Hydrogen Production via a Commercially Ready

Inorganic Membrane Reactor

Semi-Annual Technical Progress Report
Reporting Period: April 1, 2006 to September 30, 2006

Paul K. T. Liu
Project Director

January 12, 2007

<u>Disclaimer</u>

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Abstract

In the last report, we covered the experimental verification of the mathematical model we developed for WGS-MR, specifically in the aspect of CO conversion ratio, and the effect of the permeate sweep. Bench-top experimental study has been continuing in this period to verify the remaining aspects of the reactor performance, including hydrogen recovery ratio, hydrogen purity and CO contaminant level. Based upon the comparison of experimental vs simulated results in this period along with the results reported in the last period, we conclude that our mathematical model can predict reliably all aspects of the membrane reactor performance for WGS using typical coal gasifier off-gas as feed under the proposed operating condition. In addition to 250°C, the experimental study at 225°C was performed. As obtained at 250°C, the predicted values match well with the experimental results at this lower temperature.

The pretreatment requirement in our proposed WGS-MR process can be streamlined to the particulate removal only. No excess water beyond the stochiometric requirement for CO conversion is necessary; thus, power generation efficiency can be maximized. PROX will be employed as post-treatment for the elimination of trace CO. Since the CO contaminant level from our WGS-MR is projected to be 20-30 ppm, PROX can be implemented economically and reliably to deliver hydrogen with <10 ppm CO to meet the spec for PEM fuel cell. This would be a more cost effective solution than the production of on-spec hydrogen without the use of prost treatment.

WGS reaction in the presence of sulfur can be accomplished with the use of the Co/MoS_2 catalyst. This catalyst has been employed industrially as a sour gas shift catalyst. Our mathematical simulation on WGS-MR based upon the suggested pre- and post-treatment has demonstrated that a nearly complete CO conversion (i.e., 99+%) can be accomplished. Although conversion vs production cost may play an important role in an overall process optimization, no cost optimization has been taken into consideration presently. We estimate that ~90% of the hydrogen produced from the H_2+CO in the coal gasifier off-gas can be recovered via our proposed WGS-MR process. Its purity level ranges from 80 to 92% depending upon the H_2/CO_2 selectivity of 10 to 25 respectively. If the purity of 95% is required, the hydrogen recovery ratio will drop to ~80% level for the membrane with H_2/CO_2=25.

TABLE OF CONTENTS

List of Graphical Materials

Figures

Tables

1. Introduction

During this reporting period, our development activities have focused on the areas below:

(i)   Continuing the development on the fabrication of the membrane module for pilot testing in the future;

(ii)   Completing the experimental verification of the mathematical model for WGS-MR. In the previous report, we have verified the CO conversion vs W/F. In this report, we verify the mathematical prediction for CO impurity level and hydrogen recovery ratio by the MR to complete the verification of our mathematical model; and

(iii)   Optimizing hydrogen production via our proposed WGS-MR and defining its pre- and post-treatment requirements.

This report summarizes our results for items (ii) and (iii).

2. Executive Summary

In the last report, we covered the experimental verification of the mathematical model we developed, specifically in the aspect of CO conversion ratio, and the effect of the permeate sweep. Bench-top experimental study has been continuing in this period to verify the remaining aspects of the reactor performance, including hydrogen recovery ratio, hydrogen purity and CO contaminant level. About 40 to >70% hydrogen recovered was obtained for the W/F range studied with the lab-scale WGS-MR, which agrees extremely well with the simulated results. A higher than 70% recovery cannot be demonstrated due to the limitation of our lab scale reactor. The experimental CO contaminant level corresponding to this range of W/F is 3,000 to 2,200 ppm, which is consistent with the predicted value of ~2,000 ppm. Along with the experimental verification on CO conversion and sweep gas effect reported in the last report, we conclude that our mathematical model can predict reliably all aspects of the membrane reactor performance for WGS using typical coal gasifier off-gas as feed under the proposed operating condition. In addition to 250°C, the experimental study at 220°C was performed. As obtained at 250°C, the predicted values match well with the experimental results at this lower temperature.

Pretreatment requirement for our proposed WGS-MR process has been defined. To avoid the hot gas clean-up (HGCU) requirement, the target temperature for the feed to the WGS-MR is set at 250°C. Our proposed process will recover as much heat as possible from the gasifier off-gas to this target temperature via HRSG to enhance the overall power generation efficiency. Thus, particulate removal can be accomplished at this low temperature with an existing technology. The amount of water addition to the gasifier off-gas will be limited to the stochiometric requirement. The WGS efficiency under the stochiometric environment could be discounted significantly; however, the use of WGS-MR can enhance the reaction efficiency to compensate for this loss in efficiency. Since (i) our membrane has demonstrated an excellent sulfur resistance at our proposed reaction temperature, and (ii) H_2S and other sulfur removal contaminants can be rejected by our hydrogen selective CMS membrane, no sulfur pre-treatment is required. Thus, the pretreatment requirement in our proposed WGS-MR process can be streamlined to the

particulate removal only. No excess water beyond the stochiometric requirement for CO conversion is necessary; thus, power generation efficiency can be maximized.

Post treatment requirement includes the PROX for the elimination of trace CO. Since the CO contaminant level from our WGS-MR is 20-30 ppm, PROX can be implemented economically and reliably to produce hydrogen with <10 ppm CO to meet the spec for PEM fuel cells. This would be a more cost effective solution than the use of our proposed technology to produce on-spec hydrogen without post-treatment. WGS reaction in the presence of sulfur can be accomplished with the use of the Co/MoS_2 catalyst. This catalyst has been employed industrially as a sour gas shift catalyst. Our mathematical simulation on WGS-MR based upon the suggested pre- and post-treatment has demonstrated that a nearly complete CO conversion (i.e., 99+%) can be accomplished. Although conversion vs production cost may play an important role in an overall process optimization, no cost optimization has been taken into consideration presently. We estimate that ~90% of the hydrogen produced from the H_2+CO in the coal gasifier off-gas can be recovered via our proposed WGS-MR process. Its purity level ranges from 80 to 92% depending upon the H_2/CO_2 selectivity of 10 to 25 respectively. If the purity of 95% is required, the hydrogen recovery ratio will drop to ~80% level for the membrane with H_2/CO_2=25.

