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OCT O S 2016 AIR QUALITY DIV.

Marathon Petroleum Company LP 1300 South Fort Street Detroit, MI 48217

## **REPORT ON COMPLIANCE TESTING**

Performed for: MARATHON PETROLEUM COMPANY LP **DETROIT REFINERY** 

## FCCU REGENERATOR STACK (SVFCCU)

Client Reference No: 4100665755 CleanAir Project No: 12993-1 Revision 0: September 29, 2016

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.

Submitted by,

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|  | MICHIGAN DEPARTMENT (<br>AIR QUAL   | OF ENVIRONMENTAL QUALITY  | OCT 0 3 2016  |
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|  | RENEWABLE OF<br>REPORT CE   | PERATING PERMIT   | AIR QUALITY DIV.  |
| Authorized by 1994 P.A. 4  | 51, as amended. Failure to prov   | ide this information may result in c  | ivil and/or criminal penalties.   |
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| Source Name Marathon Petrol  | eum Company LP  | · · · · · · · · · · · · · · · · · · ·   | County <u>Wayne</u>   |
| Source Address 1300 South Fo   | rt Street   | City  | Detroit   |
| AQD Source ID (SRN) A9831  | ROP No.   | MI-ROP-A9831-<br>2012c  | ROP Section No.   |
| Please check the appropriate box(es):  |   | ана   | en an   |
| Annual Compliance Certification  | on (Pursuant to Rule 213(4)   | (c))  |   |
| <ul> <li>Reporting period (provide inclusive)         <ul> <li>1. During the entire reporting period (s) specified in the ROP</li> <li>2. During the entire reporting term and condition of which is deviation report(s). The method unless otherwise indicated and</li> </ul> </li> <li>Semi-Annual (or More Frequent Reporting period (provide inclusive)         <ul> <li>1. During the entire reporting period (provide inclusive)</li> <li>2. During the entire reporting period (provide inclusive)</li> <li>3. During the entire reporting period (provide inclusive)</li> <li>3. During the entire reporting period (provide inclusive)</li> <li>4. During the entire reporting period (provide inclusive)</li> <li>3. During the entire reporting period (provide inclusive)</li> <li>4. During the entire reporting period (provide inclusive)</li> <li>5. During the entire reporting period (provide inclusive)</li> </ul> </li> </ul> | re dates): From<br>beriod, this source was in com<br>dentified and included by this<br>period this source was in co<br>identified and included by th<br>d used to determine compliar<br>described on the enclosed de<br><b>it</b> ) Report Certification (Pur<br>we dates): From<br>period, ALL monitoring and assents or any other terms or cor<br>period, all monitoring and asso<br>ents or any other terms or cor | To<br>pliance with ALL terms and co<br>reference. The method(s) use<br>mpliance with all terms and co<br>is reference, EXCEPT for the<br>nce for each term and condition<br>eviation report(s).<br><b>suant to Rule 213(3)(c))</b><br>To<br>To<br>Sociated recordkeeping require<br>iditions occurred.<br>Deciated recordkeeping requiremenditions occurred, EXCEPT for | ements in the ROP were met and no the deviations identified on the ROP, |
| Other Report Certification   | nn - , , , , , , , , , , , , , , , , , ,  |   |   |
| Reporting period (provide inclusiv<br>Additional monitoring reports or of<br>Submittal of Stack Test   | e dates): From 08/02<br>her applicable documents rec<br>results.  | /2016 To 08/02/<br>quired by the ROP are attached   | 2016<br>1 as described:   |
| I certify that, based on information an<br>supporting enclosures are true, accura  | nd belief formed after reasor<br>te and complete MPC Inv  | nable inquiry, the statements restment LLC,   | and information in this report and the  |

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its General Partner

David T. Roland 313-843-9100 Deputy Assistant Secretary Name of Responsible Official (print or type) Phone Number Title 9 30/2016

Signature of Responsible Official

\* Photocopy this form as needed.

