

1 Green Process Efficiency

$$\eta_{\text{atom},i} = \frac{\nu_i, \text{desired product}}{\nu_i, \text{reactants}} \quad \eta_{\text{mass}} = \frac{(n\tilde{m})_{\text{desired product}}}{\sum_{\text{reactants}} (n_i\tilde{m}_i)}$$

2 Emissions

$$\text{Leaks: } E_{\text{VOC}} = f_E w_{\text{TOC}} N_{\text{equipment}} \frac{w_{\text{TOC}} - w_{\text{Ei}} - w_{\text{Me}}}{w_{\text{TOC}} - w_{\text{Me}}}$$

2.1 Charging an Empty Vessel

$$n_i = \frac{V_{\text{disp}} \rho_i}{\tilde{m}_i} x_i \quad E_i = \frac{p_i V_{\text{disp}}}{RT} \tilde{m}_i$$

$$\text{Pure or mixed solvent: } P = \sum_i p_i + p_{\text{inert}} \quad p_i = \gamma_i x_i p_i^*$$

2.2 Charging a Partially Filled Vessel

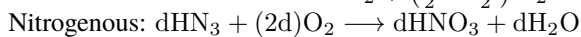
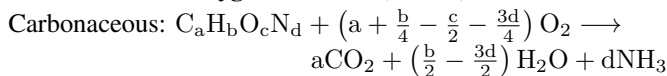
$$\phi_A = 1 + \frac{n_B}{n_A} \ln \frac{n_B}{n_A + n_B} \quad \phi_B = -\frac{n_B}{n_A} \ln \frac{n_B}{n_A + n_B}$$

$$\text{Above surface: } p_i = x_i p_i^*$$

$$\text{Subsurface: } \langle x_A \rangle = x_{A, \text{inlet}} \phi_A + x_{A, \text{tank}} \phi_B \quad p_i = \langle x_i \rangle p_i^*$$

$$\text{Immiscible, } \{x_i = 1\} : p_i = p_i^*$$

3 Theoretical Oxygen Demand (ThOD)



4 Environmental Fate of a Chemical

$$\tilde{V}_w = 1.8E-5 \frac{m^3}{mol} \quad p_i = c_i RT \quad x_i = c_{w,i} \tilde{V}_w \quad m_i = C_i V_i$$

Lipid-H₂O partition:

$$K_{ow} = \frac{C_{\text{octanol}}}{C_{\text{water}}} \quad m_T = C_o V_o + C_w V_w = C_w (K_{ow} V_o + V_w)$$

Biomass-H₂O partition:

$$K_d = \frac{C_{\text{soil/sediment}}}{C_w} \quad K_{oc} = \frac{100K_d}{\% \text{ organic carbon}} \quad BCF = \frac{C_{\text{organism}}}{C_w}$$

Air-H₂O partition:

$$\mathcal{H}_{px} \equiv \frac{p_i}{x_i} [\text{atm}] \quad \mathcal{H}_{cc} \equiv \frac{C_{\text{air},i}}{C_{w,i}}$$

$$\mathcal{H}_{pc} \equiv \frac{p_i}{C_{w,i}} = \mathcal{H}_{cc} RT = \mathcal{H}_{px} \tilde{V}_w \left[\frac{\text{atm} \cdot m^3}{mol} \right]$$

Mass balance: water, air, solids, sediment, fish

$$E_T = E_a + E_w + E_s = \sum C_x V_x \quad x \in \{w, a, s, t, f\}$$

$$C_a = C_w \mathcal{H}_{cc} \quad C_s = C_w K_d \quad C_t = C_w K'_d \quad C_f = C_w BCF$$

$$\sum C_x V_x = C_w (\mathcal{H}_{cc} V_a + V_w + K_d V_s + K'_d V_t + BCF \cdot V_f)$$

5 Industrial Hygiene

$$Y = k_1 + k_2 \ln V \quad \% (Y) = 50 \left(1 + \frac{Y-5}{|Y-5|} \operatorname{erf} \left| \frac{Y-5}{\sqrt{2}} \right| \right)$$

5.1 Volatiles

$$\text{Vapour: } C_{\text{ppm}} = 0.08205 \left[\frac{\text{atm} \cdot L}{K \cdot mol} \right] \left(\frac{T[K]}{P[\text{atm}] \tilde{m}[\text{g} \cdot mol^{-1}]} \right) C \left[\frac{\text{mg}}{m^3} \right]$$

$$TWA = \frac{1}{8} \int_0^{t_w} C(t) dt = \frac{1}{8} \sum_i C_i t_i$$

$$(\text{TLV-TWA})_{\text{mix}} = \sum_i C_i \left(\sum_i \frac{C_i}{(\text{TLV-TWA})_i} \right)^{-1}$$

$$C_{\text{ppm}} = \frac{\tilde{m} RT}{\varepsilon_m \tilde{V} P \tilde{m}} \times 10^6 \quad 0.1 \leq \varepsilon_m \leq 0.5 \quad C\% = C_{\text{ppm}} \times 10^4$$