3. Experimental

3.1. Experimental Verification of Mathematical Model Developed for WGS-MR

A lab scale CMS membrane with 0.35cm ID, 0.45cm OD, and 10" L was selected for this study. This CMS membrane was characterized with both single gas and mixed gas at the target reactor temperature, 250°C and 50 psig. Two tests were performed for the mixture separation: one with the presence of water and the other without. Thus water permeation and its effect on the permeation of other gases were quantified.

3.2. Membrane Reactor Study
The membrane was packed with the Cu/ZnO catalyst for CO conversion via WGS reaction. Feed composition and the reactor configuration and its operating condition are detailed below.

Feed Composition			Operating Condition	
	Ratio	Mol Fraction	Feed Pressure	3 atm
CO	1	0.16	Permeate Press	1 atm
CO2	0	0.00	Temperature	225-250C
H2O	1.1	0.18	Sweepratio	0.1
H2	4	0.66	Wc	30 g
N2	0	0.00	Surface Area	0.0028 m²

The experiment was performed at several selected W/F's, ranging from 250 to 500 gm-cat-hr/mol CO at 250°C and at 3 and 1 bar for the feed and permeate side pressure respectively. For each W/F, its CO conversion, hydrogen recovered ratio, CO impurity level and hydrogen purity were experimentally determined. In addition to 250°C, a lower temperature, i.e., 225°C, was

selected to evaluate the effect of reactor temperature. The experimental results obtained were then compared with the simulated values to evaluate the reliability of our mathematical model prediction.

3.3. Process Optimization

Using the mathematical model developed and verified above, we performed the optimization study on the proposed WGS-MR. Although no cost optimization was attempted here, we have configured a process scheme, which could streamline the hydrogen production via WGS-MR. The pre-treatment and post-treatment requirements were thus determined. Then a mathematical simulation was performed for WGS-MR under this proposed streamlined scheme. In addition, sensitivity analysis was performed to determine the effect of the H_2/CO_2 selectivity on the hydrogen purity. To eliminate the sulfur removal pretreatment requirement, Co/MoS_2 catalyst was employed in this optimization study. The kinetic parameters obtained from the literature [1] listed below were used for this simulation:

Preexponential factor [gmole/(gr-catal.sec.bar^0.4)]   k0=6.0
Reaction rate constant [gmole/(gr-catal.sec.atm^0.4)]   k=k0*exp(-5950/(R*(T+273)))

Rate Expression = k*(1-Beta)* PCO^0.8 * PH2O^0.29 *PCO2^-0.07

4. **Results and Discussion**

4.1. Hydrogen Permeance and Selectivity of CMS Membrane

Several CMS membranes were characterized and reported in our previous report. In this report, we select a CMS membrane with a higher hydrogen permeance in order to deliver a higher hydrogen recovery ratio under the constraint of our experimental set-up for the membrane with ≤10"L. Thus, the membrane selectivity is not as high as what reported previously. The single gas permeances along with the ideal separation factors at 250°C and 50 psig are presented in the top portion of Table 1. Its hydrogen permeance is 2.6 $m^3/m^2/hr/bar$. Its ideal selectivities are 34, and 13 for H_2/CO and H_2/CO_2 respectively. The mixture permeation was determined at a similar condition, i.e., 250°C and 50psig with the feed composition ratio of 4:1:1 of $H_2:CO:CO_2$. The hydrogen permeance is 2.1 $m^3/m^2/hr/bar$, and its selectivity over CO and CO_2 are 30 and 14 respectively. The hydrogen permeance in the mixture is somewhat lower than that obtained in the pure component while the selectivities are very close to those obtained from the pure components. In addition, the effect of water was performed. The hydrogen permeance is 2.3 $m^3/m^2/hr/bar$, and its selectivities over CO and CO_2 are 49 and 9.2 respectively. Since the hydrogen permeance obtained in this set of experiment (i.e., with H_2O) is close to the single component, we believe that the hydrogen permeance of 2.1 $m^3/m^2/hr/bar$ obtained in the first set is most likely due to the experimental error. The selectivities obtained from the presence of water exhibited the enhanced affinity toward CO while reduced affinity to CO_2. We believe that the WGS reaction may have taken place in this experimental study although no catalyst is used. As expected, the water permeance is similar to the hydrogen permeance. In summary, the

permeances in the mixture and their selectivities are consistent with those obtained from the pure components. In the reactor simulation study, the pure component permeances were adopted.

Table 1   Characterization of Hydrogen Selective CMS Membrane Used in This Reporting Period

Surface Area (m2)   0.0027928
T = 250 C

	Shell Side Feeding					
	Pure Gas					
	250 C / 50 psig					
	Permeate (cc/sec)	Permeance [m3/(m2*hr*bar)]	S.F. based on H2	Permeate (cc/sec)	Permeance [m3/(m2*hr*bar)]	S.F. based on H2
H2		2.6054	1.0			
CH4		0.0317	82.2			
CO		0.0778	33.5			
CO2		0.2046	12.7			
H2O						
N2		0.0569	45.8			
Ar		0.0650	40.1			
Ar						

	Shell Side Feeding					
	H2 : CH4 : CO : CO2 = 8.0 : 0.0 : 2.0 : 2.0			H2 : H2O : CO : CO2 = 8.0 : 2.0 : 2.0 : 2.0		
	Ar as sweep : 1.060 (cc/sec)					
	250 C / 50 psig			250 C / 50 psig		
	Permeate (cc/sec)	Permeance [m3/(m2*hr*bar)]	S.F. based on H2	Permeate (cc/sec)	Permeance [m3/(m2*hr*bar)]	S.F. based on H_2
H2		2.1187	1.0		2.3319	1.0
CH4						
CO		0.0705	30.1		0.0473	49.3
CO2		0.1552	13.7		0.2526	9.2
H2O					2.2709	1.0

4.2.   Experimental Verification of Mathematical Model

The experimental and predicted results are presented in Figures 1 to 4. In the last report, we confirmed that the mathematical model predicted well the CO conversion and the effect of sweep ratio reasonably with the feed composition typical of the coal gas. In this report, we present the comparison of experimental vs simulated results with regard to the remaining aspects of the performance parameters, i.e., hydrogen purity, CO contaminant concentration in the hydrogen recovered, and the hydrogen recovery ratio, in addition to the CO conversion by WGS-MR at 250°C. Besides the effect of the reactor temperature on CO conversion, hydrogen recovery ratio and CO contaminant level was verified at a lower temperature, i.e., 220°C.

