

CleanAir Engineering 500 W. Wood Street Palatine, IL 60067-4975 cleanair.com



RECEIVED

JUL 31 2018

AIR QUALITY DIVISION



1300 South Fort Street Detroit, MI 48217 Client Reference No. 4101379616

A2LA / STAC Certificate No. 4342.02

Revision 0, Final Report

July 27, 2018

Marathon Petroleum Company LP Detroit Refinery Report on Compliance & RATA Testing CleanAir Project No. 13599-2 Revision 0, Final Report Page ii

COMMITMENT TO QUALITY

To the best of our knowledge, the data presented in this report are accurate, complete, error free and representative of the actual emissions during the test program. Clean Air Engineering operates in conformance with the requirements of ASTM D7036-04 Standard Practice for Competence of Air Emission Testing Bodies.

Report Writer;

July 27, 2018

Date

Scott Brown, QSTI Senior Project Manager / Quality Director sbrown@cleanair.com (800) 627-0033 ext. 4544

I hereby certify that the information contained within the final test report has been reviewed and, to the best of my ability, verified as accurate.

Independent Report and Appendix Reviewer:

Ken Sullivan Project Manager ksullivan@cleanair.com (800) 627-0033 ext. 4527

July 27, 2018

Date

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

RECEIVED

1. PROJECT OVERVIEW

AIR QUALITY DIVISION

JUL 31 2018

Test Program Summary

Marathon Petroleum Company LP (MPC) contracted CleanAir Engineering (CleanAir) to successfully complete testing on the CCR Inter Heater (EU14-CCRPLINTHR-S1) at the Detroit Refinery, located in Detroit, Michigan. The test program included the following objectives:

- Perform volatile organic compounds (VOCs) 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's 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. Test program information, including the test parameters, on-site schedule and a project discussion, begins on page 2.

Table 1-1: Summary of Results - Compliance

<u>Source</u> Constituent	Sampling Method (USEPA)	Average Emission	Permit Limit ¹
CCR Inter Heater Stack			
VOC (lb/MMBtu)	25A / 18	<0.00072	0.0055

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

Table 1-2: Summary of Results - RATA

<u>Source</u>	Reference Method	Relative	Applicable	Specification Limit ²
Constituent	(USEPA)	Accuracy (%) ¹	Specification	
CCR Inter Heater				
O ₂ (% dv)	ЗA	0.13	PS3	±1.0% dv
NO _x (lb/MMBtu)	7E / 3A	7.8	PS2	20% of RM
CO (lb/MMBtu)	10	0.0	PS4A°	10% of RM

¹ Relative Accuracy is expressed in terms of comparison to the reference method (% RM) or applicable emission standard (% Std.).

² Specification limits obtained from 40 CFR 60, Appendix B, Performance Specifications.

³ For any sources emitting less than 200 ppmv of CO, PS4A applies. The PS4A RA limit is either < 10% of RM, < 5% of Standard, or ± 5 ppmv (abs. average difference plus 2.5 x confidence coefficient).

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

Test Program Details

Parameters

The test program included the following measurements:

- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THCs) minus the following constituents
 - o methane (CH₄)
 - o ethane (C₂H₆)
- nitrogen oxides (NO_x)
- carbon monoxide (CO)
- flue gas composition (e.g., O₂, CO₂, H₂O)

Schedule

Testing was performed on June 27, 2018. The on-site schedule followed during the test program is outlined in Table 1-3.