EQP 5736 (Rev 11-04)

Date

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# MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

## Client Reference No: 4100665755 CleanAir Project No: 12993-1

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## **REVISION HISTORY**

## REPORT ON COMPLIANCE TESTING

#### DRAFT REPORT REVISION HISTORY

| Revision: | Date     | Pages | Comments                            |
|-----------|----------|-------|-------------------------------------|
| D0a       | 09/06/16 | All   | Draft version of original document. |
|           |          |       |                                     |
|           |          |       |                                     |
|           |          |       |                                     |

#### FINAL REPORT REVISION HISTORY

| Revision: | Date       | Pages | Comments                            |
|-----------|------------|-------|-------------------------------------|
| 0         | 09/29/2016 | All   | Final version of original document. |
|           |            |       |                                     |
|           |            |       |                                     |
|           |            |       |                                     |

## MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

Client Reference No: 4100665755 CleanAir Project No: 12993-1

#### PROJECT OVERVIEW

#### INTRODUCTION

Marathon Petroleum Company LP (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. 63-08D, issued May 12, 2014.

### Key Project Participants

Individuals responsible for coordinating and conducting the test program were:

Crystal Davis – MPC Joe Reidy – MPC Thomas Gasloli – Michigan DEQ Chad Eilering – CleanAir

#### **Test Program Parameters**

The testing was performed at the FCCU Regenerator Stack (Emission Unit ID No. EU11-FCCU-S1; Stack ID No. SVFCCU) on August 2, 2016, and included the following emissions measurements:

- sulfuric acid (H<sub>2</sub>SO<sub>4</sub>)
- volatile organic compounds (VOCs), assumed equivalent to total hydrocarbons (THC) minus the following constituents:
  - methane (CH4)
  - $\circ$  ethane (C<sub>2</sub>H<sub>6</sub>)
- flue gas composition (e.g., O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O)
- flue gas flow rate

## MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

## **PROJECT OVERVIEW**

## **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<br>Number                               | Location               | Method                 | Analyte  | Date     | Start<br>Time | End<br>Time |
| 0   | FCCU Regenerator Stack | Draft ASTM CCM         | Sulfuric Acid  | 08/01/16 | 16:05         | 17:05       |
| 1   | FCCU Regenerator Stack | Draft ASTM CCM         | Sulfuric Acid  | 08/02/16 | 10:20         | 11:20       |
| 2   | FCCU Regenerator Stack | Draft ASTM CCM         | Sulfuric Acid  | 08/02/16 | 12:05         | 13:06       |
| 3   | FCCU Regenerator Stack | Draft ASTM CCM         | Sulfuric Acid  | 08/02/16 | 13:37         | 14:37       |
| 1   | FCCU Regenerator Stack | USEPA Method 3A/18/25A | O <sub>2</sub> /CO <sub>2</sub> /CH <sub>4</sub> /C <sub>2</sub> H <sub>6</sub> /THC | 08/02/16 | 10:19         | 11:30       |
| 2   | FCCU Regenerator Stack | USEPA Method 3A/18/25A | O <sub>2</sub> /CO <sub>2</sub> /CH <sub>4</sub> /C <sub>2</sub> H <sub>6</sub> /THC | 08/02/16 | 12:06         | 13:09       |
| 3   | FCCU Regenerator Stack | USEPA Method 3A/18/25A | O <sub>2</sub> /CO <sub>2</sub> /CH <sub>4</sub> /C <sub>2</sub> H <sub>6</sub> /THC | 08/02/16 | 13:36         | 14:42       |
| 1   | FCCU Regenerator Stack | USEPA Method 2F        | 3-D Velocity & Flow Rate   | 08/02/16 | 10:19         | 11:44       |
| 2   | FCCU Regenerator Stack | USEPA Method 2F        | 3-D Velocity & Flow Rate   | 08/02/16 | 12:12         | 12:43       |
| 3   | FCCU Regenerator Stack | USEPA Method 2F        | 3-D Velocity & Flow Rate   | 08/02/16 | 01:36         | 02:25       |