Both experimental and simulated result on CO conversion vs W/F is presented in Figure 1. The CO conversion reaches ~90% for W/F ranging from 250 to 500 gm-cat-hr/mol CO, which

matches well with the simulated results. Our previous report shows >90% conversion resulted from the use of the membrane with a higher H_2/CO selectivity than what used in this study. In summary, ~10% conversion enhancement over the thermodynamic equilibrium under this experimental condition was accomplished with the use of the membrane reactor, similar to what reported in the previous report.

| **Figure 1** | **CO conversion via WGS-MR Using Our Hydrogen Selective CMS Membrane: Experimental vs Simulated.** |
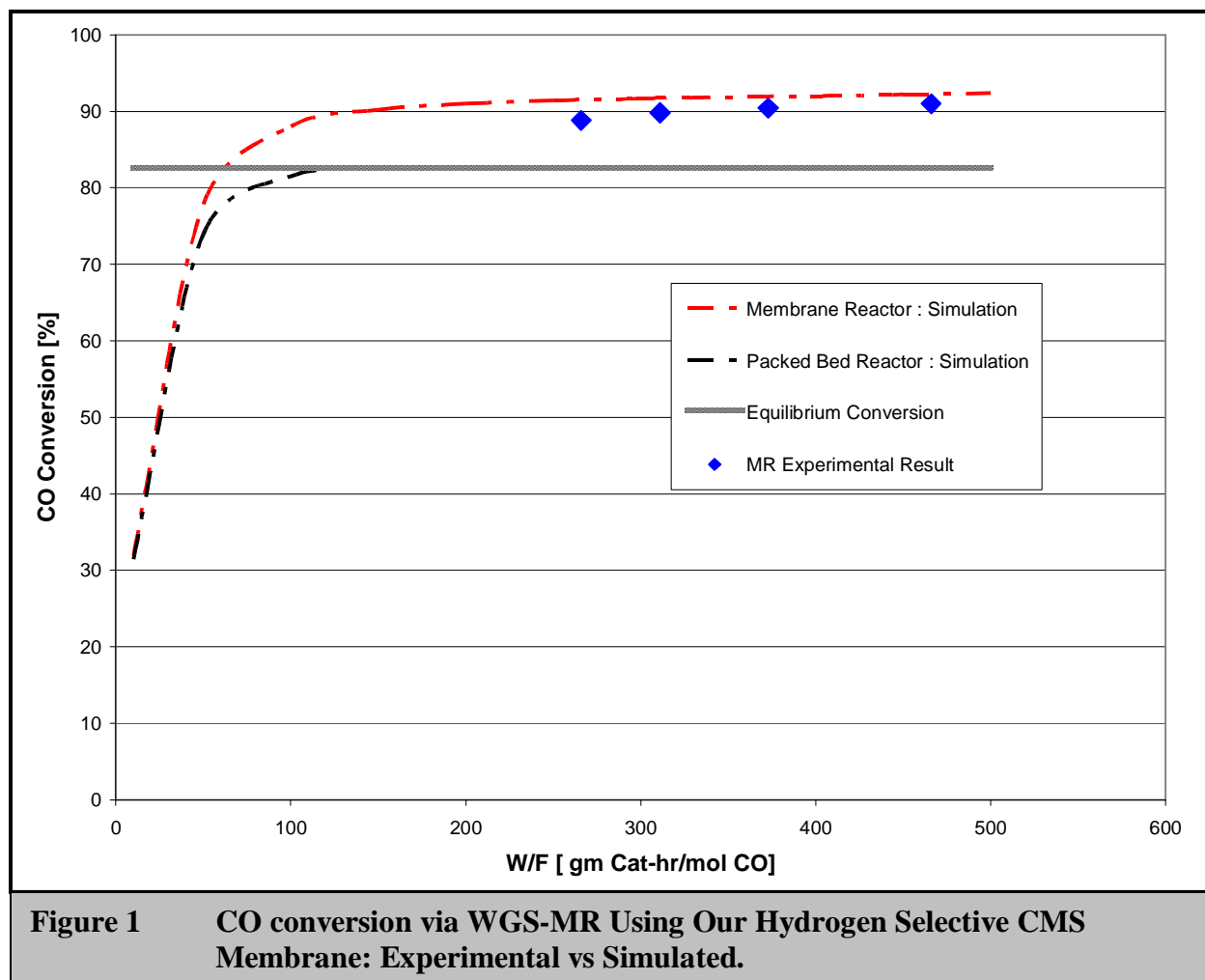
Experimental results on the hydrogen recovered and its CO contaminant concentration in the hydrogen product recovered are presented in Figure 2 along with the mathematical prediction. About 40 to >70% hydrogen recovered was obtained for the W/F range studied, which agrees extremely well with the simulated results as shown in Figure 2. The CO contaminant level corresponding to this range of W/F is 3,000 to 2,200 ppm, which is consistent with the predicted value of ~2,000 ppm. Overall the hydrogen recovery and CO contaminant level can be predicted reliably with the mathematical model we have developed although the CO contaminant level appears slightly under-estimated by our mathematical model. Based upon the permeance of our membrane, a longer membrane tube (i.e., high membrane surface area to catalyst dosage ratio, and/or lower space velocity) will be required in order to achieve the hydrogen recovered at

