

1.0 INTRODUCTION

1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct the emissions performance test the NHT Stripper in operation at the Marathon Detroit Refinery, located in Detroit, Michigan. The performance test was conducted on April 21, 2021.

1.2 Purpose of Testing

This test program was conducted to determine the nitric oxide (NO_x) emissions emitted from the NHT Stripper. All testing and audit procedures were conducted in accordance with the requirements set forth in the USEPA Title 40, Code of Federal Regulations (CFR), Part 60, Appendix B which defines the testing procedures.

1.3 Description of Source

The NHT Stripper Reboiler (EU16-NHTSTRIPREBOIL-S1) heats the liquid from the bottom of the Naphtha Hydrotreater stripper column. The vapors that form are returned to the top of the stripper column; the liquid vapor is removed as a product stream. The unit is fired by refinery fuel gas. Emissions are vented to the atmosphere via the NHT Stripper Reboiler Heater Stack where testing was performed.

1.4 Contact Information

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2.0 SUMMARY OF RESULTS

Table 2.1: NHT Stripper Emissions Results

Pollutant Measured	Mass Emission Rate	Applicable Limit	Pass/Fail
NO _x	0.118 lb/MMBtu	0.20 lb/MMBtu	<i>Pass</i>

3.0 SOURCE DESCRIPTION

3.1 Description of the process

The Naphtha Hydrotreater unit uses hydrogen to remove sulfur and nitrogen from straight-run and coker naphthas. This process, known as hydrotreating, uses a catalyst to promote the desulfurization reaction. The desulfurized or sweet naphtha is blended into gasoline or used for platformer feed. The NHT unit consists of process vessels (including exchangers, reactors, receivers, separators, and a stripper column), heaters, tanks, containers, pumps, piping, drains, and various components (pump seals, process valves, pressure relief valves, flanges, connectors, etc.).

The NHT Stripper Reboiler (EU16-NHTSTRIPREBOIL-S1) heats the liquid from the bottom of the stripper column. The vapors that form are returned to the top of the stripper column; the liquid vapor is removed as a product stream.

3.2 Applicable permit and source designation

The Marathon Detroit Refinery operates the NHT Stripper under the Permit No. MI-ROP-A9831-2012c. The NHT Stripper is also identified as EU16-NHTSTRIPREBOILS1. Under this permit, the Marathon Detroit Refinery is required to conduct an annual compliance test to demonstrate the NO_x emissions remain below the applicable limit.

3.3 Type and quantity of materials processed during tests

During the emission testing on April 21, 2021, at the Marathon Detroit Refinery, the NHT Stripper was tested at the highest achievable rate. The actual load conditions during the testing were documented by facility personnel and are summarized in Appendix A. Raw data records are provided in Appendix F.

4.0 SAMPLING AND ANALYTICAL PROCEDURES

4.1 Description of sampling and field procedures

Erthwrks completed this compliance test utilizing all applicable test methods specified in the USEPA Title 40 CFR Part 60, Appendix A. EPA Method 3A was used to determine the O₂ concentration and EPA Method 7E was used to determine the NO_x concentration.

All gaseous sampling was done utilizing three appropriate traverse points. The three traverse points were selected to ensure acquisition of a representative sample over the stack cross section.

4.2 Quality Assurance Procedures

As required by EPA Methods 3A and 10, Erthwrks followed all quality assurance and quality control procedures as defined in US EPA 40 CFR 60 Appendix A, Method 7E for the determination of the concentrations of CO and O₂.

The Calibration Error (CE) Test was conducted as specified in EPA Method 7E §8.2.3. In accordance with this requirement, a three-point analyzer calibration error test was conducted prior to sampling. The CE test was conducted by introducing the low, mid, and high level calibration gasses (as defined in EPA Method 7E §3.3.1-3) sequentially and the response was recorded. The results of the CE test are acceptable if the calculated calibration error is within $\pm 2.0\%$ of calibration span (or ≤ 0.5 ppmv).

The NO₂-NO Conversion Efficiency Test was conducted prior to each field test in accordance with EPA Method 7E §8.2.4.1. This was conducted by introducing the converter efficiency gas (~50 ppm NO₂) directly to the NO_x analyzer and recording the NO value. The NO₂-NO Conversion Efficiency test was within acceptable limits.

