1. PROJECT OVERVIEW

Test Program Summary

Marathon Petroleum Company LP contracted CleanAir Engineering (CleanAir) to complete testing on the Coker Heater (EU70-COKERHTR-S1) at the Detroit Refinery. The test program included the following objectives:

- Perform particulate matter (PM), particulate matter less than 10 microns in diameter (PM₁₀), sulfuric acid mist (H₂SO₄), and volatile organic compound (VOC) testing to demonstrate compliance with the Michigan Department of Environmental Quality (DEQ) Permit No. MI-ROP-A9831-2012c;
- Perform a relative accuracy test audit (RATA) on the facility continuous emissions monitoring system (CEMS) for oxygen (O₂), nitrogen oxides (NO_x), and carbon monoxide (CO).

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.

Table 1-1: Summary of Compliance Results

<u>Source</u>	Sampling Method	Average	
Constituent	(USEPA)	Emission	Permit Limit ¹
Coker Heater Stack			
FPM (Ib/MMBtu)	5	0.0013	N/A
PM ₁₀ (Ib/MMBtu)	5/202	0.0043	0.0076
H ₂ SO ₄ (Ib/MMBtu)	ASTM Draft CCM	0.0005	N/A
PM (Ib/MMBtu) ^{2, 3}	5 / ASTM Draft CCM	0.0009	0.0019
VOC (Ib/MMBtu)	25A/18	< 0.0008	0.0055
NSFPM (Ib/MMBtu) ⁴	5B	0.0005	N/A

¹ Permit limits obtained from MDEQ Renew able Operating Permit No. MI-ROP-A9831-2012c.

² Expressed as the average of the three (3) highest valid runs.

³ PM assumed equivalent to FPM less H₂SO₄.

⁴ NSFPM measured for supplemental purposes.

Table 1-2: Summary of RATA Results

<u>Source</u> Constituent	Reference Method	Relative Accuracy (%)	Applicable Specification	Specification Limit ¹
Coker Heater				
O ₂ (% dv)	EPA 3A	0.02	PS3	± 1.0% dv
NO _X (ppm @ 0%O2)	EPA 7E	3.3	PS4	20% of RM
NO _X (Ib/MMBtu)	EPA 7E	3.4	PS2	20% of RM
CO (lb/MMBtu)	EPA 10	0.0	PS4A	5% of Standard ²

¹ Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.

² Standard = 0.01 lb/MMBtu

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Test Program Details

Parameters

The test program included the following emissions measurements:

- filterable particulate matter (FPM)
- sulfuric acid mist (H₂SO₄) conducted concurrently with FPM measurements
- particulate matter (PM), assumed equivalent to FPM minus H₂SO₄
- total particulate matter less than 10 microns in diameter (PM₁₀), assumed equivalent to the sum of the following constituents:
 - o FPM
 - o condensable particulate matter (CPM)
- nitrogen oxides (NO_X)
- carbon monoxide (CO)
- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THCs) minus the following constituents:
 - o methane (CH₄)
 - \circ ethane (C₂H₆)
- flue gas composition (e.g., O₂, CO₂, H₂O)
- flue gas temperature
- flue gas flow rate

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Schedule

Testing was performed on July 23 and 24, 2019. The on-site schedule followed during the test program is outlined in Table 1-3.

Table	e 1-3:
Test :	Schedule

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	Coker Heater	USEPA 3A / 7E / 10	O ₂ /NO _X /CO	07/23/19	09:46	10:07
2	Coker Heater	USEPA 3A/7E/10	O ₂ /NO _X /CO	07/23/19	10:17	10:38
3	Coker Heater	USEPA 3A/7E/10	$O_2/NO_X/CO$	07/23/19	10:52	11:13
4	Coker Heater	USEPA 3A / 7E / 10	$O_2/NO_X/CO$	07/23/19	11:27	11:48
5	Coker Heater	USEPA 3A/7E/10	$O_2/NO_X/CO$	07/23/19	12:01	12:22
6	Coker Heater	USEPA 3A/7E/10	$O_2/NO_X/CO$	07/23/19	12:34	12:55
7	Coker Heater	USEPA 3A / 7E / 10	$O_2/NO_X/CO$	07/23/19	13:08	13:29
8	Coker Heater	USEPA 3A / 7E / 10	$O_2/NO_X/CO$	07/23/19	13:42	14:03
9	Coker Heater	USEPA 3A / 7E / 10	$O_2/NO_X/CO$	07/23/19	14:17	14:38
10	Coker Heater	USEPA 3A/7E/10	O ₂ /NO _X /CO	07/23/19	14:56	15:17
1	Coker Heater	USEPA Method 5 / 202	FPM/CPM	07/23/19	14:02	15:24
2	Coker Heater	USEPA Method 5 / 202	FPM / CPM	07/23/19	16:30	17:47
3	Coker Heater	USEPA Method 5 / 202	FPM / CPM	07/24/19	08:24	09:40
4	Coker Heater	USEPA Method 5 / 202	FPM/CPM	07/24/19	10:50	12:06
1	Coker Heater	USEPA Method 5B	NSFPM	07/23/19	14:02	15:24
2	Coker Heater	USEPA Method 5B	NSFPM -	07/23/19	16:30	17:48
3	Coker Heater	USEPA Method 5B	NSFPM	07/24/19	08:24	09:40
4	Coker Heater	USEPA Method 5B	NSFPM	07/24/19	10:50	12:06
1	Coker Heater	CTM-013 (mod)	H_2SO_4	07/23/19	14:02	15:02
2	Coker Heater	CTM-013 (mod)	H_2SO_4	07/23/19	16:30	17:47
3	Coker Heater	CTM-013 (mod)	H_2SO_4	07/24/19	08:24	09:40
4	Coker Heater	CTM-013 (mod)	H ₂ SO ₄	07/24/19	10:50	12:06
1	Coker Heater	USEPA Method 25A / 18	VOC	07/24/19	08:24	09:24
2	Coker Heater	USEPA Method 25A / 18	VOC	07/24/19	09:43	10:43
3	Coker Heater	USEPA Method 25A / 18	VOC	07/24/19	11:04	12:04