>>70%. Due to the experimental set up limitation, i.e., the furnace dimension, no laboratory study with a longer membrane tube (i.e., >10" L) can be performed under this project. Following the trend of the experimental vs predicted results, we believe that the CO contaminant level can be predicted closer to the simulated value at a higher hydrogen recovery level, i.e., >>70%.
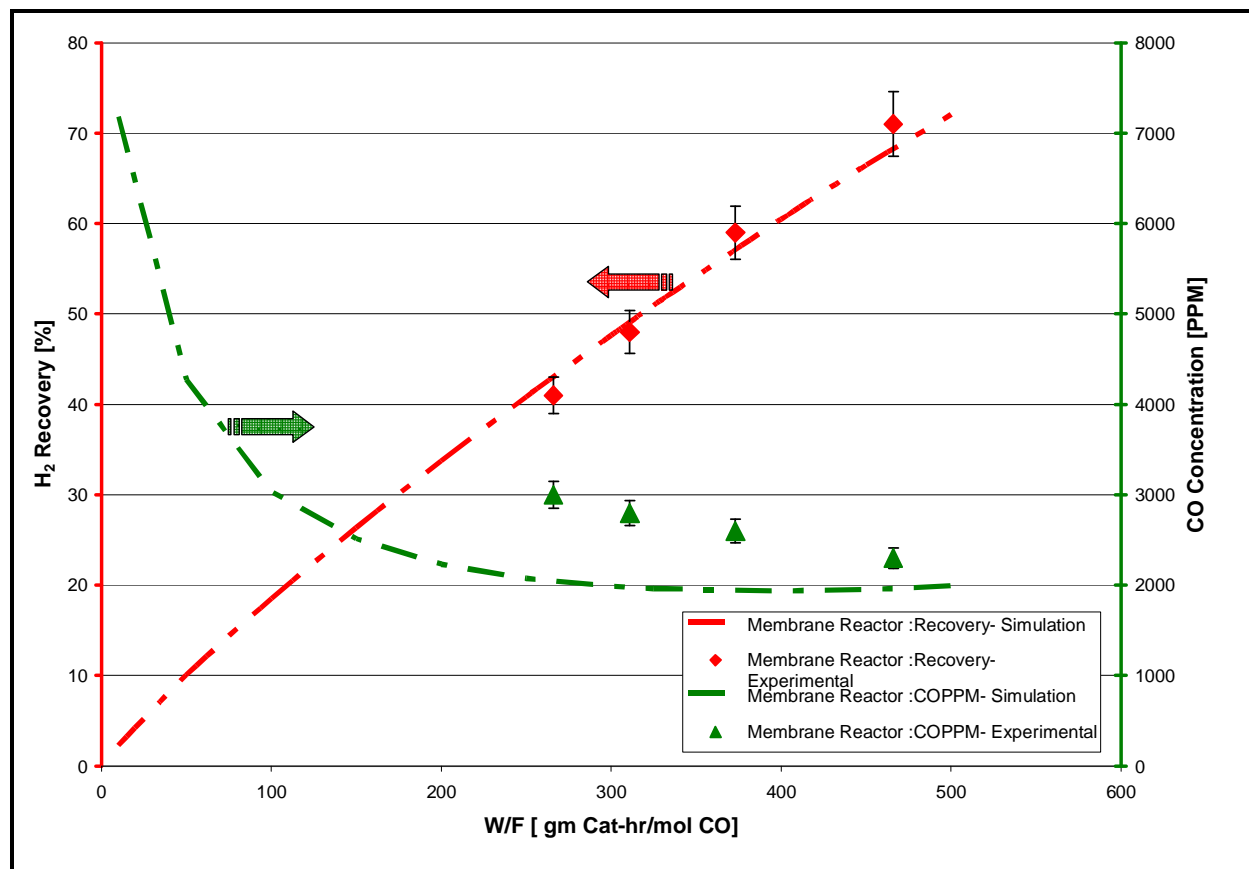

Figure 2   **Hydrogen Recovery Ratio and Its CO Contaminant Level for a Wide Range of W/F studied: Experimental vs Simulated.**

Effect of temperature was also performed both experimentally and with simulation. In addition to 250°C, the experimental study at 220°C was performed as presented in Figures 3&4 for CO conversion and hydrogen recovery and CO contaminant level respectively. As obtained at 250°C, the predicted values match well with the experimental results at this lower temperature.
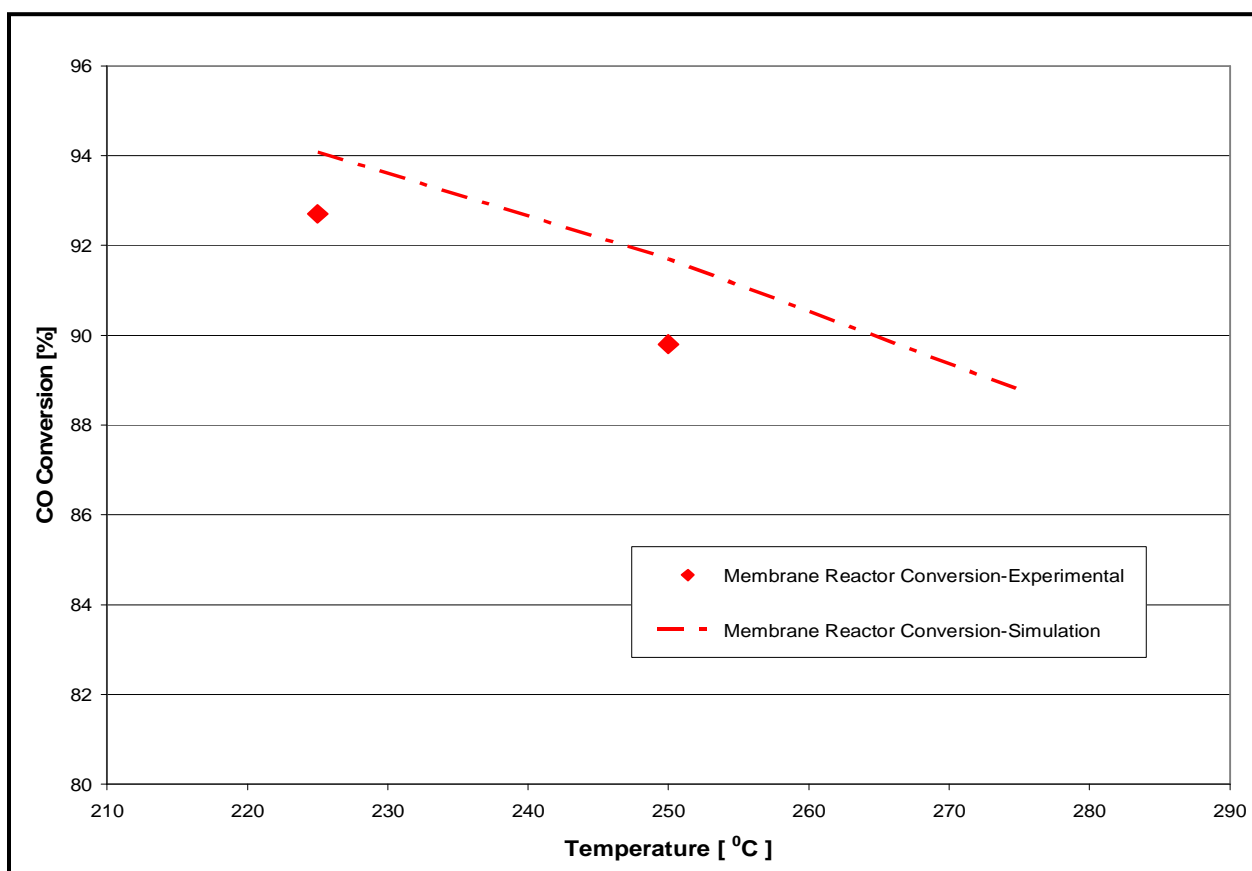
Figure 3   **Effect of Reactor Temperature on CO Conversion via WGS-MR: Experimental vs Predicted.**

