MONTROSE
AIR QUALITY SERVICES

Review and Certification

All work, calculations, and other activities and tasks performed and presented in this document were carried out by me or under my direction and supervision. I hereby certify that, to the best of my knowledge, Montrose operated in conformance with the requirements of the Montrose Quality Management System and ASTM D7036-04 during this test project.

Signature: John Nestor **Date:** 06 / 28 / 2023

Name: John Nestor **Title:** District Manager

I have reviewed, technically and editorially, details, calculations, results, conclusions, and other appropriate written materials contained herein. I hereby certify that, to the best of my knowledge, the presented material is authentic, accurate, and conforms to the requirements of the Montrose Quality Management System and ASTM D7036-04.

Signature: Andy Vella **Date:** 06 / 27 / 2023

Name: Andy Vella **Title:** Senior Reporting/QC Specialist

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1.0 Introduction

1.1 Summary of Test Program

POET Biorefining-Caro, LLC contracted Montrose Air Quality Services, LLC (Montrose) to perform a compliance test program on the CE014 Scrubber associated with the Fermentation and Distillation Processes (FGFERM&DIST) at the POET Biorefining-Caro facility (State Registration No.: N6996) located in Caro, Michigan. Testing was performed on April 29, 2023, for the purpose of satisfying the emission testing requirements pursuant to Michigan Department of Environment, Great Lakes, and Energy (EGLE) Renewable Operation Permit No. MI-ROP-N6996-2018a.

The specific objectives were to:

- Measure the emissions of total volatile organic compounds (VOC) and acetaldehyde from the CE014 Scrubber serving FGFERM&DIST
- Conduct the test program with a focus on safety

Montrose performed the tests to measure the emission parameters listed in Table 1-1.

Table 1-1
Summary of Test Program

Test Date(s)	Unit ID/ Source Name	Activity/Parameters	Test Methods	No. of Runs	Duration (Minutes)
4/29/2023	CE014 Scrubber	Velocity/Volumetric Flow Rate	EPA 1 & 2	3	10-14
4/29/2023	CE014 Scrubber	O_2	EPA 3A	3	60
4/29/2023	CE014 Scrubber	H_2O and VOC*	EPA 320	3	60

* VOC includes acetaldehyde, acetic acid, acrolein, ethanol, ethyl acetate, formaldehyde, formic acid, 2-furaldehyde, and methanol.

To simplify this report, a list of Units and Abbreviations is included in Appendix C.1. Throughout this report, chemical nomenclature, acronyms, and reporting units are not defined. Please refer to the list for specific details.

This report presents the test results and supporting data, descriptions of the testing procedures, descriptions of the facility and sampling locations, and a summary of the quality assurance procedures used by Montrose. The average emission test results are summarized and compared to their respective permit limits in Table 1-2. Detailed results for individual test runs can be found in Section 4.0. All supporting data can be found in the appendices.

The testing was conducted by the Montrose personnel listed in Table 1-3. The tests were conducted according to the test plan (protocol) dated March 17, 2023, that was submitted to and approved by the EGLE on April 14, 2023.

Table 1-2
Summary of Average Compliance Results – CE014 Scrubber

April 29, 2023

Parameter/Units	Average Results	Emission Limits
Acetaldehyde		
lb/hr	1.30	1.50
Acrolein		
lb/hr	0.27	--
Formaldehyde *		
lb/hr	<0.012	--
Methanol *		
lb/hr	<0.018	--
Acetic Acid		
lb/hr	0.92	--
Ethanol		
lb/hr	10.96	--
Ethyl Acetate		
lb/hr	2.62	--
Formic Acid *		
lb/hr	<0.019	--
2-Furaldehyde *		
lb/hr	<0.12	--
Total Volatile Organic Compounds (VOC)		
lb/hr	<16.24	19.66

* The "<" symbol indicates that the compound was below the Minimum Detection Limit (MDL) of the analytical method. See Section 4.2 for details.

