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REPORT ON COMPLIANCE TESTING

Performed for:
MARATHON PETROLEUM COMPANY
DETROIT REFINERY

COKER HEATER STACK (SV70-H1)

Client Reference No: CN00081321
CleanAir Project No: 12374
Revision 1: December 12, 2013

To the best of our knowledge, the data presented in this report are accurate, complete, error free, legible 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.

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REVISION HISTORY

REPORT ON COMPLIANCE TESTING

DRAFT REPORT REVISION HISTORY

Revision:	Date	Pages	Comments
D0a	11/25/13	All	Draft version of original document.

FINAL REPORT REVISION HISTORY

Revision:	Date	Pages	Comments
0	12/09/13	All	Final version of original document.
1	12/12/13	Cover, ii, 1-3, K-79	Corrected source name in Table 1-2.

CONTENTS

PROJECT OVERVIEW

INTRODUCTION

Marathon Petroleum Company (MPC) contracted Clean Air Engineering (CleanAir) to perform emission measurements at the Detroit Refinery for compliance purposes.

All testing was conducted in accordance with the regulations set-forth by the United States Environmental Protection Agency (USEPA) and the Michigan Department of Environmental Quality (DEQ). The permit limits are referenced in Michigan Department of Environmental Quality, Air Quality Division Permit to Install No. 63-08C, issued January 11, 2012.

Key Project Participants

Individuals responsible for coordinating and conducting the test program were:

Crystal Davis – MPC
Joe Reidy – MPC
Thomas Gasloli – DEQ
John Rooney – CleanAir

Test Program Parameters

The testing was performed at the Coker Heater Stack (Emission Unit ID No. EG70-COKERHTR; Stack ID No. SV70-H1) on October 24-25, 2013, and included the following emissions measurements:

- particulate matter (PM), assumed equivalent to filterable particulate matter (FPM) only
- total particulate matter less than 10 microns (μm) in diameter (Total PM_{10}), assumed equivalent to the sum of the following constituents:
  - filterable particulate matter (FPM)
  - condensable particulate matter (CPM)
- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THC) minus the following constituents:
  - methane (CH_4)
  - ethane (C_2H_6)
- nitrogen oxides (NO_X)
- flue gas composition (e.g., O_2, CO_2, H_2O)
- flue gas flow rate

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TEST PROGRAM SYNOPSIS

Test Schedule

The on-site schedule followed during the test program is outlined in Table 1-1.

Table 1-1:
Schedule of Activities

Run Number	Location	Method	Analyte	Date	Start Time	End Time
1	Coker Heater Stack	USEPA Method 5/202	FPM/CPM	10/24/13	14:21	16:33
2	Coker Heater Stack	USEPA Method 5/202	FPM/CPM	10/24/13	17:33	19:45
3	Coker Heater Stack	USEPA Method 5/202	FPM/CPM	10/25/13	07:27	09:41
1	Coker Heater Stack	USEPA Method 3A/18/25A	$O_2/CO_2/CH_4/C_2H_6$/THC	10/24/13	16:21	18:02
2	Coker Heater Stack	USEPA Method 3A/18/25A	$O_2/CO_2/CH_4/C_2H_6$/THC	10/24/13	18:19	20:01
3	Coker Heater Stack	USEPA Method 3A/18/25A	$O_2/CO_2/CH_4/C_2H_6$/THC	10/25/13	08:07	09:39
1	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/24/13	16:21	16:42
2	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/24/13	17:03	17:24
3	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/24/13	17:41	18:02
4	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/24/13	18:19	18:40
5	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/24/13	18:59	19:20
6	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/24/13	19:40	20:01
7	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/25/13	08:07	08:28
8	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/25/13	08:41	09:02
9	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/25/13	09:18	09:39
10	Coker Heater Stack	USEPA Method 3A/7E	$O2/CO2/NO_X$	10/25/13	09:54	10:15

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Results Summary

Table 1-2 and Table 1-3 summarize the results of the test program. A more detailed presentation of the test conditions and results of analysis are shown on pages 2-1 through 2-6.

