

DEPARTMENT OF ENVIRONMENTAL QUALITY
AIR QUALITY DIVISION
ACTIVITY REPORT: Scheduled inspection

A403337998

FACILITY: The Dow Chemical Company U.S.A., Midland		SRN / ID: A4033
LOCATION: 1790 Building, MIDLAND		DISTRICT: Saginaw Bay
CITY: MIDLAND		COUNTY: MIDLAND
CONTACT: Kayla Peacock, Environmental Specialist		ACTIVITY DATE: 10/20/2016
STAFF: Kathy Brewer	COMPLIANCE STATUS: Compliance	SOURCE CLASS: MEGASITE
SUBJECT: EU94:DVB monomers EU95 tar incinerator IR camera		
RESOLVED COMPLAINTS:		

EU94 and EU95

Dow Chemical Contact: Kayla Peacock

Attachments:

Safety Overview

DVB plant chemistry

January 2015 and January 2016 12 month rolling average for Particulate, SO₂, NO_x, and VOC emissions and associated monthly records.

List of process activities with tracked emissions

Storage tank emission calculation input elements example

Tar flow rate January and June 2016

Flue gas O₂ content for January 2015 and October 19, 2016

AQD records review

Title V Annual and semi annual reports from January 2014 through December 2015

40 CFR Part 63 Subpart FFFF (MON)

40 CFR Part 63 Subpart EEEE

40 CFR Part 63 Subpart H

PTI# 1311-90C File information

DESCRIPTION

The divinylbenzene (DVB) process (EU94) is in the specialty monomers manufacturing block with process cracker furnaces G and H, reactors, distillation/fractionation columns, separators, storage tanks/silos and related equipment. Cracker furnaces G and H burn both natural gas and process vent gas and have a heat input capacity of 6.76 MM BTU/hr each.

EU95 is the tar incinerator in the specialty monomers block with storage tanks/silos and related equipment. The tar incinerator is comprised of two series boilers each sized at 24 MM BTU/hr heat input. Each boiler is fired by natural gas and by-product fuel. By-product fuel is a blend of distillation residues (i.e., process tars).

The DVB process (EU94) and the Tar incinerator (EU95) were inspected together.

The DVB process is subject to the MON (40 CFR Part 63, Subpart FFFF) and OLD (40 CFR Part 63, Subpart EEEE). By virtue of being subject to Subpart FFFF, this emission unit is also subject to the equipment leak provisions of 40 CFR Part 63, Subpart H. The DVB process also has a storage tank (V-401) subject to the requirements of 40 CFR Part 60, Subpart Kb.

An aerial of the process area and a flow diagram are attached.

An infrared camera was used during the inspection and detected no leaking components. Areas where IR camera video was recorded include the Cracker G tank and distribution, solvent 578 distillate transfer line, accumulator 330 column and overhead pipelines, pre-330 crude DVB tanks, tank V-434 and solvent tank 578.

EU94-S1

This emission unit was permitted most recently in PTI 1311-90C. The following description is based on AQD Permit file and inspection information:

The DVB process is a high temperature reaction that removes hydrogen from the side chains of a monomer (cracking). DVB is received by rail and stored in raw material storage tank V401 which has a vapor balance system. The process has two independent reactors and cracking furnaces, G and H. The reaction uses steam as a diluent

and produces hydrogen gas as a byproduct. The monomer and steam are pre-mixed in an atomizer and pre-heated. The mixture is then passed over a catalyst. The cracking operation is done as a continuous run. Cracker operating temperatures are approximately 600 C.

The reactor effluent is quenched in a two stage process using quench water. A settling tank is used to separate the mixture of crude product and raw materials from water. The water is purged and stripped before being sent to Dow's WWT. Uncondensed gases from the reaction are compressed and sent back to the crackers to recover their fuel value.

The crude product is processed in a series of vacuum distillation towers. The primary tower removes lights from the product mix. The secondary tower removes excess monomer and sets the final product quality. The final tower separates the finished product from the remaining heavies. The heavies are collected, stored, and later combusted in a THROX burner (EU95 "Tar Incinerator") where steam is generated and recovered. All columns have side streams of inhibitor introduced into them to reduce monomer reaction and/or polymerization.

Process vents are collected and sent to carbon beds as a primary control device (V-281A & V-281B). When H-cracker is in operation the carbon beds vent to the cracker furnace combustion chamber, otherwise the carbon beds vent directly to the atmosphere.

EMISSION LIMITS

The following limits apply to the emissions from either carbon bed adsorber V-281A or V-281B through SV94001.

Pollutant	Limit	Time Period/ Operating Scenario	Monitoring/ Testing Method	On site emission records reviewed
1. VOC	1.9 tpy ¹	12-month rolling time period as determined at the end of each calendar month	SC VI.2 (carbon bed temperatures), VI.3 (emission calculations)	Jan 2016 June2016 Oct 20, 2016
2. Benzene	579 ppy ¹	12-month rolling time period as determined at the end of each calendar month	SC VI.2 (carbon bed temperatures), VI.3 (emission calculations)	Jan 2015 Jan 2016 June2016
3. Ethylvinylbenzene	429 ppy ¹	12-month rolling time period as determined at the end of each calendar month	SC VI.2 (carbon bed temperatures), VI.3 (emission calculations)	Jan 2015 Jan 2016 June2016

MATERIAL LIMITS

There are no material limit requirements specific to EU94 in the Special Conditions of the ROP.