Figure 4   Effect of Reactor Temperature on Hydrogen Recovery and CO Contaminant Level: Experimental vs Preducted.
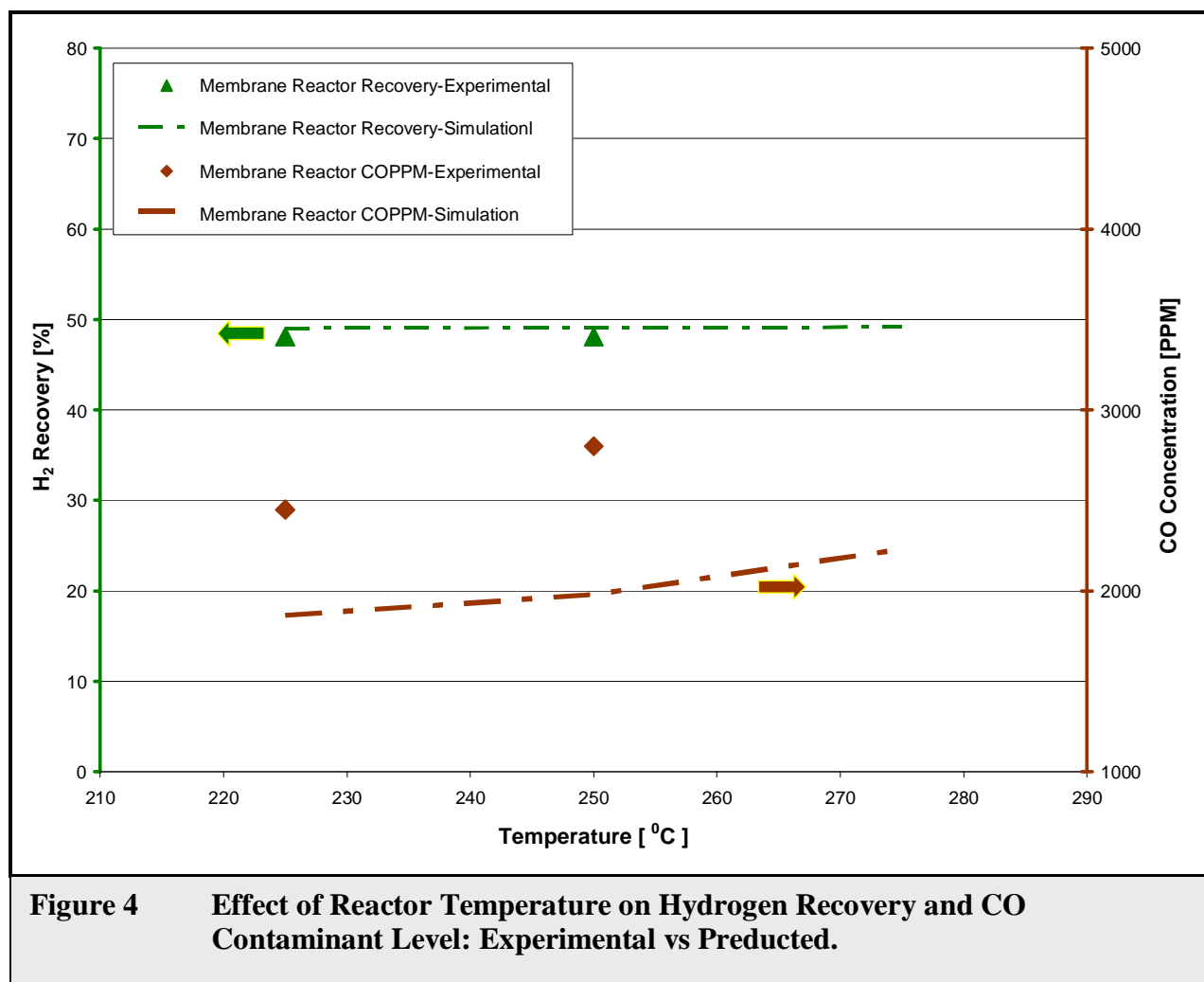
In summary, the mathematical model we have developed can predict the performance of the WGS-MR reliably for the experimental condition selected in this study using a typical feed obtained from coal gasifier off-gas.

4.3.   <u>Process Optimization for Hydrogen Production</u>

In this reporting period, we also attempted to perform process optimization, focusing on the use of our CMS membrane for WGS-MR with the mathematical model developed and verified in this project. A comprehensive process optimization is beyond the scope of this project; however, an optimization around the WGS-MR would give us valuable information, specifically an compromised hydrogen purity vs hydrogen recovery ratio. Several process variables are arbitrarily selected in order to minimize the variables involved in the optimization. These variables are listed below:

- To avoid the hot gas clean-up requirement, our process will recover as much as heat from the gasifier off-gas via HRSG. Thus, the target temperature for the feed to the WGS-MR can be set at a low temperature, e.g., 250°C. Thus, particulate removal, which is the only pre-treatment requirement for our proposed process, can be accomplished with an existing technology. No hot gas clean-up (HGCU) is required under our proposed process.

