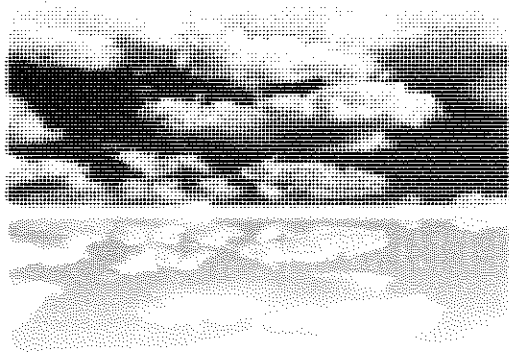




RECEIVED
APR 13 2018
AIR QUALITY DIVISION



REPORT ON DIAGNOSTIC
PARTICULATE AND SULFURIC
ACID MIST TESTING

Detroit Refinery
Crude/Vacuum Heater Stack

Marathon Petroleum Company LP
1300 South Fort Street
Detroit, MI 48217
Client Reference No. 4101379616

CleanAir Project No. 13488
STAC Certificate No. 2007.002.0113.1217
Revision 0, Final Report
March 22, 2018

1. PROJECT OVERVIEW

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to complete diagnostic testing on the Crude/Vacuum Heater Stack (SV04-H1-05-H1) at the Detroit Refinery. The test program included the following objective:

- Perform filterable particulate matter (FPM) and sulfuric acid mist (H₂SO₄) testing to quantify emissions from the Crude/Vacuum Heater Stack.

A summary of the test program results is presented below. Section 2 Results provides a more detailed account of the test conditions and data analysis. Test program information, including the test parameters, on-site schedule and a project discussion, begins on page 2.

**Table 1-1:
 Summary of Results**

Source		
Constituent (Units)	Sampling Method	Average Emission
<i>Crude/Vacuum Heater</i>		
FPM (lb/MMBtu)	USEPA M5	0.0034
H ₂ SO ₄ (lb/MMBtu)	CTM-013 / Draft ASTM CCM	0.0017
PM (lb/MMBtu) ¹		0.0017

¹ PM assumed equivalent to FPM less H₂SO₄. The letter from MDEQ referenced in Appendix K further outlines the correction of particulate emissions for H₂SO₄ bias.

RECEIVED

APR 13 2018

AIR QUALITY DIVISION

Test Program Details

Parameters

The test program included the following measurements:

- filterable particulate matter (FPM)
- sulfuric acid mist (H₂SO₄)
- particulate matter (PM), assumed equivalent to FPM minus H₂SO₄
- flue gas composition (e.g., O₂, CO₂, H₂O)
- flue gas temperature
- flue gas flow rate

Schedule

Testing was performed on February 1, 2018. The on-site schedule followed during the test program is outlined in Table 1-2.

**Table 1-2:
Test Schedule**

Run Number	Location	Method	Analyte	Date	Start Time	End Time
D1	Crude/Vacuum Heater	USEPA Method 5	FPM	02/01/18	10:16	11:25
D2	Crude/Vacuum Heater	USEPA Method 5	FPM	02/01/18	12:04	13:12
D3	Crude/Vacuum Heater	USEPA Method 5	FPM	02/01/18	13:49	14:57
D1	Crude/Vacuum Heater	CTM-013 (mod) / Draft ASTM CCM	Sulfuric Acid Mist	02/01/18	10:16	11:16
D2	Crude/Vacuum Heater	CTM-013 (mod) / Draft ASTM CCM	Sulfuric Acid Mist	02/01/18	12:04	13:04
D3	Crude/Vacuum Heater	CTM-013 (mod) / Draft ASTM CCM	Sulfuric Acid Mist	02/01/18	13:50	14:50

Discussion

Test Scope Synopsis

PM Testing

A total of three (3) 60-minute EPA Method 5 test runs were performed. The PM emission results were calculated in units of pounds per million Btu (lb/MMBtu). The final result was expressed as the average of the three (3) valid runs.

H₂SO₄ Testing

H₂SO₄ emissions were determined referencing the Draft ASTM Controlled Condensation Method (CCM). Three (3) 60-minute Draft ASTM CCM test runs were performed. H₂SO₄ emission results were calculated in units of lb/MMBtu. Flow rates from concurrent Method 5 testing were used for lb/hr emission rate calculations. The final results were expressed as the average of three (3) valid runs.

Prior to the first official test run, a 60-minute sample conditioning run (Run 0) was performed in order to minimize the absorption capacity of the front-half components of the sample train (upstream of the H₂SO₄-collecting portion of the sample train). The conditioning run was recovered and analyzed in the same manner as the official test runs but the results are not included in the average.

