MHI WGS and COS Catalyst Demonstration Test Final Report

March 19, 2018

MITSUBISHI HEAVY INDUSTRIES AMERICA, INC.
Environmental & Chemical Plant Division

MITSUBISHI HEAVY INDUSTRIES AMERICA, INC.

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MITSUBISHI HEAVY INDUSTRIES AMERICA, INC.

1. Executive Summary

Mitsubishi Heavy Industries, Ltd. (MHI) and National Carbon Capture Center (NCCC) have collaboratively conducted the demonstration project of MHI water gas shift (WGS) catalyst for the pre-combustion carbon capture and sequestration (CCS) process in the syngas clean-up test facilities of NCCC located in Wilsonville, Alabama since 2011, and successfully completed 2017 testing (Run G5) in April, 2017. The MHI WGS catalyst showed high performance (over 60% of CO conversion ratio) at higher temperature (482 °F) and at steam/CO ratio as low as 0.8-1.0 compared with current commercial WGS catalyst at NCCC. The MHI WGS catalyst was exposed to the syngas up to approximately 7,600 hours at 480 °F so far for the long-term durability testing. MHI and NCCC have also conducted the demonstration testing for MHI COS hydrolysis catalyst since November, 2013. The MHI COS hydrolysis catalyst showed over 80% COS conversion ratios.

Key findings during the WGS testing are summarized as below:

- Confirmed the low-temperature (400-430 °F) performance and the catalyst long-term durability at 480 °F for approximately 7,600 hours to date.
  - CO conversion ratio was close to equilibrium at lower temperature (400 °F) at half syngas load (25 lb/h) condition.
  - CO conversion performance was stable (over 60%) throughout the long-term durability testing at steam/CO ratio of 0.6-1.5.

Summary of COS hydrolysis catalyst test results are below:

- Confirmed high COS hydrolysis performance and the long-term durability of COS hydrolysis catalysts.
  - COS conversion ratio showed over 80% at 570°F.

2. Test Procedure

The project has been carried out by installing MHI WGS catalyst and COS hydrolysis catalyst into the existing catalyst reactor units of NCCC for the following purpose.

- To demonstrate the MHI catalyst performance in the actual syngas of NCCC gasification test facilities.
- To evaluate long-term stability of the catalyst activity in the actual syngas of NCCC gasification test facilities.

2.1 Water Gas Shift Catalyst

MHI WGS catalyst has some preferable features for high efficiency clean-up system as follows,

1) Pelletized form Sour/Sweet-shift catalyst
2) Higher performance in lower temperature; 300 – 480 deg. F
3) Higher durability for sulfur loading (applicable for both sour and sweet conditions)
4) Lower steam/CO ratio requirement

MHI WGS catalyst can be applied for wide range of sulfur loading with lower steam consumption than the conventional WGS catalyst. The following WGS catalyst was used for the testing. The photo of sample catalyst is shown in Figure 2.1.

Figure 2.1 MHI WGS Catalyst

MHI WGS catalyst has been removed and evaluated performance at MHI laboratory after 2011 test campaign. No performance degradation was seen at the laboratory. The aged catalyst was re-loaded on the bed of ceramic balls in the reactor for 2012 and 2013 testing. After 2013 test campaign, the aged catalyst was removed again and re-loaded for 2014 testing.

2.2 COS Hydrolysis Catalyst

MHI COS hydrolysis catalyst has some preferable features for high efficiency clean-up system as follows,

1) Honey-comb shape COS and HCN hydrolysis catalyst,
2) Higher performance around 570 deg. F,
3) Higher durability for halogen loading.

At the test R12 and R13, the catalyst was tested.

