Volatile Organic Compound Emissions Results from DCU Depressurization Vent Testing

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2009 Galveston Safety Seminar

Coking.com

Outline

- Why was DCU Vent testing performed?
- What data was collected?
- Is DCU Vent testing required by US EPA?
- What resources are needed to perform DCU Vent testing?

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Glossary

- **Volatile organic compound (VOC)** – any compound of carbon which participates in atmospheric photochemical reactions; generally considered to have boiling points <100°C
- **Non-methane, non-ethane volatile organic compounds (NMNE VOC)** – a subset of total VOCs excluding methane and ethane
- **Total hydrocarbons (THC)** – organic compounds made up primarily of carbon and hydrogen, categorized here as volatile or gaseous alkanes, alkenes and aromatics
- **Flame Ionization Detector (FID)** – analytical device used to quantify hydrocarbon concentrations in a sample of gas
- **Gas chromatograph (GC)** – analytical device used to separate a mixture of analytes in a sample of gas
- **Reference Method (RM)** – sampling and analytical methodology approved by US EPA or other regulatory agency
- **Mass Emission Rate (MER)** – the emission rate of a pollutant on a mass per unit time basis
- **DCU Vent** – piping used to depressurize a DCU coke drum to atmosphere prior to the de-heading and coke-cutting processes
- **DCU Venting cycle** – the release of gas from a DCU Vent to atmosphere
- **Petroleum Refinery Initiative (PRI)** – US EPA's strategy to improve environmental compliance at refineries and reduce SO_2, NO_X and VOC emissions, begun in 2005
- **New Source Performance Standards (NSPS)** – A category of US EPA regulations, under authority of the Clean Air Act (CAA), used to attain and maintain ambient air quality standards by ensuring that the best demonstrated emission control technologies (BDT) are implemented as the industrial infrastructure is modernized, while taking into account the costs to achieve emissions reductions, non-air quality health and safety impacts and energy requirements

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Acronyms

- **ppmv** – parts per million by volume
- **ppmvw** – parts per million by volume on a wet basis, the concentration of an analyte in a sample of gas
- **ppmvd** – parts per million by volume on a dry basis, the concentration of an analyte in only the dry fraction of a sample of gas
- **lbs/hr** – mass emission rate as pounds per hour
- **lbs/cycle** – mass emission rate as pounds per DCU Venting Cycle
- **tpy** – mass emission rate as tons per year
- **scf** – volume as a cubic foot of gas corrected to standard conditions (68°F/29.92" Hg)
- **scfm** – volumetric flow rate as a cubic foot of gas per minute, corrected to standard conditions
- **psig** – pressure as pounds per square inch gauge

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Why is this data relevant?

- VOCs can contribute to the formation of ground-level ozone (smog) and some specific compounds are toxic or carcinogenic
- Most refiners, regulatory agencies and the public have assumed that emissions of VOCs from DCU Vents are negligible
- DCU Vents are **extremely difficult** sources to test, emitting gas consisting almost entirely of steam at velocities of over 400 miles per hour
- Very few quantitative tests have been performed on DCU Vent emissions, and only since 2003
- These results are from the most comprehensive test program ever performed on a DCU Vent
- NSPS Subpart Ja, which includes US EPA's first regulation addressing DCU Vent emissions of SO_2 and VOCs, was promulgated in June 2008

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Hovensa 4-Coke Drum DCU – Key Parameters

- Coke Drums Tested = 1
- DCU Venting Cycles Tested = 4 (Test Runs 1-4)
- Initial Coke Drum Pressure = 7-9 psig
- DCU Venting Cycle Durations = 142-258 minutes
- Average Total Cycle Duration = 40 hours
- Average Coke Produced per Batch = 1,676 tons

Batch Process Parameters	Average Duration
	(h:min)
Steam Out to Fractionator	0:19
Steam Out to Blowdown	0:52
Quench Water	4:43
Soak	1:00
Vent and Drain	6:45
Coke Cutting	3:00

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NMNE VOC Mass Emission Rates (lbs/cycle)

	Benzene MER (lbs/cycle)	Toluene MER (lbs/cycle)	NMNE VOC MER (lbs/cycle)
Test Run 1	<17.3	<19.8	165
Test Run 2	<10.6	<13.7	354
Test Run 3	<6.90	<7.89	73.4
Test Run 4	<9.03	<10.5	120
Average	**<11.0**	**<13.0**	**178**