Discussion

PM & PM₁₀ Testing

A total of four (4) 60-minute EPA Method 5/202 test runs were performed. PM and PM₁₀ emission results were calculated in units of pounds per million Btu (lb/MMBtu). All runs were deemed valid.

PM is assumed equivalent to the difference of FPM and H_2SO_4 emissions. H_2SO_4 emissions were determined concurrently with FPM emissions, converted to units of lb/MMBtu, and subtracted from total FPM emissions from each respective run. The final result was expressed as the average of the three (3) highest valid runs.

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 PM_{10} is assumed equivalent to the sum of FPM and CPM. The Method 5/202 sample train yields a front-half, FPM result and a back-half, CPM result. The total PM result (FPM plus CPM) from Method 5/202 can be used as a worst-case estimation of total PM_{10} since Method 5 collects all FPM present in the flue gas (regardless of particle size). The final result was expressed as the average of four (4) valid runs.

H₂SO₄ Testing – Modified CTM-013

 H_2SO_4 emissions were determined referencing a modified Conditional Test Method 013 (CTM-013 (Mod.)). Four (4) 60-minute Draft ASTM CCM test runs were performed concurrently with all Method 5/202 runs. H_2SO_4 emission results were calculated in units of Ib/MMBtu. The H_2SO_4 final results were expressed as the average of four (4) valid runs.

VOC Testing – USEPA Methods 25A and 18

VOC emissions were determined using EPA Method 25A to quantify THC emissions. VOC testing was comprised of three (3) 60-minute test runs. The Method 25A test runs were performed concurrently with three (3) 60-minute Method 18 bag collections. The final result for each VOC run was expressed as the average of three (3) runs.

For all Method 25A runs, the measured concentrations of THC were below the detection limit defined as 'less than 1%' of the calibration span of the THC instrument. Assuming worst-case scenario, the resultant VOC emissions are reported as 'less than' the defined THC detection limit and Method 18 analyses are deemed extraneous. The Method 18 bag collections have been archived.

VOC emission results were calculated in units of lb/MMBtu as propane. O₂ concentrations from concurrent EPA Method 3A runs were utilized to convert VOC results to lb/MMBtu. THC data was converted from an actual (wet) basis to a dry basis using moisture data collected from nearly concurrent Method 5/202 runs.

NSFPM Testing – USEPA Method 5B

For non-sulfuric filterable particulate matter (NSFPM) testing, a total of four (4) 60-minute EPA Method 5B test runs were performed. NSFPM emission results were calculated in units of Ib/MMBtu. All runs were deemed valid. NSFPM testing was conducted for supplemental purposes. Only the front-half rinse of Run 3 was above the detection limit.

RATA Testing – USEPA Methods 3A, 7E, and 10

Minute-average data points for O₂, NO_x, and CO (dry basis) were collected over a period of 21 minutes for each run utilizing EPA Methods 3A, 7E, and 10. Unless statistically inconsequential (CO), relative accuracy was determined based on nine (9) of 10 total runs conducted per procedures outlined in Performance Specification (PS) 2, Section 8.4.4.

Sampling occurred at the three (3) points as specified in Section 8.1.3.2 of PS 2 during each run. The average result for each run was converted to identical units of measurement as the facility CEMS and compared for relative accuracy.

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Fuel Analysis

Emission results in units of dry volume-based concentration (lb/dscf, ppmdv) were converted into units of lb/MMBtu by utilizing an O₂-based fuel factor (F_d) for refinery gas provided by MPC. The heat content and F_d factor were calculated by MPC from percent volume composition analytical data 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 compliance test runs and 50% normal operating capacity during each of the RATA test runs. MPC was responsible for logging any relevant process-related data and providing it to CleanAir for inclusion in the test report.

