

10.0 VOC Emissions

Pro-Designer performs primary volatile organic compound (VOC) emission calculations from batch manufacturing facilities and secondary emission calculations from end-of-pipe treatment processes.

10.1 Primary VOC Emissions

Pro-Designer performs volatile organic compound (VOC) emission calculations for several batch operations that are common in the pharmaceutical and specialty chemical industries. Further, it enables the user to specify and track emissions of particulate and other regulated compounds for which no mathematical models are available. The initialization of emission calculations is done through appropriate dialog windows. For instance, Figure 10.1 displays the emissions dialog of the Charge operation.

CHARGE-1 (Charge)

Oper.Cond's | **Emissions** | Labor, etc. | Scheduling

☒ Perform Emission Calculations

	Component	Emitted ?	Set By User	Emission %
1	Nitrogen	<input type="checkbox"/>	<input type="checkbox"/>	0.000
2	Oxygen	<input type="checkbox"/>	<input type="checkbox"/>	0.000
3	Toluene	<input checked="" type="checkbox"/>	<input type="checkbox"/>	0.000
4	Water	<input type="checkbox"/>	<input type="checkbox"/>	0.000

Vent Condenser

☒ On at Temperature °C

☐ Off

<< OK OK >> OK Cancel Help

Figure 10.1: Emissions dialog of the “Charge” operation.

The “Emitted ?” box is checked by default for all compounds that are specified in the component database as VOCs. For particulate and non-VOC compounds, for which no mathematical models are available, the user has the option to specify the “Emission %”.

The VOC emission models are based on EPA guidelines (OAQPS, Control of Volatile Organic Emissions from Manufacture of Synthesized Pharmaceutical Products, EPA-450/2-78-029, December 1978 and OAQPS, Control of Volatile Organic Compound Emissions from Batch Processes, EPA-453/R-94-020, February 1994). A description of the current VOC emission models follows:

Displacement - Emission Model

This model is used in the “Charge” and “Transfer In” operations. It accounts for emissions when a liquid mixture is transferred into a vessel. The model assumes that the displaced gas volume is equal to the volume of liquid transferred into the vessel. The receiving vessel may be empty or contain a liquid mixture from prior operations. The displaced gas is assumed to be saturated with VOC vapor(s) at the exit temperature.

The amount of a VOC compound i emitted during a charge or transfer in operation is calculated using the following equation:

$$m_i = \frac{p_i (X_i)(MW_i)}{RT} V_r$$

where: m_i = mass of VOC component i emitted [kg]

p_i = vapor pressure of component i at T [Pa]

X_i = mole fraction of component i in the liquid mixture

MW_i = molecular weight of component

V_r = volume of displaced gas [m³]

R = ideal gas constant [8,314.5 J/kmol-K]

T = exit temperature [K]

Dividing m_i by the cycle time of the unit procedure yields the emission rate in kg/h. Please note that the rate is averaged over the cycle time of a procedure. If several operations of a unit procedure contribute to VOC emissions, the total emissions from that procedure are combined and averaged over its cycle time.

The vapor pressure, p_i , is calculated using Antoine's equation or DIPPR's polynomial expression depending on whether the component properties are retrieved from the SuperPro or DIPPR databases, respectively.

The exit temperature, T , is set equal to the temperature of the condenser. If no condenser is available, then, it is set equal to the final temperature of the liquid mixture (at the end of the addition). The temperature of the liquid mixture may change if the transferred liquid has a different temperature from that of the initial contents of the vessel.

Evacuation - Emission Model

This model is used in the “Evacuate” and “Vent” operations. It accounts for emissions when the pressure of a vessel is reduced. The model assumes that there is no leakage of air into the vessel even if the final pressure is below atmospheric. It is also assumed

that there is no temperature change during the operation and that the displaced gas is saturated with VOC compounds at the exit temperature of the vessel.