1.2 Key Personnel

A list of project participants is included below:

Facility Information

Source Location:	POET Biorefining-Caro, LLC
	1551 Empire Drive
	Caro, MI 48723
Project Contact:	Tony Paul
Role:	Regional Plant Engineer
Telephone:	--
Email:	tony.paul@poet.com

Agency Information

Regulatory Agency:	EGLE
Agency Contact:	Lindsey Wells
Telephone:	517-282-2345
Email:	WellsL8@michigan.gov

Testing Company Information

Testing Firm:	Montrose Air Quality Services, LLC
Contact:	John Nestor
Title:	District Manager
Telephone:	248-548-8070
Email:	jnestor@montrose-env.com

Test personnel and observers are summarized in Table 1-3.

Table 1-3
Test Personnel and Observers

Name	Affiliation	Role/Responsibility
John Nestor	Montrose	District Manager/ Qualified Individual (QI)
Shane Rabideau	Montrose	Field Technician/Field Support
Tony Paul	POET Biorefining-Caro	Test Coordinator
Lindsey Wells	EGLE	Agency Liaison

2.0 Plant and Sampling Location Descriptions

2.1 Process Description, Operation, and Control Equipment

The Fermentation and Distillation processes (FGFERM&DIST) at the POET Biorefining-Caro facility in Caro, Michigan, consist of multiple fermenters (EUFERMENTER1, EUFERMENTER2, EUFERMENTER3, EUFERMENTER4, EUFERMENTER5, EUFERMENTER6, EUFERMENTER7, EUFERMENTER8), a beer well (EUBEERWELL), beer strippers (EUBEERSTRIP, EUBEERSTRIP2), rectifier (EURECTIFIER), side stripper (EUSIDESTRIP), molecular sieves (EUSIEVE, EUSIEVE2), a yeast tank (EUYEAST), and an evaporator (EUEVAPORATOR). Emissions are controlled by two packed-bed wet scrubbers (CE004 or CE014), and when the scrubbers are down, emissions are handled by a regenerative thermal oxidizer (RTO) (CE012). During this test event, CE014 was in operation.

2.2 Flue Gas Sampling Location

Information regarding the sampling location is presented in Table 2-1.

Table 2-1
Sampling Location

Sampling Location	Stack Inside Diameter (in.)	Distance from Nearest Disturbance		Number of Traverse Points
		Downstream EPA "B" (in./dia.)	Upstream EPA "A" (in./dia.)	
CE014 Scrubber Exhaust Stack	24.0	49.0 / 2.0	85.0 / 3.5	Flow: 16 (8/port) Gaseous: 1

The sampling location was verified in the field to conform to EPA Method 1. Acceptable cyclonic flow conditions were confirmed prior to testing using EPA Method 1, Section 11.4. See Appendix A.1 for more information.

2.3 Operating Conditions and Process Data

Emission tests were performed while FGFERM&DIST and the CE014 Scrubber were operating at the conditions required by the permit.

Plant personnel were responsible for establishing the test conditions and collecting all applicable unit-operating data. The process data that was provided is presented in Appendix B. Data collected includes the following parameters:

- Scrubber flow, GPM
- Scrubber temperature and pressure, °F and in-H_2O
- Sodium biosulfite flow, GPM
- Ethanol product flow, GPM

3.0 Sampling and Analytical Procedures

3.1 Test Methods

The test methods for this test program have been presented in Table 1-1. Additional information regarding specific applications or modifications to standard procedures is presented below.

3.1.1 EPA Method 1, Sample and Velocity Traverses for Stationary Sources

EPA Method 1 is used to assure that representative samples or measurements of volumetric flow rate are obtained by dividing the cross-section of the stack or duct into equal areas, and then locating a traverse point within each of the equal areas. Acceptable sample locations must be located at least two stack or duct equivalent diameters downstream from a flow disturbance and one-half equivalent diameter upstream from a flow disturbance.