A Stratification Test was conducted at the beginning of the test as described in EPA Method 7E §8.1.2. Three points at 16.7%, 50%, and 83.3% of the stack diameter was used as the traverse line. The highest emitted pollutant was measured at each point for a period of at least twice the sample system response time. The concentration at each point was compared to the average concentration. The exhaust gas stream was considered unstratified because the variance at each point was $< 5.0\%$ from the average, and the sample was taken the centroid of the stack.

The Initial System Bias and System Calibration Error Check was conducted in accordance with EPA Method 7E §8.2.5. The upscale calibration gas was introduced at the probe upstream of all sample system components and the response was recorded. The procedure was repeated with the low-level gas and the response was recorded. The sample system response time was also recorded. This specification is acceptable if the calculated values of the system calibration error check are within $\pm 5.0\%$ of the calibration span value (or ≤ 0.5 ppmv).

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8681.1.B1 Marathon Detroit NHT Stripper (Reboiler) Test Report

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Version 1 (5/18/21)

After each compliance test run, the sample system bias check was conducted to validate the run data. The low-level and upscale drift was calculated using Equation 7E-4. The run data was deemed valid if the calculated drift is within $\pm 3.0\%$ of the calibration span value (or ≤ 0.5 ppmv).

Each test run, the effluent gas concentration was calculated as specified in EPA Method 7E §12.6. The arithmetic average of all valid concentration values was adjusted for bias using Equation 7E-5B.

EPA Method 19 was used for the calculation of the mass emission rates. In accordance with this method, the volumes of combustion components per unit of heat content (F_d) was calculated using the comprehensive fuel analysis (Eq. 19-13). Utilizing this “F-Factor”, the emission rates were calculated using Equation 19-1. The fuel analysis worksheets are found in Appendix C and the example calculations are found in Appendix E.

4.3 Discussion of sampling procedure or operational variances

Erthwrks, Inc. conducted the emission testing with no sampling or procedural variances. The NHT Stripper tested, operated with no operational variances.

Attachment A
Detailed Results of Emission Test

Erthwrks Summary of Results

Date: 4/21/2021
Client: Marathon
Facility: Detroit
Unit ID: NHT Stripper
Erthwrks Tech: JW, JT, JM

Run Information			
Run Number	Run 1	Run 2	Run 3
Date	4/21/2021	4/21/2021	4/21/2021
Run Start Time	8:49	9:57	11:05
Run End Time	9:49	10:57	12:05
Operating Conditions			
Unit Charge Rate	47341.1	46778.0	44467.3
MSCF/D fuel gas	798.3	801.7	733.3
NHT reboiler duty	33.7	33.4	32.2
Unit Fuel Flow Data			
Fuel F Factor (F _d) (scf/MMBtu)	8586.3	8586.3	8586.3
Emission Concentrations			
NOx (ppmv)	82.68	85.97	85.55
O ₂ (%)	5.44	5.50	5.53
Emission Concentrations O ₂ Corrected		Corrected To: 0 %O ₂	
NOx (ppmv @ %O ₂)	111.76	116.65	116.30
Emission Rates (lb/scf)			
NOx (lb/scf)	9.87E-06	1.03E-05	1.02E-05
Emission Rates (lb/MMBtu)			
NOx (lb/MMBtu)	0.1146	0.1196	0.1192

**Average
114.90 ppmv**

**Average
0.1178 lb/MMBtu**

Attachment B
Quality Control Documentation

Erthwrks Method 1 Traverse Point Location Worksheet

Client: Marathon
Project #: 8681.1.B1
Facility: Detroit
Unit ID: NHT Stripper
Technician: JW, JT, JM

Stack ID Measurements

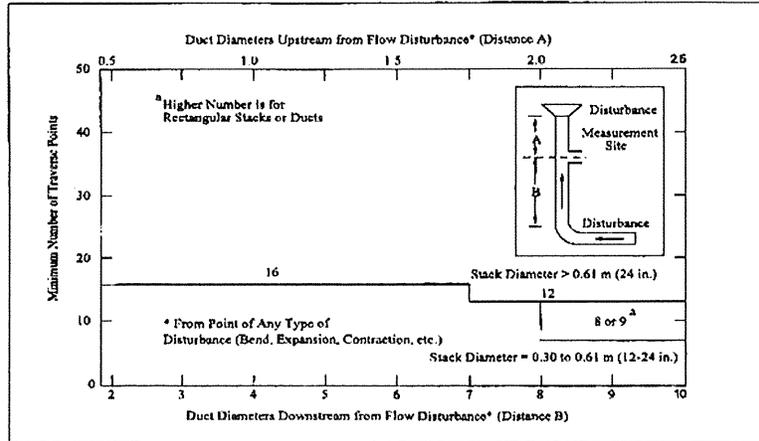
Stack ID + Port (inches): 52
 Port Extension (inches): 8
 Stack Diameter (inches): 44

