MI-ROP-B4942
Renewable Operating Permit (ROP)
Compliance Test Report

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Dow AgroSciences, LLC
Harbor Beach, Michigan

Sampling Date(s): May 13, 2014

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TABLE OF CONTENTS

Executive Summary

This report presents performance test results during heat recovery steam generator (HRSG) fresh air mode operations regulated under Renewable Operating Permit (ROP) MI-ROP-B4942 Flexible Group FG-BURNERS. The HRSG assets are located at the Dow AgroSciences, LLC (DAS) Harbor Beach Operations facility. Flexible Group FG-BURNERS is comprised of two HRSG units identified as emission units North Burner (EU_N_BURNER) and South Burner (EU_S_BURNER).

The Dow Chemical Company Stack Testing Team conducted the compliance sampling. Jennifer Lang (MDEQ Saginaw Bay District) and Nathan Hude (MDEQ Field Operations Section) observed testing on May 13, 2014. All emission units met the required permit limits.

Results of Emission Sampling				
Unit	Pollutant/Test Method	Allowable Emission Rate	Actual Emission Rate	Compliance Evaluation
EU_N_BURNER	NOx EPA Method 7E	4.5 lb/hr	3.4	Compliant
	CO EPA Method 10	4.8 lb/hr	3.4	Compliant
EU_S_BURNER	NOx EPA Method 7E	4.5 lb/hr	3.5	Compliant
	CO EPA Method 10	4.8 lb/hr	2.2	Compliant

Process Operating Rate			
Unit	Operating Condition	Proposed Operating Rate	Actual Operating Rate
EU_N_BURNER	Fresh Air	~ 27 mmBtu/hr	~ 28.7 mmBtu/hr
EU_S_BURNER	Fresh Air	~ 27 mmBtu/hr	~ 28.8 mmBtu/hr

The following are the plant and sampling contacts for questions about the information in this sample report:

Primary Dow Contact	Dow Sampling Resource
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Introduction

Description of Industrial and Unit Process -

DAS operates a pesticide active ingredient manufacturing facility in Harbor Beach, Michigan. Operations include two heat recovery steam generators (HRSG) indentified as the north and south duct burners. For the purpose of this test plan and any associated communications, the terms HRSG and duct burners are interchangeable. Both burners are fired with natural gas. The emission units are identified as EU_N_BURNER and EU_S_BURNER. Together these units make up flexible group FG-BURNERS.

Operations also include two gas fired turbines. These are commonly identified as the north and south natural gas fired turbine engines. The emission units are identified as EU_N_TURBINE and EU_S_TURBINE. Together these units make up flexible group FG-TURBINES.

Type and Quantity of Raw and Finished Materials used in Process

These HRSG and turbine assets only burn natural gas.

Description of cyclical or batch operations that impact emission profiles:

These units operate continuously. The emission profile (formation of NOx and CO) is a function of the natural gas feed rate under normal operating conditions.

Operating Parameter Requirement

The facility uses a process control computer to automatically control the process within specific ranges dictated by process limits. Operating ranges are variable and dictated by production demand. Process parameters are monitored for automatic or semi-automatic action. Parameters include, but are not limited to temperatures, pressures and flow rates. This process unit is not required to incorporate any monitoring data collection such as continuous emission monitoring systems (CEMS) into unit operations.

Process Rate

The table below summarizes process operating rates. Following the table is a description of the four operating modes.

Table 1.1 – Normal Processing Rate Summary	
Process Unit	**Typical Operating Rates**
FG-TURBINES, NORTH (Supplemental, TEG or Turbine Modes)	~ 30 to 40 Million BTU/hr
FG-TURBINES, SOUTH (Supplemental, TEG or Turbine Modes)	~ 30 to 40 Million BTU/hr
FG-BURNERS, NORTH (Supplemental Mode)	~ 5 to 20 Million BTU/hr
FG-BURNERS, NORTH (Fresh Air Mode)	~ 20 to 25 Million BTU/hr
FG-BURNERS, SOUTH (Supplemental Mode)	~ 5 to 20 Million BTU/hr
FG-BURNERS, SOUTH (Fresh Air Mode)	~ 10 to 25 Million BTU/hr