Table 1-3: Test Schedule

Run					Start	End
Number	Location	Method	Analyte	Date	Time	Time
1	CCR Inter Heater Stack	USEPA 3A, 7E, 10, 25A	O ₂ /NO _x /CO/THC	06/27/18	08:22	08:43
2	CCR Inter Heater Stack	USEPA 3A, 7E, 10, 25A	O ₂ /NO _X /CO/THC	06/27/18	08:57	09:18
3	CCR Inter Heater Stack	USEPA 3A, 7E, 10, 25A	O₂/NO _X /CO/THC	06/27/18	09:31	09:52
4	CCR Inter Heater Stack	USEPA 3A, 7E, 10, 25A	O₂/NO _X /CO/THC	06/27/18	10:05	10:26
5	CCR Inter Heater Stack	USEPA 3A, 7E, 10, 25A	O₂/NO _X /CO/THC	06/27/18	10:39	11:00
6	CCR Inter Heater Stack	USEPA 3A, 7E, 10, 25A	O ₂ /NO _X /CO/THC	06/27/18	11:14	11:35
7	CCR Inter Heater Stack	USEPA 3A, 7E, 10, 25A	O₂/NO _X /CO/THC	06/27/18	11:48	12:09
8	CCR Inter Heater Stack	USEPA 3A, 7E, 10, 25A	O₂/NO _X /CO/THC	06/27/18	12:23	12:44
9	CCR Inter Heater Stack	USEPA 3A, 7E, 10, 25A	O ₂ /NO _X /CO/THC	06/27/18	12:58	13:19
10	CCR Inter Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _X /CO	06/27/18	13:34	13:55
11	CCR Inter Heater Stack	USEPA 3A, 7E, 10	O ₂ /NO _X /CO	06/27/18	14:20	14:41
1	CCR Inter Heater Stack	USEPA 25A, 18	VOC	06/27/18	08:22	09:52
2	CCR Inter Heater Stack	USEPA 25A, 18	VOC	06/27/18	10:05	11:35
3	CCR Inter Heater Stack	USEPA 25A, 18	VOC	06/27/18	11:48	13:19
1	CCR Inter Heater Stack	USEPA4	H ₂ O	06/27/18	08:57	09:32
2	CCR Inter Heater Stack	USEPA4	H₂O	06/27/18	10:05	10:40
3	CCR Inter Heater Stack	USEPA4	H₂O	06/27/18	11:14	11:49
4	CCR Inter Heater Stack	USEPA4	H ₂ O	06/27/18	12:23	12:58

Discussion

Project Synopsis

O2, NOx and CO RATA Testing

Minute-average data points for O_2 , 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 at least nine (9) of 11 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's CEMS and compared for relative accuracy.

VOC Testing

VOC emissions were determined using EPA Method 25A to quantify THC emissions. VOC testing was comprised of three (3) 63-minute test runs. The Method 25A test runs were performed concurrently with three (3) 63-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 pounds per million Btu (lb/MMBtu) as propane. O₂ concentrations from concurrent 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 4 runs.

Moisture Testing

Four (4) 35-minute Method 4 test runs were performed using EPA Method 4. The moisture content was utilized to convert THC concentrations from a wet basis to a dry basis.

Fuel Analysis

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

<u>Test Conditions</u>

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

Marathon Petroleum Company LP Detroit Refinery Report on Compliance & RATA Testing CleanAir Project No. 13599-2 Revision 0, Final Report Page 4

Invalidated Test Runs

The facility's PI system malfunctioned during Run 10, which caused two minutes of lost data. Therefore, it was thrown out and not used in any of the RATA calculations. An eleventh run was performed in lieu of Run 10.

End of Section

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

2. RESULTS

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

Table 2-1: CCR Inter Heater Stack – VOC Emissions

Run No.	Mana ann an Anna an Ann	1	2	3	Average
Date (201	18)	Jun 27	Jun 27	Jun 27	
Start Tim	e (approx.)	08:22	10:05	11:48	
Stop Tim	e (approx.)	09:52	11:35	13:19	
Process	Conditions				
P ₁	Charge rate (bpd)	22,003	21,997	22,001	22,000
P ₂	Heat Input (MMBtu/hr)	97.8	96.6	98.5	97.6
Fd	Oxygen-based F-factor (dscf/MMBtu)	8,238	8,238	8,238	8,238
Gas Cond	ditions				
O ₂	Oxygen (dry volume %)	5.4	5.5	5.5	5.5
CO ₂	Carbon dioxide (dry volume %)	9.4	9.4	9.3	9.3
Bw	Actual water vapor in gas (% by volume) ¹	14.9	15.4	15.5	15.3
THC Resu	uits ^{2,3}				
C_{sd}	Concentration (ppmdv as C ₃ H ₈)	<0.541	<0.545	<0.546	<0.544
C_{sd}	Concentration (lb/dscf)	<6.20E-08	<6.24E-08	<6.24E-08	<6.23E-08
E. _{Fd}	Emission Rate - F _d -based (Ib/MMBtu)	<0.000711	<0.000718	<0.000722	<0.000717

¹ Moisture data used for ppmw v to ppmdv correction obtained from nearly-concurrent M-4 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 non-detect.

