



Emissions Test Report

for the
**EG70-Coker Delayed Coking Unit
Depressurization Vent**

at the
Marathon Detroit Refinery

in
Detroit, MI

subject to
**Permit No. MI-ROP-A9831-2012c
Title 40 CFR Part 60, Appendix F**

prepared for



**Marathon
Petroleum Company LP**

**Test Date: May 14-16, 2024
Erthwrks Project No. 9565.1.B4**



Endorsement Page

This report was developed in accordance with the requirements designated in the applicable regulatory permit(s) and or regulatory rules. To the best of my knowledge the techniques, instrumentation, and calculations presented in this report will serve to accurately and efficiently detail the results of the test campaign requirements.

Erthwrks, Inc.

Name: Jason Dunn

Title: QAQC Manager

Signature: 

This report has been reviewed for accuracy and completeness. The actions presented in this report are, to the best of my knowledge, an accurate representation of the results and findings of the test campaign. Erthwrks, Inc. operates in conformance with the requirements on ASTM D7036-04 Standard Practice for Competence of Air Emission Testing Bodies and is accredited as such by the Stack Testing Accreditation Council (STAC) and the American Association for Laboratory Accreditation (A2LA).

Erthwrks, Inc.

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1.0 INTRODUCTION

1.1 Identification, location and dates of tests

Erthwrks, Inc. was contracted to conduct emission testing on the EG70-Coker Delayed Coking Unit Depressurization Vent in operation at the Marathon Detroit Refinery, located in Detroit Michigan. The testing program was conducted on May 14-16, 2024.

1.2 Purpose of Testing

The purpose of this project is to determine the mass emission rate of volatile organic compounds (VOCs), filterable particulate matter (PM), and hydrogen sulfide (H₂S). VOCs were measured as total hydrocarbons (THC) and methane and ethane was subtracted to report non-methane, non-ethane (NMNE) VOCs. Emissions are reported on a pound per vent cycle (lb/cycle).

1.3 Contact Information

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2.0 SUMMARY OF RESULTS

Table 1: Coker Drum Vents Emissions Test Results

Pollutant Measured	Test Method	Test Result
PM	EPA Method 5	0.02 lb/cycle
H ₂ S	EPA Method 15	0.20 lb/cycle
VOC	EPA Method 18/25A	0.00 lb/cycle*

*Negative VOC reported as zero.

3.0 SOURCE DESCRIPTION

3.1 Description of the process

A 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 gas oil, 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 liquefied petroleum gas (LPG) and off-gas streams. The LPG and off-gas streams are sent to downstream units for additional processing.

Once a coke drum is filled with coke, the drum is isolated, purged of hydrocarbon vapors, cooled, and opened. 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 depressurized. Coke is cut from the drum with high pressure water jets and collected in pits at the base of the coke drums. A typical Delayed Coker uses at least two coking drums so that one can be filling while the other is being de-coked.

The MPC coker includes two redundant vapor recovery compressors. The compressors allow the coke drums to be vented to atmosphere only after the drum pressure has decreased to 2 pounds per square inch gauge (psig). Each venting cycle lasts for approximately 20 minutes.

During emissions testing, the process operated according to standard procedure and at maximum routine operating conditions. During each test run, the following information was recorded by MPC personnel:

- Feed rate, BPD
- Coke production, tons
- Duration of batch cycle, hr
- Duration of the total operating cycle, hr
- Duration of steam to fractionator per batch cycle, hr
- Duration of steam to blowdown quench tower per batch cycle, hr
- Duration of quenching per batch cycle, hr
- Duration of atmospheric venting per batch, hr
- Duration of soaking per batch cycle, hr
- Duration of quench water draining per cycle, hr
- Duration of coke-cutting per batch, hr
- Internal temperature and pressure of the Coke drum during the quenching, venting, soaking, draining and coke-cutting operating cycles, °F and psig
- Outage per batch cycle, ft.

4.0 SAMPLING AND ANALYTICAL PROCEDURES

The sampling occurred during venting cycles when the coke drum released through identical vents to the atmosphere. The pressurized steam that is released from the coke drum is >99% moisture by volume, which requires the use of alternative/modified EPA methodology. This venting process occurs for approximately 20 minutes every 18-24 hours.

Based on the 2019 source test, an assigned molecular weight of 16.0 lb/lb-mol was used to calculate the vent gas velocity because methane is the predominant component of the dry gas fraction.