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NMNE VOC Mass Emission Rates (tons/year)

-Based on **219** DCU Venting Cycles per Year
-**78.0** tpy NMNE VOC per 4-Coke Drum DCU

	Benzene MER (tpy)	Toluene MER (tpy)	NMNE VOC MER (tpy)
Test Run 1	<1.89	<2.17	18.1
Test Run 2	<1.17	<1.50	38.7
Test Run 3	<0.756	<0.864	8.04
Test Run 4	<0.989	<1.15	13.2
Average	**<1.20**	**<1.42**	**19.5**

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NMNE VOC Emissions In Detail

- Sample gas was diluted 30:1 and routed to two FIDs to quantify total hydrocarbon concentrations continuously
- A portion of the diluted sample gas was collected in several Tedlar bags
- The Tedlar bag samples were analyzed for methane, ethane, benzene and toluene concentrations using a GC/FID
- The total duration of each DCU Venting Cycle was separated into three 'Venting Cycle Intervals' for the interpretation of the data
- The concentrations of methane and ethane were subtracted from the concentration of total hydrocarbons during each of the three Venting Cycle Intervals during each DCU Venting Cycle
- The resulting concentrations of pollutant emissions are referred to as NMNE VOCs
- Modified EPA-approved Reference Methods were used for all NMNE VOC sampling and analyses

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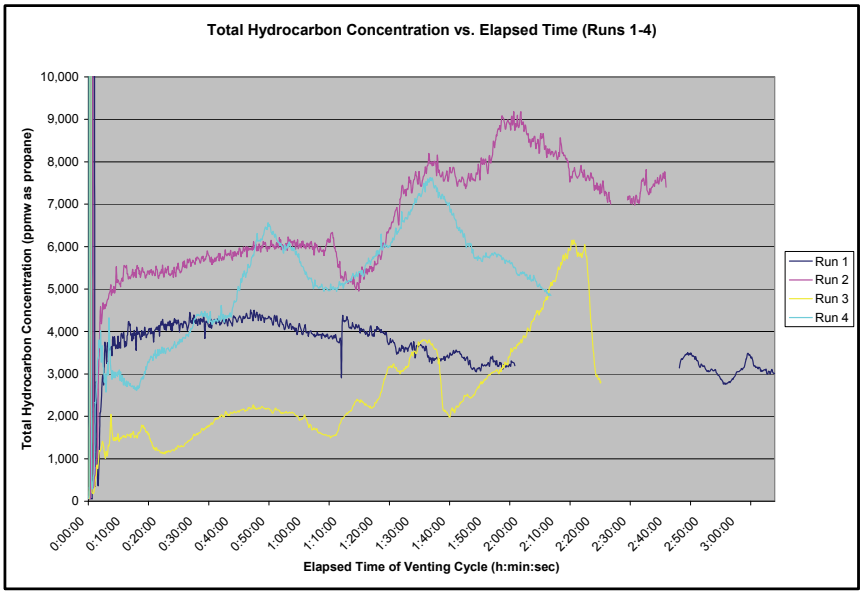

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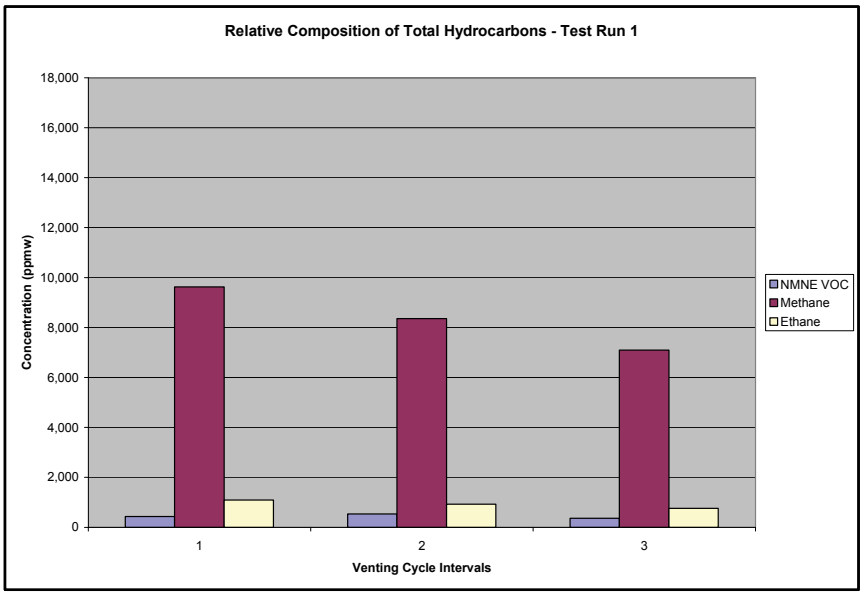
Relative Composition of Total Hydrocarbons - Test Run 1
Concentration (ppmw)
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
1
2
3
Venting Cycle Intervals
NMNE VOC
Methane
Ethane