5.2 Vapourisation

$$C_{\text{ppm}} = \frac{k A p^*}{\varepsilon_m \tilde{V} P} \quad k = k^\ominus \left(\frac{\tilde{m}^\ominus}{\tilde{m}} \right)^{1/3}$$

5.3 Filling

$$\dot{m}_i = \dot{m}_{\text{evap}} + \dot{m}_{\text{disp}} = \frac{\tilde{m}_i p_i^*}{RT} (\varepsilon_f \dot{V}_i + k_i A_\sigma) \quad \varepsilon_f = 1, \text{ splash} \\ \varepsilon_f = 0.5, \text{ subsfc.}$$

$$\{T = T_{(0)}\} : C_{\text{ppm}} = \frac{p_i^*}{\varepsilon_m \tilde{V}_i P} (\varepsilon_f \dot{V} + k_i A_\sigma) \times 10^6$$

5.4 Miscellany

$$\dot{V}_{\text{hood}} = A_\sigma \bar{v} \quad 0.406 \leq \bar{v} \leq 0.610 \text{ [m/s]} \quad L_I = -10 \log \frac{I}{I_0}$$

6 Fluid Mechanics

$$\frac{\Delta P}{\rho} + \frac{\Delta(\bar{v}^2)}{2\alpha} + g\Delta z + \sum \hat{F} = \frac{\dot{W}_{s,\text{by}}}{\dot{m}} \quad \alpha \approx 1, \text{ turbulent} \\ \alpha = 0.5, \text{ laminar}$$

$$\dot{V} = A_\sigma \langle \bar{v} \rangle = \frac{\dot{m}}{\rho} \quad (\rho \bar{v}) = \frac{\dot{m}}{A_\sigma} \quad \rho_1 A_{\sigma 1} \langle \bar{v}_1 \rangle = \rho_2 A_{\sigma 2} \langle \bar{v}_2 \rangle$$

$$\text{Hydrostatic column: } P_\perp = P_\top + \rho g h$$

6.1 Force Losses

$$\text{Re} = \frac{\langle \bar{v} \rangle \rho \ell}{\mu} \quad f = \frac{\ell}{\ell} \frac{\Delta P}{2\rho \langle \bar{v} \rangle^2}$$

$$f_{\text{smooth, lam}} = 16/\text{Re} \quad f_{\text{smooth, trb}} = 0.079 \text{Re}^{-0.25}$$

$$\hat{F}_{\text{straight pipe}} = 4f \frac{\ell}{\ell} \frac{\langle \bar{v} \rangle^2}{2} = \frac{\Delta P}{\rho} \quad \hat{F}_{\text{fitting}} = K_f \frac{\langle \bar{v} \rangle^2}{2} \quad K_{f, \text{straight}} = \frac{4f\ell}{\ell}$$

$$\sum \hat{F} = \sum_i 4f_i \frac{\ell_i}{\ell_i} \left(\frac{\langle \bar{v}_i \rangle^2}{2} \right) + \sum_j K_{f,j} \left(\frac{\langle \bar{v}_j \rangle^2}{2} \right) \quad \tilde{H}_i = \frac{\hat{F}_i}{g} \quad \tilde{H} = \frac{\Delta P}{\rho g}$$

7 Source Models

$$\langle \bar{v} \rangle = C_0 \sqrt{\frac{2P_{\text{gauge}}}{\rho}} \quad C_0 = 1, \text{ laminar} \\ C_0 = 0.61, \text{ turbulent}$$

$$\dot{m}_{\text{hole}} = \rho A \langle \bar{v} \rangle = C_0 A \sqrt{2\rho \Delta P} \quad \dot{V}_{\text{hole}} = C_0 A \sqrt{\frac{2\Delta P}{\rho}}$$

$$\text{Liquid: } \dot{m} = \rho A_{\text{hole}} C_0 \sqrt{2 \left(\frac{P_{\text{gauge}}}{\rho} + g h_L \right)}$$

$$\dot{m}(t) = \rho A_{\text{hole}} C_0 \sqrt{2 \left(\frac{P_{\text{gauge}}}{\rho} + g h_0 \right)} - \frac{\rho g C_0^2 A_{\text{hole}}^2}{A_{\sigma, \text{tank}}} t$$

