



AECOM 60544662

Source Test Report
Delayed Coking Unit
Atmospheric Depressurization Vent

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AUG 25 2017

AIR QUALITY DIVISION

Prepared for:

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June 2017

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1.0 Introduction

Marathon Petroleum Company LLC, Michigan Refining Division (MPC Detroit), operates a petroleum refinery in Detroit, Michigan. The MPC Detroit Refinery is a petroleum refinery with the capacity to convert approximately 132,000 barrels of crude oils per calendar day (bbl/cd) into finished products. The EG70-Coker delayed coking unit (DCU) was commissioned in November 2012 and is covered under the Michigan Department of Environmental Quality (MDEQ) Permit 63-08D.

AECOM prepared a Test Plan that described the sampling and analytical methodologies to be employed to measure non-methane, non-ethane volatile organic compounds (NMNE VOCs), hydrogen sulfide (H₂S), and total filterable particulate matter (FPM) mass emission rates from the DCU Vent during a normal venting cycle (see Section 1.2). Molecular weight, moisture (H₂O) concentrations, and DCU Vent exhaust gas flow rate were also measured to develop target compound mass emission rates. The Test Plan was approved by the MDEQ in June 2017.

Because of the unique nature of this intermittent process vent, modifications to existing U.S. EPA-approved reference methods were made to collect accurate and precise data from this source. Due to the extremely high moisture content (greater than 99%) and the high velocity (greater than 200 mph) of the gas stream, the dynamic nature of the gas stream's characteristics, and the variable batch nature of the delayed coking process, AECOM implemented the modified reference methods and alternative quality assurance/quality control (QA/QC) criteria discussed in the Test Plan (see Section 5.0).

This *Source Test Report* presents the results of the 2017 Source Test in the following sections:

- Section 2.0 – Summary of Results;
- Section 3.0 – Sampling and Analytical Procedures;
- Section 4.0 – Calculations; and
- Section 5.0 – Quality Assurance Objectives for Measurement Data.

Report appendices provide copies of raw data, including chain-of-custody forms, sampling logs, raw analytical instrument output, laboratory reports, DCU process data, and sampling equipment calibration forms. General information regarding the testing is summarized in Table 1-1.

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Table 1-1. Source Test Information

Facility Name	Marathon Petroleum Company, Michigan Refining Division
Contact Person(s)	Crystal Davis and Treva Formby
Telephone Number	313-297-6115 and 313-297-6356
Facility Address	1300 South Fort Street, Detroit, Michigan 48217
Types of Process Sampled	DCU Atmospheric Depressurization Vent Gas Stream
Person Responsible for Conducting Source Test	Jesse Rocha
Telephone Number	512-419-5726
Testing Company Name	AECOM Corporation
Testing Company Address	9400 Amberglenn Boulevard Austin, Texas 78729
Person(s) Conducting Source Test	Jesse Rocha Meggen DeLollis Stephen Parvaresh Dave Maxwell Jeff Frady Carl Galloway
Modified U.S. EPA Reference Methods Performed	U.S. EPA Methods 1, 2, 3, 4, 5, 18, and 25A U.S. EPA Other Test Method 12
Dates of Source Testing	June 24 through 26, 2017

1.1 Delayed Coking Unit – Process Description

The EG70 Delayed 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 (Coker Charge Heater) and then into a coke drum. The heat within the coke drum causes cracking reactions to produce the coke, which accumulates in the coke drum, and hydrocarbon vapors, which are carried overhead from the coke drum back to the fractionator. The fractionator produces gasoil, distillate, and naphtha streams which are sent to downstream units for additional processing. The fractionator overhead is directed to the Coker Gas Plant where it is separated into LPG and offgas streams. The LPG and offgas streams are sent to downstream units for additional processing.

Petroleum (pet) coke eventually fills the coke drum; subsequently the drum is isolated, purged of hydrocarbon vapors, cooled, and opened. A typical Delayed Coker uses at least two coking drums so that one can be filled while the other is being de-coked.

At the end of each coke drum filling cycle, the full coke drum is switched off-line, stripped with steam to remove residual hydrocarbons, flooded with quench water, and depressured. Coke is cut from the drum with high pressure water jets.