For this testing program, and in accordance with previous testing events, the two coke drum vents are assumed to be identical emissions. Therefore, three total test runs were conducted during three separate venting events. This resulted in two testing runs (Runs 1 and 2) being conducted on Vent A and one test run (Run 3) was conducted on Vent B. The results of the three runs were averaged together and the result is presented in Table 1 of this report.

4.1 Sampling Location – Modified Method 1 (single point)

MPC Detroit installed multiple sampling ports on both the A Coke Drum Vent and the B Coke Drum Vent to allow sequential sampling of both emission sources during the source test. The A and B Vents are identical in design and have diameters of twelve inches. The ports were installed on the same measurement plane of each DCU vent. The sampling ports are situated roughly 12” apart from one another along the horizontal run of each vent pipe.

One port was used for H₂S and THC sampling. A dilution sampling system operated according to guidance in EPA OTM- 12 was used to sample the gas stream for hydrogen sulfide, methane, ethane, total VOCs, and NMNE VOCs according to modified EPA Methods 15, 18 and 25A.

Each sampling port is located in compliance with EPA Method 1, “Sample and Velocity Traverses for Stationary Sources.” Due to health and safety concerns of the pressurized steam in the vent, EPA Method 1 was modified to allow for the use of a single traverse point at the center of the vent pipe for all test samples. This is consistent with previous testing programs including ICR test programs.

4.2 Velocity – Method 2 Modified

An S-type pitot was used to record velocity of the gas in the vent at a single point in the center 10% area of the vent. Due to the high level of moisture in the vent gas, compressed dry air was used periodically to flush moisture from the sampling apparatus.

The pressure and velocity of the vent gas stream changes greatly throughout the test period. It is expected to encounter differential pressure (ΔP) readings varying between ~ 0.25 and ~ 25.8 inH₂O. Static pressure varied between ~ 0.3 and ~ 6.0 inH₂O. Due to these variances the field technician logged a recording every 2 minutes throughout the venting process. These measurements included static pressure, ΔP , and stack temperature.

4.3 Filterable Particulate Matter – Method 5 Modified

EPA Method 5 was used to measure FPM of the vent gas from each vent. Modifications to Method 5 are necessary to address the high moisture content in the vent gas sample. The sampling probe and filter temperature were increased to $300 \pm 25^\circ\text{F}$ to assist in the prevention of condensation in the sampling equipment. In addition, the FPM sample was not collected isokinetically. The sample was collected at a low and constant rate to support sampling equipment operating temperature. It is expected that the total volume of gas collected by each Method 5 train is approximately 0.5 cubic feet (~ 14 liters).

The next section discusses why a small volume of gas was collected and why isokinetic sampling is not possible on this type of source.

4.3.1 Isokinetic Sampling Waiver – Method 5 Modified

The measurement of particulate matter loading according to EPA Method 5 requires that the sampling be within $\pm 10\%$ of 100% isokinetic. As moisture concentrations in the sample gas increase, errors in the assumed moisture fraction have a greater impact on the sampler’s ability to maintain an isokinetic sampling rate within $\pm 10\%$. For example, if a vent gas stream is assumed to be 99% moisture during sampling and the result calculated at the conclusion of sampling indicates that the moisture fraction in the vent gas stream was actually 98%, then the sampling rate will be 50% lower than 100% isokinetic sampling (e.g., 50% isokinetic) which does not meet the EPA Method 5 criterion.

Isokinetic sampling systems that provide real-time moisture concentration data during a sampling period and are suitable for use on a DCU vent source are not commercially available. Erthwrks sampling personnel had no method of accurately measuring the moisture concentration of the DCU Vent gas stream during the sampling period and therefore was not able to make any meaningful adjustment to the sampling train operation during the sampling period. The moisture concentration of the DCU vent gas stream would have to be guessed correctly within approximately $\pm 0.2\%$ moisture prior to the test run to meet EPA's criteria of $100 \pm 10\%$ isokinetic sampling.

Generally, isokinetic sampling rates above 110% have been suggested to bias pollutant concentration results low because the gas velocity at the sampling train nozzle orifice exceeds the velocity of the gas stream and a less than representative number of small particles, aerosols, or droplets, which should follow the gas flow pattern into the nozzle orifice, are collected in the sampling train.