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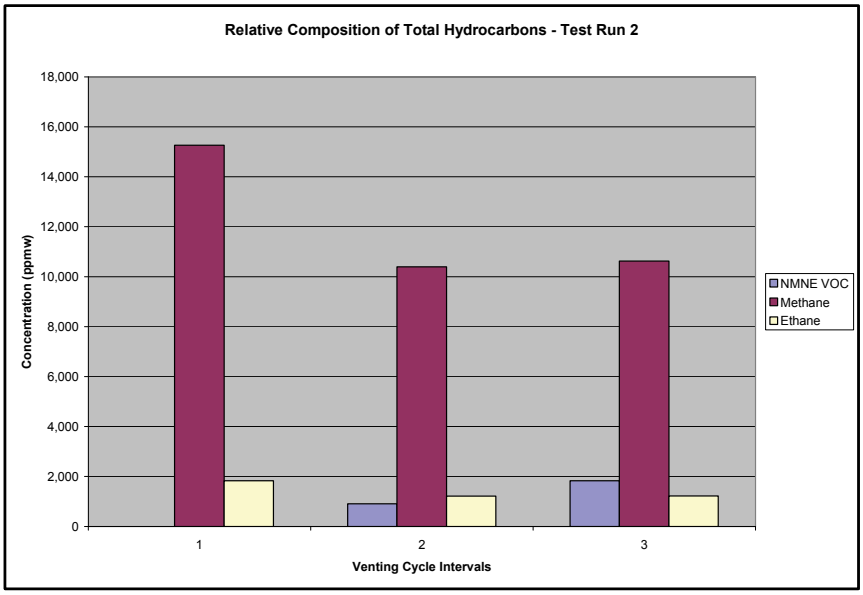
Relative Composition of Total Hydrocarbons - Test Run 2
Concentration (ppmw)
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
1
2
3
Venting Cycle Intervals
NMNE VOC
Methane
Ethane

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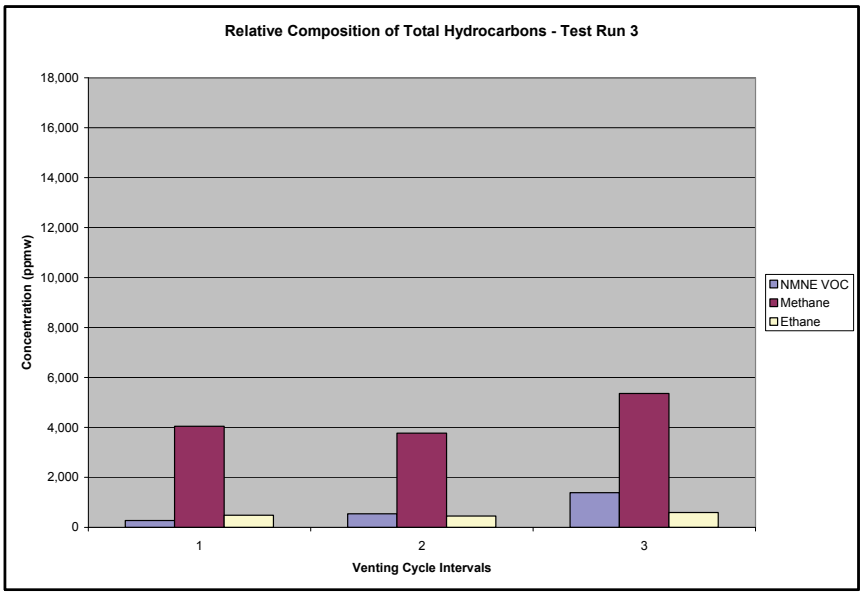
Relative Composition of Total Hydrocarbons - Test Run 3
Concentration (ppmw)
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
1
2
3
Venting Cycle Intervals
NMNE VOC
Methane
Ethane