Table 1-2:
Summary of Emission Compliance Test Results

Source Constituent	(Units)	Sampling Method	Average Emission	Permit Limit[1]
Coker Heater Stack				
PM	(lb/MMBtu)	USEPA M-5	0.0019	0.0019
PM_{10}	(lb/MMBtu)	USEPA M-5 / 202	0.0031	0.0076
VOC	(lb/MMBtu)	USEPA M-25A / 18	<0.0007	0.0055
NO_X	(lb/MMBtu)	USEPA M-7E	0.03	0.05

[1] Permit limits obtained from MDEQ Permit To Install No. 63-08C.

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Table 1-3:
Summary of RATA Results

Source Constituent (Units)	Reference Method (USEPA)	Applicable Specification	Relative Accuracy (%)	Specification Limit[1]
Coker Heater Stack				
O_2 (% dv)	M-3A	PS3	0.01	±1.0% dv
NOx (ppmdv)	M-7E	PS2	5.5	20% of RM or

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

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Discussion of Test Program

FPM and CPM Testing - USEPA Method 5/202

For this test program, PM emission rate is assumed equivalent to FPM emission rate and PM_{10} emission rate is assumed equivalent to the sum of FPM and CPM emission rates (units of lb/hr, Ton/yr, or lb/MMBtu for all constituents).

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The analytical procedures in EPA Method 202 include an ammonium titration of the inorganic sample fractions with pH less than 7.0 to neutralize acids with hygroscopic properties such as H_2SO_4 that may be present in the sample. This step speeds up the sample desiccation process and allows the samples to come to a constant weight prior to weighing. The weight of ammonium added to the sample as a result of the titration is subtracted from the analytical result.

The laboratory performing the gravimetric analysis (Clean Air Analytical Services) has determined that only samples with an initial pH less than 4.5 require a significant amount of ammonium neutralization, resulting in a correction in excess of 0.5 mg. Based on this observation, the laboratory has altered their procedures to read that a sample must have a pH lower than 4.5 in order to be titrated.

While all of the inorganic sample fractions from Runs 1, 2 and 3 had a pH less than 4.5 and were titrated, the field train reagent blank had a pH of about 5.4 and was not titrated, per Clean Air Analytical Services' modified procedure. The sample fraction was observed to come to a constant weight without having to titrate the sample.

Three (3) 120-minute M-5/202 test runs were performed on October 24-25, 2013. The final result for PM was expressed as the average of three (3) valid runs and was equivalent to the permit limit for PM. The final result for PM_{10} was expressed as the average of three (3) valid runs and was below the permit limit for PM_{10}.

The PM emission rate results for M-5/202 Run 1 yielded results that were approximately eight (8) and twelve (12) times greater than Runs 2 and 3 respectively. The front-half filter and rinse from Run 1 contained a red/brown non-magnetic particulate that was not present in the other test runs. Pictures of the front-half filter and rinse can be found in Appendix K of the report.

The source of the additional FPM from Run 1 is undetermined. The PM results from all three (3) test runs of the compliance test program performed on December 11, 2012, yielded results similar to Runs 2 and 3 performed on October 24-25, 2013. The PM results from Run 1 are not considered to be representative of the PM emission rate under standard operating conditions, but Run 1 was used in the average presented in Table 1-2.

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O_2 and NO_X Emissions / RATA Testing - USEPA Methods 3A and 7E; Performance Specifications 2 and 3

Minute-average data points for O_2, CO_2, and NO_X (dry basis) were collected over a period of 21 minutes for each RATA Reference Method (RM) run. The average result for each RM run was calculated and compared to the average result from the facility CEMs over an identical time interval in order to calculate relative accuracy (RA).

- For O_2, RA is expressed as the average absolute difference between the RM and facility CEMs runs. The final result was below the limit of ±1.0%dv set by PS3.
- For NO_X, RA is expressed as the percent difference between RM and facility CEMs runs. The final result was below the limit of 20% of the RM set by PS2.
- CO_2 data was collected only as supplemental information.

NO_X results from the RATA were converted from units of dry volume-based concentration (ppmdv) to mass-based emission rate units (lb/MMBtu) to demonstrate compliance with permit limits. The final results were expressed as the average of all ten (10) RATA runs. The final results were below the permit limit.