- The amount of water addition to the gasifier off-gas will be limited to the stochiometric requirement. Significant over-stochiometric water addition has been practiced routinely to enhance the CO conversion. However, from the power generation standpoint, the water quench to the gasifier stream is essentially a loss in the power generation efficiency. In addition, dilution of reactants and products, which are unfavorable to WGS reaction and membrane permeation in most occasions. The WGS conversion efficiency under the stochiometric environment could be discounted significantly; however, the use of WGS-MR can enhance the reaction efficiency to compensate for this loss in efficiency.

- Since our membrane has demonstrated an excellent sulfur resistance at our proposed reaction temperature, and H_2S and other sulfur contaminants removal can be rejected by our hydrogen selective CMS membrane, no sulfur pre-treatment is suggested. Instead, the acid gas removal can be implemented after the hydrogen production and recovery if necessary. Thus, the pretreatment requirement in our proposed process can be streamlined to the particulate removal only.

- WGS reaction in the presence of sulfur can be accomplished with the use of the Co/MoS_2 catalyst. This catalyst has been employed industrially for WGS in the presence of sulfur.

An example of the proposed process is presented in Figure 5. With the above assumptions in pre- and post-treatment and the reactor operation, we initiated the process simulation study for WGS-MR using the mathematical model developed.
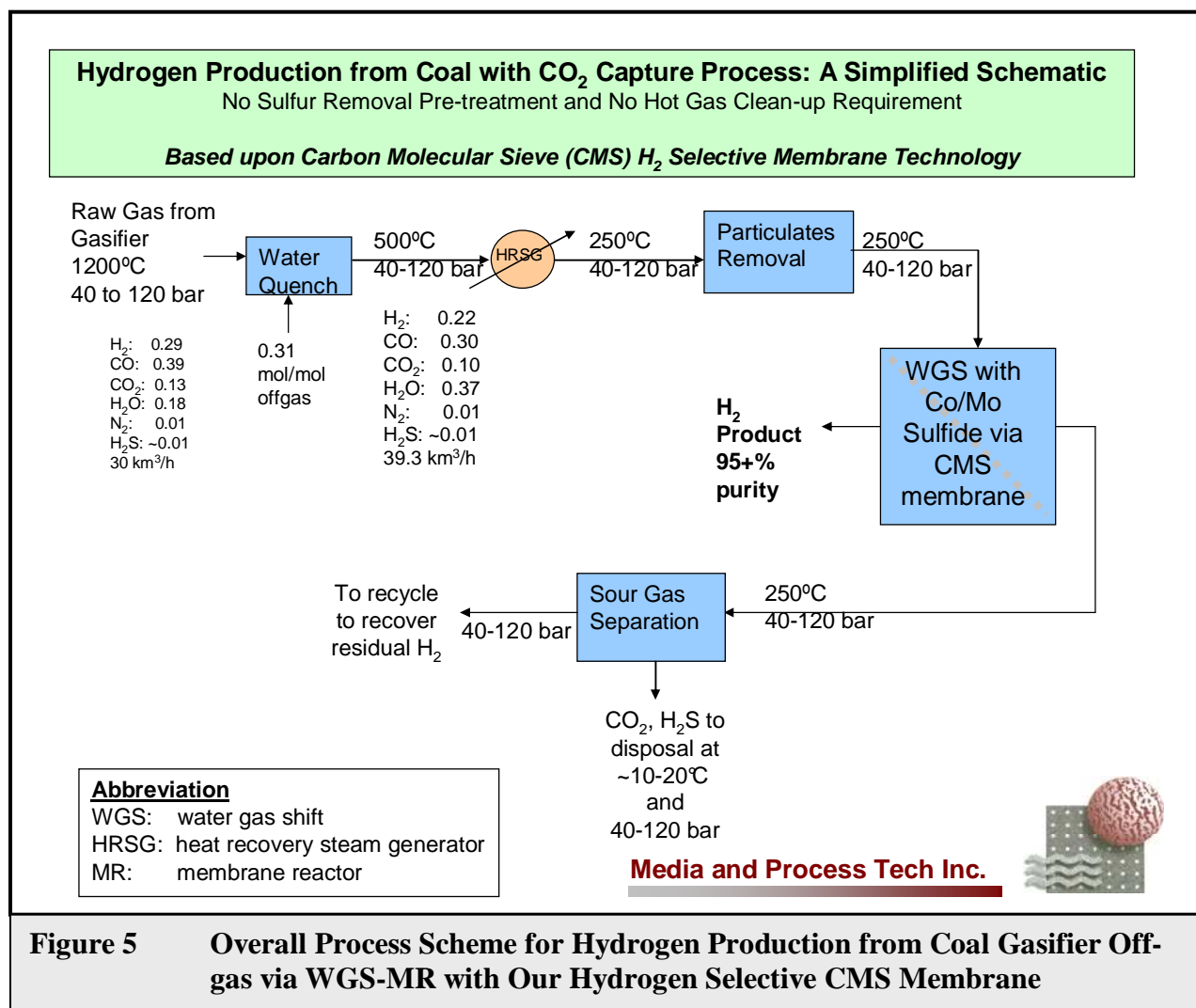
Figure 5 **Overall Process Scheme for Hydrogen Production from Coal Gasifier Off-gas via WGS-MR with Our Hydrogen Selective CMS Membrane**

Our simulation strategy is based upon the principles below:

- It is our objective to achieve a nearly complete CO conversion with the proposed CMS-MR. Although conversion vs production cost may play an important role in an overall process optimization, no cost optimization has been taken into consideration. However, a nearly complete CO conversion, i.e., >99%, can be achieved with the use of our CMS-MR.

- In our proposed process, the PROX is treated as essential post treatment to reduce the CO contaminant level of 20-30 ppm to <10 ppm to meet the PEM fuel spec. PROX can be implemented economically and reliably for this low level contaminants Therefore, our optimization does not take into consideration of minimizing the CO contaminant level with out proposed WGS process.