FG-TURBINES & FG-BURNERS comprise Flexible Group FG-UTILITES and can operate in four different operating modes. These modes are identified as Supplemental, Turbine Exhaust Gas, Fresh Air, and Turbine Modes:

- Supplemental Mode = gas turbine operating, heat recovery steam generator operating. Emissions for the north unit vent through SV00007 & the south unit through SV00009.
- Turbine Exhaust Gas (TEG) Mode = gas turbine operating & heat recovery steam generator operating (the burner is not operating). Emissions for the north unit vent through SV00007 & the south unit through SV00009.
- Fresh Air Mode = burner operating & heat recovery steam generator operating (the gas turbine is not operating). Emissions for the north unit vent through SV00007 & the south unit through SV00009.
- Turbine Running (Air Generation) = gas turbine operating (the burners & heat recovery steam generator are not operating). Emissions for the north unit vent through SV00008 & the south unit through SV00010.

Greater than 95% of the operating time these assets are operated in either Supplemental or Turbine Exhaust Gas Modes. The Fresh Air and Turbine Modes only occur when one of the associated assets are down for maintenance

Description of Air Pollution Control Equipment

These units are not equipped with air pollution control equipment.

## Sampling Conditions and Runs

The image below shows the four atmospheric vents associated with the turbine and HRGS assets.
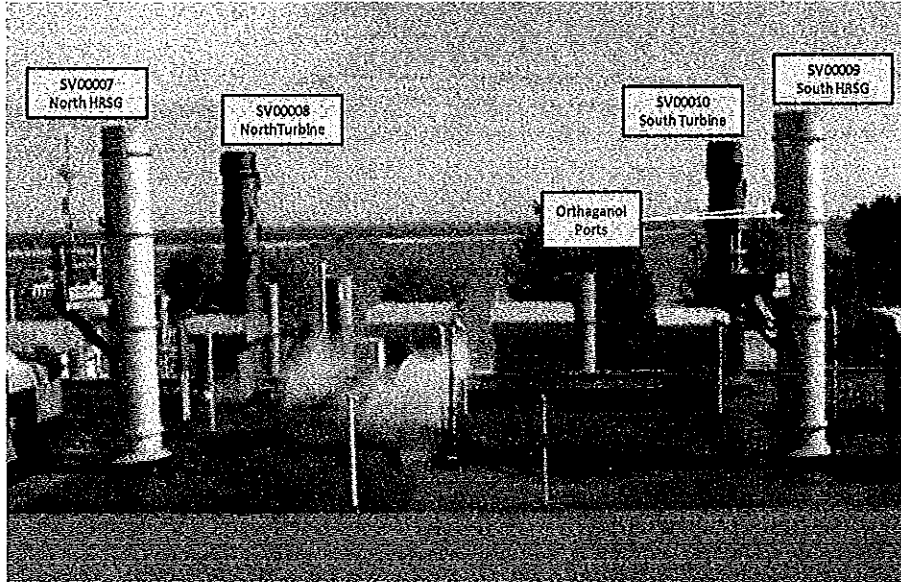
The table below summarizes the number and length of sampling runs which will constitute a complete test. The worst case emission profile occurs during Supplemental Mode because both the turbine and boiler are combusting natural gas and generating combusting by products (CO and NOx).

Test Condition Summary					
Process Units	Condition Number	Stack	Runs	Mode	Operating Rates
EU_N_BURNER	1	SV00007	3	Fresh Air	Burner $\cong$ 27 MMBTU/Hr
EU_S_BURNER	2	SV00009	3	Fresh Air	Burner $\cong$ 27 MMBTU/Hr