End of Section

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2. RESULTS

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

Table 2-1: Coker Heater – PM₁₀ Emissions

Run No).	1	2	3	4	Average
Date (2	2019)	Jul 23	Jul 23	Jul 24	Jul 24	
Start Ti	me (approx)	14:02	16:30	08:24	10:50	
Stop Time (approx.)		15:24	17:47	09:40	12:06	
Proces	ss Conditions					
R_P	Production Rate (BPD)	40,200	42,570	42,570	42,570	42,000
P ₁	Fuel Consumption (mscf/day)	4,050	4,312	4,410	4,480	4,310
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,626	8,626	8,612	8,612	
H_i	Actual heat input (MMBtu/hr)	185	197	212	230	206
Gas Co	onditions					
O ₂	Oxygen (dry volume %)	6.8	6.5	6.8	7.4	6.9
CO_2	Carbon dioxide (dry volume %)	8.3	8.5	8.2	8.8	8.5
T_{s}	Sample temperature (°F)	397	409	408	411	406
B_w	Actual water vapor in gas (% by volume)	14.3	13.9	13.6	13.6	13.8
Gas Flo	ow Rate					
Qa	Volumetric flow rate, actual (acfm)	96,000	100,000	95,300	97,300	97,100
Q_s	Volumetric flow rate, standard (scfm)	57,600	59,200	57,000	57,900	57,900
Q_{std}	Volumetric flow rate, dry standard (dscfm)	49,400	51,000	49,200	50,100	49,900
Sampli	ng Data					
V _{mstd}	Volume metered, standard (dscf)	31.46	34.49	32.79	33.71	33.11
%I	lsokinetic sampling (%)	97.4	103.5	101.8	103.0	101.4
Labora	tory Data					
mn	Total FPM(g)	0.00129	0.00174	0.00163	0.00160	
m _{CPM}	Total CPM(g)	0.00693	0.00272	0.00243	0.00180	
m _{Part}	Total particulate matter (g)	0.00822	0.00446	0.00406	0.00340	
FPM Re	esults ¹					
C_{sd}	Particulate Concentration (lb/dscf)	9.04E-08	1.11E-07	1.10E-07	1.05E-07	1.04E-07
E _{lb/hr}	Particulate Rate (lb/hr)	0.268	0.340	0.324	0.314	0.312
E_{Fd}	Particulate Rate - F _d -based (Ib/MMBtu)	0.00116	0.00139	0.00140	0.00140	0.00134
CPM Re	esults					
C_{sd}	Particulate Concentration (lb/dscf)	4.86E-07	1.74E-07	1.64E-07	1.18E-07	2.35E-07
E _{lb/hr}	Particulate Rate (lb/hr)	1.44	0.532	0.484	0.353	0.702
E_{Fd}	Particulate Rate - F_d -based (Ib/MMBtu)	0.00621	0.00218	0.00209	0.00157	0.00301
PM ₁₀ Re	esults					
C _{sd}	Particulate Concentration (lb/dscf)	5.76E-07	2.85E-07	2.73E-07	2.22E-07	3.39E-07
E _{lb/hr}	Particulate Rate (lb/hr)	1.71	0.872	0.808	0.668	1.014
E_{Fd}	Particulate Rate - F _d -based (Ib/MMBtu)	0.00737	0.00357	0.00349	0.00296	0.00435

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Table 2-2: Coker Heater – H₂SO₄ Emissions

Run No).	1	2	3	4	Average	
Date (2	2019)	Jul 23	Jul 23	3 Jul 24 Jul 24			
Start Ti	me (approx)	14:02	16:30	08:24	10:50		
Stop Ti	me (approx)	15:02	17:47	09:40	12:06		
Proces	ss Conditions						
P ₁	Charge rate (BPD)	40,199	42,570	42,570	42,570	41,977	
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,626	8,626	8,612	8,612		
H_i	Actual heat input (MMBtu/hr)	185	197	212	230	206	
Gas Co	onditions						
O ₂	Oxygen (dry volume %)	7.0	7.6	6.4	6.7	6.9	
CO ₂	Carbon dioxide (dry volume %)	8.1	7.8	8.5	9.1	8.4	
T_s	Sample temperature (°F)	400	410	405	412	407	
B_w	Actual water vapor in gas (% by volume)	12.2	12.9	13.7	13.8	13.2	
Sampli	ng Data						
V _{mstd}	Volume metered, standard (dscf)	26.50	26.46	26.72	26.64	26.58	
Labora	tory Data (Ion Chromatography)						
mn	Total H_2SO_4 collected (mg)	0.3017	0.5673	0.3580	0.8147		
Sulfuri	c Acid Vapor (H ₂ SO ₄) Results						
C_{sd}	H_2SO_4 Concentration (lb/dscf)	2.51E-08	4.73E-08	2.95E-08	6.74E-08	4.23E-08	
C_{sd}	H ₂ SO ₄ Concentration (ppmdv)	0.0987	0.186	0.116	0.265	0.166	
E_{Fd}	H_2SO_4 Rate - Fd-based (Ib/MMBtu)	0.000326	0.000641	0.000367	0.000855	0.000547	

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Table 2-3: Coker Heater – PM Emissions