VOC Testing - USEPA Method 25A and Method 18

VOC testing was performed concurrently with the RATA testing. Nine (9) 21-minute M-25 test runs for THC were performed concurrently with three (3) M-18 bag collections for CH_4 and C_2H_6, with each M-18 sample collected over a period of about 60 minutes. The M-18 samples were collected as follows:

- M-18 Run 1: Collected during M-25A Runs 1, 2 and 3
- M-18 Run 2: Collected during M-25A Runs 4, 5 and 6
- M-18 Run 3: Collected during M-25A Runs 7, 8 and 9.

VOC emission rate is normally equivalent to THC emission rate, minus CH_4, and C_2H_6 emission rates (units of lb/hr, Ton/yr, or lb/MMBtu for all constituents).

- For THC, the drift-corrected concentration was below the assumed detection limit of 1% of the instrument calibration span for Runs 1 through 3. The worst-case concentration results used to calculate mass-based emissions for these runs is defined as some number "less than" 1% of the calibration span.
- For CH_4 and C_2H_6, a non-detectable result was obtained for all runs, so no correction was made to the THC results.

Therefore, VOC emissions are equivalent to THC emissions. The final results for M-25A were expressed as the average of nine (9) valid runs and were below the permit limit.

Calculation of Final Results

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

End of Section 1 – Project Overview

RESULTS

Table 2-1:
Coker Heater Stack – FPM, CPM and Total PM_{10} Emissions (USEPA M-5/202)

Run No.		1	2	3	Average
Date (2013)		Oct 24	Oct 24	Oct 25	
Start Time (approx.)		14:21	17:33	07:27	
Stop Time (approx.)		16:33	19:45	09:41	
Process Conditions					
P_t	Fuel gas flow rate (Mscf/day)	2,603	2,645	2,547	**2,598**
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,304	8,304	8,303	**8,304**
H_i	Actual heat input (MMBtu/hr)	120	122	114	**119**
Gas Conditions					
O_2	Oxygen (dry volume %)	6.2	6.3	6.4	**6.3**
CO_2	Carbon dioxide (dry volume %)	8.4	8.3	8.5	**8.4**
T_s	Sample temperature (°F)	359	355	356	**357**
B_w	Actual water vapor in gas (% by volume)	13.6	13.5	13.6	**13.6**
Gas Flow Rate					
Q_a	Volumetric flow rate, actual (acfm)	58,900	60,300	57,600	**58,900**
Q_s	Volumetric flow rate, standard (scfm)	37,100	38,200	36,900	**37,400**
Q_{std}	Volumetric flow rate, dry standard (dscfm)	32,100	33,100	31,900	**32,300**
Q_a	Volumetric flow rate, actual (acf/hr)	3,530,000	3,620,000	3,460,000	**3,540,000**
Q_s	Volumetric flow rate, standard (scf/hr)	2,230,000	2,290,000	2,210,000	**2,250,000**
Q_{std}	Volumetric flow rate, dry standard (dscf/hr)	1,930,000	1,980,000	1,910,000	**1,940,000**
Sampling Data					
V_{mstd}	Volume metered, standard (dscf)	83.44	86.17	83.78	**84.46**
%I	Isokinetic sampling (%)	103.5	103.7	104.6	**103.9**
Laboratory Data					
m_n	Total FPM (g)	0.01534	0.00197	0.00123	
m_{CPM}	Total CPM (g)	0.00382	0.00364	0.00348	
m_{Part}	Total particulate (expressed as PM-10) (g)	0.01916	0.00561	0.00471	
n_{MDL}	Number of non-detectable fractions	N/A	1 out of 2	1 out of 2	
DLC	Detection level classification	ADL	DLL	DLL	
FPM Results					
C_{sd}	Particulate Concentration (lb/dscf)	4.05E-07	5.04E-08	3.24E-08	**1.63E-07**
$E_{lb/hr}$	Particulate Rate (lb/hr)	0.781	0.100	0.062	**0.314**
$E_{T/yr}$	Particulate Rate (Ton/yr)	3.42	0.44	0.27	**1.38**
E_{Fd}	Particulate Rate - F_d-based (lb/MMBtu)	0.0048	0.00060	0.00039	**0.0019**
CPM Results					
C_{sd}	Particulate Concentration (lb/dscf)	1.01E-07	9.32E-08	9.17E-08	**9.53E-08**
$E_{lb/hr}$	Particulate Rate (lb/hr)	0.195	0.185	0.175	**0.185**
$E_{T/yr}$	Particulate Rate (Ton/yr)	0.85	0.81	0.77	**0.81**
E_{Fd}	Particulate Rate - F_d-based (lb/MMBtu)	0.0012	0.0011	0.0011	**0.0011**
Total Particulate (as PM10) Results					
C_{sd}	Particulate Concentration (lb/dscf)	5.06E-07	1.44E-07	1.24E-07	**2.58E-07**
$E_{lb/hr}$	Particulate Rate (lb/hr)	0.975	0.285	0.237	**0.499**
$E_{T/yr}$	Particulate Rate (Ton/yr)	4.27	1.25	1.04	**2.19**
E_{Fd}	Particulate Rate - F_d-based (lb/MMBtu)	0.0060	0.0017	0.0015	**0.0031**