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## **Results Summary**

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

| Table 1-2:Summary of $H_2SO_4$ and VOC Results (Draft ASTM CCM & USEPA 18/25A) |               |                 |                     |                           |  |  |
|--|---------------|-----------------|---------------------|---------------------------|--|--|
| <u>Source</u><br>Constituent   | (Units)       | Sampling Method | Average<br>Emission | Permit Limit <sup>1</sup> |  |  |
| FCCU Regenerate  | or Stack      |                 |                     |                           |  |  |
| H₂SO₄  | (lb/Mlb coke) | Draft ASTM CCM  | 1.2E-02             | N/A                       |  |  |
| H₂SO₄  | (ppmdv)       | Draft ASTM CCM  | 0.24                | N/A                       |  |  |
| VOC  | (Ton/yr)      | USEPA 25A / 18  | 4.2                 | 21                        |  |  |
| VOC  | (Ib/MIb coke) | USEPA 25A / 18  | 0.048               | N/A                       |  |  |

<sup>1</sup> Permit limit obtained from MDEQ Permit To Install No. 63-08D.

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Client Reference No: 4100665755

CleanAir Project No: 12993-1

# MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

## Client Reference No: 4100665755 CleanAir Project No: 12993-1

## PROJECT OVERVIEW

#### Discussion of Test Program

#### Flow Rate Measurements

3-D flow traverses per Method 2F were performed during each Draft ASTM CCM test runs.

## H<sub>2</sub>SO<sub>4</sub> Testing - Draft ASTM Controlled Condensation Method

Prior to the first official test run, a 60-minute sample conditioning run (Run 0) was performed in order to minimize the absorption capacity of the front-half components of the sample train (upstream of the H<sub>2</sub>SO<sub>4</sub>-collecting portion of the sample train). The conditioning run was recovered and analyzed in the same manner as the official test runs, but was not included in the final results.

Following the conditioning run, three (3) official 60-minute test runs were performed. The final results were expressed as the average of three (3) official runs.

#### VOC Testing - USEPA Method 25A and Method 18

Three (3) approximately 60-minute Method 25 test runs for THC were performed concurrently with three (3) approximately 60-minute Method 18 bag collections for CH<sub>4</sub> and  $C_2H_6$ .

VOC emission rate is normally equivalent to THC emission rate, minus CH<sub>4</sub>, and C<sub>2</sub>H<sub>6</sub> emission rate (units of lb/hr, Ton/yr, or lb/MMBtu for all constituents). For CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, a non-detectable result was obtained for Run 1 and Run 3, so no correction was made to the THC results. Therefore, VOC emissions for Run 1 and Run 3 was equivalent to THC emissions only. The final VOC results were expressed as the average of three (3) runs.

#### Calculation of Final Results

Mass-based emission rates in units of pounds per hour (lb/hr) for Draft ASTM CCM and Method 18/25A were calculated using the concurrently measured flow rate determined by Method 2F.

Emission rates in units of tons per year (Ton/yr) were calculated using an assumed capacity factor of 8,760 operating hours per year. Emission rates in units of pounds per 1,000 pounds of coke burn (lb/Mlb coke) were calculated using coke burn rate data provided by MPC.

Ammonia (NH<sub>3</sub>) injection rates shown in Tables 2-1 and 2-2 is the aqueous ammonia, (11FC2032), multiplied by a factor of 0.2.

# MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

## Client Reference No: 4100665755 CleanAir Project No: 12993-1

| RESI               | JLTS  |          |          |          |          |
|--------------------|---|----------|----------|----------|----------|
|                    | Table   | 2-1:     |          |          |          |
|                    | H <sub>2</sub> SO <sub>4</sub> Emissions                |          | JCM)<br> |          |          |
| Run No             | ).  | 1        | 2        | 3        | Average  |
| Date (2            | 016)  | Aug 2    | Aug 2    | Aug 2    |          |
| Start Ti           | me (approx.)  | 10:20    | 12:05    | 13:37    |          |
| Stop Ti            | me (approx.)  | 11:20    | 13:06    | 14:37    |          |
| Proces             | s Conditions  |          |          |          |          |
| Rp                 | Coke burn rate (lb/hr)                                  | 21,621   | 19,143   | 19,072   |          |
| P <sub>1</sub>     | FCC charge rate (bpd)                                   | 39,483   | 35,013   | 35,002   |          |
| $P_2$              | NH3 Injection (Ib/hr)                                   | 4.7      | 4.6      | 4.4      |          |
| Сар                | Capacity factor (hours/year)                            | 8,760    | 8,760    | 8,760    |          |
| Gas Co             | onditions   |          |          |          |          |
| O2                 | Oxygen (dry volume %)                                   | 2.0      | 2.0      | 1.9      | 2.0      |
| CO2                | Carbon dioxide (dry volume %)                           | 16.0     | 16.1     | 16.2     | 16.1     |
| Τs                 | Sample temperature (°F)                                 | 525      | 514      | 509      | 516      |
| Bw                 | Actual water vapor in gas (% by volume)                 | 10.2     | 12.4     | 11.1     | 11.3     |
| Gas Flo            | ow Rate   |          |          |          |          |
| Q <sub>std</sub>   | Volumetric flow rate, dry standard (dscfm) <sup>1</sup> | 71,200   | 61,400   | 63,300   | 65,300   |
| Sampli             | ng Data   |          |          |          |          |
| Vmstd              | Volume metered, standard (dscf)                         | 24.26    | 23.17    | 24.15    | 23.86    |
| Labora             | tory Data (Ion Chromatography)                          |          |          |          |          |
| ma                 | Total H2SO4 collected (mg)                              | 1.4749   | 0.3699   | 0.1560   |          |
| Sulfuri            | c Acid Vapor (H2SO4) Results                            |          |          |          |          |
| $\mathbf{C}_{sd}$  | H2SO4 Concentration (lb/dscf)                           | 1.34E-07 | 3.52E-08 | 1.42E-08 | 6.12E-08 |
| $C_{sd}$           | H2SO4 Concentration (ppmdv)                             | 0.527    | 0.138    | 0.0560   | 0.240    |
| E <sub>lb/hr</sub> | H2SO4 Rate (lb/hr)                                      | 0.573    | 0.130    | 0.0541   | 0.252    |
| E <sub>T/yr</sub>  | H2SO4 Rate (Ton/yr)                                     | 2.51     | 0.568    | 0.237    | 1.10     |
| E <sub>Rp</sub>    | H2SO4 Rate - Production-based (lb/Mlb coke)             | 2.65E-02 | 6.78E-03 | 2.84E-03 | 1.20E-02 |
|                    |   |          |          |          |          |

Average includes 3 runs.

<sup>1</sup> Gas flow rates obtained from concurrent Method 2F test runs.

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# MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