3.1.2 EPA Method 2, Determination of Gas Velocity and Volumetric Flow Rate (Type S Pitot Tube)

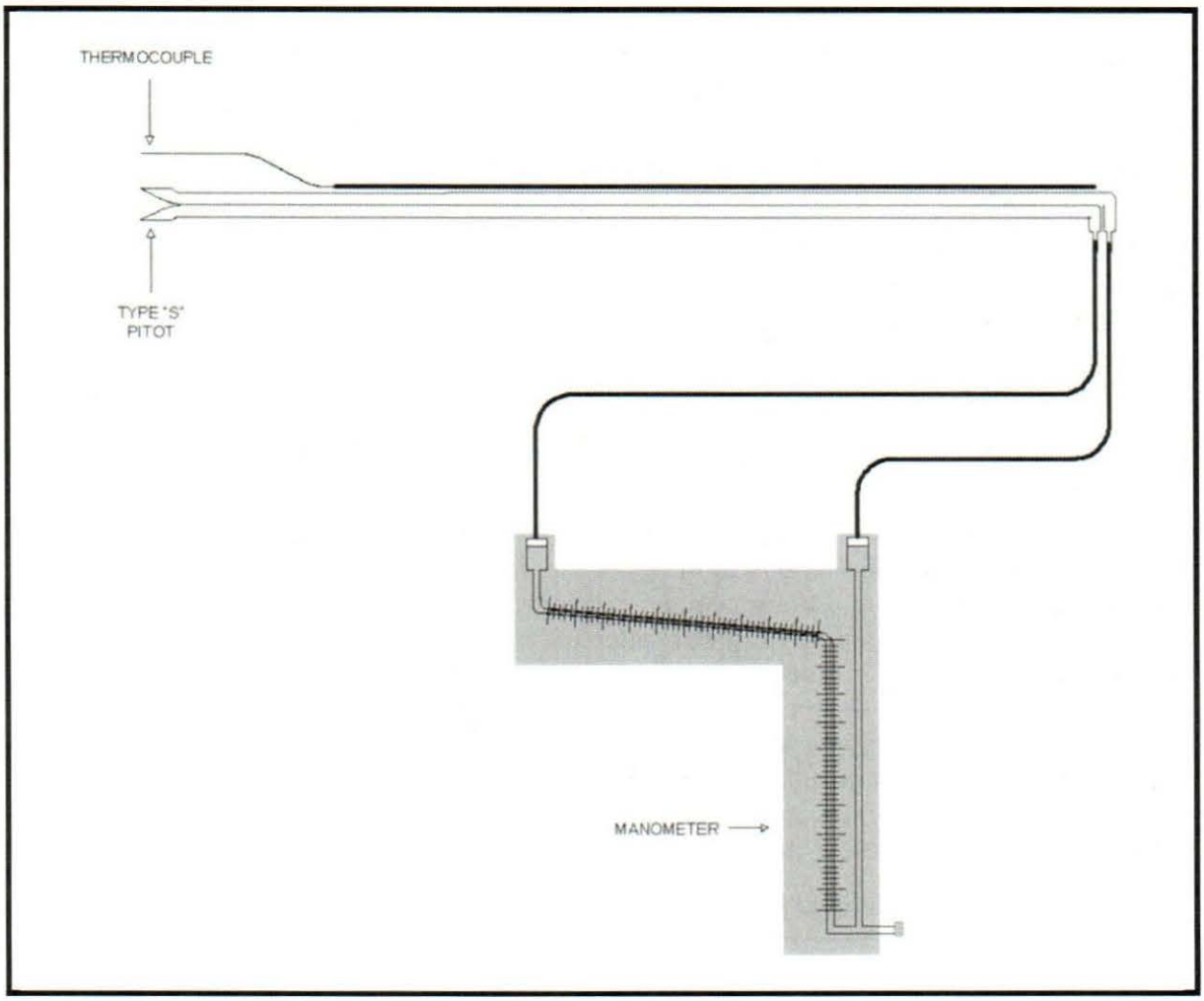
EPA Method 2 is used to measure the gas velocity using an S-type pitot tube connected to a pressure measurement device, and to measure the gas temperature using a calibrated thermocouple connected to a thermocouple indicator. Typically, Type S (Stausscheibe) pitot tubes conforming to the geometric specifications in the test method are used, along with an inclined manometer. The measurements are made at traverse points specified by EPA Method 1. The molecular weight of the gas stream is determined from independent measurements of O_2, CO_2, and moisture. The stack gas volumetric flow rate is calculated using the measured average velocity head, the area of the duct at the measurement plane, the measured average temperature, the measured duct static pressure, the molecular weight of the gas stream, and the measured moisture.

