasification temperature. The candidate membranes will be evaluated for their hydrogen flux in a laboratory permeation unit. The obtained data will provide the basis for a preliminary membrane gasifier design, process development and economic analysis. In the next stage of material screening, chemical stability of the membranes with the syngas and its contaminants generated from the coal gasification will be evaluated. When a suitable membrane material is selected, large scale membrane manufacturing, engineering design, membrane gasifier scale up will be addressed as shown in the roadmap (Figure 1).

The ceramic membrane of the perovskite type has been identified as one of the good candidate membrane for the applications in the gasification area. This material possesses a unique property of conducting both proton and electron at high temperatures, 700~1100^{o}C, under a pressure gradient of hydrogen. The hydrogen permeation property of the perovskite has been discovered since the early 1980s[1]. Significant progress has been made recently in improving the material's electronic conductivity by doping selective metal components or incorporating a separate metallic phase into the ceramic structure [2~8]. Literature review conducted in this area shows that the typical hydrogen flux across the perovskite membrane is approximately 0.05~0.1 cc/min/cm^2 in the temperature range of 600~900^{o}C at a hydrogen partial pressure across the membrane less than 1 atm with a membrane thickness about 1 mm. Higher flux has also been reported with thinner membrane. Table 1 lists typical hydrogen fluxes reported by several research groups. However, very few data were reported for temperatures higher than 900^{o}C and pressures higher than 1 atm. As coal gasification for hydrogen production takes place at temperatures above 900^{o}C and pressures above 20 atm, it is critically important to evaluate the hydrogen flux of the candidate membrane materials under these operation conditions. To this end, a high pressure/high temperature permeation unit needs to be constructed.