## Client Reference No: 4100665755 CleanAir Project No: 12993-1

| RESI               | JLTS  |           |           |           |           |
|--------------------|---|-----------|-----------|-----------|-----------|
|                    |   | 2-2:      |           | •         |           |
| Bun Ma             |   |           | A 25A/18  | )         | A         |
| Run No.            |   | 1         | z         | 3         | Average   |
| Date (20           | 16)   | Aug 2     | Aug 2     | Aug 2     |           |
| Start Tim          | e (approx.)   | 10:19     | 12:06     | 13:36     |           |
| Stop 1im           | e (approx.)   | 11:30     | 13:09     | 14:42     |           |
| Process            | Conditions  |           |           |           |           |
| Rp                 | Coke burn rate (lb/hr)                                  | 21,601    | 19,124    | 19,066    |           |
| P <sub>1</sub>     | FCC charge rate (bpd)                                   | 39,482    | 35,012    | 35,003    |           |
| P <sub>2</sub>     | NH <sub>3</sub> injection (lb/hr)                       | 4.7       | 4.6       | 4.4       |           |
| Сар                | Capacity factor (hours/year)                            | 8,760     | 8,760     | 8,760     |           |
| Gas Cor            | dítions   |           |           |           |           |
| O <sub>2</sub>     | Oxygen (dry volume %)                                   | 1.8       | 2.0       | 1.9       | 1.9       |
| $CO_2$             | Carbon dioxide (dry volume %)                           | 16.3      | 16.1      | 16.2      | 16.2      |
| Bw                 | Actual water vapor in gas (% by volume) <sup>1</sup>    | 10.2      | 12.4      | 11.1      | 11.3      |
| Gas Floy           | v Rate <sup>2</sup>                                     |           |           |           |           |
| Q <sub>std</sub>   | Volumetric flow rate, dry standard (dscfm)              | 71,200    | 61,400    | 63,300    | 65,300    |
| THC Res            | ults  |           |           |           |           |
| C <sub>sd</sub>    | Concentration (ppmdv as C <sub>3</sub> H <sub>8</sub> ) | 2.34      | 1.97      | 2,24      | 2.18      |
| C <sub>sd</sub>    | Concentration (lb/dscf)                                 | 2.68E-07  | 2.25E-07  | 2.56E-07  | 2.50E-07  |
| E <sub>tb/hr</sub> | Emission Rate (lb/hr)                                   | 1.14      | 0.830     | 0.973     | 0.982     |
| E <sub>T/y</sub>   | Emission Rate (Ton/yr)                                  | 5.01      | 3.63      | 4.26      | 4.30      |
| E <sub>Rp</sub>    | Emission Rate - Production-based (lb/Mlb coke)          | 5,30E-02  | 4.34E-02  | 5.11E-02  | 4.91E-02  |
| Methane            | Results   |           |           |           |           |
| C <sub>sd</sub>    | Concentration (ppmdv)                                   | <0.210    | 0,480     | <0.210    | <0.300    |
| C <sub>sd</sub>    | Concentration (lb/dscf)                                 | <8.74E-09 | 2.00E-08  | <8.74E-09 | <1.25E-08 |
| E <sub>ib/hr</sub> | Emission Rate (lb/hr)                                   | < 0.0373  | 0.0737    | < 0.0332  | < 0.0481  |
| ETAYI              | Emission Rate (Ton/yr)                                  | < 0.164   | 0.323     | < 0.145   | < 0.211   |
| E <sub>Rp</sub>    | Emission Rate - Production-based (Ib/Mlb coke)          | <1.73E-03 | 3.85E-03  | <1.74E-03 | <2.44E-03 |
| Ethane F           | lesults   |           |           |           |           |
| C <sub>sd</sub>    | Concentration (ppmdv)                                   | <0.390    | <0,390    | <0.390    | <0.390    |
| C <sub>sd</sub>    | Concentration (lb/dscf)                                 | <3.04E-08 | <3.04E-08 | <3.04E-08 | <3.04E-08 |
| E <sub>ib/hr</sub> | Emission Rate (lb/hr)                                   | < 0.130   | < 0.112   | < 0.116   | < 0.119   |
| ETAY               | Emission Rate (Ton/yr)                                  | < 0.569   | < 0.491   | < 0.506   | < 0.522   |
| E <sub>RP</sub>    | Emission Rate - Production-based (lb/Mlb coke)          | <6.02E-03 | <5.87E-03 | <6.06E-03 | <5.98E-03 |
| VOC Res            | sults   |           |           |           |           |
| E <sub>lb/hr</sub> | Emission Rate (lb/hr)                                   | 1.14      | 0.756     | 0.973     | 0.958     |
| ETA                | Emission Rate (Ton/yr)                                  | 5.01      | 3.31      | 4,26      | 4.20      |
| ERP                | Emission Rate - Production-based (Ib/MIb coke)          | 5.30E-02  | 3.95E-02  | 5.11E-02  | 4.79E-02  |

Average includes 3 runs.

<sup>1</sup> Moisture data used for ppmwv to ppmdv correction obtained from nearly-concurrent Draft ASTM CCM runs.

<sup>2</sup> Flow data used in lb/hr calculations was obtained from nearly-concurrent M-2F test runs.

For methane and ethane, '<' indicates a measured response below the analytical detection limit determined by the laboratory. For all calcuated averages, "<' values are treated as the entire value of the detection limit.

End of Section 2 – Results

## MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

## Client Reference No: 4100665755 CleanAir Project No: 12993-1

## 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 Fluid Catalytic Cracking Unit (EU11-FCCU-S1) utilizes a primary reactor, a distillation column and a catalyst regeneration unit to continuously generate light hydrocarbon products from heavy crude oil feeds. The FCCU is equipped with an ESP with two (2) bays and variable aqueous NH<sub>3</sub> injection to control emissions. Emissions are vented to the atmosphere via the FCCU Regenerator Stack (SVFCCU).