Run No.		1	2	3	4	Average
Date (2	2019)	Jul 23	Jul 23	Jul 24	Jul 24	
Start Ti	me (approx.)	14:02	16:30	08:24	10:50	
Stop Ti	me (approx.)	15:24	17:47	09:40	12:06	
Proces	ss Conditions					
R _P	Production Rate (BPD)	40,200	42,570	42,570	42,570	42,000
P ₁	Fuel Consumption (mscf/day)	4,050	4,312	4,410	4,480	4,310
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,626	8,626	8,612	8,612	
H_i	Actual heat input (MMBtu/hr) ¹	185	197	212	230	206
Gas Co	onditions					
O ₂	Oxygen (dry volume %)	6.8	6.5	6.8	7.4	6.9
CO_2	Carbon dioxide (dry volume %)	8.3	8.5	8.2	8.8	8.5
T_s	Sample temperature (°F)	397	409	408	411	406
FPM Re	esults					
E_{Fd}	Particulate Rate - F _d -based (Ib/MMBtu)	0.00116	0.00139	0.00140	0.00140	0.00134
Sulfuri	c Acid Vapor (H ₂ SO ₄) Results					
E_{Fd}	H ₂ SO ₄ Rate - F _d -based (Ib/MMBtu)	0.000326	0.000641	0.000367	0.000855	0.000547
Particu	llate Matter (as PM ₁₀) Results ¹					
E_{Fd}	Particulate Rate - F _d -based (lb/MMBtu) ²	0.000830	0.000752	0.00103	0.000541	0.000872

¹ Final PM results average of three (3) highest valid runs.

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Table 2-4: Coker Heater – VOC Emissions

Run No.		1	2	3	Average
Date (20	019)	Jul 24	Jul 24	Jul 24	
Start Tin	ne (approx.)	08:24	09:43	11:04	
Stop Tin	ne (approx.)	09:24	10:43	12:04	
Process	s Conditions				
P ₁	Production Rate (BPD)	42,570	42,570	42,570	42,570
P_2	Fuel Consumption (mscf/day)	4,373	4,547	4,463	4,461
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,612	8,612	8,612	
H_i	Actual heat input (MMBtu/hr)	205	234	230	223
Gas Con	nditions				
O ₂	Oxygen (dry volume %)	6.1	6.9	6.8	6.6
CO2	Carbon dioxide (dry volume %)	8.8	7.9	8.0	8.2
B_{w}	Actual water vapor in gas (% by volume) ¹	13.6	13.6	13.6	13.6
THC Res	sults ²				
C_{sd}	Concentration (ppmdvas C ₃ H ₈)	<0.544	<0.544	<0.544	<0.544
C_{sd}	Concentration (Ib/dscf)	<6.22E-08	<6.22E-08	<6.22E-08	<6.22E-08
E_{Fd}	Emission Rate - F _d -based (Ib/MMBtu)	< 0.000759	< 0.000763	< 0.000776	< 0.000766
VOC Res	sults ³				
C_{sd}	Concentration (ppmdv as C ₃ H ₈)	< 0.544	< 0.544	< 0.544	< 0.544
C_{sd}	Concentration (Ib/dscf)	<6.22E-08	<6.22E-08	<6.22E-08	<6.22E-08
E_{Fd}	Emission Rate - F _d -based (Ib/MMBtu)	< 0.000759	< 0.000763	< 0.000776	< 0.000766

¹ Moisture data used for ppmw v to ppmdv correction obtained from nearly-concurrent EPA M5-202 runs.

² For THC, '<' indicates a measured response below the detection limit (assumed to be 1% of the instrument calibration span).

 3 VOC is reported as THC since all THC results were less than VOC limit.

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Table 2-5:

Coker Heater – NSFPM Emissions

Run No).	1	2	3	4	Average
Date (2	2019)	Jul 23	Jul 23	Jul 24	Jul 24	
Start Ti	me (approx)	14:02	16:30	08:24	10:50	
Stop Ti	me (approx)	15:24	17:48	09:40	12:06	
Proces	ss Conditions					
R_P	Production Rate (BPD)	40,200	42,570	42,570	42,570	42,000
P ₁	Fuel Consumption (mscf/day)	4,050	4,312	4,410	4,480	4,310
F_{d}	Oxygen-based F-factor (dscf/MMBtu)	8,626	8,626	8,612	8,612	
H _i	Actual heat input (MMBtu/hr)	185	197	212	230	206
Gas Co	onditions					
O ₂	Oxygen (dry volume %)	6.8	6.4	6.3	7.1	6.7
CO_2	Carbon dioxide (dry volume %)	8.2	8.6	8.6	9.0	8.6
T_s	Sample temperature (°F)	397	407	406	409	404
B_w	Actual water vapor in gas (% by volume)	12.8	14.4	14.7	14.3	14.1
Gas Flo	w Rate					
Qa	Volumetric flow rate, actual (acfm)	91,800	96,900	99,200	97,100	96,300
Q_s	Volumetric flow rate, standard (scfm)	55,200	57,600	59,400	58,000	57,500
Q_{std}	Volumetric flow rate, dry standard (dscfm)	48,100	49,300	50,700	49,700	49,400
Sampli	ng Data					
V _{mstd}	Volume metered, standard (dscf)	31.67	32.93	34.13	33.23	32.99
%I	Isokinetic sampling (%)	100.7	102.2	102.9	102.3	102.0
Labora	tory Data					
m _n	Total NSFPM(g)	0.00061	0.00061	0.00061	0.00061	
NSFPM	Results					
C_{sd}	Particulate Concentration (lb/dscf)	4.25E-08	4.08E-08	4.72E-08	4.05E-08	4.27E-08
E _{lb/hr}	Particulate Rate (lb/hr)	0.123	0.121	0.144	0.121	0.127
E_{Fd}	Particulate Rate - F _d -based (Ib/MMBtu)	0.000543	0.000508	0.000581	0.000528	0.000540