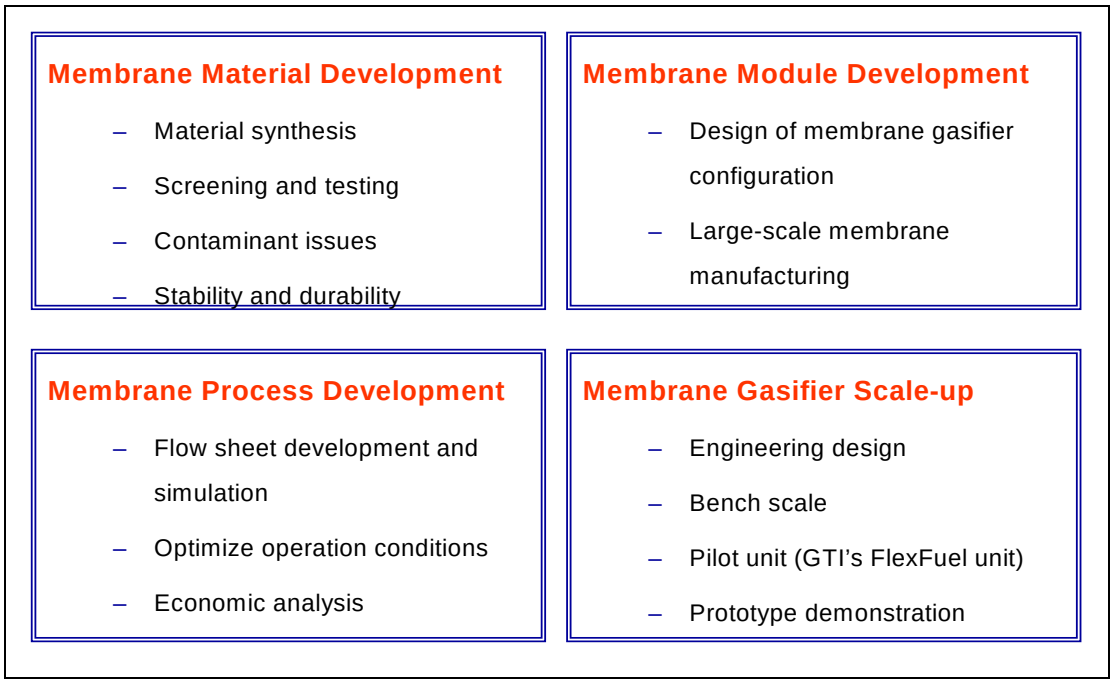

Figure 1. Roadmap for successful membrane gasifier development

During this reporting period, design of a high pressure/high temperature permeation unit was completed. The unit will be capable of operating at temperatures and pressures up to 1100°C and 60 atm respectively. The unit will allow screening and testing of the membrane materials at more realistic gasification temperature and pressure conditions. Furthermore, it will be able to demonstrate much higher hydrogen flux from the membranes than what have been reported in the literature. It is anticipated that the hydrogen flux in the order of 10 to 50 cc/min/cm^2 can be achieved with the perovskite membrane under the gasification temperature and pressure conditions.

Table 1. Comparison of Hydrogen Flux from Various Membranes.

	Flux, cc/min/cm^2	Temp, °C	Pressure*, atm	Thickness, mm	Membrane Material
Roark et al.[2]	1.8	950	1	0.43	cermet
Guan et al.[3]	.072	800	1	1.1	$SrCe_{0.95}Y_{0.05}O_{3-\alpha}$
Balachandran et al.[4]	20	900	1	0.04	cermet
Hamakawa et al.[5]	1.3	680	0.4	0.002	$SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$
Qi and Lin[6]	.04	900	0.1	1.6	$SrCe_{0.95}Tm_{0.05}O_{3-\alpha}$
Hamakawa, et. al.[7]	.056	900	.05	1	$SrCe_{0.95}Tm_{0.05}O_{3-\alpha}$
Wachsman et al.[8]	.05	600	.04	2	$BaCe_{0.85}Gd_{0.15}O_{3-\alpha}$
Wachsman et al.[8]	.42	600	.04	2	$BaCe_{0.85}Eu_{0.15}O_{3-\alpha}$

*Note: hydrogen partial pressure at the feed side.

EXECUTIVE SUMMARY

The gas permeation flux through a membrane generally is measured at room temperature under a certain pressure differential across the membrane as in the case of polymeric membranes. For high temperature membranes such as ceramic membranes, the flux is generally measured at ambient pressure with a sweeping gas on the other side of the membrane to remove the permeate so a partial pressure gradient can be established. There has not been much data from high temperature (to 1000^{o}C) and high pressure (to 60 atm) permeation units in the literature. Consequently, the hydrogen flux from the high temperature ceramic membranes, which are ideal for the membrane gasifier application, is lower than other low or medium temperature membranes such as the Palladium membrane. As coal gasification for hydrogen production takes place at temperatures above 900^{o}C and pressures above 20 atm, it is critically important to evaluate the hydrogen flux of the candidate membrane materials under these operation conditions.

The design challenge for the high pressure/high temperature permeation unit is mainly in the membrane sealing and the materials of construction for the cell. The high pressure sealing issue can be addressed by using a sweeping gas as mentioned earlier. Proper sealing between the ceramic membrane and its supporting tube at high temperatures remains a challenge, due to the different thermal expansion coefficients for the sealing material and the membrane. Pressure rating for the materials of construction can be reduced if the pressures are balanced between the inside and the outside of the permeation cell, as in the current design for this project.

We have completed a design for a high temperature/high pressure permeation unit for measuring hydrogen flux through the high temperature ceramic membranes. The unit was designed to operate at temperatures up to 1100^{o}C and pressures to 60 atm for evaluation of disc membranes with a diameter of about 3 cm. The permeation assembly consists of a tubular permeation cell, a surrounding cylindrical heater, and an enclosing pressure vessel. A simplified schematic illustrating the concept of the permeation cell design is shown in Figure 2. The membrane to be tested will be attached or cemented to a holding tube. A hydrogen gas flowing through an inner tube will be in contact with the membrane and exit the system as a non-permeate gas diverted by an outer tube. An inert sweeping gas passing through another inner tube is used to sweep the hydrogen permeate from the membrane. Therefore, the pressure differential across the membrane will be insignificant, which would make the membrane sealing less difficult.

