

DIRECT HYDROGEN PRODUCTION FROM BIOMASS GASIFIER USING H₂ SELECTIVE MEMBRANE

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1. Introduction

Biomass represents an abundant and renewable feedstock that can be converted into a gaseous mixture of hydrogen, carbon monoxide, carbon dioxide, methane and other products by applying heat under pressure in the presence of steam and a controlled amount of oxygen. Adsorbers or hydrogen selective membranes can separate the hydrogen from the gas stream. The produced hydrogen can be sent directly to a fuel cell for highly efficient and environmentally clean power generation. Biomass offers a secure and self-sufficient way of electricity generation via gasification due to its renewable nature. However, the cost of hydrogen from biomass based on the current technologies is still uneconomical. There is a great need to develop a more efficient process to reduce the cost of hydrogen from biomass, if biomass is to become an economic and viable source of hydrogen.

An important challenge to realize the highly efficient and renewable energy production from the biomass gasification/fuel cell combination is clean, efficient and low cost hydrogen production from biomass. Biomass gasification is perceived as a means of central production of hydrogen. However, due to the distributed nature of the biomass resources, the size of these systems will be smaller than the current steam reformers from natural gas or future hydrogen plants from coal. The economy of scale makes the current hydrogen production technologies from biomass uneconomical. Biomass has the potential to accelerate the realization of hydrogen as a major fuel of the future. Since biomass is renewable and consumes atmospheric CO₂ during growth, it can have a positive impact on greenhouse gas emissions compared to fossil fuels.

GTI in collaboration with Natural Resources Research Institute (NRRI), Coleraine Minerals Research Laboratory has demonstrated a low cost, highly efficient hydrogen production process from biomass gasification using a hydrogen-selective membrane. This was accomplished through the following tasks:

- Task 1. Identify and select the candidate membrane
- Task 2. Construct a hydrogen permeation cell unit
- Task 3. Install, instrument and shake down a down draft biomass gasification unit
- Task 4. Test the hydrogen permeation unit under simulated gas conditions

Task 5. Integrated testing of hydrogen permeation unit and the down draft biomass gasifier

2. Project Overview

Biomass as an energy source has several important advantages. Renewability and an infinite list of plant, byproducts, and waste materials that can be used as feedstock are very attractive features. Also, biomass consumes atmospheric CO₂ during growth and therefore may have no net generation of CO₂ through a life cycle analysis and, therefore no negative impact on global warming due to greenhouse gas generation.

The syngas generated from biomass gasification is usually converted to power and heat via Integrated Gasification Combined Cycle (IGCC) for larger plants or Reciprocating Internal Combustion Engine (RICE) for smaller units. Combination of gasification processes with advanced technologies such as fuel cells may produce electricity with no pollution. In the future, advanced fuel cell technologies may be combined with biomass gasification technologies to produce electricity very efficiently with virtually no pollution.

Fuel cells are considered as promising options because their efficiency is generally higher (between 40 and 75%) than present conversion technologies. A fuel cell uses hydrogen as the main fuel source. One scenario for the fuel cells to operate with biomass as the energy source is to use the hydrogen produced from the proposed membrane gasifier to generate electricity. If the hydrogen produced from biomass is clean and of high purity, a Proton Exchange Membrane (PEM) fuel cell can be integrated directly with the biomass gasification process for electricity generation, as shown in Figure 1. The PEM fuel cell typically requires a hydrogen fuel with CO content less than 3 ppm. The hydrogen produced from biomass gasification must be free of CO and other contaminants. The hydrogen produced from the proposed membrane gasifier concept can meet this stringent requirement because the membrane materials identified for its application are 100% selective to hydrogen.

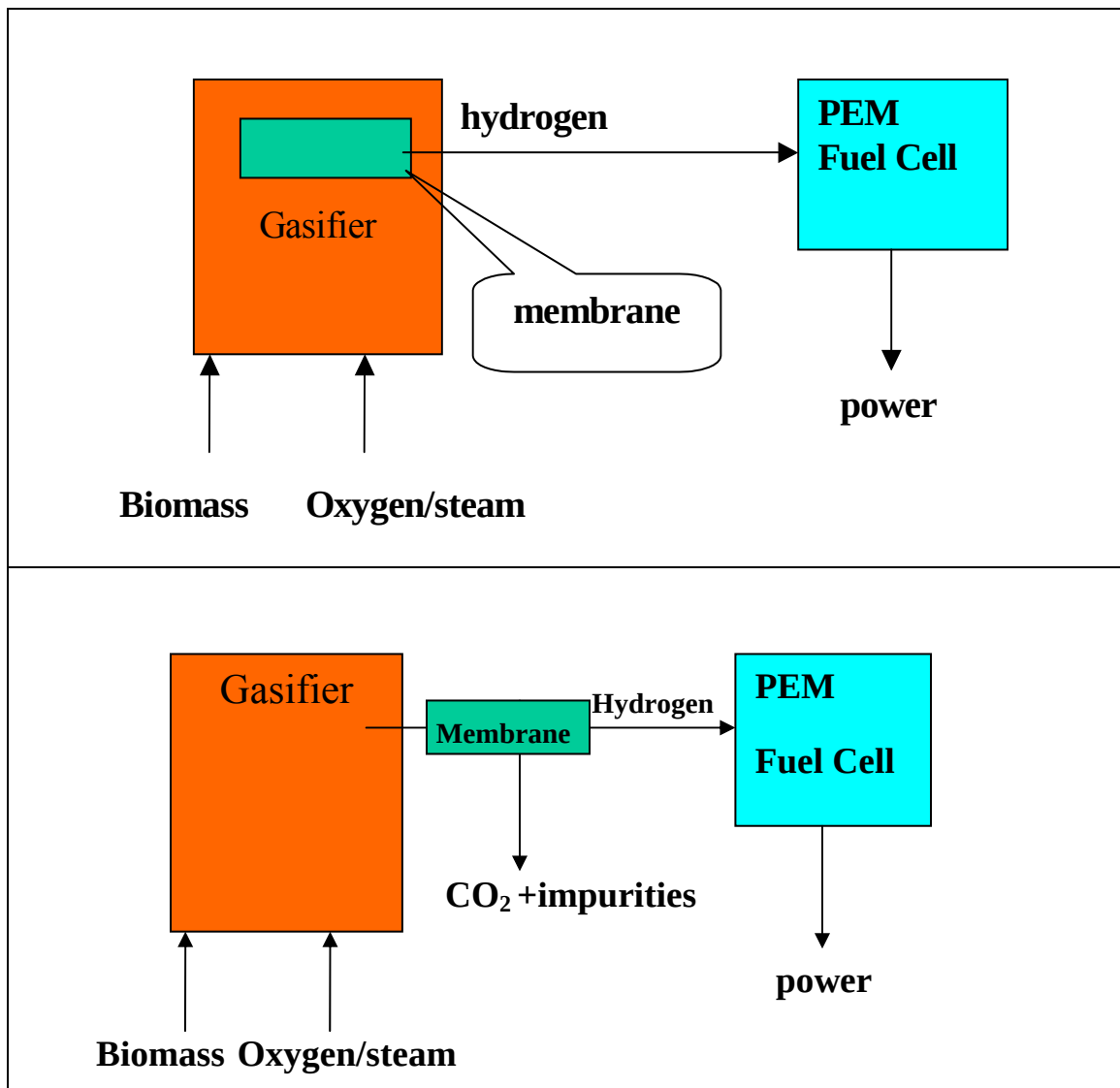


Figure 1. Biomass Gasifier with Internal Membrane or Close-Coupled Integrated with PEM Fuel Cell

Biomass is first converted to syngas by reacting with oxygen and steam in a gasification reactor at elevated temperature, 500~1200° C, and pressures ranging from 1 to 100 atm. The produced syngas from the gasifier must go through a series of processing steps such as cleaning, reforming, shifting, cooling, and separation before a purified hydrogen stream is produced. A cost breakdown for a typical hydrogen biomass gasification process is approximately 25% from the biomass feedstock, 50% from capital cost, and 25% from operation and maintenance. Major capital equipment components are 15% for biomass feed handling, 20% for gasifier, 20% for air separation, 20% for the reformer, shift reactor and hydrogen separation, and 25% for the balance of the plant. Therefore, a technology that can increase the hydrogen production efficiency from the biomass can reduce the cost of the biomass feedstock and its handling since less feedstock is consumed for the same quantity of hydrogen product. The gasifier size and its associated costs will also be lower. If hydrogen can be produced from the gasifier directly such as through the proposed membrane gasifier concept, all the downstream process steps can be reduced or eliminated, resulting in an additional 20% decrease in capital and a significant reduction in operating costs.