Port Location Measurements

Distance Upstream (A) (inches): 125
 Distance Downstream (B) (inches): 135
 Stack Diameters Upstream (A): 2.8
 Stack Diameters Downstream (B): 3.1

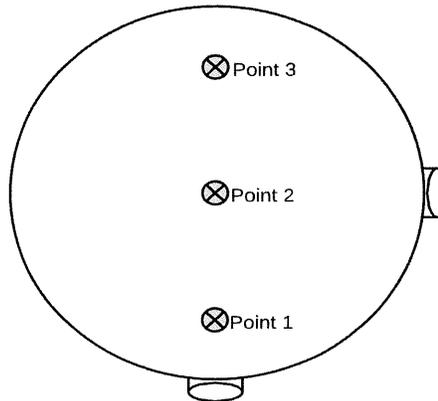
Total Traverse Points to be used: 3
 Traverse Points per Diameter: 3

Traverse Point Table and Stack Side View



Stack Cross Section View

Traverse Point Locations ⁽¹⁾⁽²⁾	
Point 1:	7.35"
Point 2:	22.00"
Point 3:	36.65"



⁽¹⁾For stack diameter >4.0" and <2.4 meters, stratification is measured at 16.7%, 50.0%, and 83.3" of stack diameter (M7E, §8.1.2).

⁽²⁾For stack diameter >2.4 meters, stratification is measured at 0.4, 1.2, and 2.0 meters from stack wall (M7E, §8.1.2).

Erthwrks Gaseous Sample Collection and Quality Assurance Worksheet

Date: 4/21/2021
 Client: Marathon
 Facility: Detroit
 Unit ID: NHT Stripper
 Erthwrks Tech: JW, JT, JM

Calibration Gas Verification

Pollutant	Low-Level Gas Conc. (CV)	Cylinder Serial #	Mid-Level Gas Conc. (CV)	Cylinder Serial #	High-Level Gas Conc. (CV/CS)	Cylinder Serial #	Diluter Root Gas
NOx	NA	NA	50.28	ALM049993	95.02	XC036040B	NA
O2	NA	NA	12.25	CC235646	20.59	EB0013408	NA

Reference Method Analyzer Info

Make	Model	Serial No.
Teledyne	T200H	600
Teledyne	T200H	600

Direct Calibration Error Test

Pollutant	Zero Gas Response (C _{0i})	Calibration Error (ACE)*	Low-Level Response (C _{0i})	Calibration Error (ACE)*	Mid-Level Response (C _{0i})	Calibration Error (ACE)*	High-Level Response (C _{0i})	Calibration Error (ACE)*
NOx	-0.19	-0.19%	NA	NA	49.70	-0.61%	94.76	-0.28%
O2	-0.03	-0.14%	NA	NA	12.30	0.23%	20.61	0.10%

*ACE must either be within ± 2.0% or ≤ 0.5 ppmv absolute difference

Conversion Efficiency Test

NO ₂ Cal Gas Concentration	60.93
NO ₂ Cal Gas Cyl. Number	CC506641
NOx Analyzer Response	59.21
NO ₂ -NO Conv. Efficiency (Eff _{NO2})*	97.18%

*Eff_{NO2} must be ≥ 90%

Traverse Points				Nox Stratification Test		
Stack ID	% of Stack	Inches from ID	Inch port ext	Point 1	Point 2	Point 3
44	Point 1	16.7%	7.35	79.131	79.993	79.703
Port Extension	Point 2	50.0%	22.00	79.703	79.703	79.609
8	Point 3	83.3%	36.65	79.609	79.609	79.609
				Average	79.609	0.60%

*Stratification Test results must be <5%

Initial Sample System Bias and Response Time

Pollutant	Upscale Gas Cert. Conc. (C _{MA})	Upscale Gas Direct (C _{0i})	Upscale Response (C _s)	Sample System Bias (SB)*	Response Time (sec)	Downscale Response (C _s)	Sample System Bias (SB)*	Response Time (sec)
NOx	50.28	49.70	48.60	-1.16%	45	-0.32	-0.14%	45
O2	12.25	12.30	12.39	0.43%	45	0.11	0.67%	45