The hydrogen content of the permeate will be analyzed by a GC to determine the hydrogen flux through the membrane. The inner tube, outer tube and the membrane holding tube will be made of Inconel material for its good resistance to heat and easy machining and welding. The entire permeation cell assembly will be heated by a cylindrical heater, which will be enclosed in a pressure vessel purged with inert gas.

A GTI internal meeting was held to review the design and the safety aspect of the high pressure permeation unit. Consultant meetings were also held to discuss the potential candidate membranes and the design of the permeation unit. Construction of the unit is expected to be completed by the end of the next reporting period.

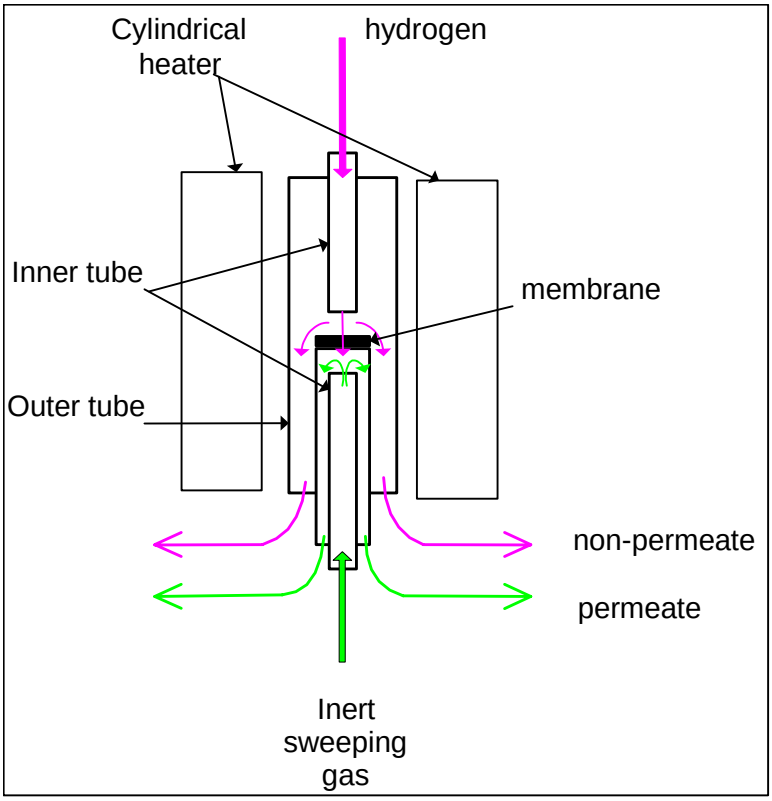

Figure 2. Simplified schematic for the membrane assembly

EXPERIMENTAL

The major process design parameters are listed below:

Membrane : ceramic or metallic membranes, ~3 cm diameter
Maximum Temperature: 1100^{o}C
Maximum Pressure: 60 atm
Maximum Hydrogen partial pressure: 24 atm (feed side)
Maximum hydrogen feed flow: 5 slpm
Sweeping gas (nitrogen) flow: 2 slpm
Target hydrogen flux: 50 cc/min/cm2
Permeate side hydrogen composition: less than 20%