The moles of a VOC compound i emitted during an Evacuation operation are calculated using the following equation:

$$n_i = \frac{p_i (X_i)}{P_{\text{inert}}} n_{\text{inert}}$$

where: n_i = VOC component i emitted [kmoles]

p_i = vapor pressure of component i at T [Pa]

X_i = mole fraction of component i in the liquid mixture

n_{inert} = inert gas(es) removed during the operation [kmoles]

P_{inert} = average partial pressure of inert gas(es) during the operation [Pa]

Dividing n_i by the cycle time of the unit procedure yields the emission rate in kg/h. Please note that the rate is averaged over the cycle time of a procedure. If several operations of a unit procedure contribute to VOC emissions, the total emissions from that procedure are combined and averaged over its cycle time.

The partial pressure of inert gas(es) is estimated by considering the initial and final pressure of the system as well as the vapor pressure of the volatile compounds (which does not change during the operation). The amount of inert gas(es) removed is estimated using the following equation:

$$n_{\text{inert}} = V \Delta P / RT$$

Where V is the gas space volume, ΔP is the system pressure change, and T is the exit temperature. Essentially, it is assumed that during the operation the total number of VOC moles in the gas space does not change (the emitted moles are replaced by the newly vaporized ones) and that the pressure change is entirely due to removal of inert gases.

Gas Sweep - Emission Model

This model is available in the “Gas Sweep”, “React”, “Crystallize”, and “Vaporize / Concentrate” operations. It accounts for emissions that are associated with sweeping a vessel with an inert gas (e.g., nitrogen, air, etc.). The model assumes that the sweeping gas leaves the system saturated with VOCs at the exit (condenser) temperature.

The moles of a VOC compound i emitted during a Sweeping operation are calculated using the following equation:

$$n_i = \frac{p_i (X_i)}{P - \sum_j X_j p_j} n_{\text{inert}}$$

where: n_i = VOC component i emitted [kmoles]

p_i = vapor pressure of component i at T [Pa]

p_j = vapor pressure of component j at T [Pa]

P = vessel pressure during the operation [Pa]

X_i = mole fraction of component i in the liquid mixture

n_{inert} = inert gas flown through the vessel during the operation [kmoles]

If the vessel contains no liquid material but VOCs are present in its vapor space, then the emission calculations are done using the following equation:

$$n_i = \frac{P_i (X_i)(V_r)}{RT} (1 - 0.37^N)$$

where: N = number of volumes (multiple of vessel volumes) of sweeping gas

V_r = vessel volume [m^3]

Dividing n_i by the cycle time of the unit procedure yields the emission rate in kg/h. Please note that the rate is averaged over the cycle time of a procedure. If several operations of a unit procedure contribute to VOC emissions, the total emissions from that procedure are combined and averaged over its cycle time.

Heating - Emission Model

This model accounts for emissions that are associated with heating a vessel that contains a mixture of volatile components. During heating under constant pressure, the gas of the vapor space undergoes expansion and a fraction leaves the vessel through the vent. Further, during heating there is an increase in the vapor pressure of VOC compounds. The removed gas (due to expansion) is assumed to be saturated in VOCs at the average vessel temperature.

The moles of a VOC compound i emitted during a Heating operation are calculated using the following equation:

$$n_i = \frac{n_{\text{inert}}}{2} \left[\frac{(p_i)_{T_1} X_i}{P - \sum_j X_j (p_j)_{T_1}} - \frac{(p_i)_{T_2} X_i}{P - \sum_j X_j (p_j)_{T_2}} \right]$$

where: n_i = VOC component i emitted [kmoles]

p_i = vapor pressure of component i at T_1 (inial) or T_2 (final) temperature [Pa]

p_j = vapor pressure of component j at T_1 (inial) or T_2 (final) temperature [Pa]

P = vessel pressure during the operation [Pa]

X_i = mole fraction of component i in the liquid mixture

n_{inert} = inert gas leaving the vessel during the operation [kmoles]