*SB must either be within ± 5.0% or ≤ 0.5 ppmv absolute difference

Sample Collection Raw Data--Pre and Post Sample System Calibration (SSC) and Raw Run Results

Pollutant	Run 1					Run 2				
	Initial Zero SSC (C _{0i})	Initial Upscale SSC (C _s)	Raw Results (C _{AVG})	Final Zero SSC (C _{0i})	Final Upscale SSC (C _s)	Initial Zero SSC (C _{0i})	Initial Upscale SSC (C _s)	Raw Results (C _{AVG})	Final Zero SSC (C _{0i})	Final Upscale SSC (C _s)
NOx	-0.32	48.60	79.98	-0.11	48.50	-0.11	48.50	82.45	-0.06	47.88
O2	0.11	12.39	5.49	0.05	12.15	0.05	12.15	5.48	0.05	12.15

Sample Collection Raw Data--Pre and Post Sample System Calibration (SSC) and Raw Run Results

Pollutant	Run 3				
	Initial Zero SSC (C _{0i})	Initial Upscale SSC (C _s)	Raw Results (C _{AVG})	Final Zero SSC (C _{0i})	Final Upscale SSC (C _s)
NOx	-0.06	47.88	81.72	0.08	48.19
O2	0.05	12.15	5.54	0.08	12.26

Run 1 Sample Collection Calculations--Pre- and Post-Run Sample System Bias Check, Drift Assessment, Corrected Results

Pollutant	Initial Zero Sys. Bias (SB)*	Initial Upscale Sys. Bias (SB)*	Final Zero Sys. Bias (SB)*	Final Upscale Sys. Bias (SB)*	Avg. Zero Sys. Bias (C ₀)	Avg. Upscale Sys. Bias (C _M)	Zero Drift Assessment (D) [†]	Upscale Drift Assessment (D) [†]	Corrected Results (C _{0i})
NOx	-0.14%	-1.16%	0.08%	-1.26%	-0.22	48.55	0.22%	0.11%	82.68
O2	0.67%	0.43%	0.35%	-0.69%	0.08	12.27	0.31%	1.13%	5.44

*SB must either be within ± 5.0% or ≤ 0.5 ppmv absolute difference
[†]D must either be within ± 3.0% or the pre- and post-run bias responses are ≤ 0.5 ppmv absolute difference

Run 2 Sample Collection Calculations--Pre- and Post-Run Sample System Bias Check, Drift Assessment, Corrected Results

Pollutant	Initial Zero Sys. Bias (SB)*	Initial Upscale Sys. Bias (SB)*	Final Zero Sys. Bias (SB)*	Final Upscale Sys. Bias (SB)*	Avg. Zero Sys. Bias (C ₀)	Avg. Upscale Sys. Bias (C _M)	Zero Drift Assessment (D) [†]	Upscale Drift Assessment (D) [†]	Corrected Results (C _{0i})
NOx	0.08%	-1.26%	0.13%	-1.92%	-0.09	48.19	0.05%	0.66%	85.97
O2	0.35%	-0.69%	0.35%	-0.70%	0.05	12.15	0.00%	0.00%	5.50

*SB must either be within ± 5.0% or ≤ 0.5 ppmv absolute difference
[†]D must either be within ± 3.0% or the pre- and post-run bias responses are ≤ 0.5 ppmv absolute difference

Run 3 Sample Collection Calculations--Pre- and Post-Run Sample System Bias Check, Drift Assessment, Corrected Results

Pollutant	Initial Zero Sys. Bias (SB)*	Initial Upscale Sys. Bias (SB)*	Final Zero Sys. Bias (SB)*	Final Upscale Sys. Bias (SB)*	Avg. Zero Sys. Bias (C ₀)	Avg. Upscale Sys. Bias (C _M)	Zero Drift Assessment (D) [†]	Upscale Drift Assessment (D) [†]	Corrected Results (C _{0i})
NOx	0.13%	-1.92%	0.27%	-1.59%	0.01	48.03	0.15%	0.33%	85.55
O2	0.35%	-0.70%	0.51%	-0.20%	0.06	12.20	0.15%	0.50%	5.53

*SB must either be within ± 5.0% or ≤ 0.5 ppmv absolute difference
[†]D must either be within ± 3.0% or the pre- and post-run bias responses are ≤ 0.5 ppmv absolute difference

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