Marathon Petroleum Company LP

Detroit Refinery

Report on Compliance & RATA Testing

CleanAir Project No. 13599-2 **Revision 0, Final Report** Page 6

Table 2-2: CCR Inter Heater Stack - O₂ (% dv) RATA

Run No.	Start Time	Date (2018)	RM Data	(%dv)	CEMS Data (%dv)	Difference (%dv)	Difference Percent
1	08:22	Jun 27		5.37	5.50	-0.13	-2.4%
2	08:57	Jun 27		5.36	5.50	-0.14	-2.6%
3	09:31	Jun 27		5.50	5.63	-0.13	-2.4%
4	10:05	Jun 27		5.51	5.65	-0.14	-2.5%
5	10:39	Jun 27		5.55	5.68	-0.13	-2.4%
6	11:14	Jun 27		5.38	5.52	-0.14	-2.7%
7	11:48	Jun 27		5.51	5.65	-0.14	-2.5%
8	12:23	Jun 27		5.44	5.55	-0.11	-1.9%
9	12:58	Jun 27		5.64	5.77	-0.13	-2.3%
10 *	13:34	Jun 27		5.36	5.55	-0.19	-3.5%
11 *	14:20	Jun 27		5.40	5.55	-0.15	-2.7%
	Average			5.47	5.61	-0.13	-2.4%

Relative	Accuracy	Test	Audit	Results

eference Method (CleanAir Data)			071818 133043
Avg. Abs. Diff. (%dv)	0.13	1.0	
		Limit	
t-Value for 9 Data Sets	2.306		
Confidence Coefficient (CC)	0.0086		
Standard Deviation of Differences	0.0112		

RM = Reference Method (CleanAir Data)

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data) RATA calculations are based on 9 of 11 runs.* indicates the excluded runs.



Marathon Petroleum Company LP

Detroit Refinery

Report on Compliance & RATA Testing

CleanAir Project No. 13599-2 Revision 0, Final Report Page 7

Table 2-3:

Run No.	Start Time	Date (2018)	RM Data (Ib/MMBtu)	CEMS Data (Ib/MMBtu)	Difference (Ib/MMBtu)	Difference Percent
1	08:22	Jun 27	0.0319	0.0343	-0.0024	-7.5%
2	08:57	Jun 27	0.0330	0.0351	-0.0021	-6.4%
3	09:31	Jun 27	0.0335	0.0360	-0.0025	-7.5%
4	10:05	Jun 27	0.0335	0.0362	-0.0027	-8.1%
5	10:39	Jun 27	0.0336	0.0360	-0.0024	-7.1%
6 *	11:14	Jun 27	0.0323	0.0350	-0.0027	-8.4%
7	11:48	Jun 27	0.0328	0.0353	-0.0025	-7.6%
8	12:23	Jun 27	0.0321	0.0345	-0.0024	-7.5%
9	12:58	Jun 27	0.0321	0.0345	-0.0024	-7.5%
10 *	13:34	Jun 27	0.0321		NA	NA
11	14:20	Jun 27	0.0317	0.0342	-0.0025	-7.9%
	Average)	0.0327	0.0351	-0.0024	-7.4%

4----

. . .

...

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.000158	
Confidence Coefficient (CC)	0.000122	
t-Value for 9 Data Sets	2.306	
		Limit
Relative Accuracy (as % of RM)	7.8%	20.0%
Relative Accuracy (as % of Appl. Std.)	5.1%	10.0%
Appl. Std. = 0.05 lb/MMBtu		

RM = Reference Method (CleanAir Data)

Sandrus

072018 150433

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data) RATA calculations are based on 9 of 11 runs.* indicates the excluded runs.



Marathon Petroleum Company LP

Detroit Refinery

Report on Compliance & RATA Testing

CleanAir Project No. 13599-2 Revision 0, Final Report Page 8

Table 2-4:

CCR Inter Heater Stack - CO (Ib/MMBtu) RATA

Run No.	Start Time	Date (2018)	RM Data (Ib/MMBtu)	CEMS Data (Ib/MMBtu)	Difference (lb/MMBtu)	Difference Percent
1	08:22	Jun 27	0.00	0.00	0.00	0.0%
2	08:57	Jun 27	0.00	0.00	0.00	0.0%
3	09:31	Jun 27	0.00	0.00	0.00	0.0%
4	10:05	Jun 27	0.00	0.00	0.00	0.0%
5	10:39	Jun 27	0.00	0.00	0.00	0.0%
6	11:14	Jun 27	0.00	0.00	0.00	0.0%
7	11:48	Jun 27	0.00	0.00	0.00	0.0%
8	12:23	Jun 27	0.00	0.00	0.00	0.0%
9	12:58	Jun 27	0.00	0.00	0.00	0.0%
10 *	13.34	Jun 27	0.00		NA	NA
11	14:20	Jun 27	0.00	0.00	0.00	0.0%
	Average]	0.00	0.00	0.00	0.0%