Fuel Analysis

Emission results in units of dry volume-based concentration (lb/dscf, ppm_{dv}) were converted into units of lb/MMBtu by calculating an oxygen-based fuel factor (F_d) for refinery gas per EPA Method 19 specifications. The F_d factor was calculated from percent volume composition analytical data provided by MPC and tabulated heating values for each of the measured constituents.

Test Conditions

The unit was operated at the maximum normal operating capacity during each of the emissions test runs. MPC was responsible for logging any relevant process-related data and providing it to CleanAir for inclusion in the test reports.

Modifications to Test Methodology

The connection between the Method 5 particulate filter holder and the water-cooled condenser, which were knock-outs jars rather than impingers, was a flexible Teflon line as allowed by the method.

The integrated gas sample (IGS) bags that were analyzed for O₂ and CO₂ content by EPA Method 3, as referenced in Method 5, were vinyl instead of Tedlar. The O₂ and CO₂ concentrations were measured using O₂ and CO₂ analyzers instead of an Orsat analyzer. The analyzers were calibrated on-site using certified calibration gases, as described in EPA Method 3A. A description of the analyzers that were used can be found in Appendix A of this report.

End of Section

2. RESULTS

This section summarizes the test program results. Additional results are available in the report appendices, specifically Appendix C Parameters.

**Table 2-1:
 Crude/Vacuum Heater Stack – FPM**

Run No.	D1	D2	D3	Average
Date (2018)	Feb 1	Feb 1	Feb 1	
Start Time (approx.)	10:16	12:04	13:49	
Stop Time (approx.)	11:25	13:12	14:57	
Process Conditions				
P ₁ Charge rate (BPD)	144,330	144,036	144,005	144,124
F _d Oxygen-based F-factor (dscf/MMBtu)	8,272	8,272	8,272	8,272
Gas Conditions				
O ₂ Oxygen (dry volume %)	7.8	8.1	8.0	8.0
CO ₂ Carbon dioxide (dry volume %)	7.8	7.6	7.7	7.7
T _s Sample temperature (°F)	286	285	286	285
B _w Actual water vapor in gas (% by volume)	12.3	11.9	11.8	12.0
Gas Flow Rate				
Q _a Volumetric flow rate, actual (acfm)	124,000	122,000	123,000	123,000
Q _s Volumetric flow rate, standard (scfm)	87,000	85,600	86,000	86,200
Q _{std} Volumetric flow rate, dry standard (dscfm)	76,300	75,300	75,800	75,800
Sampling Data				
V _{mstd} Volume metered, standard (dscf)	37.69	37.52	37.85	37.68
%I Isokinetic sampling (%)	101.1	101.9	102.2	101.7
Laboratory Data				
m _{filter} Matter collected on filter(s) (g)	0.00120	0.00128	0.00137	
m _s Matter collected in solvent rinse(s) (g)	0.00534	0.00221	0.00149	
m _n Total FPM (g)	0.00654	0.00349	0.00286	
FPM Results				
C _{sd} Particulate Concentration (lb/dscf)	3.8E-07	2.1E-07	1.7E-07	2.5E-07
E _{lb/hr} Particulate Rate (lb/hr)	1.8	0.93	0.76	1.1
E _{Fd} Particulate Rate - F _d -based (lb/MMBtu)	0.0050	0.0028	0.0022	0.0034

Average includes 3 runs.

**Table 2-2:
 Crude/Vacuum Heater Stack – H₂SO₄ Emissions**

Run No.		D1	D2	D3	Average
Date (2018)		Feb 1	Feb 1	Feb 1	
Start Time (approx.)		10:16	12:04	13:50	
Stop Time (approx.)		11:16	13:04	14:50	
Process Conditions					
P ₁	Charge rate (BPD)	144,324	144,039	144,004	144,122
F _d	Oxygen-based F-factor (dscf/MMBtu)	8,272	8,272	8,272	8,272
Gas Conditions					
O ₂	Oxygen (dry volume %)	8.3	8.4	9.4	8.7
CO ₂	Carbon dioxide (dry volume %)	7.5	7.4	6.8	7.2
T _s	Sample temperature (°F)	282	282	282	282
B _w	Actual water vapor in gas (% by volume)	12.4	12.3	11.6	12.1
Sampling Data					
V _{mstd}	Volume metered, standard (dscf)	26.69	26.62	26.96	26.76
Laboratory Data (Ion Chromatography)					
m _n	Total H ₂ SO ₄ collected (mg)	1.4546	1.3629	1.5170	
Sulfuric Acid Vapor (H₂SO₄) Results					
C _{sd}	H ₂ SO ₄ Concentration (lb/dscf)	1.2E-07	1.1E-07	1.2E-07	1.2E-07
C _{sd}	H ₂ SO ₄ Concentration (ppm _{dv})	0.47	0.44	0.49	0.47
E _{Fd}	H ₂ SO ₄ Rate - F _d -based (lb/MMBtu)	0.0016	0.0016	0.0019	0.0017