The ultimate concept envisioned by GTI incorporates a hydrogen-selective membrane within a gasifier for direct extraction of hydrogen from biomass synthesis gases. As more than 50~60% of the final hydrogen product is generated in the gasification stage, there is great potential of maximizing hydrogen production by separating this hydrogen directly from the gasifier. By incorporating a hydrogen-selective membrane into a gasification reactor, both gasification reactions and hydrogen separation can be accomplished simultaneously within the gasifier thus increasing hydrogen production and simplifying process operation. Because of gasifier limitations and the current membrane development effort, a close-coupled membrane was used in conjunction with the gasifier i. e. the membrane was installed in a gas slipstream line downstream of the biomass gasifier. In this manner, many of the concepts could still be tested at this stage of development, including using an actual product gas stream from a biomass gasifier rather than a synthesized gas stream.

The advantages of the membrane gasifier concept are summarized below:

- High efficiency: more than 40% higher than the conventional biomass gasification systems in terms of hydrogen production.
- Low cost: reduced biomass feed and its handling cost for the same quantity of hydrogen produced; reduce/eliminate downstream processing steps
- Clean: no further gas cleaning needed for the hydrogen product
- High purity: No further hydrogen separation/purification required.
- CO₂ sequestration ready: simplify CO₂ capture process
- Power/heat co-generation: utilization of non-permeable syngas

3. Selection of Candidate Membrane Materials

The candidate membranes were selected from ceramic and/or metallic class of materials. The work involved in this task included:

- Identification of candidate membranes
- Procurement and preparation of membranes
- Testing of membranes for thermo and chemical stability
- Testing of membranes for hydrogen permeability
- Selection of final candidate membrane

Candidate membrane materials were subjected to two separate tests: thermo stability and hydrogen permeability. For the hydrogen permeability test, the membranes were tested in a high temperature permeation apparatus under ambient pressure conditions. Figure 2 shows a picture of this apparatus.



1= feed inlet, 2=feed exhaust, 3=sweep inlet, 4=product gas out

Figure 2. Existing laboratory scale hydrogen permeation unit

The results observed from the stability tests together with the permeability data were used to assess if a material was qualified for further evaluation under real biomass gasification conditions.

The GTI team has researched hydrogen selective membranes extensively. Palladium-based alloy foils with different composition and foils from refractory metals (vanadium, tantalum, zirconium, titanium etc) were chosen as the membrane candidates. While Pd-based foils were tested for hydrogen permeation properties without any modification, foils from refractory metals were subjected to electroless plating or an electroplating method.

Palladium is a metal well-known for its hydrogen permeability[1]. Hydrogen permeation involves such steps as adsorption of hydrogen on palladium surface, dissociation of molecular hydrogen into atoms, bulk diffusion and reverse steps as recombination of hydrogen atom into a molecule and desorption of hydrogen from the metal surface. Unfortunately, pure palladium along with high hydrogen permeability is not resistant to such poisons as carbon monoxide and hydrogen sulfide which are typical components of producer gas from a gasification process. Also, pure palladium is subjected to lattice expansion during thermal cycling and cannot be used below 298°C. Incorporation of another metal into palladium may improve chemical stability. One promising material is the Pd-Cu alloy membrane, which has been assessed over a wide range of temperatures (to 900°C) and pressures (to 35 atm) for its hydrogen permeability[2,3]. The other positive characteristic of the Pd-Cu membrane is its potential resistance to sulfur poisoning. The alloys containing 53%, 60% and 80% of Pd by weight have

demonstrated negligible decreases in flux in the presence of 1000 ppm H_2S [4]. The feasibility for use of these membranes in gasification applications is uncertain at this time.

Also, refractory metals have a high hydrogen solubility and diffusivity[5]. Due to their high reactivity, all refractory metals in air are covered with a surface oxide layer that is impermeable to hydrogen. Therefore to have a hydrogen selective membrane, the refractory metals oxide layer should be removed and a protective, catalytically active (to hydrogen dissociation) coating should be applied. Such methods as chemical etching and reduction by electroplating were used for surface oxide removal. A palladium layer was deposited by electroless plating or electroplating. The theory and practice of electroless plating is similar to electroplating. The actual metal reduction and film development occurs at the interface of the solution and the object being plated in both methods, but the electrons in electroless plating are supplied by a chemical reducing agent[6].

Experiments to test permeation properties of Pd-Cu and Pd-V-Pd membranes were conducted. Based on test results, vanadium coated by a palladium layer was chosen as a final candidate. Preference was given to the vanadium membrane because at equal conditions, it has a higher hydrogen flux than the palladium-copper membrane. An optimization of a membrane synthesis method was conducted to achieve higher hydrogen flux and a more chemically stable membrane.

4. Construction of a Hydrogen Permeation Cell Unit

The objective of this task was to design and build a hydrogen permeation cell unit that could be transported to the NRRI facility for testing with their downdraft biomass gasifier unit. The work planned for this task included:

- Large size membrane fabrication
 - Fabricate 10-20 cm^2 flat plate membranes
 - Fabricate 10-20 cm^2 surface area tubular membranes
 - Decide membrane size and geometry to be tested
 - Fabricate final membranes for the permeation cell
- Permeation unit construction
 - Design
 - Parts procurement
 - Construction
 - Shakedown

The selected candidate membranes were scaled up to about 10-20 cm² for their active areas. The size and geometry of the membranes for the permeation cell were decided based on ease of fabrication and ease of sealing in the permeation cell. The objective of this activity was to design and build a hydrogen permeation cell unit that could be transported to the NRRI facility for testing with their biomass gasifier unit.

The hydrogen permeation cell unit was fabricated. The unit was mounted on a skid for easy transport to the NRRI site for testing of hydrogen production from biomass gasification. Based on the gasifier information provided by NRRI, the product syngas from the NRRI's down draft gasifier was expected to have a temperature in the range of 315 to 400°C, a pressure near atmosphere pressure and a composition containing about 20-30% of H₂ and CO. Therefore, the biomass syngas required compression to the range of 300-400 psig for permeation testing. A catalytic water-gas-shift reactor was also needed to increase the hydrogen content. A guard bed packed with sorbent material was used to remove sulfur and other contaminants. A booster compressor was used for the slip stream to increase the partial pressure of hydrogen in the feed side of the membrane to simulate the realistic hydrogen feed pressure from a commercial gasifier. After construction of the unit was completed, check-out and shakedown tests were performed to ensure that the unit was functional before being transported to NRRI.