The amount of inert gas leaving the system is estimated using the following equation:

$$n_{\text{inert}} = \frac{V_r}{R} \left[\frac{P - \sum_j X_j (p_j)_{T_1}}{T_1} - \frac{P - \sum_j X_j (p_j)_{T_2}}{T_2} \right]$$

where: R = ideas gas constant [8,314.5 J/kmol-K]

V_r = gas space volume [m^3]

T_1 = initial system temperature [K]

T_2 = final system temperature [K]

Dividing n_i by the cycle time of the unit procedure yields the emission rate in kg/h. Please note that the rate is averaged over the cycle time of a procedure. If several operations of a unit procedure contribute to VOC emissions, the total emissions from that procedure are combined and averaged over its cycle time.

Gas Evolution - Emission Model

This model accounts for emissions from reaction operations that involve generation and release of an inert gas. It is assumed that the gas that leaves the system is saturated with VOCs at the exit temperature. The mathematical model is identical to the Gas Sweep model. Simply, the released gas plays the role of the sweeping gas.

Vacuum - Emission Model

In chemical processing, some operations (e.g., reaction, distillation, etc.) are carried out under vacuum. Under such conditions, a small amount of air leaks into the vessel and comes into contact with the contents of the vessel. The model assumes that the air that leaves the system is saturated with VOCs at the exit temperature. The mathematical model is identical to the Gas Sweep model. Simply, the leaking air plays the role of the sweeping gas. The leak rate must be specified by the user.

Drying - Emission Model

Wet cakes recovered from filtration and centrifugation operations frequently contain solvents in their interstitial space. The drying of such cakes results in emissions. The emission calculations are based on simple material balances (inlet minus outlet flow). By default no control device is associated with drying operations. If a control device (e.g., condenser, absorber, activated carbon column) is required, it should be added explicitly using a separate unit and directing the vent streams of the dryer to the control device.

10.2 Secondary VOC Emissions

Pro-Designer is equipped with rigorous models for calculating VOC emissions from wastewater treatment plants. There are four types of emission calculation models in the current version of the software. The first type includes emissions from tanks and basins with quiescent surfaces (e.g., equalizers, neutralizers, clarifiers, thickeners, flotation, and oil separation units). The removal of VOCs from tanks with quiescent surfaces occurs due to natural volatilization, i.e., mass transfer across open surfaces. The second type includes emissions from aerated tanks equipped with surface or diffused aeration systems. The removal of VOCs from such tanks occurs due to surface volatilization for mechanically aerated systems or due to stripping for tanks with diffused aeration systems. The third type includes emissions from trickling filters. Trickling filters are modeled as packed-media systems in which volatilization is the primary removal mechanism for all VOCs, a conservative assumption for VOCs that are biodegradable. Finally, the fourth type includes emission calculation models for junction boxes. Junction boxes combine wastewater streams flowing into a treatment

plant. These boxes are usually open to the atmosphere and VOC emissions occur in a similar manner as emissions from quiescent surface tanks. A description of the VOC emission models for quiescent and agitated tanks follows below. The emission models for trickling filters and junction boxes are described as part of their operation models in the Help Facility (search for the name of those operations).

Quiescent Tanks - Emission Model

Emissions of volatile organic compounds (VOCs) from tanks with quiescent surfaces (clarifiers, thickeners, equalizers, neutralizers, etc.) occur due to natural volatilization, i.e., mass transfer across open surfaces. The rate of mass transfer across the air-wastewater interface is written as follows:

$$R_{\text{vol}} = K_L C_L A$$

where: R_{vol} (kg/s) = rate of compound removal by volatilization

K_L (m/s) = overall mass transfer coefficient

C_L (kg/m³) = VOC concentration in bulk liquid

A (m²) = surface area of the tank

K_L depends upon both the gas phase as well as the liquid-phase resistances:

$$\frac{1}{K_L} = \frac{1}{k_\lambda} + \frac{1}{H_C k_g}$$

where k_λ and k_g are the liquid-phase and gas-phase mass transfer coefficients in (m/s), respectively, and H_C is the dimensionless Henry's law constant. The value of H_C is retrieved from the chemical component databank.

