

Refinery Emission Overview



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A presentation for the Taiwan EPA delegation

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Emission Pollutants

- VOC
- NO_x
- SO_x
- PM₁₀
- CO
- NH₃
- HAPs

Emission Source Types

- Point Source
 - Exhaust stacks, process vents
- Volume Source
 - Storage tanks, fugitive components
- Area Source
 - Coke handling

Refinery Processes

- Heater
- Process Equipment
- FCCU
- Hydrogen Plant
- Sulfur Recovery Plant
- Storage Tank

Refinery Processes (cont.)

- Wastewater Treatment
- Delayed Coking Unit
- Flare
- Loading Rack
- Process Turnaround
- Tank Degassing

Emission Factors

- Default Factors
 - AP-42
 - AER
- Rule Limits
 - AQMD
 - Federal
- BACT
 - Achieved in Practice
 - Technologically Feasible
- Manufacturer Guarantee

Heater

- Stack Emissions: NO_x, SO_x, PM₁₀, CO, VOC
- SCR: NH₃
- CEMS for NO_x and SO_x
- Source Test for PM₁₀, CO, VOC, and NH₃

Heater (cont.)

- NOx 7 ppmv
- SOx 40 ppmv S content
- PM₁₀ 7.5 lbs/mmscf
- CO 50 ppmv
- VOC 7.0 lbs/mmscf
- NH₃ 5 ppmv

Process Equipment

- Fugitive VOC Emission
 - Rule 1173: 500 ppmv as CH₄
 - Component Counts
 - Correlation Equations (lb/hr)
- HAP Emissions: BTEX, C₆H₁₄, others
- PRV Releases
 - Release Time Duration
 - Pressure and Temperature

Process Equipment (cont.)

Correlation Equations, lb/hr

Valves	$5.00E-06(SV)^{0.747}$
Pump seals	$1.12E-04(SV)^{0.622}$
Others	$1.92E-05(SV)^{0.642}$
Connectors	$3.37E-06(SV)^{0.736}$
Flanges	$9.92E-06(SV)^{0.706}$
Open-ended lines	$4.19E-06(SV)^{0.724}$

SV = screening value, ppm

Process Equipment (cont.)

PRD Equation for Gas Service

$$W_v = \frac{(ACK_r K_s K_o)(P^{1.47})}{3600 \sqrt{\frac{(T+460)Z}{M}}}$$

$$W_{voc} = W_s * VOC * \eta$$

$$W_{rvoc} = \sum W_{voc}$$

Where:

A = Relief Valve Orifice Size, sq in

$$C = \text{Sizing Coefficient} = 520 \sqrt{k \left(\frac{2}{k+1} \right)^{\frac{k+1}{k-1}}}$$

Process Equipment (cont.)

$k = C_p/C_v$ = Specific Heat Ratio for the released gas
 K_d = Effective Coefficient of Discharge (use $K_d = 0.975$ in absence of manufacturer's PRD specific data)
 K_b = Capacity Correction Factor
 K_c = Combination Correction Factor. ($K_c = 1$ if no rupture disk; $K_c = 0.9$ if rupture disk)
 M = Molecular Weight of the released gas
 P = Pressure (psig), as measured with Process Pressure Monitoring System
 T = Temperature (°F)
 t = Recorded Duration of Release in Seconds by Electronic Monitoring Device
 VOC = weight percent VOC in the released gas
 W_s = Flow through the PRD, lb/sec
 W_{VOC} = Flow of VOCs through the PRD
 W_{TVOC} = Total VOC Released during the Event, lbs
 Z = Compressibility Factor

Process Equipment (cont.)

PRD Equation for Liquid Service

$$Q = 0.63AK_dK_bK_c\sqrt{\frac{P}{G}}$$

$$M = Q^*8.34^*G^*t$$

Q = flow rate, gal/sec
 K_d = Rated Coefficient of Discharge (use $K_d = 0.65$ in absence of manufacturer's PRD specific data)
 K_b = Capacity Correction Factor ($K_b = 1$ for atmospheric back pressure)
 K_c = Correction Factor due to Viscosity (assume = 1)
 P = Pressure (psig), as measured with Process Pressure Monitoring System
 G = Specific Gravity of the liquid at flowing temperature
 M = Release per Event, lbs
 t = Recorded Duration of Release in Seconds by Electronic Monitoring Device

American Petroleum Institute 520 (1993) Sizing, Selection and Installation of Pressure Relieving Devices in Refineries, Part I: Sizing and Selection, 6th Ed.