The design was based on a planar configuration with a total active membrane surface area of about 112.5 cm². Preference was given to planar design due to the easy membrane manufacture and availability of metallic foils. The unit was expected to process a syngas feed flow of about 2 slpm (standard liter per minute) and produce a pure hydrogen stream of about 0.2 slpm. Figure 3 is a photo showing three pieces of the metal frames for the membrane cell module. The middle plate houses the syngas feed and exit lines. The top and bottom plates are for hydrogen product off-take. Figure 4 is the photo for the unassembled cell including the membrane foil and the porous stainless steel plate. Two sets of the membrane foils and the support structures that were used in the cell module. Copper rings (not shown) were placed in the grooves along the edges of the metal frames to seal the membrane foils. Figure 5 shows the unit completely assembled without the gas tubing connected. The unit was tested in GTI's laboratory with simulated syngas before conducting the integrated testing with NRRI's gasifier.

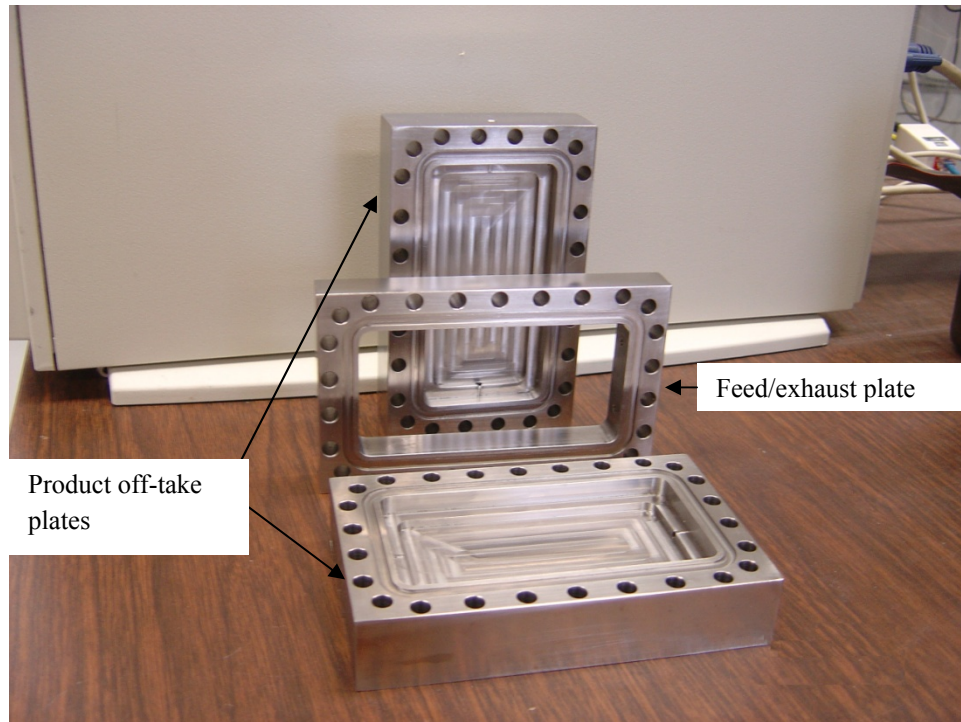


Figure 3. The membrane cell consists of three metal frames, one plate for the feed and exhaust and top/bottom plates for the hydrogen off-takes.

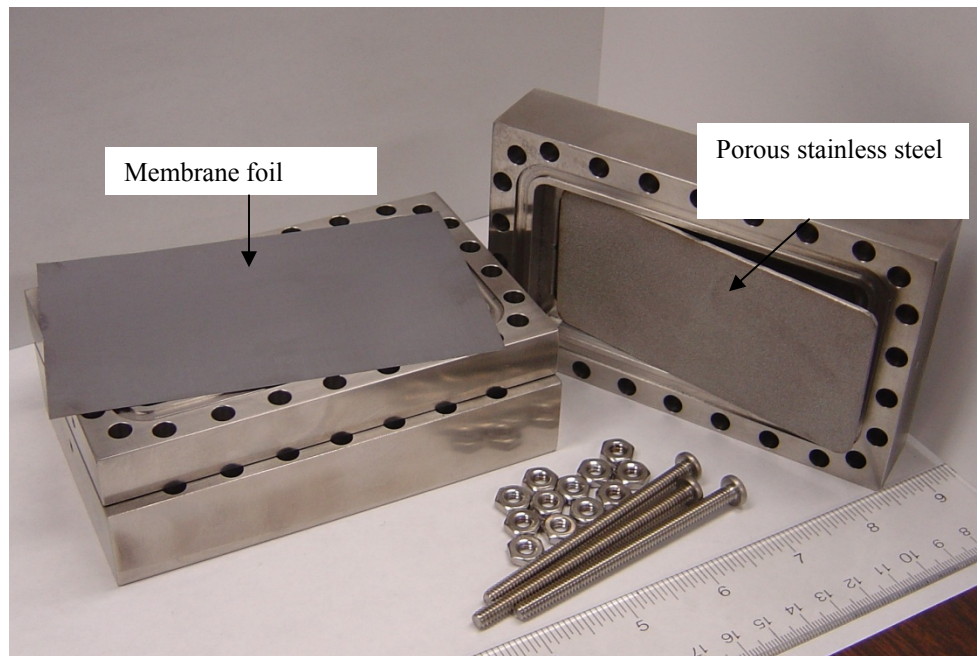


Figure 4. The unassembled cell showing the membrane foil and the porous stainless steel plate.

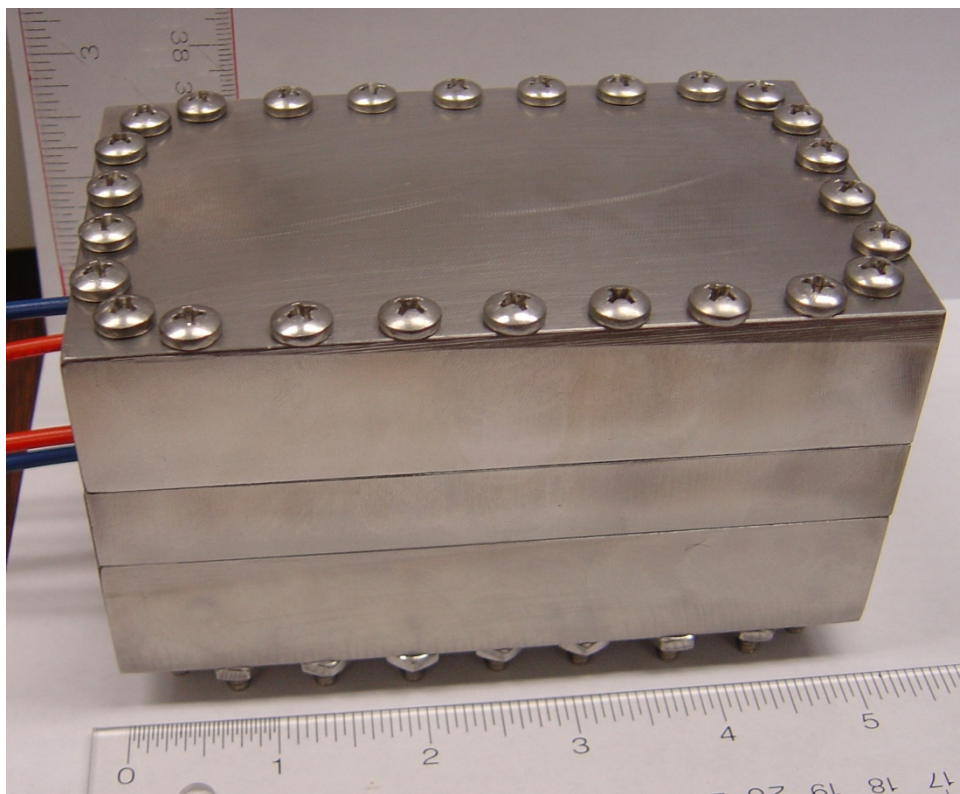


Figure 5. Completely Assembled Membrane Module

The sizes of the membranes have been gradually scaled up from about 2.5 cm in diameter to about 12x7 cm, which is the membrane size required to fit into the module (Figure 6). Two palladium-coated vanadium membranes with sized 12x7 cm were also fabricated by the electro plating technique. One of the concerns for scaling up the membrane was whether the property of the larger membrane is uniform throughout the entire area. The membrane was cut into several pieces so that each piece could fit into the laboratory permeation unit for hydrogen permeation testing. In general, reasonably good fluxes were obtained with small variations among all individual pieces tested. Although the hydrogen fluxes measured for the membranes fabricated with a larger size are still lower than those fabricated with a smaller size, further optimization for the membrane fabrication procedures were performed to minimize flux reduction from the scale-up.