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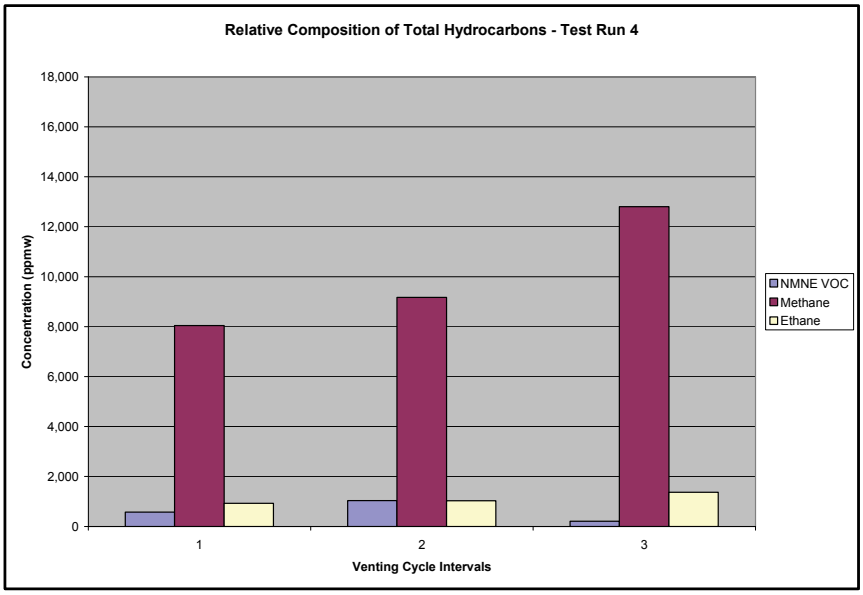
Relative Composition of Total Hydrocarbons - Test Run 4
Concentration (ppmw)
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
1
2
3
Venting Cycle Intervals
NMNE VOC
Methane
Ethane

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What is NSPS Subpart Ja?

- Authorized under Clean Air Act
- Required to be periodically reviewed and revised by US EPA
- Attain and maintain ambient air quality standards for specific pollutants by implementing best demonstrated emission control technologies (BDT)
- Should include cost/benefit analyses for emission reductions
- May include emissions limits and/or work practice standards
- **Subpart J**: Petroleum Refinery process units since June 11, 1973
- **Subpart Ja**: Petroleum Refinery process units since May 14, 2007

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What is the new DCU work practice standard in Subpart Ja?

- **40 CFR 60.103(c):** "*Each owner or operator of a delayed coking unit shall depressurize to 5 lb per square inch gauge (psig) during reactor vessel depressurizing and vent the exhaust gases to the fuel gas system for combustion in a fuel gas combustion device.*"

- Imposed to reduce VOC and SO_2 emissions from DCUs
- Based on US EPA's estimate of VOC and SO_2 emissions from either **2 new** DCUs or **3 modified or reconstructed** DCUs that would be subject to the rule within 5 years
- US EPA assumed **1** of the 3 modified or reconstructed DCUs would have to install a new fuel gas compressor to allow 5 psig depressurization
- Estimated baseline emissions of **3.5 tpy** VOC and **250 tpy** SO_2 per 2-Coke Drum DCU
- Cost of emissions reductions by requiring this work practice standard?
- New DCU: $1,300 per ton combined VOC/SO_2
- Modified or Reconstructed DCU: $5,100 per ton combined VOC/SO_2

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3.5 tpy VOC (US EPA) vs. 39.0 tpy VOC (URS)?

- Estimated emissions vs. direct measurement of emissions
- US EPA used DCU Vent emissions data from test programs performed by SCAQMD in 2003
- SCAQMD admitted in test reports that this data was biased low
- Inaccurate estimate of volumetric flow rate of DCU Vent gas
- US EPA assumed that the volume of gas emitted through a DCU Vent could be no greater than the internal volume of an empty coke drum, corrected to a nominal pressure between 0 and 15 psig
- US EPA's "average" volume of an empty coke drum = 34,400 cf
- US EPA's "average" volume of gas released from a coke drum pressurized to 15 psig = 69,400 scf
- URS' direct, semi-continuous measurement of average volumetric flow rate = 2,220,000 scf