The MPC Detroit coker includes two redundant vapor recovery compressors. The compressors allow the coke drums to be vented to atmosphere only after the drum pressure decreases to two pounds per square inch gauge (psig).

1.2 Source Test Objectives

The objective of the source test is to quantify emissions from the DCU vent. The sampling and analytical methods employed during the source test and any modifications to the EPA-approved reference methods (RMs) are presented in subsequent sub-sections.

The DCU vent gas stream was sampled pursuant to the Test Plan using direct source testing methodologies to quantify the emissions of the following target compounds:

- NMNE VOC;
- Methane;
- Ethane;
- Hydrogen sulfide (H₂S); and
- Total particulate matter (Total PM).

Table 1-2 presents the sampling durations for each target compound during the batch cycle of the DCU vent.

Valid gas samples were collected during three (3) separate venting cycles of the DCU (Runs 1, 2, and 3).

1.3 Source Test Strategy

A venting cycle is defined in the Test Plan as the period of time between the activation of the vent (i.e., opening) and the optimal depressurization of a coke drum to atmosphere that is necessary before the draining and coke-cutting cycles can begin.

Table 1-2 presents the test run durations of each modified sampling system during a given test run. Modified sampling methods are described in detail in Section 3.0. AECOM began collecting all gas samples within one (1) minute of vent activation during each test run unless otherwise noted. Gas samples were collected until the coke drum reached optimal depressurization, for as long as the sampling equipment remained operable within acceptable performance ranges, or until health and safety limitations were encountered.

Section 2.0 of this report presents the averages of target compound mass emission rates measured during each venting condition.

Table 1-2. Sampling Train Durations

Run No.	Drum	Date	Time	Sampling Duration (min)	Sampling Method	Selected Sampling Train & CEMS Analyzer
1	A	6/24/17	12:58 – 13:19	21	U.S. EPA Method 5	Train 1
	A	6/24/17	12:58 – 13:19	21	U.S. EPA Methods 18/25A/OTM 12	THC 2
2	B	6/25/17	08:14 – 08:39	25	U.S. EPA Method 5	Train 1
	B	6/25/17	08:14 – 08:39	25	U.S. EPA Methods 18/25A/OTM 12	THC 1
3	A	6/26/17	04:20 – 04:36	16	U.S. EPA Method 5	Train 2
	A	6/26/17	04:20 – 04:36	16	U.S. EPA Methods 18/25A/OTM 12	THC 1

1.4 Quality Assurance Summary

Any sampling and/or analytical QA/QC issues associated with the data obtained through the 2017 Source Test are described in Section 5.0. Table 1-3 presents QA summaries for each of the modified U.S. EPA reference methods performed on the DCU.

A review of the data quality associated with the measurements performed during all runs indicates that these data are supportable and usable for the purpose intended.

Table 1-3. Quality Assurance Summary

Parameter	Deviations from the Test Plan and Quality Assurance/Quality Control Issues
Sampling Points, Velocity and Volumetric Flow Rate, Dry Gas Molecular Weight, and Moisture Concentration	None
Total Particulate Matter Determination	The Test Plan describes a single PM sampling train per vent cycle. During the 2017 Source Test, two PM sampling trains (1 and 2 for each run) were collected simultaneously to minimize the potential for collecting an incomplete set of data for a given vent cycle. The replicate sample that resulted in the greater sample volume was chosen for analysis, and the other sample was archived. As a result, the reported PM results from Runs 1 and 2 were derived using Train 1 and Run 3 was derived using sample Train 2.
Methane and Ethane Concentrations and Dilution Sampling System	None
Hydrogen Sulfide Concentrations and Dilution Sampling System	None
Total Hydrocarbon Concentration and Dilution Sampling System	<p>Near the end of Run 1, the data acquisition signal was lost for THC 1 and THC ND. As a result, final quality activities were not recorded. The values measured on THC 1 were not reported for this run. The results and quality check for THC ND, used only for the determination of dilution factor, were recorded by hand at the end of the run.</p> <p>The span drift for THC 2 on Run 1 failed with a drift check of 7.6% (limit is 3%).</p>

2.0 Summary of Results

This section presents a summary of process operations during the Source Test as well as selected methane, ethane, hydrogen sulfide, NMNE VOC, and PM emissions data. Table 2-1 presents the summary of results for this test program.