Two different models have been implemented in order to calculate the individual mass transfer coefficients of VOCs from quiescent surface tanks. You can either select the emission calculation model or simply specify the emission percent for a VOC component.

The first model, which is accepted by the US EPA, utilizes three correlations formulated by Springer et. al. (1984) to estimate the liquid phase mass transfer coefficient for a VOC component. These correlations are based upon the wind speed at ten meters (U_{10}) above the liquid surface and the fetch-to-depth ratio (F/D) of the tank under consideration. "Fetch" is the linear distance across the impoundment (EPA, 1994).

For $F/D < 51.2$ (originally developed for $14 < F/D < 51.2$),

$$k_\lambda = \left(2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7} \right) U_{10}^2 \left(\frac{D_w}{D_{\text{ether}}} \right)^{0.67}$$

And, for $F/D > 51.2$,

$$k_{\lambda} = 2.611 \times 10^{-7} U_{10}^2 \left(\frac{D_w}{D_{\text{ether}}} \right)^{0.67}$$

where D_w and D_{ether} are the diffusivities of the VOC and ether in water, respectively, in (m^2/s). The above equations were validated by Springer et al. for $U_{10} > 3.25$ m/s and may lead to lower accuracy for $U_{10} < 3.25$ m/s.

The second model estimates k_{λ} using the correlations developed by Mackay and Yeun (1983):

$$k_{\lambda} = 1.0 \times 10^{-6} + 34.1 \times 10^{-4} (U^*) Sc_L^{-0.5} \quad \text{for } U^* > 0.3$$

$$k_{\lambda} = 1.0 \times 10^{-6} + 144 \times 10^{-4} (U^*)^{2.2} Sc_L^{-0.5} \quad \text{for } U^* < 0.3$$

Where,

$$U^* = (6.1 + 0.63 U_{10})^{0.5} U_{10}$$

$$Sc_L = \frac{\mu_L}{\rho_L D_w}$$

In both cases, the gas phase mass transfer coefficient is calculated using the equation developed by Mackay and Matasugu (Hwang, 1982):

$$k_g = 1.0 \times 10^{-3} + 46.2 \times 10^{-3} U^* Sc_G^{-0.67} \quad \text{where } Sc_G = \frac{\mu_G}{\rho_G D_a}$$

Where μ_L and μ_G are the viscosities of water and air in ($\text{kg}/\text{m}\cdot\text{s}$), respectively. ρ_L and ρ_G are the densities of air and water in (kg/cm^3), respectively, and D_w and D_a are the diffusivities of the VOC in water and in air in (m^2/s), respectively. The values of μ_L , μ_G , ρ_L , ρ_G , D_w , D_a , and D_{ether} are retrieved from the component databank.

The above equations are combined with an overall material balance equation to solve for C_L and R_{vol}

References

1. Hwang, S. T. 1982. "Toxic Emissions from Land Disposal Facilities," *Environmental Progress*. 1: 46-52.
2. Mackay, D., and A. T. K. Yeun. 1983. "Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water," *Environmental Science and Technology*. 17: 211-217.
3. Springer, C., P. D. Lunney, and K. T. Valsaraj. 1984. "Emission of Hazardous Chemicals from Surface and Near Surface Impoundments to Air," Project Number 808161-02. Cincinnati, OH: U.S. Environmental Protection Agency (EPA), Solid and Hazardous Waste Research Division.
4. U. S. Environmental Protection Agency (EPA). 1994. "Air Emissions Models for Waste and Wastewater," *Rep. EPA-453/R-94-080A*. Research Triangle Park, NC: Office of Air Quality Planning and Standards.