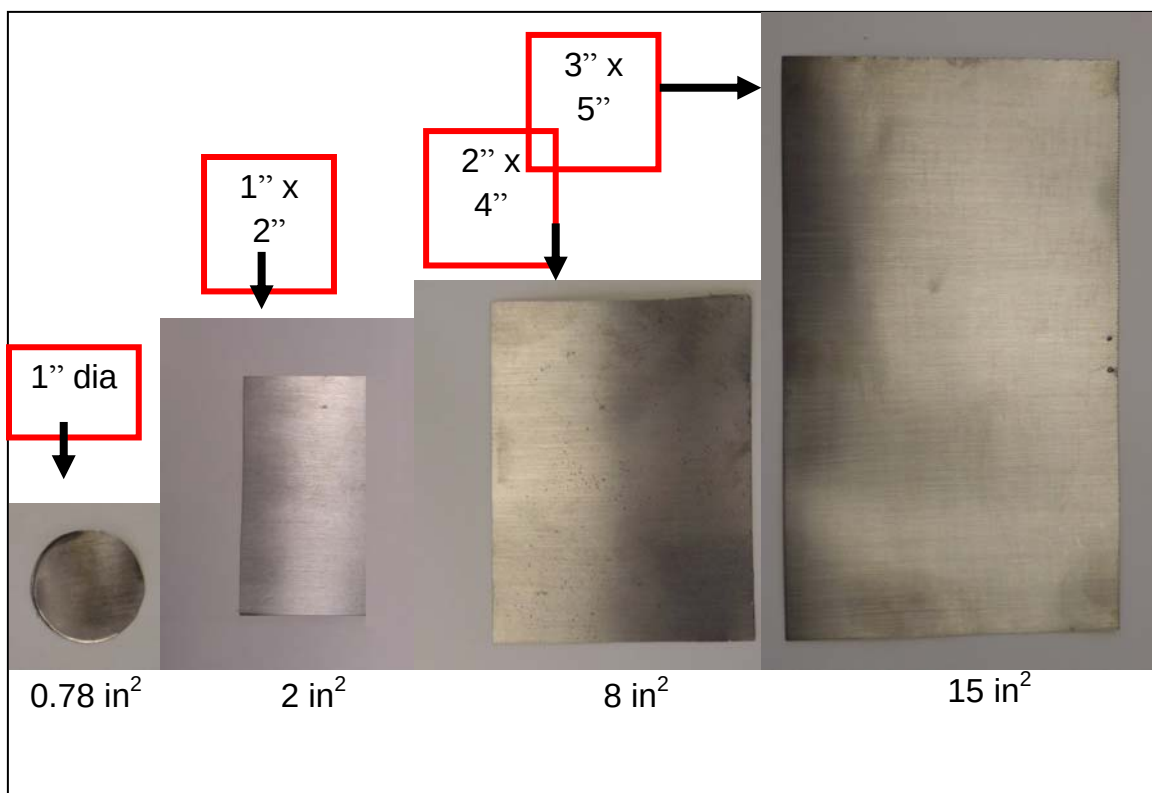


Figure 6. Membrane Scale-Up

Tests were conducted to verify the mechanical strength of the porous ceramic/stainless steel support system for the membrane foil. Experiments showed that ceramic support (Small Parts Company, thickness=6 mm, pore size =6 microns) cannot handle high pressures (350 psig). Because an increase in the thickness of ceramic substrate may lead to a better mechanical stability but also may lead to transport resistance and as a result, to a decrease of hydrogen flux, we decided to use stainless steel supports. The stainless steel porous support (Applied Porous Technologies, thickness=1.5 mm, pore size = 0.5 microns) was introduced for experiments. The stainless steel support withstood operating pressures and temperatures but were bent which lead to rupture of membranes along the edges. New supports from stainless steel with holes made along the surface were used to provide the necessary mechanical strength.

5. Installation of a Down Draft Biomass Gasifier Unit

A pilot-scale down draft gasifier was installed and commissioned for testing of Minnesota's biomass feedstocks to demonstrate the production of hydrogen using selective membrane technology. This task was performed by NRRI. The work was

divided into three subtasks. These subtasks were modified based on purchase of a downdraft gasifier from Community Power Corporation of a smaller modular unit.

The BioMax gasification system is capable of processing 25 kg/hr of feed materials. It was anticipated that 5-10 tons of woody biomass would be processed. The NRRI procured about fifty tons of woody biomass for the project. This material was shipped from Northern Minnesota. Feed materials were characterized according to ASTM proximate and ultimate analyses for biomass fuels. Proximate analyses (wt. %) included; moisture, volatile matter, fixed carbon content, ash, sulfur, and BTU/lb on both “as received” and dry basis. Ultimate analyses included ash, carbon, hydrogen, nitrogen, sulfur and oxygen.

The Biomax 25 downdraft gasifier was purchased from Community Power Corporation (CPC), in Littleton, CO. This is a fully instrumented downdraft gasifier capable of processing 25 kg/hr of biomass feedstock. The unit was installed at the Natural Resources Research Institute (NRRI) Coleraine Mineral Research Laboratory. University Building Codes division reviewed the installation and provided the necessary permits for operation of the gasifier.

After installation, “shake-down” of the unit was performed to assess its operability. Compliance with the University environmental standards was addressed through the University of Minnesota Health and Safety groups. Safety procedures were developed and established to be in compliance with the Coleraine Minerals Research Laboratory’s safety rules and regulations.

The BioMax[®] 25, downdraft gasifier was purchased from Community Power Corporation (CPC), in Littleton, CO. Downdraft gasification, also known as co-current gasification, has the oxidant and producer gases passing through the reactor in the same direction as the biomass. Biomass gasification proceeds primarily through a two step process, pyrolysis followed by gasification. Pyrolysis or devolatilization occurs in the initial stage of the process and decomposes the biomass feedstock with heat. This process is endothermic and produces 75-90% of the volatile materials in the form of hydrocarbons. The remaining, non-volatile material contains high carbon content and is described as char. The volatile hydrocarbons and char are converted to producer gas in the second stage of the process, gasification. Significant chemical reactions involved in the process are described below:

- | | |
|--------------------------|---|
| 1) Combustion | $\{\text{biomass volatiles/char}\} + \text{O}_2 \rightarrow \text{CO}_2$ |
| 2) Partial Oxidation | $\{\text{biomass volatiles/char}\} + \text{O}_2 \rightarrow \text{CO}$ |
| 3) Methanation | $\{\text{biomass volatiles/char}\} + \text{H}_2 \rightarrow \text{CH}_4$ |
| 4) Water-Gas Shift | $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ |
| 5) CO Methanation | $\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ |
| 6) Steam-Carbon Reaction | $\{\text{biomass volatiles/char}\} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2$ |
| 7) Boudouard Reaction | $\{\text{biomass volatiles/char}\} + \text{CO}_2 \rightarrow 2\text{CO}$ |

Unconverted char and ash are removed and sent to the storage containers or disposal. Downdraft gasification provides the following advantages[7]:

- Up to 99% of the tars are converted, requiring minimal tar clean-up
- Minerals remain with the char/ash residues
- Proven, simple and low cost process

BioMax[®] 25

The NRRI pilot gasifier is a state of the art modular biopower system that has been designed for research and development. The BioMax[®] 25 system consists of three main modules:

1. Feedstock Conditioning Module
 - Drying Bins
 - Screener
 - Conveyor
2. Gas Production Module
 - Gasifier
 - Control System
 - Heat Exchanger
 - Filter
3. 25 kW Genset and Gas Flare

The unit is capable of processing 25 kg/hr of feed materials and generating ~250,000 Btu/hr. The gasifier uses a fully automated fuel feed system, ash removal and gas control systems. The gasifier is an open top (low pressure) reactor and the reaction is >99% efficient when the product is raw hot gas. The producer gas can be used as a fuel for boilers, dryers, internal combustion engines, gas turbines, liquid fuels and fuel cells. The gasifier can accommodate almost any woody biomass fuels (wood chips, pellets and scrapes, nut shells, etc.). The BioMax[®] 25 specifications are listed below and further described at www.gocpc.com.