Average includes 3 runs.

Detection level classifications are defined as follows:

ADL = Above Detection Level - all fractions are above detection limit

DLL = Detection Level Limited - some fractions are below detection limit

RESULTS

Table 2-2:
Uncertainty Analysis – FPM, CPM and Total PM_{10} (USEPA M-5/202)

		FPM Results (lb/MMBtu)		CPM Results (lb/MMBtu)		Total PM (as PM10) Results (lb/MMBtu)
Method		**5/202**		**5/202**		**5/202**
Run No.	**1**	0.0048	**1**	0.0012	**1**	0.0060
	2	0.0006	**2**	0.0011	**2**	0.0017
	3	0.0004	**3**	0.0011	**3**	0.0015
SD		0.0025		0.0001		0.0025
AVG		**0.0019**		**0.0011**		**0.0031**
RSD		128.9%		4.6%		82.9%
N		3		3		3
SE		0.0014		0.0000		0.0015
RSE		74.4%		2.7%		47.8%
P		95.0%		95.0%		95.0%
TINV		4.303		4.303		4.303
CI +		0.0081		0.0013		0.0093
AVG		**0.0019**		**0.0011**		**0.0031**
CI -		-0.0042		0.0010		-0.0032
TB +		0.0209		0.0015		0.0225

AVG (average) is the mean value of the runs; N is the number of individual runs.

SD (standard deviation) and RSD (relative standard deviation) are measures of the variability of individual runs.

SE (standard error) and RSE (relative standard error) are measures of the variability of the average of the runs.

P (probability) is the confidence level associated with the two-tailed Student's t-distribution.

TINV (t-value) is the value of the Student's t-distrubution as a function of P (probability) and N-1 (degrees of freedom).

CI (confidence interval) indicates that if the test is conducted again under the same conditions, the average would be expected to fall within the interval (CI- to CI+) about 95% of the time.

TB+ (upper tolerance bound) is the value below which 95% of future runs are expected to fall (assuming testing at the same conditions).

RESULTS

Table 2-3:
Coker Heater Stack – THC, CH_4, C_2H_6, and VOC Emissions (USEPA M-25A/18)