PROCESS OPERATIONAL RESTRICTION

The permittee requires that EU94-S1 shall comply with the requirements of 40 CFR Part 60, Subpart Kb for raw material storage tank V 401. Raw material storage tank V401 has a vapor balance system and emissions are vented to a control device that reduces inlet VOCs by at least 95%.

DESIGN/EQUIPMENT PARAMETERS

The permittee requires that the portions of EU94-S1 that vent to the Dow Sorbathene adsorber are only operated if the Dow Sorbathene adsorber is installed, maintained, and operated in a satisfactory manner.

Satisfactory operation includes, but is not limited to, maintaining a carbon bed operating temperature (top section) of less than 50°C in either carbon bed adsorber V-281A or V-281B (whichever is receiving process exhaust). A partial review of site records indicate the process was complying with this condition.

Carbon bed	Limit	Jan 2015 range of operating temperatures	Jan 2016 range of operating temperatures	June 2016 range of operating temperatures	Oct 20 2016 range of operating temperatures
V281A	<50C	< 5 C	< 20 C	<40 C	< 25 C
V281B	<50C			<40 C	< 25 C

TESTING/SAMPLING

There are no testing requirements specific to EU94 in the Special Conditions of the ROP.

MONITORING/RECORDKEEPING

The permittee requires that a device to monitor and record the temperature of the top section of either carbon bed adsorber V-281A or V-281B (whichever is receiving process exhaust) shall be installed, calibrated, maintained and operated in a satisfactory manner on a continuous basis.

On site record and process equipment review indicate the process is in compliance with this condition.

The permit also requires the emissions to be calculated and recorded to demonstrate compliance with the 12 month rolling time period limits in Special Condition I. Emission calculations are based on activity generated emissions including raw materials recycle streams, filling tank losses, breathing losses, purging, device temperatures, and hours of operation. The process activities tracked for emissions and an example of how emissions from storage tanks would be evaluated is attached.

On site review of records from January 2015, January 2016 and June 2016 indicate emissions were within permitted limits and required records were maintained

REPORTING

A review of 40 CFR Part 63 periodic reports found the following:

Jan – June 2016 Subpart FFFF No Deviations

12 valves monitored, no leaks; 15 difficult to monitor reported; 3 pumps monitored, no leaks

No SSMPs of Malfunctions w/potential or actual excess emissions

Updated Section VIII with component counts for valves and pumps

No change in method of compliance

A review of 40 CFR Part 63 NOCSR updates found the following:

Updated continuous process vents HAP emission analysis results. All are Group 2.

H Cracker and G Cracker vent gas listed as exempt. The gas stream goes to a fuel gas system

All storage tanks are existing Group 2

34 exempt tanks, vessels, & recovery are listed

Railcar & truck transfer racks are listed as Group 2

Steam stripper discharge to the WWTP is a Group 2 wastewater

(4) exempt process wastewaters and (2) exempt maintenance wastewaters are listed.

(33) exempt heat exchange systems are listed

STACK/VENT RESTRICTIONS

The following stacks/vents information was reviewed during the inspection.

Stack & Vent ID	Maximum Exhaust Dimensions (inches)	Minimum Height Above Ground (feet)	Description
1. SV94001	6 ¹	50 ¹	PSA
1. SV94002	37 ¹	60 ¹	G cracker
2. SV94003	30 ¹	103 ¹	H cracker
3. SV94004	6 ¹	28 ¹	North Tank Storage (model as one vent but actually 4 tanks)
4. SV94005	4 ¹	1 ¹	West tank farm(final product storage tank, modeled as one but are eight tanks)

Stack & Vent ID	Maximum Exhaust Dimensions (inches)	Minimum Height Above Ground (feet)	Description
5. S, SV94006	2 ¹	20 ¹	Diethylbenzene tank for start up & shutdown
6. SV94007	4 ¹	1 ¹	Process day tanks for product or intermediate
7. SV94008	18 ¹	18 ¹	HVAC worker health & safety vent for drum loading area
8. SV94009	24 ¹	9.8 ¹	Manway on tank trucks in Truck Tanker loading area (not a stationary point)
9. SV94010	3 ¹	21 ¹	Product storage
10. SV94011	2 ¹	0.03 ¹	Makeup tanks, inhibitor storage

EU95

The heavies from distillation towers are collected, stored, and combusted in two 24 MM BTU/hr boilers in series (THROX burner/EU95 "Tar Incinerator") where steam is generated and recovered. The boilers are equipped with low NOx burner technology and low excess air firing for NOx control.

This emission unit was permitted in PTI 694-88A.