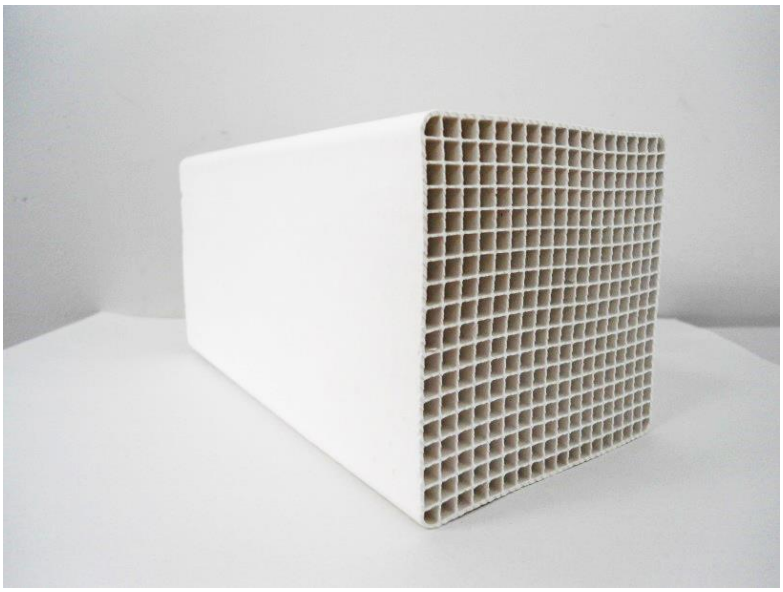

Figure 2.2 MHI COS Hydrolysis Catalyst

2.3 Test Facilities

The following existing slip stream catalyst reactors in NCCC's Power Systems Development Facility (PSDF) were used to evaluate the catalyst performance as shown in Figure 2.3 and Figure 2.4.

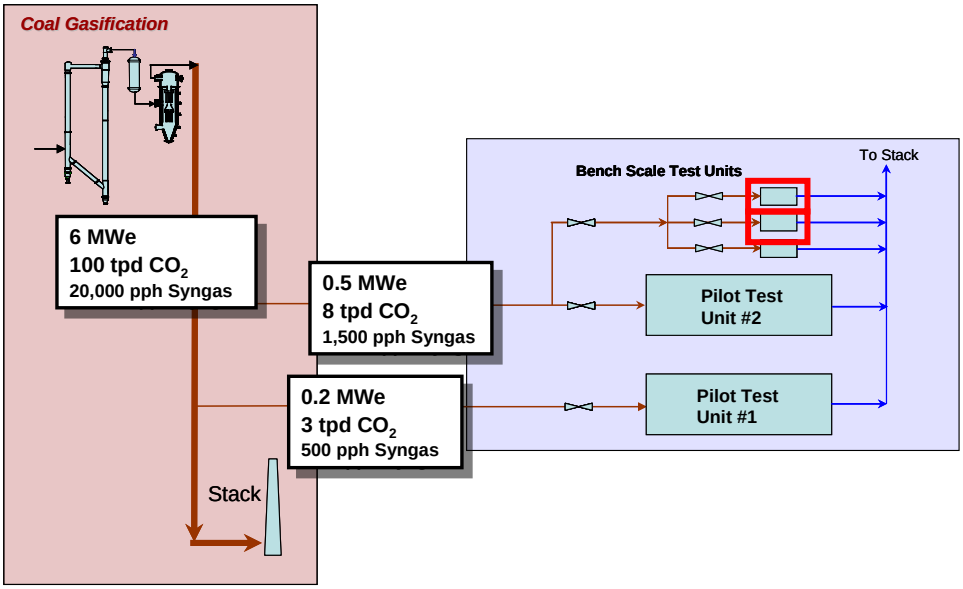

Figure 2.3 Test Facilities Process Flow

(a)Catalyst Reactors (b)RX700E Vessel

Figure 2.4 Catalyst Reactor

2.4 Test Items and Conditions

Parametric and long-term durability tests were performed to evaluate WGS and COS hydrolysis catalyst performance. The test conditions and gas measurement items are shown in Table 2.1, Table 2.2 and Table 2.3.

