University of Mosul
College of Petroleum & Mining Engineering

# Petroleum Pollution

Lecture …(4)….

Petroleum and Refining Engineering Department

# Air Emissions and Estimation

vapors as a result of tank vapor space breathing. Standing storage losses for these tanks can be predicted from the following equation:

$$L_S = 365 V_V W_V K_E K_S \qquad (2.14)$$

where 365 is the number of daily events in a year (year$^{-1}$), $V_V$ denotes the vapor space volume (ft$^3$), $W_W$ is the stock vapor density (lb/ft$^3$), $K_E$ is the vapor space expansion factor (dimensionless), and $K_S$ denotes the vented vapor saturation factor (dimensionless) (for more information about these parameters see US EPA, 2006).

The working loss refers to the loss of stock vapors as a result of tank filling or emptying operations. Working losses for these tanks can be predicted from the following equation:

$$L_S = 0.0010 M_V P_{VA} Q K_N K_P \qquad (2.15)$$

where $M_V$ is the vapor molecular weight (lb/lb-mole), $P_{VA}$ denotes the vapor pressure at daily average liquid-surface temperature (psia), $Q$ depicts the annual net throughput [tank capacity (bbl) times annual turnover rate] (bbl/year), $K_N$ is the working loss turnover (saturation) factor (dimensionless), and $K_P$ denotes the working loss product factor (dimensionless). For crude oils and all other organic liquids, $K_P$ are 0.75 and 1, respectively (for more information about these parameters and also for the total losses from the other types of tanks see US EPA, 2006).

For fixed-roof tanks that are vented to a control device, the precontrol emissions from these tanks can be predicted using AP−42 equations (Eqs. (2.11), (2.12), and (2.13)). The postcontrol device emissions can be calculated from the precontrol emission estimates and the control device efficiency using the following formula:

$$E_i = E_{\text{unc},i} \times \left(1 - \frac{CD_{\text{eff}}}{\ldots}\right) \qquad (2.16)$$

### *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):

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

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

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

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

Hourly TOC emissions for valves in gas service:

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

Hourly TOC emissions for valves in light liquid service:

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

Hourly TOC emissions for valves in heavy liquid service:

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

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):

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

**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).

### *Example 2.5*

Assume that vessel, cargo description, and compartment conditions in a crude-oil cargo ship are as follows: 80,000 dead-weight-ton tanker, crude-oil capacity 500,000 barrels (bbl); 20% of the cargo capacity is filled with ballast water after cargo discharge; the crude oil has an RVP of 6 psia and is discharged at 75°F; 70% of the ballast water is loaded into compartments that had been fully loaded to 2 ft ullage, and 30% is loaded into compartments that had been lightered to 15 ft ullage before arrival at dockside; and true vapor pressure of crude oil is 4.6 psia. What are the total ballasting emissions and VOC emissions?

### Solution

$U_A$ or true cargo ullage for the full compartments is 2 ft and this parameter for the lightered compartments is 15 ft. Thus ballasting emissions can be estimated using Eq (2.21) as follows:

$$
\begin{aligned}
L_B &= 0.31 + 0.20P + 0.01PU_A \\
&= 0.7[0.31 + (0.20)(4.6) + (0.01)(4.6)(2)] + 0.3[0.31 + (0.20)(4.6) \\
&\quad + (0.01)(4.6)(15)] \\
&= 1.5\ \text{lb}/10^3\ \text{gal}
\end{aligned}
$$

**Figure 2.2** Nowruz oil-field spill in Persian Gulf of Iran (Courtesy of bing copyright free images. From http://envgeology.wikispaces.com/).

**Figure 2.3** Amoco Cadiz oil spill in Porstall, France (https://en.wikipedia.org/wiki/Amoco

**Table 2.24 Incidence of Spills <7 tons, Spills 7−700 tons, and Spills >700 tons by Operation at Time of Incident and Primary Cause of Spill During 1970−2014 (ITOPF, 2015)**

| Group | Item | Incidence of Spills <7 tons | Incidence of Spills 7−700 tons | Incidence of Spills >700 tons |
|---|---|---|---|---|
| Operations | At anchor (inland/ restricted) | | | 4% |
| | At anchor (open water) | | | 2% |
| | Underway (inland/ restricted) | | | 17% |
| | Underway (open water) | | | 50% |
| | Loading/discharging | 40% | 29% | 9% |
| | Bunkering | 7% | 2% | <1% |
| | Other operations/ unknown | 53% | 69% | >17% |
| Cause | Allision/collision | 2% | 26% | 30% |
| | Grounding | 3% | 20% | 33% |
| | Hull failure | 7% | 7% | 13% |
| | Equipment failure | 21% | 15% | 4% |
| | Fire/explosion | 2% | 4% | 11% |
| | Other | 23% | 13% | 6% |
| | Unknown | 41% | 15% | 3% |