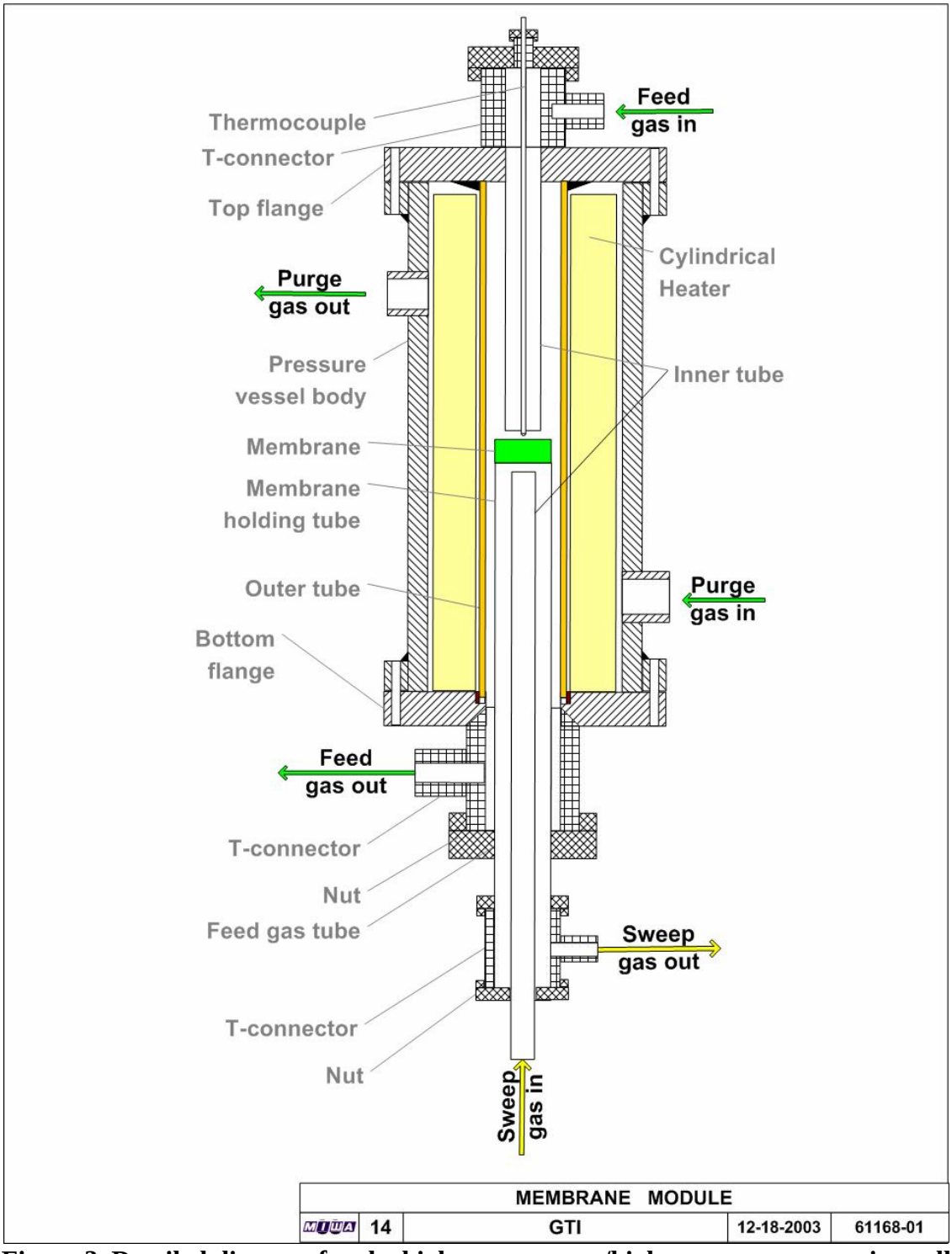

Figure 3. Detailed diagram for the high temperature/high pressure permeation cell

Figure 3 is a detailed diagram of the membrane cell assembly. The pressure vessel body will be made of 316 stainless steel, 5" schedule 80 pipe. The cylindrical ceramic heater, 11.7 cm O.D. and 5.1 cm I.D., will be made by Internal Ceramics & Heating System,

with the temperature of the heating element up to 1200°C. The membrane temperature is, therefore, expected to reach 1100 to 1150°C range. The cold side or the outer diameter of the cylindrical heater will be in the range of 200 to 250°C, according to the vendor. It is important to maintain the pressure vessel and its flanges below 300°C so that they can withstand a pressure of 60 atm. The heater and the vessel will be about 61 cm (2 feet) long. The hydrogen feed flow rate will be much higher than the expected flux through the membrane so that the hydrogen compositions at the vicinity of the membrane can be maintained constant.