Block Flow Diagrams
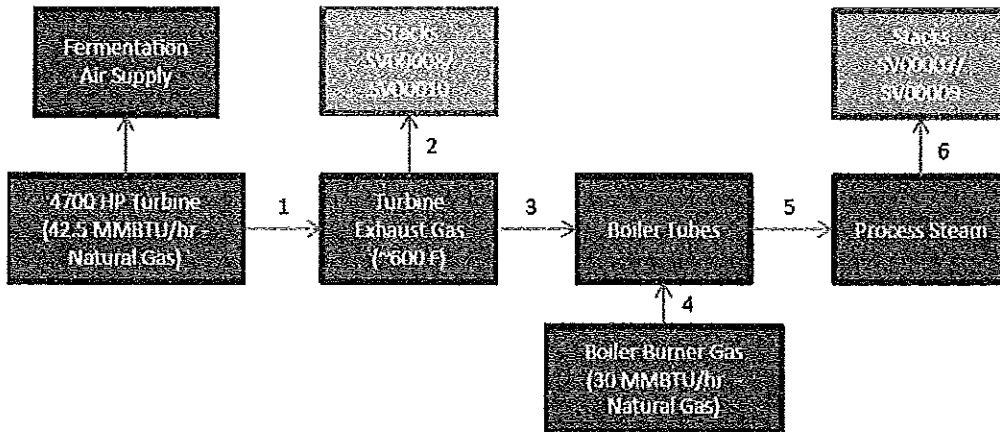
Turbine Mode - Air production without steam production. Pt 1 is active. Pt 3 is closed. Emission vent through Pt 2 (SV00008 for North Unit and SV00010 for South Unit.) Approx 1% of operating time.

Supplemental Mode - Air production and steam production. Pt 1 is active. Pt 2 in closed. Pt 3 is open. Pt 4 is active. Pt 5 is open. Emission vent through Pt 6 (SV00007 for North Unit and SV00009 for South Unit.) Approx 40% - 50% of operating time.

Turbine Exhaust Gas Mode - Air production and steam production without the boiler burner operating. Pt 1 is active. Pt 2 in closed. Pt 3 is open. Pt 4 is closed. Pt 5 is open. Emission vent through Pt 6 (SV00007 for North Unit and SV00009 for South Unit.) Approx 40% - 50% of operating time.

Fresh Air Mode - Steam production without air production. Pt 1 is closed. Pt 2 in closed. Pt 3 is closed. Pt 4 is active. Pt 5 is open. Emission vent through Pt 6 (SV00007 for North Unit and SV00009 for South Unit.) Approx 1% of operating time.

Test Results

The boiler and turbine assets are regulated by equipment type and in combination. FG-Burner regulates the natural gas fired HRSG. FG-Turbine regulates the natural gas fired turbines. FG-Facility regulates the assets in combination. Compliance testing is required under FG-Facility for the assets operated in combination. The tables below summarize the test results.

Results of Emission Sampling				
Unit	Pollutant/Test Method	Sampling Time (Minutes)	Actual Emission Rate	Allowable Emission Rate
FG Burner Emission Limits				
EU_N_BURNER	NOx EPA Method 7E	60	3.4	4.5 lb/hr
	CO EPA Method 10	60	3.4	4.8 lb/hr
EU_S_BURNER	NOx EPA Method 7E	60	3.5	4.5 lb/hr
	CO EPA Method 10	60	2.2	4.8 lb/hr

Sampling and Analytical Procedures

The table below lists all the pollutants and sampling trains used to collect measurements and samples during the performance test. These methods were performed according to the protocol listed in the appropriate Appendix A, 40 CFR 60 EPA Reference Test Method. Schematic diagrams can be found in the EPA Reference Test Methods.

Test Matrix for Emission Sampling:						
Sampling Location	No. of Runs	Sample/Type Pollutant	Sampling Organization	Sample Run Time (Min)	Reference Method	Target Reported Units Of Measure
Stack Exhaust	3/unit	Flow Rate	Dow Stack Testing Team	~ 60 Min	US EPA Method 1 through 4	acfm
Stack Exhaust	3/unit	Nitrogen Oxides (NOx)	Dow Stack Testing Team	~ 60 Min	US EPA Method 7E	ppmv
Stack Exhaust	3/unit	Carbon Monoxide (CO)	Dow Stack Testing Team	~ 60 Min	US EPA Method 10	ppmv
Stack Exhaust	3/unit	Oxygen (O$_2$)	Dow Stack Testing Team	~ 60 Min	US EPA Method 3A	%

Detailed Sampling and Analytical Procedures

The sampling and analytical procedure to be followed during the performance test is designed to demonstrate compliance with emission limits.