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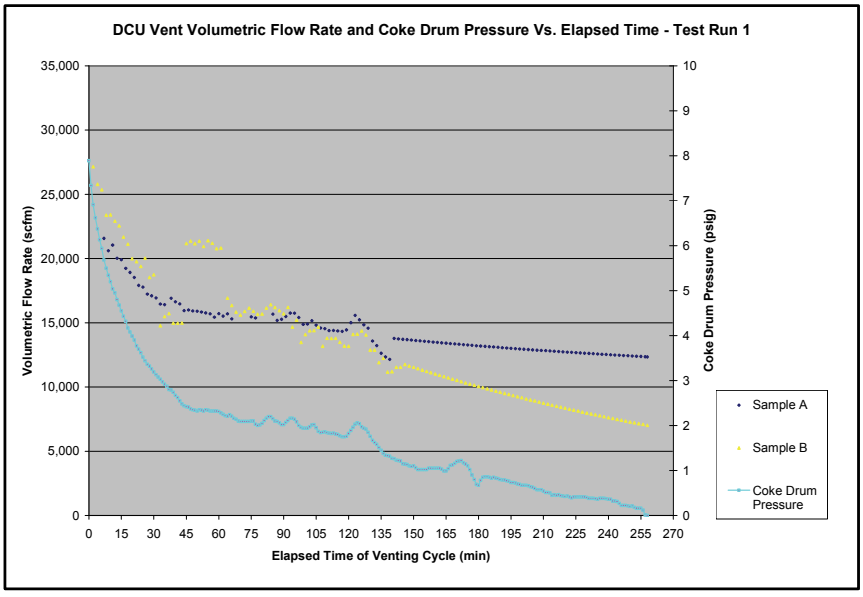

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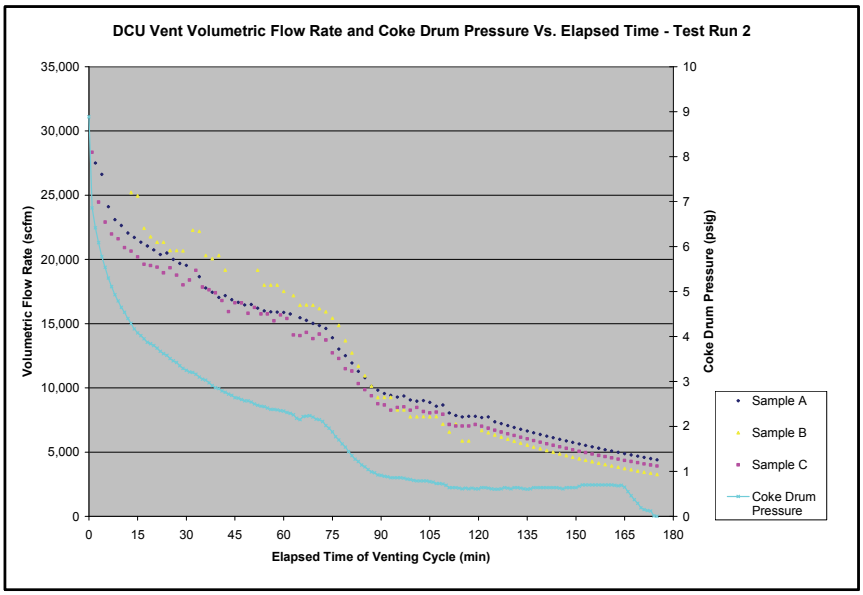
DCU Vent Volumetric Flow Rate and Coke Drum Pressure Vs. Elapsed Time - Test Run 2
Volumetric Flow Rate (scfm)
Coke Drum Pressure (psig)
Elapsed Time of Venting Cycle (min)
Sample A
Sample B
Sample C
Coke Drum Pressure