The testing described in this document was performed at the FCCU Regenerator Stack.

#### **DESCRIPTION OF SAMPLING LOCATIONS**

Sampling point locations were determined according to USEPA Method 1.

Table 3-1 outlines the sampling point configurations. The figures shown on pages 3-2 and 3-3 illustrate the sampling points and orientation of sampling ports.

| Table 3-1:<br>Sampling Points       |                     |            |       |                    |                      |                  |                  |
|-------------------------------------|---------------------|------------|-------|--------------------|----------------------|------------------|------------------|
| <u>Source</u><br>Constituent        | Method              | Run<br>No. | Ports | Points per<br>Port | Minutes per<br>Point | Total<br>Minutes | Figure           |
| FCCU Regenerator Stack<br>Flow Rate | USEPA 2F            | 1-3        | 2     | 12                 | varied               | varied           | 3-1              |
| H₂SO₄                               | Draft ASTM CCM      | 1-3        | 1     | 1                  | 60                   | 60               | N/A <sup>1</sup> |
| $O_2 / CO_2 / CH_4 / C_2H_6 / THC$  | USEPA 3A / 18 / 25A | 1-3        | 1     | 1                  | 60                   | 60               | N/A <sup>1</sup> |

<sup>1</sup> Sampling occured at a single point near the center of duct.

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## MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

## Client Reference No: 4100665755 CleanAir Project No: 12993-1



End of Section 3 - Description of Installation

## MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

## Client Reference No: 4100665755 CleanAir Project No: 12993-1

## METHODOLOGY Clean Air Engineering followed procedures as detailed in USEPA Methods 1, 2, 2F, 3, 3A, 4, 18, 25A, and the Draft ASTM Controlled Condensation Method (CCM). The following table summarizes the methods and their respective sources. Table 4-1: **Summary of Sampling Procedures** Title 40 CFR Part 60 Appendix A "Sample and Velocity Traverses for Stationary Sources" Method 1 "Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)" Method 2 Method 2F "Determination of Stack Gas Velocity And Volumetric Flow Rate with Three-Dimensional Probes" 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)' "Gas Analysis for the Determination of Emission Rate Correction Factor or Excess Air" Method 3B Method 4 "Determination of Moisture Content in Stack Gases" "Measurement of Gaseous Organic Compound Emissions by Gas Chromatography" Method 18 Method 25A "Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer" **Draft Methods** Draft ASTM CCM "Standard Test Method for Determination of Sulfur Trioxide and Sulfuric Acid Vapor and Mist, from Stationary Sources Using a Controlled Condensation Sampling System" These methods appear in detail in Title 40 of the Code of Federal Regulations (CFR) and are located on the internet at http://ecfr.gpoaccess.gov. Diagrams of the sampling apparatus and major specifications of the sampling, recovery and analytical procedures are summarized for each method in Appendix A. CleanAir followed specific quality assurance and quality control (QA/QC) procedures as outlined in the individual methods and as prescribed in CleanAir's internal Quality Manual. Results of all QA/QC activities performed by CleanAir are summarized in Appendix D.

## MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

## Client Reference No: 4100665755 CleanAir Project No: 12993-1

## METHODOLOGY

H<sub>2</sub>SO<sub>4</sub> Testing - Draft ASTM Controlled Condensation Method H<sub>2</sub>SO<sub>4</sub> emissions were determined referencing the Draft ASTM Controlled Condensation Method.

A gas sample was extracted from the source at a constant flow rate using a quartz-lined probe maintained at 650°F and a quartz fiber filter maintained at 650°F to remove particulate matter.