Changes made in the definition of 40 CFR Part 60 Subpart DDDD (CISWI) to no longer exempt waste heat recovery units will require the emission unit to achieve final compliance with the Subpart DDDD by February 7, 2018.

EMISSION LIMITS

The following limits apply to the emissions from either boiler through SV95008.

Pollutant	Limit	Time Period/ Operating Scenario	Monitoring/ Testing Method	On Site record review
1. Particulate Matter (PM)	0.8 pph ²	Test protocol	SC VI.1 (% O ₂ gen)	Jan 2015, Jan 2016, June 2016
2. PM	3.36 tpy ²	12-month rolling time period as determined at the end of each calendar month	SC VI.2 (emission calculations)	Jan 2015, Jan 2016, June 2016
3. Sulfur Dioxide (SO ₂)	0.61 pph ²	Test protocol	SC IX.1(fuel sulfur content)	Mar 2015, Mar 2016, June 2016
4. SO ₂	2.67 tpy ²	12-month rolling time period as determined at the end of each calendar month	SC VI.2 (emission calculations)	Mar 2015, Mar 2016, June 2016
5. Nitrogen Dioxide (NO ₂) [*]	1.3 lbs/MMBTU heat input ²	Test protocol	SC VI.1 (% O ₂ gen)	Jan 2015, Jan 2016, June 2016
6. NO ₂ [*]	23 pph ²	Test protocol	SC VI.1 (% O ₂ gen)	Jan 2015, Jan 2016, June 2016
5. NO ₂ [*]	87 tpy ²	12-month rolling time period as determined at the end of each calendar month	SC VI.2 (emission calculations)	Jan 2015, Jan 2016, June 2016
8. VOC ^{**}	0.0023 lb/MMBTU heat input ²	Test protocol	SC VI.1 (% O ₂ gen)	Jan 2015, Jan 2016, June 2016

Pollutant	Limit	Time Period/ Operating Scenario	Monitoring/ Testing Method	On Site record review
9. VOC**	0.16 pph ²	Test protocol	SC VI.1 (% O ₂ gen)	Jan 2015, Jan 2016, June 2016
10. VOC**	0.058 tons/month ²	12-month rolling time period as determined at the end of each calendar month	SC VI.2 (emission calculations)	Jan 2015, Jan 2016, June 2016

MATERIAL LIMITS

No material limits are required by the ROP conditions.

PROCESS/OPERATIONAL RESTRICTIONS

The permit requires corrective action if the exhaust gas O₂ % from the incinerator is less than 1.5% or greater than 16%. Records review found the following:

	Limit	Jan 2015	Jan 2016	June 2016	Oct 20 2016
Throx Flue gas O ₂ %	<1.5 % or >16%	>2.5 and <7.5	>5% and <15%	>5% and <15%	>5% and <10%

During the inspection the instantaneous read out for the Throx % Oxygen was 8% at 12:22 PM.

The tar flow is reduced and stopped if necessary if O₂ levels rise above 7%. Incinerator process monitoring has periods above 7% but below 16% during low or no flow tar conditions followed by resumption of tar flow when O₂ levels returned to less than 7%..

DESIGN/EQUIPMENT PARAMETERS

No design/equipment parameters are required by the ROP.

TESTING/SAMPLING

No testing or sampling requirements are required by the ROP conditions

MONITORING/RECORDKEEPING

The permittee is required to monitor and record, on a continuous basis, the oxygen content in the exhaust gas stack from the incinerator. All %oxygen records reviewed indicate required monitoring and recordkeeping has been performed.

The permit also requires the emissions to be calculated and recorded to demonstrate compliance with the 12 month rolling time period limits in Special Condition I. Emission calculations are based on activity generated emissions including tank losses, device temperatures, and hours of operation. The process activities tracked for calculating emissions is attached.

On site review of records from January 2015, January 2016 and June 2016 indicate emissions were within permitted limits and required records were maintained

REPORTING

A review of annual and semi annual deviation reports found the following:

2014 reported emissions were corrected and submitted to MDEQ on October 30, 2015 after an audit of the sites emission reporting calculations did match the facility reasonable inquiry calculations used to demonstrate compliance.

STACK/VENT RESTRICTION

The exhaust gases from the stacks listed in the table below were discharged unobstructed vertically upwards to the ambient air.

Stack & Vent ID	Maximum Exhaust Dimensions (inches)	Minimum Height Above Ground (feet)	
1. SV95008	35 ²	40 ²	THROX

OTHER REQUIREMENTS

The permit requires that a copy of the sulfur content of natural gas for each specific contract shall be made available to the AQD upon request. I reviewed the vendor provided natural gas analysis for 2015 and 2016. The sulfur dioxide emission limits are based on the use of natural gas with a maximum sulfur content of 5.5 grains per 100 standard cubic feet. The total sulfur reported was 11.8 ppm for 2015 and 12.7 ppm for 2016 resulting less than 0.008 grains per cubic feet for each year based on my calculations.

NAME 

DATE 3/3/17

SUPERVISOR 