FCCU

- Stack Emissions
- Rule 1105.1
 - Filterable PM_{10} - 0.005 gr/dscf
 - NH_3 - 10 ppmv
- CEMS for NO_x , SO_x , CO, and Opacity
- Annual Test for PM_{10} , VOC, and NH_3
- Fugitive Emissions

FCCU (cont.)

- 40CFR60 Subpart J/Ja and 40CFR63 Subpart UUU
 - CO - 500 ppmv (1-hr avg.)
 - PM - 1 kg/Mg of coke burn & Opacity - 30%;
Ja only - 0.5 kg/Mg of coke burn (new unit);
UUU - Optional Ni limits.
 - SO_2 (J & UUU) - 50 ppmv (or 90% control)(unit with add-on control); or 9.8 kg/Mg coke burn (unit w/o add-on control); or Feed Sulfur ≤ 0.3 wt%.
 - SO_2 (Ja) - 50 ppmv (7-day avg.) and 25 ppmv (365-day avg.)
 - NO_x (Ja) - 80 ppmv (7-day rolling avg.)

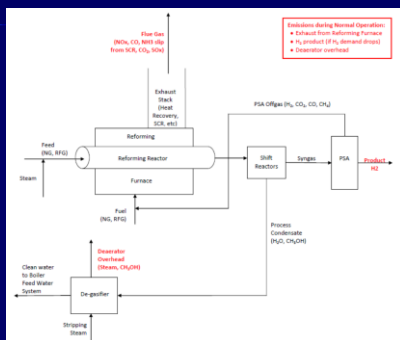
FCCU (cont.)

- EPA Consent Decrees
 - Similar CO, PM and SO₂ Limits
 - Lower NO_x Limits for Some FCCUs:
40 ppmv (7-day avg.) and 20 ppmv (365-day avg.)

Hydrogen Plant

- Exhaust Stack Emissions
- Process Vents
- Rule 1189: VOC - 2.5 lbs/10⁶scf H₂
- Annual Test for VOC
- Fugitive Emissions

Hydrogen Plant (cont.)



Sulfur Recovery Plant

- Stack Emissions (SO₂, H₂S, S)
- Sulfur Pit Vent
- Rule 468:
 - 500 ppm S
 - 10 ppm H₂S
- CEMS for SO₂ or S and H₂S

Sulfur Recovery Plant (cont.)

- 40CFR60 Subpart J/Ja and 40CFR63 Subpart UUU
 - 250 ppmv SO₂ for SRUs with an oxidation system or reduction system with incineration
 - 300 ppmv S and 10 ppmv H₂S for SRUs with a reduction system w/o incineration
- BACT
 - 12 ppmv SO₂ (72-hr avg.)
 - 2.5 ppmv H₂S (24-hr avg.)

Storage Tank

- Rules 463 and 1178
- VOC Emission
 - Throughput
 - Vapor Pressure
 - Type of Tank: FR, IFR, EFR, DEFR
 - USEPA Program Tanks 4.0.9d
 - Volume source; point source; closed vent

Storage Tank (cont.)

TANKS 4.0.9d Emissions Report - Detail Format Tank Identification and Physical Characteristics