The performance test will be conducted while the process unit is in the operating step that generates the worst case emission profile. The sampling procedure includes the following steps:

1. Documenting the sample location dimensions and using the EPA Reference Method 1 Duct Dimension and Flow Disturbance Chart to determine traverse points.
2. For nitrogen oxides (EPA Method 7E), carbon monoxide (EPA Method 10) and oxygen (EPA Method 3A) sampling, one sampling train per location, per run, will be continuously extracted from the stack and transported through a heat-traced sample line to a mobile analytical laboratory. The mobile analytical laboratory will have a sample header that will be shared by other instruments in the trailer. A minimum of 3 runs will be collected. Each run will be a minimum of sixty-minutes in duration.
3. The methods provided in the table below will be used to collect samples for demonstration of compliance. Samples will be collected by the Dow Stack Testing Team.

Sampling and Analytical Plan			
Sampling Method	Sampling Plan	Analytical Method	Analytical Plan
Method 1	Traverse locations will be determined prior to sampling.	Not applicable	Not applicable
Method 2	Velocity measurements will be collected by traversing the stack.	Not applicable	Not applicable
Method 3	Carbon dioxide concentration will be determined by FYRITE analysis	Method 3 – FYRITE	Samples will be completed on-site.
Method 4	Samples will be collected from a single center point.	Method 4 – Gravimetric	Samples will be completed on-site.
Method 3A	Samples will be collected from a single center point routed to a header to be used by analyzer system.	Method 3A – Paramagnetic	Samples will be completed on-site.
Method 7E	Samples will be collected from a single center used by analyzer system.	Method 7E – Chemiluminescent	Samples will be completed on-site.
Method 10	Samples will be collected from a single center used by analyzer system.	Method 10 - Infrared	Samples will be completed on-site.

EPA Method 1-4

The number and location of traverse points in the stack were determined according to the procedures outlined in EPA Method 1. The flue gas velocity and volumetric flow rate were determined according to the procedure outline in 40 CFR 60, Appendix A, EPA Method 2. Velocity measurements were made using S-type pitot tubes conforming to the geometric specifications outlined in EPA Method 2. Differential pressures were measured with fluid manometers. Flue gas temperature, velocity, and volumetric flow rate data were recorded. Flue gas analysis for oxygen (3A) and carbon dioxide (3) and the calculation of flue gas molecular weight was performed in accordance with 40 CFR 60, EPA Methods 3 and 3A. The flue gas moisture content was determined in according to the procedures outlined in 40 CFR 60, Appendix A, EPA Method 4. The impingers were connected in series and contained reagents as described in Method 4. The impingers were contained in an ice bath in order to assure condensation of the moisture in the flue gas stream. Any moisture that was not condensed in the impingers was captured in the silica gel; therefore, all moisture was weighed and entered into moisture content calculations. The flue gas moisture content data was recorded.

EPA Method 7E

Emission sampling was conducted on the stack for NOx. The NOx sampling was conducted by continuously extracting sample from a single point in the centroidal area of the stack and analyzing a portion of the sample with a chemiluminescent analyzer. The sample was delivered to the analyzer via a heated probe and sample line. This prevents any condensation of water vapor and/or pollutant in the gas stream. The gas stream was then directed into a gas conditioning system where the moisture content of the stream is removed. The sample gas that exits the gas conditioning system was then routed to the chemiluminescent analyzer for analysis on a dry basis. Three runs of approximately one-hour duration each were conducted for each condition. The instrument was calibrated before and after each run using Protocol 1 standards.

EPA Method 10

Emission sampling was conducted on the outlet stack. The CO sampling was conducted by continuously extracting sample from a single point in the center of the stack and analyzing a portion of the sample by infrared. Three runs of approximately one-hour duration each were conducted for each condition..