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Table 2-6:

Coker Heater –	· O 2	(%dv)	Relative	Accuracy
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Run No.	Start Time	Date (2019)	RM Data (%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	09:46	Jul 23	6.66	6.70	-0.04	-0.6%
2	10:17	Jul 23	6.70	6.73	-0.03	-0.4%
3	10:52	Jul 23	6.75	6.75	0.00	0.0%
4	11:27	Jul 23	6.65	6.65	0.00	0.0%
5	12:01	Jul 23	6.78	6.74	0.04	0.6%
6	12:34	Jul 23	6.74	6.77	-0.03	-0.4%
7	13:08	Jul 23	6.73	6.75	-0.02	-0.3%
8 *	13:42	Jul 23	6.67	6.71	-0.04	-0.6%
9	14:17	Jul 23	6.73	6.73	0.00	0.0%
10	14:56	Jul 23	6.62	6.63	-0.01	-0.2%
	Average		6.71	6.72	-0.01	-0.1%

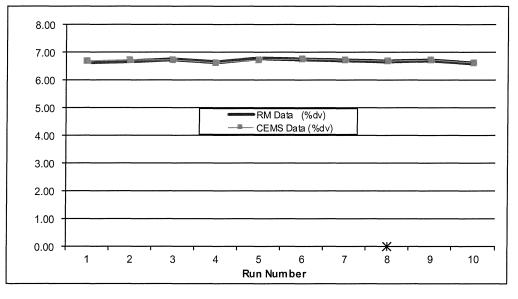
Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.0240		
Confidence Coefficient (CC)	0.0184		
t-Value for 9 Data Sets	2.306		
		Limit	
Avg. Abs. Diff. (%dv)	0.02	1.0	

RM = Reference Method (CleanAir Data)

081419 112537

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data) RATA calculations are based on 9 of 10 runs.* indicates the excluded run.



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Table 2-7:

Coker Heater – NO_X (ppmdv @ 0% O₂) Relative Accuracy

Run No.	Start Time	Date (2019)	RM Data (ppm@0%O2)	CEMS Data (ppm@0%O2)	Difference (ppm@0%O2)	Difference Percent
1 *	09:46	Jul 23	36.34	37.61	-1.27	-3.5%
2	10:17	Jul 23	36.75	37.99	-1.24	-3.4%
3	10:52	Jul 23	37.68	38.83	-1.15	-3.1%
4	11:27	Jul 23	37.01	37.94	-0.93	-2.5%
5	12:01	Jul 23	37.40	38.58	-1.18	-3.2%
6	12:34	Jul 23	37.52	38.69	-1.17	-3.1%
7	13:08	Jul 23	37.63	38.84	-1.21	-3.2%
8	13:42	Jul 23	37.96	38.84	-0.88	-2.3%
9	14:17	Jul 23	38.66	39.99	-1.33	-3.4%
10	14:56	Jul 23	38.11	39.16	-1.05	-2.8%
	Average	:	37.64	38.76	-1.13	-3.0%

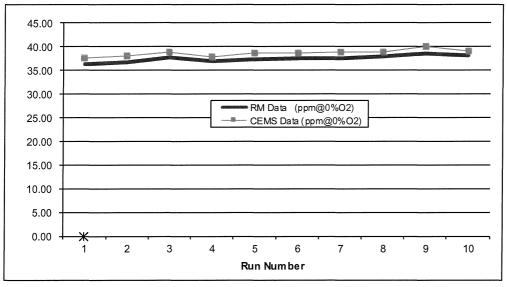
Relative Accuracy Test Audit Results

Star	ndard Deviation of Differences	0.1465	
	Confidence Coefficient (CC)	0.1126	
	t-Value for 9 Data Sets	2.306	
			Limit
F	Relative Accuracy (as % of RM)	3.3%	20.0%

RM = Reference Method (CleanAir Data)

081419 112537

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data) RATA calculations are based on 9 of 10 runs.* indicates the excluded run.