Specifications –

- Electrical Power: 25 kW_e
- Thermal Power: ~250,000 Btu/hr
- Footprint: 5m x 5m
- Weight: ~1,500 kg
- Gas: LHV 5mj/m³ <5ppm Tars/Particulates
- Fuel Conversion: ~1.5kg Wood per kWh_e
- Dispatchable Power Within 30 Seconds
- Full Cold Startup on Wood Gas: ~15 minutes

Wood Chip Preparation / Characterization

Approximately 32 tons of Northern Minnesota wood chips (wet basis) were procured for use during the commissioning and operation of the gasifier. These chips were primarily Aspen chips, screened to -1 1/2" obtained from Blandin Paper Co. and McCabe Forest Products, Inc. Proximate and ultimate analyses were performed by Standard Laboratories Inc., Cresson, PA and are provided in Table 1:

Table 1. Proximate and Ultimate Wood Chip Characterization

WOOD CHIPS – PROXIMATE ANALYSIS	ASTM METHOD	AS RECEIVED	DRY BASIS
Moisture	D2961 D3302 D3173	36.31%	
Volatile	D3175M	53.96%	84.73%
Fixed Carbon	D3172	9.11%	14.29%
Ash	D3174	0.62%	0.98%
Sulfur	D4293 Method B	0.20%	0.31%
BTU/lb		5566	8740
lbs SO ₂ /MM BTU			0.71
lbs Sulfur/MM BTU		0.359	
WOOD CHIPS – ULTIMATE ANALYSIS	ASH MINERAL D2795 D3682		
Silicon Dioxide	13.65%		
Aluminum Oxide	3.95%		
Ferric Oxide	6.15%		
Titanium Oxide	0.22%		
Phosphorous Pentoxide	1.54%		
Calcium Oxide	45.78%		
Magnesium Oxide	3.84%		
Sodium Oxide	0.49%		
Potassium Oxide	15.98%		
Sulfur Trioxide	6.47%		

The wood chips were dried from 45-50% moisture to approximately 25-35% moisture prior to final drying in the feed bins. The chips were shoveled into barrels and placed in drying ovens at low temperature. To expedite the process, the barrels were mixed at regular time intervals. After the fuel was pre-dried to the desired moisture range, it was placed into two drying bins for further drying.

Installation and Commissioning at CMRL –

The installation of the BioMax® 25 was conducted from May 21-25, 2007. An Installation Engineer from CPC assisted NRRI employees and on-site electricians with the installation. Ports were installed for sampling both hot and cold gas. Components of the system were assembled sequentially according to the processing of the biomass fuels. A Biopower Systems Engineer-CPC, was on site for software installation and commissioning of equipment, as well as training from May 30 to June 7, 2007. Initial operation of the gas analyzer and gas analyses indicate the gas contained unusually high oxygen levels ($> 5\%$). Trouble shooting the system found loose connections caused during shipping creating leakage around the gas filter bags. The interior plumbing of the gasifier was disconnected and reinstalled to resolve this issue. Subsequent gas analysis showed increased levels of CO and H₂ and decreased O₂, (est. 15-20% CO, 15-20% H₂, 10% CO₂, 4-5% CH₄ and $< 1\%$ O₂). Approximately 8-10 tons of wood chips were processed, and the gasifier was operated approximately 30-35 hrs/week for a 6-7 week period during the commissioning phase of this effort. The objective during this phase was to determine the operating parameters necessary to obtain a stable operating temperature and pressure regime and consistent gas chemistry. With assistance from CPC, the stability of the reactor operation was found to be a balance of operating temperatures and pressures within the process control system configuration.

6. Testing of the Hydrogen Permeation Unit Under Simulated Gas Conditions

The objective of this task was to collect initial permeation data in the new permeation unit under the controlled laboratory environment for the membranes selected and fabricated in Task 2. The permeation unit was first commissioned at GTI's facility. Membrane sealing issues were addressed and solved in this task. Initial tests were performed using H₂/N₂ binary gas mixture to obtain hydrogen permeability data for comparison with the results from Task 1. Further tests were conducted using simulated gas mixtures prepared from gas cylinders. Potential contaminants as hydrogen sulfide generated from biomass gasification were present in the product gas. When syngas was used for the permeation tests, reforming and shift reactions took place in the feed stream prior to contact with the membrane. Membrane samples after tests were analyzed for any chemical and physical degradation, especially if contaminants were added in the feed stream. The experience learned from this task helped to define test plan and procedures for integration tests.

The objective of this task was to collect initial permeation data in the new permeation unit under the controlled laboratory environments for the membranes selected and fabricated in Task 2. The permeation unit was commissioned at GTI's facility. The schematic of the permeation unit is shown in Figure 7.

membranes were tested and hydrogen permeability for membranes was about 5×10^{-9} moles/m²-s-Pa^{0.5}, which was consistent with previous results.

Long-term experiments were conducted to test stability of palladium-vanadium membranes. Unfortunately, palladium-vanadium membranes failed due to inferior chemical and mechanical stability of membranes after long-term operation. Because of the failure, palladium-vanadium membranes were replaced by the other initial candidate-palladium-copper alloy membranes. The membrane module reactor was operated for about 40 hours using Pd-Cu membranes. Changes in pressure and temperature or shutdown and startup didn't affect the Pd-Cu membrane properties.

The membrane module was incorporated into the permeation unit system and components such as the carbon reactor/cleaning bed, air-driven booster and packed bed Water-Gas shift reactor were connected in accord with schematic shown in Figure 7. Components of the permeation unit were tested separately.

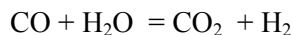
The carbon bed reactor shown in Figure 8 is constructed from molded polycarbonate. The maximum working pressure is approximately 100 psig. The operating temperature is less than 50°C. The column is filled with FCA granular activated carbon which has been specifically developed for use in vapor phase applications by Calgon Carbon Corporation. Activated carbon is placed between felt filters. Impurities such as hydrogen sulfide and low molecular weight organic sulfur compounds are absorbed from the gas stream. The gas inlet is located at the bottom of the column. The producer gas slip stream is connected to the inlet of the column and the cleaned gas stream exits from the top of the reactor and proceeds to the water-gas shift reactor (see Figure 7). Complete hydrogen sulfide removal was obtained



Figure 8. Carbon Bed Reactor

when feed concentration was 300 pm for about 30 hours of operation. Complete (100%) hydrogen sulfide removal was achieved for about 12 hours when hydrogen sulfide concentration was equal to 1000 ppm.