$$h_L(t) = h_0 - t \frac{A_{\text{hole}} C_0}{A_{\sigma, \text{tank}}} \sqrt{\frac{P_{\text{gauge}}}{\rho} + 2g h_0} + \frac{g}{2} \left(\frac{C_0 A_{\text{hole}}}{A_{\sigma, \text{tank}}} t \right)^2$$

$$t_{\text{empty}} = \frac{1}{C_0 g} \frac{A_{\sigma, \text{tank}}}{A_{\text{hole}}} \left[\sqrt{2 \left(\frac{P_{\text{gauge}}}{\rho} + g h_0 \right)} - \sqrt{\frac{2P_{\text{gauge}}}{\rho}} \right]$$

$$\text{Gas: } \dot{m} = \rho A_{\text{hole}} C_0 \sqrt{\frac{2\tilde{m}}{RT_G} \frac{\gamma}{\gamma-1} \left[\left(\frac{P}{P_G} \right)^{\frac{2}{\gamma}} - \left(\frac{P}{P_G} \right)^{\frac{\gamma+1}{\gamma}} \right]}$$

$$\dot{m}_{\text{choked}} = P_G A_{\text{hole}} C_0 \sqrt{\frac{\gamma \tilde{m}}{RT_G} \left(\frac{2}{\gamma-1} \right)^{\frac{\gamma+1}{\gamma-1}}}$$

$$\text{Breather vent: } m = \frac{\tilde{m} p^* U}{RT_L} \left(\frac{T_H}{T_L} - 1 \right)$$

8 Dispersion Models

Puff with instantaneous point source at h_R above ground level and coordinate system on ground that moves with puff:

$$\langle C \rangle(x, y, z, t) = \frac{m}{(2\pi)^{1.5} \sigma_x \sigma_y \sigma_z} e^{-0.5 \left(\frac{y}{\sigma_y} \right)^2} \times \\ \left[e^{-0.5 \left(\frac{z-h_R}{\sigma_z} \right)^2} + e^{-0.5 \left(\frac{z+h_R}{\sigma_z} \right)^2} \right]$$

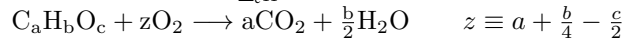
Plume with continuous steady-state source at h_R above ground level and wind moving in x direction at $\vec{v}_{\text{wind}}$:

$$\langle C \rangle(x, y, z) = \frac{\dot{m}}{\pi \sigma_y \sigma_z \bar{v}_{x, \text{wind}}} e^{-0.5 \left(\frac{y}{\sigma_y} \right)^2} \times \\ \left[e^{-0.5 \left(\frac{z-h_R}{\sigma_z} \right)^2} + e^{-0.5 \left(\frac{z+h_R}{\sigma_z} \right)^2} \right]$$

9 Fires and Explosions

$$L = \left(\sum_i \frac{y_i}{L_i} \right)^{-1} \quad L \in \{\text{LFL, UFL}\}$$

$$L(T) = L(25^\circ\text{C}) - \frac{0.75}{\Delta_c \tilde{H}} (T - 25^\circ\text{C}) \quad \Delta_c \tilde{H} = \sum_i y_i \Delta_c \tilde{H}_i \frac{\text{kcal}}{\text{mol}}$$



$$\text{LOC} = \text{LFL} \frac{n_{O_2}}{n_{\text{fuel}}} = z(\text{LFL})$$

$$z_c \equiv \frac{r}{m_{\text{TNT}}^{1/3}} \quad m_{\text{TNT}} = \frac{\eta_{\text{explosion}} m_{\text{hydrocarbon}} \Delta_c \tilde{H}}{E_{\text{TNT}}} \quad P^* = \frac{\text{peak overpressure}}{P_{\text{ambient}}}$$

$$E = RT \left[\ln \frac{P_g}{P} - 1 + \frac{P}{P_g} \right]$$

9.1 Purging

$$y_i - y_{\text{oxygen}} = \left(\frac{P_i}{P_H} \right)^i (y_0 - y_{\text{oxygen}}) \quad \Delta n_{\text{nitrogen}} = i(P_H - P_L) \frac{V}{RT}$$

$$\dot{V}_{\text{inert}} t = V \ln \frac{C_1 - C_0}{C_2 - C_0} \quad \text{OSFC} = \frac{\text{LOC}}{z - z_{\frac{\text{LOC}}{21}}}$$

References

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https://www.epa.gov/sites/default/files/2020-11/documents/protocol_report_2015.pdf