Run No.		1	2	3	Average
Date (2013)		Oct 24	Oct 24	Oct 25	
Start Time (approx.)		16:21	18:19	08:07	
Stop Time (approx.)		18:02	20:01	09:39	
Process Conditions					
P_t	Fuel Gas Flow rate (Mscf/Day)	2,695	2,618	2,566	**2,626**
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,304	8,304	8,303	**8,304**
H_i	Actual heat input (MMBtu/hr)	125	121	115	**120**
Gas Conditions					
O_2	Oxygen (dry volume %)	6.3	6.3	6.4	**6.3**
CO_2	Carbon dioxide (dry volume %)	8.2	8.3	8.2	**8.2**
B_w	Actual water vapor in gas (% by volume)[1]	13.5	13.5	13.6	**13.6**
THC Results					
C_{sd}	Concentration (ppmdv as C_3H_8)	<0.52	<0.52	<0.52	**<0.52**
C_{sd}	Concentration (lb/dscf)	<5.94E-08	<5.94E-08	<5.95E-08	**<5.94E-08**
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	< 0.0007	< 0.0007	< 0.0007	**< 0.0007**
Methane Results					
C_{sd}	Concentration (ppmdv)	<0.23	<0.23	<0.23	**<0.23**
C_{sd}	Concentration (lb/dscf)	<9.58E-09	<9.58E-09	<9.58E-09	**<9.58E-09**
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	< 0.0001	< 0.0001	< 0.0001	**< 0.0001**
Ethane Results					
C_{sd}	Concentration (ppmdv)	<0.17	<0.17	<0.17	**<0.17**
C_{sd}	Concentration (lb/dscf)	<1.33E-08	<1.33E-08	<1.33E-08	**<1.33E-08**
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	< 0.0002	< 0.0002	< 0.0002	**< 0.0002**
VOC Results					
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	<0.0007	<0.0007	<0.0007	**< 0.0007**

Average includes 3 runs.

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[1] Moisture data used for ppmwv to ppmdv correction obtained from nearly-concurrent M-5/202 runs.

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

For methane and ethane, '<' indicates a measured response below the analytical detection limit determined by the laboratory.

RESULTS

Table 2-4:
Coker Heater Stack – NO_X Emissions (USEPA M-7E)

Run No.		1	2	3	4	5	6
Date (2013)		Oct 24	Oct 24	Oct 24	Oct 24	Oct 24	Oct 24
Start Time (approx.)		16:21	17:03	17:41	18:19	18:59	19:40
Stop Time (approx.)		16:42	17:24	18:02	18:40	19:20	20:01
Process Conditions							
P_1	Fuel Gas Flow rate (Mscf/Day)	2,707	2,694	2,683	2,636	2,640	2,577
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,304	8,304	8,304	8,304	8,304	8,304
H_i	Actual heat input (MMBtu/hr)	125	125	124	122	122	119
Gas Conditions							
O_2	Oxygen (dry volume %)	6.2	6.3	6.4	6.2	6.2	6.3
CO_2	Carbon dioxide (dry volume %)	8.3	8.2	8.1	8.3	8.3	8.3
Nitrogen Oxides Results							
C_{sd}	Concentration (ppmdv)	19.7	19.7	19.5	19.9	19.8	19.8
C_{sd}	Concentration (lb/dscf)	2.35E-06	2.35E-06	2.33E-06	2.37E-06	2.36E-06	2.36E-06
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	0.0278	0.0280	0.0280	0.0280	0.0279	0.0282

Table 2-4:
Coker Heater Stack – NO_X Emissions (USEPA M-7E)

Run No.		7	8	9	10	Average
Date (2013)		Oct 25	Oct 25	Oct 25	Oct 25	
Start Time (approx.)		08:07	08:41	09:18	09:54	
Stop Time (approx.)		08:28	09:02	09:39	10:15	
Process Conditions						
P_1	Fuel Gas Flow rate (Mscf/Day)	2,544	2,575	2,580	2,564	**2,620**
F_d	Oxygen-based F-factor (dscf/MMBtu)	8,303	8,303	8,303	8,303	**8,304**
H_i	Actual heat input (MMBtu/hr)	114	115	115	115	**120**
Gas Conditions						
O_2	Oxygen (dry volume %)	6.5	6.3	6.5	6.5	**6.4**
CO_2	Carbon dioxide (dry volume %)	8.2	8.2	8.2	8.2	**8.2**
Nitrogen Oxides Results						
C_{sd}	Concentration (ppmdv)	19.4	19.2	19.1	19.2	**19.5**
C_{sd}	Concentration (lb/dscf)	2.32E-06	2.29E-06	2.28E-06	2.29E-06	**2.33E-06**
E_{Fd}	Emission Rate - F_d-based (lb/MMBtu)	0.0279	0.0273	0.0275	0.0277	**0.0278**

Average includes 10 runs.

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