Relative Accuracy Test Audit Results

Standard Deviation of Differences	0.000		
Confidence Coefficient (CC)	0.000		
t-Value for 10 Data Sets	2.262		
		Limit	
Relative Accuracy (as % of RM)	0.0%	10.0%	
Relative Accuracy (as % of Appl. Std.)	0.0%	5.0%	
Appl. Std. = 0.013 lb/MMBtu			
Avg. Abs. Diff. (lb/MMBtu)	0.00	5.0	

RM = Reference Method (CleanAir Data)

072018 150433

CEMS = Continuous Emissions Monitoring System (Marathon Petroleum Company Data) RATA calculations are based on 10 of 11 runs.* indicates the excluded run.



RECEIVED

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

JUL 31 2018

CleanAir Project No. 13599-2 Revision 0, Final Report Page 9

AIR QUALITY DIVISION

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 Continuous Catalytic Regeneration Platformer Unit (EG14-CCRPLATFORMER) is a catalytic reformer that rearranges the structure of low octane naphtha feed into higher-octane reformates. Hydrogen is produced as a product of the reaction and is used in other refinery processes. The CCR Inter Heater (EU14-CCRPLINTHTR) heats the intermediate reformate reactants prior to its re-entry into the multi-staged reactor system.

The unit is fired by refinery fuel gas. Emissions are vented to the atmosphere via the CCR Inter Heater Stack (SV14-H4A) where testing was performed.

Test Location

The sample point locations were determined by EPA Method 7E and Performance Specification 2. Table 3-1 presents the sampling information for the test location described in this report. The figure shown on page 10 represents the layout of the test location.

Table 3-1: Sampling Information

Source Constituent	Method (USEBA)	Run	Ports	Points per	Minutes per Roint	Total Minutes	Figure
			FUILS	FOIL			* iyule
CCR mer neater	01 140 1001	4.0	4	0	04	<u></u>	0.4
$O_2 / CO_2 / CH_4 / C_2 H_6 / THC$	3A/18/25A	1-3	1	3	21	63	3-1
$O_2 / CO_2 / NO_X / CO$	3A / 7E / 10	1-10	1	3	7	21	3-1
H ₂ O	4	1-4	1	1	35	35	N/A ¹

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

Marathon Petroleum Company LP

Detroit Refinery

Report on Compliance & RATA Testing

CleanAir Project No. 13599-2 **Revision 0, Final Report** Page 10



Sampling Point	% of Stack Diameter	Port to Point Distance (inches)	
1	83.3	55.0	
2	50.0	33.0	
3	16.7	11.0	
Duct diamete	rs upstream fro	m flow disturbance (A): 13.1	Limit: 0.5
Duct diamete	rs downstream	from flow disturbance (B):3.6	Limit: 2.0

End of Section

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

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 3A	"Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure)"		
Method 4	"Determination of Moisture Content in Stack Gases"		
Method 7E	"Determination of Nitrogen Oxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)"		
Method 10	"Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyze Procedure)"		
Method 19	"Determination of Sulfur Dioxide Removal Efficiency and Particulate Matter, Sulfur Dioxide and Nitrogen Oxide Emission Rates"		
Method 25A	"Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer"		
Title 40 CFR Part 60, Appendix B Performance Specifications PS 2 "Specifications and Test Procedures for SO ₂ and NOx Continuous Emission Monitor in Stationary Sources"			
PS 3	"Specifications and Test Procedures for O_2 and CO_2 Continuous Emission Monitoring Systems in Stationary Sources"		
PS 4A	"Specifications and Test Procedures for Carbon Monoxide Continuous Emission Monitoring Systems in Stationary Sources"		

Methodology Discussion

*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 nitrogen (N₂), 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 NO₂ converter efficiency checks are included in this report. Per EPA Methods 3A, 7E and 10, the average results for each run were drift-corrected.

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 63 minutes for each test run. Tedlar bags were not analyzed because THC was non-detect.

Moisture Testing – USEPA Method 4 (Modified)

Flue gas was extracted at a single point and constant rate through an unheated, stainless steel tubing sampling probe. After exiting the unheated sampling probe, the flue gas passed through a series of knock-out jars. Condensate in the knock-out jars was 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.