Table 2-1. Summary of Results

Run No.	Date	Methane Mass Emission Rate (lbs/cycle)	Ethane Mass Emission Rate (lbs/cycle)	H ₂ S Mass Emission Rate (lbs/cycle)	NMNE VOC Mass Emission Rate (lbs/cycle)	Particulate Matter Mass Emission Rate (lbs/cycle)
1	6/24/17	8.72	1.54	0.739	0*	0.0196
2	6/25/17	37.6	6.03	3.14	0*	<0.025
3	6/26/17	14.4	2.24	1.17	0*	<0.019

*Negative number represented by 0

2.1 DCU Process Operations

The DCU was operated at conditions reflective of “normal” unit operations during the source test. The DCU was vented to atmosphere after the internal pressure of the coke drum reached approximately 2 psig. This venting pressure is consistent with the normal operation of the DCU.

Sampling durations were determined using the venting cycle start and end times recorded by AECOM scientists. The venting cycle start times corresponded to the initial differential pressure increase within the vent duct, as reported by sampling instrumentation, rounded to the nearest whole minute. In many cases, the venting cycle end times corresponded to the measurement of zero (0) differential pressure in the vent pipe using U.S. EPA Method 2, “*Determination of Stack Gas Velocity and Flow Rate from Stationary Sources (Type-S Pitot Tube)*.”

2.2 Data Reduction Approach

Mass emission rates are typically expressed using an industry standard of mass per unit time, such as pounds per hour (lbs/hr), by relating the average concentration of a target compound to the average volumetric flow rate of a gas stream through a stack or vent. However, the use of a simple average is inappropriate for developing an emissions profile for the intermittent and dynamic characteristics of the atmospheric depressurization vent source, so the duration and profile of each complete venting cycle varied according to the batch process.

The data reduction approach used in this report integrates target compound mass emission rates as pounds per minute (lbs/min) throughout the complete venting cycle, starting at the point of vent activation and ending at the point of optimal depressurization of the coke drum. Total mass emission rates are expressed in this report as mass per batch cycle (lbs/cycle).

2.3 Results for Vent Gas Volumetric Flow Rate

Vent gas volumetric flow rate was measured according to modified U.S. EPA Methods 2, “*Determination of Stack Gas Velocity and Volumetric Flow Rate*,” 3, “*Gas Analysis for the Determination of Dry Molecular Weight*,” and 4, “*Determination of Moisture Content in Stack Gases*.” These methods were performed in conjunction with each modified U.S. EPA Method 5 sampling train. Table 2-2 presents average volumetric flow rate and other operating data associated with the modified sampling train.

It was not practicable to measure the oxygen or carbon dioxide concentrations in the sample gas using U.S. EPA Method 3 due to the low dry gas percentage (less than 2% of the total). The molecular weight of the dry fraction of the DCU gas was therefore assumed to be equal to methane (16.0 g/g-mol), the most abundant compound detected in the vent gas stream after water. The estimated dry gas molecular weight had an insignificant impact on the calculation of wet gas molecular weight as the average moisture concentration was slightly in excess of 99%.

Table 2-2. Isokinetic Sampling Data

Run No.	Analytical Parameter	Average Vent Temperature (°F)	Velocity (ft/sec)	Vent Gas Moisture (%)	Avg Flow Rate (acfm)	Avg Flow Rate (dscfm)	Volume at Meter (dscf)	Isokinetic Sampling Rate (%)
1 ^a	Particulate Matter	216	223	99.45	10,500	43.3	0.362	74.2
2 ^a	Particulate Matter	226	300	99.16	14,200	88.9	0.705	59.0
3 ^b	Particulate Matter	221	374	99.20	17,600	108	0.402	44.1

^a Results from PM Train 1

^b Results from PM Train 2

2.4 Results for Methane, Ethane, and Hydrogen Sulfide Emissions

Methane, ethane, and hydrogen sulfide concentrations were measured according to modified U.S. EPA Method 18, "*Measurement of Gaseous Organic Compound Emissions by Gas Chromatography*" and the dilution sampling system procedures described in U.S. EPA Other Test Method 12, "*Protocol for the Source Testing, Analysis, and Reporting of VOC Emissions from Hot Mix Asphalt Plant Dryers.*"