Table 2.1 Summary of WGS Test Conditions

Items	Parametric Test	Long-term Durability Test
Syngas Flow Rate	25 – 60 lb/h	50-60 lb/h
Syngas Temp. of Inlet	400 – 430 degF	482 deg F
Steam/CO ratio	0.7 – 1.2 mol/mol*	0.7 – 1.2 mol/mol*
Syngas pressure	180 psig	180 psig

Underlined conditions: Standard and long-term test conditions

Table 2.2 Summary of COS Hydrolysis Test Conditions

Items	Parametric Test
Syngas Flow Rate	25 – 50 lb/h
Syngas Temp. of Inlet	480 – 650 degF
Syngas pressure	180 psig

Table 2.3 Summary of Gas Measurement Items

Items	Reactor Inlet	Reactor Outlet	Method
CO, CO_2	A	A	NDIR
H_2, CH_4, H_2S,	A	A	Continuous-GC
H_2O	B	B	Wet chemical
COS	C	C	Continuous-GC

Frequency ; A : Continuous measurement
B : Once per day for parametric testing and twice per week for long-term durability testing
C : Continuous measurement either inlet or outlet

3. WGS Catalyst Test Results and Discussion

3.1 Test Duration

Parametric test and Long-term durability test were performed during separate runs. The test duration is summarized in Table 3.1.

Table 3.1 Summary of Test Duration

NCCC Run No.	Fuel coal	Start date	End date	Duration (hr)	Total duration (hr)
R7	PRB	2011/10/24	2011/12/12	861	861
R8	PRB	2012/6/23	2012/7/3	245	1,106
R8	PRB	2012/7/24	2012/7/25	26	1,132
R9	PRB	2012/11/29	2012/12/11	286	1,418
R9	PRB	2012/12/12	2012/12/19	178	1,596
R10	PRB	2013/3/21	2013/4/22	738	2,334
R11	MS Lignite	2013/8/4	2013/9/2	736	3,070
R12	PRB	2013/11/21	2013/12/12	447	3,517
R13	PRB	2014/03/19	2014/04/19	734	4,251
G1	PRB	2014/10/6	2014/11/6	735	4,986
G2	PRB	2015/9/21	2015/10/13	694	5,680
G3-4	PRB	2016/3/22	2016/6/2	1,121	6,801
G5	PRB	2017/3/29	2017/4/13	802	7,603

*2015/9/26: Oxygen break through occurred.
2016/4/10: Burned up to 1500 F because of the heater failure.

CO conversion ratio was calculated from the following equation.

$$\text{CO Conversion ratio (\%)} = \left(1 - \frac{\dfrac{\text{Outlet CO conc.}}{(\text{Outlet CO conc.} + \text{CO2 conc.} + \text{CH4 conc.})}}{\dfrac{\text{Inlet CO conc.}}{(\text{Inlet CO conc.} + \text{CO2 conc.} + \text{CH4 conc.})}}\right) \times 100$$

3.2 Parametric Test Results

All the parametric test results are summarized in the chart of relationship between CO conversion ratio and steam/CO ratio as shown in Figure 3.1. Steam/CO ratio was varied depending on the fuel type and gasifier operating conditions even though there was no additional steam injection during the test campaign. The curve of equilibrium CO conversion ratio at 400 degF is shown in the chart, the CO conversion of half syngas load (25 lb/h) conditions are close to the equilibrium because of lower space velocity. However, the other data show the lower CO conversion performance because of higher space velocity. It was confirmed that this catalyst showed higher activity at low temperature (400-430 degF) compared with conventional WGS catalysts.