Identification			
User Identification:	94-76-0012 (Fuel Mod)		
City:	Wilmington		
State:	California		
Company:	Shuram		
Type of Tank:	External Floating Roof Tank		
Designation:	0066		
Tank Dimensions			
Diameter (ft):	127.50		
Volume (gallons):	4,200,000.00		
Turnover:	109.50		
Paint Characteristics			
Internal Shell Condition:	Light Rust		
Shell Color/Grade:	White/White		
Shell Condition:	Good		
Roof Characteristics			
Type:	Poricon		
Fitting Category:	Detail		
Tank Construction and Rim-Seal System			
Construction:	Welded		
Primary Seal:	Mechanical Shoe		
Secondary Seal:	Rim-mounted		
Deck Fittings/Status			Quantity
Access Hatch (24-in. Dia.)/Hatched Cover: Gas/Water			1
Venturi Breaker (15-in. Diam.)/Winged Mech. Actuation: Gas			2
Steam-Heated/Temp. Well (24-in. Diam.)/Winged Mech. Actuation: Gas			1
Roof Leg (3-in. Diameter)/Adjustable: Center Area: Sock			20
Roof Leg (3-in. Diameter)/Adjustable: Perimeter Area: Sock			22
Sloster Guide-Pole/Sample Well/Gask. Sliding Cover: w/ Float, Wiper			1

Wastewater Treatment

- Process Vent Emissions
- Rule 1176
 - 500 ppm as CH₄
 - Grab Sample
- BACT: 50 ppm
- Fugitive Emissions
- HAP Emissions: C₆H₆

Delayed Coking Unit

- Coke Drum Vent
 - 40CFR60 Subpart Ja: Vent gas to VRS until drum pressure reaches 5 psig
 - BACT: Vent gas to VRS until drum pressure reaches 2 psig
- Fugitive Emissions

Delayed Coking Unit (cont.)

- Coke Handling System (PM)
 - Rule 1158
 - 10% Opacity from Fugitive Dust
 - Coke piles and coke unloading occur in enclosed storage equipped with dust control such as water spray
 - Conveyor belts covered. Transfer points equipped with total enclosure, water spray, or venting to control equipment

Delayed Coking Unit (cont.)

- Coke Handling Emissions
 - PM emissions for each transfer point

$$E = k(0.0032) \frac{\left(\frac{U}{5}\right)^{1.3}}{\left(\frac{M}{2}\right)^{1.4}}$$

where:

E = emission factor (lb/ton)

k = particle size multiplier (dimensionless)

U = mean wind speed, (miles per hour)

M = material moisture content (%)

- 90% reduction

Flare

- Rule 1118
 - No Flaring except for SU, SD, T/A, Emergency, and EONs
- Monitor
 - Flow
 - HHV
 - Sulfur

Flare (cont.)

- EONS
 - Temporary Fuel Gas Imbalance
 - Incompatible Gas
 - Intermittent Minor Vent from Equipment
 - PRV releases
- Performance Target
 - 2010 : 0.7 ton SO₂/mm bbl of crude
 - 2012 : 0.5 ton SO₂/mm bbl of crude

Flare (cont.)

▪ Stack Emissions

Air Pollutant	Equation	Emission Factor
ROG	$E = V \times HHV \times EF$	0.063 lb/mmBtu
NO _x	$E = V \times HHV \times EF$	0.068 lb/mmBtu
CO	$E = V \times HHV \times EF$	0.37 lb/mmBtu
PM ₁₀	$E = V \times EF$	21 lb/mmscf
SO _x	$E = V \times Cs \times 0.1662$	

Where:
 E = Calculate vent gas emissions, lbs
 V = Volume flow of vent gas, scf
 HHV = Higher Heating Value, Btu/scf
 EF = Emission Factor
 Cs = The concentration of total sulfur in the vent gas, SO₂ ppmv

Loading Rack

▪ Uncontrolled VOC Emission

$$ER = 12.46 \frac{S \times P \times MW}{T}$$

Where:
 ER = Loading emission factor, lb/1000 gal
 S = Saturation Factor, 1.0
 P = Vapor pressure, psia
 MW = Molecular weight
 T = Temperature, °R

Loading Rack (cont.)

- Controlled VOC Emission
 - Rule 462: 0.08 lb/1000 gal
 - BACT: 0.02 lb/1000 gal
- Combustion Emissions
- Fugitive Emissions
- HAP Emissions

Tank Degassing

- Rule 1149: 500 ppm as CH₄
- Stack Emissions
- HAP Emissions

Process Turnaround

- Rule 1123
- Flare Emissions
- Atmospheric Releases
 - Depressurize any vessel containing VOC
 - Submit Plan

The End