2.4.1 Results for Methane and Ethane

Bag samples were collected from the same dilution sampling system used for the measurement of total hydrocarbon (THC) concentrations by modified U.S. EPA Method 25A, "*Determination of Total Gaseous Organic Concentrations Using a Flame Ionization Analyzer,*" and modified Other Test Method 12. An integrated bag sample of vent gas was collected during a venting cycle and analyzed for methane and ethane by gas chromatograph with flame ionization detector (GC/FID) and for hydrogen sulfide (H₂S) by a gas chromatograph with flame photometric detector (GC/FPD). All analyses were performed in triplicate. Concentration results are presented as parts per million by volume, wet basis (ppmvw).

Raw GC/FID results were multiplied by the dilution ratios (DR) developed on a test run-specific basis through the operation of the dilution sampling system (see Section 2.5).

Based on past practices, AECOM assumed methane/propane and ethane/propane equivalency factors to be 1/3 and 2/3, respectively. These factors were multiplied by the methane and ethane concentrations (quantified by GC/FID), respectively, to determine methane/propane equivalent and ethane/propane equivalent concentrations. Methane/propane equivalent and ethane/propane equivalent concentrations were then subtracted from average THC concentrations to develop average NMNE VOC concentrations during a given sampling interval.

The methane and ethane concentration data from each test run are presented in Table 2-3. Methane/propane and ethane/propane equivalent concentrations are presented in Table 2-4. Raw data associated with the operation of the GC/FID, including all chromatograms, are included in Appendix 2-1.

Methane and ethane mass emission rates are presented in Tables 2-5 and 2-6, respectively. Section 2.2 discusses the development of target compound mass emission rates. The individual bag results, as well as the time-weighted average are presented in Appendix 2-1.

Table 2-3. Concentration Results for Methane and Ethane

Run No.	Date	Sampling Interval (hh:mm)	Methane Conc. Undiluted (ppmvw)	Ethane Conc. Diluted (ppmvw)	Average Dilution Ratio	Methane Conc. Corrected (ppmvw)	Ethane Conc. Corrected (ppmvw)
1	6/24/17	12:58 – 13:19	46.9	4.15	29.3	1,370	121
2	6/25/17	08:14 – 08:39	148	12.7	23.2	3,440	294
3	6/26/17	04:20 – 04:36	60.3	5.00	26.6	1,600	133

Table 2-4. Methane/Propane and Ethane/Propane Equivalent Concentrations

Run No.	Date	Sampling Interval (hh:mm)	Methane Conc. (ppmvw)	Methane/Propane Equivalent Conc. (ppmvw)	Ethane Conc. (ppmvw)	Ethane/Propane Equivalent Conc. (ppmvw)
1	6/24/16	12:58 – 13:19	1,370	458	121	80.9
2	6/25/16	08:14 – 08:39	3,440	1,150	294	196
3	6/26/16	04:20 – 04:36	1,600	534	133	88.6

Table 2-5. Mass Emission Rate Results for Methane

Run No.	Date	Sampling Interval (hh:mm)	Sampling Duration (min)	Wet Methane Conc. (ppmvw)	Vent Gas Moisture (%)	Dry Methane Conc. (ppmvd)	Volumetric Flow Rate (dscfm)	Methane Mass Emission Rate (lbs/min)	Methane Mass Emission Rate (lbs/cycle)
1	6/24/17	12:58 – 13:19	21	1,370	99.45	252,000	43.3	0.453	9.51
2	6/25/17	08:14 – 08:39	25	3,440	99.16	407,000	88.9	1.50	37.6
3	6/26/17	04:20 – 04:36	16	1,600	99.20	200,000	108	0.899	14.4