Agitated Tanks - Emission Model

In agitated tanks, such as aeration basins, VOC emissions result from surface volatilization and diffused air stripping (if diffused air is used for aeration). The general material balance equation for a component that biodegrades and is emitted is given by the following equation:

$$0 = (\text{Input}) - (\text{Output}) - \left(\begin{matrix} \text{Biochemical} \\ \text{Oxidation} \end{matrix} \right) - \left(\begin{matrix} \text{Surface} \\ \text{Volatilization} \end{matrix} \right) - \left(\begin{matrix} \text{Diffused} \\ \text{Air} \\ \text{Stripping} \end{matrix} \right)$$

$$\text{or} \quad 0 = QC_{in} - QC - Vr_b - K_L a VC - Q_a K_{eq} CF_{st}$$

where Q is the liquid flow rate, V is the reactor volume, C_{in} is the inlet concentration, C is the outlet concentration which is the same as the concentration in the reactor, r_b is the biodegradation rate, $K_L a$ is the overall mass transfer coefficient, Q_a is the air flow rate (in case of diffused aeration), K_{eq} is the equilibrium constant, and F_{st} is the saturation term (it represents the extent of saturation of the exiting gas stream). In general, the biodegradation rate is a function of substrate concentration, oxygen concentration, and biomass concentration. Various expressions are available for the effect of substrate. The overall equation with a Monod-type substrate expression is written as follows:

$$r_b = K_{max} \left(\frac{C}{K_s + C} \right) \left(\frac{C_o}{K_o + C_o} \right) X$$

where K_{max} is the maximum rate constant, K_s is the half saturation constant for the substrate, C_o is the oxygen concentration, K_o is the half saturation constant for oxygen, and X is the biomass concentration. Alternative expressions for the substrate and oxygen terms are also available. The component databank includes data for K_{max} and K_s for a large number of chemical components.

The overall mass transfer coefficient of a VOC component is estimated as a function of the oxygen mass transfer coefficient in wastewater, using a proportionality coefficient, ψ_M . In other words,

$$(k_1 a)_{\text{VOC}} = \psi_M (k_1 a)$$

The value of $(K_L a)_{\text{O}_2}$ in the wastewater is a user input to the program. ψ_M is given by the following equation (Hsieh et. al., 1993):

$$\psi_M = \psi \left\{ 1 + \frac{1}{H_c \frac{k_g a}{k_l a}} \right\}^{-1}$$

ψ is the dimensionless transfer coefficient proportionality constant and it is calculated by the following equation (Corsi and Card, 1991):

$$\psi = \left\{ \frac{D_{\text{voc}}}{D_{\text{O}_2}} \right\}^n$$

where D_{voc} and D_{O_2} are the liquid diffusion coefficients for a VOC and oxygen in (m^2/s), respectively. The exponent n varies from 0.5 for penetration and surface renewal theories to 1.0 for two-film theory (Corsi and Card, 1991) and is typically 0.5 to 0.6 (Mihelcic et. al., 1993). The diffusion coefficients of VOC components are retrieved from the component databank of the program.

$k_g a$ and $k_l a$ are the individual mass transfer coefficients of the VOC in the gas and liquid phases, respectively, in (s^{-1}). For mechanically aerated systems, the value of $\frac{k_g a}{k_l a}$ is estimated using the following empirical equation (Hsieh et. al., 1993):

$$\log \left(\frac{k_g a}{k_l a} \right) = -0.39664 \log_{10} (P / V) + 2.6776$$

(P/V) represents the mechanical power consumed for surface aeration divided by the liquid volume of the aeration basin and it is calculated by the program. Alternatively, you have the option to set the value of $k_g a/k_l a$ or set the value of the term in parenthesis (denoted by Rl/Rt on the emission i/o dialog window).

For diffused aerated systems, the F_{st} term is calculated by the following equation:

$$F_{st} = 1 - \exp \left(\frac{\psi_M (K_L a)_{\text{O}_2} V}{H_c Q_g} \right)$$

To calculate ψ_M , you have the option to set either the $k_g a/k_l a$ ratio or the term in parenthesis (called Rl/Rt on the emission i/o dialog window).