Pertinent information regarding the performance of the method is presented below:

- Method Options:
  - S-type pitot tube coefficient is 0.84

The typical sampling system is detailed in Figure 3-1.

Figure 3-1
EPA Method 2 Sampling Train



3.1.3 EPA Method 3A, Determination of Oxygen and Carbon Dioxide in Emissions from Stationary Sources (Instrumental Analyzer Procedure)

EPA Method 3A is an instrumental test method used to measure the concentration of O_2 and CO_2 in stack gas. The effluent gas is continuously or intermittently sampled and conveyed to analyzers that measure the concentrations of O_2 and CO_2. The performance requirements of the method must be met to validate data.

Pertinent information regarding the performance of the method is presented below:

- Method Options:
  - A dry extractive sampling system is used to report emissions on a dry basis
  - A paramagnetic analyzer is used to measure O_2

The typical sampling system is detailed in Figure 3-2.

3.1.4 EPA Method 320, Measurement of Vapor Phase Organic and Inorganic Emissions by Extractive FTIR Spectroscopy

EPA Method 320 is an instrumental test method used to measure specific analyte concentrations for which EPA reference spectra have been developed or prepared. Extractive emission measurements are performed using FTIR spectroscopy. The FTIR analyzer is composed of a spectrometer and detector, a high optical throughput sampling cell, analysis software, and a quantitative spectral library. The analyzer collects high resolution spectra in the mid infrared spectral region (400 to 4,000 cm^{-1}), which are analyzed using the quantitative spectral library. This provides an accurate, highly sensitive measurement of gases and vapors.

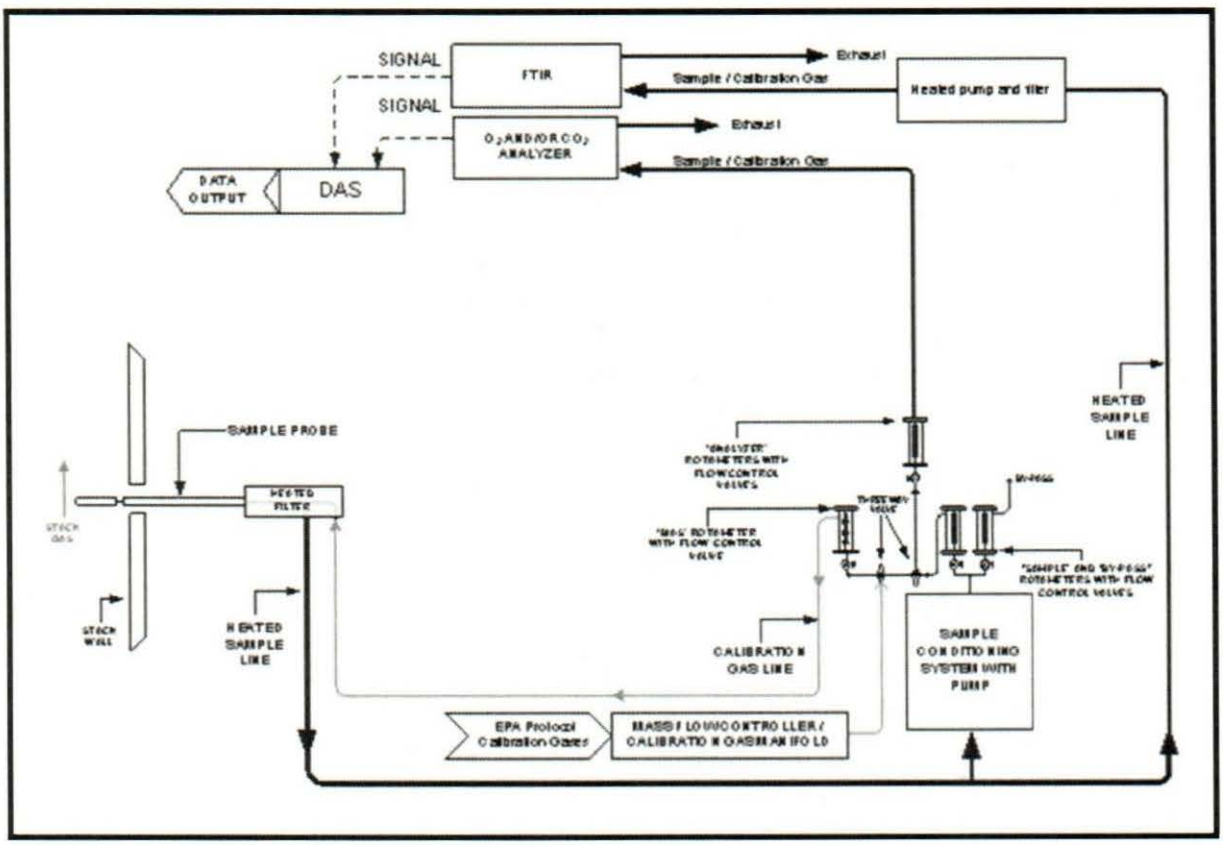
Pertinent information regarding the performance of the method is presented below:

- Method Options:
  - The specific analyte concentrations include H_2O, acetaldehyde, acetic acid, acrolein, ethanol, ethyl acetate, formaldehyde, formic acid, 2-furaldehyde, and methanol
  - Continuous static sampling is performed at a flow rate of approximately 6 liters per minute
  - Previous spiking studies validate the use of FTIR spectroscopy to accurately measure the concentrations of the specific analytes from similar sources
  - A dynamic matrix spike is performed using acetaldehyde and methanol with SF_6 as a tracer gas

- Method Exceptions:
  - To calculate the MDL for the target analytes, the guidelines in Appendix B of 40 CFR 136 are followed using the Student t-test to calculate the MDL for each analyte at a 99% confidence level. This follows EPA guidelines for reporting of zeroes or non-detects and also meets the NELAC requirements for determination of MDL values.
  - Independent calculations of optical path length are not performed because the instrument has a fixed path of 5.11 meters
- Target and/or Minimum Required Sample Duration: 60 minutes

The typical sampling system is detailed in Figure 3-2.

Figure 3-2
EPA Method 3A and FTIR Sampling Train



3.2 Process Test Methods

The test plan did not require that process samples be collected during this test program; therefore, no process sample data are presented in this test report.

4.0 Test Discussion and Results

4.1 Field Test Deviations and Exceptions

No field deviations or exceptions from the test plan or test methods occurred during this test program.

4.2 Presentation of Results

The average results are compared to the permit limits in Table 1-2. The results of individual compliance test runs performed are presented in Table 4-1. Emissions are reported in units consistent with those in the applicable regulations or requirements. Additional information is included in the appendices as presented in the Table of Contents.

Concentration values in Tables 1-2 and 4-1 denoted with a '<' were measured to be below the minimum detection limit (MDL) of the applicable analytical method. Mass emission rates denoted with a '<' in Tables 1-2 and 4-1 were calculated utilizing the applicable MDL concentration value instead of the "as measured" concentration value.