Table 2-6. Mass Emission Rate Results for Ethane

Run No.	Date	Sampling Interval (hh:mm)	Sampling Duration (min)	Wet Ethane Conc. (ppmvw)	Vent Gas Moisture (%)	Dry Ethane Conc. (ppmvd)	Volumetric Flow Rate (dscfm)	Ethane Mass Emission Rate (lbs/min)	Ethane Mass Emission Rate (lbs/cycle)
1	6/24/17	12:58 – 13:19	21	121	99.45	22,300	43.3	0.0734	1.54
2	6/25/17	08:14 – 08:39	25	294	99.16	34,800	88.9	0.241	6.03
3	6/26/17	04:20 – 04:36	16	133	99.20	16,600	108	0.140	2.24

2.4.2 Results for Hydrogen Sulfide

Bag samples were collected from the same dilution sampling system used for the measurement of total hydrocarbon (THC) concentrations by modified U.S. EPA Method 25A, and modified U.S. EPA Other Test Method 12. As discussed earlier, one integrated bag sample of vent gas was collected during a venting cycle. The bag was analyzed for methane and ethane by gas chromatograph with flame ionization detector (GC/FID) and for hydrogen sulfide (H₂S) by a gas chromatograph with flame photometric detector (GC/FPD). All analyses were performed in triplicate. Concentration results are presented as parts per million by volume, wet basis (ppmvw).

Raw GC/FPD results were multiplied by the dilution ratios (DR) developed on a test run-specific basis through the operation of the dilution sampling system (see Section 2.5).

The hydrogen sulfide concentration data from each test run are presented in Table 2-7. Raw data associated with the operation of the GC/FPD, including all chromatograms, are included in Appendix 2-2.

Hydrogen sulfide mass emission rates are presented in Table 2-8. Section 2.2 discusses the development of target compound mass emission rates.

Table 2-7. Concentration Results for Hydrogen Sulfide

Run No.	Date	Sampling Interval (hh:mm)	Hydrogen Sulfide Conc. Diluted (ppmvw)	Average Dilution Ratio	Hydrogen Sulfide Conc. Corrected (ppmvw)
1	6/24/17	12:58 – 13:19	1.71	29.3	50.2
2	6/25/17	08:14 – 08:39	5.83	23.2	135
3	6/26/17	04:20 – 04:36	2.30	26.6	61.2

Table 2-8. Mass Emission Rate Results for Hydrogen Sulfide (H₂S)

Run No.	Date	Sampling Interval (hh:mm)	Sampling Duration (min)	Wet H ₂ S Conc. (ppmvw)	Vent Gas Moisture (%)	Dry H ₂ S Conc. (ppmvd)	Volumetric Flow Rate (dscfm)	H ₂ S Mass Emission Rate (lbs/min)	H ₂ S Mass Emission Rate (lbs/cycle)
1	06/24/17	12:58 – 13:19	21	50.2	99.45	9,200	43.3	0.0352	0.739
2	06/25/17	08:14 – 08:39	25	135	99.16	16,000	88.9	0.126	3.14
3	06/26/17	04:20 – 04:36	16	61.2	99.20	7,630	108	0.0729	1.17

2.5 Results for NMNE Volatile Organic Compounds (NMNE VOC)

The total hydrocarbon (THC) concentration in the DCU gas stream was measured conservatively during the 2017 Source Test as THC using FID-based portable gas analyzers. THC concentrations were measured according to modified U.S. EPA Method 25A and the dilution sampling system procedures described in U.S. EPA Other Test Method 12.

Samples of the DCU gas stream were extracted using the same dilution sampling system used to collect methane, ethane, and hydrogen sulfide samples by modified U.S. EPA Method 18 (see Section 2.4). The diluted sample gas was routed to two (2) gas analyzers that measured THC concentrations as parts per million by volume, wet basis (ppmvw), continuously during the venting cycle. Standards of propane in a balance of nitrogen were used to calibrate two (2) THC analyzers at three (3) different ranges (0-3,500, 0-10,000, and 0-35,000 ppmvw). Nitrogen was also used as the diluent with the dilution sampling system. The dilution ratio developed on a test run-specific basis was multiplied by the average THC concentration result per sample run.

Based on prior experience and as presented in the Test Plan, AECOM assumed methane/propane and ethane/propane equivalency factors to be 1/3 and 2/3, respectively. Methane/propane equivalent and ethane/propane equivalent concentrations were subtracted from THC concentrations to develop NMNE VOC concentrations during a given sample run. Section 2.4.1 describes this calculation process in detail.