The equilibrium constant is estimated by:

$$K_{eq} = \frac{H_C}{RT}$$

where H_C is Henry's law constant, R is the universal gas constant, and T is temperature.

The above equations written for each chemical component entering an aeration basin constitute a set of non-linear equations, which is solved numerically to calculate the exit concentration and the emission rate of each component.

References

1. Corsi, R. L., and T. R. Card. 1991. "Estimation of VOC Emissions Using the BASTE Model," *Environmental Progress*. 10: 290-299.
3. Hsieh, C.-C., K. S. Ro, and M. K. Stenstrom, "Estimating Emissions of 20 VOCs. I: Surface Aeration, II: Diffused Aeration", *J. of Env. Engr.*, Vol. 119, No. 6, Nov./Dec. 1993, ASCE, ISSN 0733-9372.
4. Mihelcic, J. R., C. R. Baillod, J. C. Crittenden, and T. N. Rogers. 1993. "Estimation of VOC Emissions from Wastewater Facilities by Volatilization and Stripping," *Journal of Air and Waste Management Association*. 43: 97-105.
5. Melcer, H, J. P. Bell, D. J. Thomas, C. M. Yendt, J. Kemp, and P. Steel. 1994. "Modeling Volatile Organic Contaminants' Fate in Wastewater Treatment Plants," *Journal of Environmental Engineering*. 120: 588-609.
6. Melcer, H. 1994. "Monitoring and Modeling VOCs in Wastewater Facilities," *Environmental Science and Technology*. 28: 328A-335A.
7. Tchobanoglous G. and F.L. Burton (1991). "Wastewater Engineering: Treatment, Disposal, and Reuse", Third edition, Metcalf & Eddy, Inc., McGraw-Hill, Sec. 10-1.
8. Wong-Chong, G.M., and R.C. Loeht: *Water Res.*, vol. 9, p. 1099, 1975.

10.3 Emissions Report Structure

This report presents information on air pollutant flow from the various procedures of a flowsheet. For batch processes, the flowrates (in kg/h) represent average flows during the cycle of a procedure. For each procedure, the Actual and Permit Allowable flowrates of the following pollutant categories are included:

- a. Total Particulate (and its various subcategories),
- b. Total VOC (and its various subcategories),
- c. Acid Gases (and its two subcategories),
- c. Extremely Toxic Gases (ETG) and its two subcategories,
- d. Carbon Monoxide (CO),
- e. NO_x,
- f. SO₂ and
- g. BASES

The bottom table of the Emissions Report provides info on total pollutant amounts.

10.4 Emission Limits

You can set emission limits for the various pollutant categories, except for volatile organic compounds (VOCs) through the dialog that is shown below (select **Edit / Flowsheet Options / Preferences / Emission Limits...** to bring it up). For VOCs the emission limit is calculated by the program based on the composition of the various vent (emission) streams. The emissions report will include warnings if the accumulated emissions for any of the above categories exceeds the set limit.

Emission Limits

Particulates

Total Particulate kg/h

Biological kg/h

Radionuclide kg/h

Asbestos kg/h

Dioxin kg/h

LOC kg/h

HAP kg/h

Cr+6 kg/h

Metal kg/h

Other Particulate kg/h

Acid Gases

Total Acid Gas kg/h

HAP-Acid kg/h

Acid (non-HAP) kg/h

ETG

Total ETG kg/h

HAP-Gas kg/h

Gas (non-HAP) kg/h

Other

CO kg/h

NOx kg/h

SO2 kg/h

Base kg/h

User Defined Categories

☐ kg/h

☐ kg/h

☐ kg/h

☐ kg/h

OK Cancel Help

Through the above dialog you can introduce four additional used-defined pollutant categories and specify their limits. Once a user-defined pollutant category has been introduced, you can classify any component present in this design case as contributing to that category (see Pure Component Properties in Chapter 3: Pollutant Categorization).

GO TO TOP LEVEL CONTENTS