- In stead of the maximized hydrogen purity and the minimized CO contaminant level, a relationship for hydrogen purity and its CO contaminant vs % hydrogen recovered will be established to demonstrate the trade-off relationship.
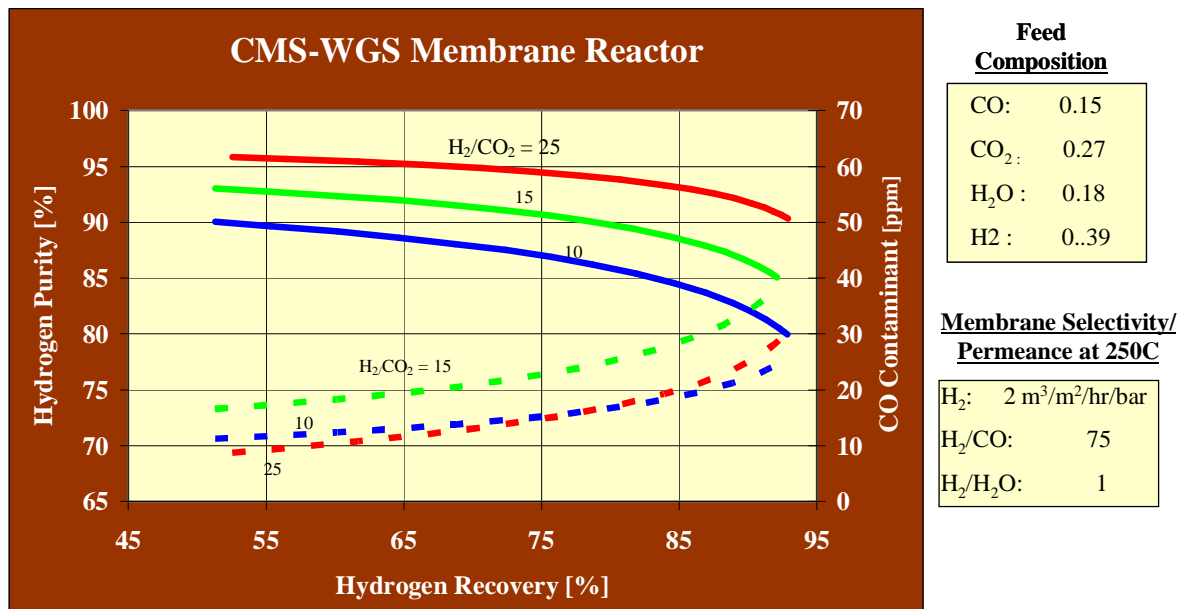
Figure 6 **Hydrogen Purity and CO Contaminant Level for the WGS-MR with A Nearly Complete Conversion of CO and the Use of Nearly Stochiometirc H_2O/CO Ratio.**

Hydrogen purity and CO contaminant level vs % hydrogen recovered is presented in Figure 6 for the membrane with hydrogen permeance of 2 $m^3/m^2/hr/bar$ and the selectivity of H_2/CO=75. In comparison with the membrane property employed in Sec. 4.2 for verification, the hydrogen permeance used here is lower while the selectivity is higher. As indicated in Sec. 4.2, a membrane with a higher hydrogen permeance was selected to maximize the hydrogen recovery ratio with the lab scale reactor we used there. Thus, a lower hydrogen permeance with a higher selectivity used here is in-line with the CMS membranes we have produced thus far. In addition, our typical H_2/CO_2 selectivities range from <5 to >25 at this temperature are selected, depending upon the hydrogen permeance required. For hydrogen permeance of 2 $m^3/m^2/hr/bar$, a H_2/CO_2=10 is considered as our base case. A typical coal gasifier off-gas composition was adopted here (see Figure 6). The H_2O/CO ratio used in this simulation is 1.2.

For the selectivitiy of H_2/CO_2=10, our simulation shows that the hydrogen purity of 80% and CO contaminant of 25 ppm can be produced at 90% hydrogen recovered. To enhance the purity to 90% the recovered ratio diminishes to ~55%. Thus, it is not practical to enhance the hydrogen purity using the membrane with H_2/CO_2=10. Since majority of impurity is CO_2, to enhance the purity can be most effectively accomplished with the use of the membrane with a higher H_2/CO_2, we perform some sensitivity analysis on the variation of H_2/CO_2 on the hydrogen purity vs hydrogen recovered. The hydrogen purity can be enhanced to 92% with the 90% hydrogen recovered. Its corresponding CO contaminant level is ~30 ppm. On the other hand, if the

hydrogen recovered of 80% is acceptable, hydrogen purity approaches 95%. Figure 7 presents the effect of H_2/CO_2 selectivity on hydrogen purity at the recovery ratio of 92%. The purity will increase from 80 to 90% with the H_2/CO_2 selectivity increase from 10 to 25. In summary, 90% hydrogen produced from the H_2+CO in the feed can be recovered via our proposed WGS-MR process. Its purity level ranges from 80 to 92% depending upon the H_2/CO_2 ratio. If the purity of 95% is required, the hydrogen recovery ratio will drop to 80% level for the membrane with $H_2/CO_2=25$.

