University of Mosul
College of Petroleum & Mining Engineering

Petroleum Pollution

Lecture …(3)….

Petroleum and Refining Engineering Department

Refinery Screening Range Emission Factors (For Nonmethane Organic Compound Emission Rates)

(The Light Liquid Pump Seal Factor Can Be Used to Predict the Leak Rate From Agitator Seals) (US EPA, 1995b)

Equipment Type	Service	≥10,000 ppmv Emission Factor (kg/h/source)	<10,000 ppmv Emission Factor (kg/h/source)
Valves	Gas	0.2626	6×10^{-4}
	Light liquid	0.0852	1.7×10^{-3}
	Heavy liquid	0.00023	2.3×10^{-4}
Pump seals	Light liquid	0.437	1.2×10^{-2}
	Heavy liquid	0.3885	1.35×10^{-2}
Compressor seals	Gas	1.608	8.94×10^{-2}
Pressure relief valves	Gas	1.691	4.47×10^{-2}
Connectors	All	0.0375	6×10^{-5}
Open-ended line	All	0.01195	1.5×10^{-3}

Example 2.1

At a refinery, assume there are 100 gas valves in a stream that, on average, contain 80 wt% nonmethane organic compounds, 10 wt% water vapor, 10 wt% methane, and no ethane (thus the TOC wt% would be 90). If the process operates 8000 h per year (h/year), what are the hourly and annual TOC and VOC emissions from the 100 gas valves?

Solution

The average hourly TOC emissions from the gas valves in the stream can be calculated using the applicable EF from Table 2.9 and Eq. (2.6):

$$E_{\mathrm{TOC}} = F_{\mathrm{A}} \times \left(\frac{\mathrm{WF}_{\mathrm{TOC}}}{\mathrm{WF}_{\mathrm{TOC}} - \mathrm{WF}_{\mathrm{methane}}}\right) \times \mathrm{WF}_{\mathrm{TOC}} \times N$$

$$= 0.0268 \times \left(\frac{0.9}{0.9 - 0.1}\right) \times 0.9 \times 100 = 2.71\ \mathrm{kg\ TOC/h}$$

The average annual TOC emissions from the gas valves in the stream can also be calculated as follows:

$$E_{\mathrm{TOC,\ annual}} = 2.71\ \mathrm{kg\ TOC/h} \times 8000\ \mathrm{h/year} = 21680\ \mathrm{kg\ TOC/year}$$

Table 2.7 Main Air Emissions and Their Sources in Refineries (US EPA, 1995c, 2004; Speight, 2005; European Commission and Joint Research Center, 2013)—cont'd

Air Emissions	Sources and/or Processes
Sulfur oxides (SO_x)	Process furnaces and boilers, fluidized catalytic cracking regenerators, CO boilers, sulfur recovery units, flare systems, incinerators, or in processes such as crude-oil desalting, atmospheric distillation, vacuum distillation, thermal cracking/visbreaking, coking, catalytic cracking, catalytic hydrocracking, hydrotreating/hydroprocessing, alkylation, isomerization, catalytic reforming, and propane deasphalting
Volatile organic compounds (VOCs)	Storage and handling facilities, as separation units, oil/water separation systems, fugitive emissions (valves, flanges, etc.), vents, flare systems
Fugitive hydrocarbons	Crude-oil desalting, atmospheric distillation, vacuum distillation, thermal cracking/visbreaking, coking, catalytic cracking, catalytic hydrocracking, hydrotreating/hydroprocessing, alkylation, isomerization, catalytic reforming, propane deasphalting, and wastewater treatment
Catalyst dust	Catalytic hydrocracking
HCl (potentially in light ends)	Isomerization
H_2S	From caustic washing in polymerization and wastewater treatment
NH_3	Wastewater treatment
Fugitive solvents	Solvent extraction and dewaxing
Fugitive propane	Propane deasphalting

Example 2.2

At an SOCMI process unit, assume there are 100 gas valves in a stream that, on average, contain 80 wt% nonmethane organic compounds, 10 wt% water vapor, 10 wt% methane, and no ethane (thus the TOC wt% would be 90). If the process operates 7900 h per year, what are the hourly and annual TOC emissions from the 100 gas valves?

Solution

The average hourly TOC emissions from the gas valves in the stream can be calculated using the applicable EF from Table 2.9 and Eq. (2.2):

$$E_{\text{TOC}} = F_{\text{A}} \times \text{WF}_{\text{TOC}} \times N = 0.00597 \times 0.9 \times 100 = 0.5373 \text{ kg TOC/h}$$

The average annual TOC emissions from the gas valves in the stream can also be calculated as follows:

$$E_{\text{TOC, annual}} = 0.5373 \text{ kg TOC/h} \times 7900 \text{ h/year} = 4244.67 \text{ kg TOC/year}$$

(US EPA, 1995b; RTI International, 2015).

