



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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OFFICE OF
AIR AND RADIATION

James M. Nelson
Division Manager
Marathon Ashland Petroleum LLC
1300 South Fort Street
Detroit, Michigan 48217-1294

Re: Petition to Use an Alternate NO_x Mass Monitoring Configuration
at MAP's Refinery in Detroit, Michigan

Dear Mr. Nelson:

EPA reviewed your October 11, 2001 petition under §§75.66 and 97.75 of EPA's regulations in which Marathon Ashland Petroleum, LLC (MAP) requests to use a subtractive apportionment methodology to determine the NO_x mass emissions of the carbon monoxide (CO) boiler. The CO boiler combusts CO from a fluid catalytic cracker unit regenerator (FCCU) and some other fuels, and the CO boiler and the FCCU exhaust through a common stack. The CO boiler, but not the FCCU, is subject to the NO_x Budget Trading Program under Part 97.¹

MAP's proposed apportionment would be accomplished by using: NO_x, carbon dioxide (CO₂), and CO continuous emissions monitoring systems (CEMS) and a moisture monitoring system on the common stack to determine NO_x mass emissions in the combined flue gas from the CO boiler and the FCCU; and NO_x, CO₂, and CO CEMS in the duct exhausting from the FCCU to the CO boiler to determine NO_x mass emissions from the FCCU alone. MAP would utilize a CO₂ mass balance approach to determine the flow from the FCCU exhaust duct to the CO boiler. MAP would subtract NO_x mass emissions for the FCCU from the NO_x mass emissions at the common stack and use the heat input of the fuels combusted in the CO boiler, which includes the combustible components of the flue gases from the FCCU. EPA approves MAP's request to use a subtractive apportionment methodology for the CO boiler, with the modifications and conditions described below.

Background

¹ EPA's determination in this letter also applies if these units become subject the NO_x Budget Trading Program under a State Implementation Plan approved by EPA under §51.121.

MAP operates a FCCU that combusts the petroleum coke residue deposited on catalyst during the petroleum cracking process. The FCCU is not subject to the NO_x Budget Trading Program. However, the FCCU exhaust includes CO that is combusted in the CO boiler, which unit is subject to the program.

According to MAP, the high temperature (e.g., 1200 to 1400 degrees Fahrenheit) of exhaust from the FCCU precludes the use of a flow monitor at the FCCU exhaust duct. MAP maintains that the volumetric flow of flue gases in the FCCU exhaust duct entering the CO boiler can be determined by performing a CO₂ balance on the FCCU and CO boiler combination. The volumetric flow from FCCU can be used in conjunction with a NO_x concentration monitor to measure NO_x mass emissions for the FCCU in accordance with §75.72. The CO boiler generates process steam from: the waste heat provided by the FCCU; and the heat produced from combusting refinery gas (RFG), No. 6 fuel oil, pipeline natural gas (PNG), and CO from the FCCU. The heat input to the CO boiler from RFG, fuel oil, and PNG is measured by fuel flowmeters in the supply lines.

In its October 11, 2001 petition, MAP states the following:

- 1) MAP proposes to subtract the NO_x mass emissions from the FCCU from the NO_x mass emissions of the CO boiler utilizing the following equations:

$$(a) \text{NO}_x \text{ Mass}_{\text{co}} = \text{NO}_x \text{ Mass}_{\text{cs}} - \text{NO}_x \text{ Mass}_r$$

Where:

NO_x Mass_{co} = NO_x mass emissions reported for the affected CO boiler, lb/hr

NO_x Mass_{cs} = Combined NO_x mass emissions at the common stack, lb/hr

NO_x Mass_r = NO_x mass emissions at the FCCU exhaust duct, lb/hr

$$(b) \text{NO}_x \text{ Mass}_r = (1.194 \times 10^{-7}) \text{NO}_{\text{xr}} Q_r$$

$$(c) \text{NO}_x \text{ Mass}_{\text{cs}} = (1.194 \times 10^{-7}) \text{NO}_{\text{xcs}} [1 - (\text{H}_2\text{O}\%_{\text{cs}}/100)] Q_{\text{cs}}$$