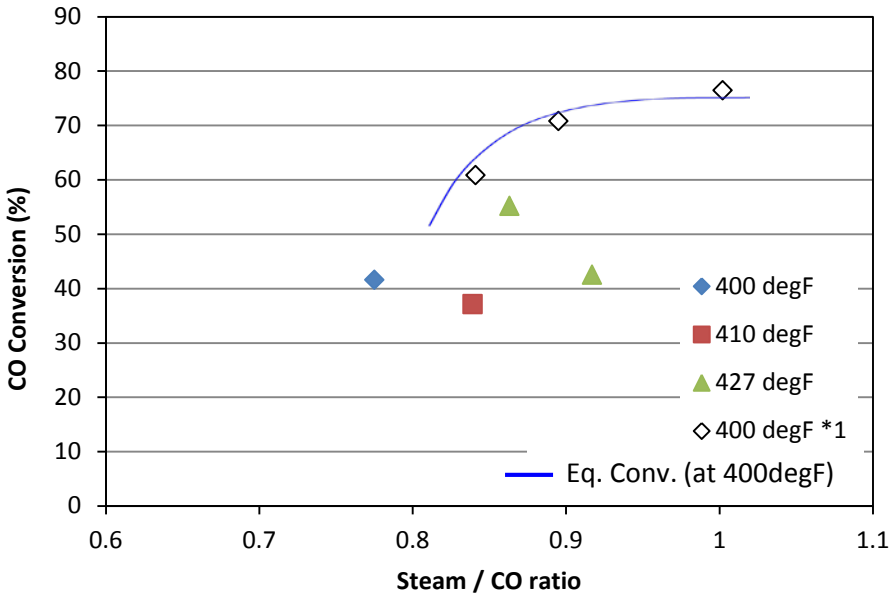

Figure 3.1 Parametric test results

*1 Half syngas load (25 lb/h) condition

3.3 Long-term Durability Test Results

Data trend of long-term durability test is shown in Figure 3.2. CO conversion ratio was stable and over 60% at steam/CO ratio of 0.6-1.5 during the PRB coal testing from R7 to G1. At G2 test, the conversion decreased by 55%, because of oxygen break thorough occurred. At G5 test, the catalyst seems to be degraded due to failure of the reactor that accidentally burned the catalyst up to 1500 F. At the end of G5 test, the catalyst performance made a recovery and the test was completed.

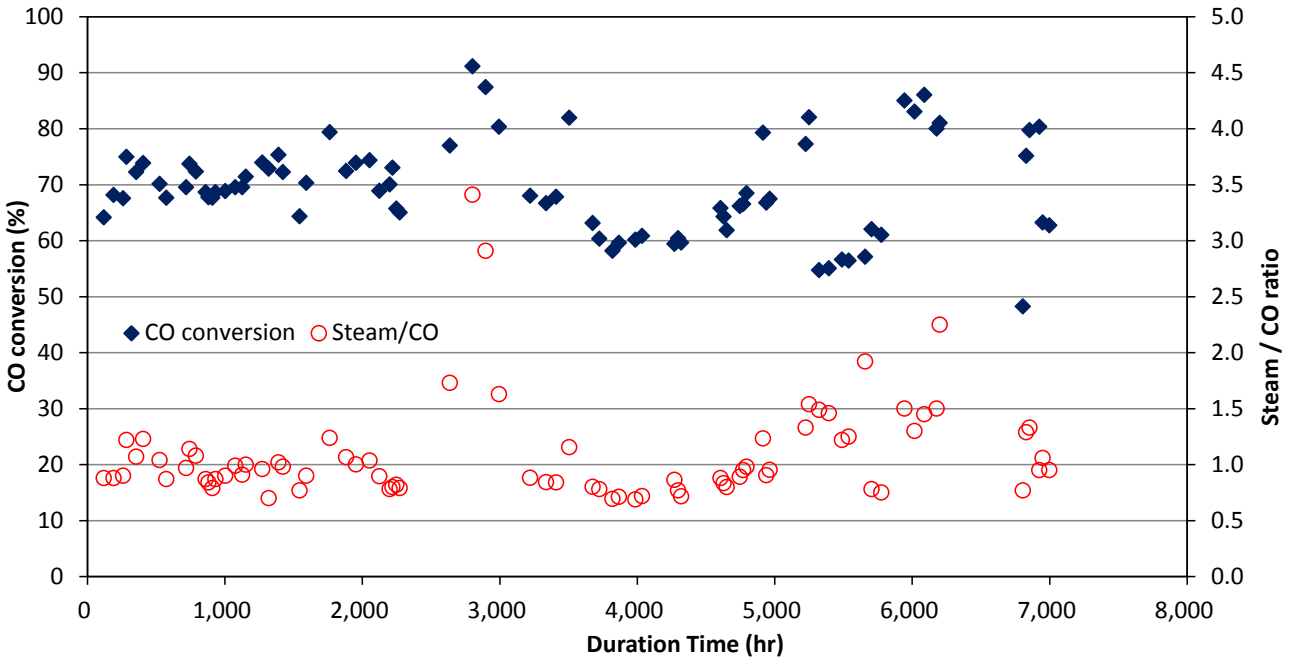

Figure 3.2 Long-term Durability Test Data Trend

4. COS Hydrolysis Catalyst Test Results and Discussion

4.1 Test results

Parametric test was performed with COS hydrolysis catalyst during March-April timeframe in 2014. COS conversion ratio was calculated from the following equation.