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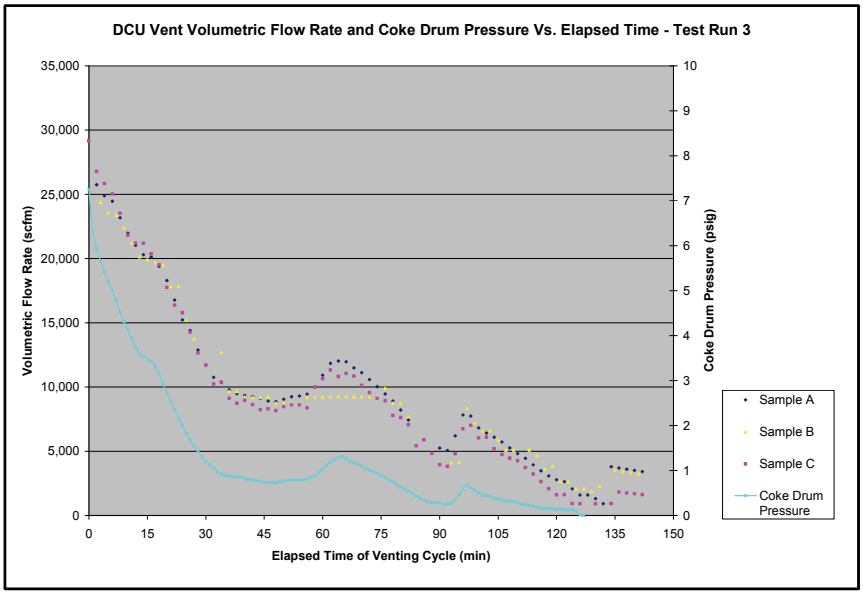
DCU Vent Volumetric Flow Rate and Coke Drum Pressure Vs. Elapsed Time - Test Run 3
Volumetric Flow Rate (scfm)
Coke Drum Pressure (psig)
Elapsed Time of Venting Cycle (min)
Sample A
Sample B
Sample C
Coke Drum Pressure

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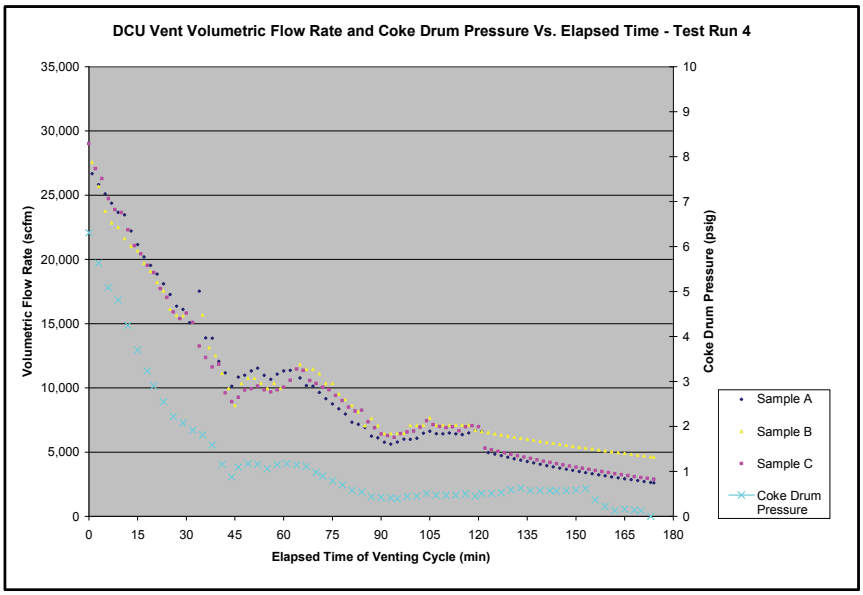

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Is DCU Vent Emissions Testing Required?

- *Not yet*
- NSPS Subparts J and Ja do not require refiners to perform emissions testing on DCU Vents or for DCU Vent emissions to comply with any limit

-However-

- US EPA has demonstrated interest in DCU Vent emissions
- One goal of US EPA's Petroleum Refinery Initiative is to reduce VOC emissions through settlement or filed civil action
- Some refiners have received specific requests from US EPA to perform DCU Vent testing, citing the authority of the Clean Air Act
- Hovensa voluntarily submitted their test report to US EPA in September 2008
- At least **2** refiner's operating permits (issued at the state level) for specific DCUs require at least annual testing for particulate matter, NMNE VOCs and H_2S emissions
- Operating permits are periodically reviewed and renewed and should include accurate emissions data

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Resources Needed for DCU Vent Emissions Testing

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At least two 4-inch Sampling Ports with Gate Valves

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Extensive Scaffolding with Easy Access

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Sufficient Space for Operating Complex Testing Equipment

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Sufficient Electrical Resources Near DCU Vent

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Sufficient Ventilated Laboratory Space for Sample Recovery

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An Experienced Contractor

- Performed 16 DCU Vent emissions tests since 2006
- Tested DCU Vents in Texas, Louisiana, California and USVI
- Experienced quantifying NMNE VOCs, SVOCs, H_2S, total reduced sulfur, CO and particulate matter emissions from DCU Vents
- DCU Vents cannot be tested using any current US EPA-approved Reference Methods without **extensive** technical modifications

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