Where:

NO_{xr} = NO_x concentration in FCCU exhaust duct, ppm, dry

Q_r = Flue gas volumetric flow rate in FCCU exhaust duct, dscf/hr

H₂O%_{cs} = Moisture concentration at the common stack, %

NO_{xcs} = NO_x concentration at the common stack, ppm, dry

Q_{cs} = Combined flue gas volumetric flow rate at the common stack, scf/hr

- (2) MAP proposes to calculate the volumetric flow rate in the FCCU exhaust duct (Q_r) from a CO₂ mass balance on the FCCU and CO boiler combination utilizing the following equations:

$$(a) \text{CO}_2 \text{ Mass}_r = \text{CO}_2 \text{ Mass}_{\text{cs}} - \text{CO}_2 \text{ Mass}_{\text{co}}$$

Where:

$CO_2 \text{ Mass}_r$ = CO_2 mass emissions contributed by the FCCU exhaust, ton/hr
 $CO_2 \text{ Mass}_{cs}$ = Combined CO_2 mass emissions at the common stack, ton/hr
 $CO_2 \text{ Mass}_{co}$ = CO_2 mass emissions from fuel combusted in the CO boiler, ton/hr

(b) $CO_2 \text{ Mass}_r = (5.7 \times 10^{-7}) CO_{2r} Q_r$

(c) $CO_2 \text{ Mass}_{cs} = (5.7 \times 10^{-7}) CO_{2cs} [1 - (H_2O\%_{cs}/100)] Q_{cs}$

Where:

CO_{2r} = CO_2 concentration in the FCCU exhaust duct, %, dry

Q_r = Flue gas volumetric flow rate in the FCCU exhaust duct, dscf/hr

$H_2O\%_{cs}$ = Moisture concentration at the common stack, %

CO_{2cs} = CO_2 concentration at the common stack %, dry

Q_{cs} = Combined flue gas volumetric flow rate at the common stack, scf/hr

(d) $CO_2 \text{ mass}_{co} = CO_2 \text{ mass from RPG, PNG, and fuel oil} + CO_2 \text{ mass from CO}$

Where:

$CO_2 \text{ mass from RPG, PNG, and fuel oil}$ = CO_2 mass calculated using Equation G-4 from Appendix G.

$CO_2 \text{ mass from CO} = (5.7 \times 10^{-7}) CO_r Q_r$

CO_r = CO concentration measured at FCCU exhaust duct, %, dry

(e) Combining equations (b), (c), and (d) and solving for Q_r gives the volumetric flow rate from the FCCU exhaust as follows:

$$Q_r = [(CO_{2cs})[1 - (H_2O\%_{cs}/100)]Q_{cs} - 100(F_c)(HI_{co})] / (CO_{2r} + CO_r)$$

Where:

F_c = a factor representing a ratio of the volume of CO_2 generated to the calorific value of RPG, NPG, and fuel oil combusted, scf/mmBtu.

HI_{co} = heat input from RPG, NPG, and fuel oil combusted, mmBtu/hr.

- 3) MAP proposes to certify and quality assure each CEMS in accordance with Part 75, except the CO CEMS, which would be certified in accordance with the performance criteria specified in Performance Specification 4 of Part 60.
- 4) MAP maintains that the boiler load in the CO boiler is not related to the heat input from the fuel combusted in that boiler because much of the heat in the CO boiler is from the flue gases produced by fuel combusted in the FCCU. Therefore, MAP states that the flow-to-load test required by Appendix B, section 2.2.5 would not be valid. MAP requests to be relieved from the requirement to perform the test.
- 5) MAP states that it cannot use the load-based missing data procedures in Part 75 because there is no operating parameter analogous to load for the FCCU. MAP

proposes instead to use the average of the hour before and hour after to substitute data for missing data periods for the FCCU CEMS.

- 6) MAP proposes to calculate the heat input to the CO boiler by first calculating the heat input of the CO from the FCCU by using the gross calorific value of CO of 328 Btu/scf and the volumetric flow of CO from the FCCU (scf/hr) determined from the CO₂ balance approach and adding to that the heat input from the RPG, NPG, and fuel oil supplied to the CO boiler by the fuel supply lines. The heat input of the fuel supplied to the CO boiler from the fuel supply lines would be measured utilizing the procedures in Part 75, Appendix D.