Hourly TOC emissions for valves in gas service:

$$E_{\text{TOC}} = \left(\left[0.2626 \times \left(\frac{100}{100-3}\right) \times 3\right] + \left[0.0006 \times \left(\frac{100}{100-3}\right) \times 236\right]\right)$$
$$= 0.9581 \text{ kg TOC/h}$$

Hourly TOC emissions for valves in light liquid service:

$$E_{\text{TOC}} = \left(\left[0.0852 \times \left(\frac{100}{100-3}\right) \times 3\right] + \left[0.0017 \times \left(\frac{100}{100-3}\right) \times 293\right]\right)$$
$$= 0.7770 \text{ kg TOC/h}$$

Hourly TOC emissions for valves in heavy liquid service:

$$E_{\text{TOC}} = \left(\left[0.00023 \times \left(\frac{100}{100-3}\right) \times 0\right] + \left[0.00023 \times \left(\frac{100}{100-3}\right) \times 65\right]\right)$$
$$= 0.0154 \text{ kg TOC/h}$$

Thus the total hourly TOC emissions for all valves are $0.9581 + 0.7770 + 0.0154 = 1.7505$ kg TOC/h. The hourly VOC emissions from all valves can be calculated using Eq. (2.3):

$$E_{\text{VOC}} = E_{\text{TOC}} \times \left(\frac{\text{WF}_{\text{VOC}}}{\text{WF}_{\text{TOC}}}\right) = 1.7505 \times \left(\frac{96}{100}\right) = 1.6804 \text{ kg VOC/h}$$

Table 2.13 Number of Valves, the Screening Value, and Hourly TOC and VOC Emission Rates From the Valves in Example 2.4 (US EPA, 1995b; RTI International, 2015)

Number of Valves	Screening Value (ppmv)	Emissions (kg/h)	
		TOC	VOC
580	0	0.00452	0.00434
5	200	0.00012	0.00011
5	400	0.00020	0.00019
2	1,500	0.00054	0.00051
2	7,000	0.00169	0.00162
2	20,000	0.00370	0.00355
2	50,000	0.00733	0.00704
2	Pegged at 100,000	0.28000	0.26880
	Total	0.30	0.29

screening value of 0 ppmv. The pegged emission rate for the valves in Table 2.4 (0.140) is used to estimate the TOC emission rate for the two valves with pegged readings. The correlation equation for the valves in Table 2.4 ($2.29 \times 10^{-6}C^{0.746}$) is used to estimate the emissions for each of the valves with a measured screening value. In each case, the calculated TOC emissions are multiplied by $(100 - 4)/100$ to calculate the VOC emissions (US EPA, 1995b; RTI International, 2015).

Table 2.14 Major Water Pollutants and Their Sources in Refineries (CONCAWE, 1999; European Commission and Joint Research Center, 2013)

Water Pollutant	Sources
Oil	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain)
H_2S (RSH)	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, spent caustic
NH_3 (NH_4^+)	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, sanitary blocks
Phenols	Distillation units, visbreaking, catalytic cracking, spent caustic, ballast water
Organic chemicals (BOD, COD, TOC)	Distillation units, hydrotreating, visbreaking, catalytic cracking, hydrocracking, lube oil, spent caustic, ballast water, utilities (rain), sanitary blocks
CN^-(CNS^-)	Visbreaking, catalytic cracking, spent caustic, ballast water
TSS	Distillation units, hydrotreating, visbreaking, catalytic cracking, spent caustic, ballast water, sanitary blocks
Amines compounds	CO_2 removal in LNG plants

Table 2.15 **Details of Refinery and Petrochemical Wastewaters From Different References**

Parameters	Refinery and Petrochemical Wastewaters From Different References												
	Almasi et al. (2014)	Gasim et al. (2012)	Zhidong et al. (2009)	Xianling et al. (2005)	Nkwocha et al. (2013)	Coelho et al. (2006)	Dold (1989)	Ma and Guo (2009)	Khaing et al. (2010)	Amin et al. (2012)	Mohr et al. (1998)	Benyahia et al. (2006)	Shabir et al. (2013)
BOD (mg/L)	204	3378	90−188		138	570	150−350	150−350					685
SBOD (mg/L)	126												
COD (mg/L)	622	7896	72.1−296.1	250−613	350	850−1020	300−800	300−600	330−556	1200			1965
SCOD (mg/L)	495												
pH	7.9	8.48		7.80−8.79	8	8−8.2		7−9	7.5−10.3	6.7		9.25−10.8	8.31
T (°C)					39.7								
Oil & grease (mg/L)			20−87	35−55	14.75	12.7	3000	50	40−91		20,223	466−3428	1057
Ammonia (mg/L)	13.1	13.5	12.05−19.79	56−125		2.1−5.1		10−30	4.1−33.4	9.3		0.76−4.96	
Nitrate (mg/L)		2.23								9.3			
Total Kjeldahl nitrogen (TKN)		40.6											
Total phosphorus (mg/L)		10.2	0.82−2.96	<0.5	16.25					3.7			0.67
Total alkalinity (mg/L)		990											

[illegible] (mg/L)		[illegible]											
Turbidity (NTU)						22−52			10.5−159.4				
TSS (mg/L)	56		245−950	108−159	60		100	150	130−250			28.9−372	315
Volatile suspended solids (VSS) (mg/L)	44												
Total dissolved solids (TDS) (mg/L)					2100							3272	6267
Phenol (mg/L)	69.6				7.35	98−128	20−200					0.2	18.32
BTEX (mg/L)						23.9	1−100						
Volatile fatty acids (VFA) (mg/L)		198											
Heavy metals (mg/L)							0.1−100					0.01−11.7	4.3−6.48