The Water-Gas Shift reactor is a packed bed catalytic tubular reactor (Figure 9). The catalyst utilized for the WGS reaction is CuO/ZnO (Shiftmax-230, Sud-Chemie) that is effective at low temperatures. Carbon monoxide reacts with water/steam to produce hydrogen and carbon dioxide:



The WGS reaction occurs at 200-300°C and atmospheric pressure. The cleaned producer gas (hydrogen sulfide removed) flows through the tubular reactor where the CO and steam are converted to CO₂ and H₂. An electrically heated line converts a water feed to steam before introduction into the tubular reactor. The length of preheated stainless tubing provides sufficient heat transfer surface area to convert the water to steam. The excess steam exiting from the WGS tubular reactor is condensed and removed via a knock out/water collection pot. A sample port for GC analysis is located after the steam condensate (water collection) pot. A drierite bed is located before the GC to remove any water which is harmful to the micro gas chromatograph.



Figure 9. Water-Gas Shift Reactor Filled With Catalyst.

Experiments on water-gas shift reaction were conducted by using a producer gas simulated mixture consisting of carbon monoxide – 20%, hydrogen- 20%, carbon monoxide-10% and balance of nitrogen. No hydrogen sulfide was included in the simulated mixture since the producer gas will pass through a carbon bed where all hydrogen sulfide will be removed before entering the WGS reactor. Carbon monoxide conversion was from 90 to 100% depending upon gas space velocity. So, as a result of the gas cleaning unit, WGS reactor and steam condenser, the producer gas will consist of hydrogen (~30-35%), carbon dioxide (~25%), carbon monoxide (less than 2%) and nitrogen.

A booster compressor is used for the slip stream to increase the partial pressure of hydrogen in the feed side of the membrane to simulate a realistic hydrogen feed pressure from a commercial gasifier. Haskel Gas booster (Model AG-62) consists of a large area reciprocating air driven piston directly coupled by a connecting rod to a small gas piston. The gas piston operates in a high-pressure gas barrel

section. Each gas barrel end cap contains high-pressure inlet and outlet check valves. A single acting single stage model AG-62 booster provides the means of boosting producer gas pressure. The booster compressor uses house air at about 60 psig. The gas supply line has two surge tanks to insure uniform flow on both low and high pressure sides (Figure 10).

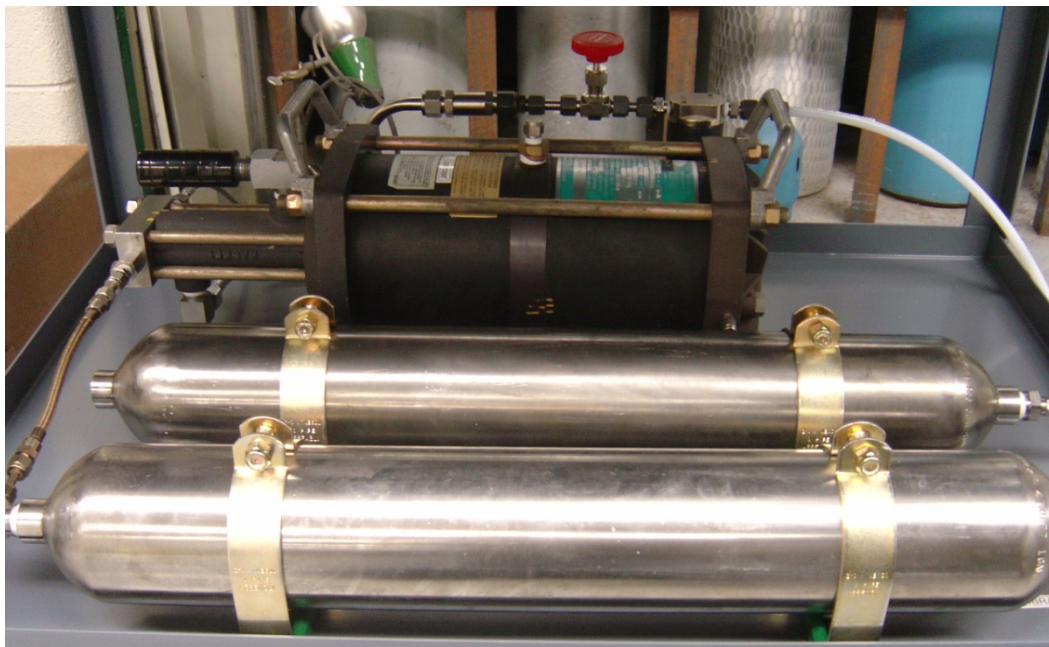


Figure 10. Booster With Two Surge Tanks.

Testing of the permeation unit with a mixture of gases simulating syngas was conducted successfully. Composition of gases was equivalent to composition of syngas typical after biomass gasification: carbon monoxide- 20%, hydrogen-20%, carbon monoxide-10%, 300 ppm of hydrogen sulfide and balance of nitrogen. Experiments were conducted with the permeation unit and the syngas mixture of gases. The gas streams were analyzed after each unit by a micro gas chromatograph (μ -GC). After passing through the gas cleaning bed, the gas mixture is the same except no hydrogen sulfide was present. After WGS reactor, composition of gas has changed: no carbon monoxide was observed and only hydrogen and carbon dioxide were observed together with nitrogen. This mixture was directed to membrane module through booster where pressure was increased up to 350 psig (~25 atmospheres). The pressurized gas mixture was introduced to membrane module at the feed side, which was heated up to 350°C. Hydrogen permeated through the membranes and only hydrogen was observed on the sweep side. To analyze purity of permeated gas, nitrogen was introduced into sweep side of membrane module. Micro GC shows that only hydrogen is present on the permeate side. Also, hydrogen flow rate was calculated using a bubble meter. When no nitrogen is present on the sweep side of the membrane module, reactor hydrogen flow rate equals 1.04 ml/min-cm^2 when feed side pressure = 25

atmospheres, concentration of hydrogen in feed is 30% by volume at membrane module temperature of 350°C.

The permeation unit was able to extract hydrogen from simulated producer gas mixture. The next step of the project was to transport the hydrogen permeation cell unit to the NRRI facility for testing with their downdraft biomass gasifier unit.

7. Integrated Testing of the Hydrogen Permeation Unit With Down Draft Biomass Gasifier

The permeation unit was shipped to NRRI and installed downstream of the down draft gasifier for demonstration of hydrogen production from biomass. A slip stream from the syngas product of the down draft biomass gasifier was used to feed the permeation unit. GTI and NRRI designed a testing plan and jointly conducted the testing. The task work involved included:

- **Test Plan** – A test plan for the integration test was prepared. Data and experience learned from Task 4 was utilized to formulate the test plan. In addition to test conditions such as temperature, pressure, oxygen/carbon and steam/carbon ratios for the gasifier, the plan included schedules, procedures, operating instructions, measurement techniques, sample analyses and reporting requirements.
- **Install slip stream piping** – Piping for a slip stream from the gasifier was provided to supply biomass gas to the membrane unit. Additional instrumentation and control was also added.
- **Transport permeation cell** – The permeation cell was packed and transported to the NRRI site.
- **Integrate permeation cell to gasifier** – The permeation unit was connected to the gasifier.
- **Conduct integration tests** - NRRI provided operators for the gasification system and technical support as required. Operating parameters were optimized according to the test plan and gas analyses obtained. It is estimated that a total of 3-4 tons of biomass feed material (wood) was gasified. Initially the gasifier was operated over a five-day work week, several hours a day intermittently for several weeks to develop an optimal operating strategy for maximizing production of hydrogen. During this phase of continuous operation, solid sample collection and analysis was conducted by NRRI, as well as flue gas characterization, producer gas assessment and performance criteria evaluation. Initial flue gas characterization was conducted using available emission analyzers capable of measuring NO, NO₂, CO, O₂, SO₂ and Hg. Additional measurements were determined according to the requirements and parameters set by the testing protocol. The engine and generator set were not available to consume any excess synthesis gas that was not processed through the membrane. Excess gas went to the flare instead.