End of Section

3. DESCRIPTION OF INSTALLATION

Process Description

MPC's facility in Detroit, Michigan, produces refined petroleum products from crude oil. MPC must continue to demonstrate that select process units are in compliance with permitted emission limits.

The Crude Unit (EU05-CRUDE) separates crude oil into various fractions through the use of distillation processes. These fractions are sent to other units in the refinery for further processing. The Crude Unit consists of process vessels (including heat exchangers and fractionation columns), the Alcorn Heater (EU05-CRUDEHTR-S1), tanks, containers, compressors, pumps, piping, drains, and various components (pump and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

The Vacuum Unit (EU04-VACUUM) separates the reduced crude from the crude unit through the use of a vacuum column. The reduced crude is separated into light vacuum gas oil, medium vacuum gas oil, heavy vacuum gas oil and a bottoms product called flux. The various fractions are sent to other units in the refinery for further processing. The vacuum unit consists of process vessels (including heat exchangers and vacuum column), two process heaters, tanks, containers, two cooling towers, flare, compressors, pumps, piping drains and various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.).

Both the Crude Heater (EU05-CRUDEHTR-S1) and the Vacuum Heater (EU04-VACHTR-S1) are fired by refinery fuel gas. Emissions are vented to the atmosphere via a common stack known as the Crude/Vacuum Heater Stack (SV04-H1-05-H1) where testing was performed.

Test Location

The sample point locations were determined by EPA Method 1 specifications. Table 3-1 presents the sampling information for the test location described in this report. The figure shown on page 7 represents the layout of the test location.

**Table 3-1:
 Sampling Information**

Source Constituent	Method	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
<i>Crude/Vacuum Heater</i>							
FPM	EPA M5/202	1-3	2	6	5	60	3-1
H ₂ SO ₄	Draft ASTM CCM	1-3	1	1	60	60	NA ¹

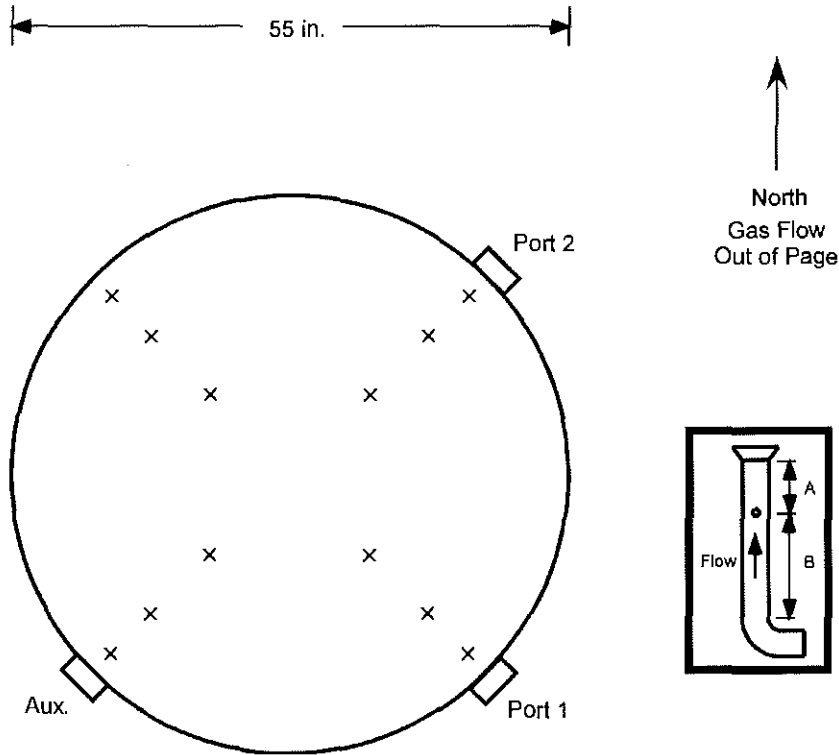
¹ Sampling occurred at a single point near the center of the duct.