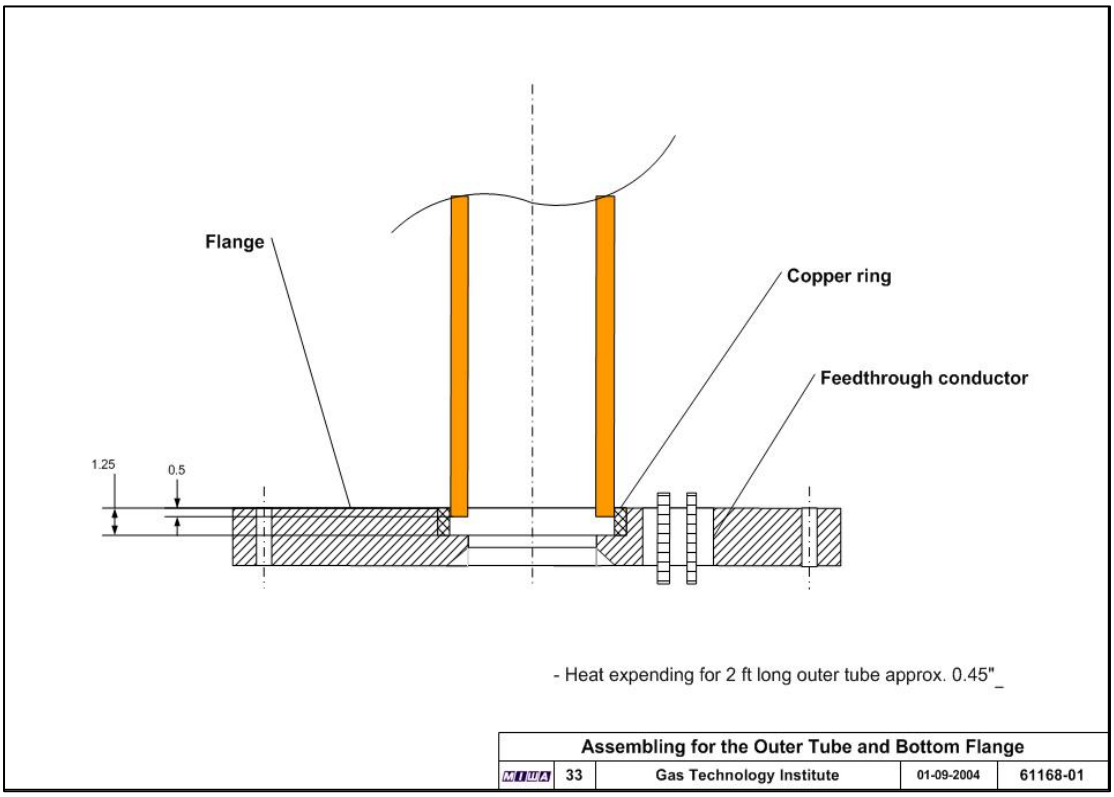

Figure 4. Assembly of the outer tube and bottom flange

The hydrogen-containing feed gas will enter the permeation cell through a tee connector at the top of the vessel. The hydrogen feed gas after entering the vessel will be heated by one of the inner tune above the membrane. The membrane will be attached to a holding tube by high temperature sealing materials such as ceramics, glass. The sweeping gas will enter the vessel from the bottom of the vessel and be heated by the inner tube below the membrane. The permeate hydrogen will be removed by the sweeping gas and exit from the bottom of the vessel. The membrane cell section will be separated from the heater by an outer tube, which will also prevent the hydrogen feed gas from entering the heater section. One end of the outer tube will be welded to the top flange while the other end will be allowed to expand when heated up. Figure 4 shows the details of the outer tube attached to the bottom flange by a copper O-ring, which will provide sealing when it is thermally expanded. Also shown in Figure 4 is a feedthrough opening at the bottom

flange for the connector of the electrical wires of the heater. A thermocouple will be installed vertically close to the membrane to measure the cell temperature.