Isokinetic sampling train operating parameters such as the sampling nozzle orifice size were determined during preliminary project activities to achieve isokinetic sampling percentages $\leq 110\%$ during the source test. An isokinetic rate of $\leq 110\%$ can be ensured by using a nozzle with a large enough orifice diameter such that the velocity of the sample gas through the nozzle orifice will always be less than the velocity of the vent gas stream. This criterion is based upon guidance in Attachment A to Rule 1189, "Source Test Protocol for VOC Emissions from High Moisture Hydrogen Plant Process Vents," developed by California's South Coast Air Quality Management District (SCAQMD).

4.4 Total Hydrocarbon Measurement – EPA Method 25A

The determination of the VOC concentration was determined by measuring total hydrocarbon compound (THC) and followed all QAQC procedures as specified in the US EPA 40 CFR 60 Appendix A, Method 25A with the exception of the EGLE requirement to adjust the final results for drift using Equation 7E-5B. The calibration error (CE) test was conducted following the procedures specified in EPA Method 25A §8.4. In accordance with this requirement, a four-point analyzer calibration error test was conducted prior to exhaust sampling. This CE test was conducted by introducing the zero, low, mid, and high-level calibration gases (as defined by EPA Method 25A §7.1.2-5) and the response recorded. The results of the CE test are acceptable if the results for the low and mid-level calibration gasses are within $\pm 5.0\%$ of the predicted responses as defined by the linear curve from the zero and high-level results. The sample system response time was also recorded at this time in accordance with EPA Method 25A §8.5.

Immediately following the completion of each test run, the drift determination was conducted to validate the test data in accordance with EPA Method 25A §8.6.2. The test data is valid if the calculated drift is within $\pm 3.0\%$ of the span value (EPA Method 25A §13.1.2).

4.4.1 VOC – Bag Sampling and Dilution System Operation

In order to reduce the moisture in the sample stream, OTM-12 was utilized to dilute the sample stream. Samples of the DCU vent gas stream were extracted continuously using a sampling system equipped with a glass critical orifice and diluted with high-purity nitrogen. The actual dilution ratio was measured by direct calibration and calibration of the total hydrocarbon analyzer through the dilution system. A heated particulate filter was placed immediately downstream of the inlet to the stainless steel dilution sampling probe tip and upstream of the glass critical orifice. The diluted sample gas passed from the glass critical orifice through a heated Teflon sampling line and into a Tedlar bag for methane, ethane, and H₂S sample collection and analysis.

An EPM Dilution Probe and Apex Instruments Flow Panel was used as the dilution sampling system. A stable dilution air pressure and critical orifice vacuum greater than 14.7” Hg (or manufacturer’s specification) was maintained throughout the sampling period for all test runs. It is important to note that with an anticipated DR of 17:1 during each test run, the moisture concentrations in the bag samples were <10%. All applicable dilution sampling system components were heated to approximately 300°F, and the dew point of the sample gas was maintained lower than the operating temperature of the GC/FID and GC/FPD analyzers to minimize sample loss or interferences due to moisture. The dilution sampling system was leak checked before the test run and placed at a single sampling point within the 10% centroid of the DCU Vent cross section. However, since target compound concentrations were expected to be highest during the first few minutes of the venting cycle, the dilution sampling system was not flushed with sample gas prior to beginning collection in the sample bag.

Integrated bag samples were collected once every venting cycle. The bag samples (~6L) were transported from the DCU vent sampling location to a mobile laboratory for analysis by gas chromatography (GC). Methane and ethane concentrations were measured using a GC/FID (flame ionization detector). A GC/FPD (flame photometric detector) was used to quantify the concentration of hydrogen sulfide. All GC sample analyses were performed within 72 hours of sample collection.

Attachment A
Detailed Results of Emission Test

Summary of Results

Client: Marathon Petroleum Company
Facility: Detroit Refinery
Unit ID: Vent A (Run 1-2) Vent B (Run 3)