EPA's Determination

EPA approves MAP's petition to use the subtractive apportionment methodology to determine the NO_x mass emissions of the CO boiler, with the following modifications and conditions:

- 1) MAP shall use the equations cited in the October 11, 2001 petition.
- 2) The flow, NO_x, moisture, and CO₂ CEMS on the common stack shall be certified in accordance with Part 75 and the quality assurance and quality control procedures shall conform with Appendix B of Part 75.
- 3) The NO_x, CO₂, and CO CEMS on the FCCU exhaust duct shall be certified in accordance with Part 75 and the quality assurance and quality control procedures shall conform with Appendix B of Part 75 with following modifications:
 - A) To certify and quality assure the CO CEMS, wherever the term "CO₂ gas monitor or CO₂ monitor" is used in Appendix A or B of Part 75, substitute the term "CO gas monitor or CO monitor".
 - B) The maximum potential concentration (MPC) for CO is to be determined based on expected CO concentrations. The MPC is not to be determined in accordance with Appendix A, section 2.1.3. The span for the CO monitor is determined by multiplying the MPC by 1 to 1.25 %. Select the range such that the readings obtained during typical unit operation are kept, to the extent practicable, between 20.0 and 80.0 percent of full-scale range of the instrument.
 - C) With respect for to the relative accuracy test audits (RATA), the following criteria will apply:
 - i) The relative accuracy (RA) for certification and quality assurance shall not exceed 10.0 percent.
 - ii) The alternative standard in Appendix A, section 3.3.3 shall not apply. If

the mean difference of the monitor measurements and the corresponding reference method measurement, calculated using the Equation A-7 of Appendix A, is within 1.0 percent CO, and the RA exceeds 10.0 percent, the results of the relative accuracy test audit (RATA) are not acceptable for certification.

- iii) The RA shall be less than 7.5 percent to qualify of the reduced RATA frequency in section 2.3.1.2 of Appendix B. The alternative specification in section 2.3.1.2(h) of Appendix B (i.e., where the mean difference between the reference method values from the RATA and the corresponding monitor values is ± 0.7 percent CO₂ or O₂) shall not be used to qualify for reduced RATA frequencies for the CO CEMS.
 - D) The alternative standard for calibration error (CE) in section 3.1(b) of Appendix A that allows the monitor reading to deviate from the reference gas by no more than 0.5% (as determined by $|R-A|$ in the numerator of Equation A-5 of Appendix A) shall not apply to the CE test performed on the CO CEMS. The standard that shall apply to the daily CE error test on the CO CEMS for data validation in section 2.1.4(a) of Appendix B shall be that an out-of-control period occurs when the CE exceeds 5.0 percent of the span value (not 1.0% CO).
 - E) The alternative standard for linearity error in section 3.2(2) of Appendix A shall not apply to linearity checks performed on the CO CEMS.
 - F) The reference method for the CO RATA shall be specified by section 8.2 of Performance Specification 4 of Part 60. All gases used to certify and quality assure the CO CEMS shall be EPA protocol gases, including those used to calibrate the reference method. Gases meeting the definition of zero air material in §72.2 are acceptable.
- 4) The flow-to-load test in Appendix B of Part 75 relates the flow at the common stack to the steam load or gross heat rate at the time of the RATA. It evaluates the condition of the flow monitor on a quarterly basis as a quality assurance test for the flow monitor. In MAP's case, because a significant part of the flow in the common stack is from flue gases contributed by the FCCU and because the steam load of the CO Boiler is impacted by the heat from the FCCU flue gases, as well as the heat from combustion of RPG, PNG, fuel oil, and CO in the CO boiler, it is possible that neither the steam load or the gross heat rate will be proportional to the flow measured by the flow monitor. EPA therefore agrees that MAP is not required to perform the flow-to-load test of Appendix B of Part 75.
 - 5) For the common stack CEMS, MAP shall use the standard missing data procedures in §§75.31, 75.33, 75.35, 75.36 and 75.37.
 - 6) For the CEMS at the FCCU exhaust duct, MAP's proposal to substitute the average of the