Marathon Petroleum Company LP Detroit Refinery - Coker Heater

Report on Compliance & RATA Testing

Table 2-8:

Coker Heater -	NOx	(lb/MMBtu) Relative	Accuracy
----------------	-----	-----------	------------	----------

Run No.	Start Time	Date (2019)	RM Data (Ib/MMBtu)	CEMS Data (Ib/MMBtu)	Difference (Ib/MMBtu)	Difference Percent
1 *	09:46	Jul 23	0.03743	0.03878	-0.00135	-3.6%
2	10:17	Jul 23	0.03785	0.03917	-0.00132	-3.5%
3	10:52	Jul 23	0.03881	0.04003	-0.00122	-3.1%
4	11:27	Jul 23	0.03812	0.03911	-0.00099	-2.6%
5	12:01	Jul 23	0.03852	0.03978	-0.00126	-3.3%
6	12:34	Jul 23	0.03865	0.03989	-0.00124	-3.2%
7	13:08	Jul 23	0.03875	0.04005	-0.00130	-3.4%
8	13:42	Jul 23	0.03910	0.04005	-0.00095	-2.4%
9	14:17	Jul 23	0.03982	0.04123	-0.00141	-3.5%
10	14:56	Jul 23	0.03925	0.04038	-0.00113	-2.9%
	Average		0.03876	0.03997	-0.00120	-3.1%

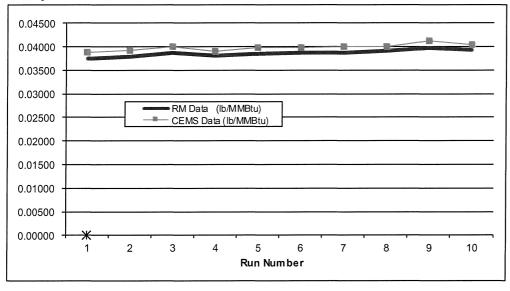
Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.0001523		
Confidence Coefficient (CC)	0.0001171		
t-Value for 9 Data Sets	2.306		
		Limit	
Relative Accuracy (as % of RM)	3.4%	20.0%	

RM = Reference Method (CleanAir Data)

081419112537

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data) RATA calculations are based on 9 of 10 runs.* indicates the excluded run.



Marathon Petroleum Company LP Detroit Refinery - Coker Heater

Report on Compliance & RATA Testing

Table 2-9:

Run No.	Start Time	Date (2019)	RM Data (Ib/MMBtu)	CEMS Data (Ib/MMBtu)	Difference (Ib/MMBtu)	Difference Percent
1	09:46	Jul 23	0.0000	0.0000	0.0000	100.0%
2	10:17	Jul 23	0.0000	0.0000	0.0000	100.0%
3	10:52	Jul 23	0.0000	0.0000	0.0000	100.0%
4	11:27	Jul 23	0.0000	0.0000	0.0000	100.0%
5	12:01	Jul 23	0.0000	0.0000	0.0000	100.0%
6	12:34	Jul 23	0.0000	0.0000	0.0000	100.0%
7	13:08	Jul 23	0.0000	0.0000	0.0000	100.0%
8	13:42	Jul 23	0.0000	0.0000	0.0000	100.0%
9	14:17	Jul 23	0.0000	0.0000	0.0000	100.0%
10	14:56	Jul 23	0.0000	0.0000	0.0000	100.0%
	Average		0.0000	0.0000	0.0000	100.0%

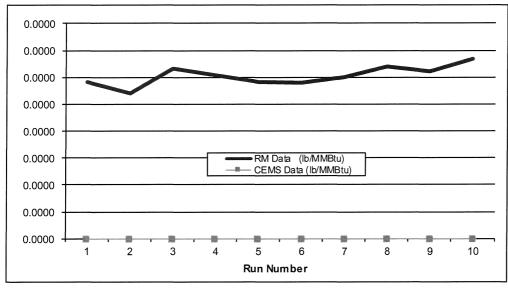
Relative Accuracy Test Audit Results

Standard Deviation of Differences Confidence Coefficient (CC)	0.000000 0.000000	
t-Value for 10 Data Sets	2.262	
Relative Accuracy (as % of Appl. Std.) Appl. Std. = 0.01 lb/MMBtu	0.0%	Limit 5.0%

RM = Reference Method (CleanAir Data)

081419 112537

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data) RATA calculations are based on all 10 runs.



End of Section

CleanAir.

Marathon Petroleum Company LP Detroit Refinery - Coker Heater Report on Compliance & RATA Testing

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 Coker unit (EU70-COKER) converts Vacuum Resid (Crude Vacuum Tower Bottoms), a product normally sold as asphalt or blended into residual fuel oil, into lighter, more valuable products. The Vacuum Resid feedstock is heated before it enters the main fractionator, where lighter material vaporizes. The fractionator bottoms are routed through a fired heater and then into a coke drum. This emission unit consists of process vessels (fractionators), coke drums, heater (EU70-COKERHTR-S1), cooling tower, compressors, pumps, piping, drains, and various components (pumps and compressor seals, process valves, pressure relief valves, flanges, connectors, etc.). This emission group includes the Coke Handling System, which collects, sizes, and transports the petroleum coke created during the coking process. The system consists of a coke pit, storage pad, enclosed crusher, enclosed conveyors, and surge bins.

The Coker Heater is fired by refinery fuel gas. Emissions are vented to the atmosphere via the Coker Heater Stack (SV70-H1), where testing was performed.

Test Location

The sample point locations were determined by EPA Method 1 and PS 2. Table 3-1 presents the sampling information for the test location described in this report. The figures shown on pages 16 and 17 represent the layout of the test location.