Run Information				
Run Number	Run 1	Run 2	Run 3	
Date	5/14/2024	5/16/2024	5/16/2024	
Run Start Time	22:09	6:21	21:12	
Run End Time	22:30	6:56	21:30	
Cycle Time (minutes)	20	35	18	
Stack Gas Flow Rate (Method 1-4)				Averages
Moisture Content (Bws)	0.996	0.995	0.992	0.994
Stack Gas Flow Rate, Q, (dscfh)	2669.42	2310.11	3661.67	2880.40
Diluted Emission Concentrations				
THC, as propane (ppmvw)	65.99	70.15	39.57	58.57
CH4, as propane (ppmvw)	59.63	68.89	40.19	56.24
C2H6, as propane (ppmvw)	10.68	8.85	3.91	7.81
H ₂ S (ppmvw)	0.52	0.51	0.52	0.52
Emission Concentrations		Dilution Ratio:		16.80
THC, as propane (ppmvw)	1108.74	1178.63	664.84	984.07
CH4, as propane (ppmvw)	1001.88	1157.46	675.26	944.87
C2H6, as propane (ppmvw)	179.44	148.69	65.69	131.28
H ₂ S (ppmvw)	8.74	8.57	8.74	8.68
Emission Concentrations				
THC, as propane (ppmvd)	266,040	282,811	159,527	236,126
CH4, as propane (ppmvd)	240,399	277,731	162,027	226,719
C2H6, as propane (ppmvd)	43,057	35,679	15,763	31,500
H ₂ S (ppmvd)	2,096	2,056	2,096	2,083
Emission Rates (lb/scf)				
THC (lb/scf)	3.04E-02	3.24E-02	1.83E-02	2.702E-02
CH4 (lb/scf)	2.75E-02	3.18E-02	1.85E-02	2.595E-02
C2H6 (lb/scf)	4.93E-03	4.08E-03	1.80E-03	3.605E-03
H ₂ S (lb/scf)	1.85E-04	1.82E-04	1.85E-04	1.842E-04
Emission Rates (lb/hr)				
THC (lb/hr)	81.27	74.77	66.85	74.29
CH4 (lb/hr)	73.44	73.42	67.90	71.59
C2H6 (lb/hr)	13.15	9.43	6.61	9.73
VOC (NMNEHC) (lb/hr)	-5.32	-8.09	-7.65	-7.02
H ₂ S (lb/hr)	0.49	0.42	0.68	0.53
Emission Rates (lb/cycle)				
VOC (NMNEHC) (lb/cycle)	-1.77	-4.72	-2.30	-2.93
H ₂ S (lb/cycle)	0.16	0.25	0.20	0.20

*VOC is defined as total hydrocarbons in pounds per hour, minus methane and ethane (NMNEHC)

Erthwrks Particulate Matter Summary of Results

Client: Marathon Petroleum
Project: 9565.1.B4
Facility: Detroit Refinery
Unit ID: Coker Vent Drum A & B

Run Designation						
Run Number		1	2	3	Average	
Date		5/14/2024	5/16/2024	5/16/2024		mm:dd:yyyy
Run Start Time		22:09	6:21	21:12		hh:mm
Run End Time		22:30	6:56	21:30		hh:mm

Stack Gas Composition						
Stack Moisture Content	(B_{ws})	0.996	0.995	0.992	0.99	
Stack Dry Molecular Weight	(M_d)	16.00	16.00	16.00	16.00	lb/lb-mole
Stack Wet Molecular Weight	(M_s)	17.99	17.99	17.98	17.99	lb/lb-mole

Stack Gas Volumetric Flow Calculations						
Absolute Stack Pressure	(P_s)	29.78	28.48	29.51	29.26	in Hg
Average Stack Temperature	(t_s) _{avg}	675.6	690.2	703.3	689.7	°R
Average Square Root of ΔP 's	($\Delta p^{1/2}$) _{avg}	4.2982	3.0531	3.2436	3.5316	%
Average Stack Gas Velocity	(v_s)	20797.20	15266.71	16089.92	17384.61	ft/min
Average Stack Gas Flow	(Q_{gw})	13,725	10,075	10,619	11,473	acfm
Wet Standard Stack Flow Rate	(Q_{sw})	640520.41	440284.22	471665.75	517490.13	wscfh
Dry Standard Stack Flow Rate	(Q_{sd})	2669.42	2310.11	3661.67	2880.40	dscfh

Particulate Matter Emission Rate Calculations						
Mass of Filterable PM (M.5)	mg	3.8	1.6	12.6	6.0	mg
Filterable PM Mass Concentration	lb/dscf	1.55E-05	5.93E-06	2.82E-05	1.65E-05	lb/dscf
Filterable PM Mass Emission Rate	lb/hr	0.041	0.014	0.103	0.05	lb/hr
Filterable PM Mass Emission Rate	lb/cycle	0.014	0.008	0.031	0.02	lb/cycle