COS conversion ratio (%) = (1- Outlet COS conc. / Inlet COS conc.) × 100

The data trend of COS concentration is shown in Figure 4.1 and 4.2.

The COS conversion ratio was higher than 80% all through the test conditions.

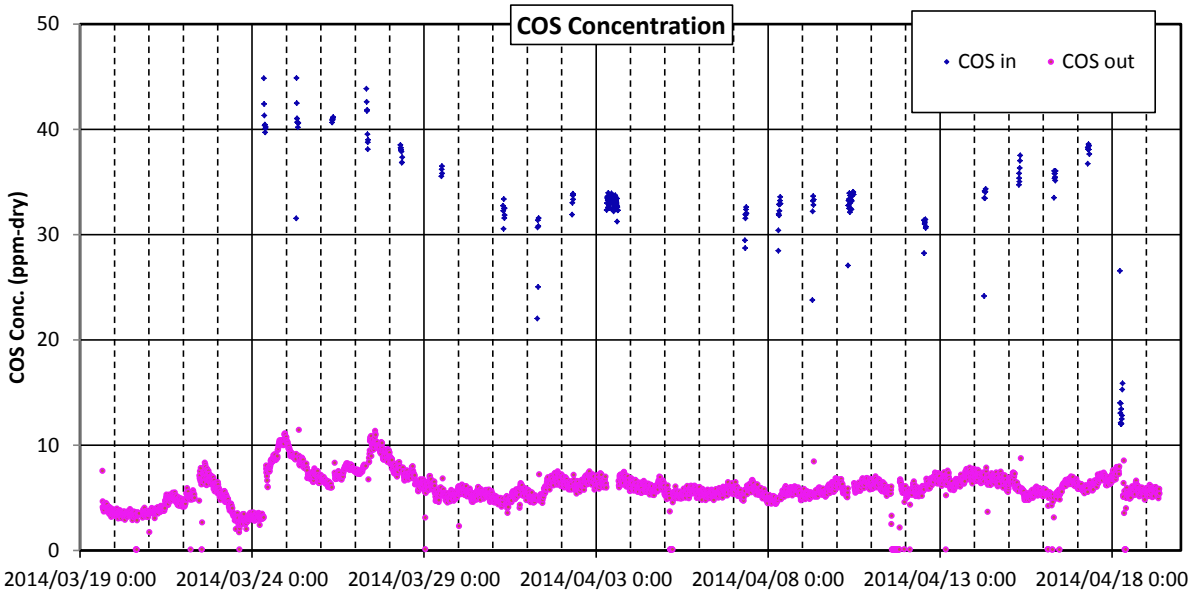

Figure 4.1 COS Hydrolysis Test Data Trend

5. Summary

MHI and NCCC are collaboratively conducting the demonstration project of MHI WGS catalyst for the pre-combustion carbon capture and sequestration process in the syngas clean-up test facilities of NCCC located in Wilsonville, Alabama since 2011, and successfully completed 2017 testing (Run G5) in April, 2017. The MHI WGS catalyst showed high performance (over 60% of CO conversion ratio) at higher temperature (482 °F) and at steam/CO ratio as low as 0.8-1.0 compared with current commercial WGS catalyst at NCCC. The catalyst seems to be degraded due to heater failure of the reactor that accidentally burned the catalyst up to 1500 °F on April 10th, 2016 even though sulfidation processing was conducted before the testing of Run G5. The MHI WGS catalyst was exposed to the syngas up to approximately 7,600 hours at 480 °F so far for the long-term durability testing. MHI and NCCC have also conducted the demonstration testing for MHI COS hydrolysis catalyst since November, 2013. The MHI COS hydrolysis catalyst showed over 80% COS conversion ratios.

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