The gasifier was operated with air at near ambient pressure. Consequently, the expected hydrogen contents in the produced biomass syngas was less than 10% with nitrogen as a major diluent. Use of oxygen or enriched air instead of air as an oxidant for the downdraft gasifier is technically feasible and should be tested in a future project. A booster compressor was used for the slip stream to increase the partial pressure of hydrogen in the feed side of the membrane to simulate the realistic hydrogen feed pressure from a commercial gasifier. A small catalytic reforming and/or shift reactor was also used upstream of the permeation cell to increase the hydrogen content. An inert gas was used to sweep the hydrogen permeate. The hydrogen permeability that was demonstrated through this testing is 2.1 cc/min per cm² of membrane area under a hydrogen partial pressure difference of 390 psig (27 atmospheres) and at 390° C for a membrane thickness of 200 microns, which was **twice** the targeted flux value.

The goal of this task was to show that the permeation unit incorporated into the downstream line of the biomass gasifier will extract pure hydrogen from producer gas.

A test plan was developed based on results and experience learned from Task 4. An operational manual with description of safety issues, procedures, and the permeation unit was prepared.

Integrated testing of the permeation cell and gasifier was conducted August 13-15, 2007 at the NRRI site in Coleraine, MN. The permeation unit was transported to NRRI and installed downstream of the down draft gasifier exit line for demonstration of hydrogen production from biomass. A slip stream from the syngas product of the down draft biomass gasifier was fed into the permeation unit by using a vacuum pump to ensure a stable flow rate of producer gas (see Figure 11).

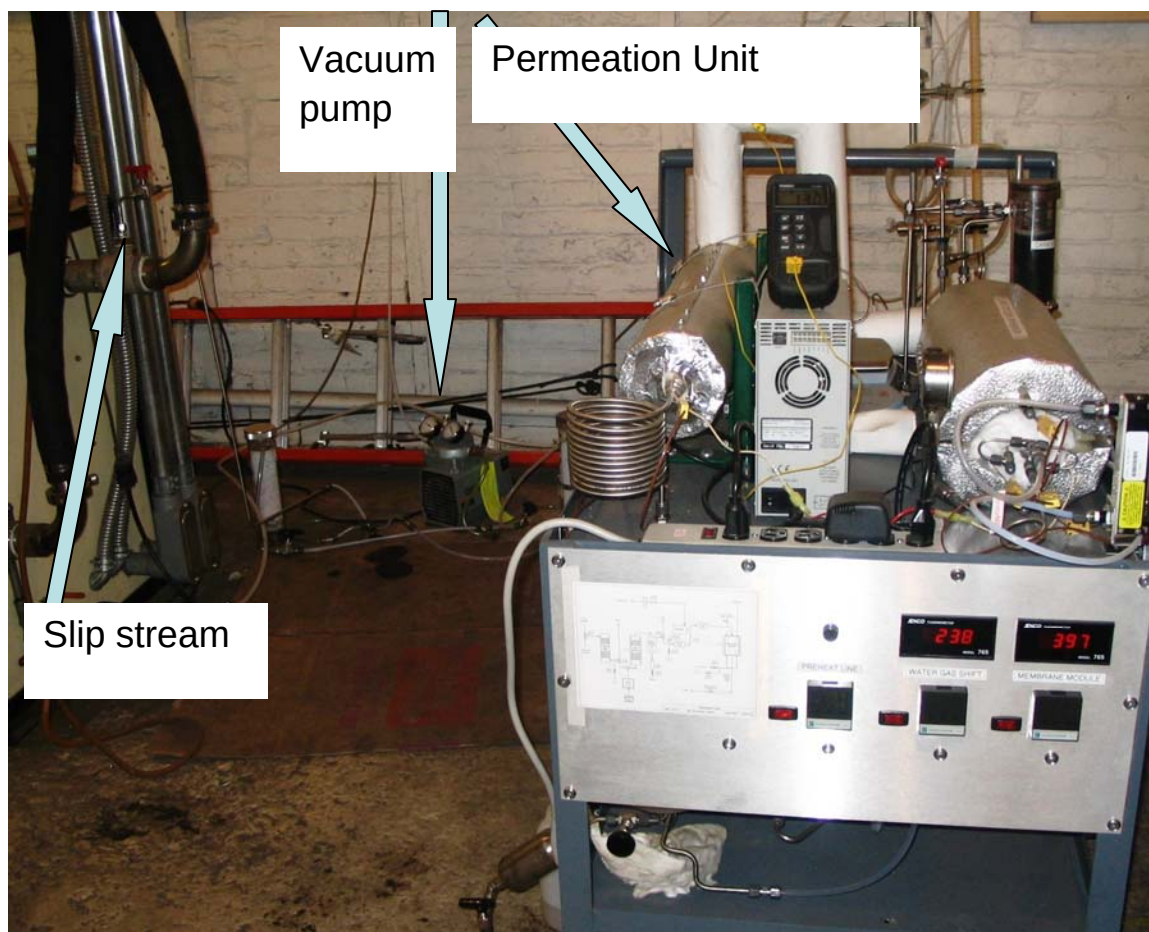


Figure 11. Permeation unit is connected to slip stream from gasifier using vacuum pump.

NRRI provided operators for the gasification system and technical support as required. The gasifier was operated with air at near ambient pressure using wood chips obtained from northern Minnesota sources. Consequently, the expected hydrogen contents in the produced biomass syngas were less than 20% with nitrogen as a major diluent. Composition of producer gas was analyzed continuously by a NOVA analytical system. Typical producer gas composition was 18-20% of carbon monoxide, 18-20% of hydrogen, 10 % of carbon dioxide, 2-4% of methane and 50% of nitrogen (see Figure 12). Constituents as hydrogen sulfide, ammonia, sulfur oxides were present at less than a 1% level.



Figure 12. Producer Gas Composition by NOVA Analytical System.

Figure 13 shows gas composition recorded over time with temperature profile data obtained during the integrated testing of the biomass gasifier and the membrane unit. This figure also shows the stability/variability of the temperature profile and gas composition during the day and represents a typical profile observed during gasifier operation. The profile shows that the exit oxygen content was nearly zero indicating that indeed the wood was being gasified rather than combusted. Typically, the first part of the reactor is utilized for combustion between the air and the fuel. The combustion reaction is a large exothermic reaction that is necessary to provide the heat to drive the endothermic gasification reactions. This reducing atmosphere also determines the form of some of the trace contaminants that are formed such as H_2S , HCN , NH_3 , etc. Fortunately, the gas conditioning system provided by GTI for the membrane system either removed these contaminants or they were not detrimental to the membrane operation at the concentrations generated during operations.