Calculation Example

Analyzer Calibration Error Calculations

The calibration error test consisted of challenging each reference monitor at three measurement points against known calibration gas values. Calibration error is calculated using the following equation:

$$CE_{RM} = \frac{|Analyzer\ Response - Calibration\ Gas\ Value|}{Span\ of\ Analzyer} \times 100$$

South NOx Zero Calibration Error Example

$$CE_{RM} = \frac{|0.2\ ppmv - 0.0\ ppmv|}{60.1\ ppmv} \times 100 = \underline{0.3\ \%}$$

South NOx Mid-Gas Calibration Error Example

$$CE_{RM} = \frac{|30.2\ ppmv - 30.1\ ppmv|}{60.1\ ppmv} \times 100 = \underline{0.2\ \%}$$

South NOx High-Gas Calibration Error Example

$$CE_{RM} = \frac{|60.5\ ppmv - 60.1\ ppmv|}{60.1\ ppmv} \times 100 = \underline{0.7\ \%}$$

System Calibration Bias Calculations

The system bias calibration test consisted of challenging the reference sample system at two measurement points against the local calibration values. Calibration bias calculations for the reference sample system are calculated using the following equation:

$$CB_{RM} = \frac{|System\ Calibration\ Response - Analzyer\ Calibration\ Response|}{Span\ of\ Analzyer} \times 100$$

South NOx Zero Initial System Bias Run #1 Example

$$CB_{RM} = \frac{|0.0\ ppmv - 0.2\ ppmv|}{60.1\ ppmv} \times 100 = \underline{0.3\ \%}$$

South NOx Mid-Gas Initial System Bias Run #1 Example

$$CB_{RM} = \frac{|29.5\ ppmv - 30.2\ ppmv|}{60.1\ ppmv} \times 100 = \underline{1.2.\ \%}$$

Calibration Drift Calculations

The calibration drift tests were conducted at the beginning and end of each run. Analyzer maintenance, repair or adjustment could not be completed until the system calibration response was recorded. Calibration drifts for the reference is calculated using the following equation:

$$CD_{RM} = \frac{|Final\ System\ Cal\ Response - Initial\ System\ Cal\ Response|}{Span\ of\ Analzyer} \times 100$$

South NOx Zero Calibration Drift Run #1 Example

$$CD_{RM} = \frac{|0.2\ ppmv - 0.0\ ppmv|}{60.1\ ppmv} \times 100 = \underline{0.3\ \%}$$

South NOx Mid-Gas Calibration Drift Run #1 Example

$$CD_{RM} = \frac{|29.6\ ppmv - 29.5\ ppmv|}{60.1\ ppmv} \times 100 = \underline{0.2\ \%}$$

System Calibration Drift Correction

The gas concentrations are corrected for the system calibration bias. The concentrations are calculated using the following equations:

$$C_{Gas} = (\overline{C} - C_O)\left(\frac{C_{MA}}{C_M - C_O}\right)$$

where: C_{Gas} = Effluent Concentration, dry ppm or %
$\overline{C}$ = Average Analyzer Concentration, ppm or %
C_O = Average Initial and Final System Calibration Responses for Zero Gas, ppm or %
C_M = Average Initial and Final System Calibration Responses for Upscale Calibration Gas, ppm or %
C_{MA} = Actual Concentration of Upscale Calibration Gas, ppm or %

CO System Calibration Drift Correction for South Run #1 Example

$$C_{Gas} = (15.4\ ppmv - 0.1\ ppmv)\left(\frac{30.1\ ppmv}{29.6\ ppmv - 0.1\ ppmv}\right) = \underline{15.9\ ppmv}$$

O2 System Calibration Drift Correction for Run #1 Example

$$C_{Gas} = (17.9\ \% - (-0.1\ \%))\left(\frac{12.1\ \%}{12.0\ \% - (-0.1\ \%)}\right) = \underline{18.0\ \%}$$

NOx System Calibration Drift Correction for Run #1 Example

$$C_{Gas} = (15.7\ ppmv - 0.1\ ppmv)\left(\frac{30.1\ ppmv}{29.6\ ppmv - 0.1\ ppmv}\right) = \underline{15.9\ ppmv}$$

Stack Gas Velocity & Volumetric Rates (EPA M2)