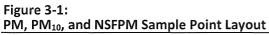
Table 3-1: Sampling Point Information

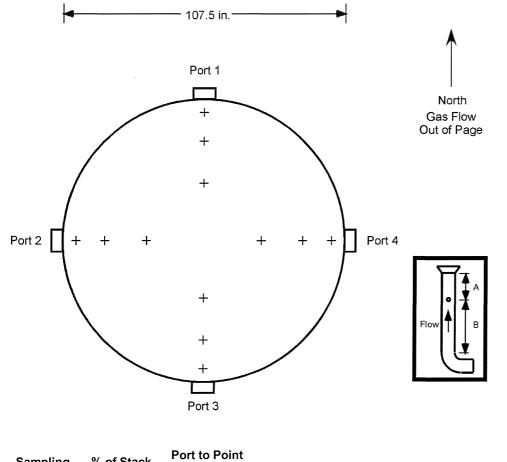
<u>Source</u> Constituent	Method (USEPA)	Run No.	Ports	Points per Port	Minutes per Point	Total Minutes	Figure
Coker Heater Stack							
FPM/CPM	5 / 202	1-4	4	3	5	60	3-1
H ₂ SO ₄	CTM-013 (Mod.)	1-4	1	1	60	60	N/A ¹
NSFPM	5B	1-4	4	3	5	60	3-1
$O_2 / CO_2 / CH_4 / C_2 H_6 / THC$	3A/18/25A	1-3	1	3	21	60	N/A ¹
$O_2/CO_2/NO_X/CO$	3A/7E/10	1-10	1	3	7	21	3-2

¹ CTM-013 (Mod.) and EPA M-25A sampling occurred at a single point near the center of the duct.

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Sampling Point	% of Stack Diameter	Port to Point Distance (inches)
1	29.6	31.8
2	14.6	15.5
3	4.4	4.7

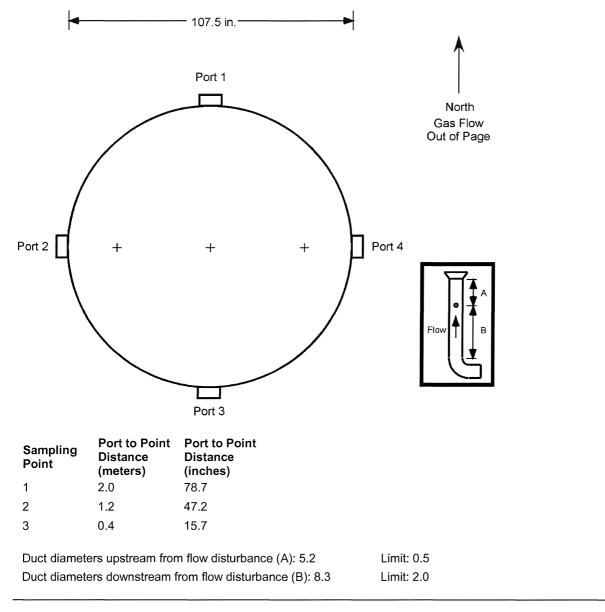
Duct diameters upstream from flow disturbance (A): 5.2	Limit: 0.5
Duct diameters downstream from flow disturbance (B): 8.3	Limit: 2.0

CleanAir.

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Figure 3-2:





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 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. In accordance with ASTM D7036 requirements, CleanAir included a description of any such modifications along with the full context of the objectives and requirements of the test program in the test protocol submitted prior to the measurement portion of this project. 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 3A	"Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 3B	"Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air"
Method 4	"Determination of Moisture Content in Stack Gases"
Method 5	"Determination of Particulate Matter Emissions from Stationary Sources"
Method 5B	"Determination of Nonsulfuric Acid Particulate Matter Emissions from Stationary Sources"
Method 7E	"Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 10	"Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"
Method 18	"Measurement of Gaseous Organic Compound Emissions by Gas Chromatography"
Method 25A	"Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer"
Title 40 CFF	R Part 51, Appendix M

Method 202 "Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources"

Title 40 CFR Part 60, Appendix B Performance Specifications

- PS 2 "Specifications and Test Procedures for SO₂ and NOx Continuous Emission Monitoring Systems in Stationary Sources"
 PS 3 "Specifications and Test Procedures for O₂ and CO₂ Continuous Emission Monitoring Systems in Stationary Sources"
- PS 4A "Specifications and Test Procedures for CO Continuous Emission Monitoring Systems in Stationary Sources"

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

PM and PM₁₀ Testing – USEPA Method 5/202

PM and PM_{10} emissions were determined using EPA Method 5/202.

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

The back-half (Method 202 portion) of the sampling train is designed to mimic ambient conditions and collect only the particles that would truly form CPM in the atmosphere by minimizing the sulfur dioxide (SO_2) and NO_X interferences observed with earlier versions of the method, in which flue gas was bubbled through cold water, and SO_2 and NO_X were absorbed and partially oxidized before they could be purged out with nitrogen (N_2).

Flue gas exiting the front-half heated filter passes through a coiled condenser and dry impinger system jacketed by water continually circulated at ambient temperature. Moisture is removed from the flue gas without bubbling through the condensed water. Flue gas then passes through a tetrafluoromethane (TFE) membrane filter at ambient temperature. The temperature of the flue gas at the exit of the filter was directly measured with an in-line thermocouple and maintained in the temperature range of 65°F to 85°F.