The sample 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) located at the condenser outlet collected any residual sulfuric acid mist that passed through the condenser. The condenser temperature was regulated by a circulating water jacket; the SAM filter temperature was regulated by a closed oven. Both the water jacket and SAM filter oven were maintained at 140°F  $\pm$ 9°F (above the water dew point, which eliminates the oxidation of dissolved SO<sub>2</sub> into the H<sub>2</sub>SO<sub>4</sub>-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 was maintained below 68°F. The sample gas then flowed into a calibrated dry gas meter where the collected sample gas volume was determined.

The H<sub>2</sub>SO<sub>4</sub>-collecting portion of the sample train (condenser and SAM filter) was recovered into a single fraction using DI H<sub>2</sub>O as the recovery/extraction solvent; any H<sub>2</sub>SO<sub>4</sub> disassociated into sulfate ion (SO<sub>4</sub><sup>2-</sup>) was stabilized in the H<sub>2</sub>O matrix until analysis.

A field train blank was assembled, transported to the location, heated, leak-checked and recovered as if it were an actual test sample. Reagent blanks were collected to quantify background contamination.

Samples and blanks were returned to CleanAir Analytical Services for ion chromatography (IC) analysis.

## O<sub>2</sub>, CO<sub>2</sub>, and VOC Testing - USEPA Methods, 3A, 18, and 25A

 $O_2$  and  $CO_2$  emissions were determined using a paramagnetic/NDIR analyzer per EPA Method 3A. VOC emissions were determined using USEPA Method 25A to quantify total hydrocarbon emissions (THC) and USEPA Method 18 to quantify methane (CH4) and ethane (C<sub>2</sub>H<sub>6</sub>) emissions. VOC emissions are equivalent to THC emissions, minus CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> emissions.

## 4-2

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## MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

Client Reference No: 4100665755 CleanAir Project No: 12993-1

## METHODOLOGY

The Method 3A/18/25A sampling system consisted of a heated probe, heated filter and heated sample line. Flue gas was extracted at a constant rate and delivered at 250°F to a tee at the end of the heated sample line.

- One leg of the tee was connected to a flame ionization analyzer (FIA) which continuously measured minute-average THC concentration expressed in terms of propane (C<sub>3</sub>H<sub>8</sub>) on an actual (wet) basis.
- The other leg of the tee was connected to a gas conditioner which removed moisture before delivering the gas to a flow panel and the O<sub>2</sub>/CO<sub>2</sub> analyzers which measured concentration on a dry basis (units of %dv or ppmdv).
- The Method 18 gas sample was collected by pulling a slipstream from the flow panel 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 approximately one (1) hour for each test run.

THC analyzer 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.

 $O_2/CO_2$  calibration error checks were performed by introducing zero nitrogen (N<sub>2</sub>), high-range 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. Per Method 3A, the average results for each run were drift-corrected.

Analysis for CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> was performed off-site by CleanAir Analytical Services using gas chromatography (GC). Since moisture was removed from the sample prior to collection and GC analysis, the concentration results were on a dry basis. At least five (5) sample injections were analyzed for each run.

GC calibration was performed by generating a calibration curve from triplicate injections of three (3) distinct CH<sub>4</sub> and  $C_2H_6$  concentrations introduced directly into the GC. Upon completion of calibration, a recovery study was performed by spiking two (2) of the bag samples with a known concentration of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub>, storing the bags for the same period of time prior to analysis as the field samples and analyzing the bags to determine percent recovery.

## MARATHON PETROLEUM COMPANY LP DETROIT REFINERY

### Client Reference No: 4100665755 CleanAir Project No: 12993-1

## METHODOLOGY

#### General Considerations

A traditional verification of the absence of cyclonic flow following Method 1 specifications was not performed. However, the resultant angle of flow was determined from each Method 2F flow traverse and found to be less than 20° in all instances. Data is included in Appendix G.

H<sub>2</sub>O data used for moisture correction of concentration data was obtained (when required) in the following manner during the test program:

- For Method Draft ASTM CCM, Method 4 measurements are incorporated into the sampling train and recovery procedures.
- For Method 3A/18/25A, H<sub>2</sub>O data was obtained from most concurrentlyoperated Draft ASTM CCM sample trains.

O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O data used for Method 2F flow calculations was obtained from the most concurrently operated Draft ASTM CCM sample trains.

End of Section 4 – Methodology