| Figure 7 | Effect of H_2/CO_2 Selectivity on Hydrogen Purity on WGS-MR with Complete CO Conversion |
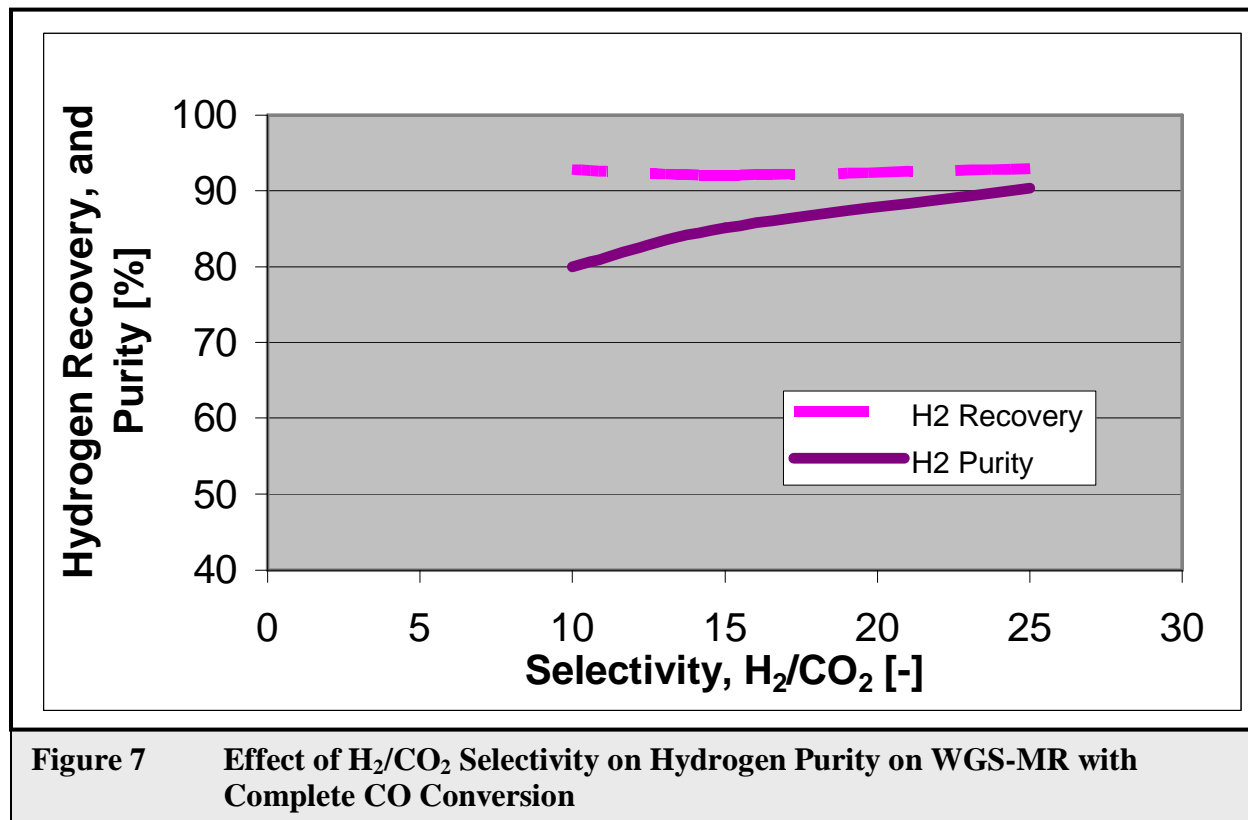
5. Conclusions

Based upon the results obtained in this reporting period, several conclusions can be drawn as follows:

- About 40 to >70% hydrogen recovered was obtained for the W/F range studied with the lab-scale WGS-MR, which agrees extremely well with the simulated results. The experimental CO contaminant level corresponding to this range of W/F is 3,000 to 2,200 ppm, which is consistent with the predicted value of ~2,000 ppm in this range. Along with the experimental verification on CO conversion and sweep gas effect reported in the last report, we conclude

that our mathematical model can predict reliably all aspects of the membrane reactor performance for WGS using the coal gasifier off-gas as feed under the proposed operating condition.

- In addition to 250°C, the experimental study at 220°C was performed. As obtained at 250°C, the predicted values match well with the experimental results at this lower temperature.

- Pretreatment requirement for our proposed WGS-MR process has been defined as follows:

    o To avoid the hot gas clean-up (HGCU) requirement, our process will recover as much heat as possible from the gasifier off-gas via HRSG to enhance the overall power generation efficiency. Thus the target temperature for the feed to the WGS-MR can be set at a low temperature, e.g., 250°C. Thus, particulate removal can be accomplished with an existing technology.

    o The amount of water addition to the gasifier off-gas will be limited to the stochiometric requirement. The WGS efficiency under the stochiometric environment could be discounted significantly; however, the use of WGS-MR can enhance the reaction efficiency to compensate for this loss in efficiency.

    o Since (i) our membrane has demonstrated an excellent sulfur resistance at our proposed reaction temperature, and (ii) H_2S and other sulfur removal contaminants can be rejected by our hydrogen selective CMS membrane, no sulfur pre-treatment is required.

Thus, the pretreatment requirement in our proposed WGS-MR process can be streamlined to the particulate removal only. No excess water beyond the stochiometric requirement for CO conversion is necessary in our pre-treatment; thus, power generation efficiency can be maximized.

- Post treatment requirement includes the PROX for the elimination of trace CO. Since the CO contaminant level from our WGS-MR is very low, e.g., 20-30 ppm, PROX can be implemented economically and reliably to reduce the CO to <10 ppm to meet the PEM fuel spec. This would be a more cost effective solution than the use of our proposed process to produce on-spec hydrogen without post treatment.

- WGS reaction in the presence of sulfur can be accomplished with the use of the Co/MoS_2 catalyst. This catalyst has been employed industrially for WGS in the presence of sulfur. Our mathematical simulation on WGS-MR based upon the suggested pre- and post-treatment has demonstrated that

    o A nearly complete CO conversion (i.e., 99+%) with the proposed CMS-MR can be accomplished. Although conversion vs production cost may play an important role in an overall process optimization, no cost optimization has been taken into consideration.

- ~90% of the hydrogen produced from the H_2+CO in the coal gasifier off-gas can be recovered via our proposed WGS-MR process. Its purity level ranges from 80 to 92% depending upon the H_2/CO_2 ratio of 10 to 25 respectively. If the purity of 95% is required, the hydrogen recovery ratio will drop to 80% level for the membrane with H_2/CO_2=25.

References:

1. Lund, C. R. F., "Effect of adding Co to MoS_2/Al_2O_3 upon the kinetics of the Water-Gas Shift", I&EC Res., 35, 3067(1996).

List of Acronyms:

WGS: water gas shift reaction
MR: membrane reactor
PFR: packed fixed-bed reactor
Ea: activation energy
HGCU: hot gas clean up
HRSG: heat recovery steam generator
CMS: carbon molecular sieve
SGS: sour gas shift
PROX: Preferential oxidation
W/F: Ratio of catalyst dosage to feed rate
PEM: Proton exchange membrane