The entire flow diagram for the high temperature/high pressure permeation unit is shown in Figure 5. All gas flows will be measured and controlled by Brooks mass flow controllers. Although there are three gas inlets into the vessel, feed, purge and sweep gases, all three gas streams eventually will vent out of the system through a back pressure regulator, which would control the system pressure and maintain the same pressure for all three gas streams. Steam generators will be added for both feed and sweep sides to study the effect of steam on hydrogen permeation performance. The gases will also be preheated by the heating tapes wrapped around the tubing before entering into the vessels. Two pressure relief valves will be installed on the hydrogen feed line and the vessel purge gas line respectively. Heater temperature control (TIC-004) will be provided by the vendor. The temperatures on the vessel body, the top and the bottom flanges (TI005-007) will also be monitored to ensure no overheating. The hot exhaust gases, both permeate and non-permeate, from the vessel will be cooled down by water coolers before venting out of the system. A fraction of the permeate gas will be diverted to a GC for analysis of its hydrogen content.

The major operating procedures of this permeation unit are summarized below:

1. Open the purge gas for the vessel, line SS316-003 and SS316-008
2. Open the sweeping gas flow, line SS316-002 and SS316-006
3. Open the inert gas of the feed side, line 316-001 and SS316-007
4. Open the water flow for the water coolers
5. Turn the heaters on, TIC-001, TIC-002 and TIC-004
6. Raise system pressure by adjusting Back Pressure Regulator (BPR).
7. Open the hydrogen feed gas via the bypass line, SS316-004.
8. Adjust the system temperature and pressure to the desired values.
9. Throttle valve nv-6 at the outlet of the vessel purge gas to ensure its pressure slightly higher than the feed gas by monitoring DPT-001.
10. Switch the hydrogen feed gas to the membrane cell, SS316-001.
11. The experiment is finished when the hydrogen composition in the permeate gas becomes constant as verified by GC analysis of the gas.

A location in one of the GTI laboratories has been identified and is being prepared for the construction of the high pressure permeation unit. Additional power was added to the area to accommodate the high temperature heater electrical requirements. A meeting was held to review the overall design and safety of the high pressure permeation unit.