After exiting the ambient filter, the flue gas passes through two (2) additional impingers surrounded by ice in a "cold" section of the impinger bucket. The moisture collected in these impingers is not analyzed for CPM and is only collected to determine the flue gas moisture and to thoroughly dry the gas. The sample gas then flows into a calibrated dry gas meter where the collected sample gas volume is 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. The back-half of the sample train (heated filter outlet, condenser, dry impingers, and TFE membrane filter) was recovered per Method 202 requirements. The impinger train was purged with N₂ at a rate of 14 liters per minute (lpm) for one (1) hour following each test run and prior to recovery.

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A field train blank was assembled, purged, and recovered as if it were an actual test sample; analysis of the field train blank was used to blank-correct the test run results. Reagent blanks were collected to quantify background contamination. All samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for gravimetric analysis. Method 202 samples were maintained at a temperature < 85°F during transport to the laboratory.

All samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for gravimetric analysis. Upon receipt, the filters dessicated 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.

NSFPM Testing – USEPA Method 5B

NSFPM emissions were determined using EPA Method 5B.

The front-half of the sampling train consisted of a glass nozzle, glass liner and filter holder heated to $320^{\circ}F \pm 25^{\circ}F$, and a quartz fiber filter. Flue gas samples were extracted isokinetically per Method 5B requirements. The front-half portion of the sample train (nozzle, probe, and heated filter) was recovered per Method 5B requirements, using acetone as the recovery solvent.

All samples and blanks were returned to CleanAir Analytical Services in Palatine, Illinois, for gravimetric analysis.

H₂SO₄ Testing – CTM-013 Modified

H₂SO₄ emissions were determined referencing CTM-013 (Mod.).

A gas sample was extracted from the source at a constant flow rate using a quartz-lined probe maintained at a temperature of $650^{\circ}F \pm 25^{\circ}F$ and a quartz fiber filter (to remove particulate matter) maintained at the same temperature as the probe. The sample was 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) is located at the condenser outlet for the collection of residual SAM not collected by the condenser. The condenser temperature is regulated by a water jacket and the SAM filter is regulated by a closed oven. Both the water jacket and SAM filter oven were maintained at 140°F \pm 9°F plus 2°F for each 1% moisture above 16% flue gas moisture (above the water dew point, which eliminates the oxidation of dissolved SO₂ into the H₂SO₄-collecting fraction of the sample train).

After exiting the SAM filter, the sample gas then 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 is 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 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 in Palatine, Illinois, for ion chromatography (IC) analysis.

*O*₂, *CO*₂, *NO*_X, and *CO* Testing – USEPA Methods 3A, 7E, and 10; Performance Specifications 2, 3, and 4A

Reference method (RM) O_2 concentrations were determined using a paramagnetic analyzer per EPA Method 3A. RM NO_X emissions were determined using a chemiluminescent analyzer per EPA Method 7E. RM CO emissions were determined using an infrared analyzer per EPA Method 10. Carbon dioxide (CO₂) concentrations were determined using an NDIR analyzer per EPA Method 3A for supplemental purposes.

Sample gas was extracted at a constant rate, conditioned to remove moisture, and delivered to an analyzer bank, which measured concentration on a dry basis (units of %dv or ppmdv).

Calibration error checks were performed by introducing zero N_2 , high and mid-range calibration gases to the inlet of each analyzer during calibration error checks. Bias checks were performed before and after each sampling run by introducing calibration gas to the inlet of the sampling system's heated filter. Documentation of interference checks and NO_2 converter efficiency checks are included in Appendix D of this report.

Minute-average data points for O_2 , NO_X , and CO (dry basis) were collected over a period of 21 minutes for each RATA run. Sampling occurred at the three points specified in Section 8.1.3.2 of PS 2 during each run. A single port was used for each run.

Per Methods 3A, 7E, and 10, the average result for each run was drift-corrected, converted to identical units of measurement as the facility CEMS, and compared for relative accuracy (RA).

VOC Testing – USEPA Methods 18 and 25A

VOC emissions were determined using EPA Method 25A to quantify THC emissions, which were assumed equivalent to VOC emissions.

The Method 25A sampling system consisted of a heated probe, heated filter and heated sample line. Flue gas was delivered at 250°F to a flame ionization analyzer (FIA), which continuously measured minute-average THC concentration expressed in terms of propane (C_3H_8) on an actual (wet) basis. FIA calibration was performed by introducing zero air, high, mid- and low range C_3H_8 calibration gases to the inlet of the sampling system's heated filter. Bias checks were performed before and after each sampling run in a similar manner.

The Method 18 sampling system consisted of a gas conditioner (for moisture removal), TFE sample lines, TFE-coated diaphragm pump and a mass flow meter ("Direct Pump Sampling Procedure"). This system pulled a slipstream of the flue gas from the Method 25A sample delivery system and delivered it into a Tedlar bag at a constant rate. The moisture condensate was not collected for analysis as CH_4 and C_2H_6 are insoluble in water. Each bag was filled over a period of 60 minutes for each test run. The Tedlar bags were not analyzed because all Method 25A runs resulted in non-detect concentrations.

End of Section