hour before and the hour after missing data, regardless of the percentage of monitor availability of the FCCU CEMS, is not acceptable because the proposal fails to provide any incentive to keep monitor availability above 90%. The purposes of the substitute data provisions are, among other things, to ensure that emissions from the affected unit are not understated and to provide strong incentives to maintain CEMS so that they are available to the maximum extent possible. See 58 Fed. Reg. 3590, 3635 (1993). Standard missing data procedures in Part 75, which tend to overstate emissions, cannot be used for the FCCU CEMS because the NO_x mass emissions from the FCCU are subtracted from the NO_x mass emissions at the common stack to determine the CO boiler's emissions. In order to ensure that the CO boiler emissions are not understated, MAP needs to use inverse missing data procedures for the NO_x concentration CEMS at the FCCU exhaust duct, which, for example, substitute the 10th percentile value when the standard missing data procedures in §75.33 require the 90th percentile value and use the 5th percentile value in lieu of the 95th percentile value. Should it become necessary for MAP to substitute maximum potential values due to continued monitor outages, MAP shall use zeros for the NO_x CEMS in the FCCU exhaust duct. Further, the missing data procedures must reflect the fact that the FCCU does not have a clearly definable load. The following table summarizes these points:

Non-Load Based Missing Data Procedure for NO_x Concentration CEMS at FCCU Exhaust Duct

Trigger conditions		Calculation routines	
Monitor data availability (percent)	Duration (N) of CEMS outage (hours) ¹	Method	Lookback period
95 or more	N ≤ 24	Average	2160 hours*
	N > 24	10th percentile	2160 hours*
90 or more, but below 95	N ≤ 8	Average	2160 hours*
	N > 8	5th percentile	2160 hours*
80 or more, but below 90	N > 0	Minimum Value	2160 hours*
Below 80, or operational bin indeterminable	N > 0	Use 0 ppm	None

* Quality-assured CEMS hours during unit operation

¹ During unit operation.

Similarly, because the CO₂ and CO concentrations in the FCCU exhaust duct are inversely related to the flow, MAP shall use the following non-load-based missing data procedures for the CO₂ and CO CEMS on the FCCU exhaust duct:

Non-load-based Missing Data Procedure for CO₂ and CO CEMS at the FCCU Exhaust Duct

Trigger conditions		Calculation routines	
Monitor data availability (percent)	Duration (N) of CEMS outage (hours) ¹	Method	Lookback period
95 or more	N ≤ 24	Average	2160 hours*
	N > 24	10th percentile	2160 hours*
90 or more, but below 95	N ≤ 8	Average	2160 hours*
	N > 8	5th percentile	2160 hours*
80 or more, but below 90	N > 0	Minimum value	2160 hours*
Below 80, or operational bin indeterminable	N > 0	Minimum value	2160 hours*

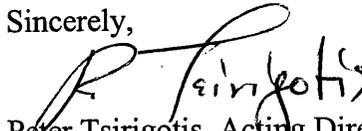
* Quality-assured CEMS hours during unit operation

¹ During unit operation.

- 7) MAP shall calculate the heat input to the CO boiler by first calculating the heat input of the CO from the FCCU by using the gross calorific value of CO of 328 Btu/scf and the volumetric flow of CO from the FCCU (scf/hr) determined from the CO₂ balance approach (discussed above) and adding to that the heat input from the RPG, NPG, and fuel oil supplied to the CO boiler by the fuel supply lines. The heat input of the fuel supplied to the CO boiler from the fuel supply lines will be measured utilizing the procedures in Part 75, Appendix D.

EPA's determination in this letter relies on the accuracy and completeness of MAP's submission on October 11, 2001 and is appealable under Part 78. If you have any questions regarding this correspondence, please contact Louis Nichols at (202) 564-0161.

Sincerely,



Peter Tsirigotis, Acting Director
Clean Air Markets Division

cc: Constantine Blathras, Region 5
Karen Kajiyi-Mills, MDEQ