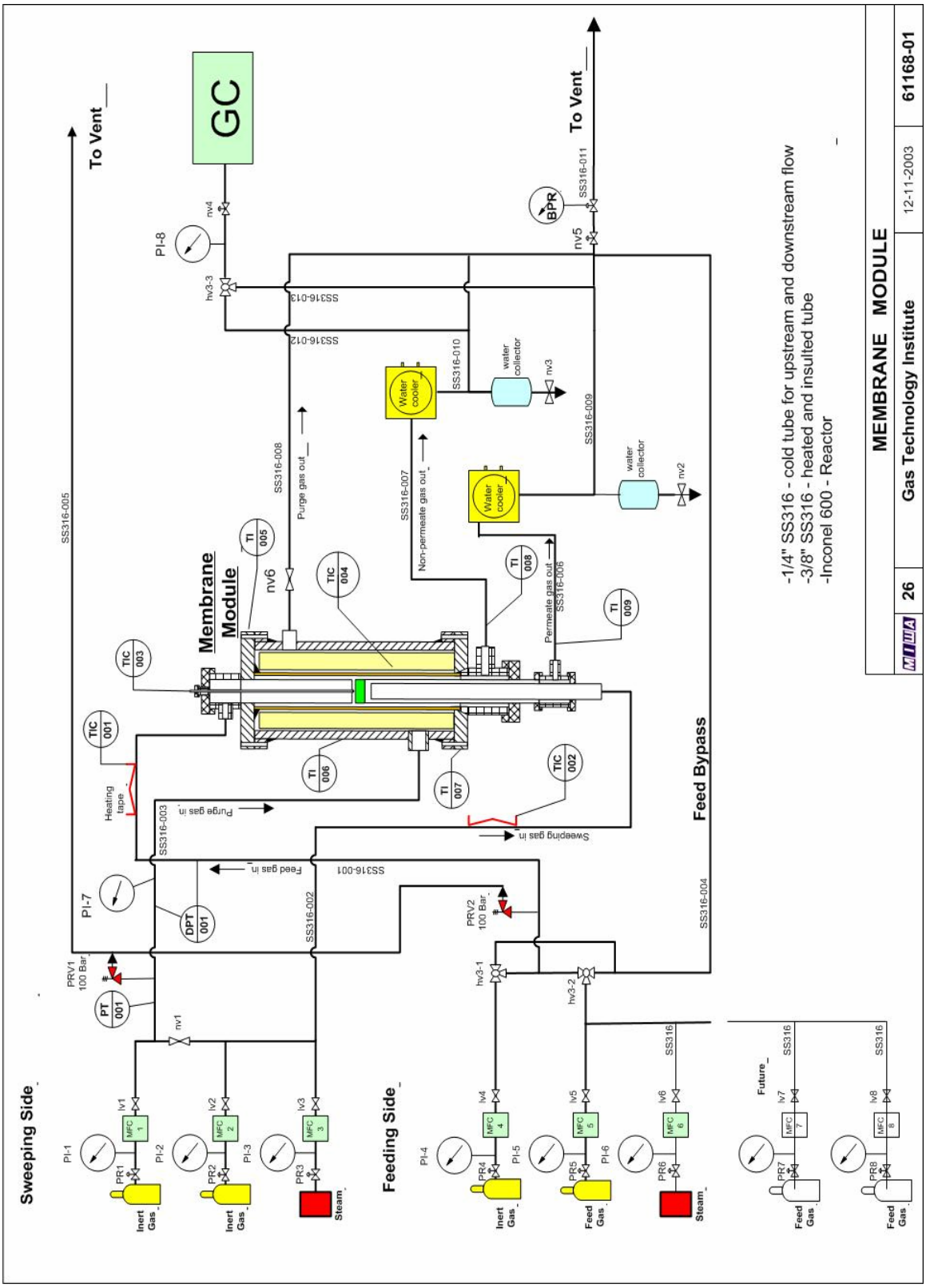

Figure 5. Flow diagram for the high temperature/high pressure permeation unit

RESULTS AND DISCUSSION

No experimental data have been collected during this reporting period.

OTHER ACTIVITIES

A consultant meeting was held with Dr. Jerry Lin of University of Cincinnati on December 5. A second consultant meeting was held with Dr. Wachsman of University of Florida on December 22. In addition to discussion on the current state-of-the-art in the area of high temperature hydrogen membrane materials, the high pressure permeation unit was also reviewed by both consultants. They provided especially useful information for the membrane sealing issues based on their past experience. Both consultants will also provide perovskite membrane materials for GTI to evaluate, initially for the purpose of calibrating the permeation unit and establishing a baseline for the hydrogen flux. GTI will also evaluate certain in-house membrane materials prepared under a separate project funded by Illinois Clean Coal Institute.

CONCLUSION

The design of the high pressure/high temperature permeation unit was completed. The unit will allow screening and testing of the membrane materials at the coal gasification temperature and pressure conditions up to 1100^{o}C and 60 atm respectively. The hydrogen flux that will be obtained from this unit will provide meaningful and realistic basis for the membrane gasifier design and economic analysis. This is a first step that is critically important for the successful development of the membrane gasifier technology.

PLAN FOR NEXT QUARTER

Construction for the high pressure/high temperature unit will be completed. The unit will be commissioned and ready for the membrane testing. Modeling work for the membrane gasifier will also begin by reviewing the reaction kinetics information for the chemical reactions in the gasifier.

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