RECEIVED

APR 13 2018

AIR QUALITY DIVISION

**Figure 3-1:
 FPM Sample Point Layout (EPA Method 1)**



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	95.6	52.6
2	85.4	47.0
3	70.4	38.7
4	29.6	16.3
5	14.6	8.0
6	4.4	2.4

Duct diameters upstream from flow disturbance (A): 9.2 Limit: 0.5
 Duct diameters downstream from flow disturbance (B): 12.0 Limit: 2.0

End of Section

4. METHODOLOGY

Procedures and Regulations

The test program sampling measurements followed procedures and regulations outlined by the United States Environmental Protection Agency (USEPA) and the Michigan Department of Environmental Quality (DEQ). These methods appear in detail in Title 40 of the CFR and at <https://www.epa.gov/emc>. Appendix A includes diagrams of the sampling apparatus, as well as specifications for sampling, recovery and analytical procedures. Any modifications to standard test methods are explicitly indicated in this appendix. Modifications to standard methods are not covered by the ISO 17025 and TNI portions of CleanAir's A2LA accreditation.

CleanAir follows specific QA/QC procedures outlined in the individual methods and in USEPA "Quality Assurance Handbook for Air Pollution Measurement Systems: Volume III Stationary Source-Specific Methods," EPA/600/R-94/038C. Appendix D contains additional QA/QC measures, as outlined in CleanAir's internal Quality Manual.

Title 40 CFR Part 60, Appendix A

- Method 1 "Sample and Velocity Traverses for Stationary Sources"
- Method 2 "Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)"
- Method 3 "Gas Analysis for the Determination of Dry Molecular Weight"
- Method 4 "Determination of Moisture Content in Stack Gases"
- Method 5 "Determination of Particulate Matter Emissions from Stationary Sources"
- Method 19 "Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide and Nitrogen Oxide Emission Rates"

CTM-013 (Mod.)/Draft ASTM Controlled Condensation Method (Draft ASTM CCM)

"Determination of Sulfur Oxides Including Sulfur Dioxide, Sulfur Trioxide and Sulfuric Acid Vapor and Mist from Stationary Sources Using a Controlled Condensation Sampling Apparatus"

Methodology Discussion

FPM Testing – USEPA Method 5

The front-half of the sampling train consisted of a glass nozzle, glass liner and filter holder heated to $248^{\circ}\text{F} \pm 25^{\circ}\text{F}$ and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5 requirements.

After exiting the front-half filter, the flue gas passed through a series of knock-out jars. Condensate in the knock-out jars were collected to determine the flue gas moisture and thoroughly dry the gas. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.

The front-half portion of the sample train (nozzle, probe and heated filter) was recovered per Method 5 requirements, using acetone as the recovery solvent.

All samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for gravimetric analysis. Upon receipt, the filters were desiccated for 24 hours at ambient temperature. The front-half rinses were evaporated at ambient temperature and pressure. The masses from each fraction were then summed for a total FPM mass.

H₂SO₄ Testing – Draft ASTM CCM

A gas sample was extracted from the source at a constant flow rate using a quartz-lined probe maintained at a temperature of $650^{\circ}\text{F} \pm 25^{\circ}\text{F}$ (depending on the required probe length) and a quartz fiber filter maintained at the same temperature as the probe to remove particulate matter.

The sample then passed through a glass coil condenser for collection of sulfuric acid vapor and/or mist. A second quartz fiber filter (referred to as the sulfuric acid mist (SAM) filter) was located at the condenser outlet for the collection of residual SAM not collected by the condenser. The condenser temperature was regulated by a water jacket and the SAM filter was regulated by a closed oven. Both the water jacket and SAM filter oven were maintained at $140^{\circ}\text{F} \pm 9^{\circ}\text{F}$.

After exiting the SAM filter, the sample gas continued through a series of four (4) glass knock-out jars: two (2) containing water, one (1) empty and one (1) containing silica gel for residual moisture removal. The exit temperature from the knock-out jar set was maintained below 68°F . The sample gas then flowed into a dry gas meter, where the collected sample gas volume was determined by means of a calibrated, dry gas meter or an orifice-based flow meter.

The H₂SO₄-collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using deionized (DI) H₂O as the recovery/extraction solvent; any H₂SO₄ disassociates into sulfate ion (SO₄²⁻) and is stabilized in the H₂O matrix until analysis.

Samples and blanks were returned to CleanAir Analytical Services for ion chromatography (IC) analysis.

End of Section