The velocity and volumetric flow rate of the stack gas are calculated using the following equations:

$$V_S = K_P C_P \left(\sqrt{\Delta p}\right)_{AVG} \sqrt{\frac{T_{S(AVG)}}{P_S M_S}}$$

$$Q_W = V_S A_S (3600 \ sec/hr)$$

$$Q_{SW} = Q_W \left(\frac{528 \ °R}{T_S}\right)\left(\frac{P_S}{29.92" \ Hg}\right)$$

$$Q_{SD} = Q_{SW}(DGF)$$

Where:
V_S = Stack gas velocity (ft/sec)

K_P = Pitot Tube Constant, $85.49 \ \frac{ft}{sec}\sqrt{\frac{(lb/lb \ mol)(" \ Hg)}{(°R)("H_2O)}}$

C_P = Pitot Tube Coefficient, 0.84 (dimensionless)

Δp = Velocity Head of Stack Gas, ("H₂O)

T_S = Stack Temperature (°R)

P_S = Absolute Stack Pressure ("Hg)

M_S = Molecular weight of stack gas, wet basis (lb/lb-mole)

Q_W = Stack Gas Wet Volumetric Flow at Stack Conditions (ft³/hr)

Q_{SW} = Stack Gas Wet Volumetric Flow at Standard Conditions (ft³/hr)

A_S = Stack Area (ft²)

Q_{SD} = Stack Gas Flow @ Std. Conditions, dry basis (dscf/hr)

DGF = Dry Gas Fraction

Volumetric Flow

South Run 1 Example

$$V_S = \left(85.49 \ \frac{ft}{sec}\sqrt{\frac{(lb/lb \ mol)(" \ Hg)}{(°R)("H_2O)}}\right)(0.84)(1.201 \ " \ H_2O)\sqrt{\frac{764 \ °R}{(29.72 \ " \ Hg)(28.3 \ lb/lb \ mol)}} = \underline{82.18 \ ft/sec}$$

$$Q_W = \left(\frac{82.18 \ ft}{sec}\right)\left(\frac{9.621 \ ft^2}{1}\right)\left(\frac{3600 \ sec}{hr}\right) = \underline{2.85 \ x \ 10^6 \ cf/hr}$$

$$Q_{SW} = \left(\frac{2.85 \ x \ 10^6 \ cf}{hr}\right)\left(\frac{528 \ °R}{761 \ °R}\right)\left(\frac{29.72 \ " \ Hg}{29.92" \ Hg}\right) = \underline{1.95 \ x \ 10^6 \ scf/hr}$$

$$Q_{SD} = (1.95 \ x \ 10^6)(0.948) = \underline{1.85 \ x \ 10^6 \ dscf/hr}$$

NOx and CO Concentration and Emission Rate

$$E_{Gas} = \frac{(C_{Gas})(Q_{SD})(Gas_{MW})(28.32 \ L/ft^3)}{(10^6 \ ppmv)(24.056 \ L/mol)(453.6 \ g/lb)}$$

where: C_{Gas} = Effluent Concentration $(dry \ ppmv)$
E_{Gas} = Emission of Gas, (lb/hr)
C_{Gas} = Concentration of Gas, $(dry \ ppmv)$
Q_{SD} = Stack Gas Flow @ Std. Conditions, dry basis $(dscf/hr)$
Gas_{MW} = Molecular Weight of Gas $(g/g \ mol)$ Where:
$\quad NOx_{MW}$ = Molecular Weight of NOx (46.01 $g/g \ mol$)
$\quad CO_{MW}$ = Molecular Weight of CO (28.01 $g/g \ mol$)

Pollutant Gas Emissions South Run #1 Example

$$E_{NOx} = \frac{(15.9 \ ppmv \ NOx)(1.85 \times 10^6 \ dscf/hr)(46.01 \ g/gmol)(28.32 \ L/ft^3)}{(10^6 \ ppmv)(24.056 \ L/mol)(453.6 \ g/lb)} = \underline{3.52 \ lb/hr}$$

$$E_{CO} = \frac{(16.2 \ ppmv \ CO)(1.85 \times 10^6 \ dscf/hr)(28.01 \ g/gmol)(28.32 \ L/ft^3)}{(10^6 \ ppmv)(24.056 \ L/mol)(453.6 \ g/lb)} = \underline{2.18 \ lb/hr}$$