THC and NMNE VOC concentrations data for each test run are presented in Table 2-9. Raw data associated with the operation of the THC analyzers is included in Appendix 2-3. NMNE VOC (as propane) mass emission rates are presented in Table 2-10. Section 2.2 discusses the development of target compound mass emission rates.

Table 2-9. Concentration Results for NMNE VOC, as Propane

Run No.	Date	Sampling Interval (hh:mm)	THC Conc. (ppmvw, as propane)	Methane/Propane Equivalent Conc. (ppmvw)	Ethane/Propane Equivalent Conc. (ppmvw)	NMNE VOC Conc. (ppmvw, as propane)
1	6/24/17	12:58 – 13:19	508	458	80.9	0*
2	6/25/17	08:14 – 08:39	1,280	1,150	196	0*
3	6/26/17	04:20 – 04:36	521	534	88.6	0*

* Negative number represented by 0

Table 2-10. Mass Emission Rate Results for NMNE VOC, as Propane

Run No.	Date	Sampling Interval (hh:mm)	Sampling Duration (min)	Wet NMNE VOC Conc. (ppmvw, as propane)	Vent Gas Moisture (%)	Dry NMNE VOC Conc. (ppmvd)	Volumetric Flow Rate (dscfm)	NMNE VOC Mass Emission Rate (lbs/min)	NMNE VOC Mass Emission Rate (lbs/cycle)
1	6/24/17	12:58 – 13:19	21	0*	99.45	0*	43.3	0*	0*
2	6/25/17	08:14 – 08:39	25	0*	99.16	0*	88.9	0*	0*
3	6/26/17	04:20 – 04:36	16	0*	99.20	0*	108	0*	0*

* Negative number represented by 0

2.6 Results for Particulate Matter

Total particulate matter was measured according to modified U.S. EPA Method 5, “*Determination of Particulate Matter Emissions from Stationary Sources*.” Particulate matter samples were extracted from the DCU gas stream isokinetically.

Following each test run, the PM samples were recovered separately into the following components:

- Front-half (nozzle, probe liner, and front-half of the filter holder) rinse with acetone; and
- Quartz-fiber filter.

The minimum dry gas sample volumes typically associated with sampling for total PM were not obtained due to the limited sampling durations, the minimal dry gas fraction of the vent gas stream (less than 2%), and the large volume of water that was condensed in a relatively short period of time. As an alternative, the target wet gas sample volume of greater than 0.25 cubic feet (corrected to standard conditions) was used for this source testing project.

Table 2-2 presents a summary of modified U.S. EPA Method 5 sampling train operating data such as dry and wet gas volumes collected and isokinetic sampling rates achieved. Particulate mass loadings are presented in Table 2-11. The full laboratory report detailing the analyses of vent gas samples for particulate loading is presented in Appendix 2-4.

Total PM mass emission rates are also presented in Table 2-11. Section 2.2 discusses the development of target compound mass emission rates.

Table 2-11. Mass Loading and Mass Emission Rate Results for Total PM

	Run 1 ^a	Run 2 ^a	Run 3 ^b	Average
Date	6/24/2017	6/25/2017	6/26/2017	-
Time	12:58 – 13:19	08:14 – 08:39	04:20 – 04:36	-
Duration (mins)	21	25	16	-
Volume Collected (dscf)	0.362	0.705	0.402	-
Flow Rate (dscfm)	43	89	108	-
Mass Found (mg)				
PM - Filter	0.930	<0.50	<0.50	-
PM - PNR	2.62	3.13	1.51	-
Particulate Matter - Total	3.55	<3.63	<2.01	-
Stack Gas Concentration (mg/dscm)				
Particulate Matter	346	<180	<180	<235
Mass Emission Rate (lb/min)				
Particulate Matter	0.000935	<0.0010	<0.0012	<0.0010
Mass Emission Rate (lb/cycle)				
Particulate Matter	0.0196	<0.025	<0.019	<0.021

^a Results from PM Train 1

^b Results from PM Train 2