Table 4-1
Acetaldehyde and Total VOC Emissions Results - CE014 Scrubber

Parameter/Units	Run 1	Run 2	Run 3	Average
Date	4/29/2023	4/29/2023	4/29/2023	--
Time	10:15-11:15	12:35-13:35	14:09-15:09	--
Process Data *				
Ethanol product flow, GPM	151.99	155.08	155.26	154.11
Sampling & Flue Gas Parameters				
sample duration, minutes	60	60	60	--
O_2, % volume dry	0.00	0.00	0.00	0.00
CO_2, % volume dry	96.10	96.57	96.78	96.49
flue gas temperature, °F	65.6	66.6	67.1	66.4
moisture content, % volume	1.65	1.84	1.72	1.74
volumetric flow rate, dscfm	8,880	8,727	8,655	8,754
Acetaldehyde				
ppmvd	20.35	24.05	20.41	21.60
lb/hr	1.24	1.44	1.21	1.30
Acrolein				
ppmvd	3.39	3.49	3.90	3.59
lb/hr	0.26	0.27	0.29	0.27
Formaldehyde †				
ppmvd	<0.31	<0.31	<0.31	<0.31
lb/hr	<0.013	<0.012	<0.012	<0.012
Methanol †				
ppmvd	<0.41	<0.41	<0.41	<0.41
lb/hr	<0.018	<0.018	<0.018	<0.018

* Process data was provided by POET Biorefining-Caro personnel.

† The "<" symbol indicates that the compound was below the Minimum Detection Limit (MDL) of the analytical method. See Section 4.2 for details.

Table 4-1 continued
Acetaldehyde and Total VOC Emissions Results -
CE014 Scrubber

Parameter/Units	Run 1	Run 2	Run 3	Average
Date	4/29/2023	4/29/2023	4/29/2023	--
Time	10:15-11:15	12:35-13:35	14:09-15:09	--
Process Data *				
Ethanol product flow, GPM	151.99	155.08	155.26	154.11
Acetic Acid				
ppmvd	11.76	10.80	11.18	11.25
lb/hr	0.98	0.88	0.91	0.92
Ethanol				
ppmvd	158.3	157.5	208.5	174.8
lb/hr	10.09	9.86	12.95	10.96
Ethyl Acetate				
ppmvd	21.11	21.43	22.88	21.81
lb/hr	2.57	2.57	2.72	2.62
Formic Acid †				
ppmvd	<0.31	<0.31	<0.31	<0.31
lb/hr	<0.019	<0.019	<0.019	<0.019
2-Furaldehyde †				
ppmvd	<0.92	<0.92	<0.92	<0.92
lb/hr	<0.12	<0.12	<0.12	<0.12
Total Volatile Organic Compounds (VOC)				
lb/hr	<15.31	<15.18	<18.24	<16.24

* Process data was provided by POET Biorefining-Caro personnel.

† The "<" symbol indicates that the compound was below the Minimum Detection Limit (MDL) of the analytical method. See Section 4.2 for details.

5.0 Internal QA/QC Activities

5.1 QA/QC Audits

EPA Method 3A calibration audits were all within the measurement system performance specifications for the calibration drift checks, system calibration bias checks, and calibration error checks.

The EPA Method 320 performance parameters measured included signal to noise tests, noise equivalent absorbance (NEA), detector linearity, background spectra, potential interferents, and cell and system leakage. Quality assurance procedures included baseline measurement with ultra-high purity nitrogen, measurement of a calibration transfer standard (~100 ppm ethylene), direct analyte calibration measurements, and measurements to determine baseline shift. SF_6 was also used as a tracer gas in the calibration gases to evaluate dilution ratios and verify the sample delivery system integrity. A dynamic matrix spike was performed using SF_6 as a tracer gas. The method QA/QC criteria were met.

5.2 QA/QC Discussion

All QA/QC criteria were met during this test program.

5.3 Quality Statement

Montrose is qualified to conduct this test program and has established a quality management system that led to accreditation with ASTM Standard D7036-04 (Standard Practice for Competence of Air Emission Testing Bodies). Montrose participates in annual functional assessments for conformance with D7036-04 which are conducted by the American Association for Laboratory Accreditation (A2LA). All testing performed by Montrose is supervised on site by at least one Qualified Individual (QI) as defined in D7036-04 Section 8.3.2. Data quality objectives for estimating measurement uncertainty within the documented limits in the test methods are met by using approved test protocols for each project as defined in D7036-04 Sections 7.2.1 and 12.10. Additional quality assurance information is included in the report appendices. The content of this report is modeled after the EPA Emission Measurement Center Guideline Document (GD-043).