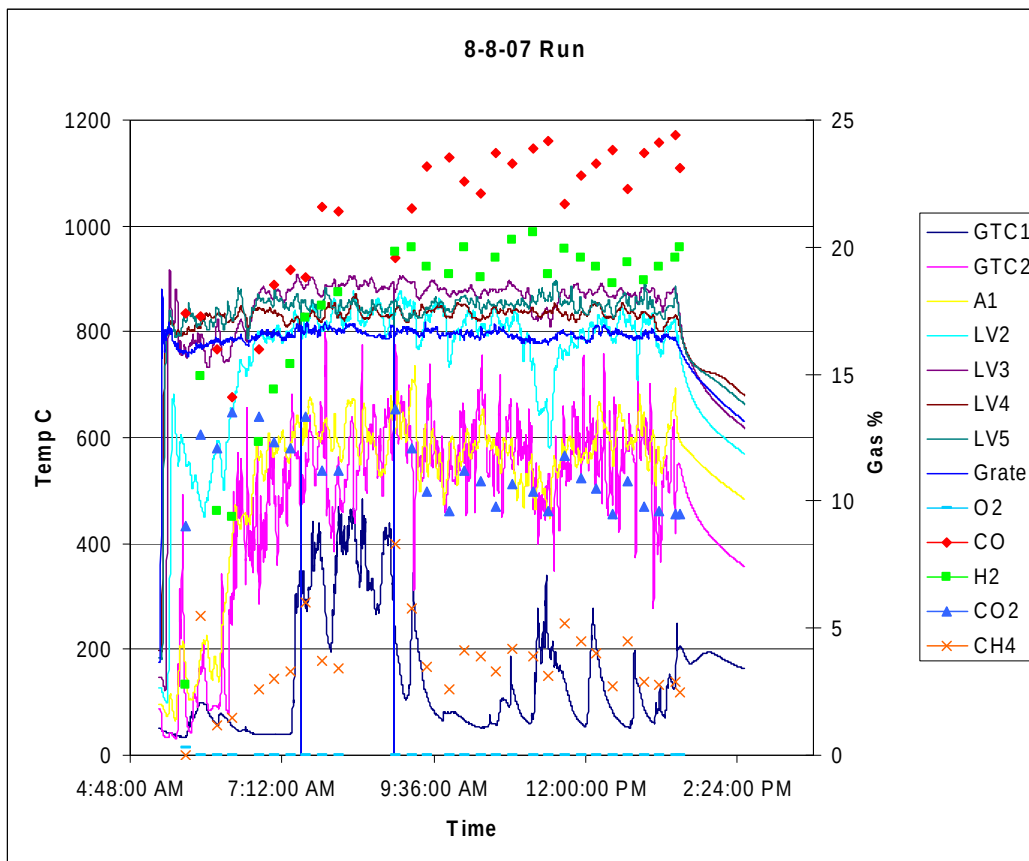


Figure 13. Operating data and producer gas composition on August 8, 2007.

The Carbon Bed contains the vessel where contaminants such as particulates, sulfides, ammonia etc. are removed (cleaned) from the producer gas. The water-gas shift reactor uses carbon monoxide and water/steam to produce hydrogen and carbon dioxide. As a result of the shift reaction, the hydrogen content increases and the carbon monoxide concentration becomes negligible. A booster compressor is needed to pressurize the producer gas because the hydrogen flux through the membrane depends upon the partial pressure difference of hydrogen on the feed and permeate sides. By increasing the differential pressure, the hydrogen flux increases too. The membrane module which contains a hydrogen selective membrane serves as a barrier through which only hydrogen can pass. As a result, pure hydrogen is on one side of the membrane and carbon dioxide with impurities is on the other side.

The carbon bed and water-gas shift reactors were tested first. The producer gas stream passed through the carbon bed to remove hydrogen sulfide and through the water-gas shift reactor to increase hydrogen content and to decrease carbon monoxide. Hydrogen sulfide concentration was analyzed by the μ -GC. The μ -GC shows complete hydrogen

sulfide removal from the gas stream. The product gas after the WGS reaction was tested by using a μ -GC and NOVA analytical system. Carbon monoxide reacts with water to form hydrogen and carbon dioxide. The hydrogen content was increased up to 35% while carbon monoxide concentration decreased to 2-3%. After successful testing of the carbon bed and WGS reactor, producer gas was directed to membrane module reactor, where hydrogen separation occurs. Permeated gas was analyzed by the μ -GC and NOVA analytical system. The flow rate of the gas was measured by a bubble meter and also calculated using μ -GC and NOVA analytical system data. Results obtained by different analysis methods agreed with each other and show that only hydrogen permeates through the membranes.

To optimize the hydrogen extraction process, such parameters as gasification temperature and biomass moisture were varied. Operating temperature and pressure of membrane module were adjusted to produce hydrogen from producer gas more efficiently. For the membrane module, temperature was changed from 350 to 400°C while pressure on the feed side was increased to 458 psig. When nitrogen was used as sweep gas, more hydrogen was separated from syngas when temperature was 390°C and pressure 390 psig.

When no sweep gas was used, more hydrogen was extracted when temperature and pressure were at their maximum value (400°C, 460 psig). Hydrogen permeation flux measured by μ -GC was 293 ml/min and 301 ml/min by NOVA analytical system (agreed within 4%). A bubble meter was used to measure pure the hydrogen flux of 235 ml/min. Nitrogen sweep causes a difference of hydrogen flux as measured by GC or NOVA and bubble meter. When permeated hydrogen is swept by nitrogen, the hydrogen flow is increased and higher nitrogen flowrate leads to more hydrogen permeation flux.

The efficiency of the hydrogen separation process is easily calculated. The flowrate of producer gas is 2 slpm and hydrogen concentration averages 20%, so pure hydrogen flow is 0.4 slpm. When nitrogen is used as sweep gas, efficiency is 70% and when no nitrogen is used, efficiency of hydrogen separation from syngas is 59%.

The target for pure hydrogen extraction was achieved and the integrated operation of gasifier and permeation unit occurred for 20 hours. Results show the proof of feasibility for separating hydrogen from producer gas (obtained by biomass gasification) using a hydrogen selective membrane.

Major achievements and Recommendations

The major achievements from this project can be summarized as follows:

- Identified palladium-based membranes as a leading material for hydrogen permeation in biomass-derived syngas environment.
- Designed, constructed and commissioned a new membrane module unit capable of operating at up to 500°C and 30 bar, allowing screening and testing of hydrogen membranes under gasification conditions.
- Constructed and commissioned a permeation cell with carbon bed, water-gas shift reactor, booster compressor and membrane module to increase efficiency of hydrogen extraction from producer gas of biomass gasification. Installed and commissioned a biomass gasifier that allows processing of biomass and the generation of a syngas feed to the close-coupled hydrogen membrane unit. The downdraft gasifier is sufficiently large that the current membrane will only be able to take a slipstream of the producer gas. The gasifier is thus of adequate capacity to test a larger scaled-up membrane in the future.
- Tested integrated permeation unit with hydrogen permselective membrane into downstream process of biomass gasifier successfully. Target for hydrogen extraction flux was exceeded.
- The proposed membrane reactor process could potentially decrease the hydrogen cost by about 40% from the conventional biomass to hydrogen process, based on a preliminary economic analysis.

The Gas Technology Institute (GTI) and Natural Resources Research Institute (NRRI) have developed a novel concept for direct extraction of hydrogen from biomass by close-coupling a hydrogen-selective membrane with a biomass gasifier. The concept of joint work of gasifier and permeation unit was successfully tested. Integrated operation of the biomass gasifier and the permeation cell exceeded 20 hours during which time the hydrogen flux through the membrane cell was up to nearly double the targeted value.

The commercial development plan calls for development efforts in four major areas: membrane material development, integration of membrane into water-gas shift process, scale-up of permeation cell and optimization of gasifier operation closely-coupled with membrane. In the initial phase of the program, the membrane material development is the key effort to increase hydrogen permeability together with mechanical and chemical stability. Integration of membrane into equilibrium-limited water-gas shift process allows to increase

hydrogen content in producer gas to maximum. Optimization of gasifier operation with close-coupled membrane cell is essential to realize the maximum performance from the selected membrane materials and achieve the overall cost effectiveness.

Recommendations for future work includes:

- Improve the hydrogen permeability, chemical and mechanical stability by incorporation of a third metal into the palladium-copper alloy membrane.
- Scale-up the existing membrane module to have a larger surface area.
- Incorporate membrane into water-gas shift reactor to increase efficiency of process.
- Conduct longer term permeation testing with simulated syngas.
- Conduct longer term permeation testing with real syngas from a biomass gasifier.
- Optimize gasifier operation closely coupled with permeation unit to increase hydrogen extraction efficiency.
- Scale-up the size of the membrane disks.

ACKNOWLEDGEMENT

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