Improved Algorithm for Estimating Process Emissions from Batch Heating

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An improved algorithm is proposed for more accurately esti-mating process emissions from chemical batch heating opera-tions. Results using the derived algorithm are compared to those obtained from the current 1994 EPA standard calcula-tions [1] and from the newly proposed NESHAP standards [4]. The new approach is shown to result in lower emission estima-tions from process vents for volatile components, especially when the final temperature is near the boiling point tempera-ture of the liquid in the vessel.

INTRODUCTION

Estimating the environmental impact of chemical processes has become a routine practice for the chemical process industry. In 1978 the EPA issued a guidance document [2] aimed at providing stan-dardized vent emission calculations for many of the different types of operations. These basic process operations include charging, depressurization, gas sweep, heating, gas evolution, vacuum distilla-tion, and drying operations. Later, in 1994, the EPA issued revised calculations and included many worked examples for the different methods.

One of these 1994 EPA models applies to the heating of a liquid in a process vessel. For this model the gas phase in the vessel head-space contains a noncondensable gas (i.e., air or nitrogen) and vapors, which are in equilibrium with the volatile liquid compo-nents. When the batch is heated at constant pressure a portion of gas phase in the vessel headspace exits the system through the process vent due to thermal expansion of the gas and an increase in liquid-phase vapor pressure. Emission calculations for the heating model are based on the premise that the amount of noncondens-able component displaced from the still or receiver can be deter-mined by the initial and final gas space composition. It is assumed that the exiting gas is at equilibrium with the contents of the vessel at the time of venting. The amount of solvent vapor in the dis-charged vent gas is calculated by multiplying the moles of non-con-densable gas (air or nitrogen) by the average ratio between the par-tial pressure of the solvent vapors and the partial pressure of the non-condensable component for the heating process.

This basic technique is similar to the approach taken in the EPA literature for the depressurization model. While this estimation approach appears to be reasonable on the surface, it can lead to

emission levels that are significantly higher than can be obtained through theoretical considerations. Proposed revisions to the heat-ing model, as contained in recent EPA literature [4], more closely approximate vent losses due to heating by applying the standard 1994 EPA equations over smaller temperature increments and sum-ming up the overall result.

In presenting the findings of this investigator, the basis for the original 1994 EPA model is presented and then the proposed new model is developed. The results that form the proposed new model are then presented and compared to the standard 1994 EPA model applied over 5°C and 1°C increments.

CURRENT EPA METHODOLOGY

At any time during the heating operation, the total system pres-sure for the vessel is equal to the sum of the partial pressures of nitrogen and toluene.

$$P_T = p_{nc} + p_i \tag{1}$$

where P_T is the system pressure, p_{nc} is the nitrogen (or non-con-densable) pressure, and p_i is the partial pressure of the solvent vapor.

The total amount of gas in the vessel headspace at any time dur-ing the heating is equal to the moles of nitrogen plus the moles of solvent vapor.

$$n_T = n_{nc} + n_i \tag{2}$$

where n_T is the system pressure, n_{nc} is the nitrogen (or non-condensable) partial pressure, and n_i is the toluene partial pressure.

Material Balance on Nitrogen in the Vessel Headspace

For this problem, nitrogen is not entering the vessel during the heating process so the amount of nitrogen or noncondens-able component that is emitted from the vessel may be deter-mined from the initial and final conditions.

$$n_{nc}(out) = \left[\left(\frac{p_{nc,1} V}{RT_1} \right) - \left(\frac{p_{nc,2} V}{RT_2} \right) \right] \tag{3}$$

$$n_{nc}(out) = \left(\frac{V}{R}\right)\left[\left(\frac{P_T - p_{i,1}}{T_1}\right) - \left(\frac{P_T - p_{i,2}}{T_2}\right)\right] \qquad (4)$$

where $n_{nc(out)}$ are the moles of noncondensable component exiting the vessel through the vent between conditions 1 and 2. $p_{nc,1}$ and $p_{nc,2}$ are the partial pressures of the noncondensable component at temperature conditions 1 and 2. V, T, and R are the vessel headspace volume, system temperature, and universal gas constant, respectively.

Calculating the Solvent Vapor Vent Losses.

The gas phase in the vessel contains only nitrogen and the solvent vapor component. During heating, the vapor pressure of the volatile liquid component increases. The moles of solvent vapor which are contained in an incremental amount of vent gas can be calculated from the moles of nitrogen that are present and the partial pressure ratio between the solvent vapors and nitrogen.

$$dn_i(out) = \frac{p_i}{p_{nc}} dn_{nc}(out) \qquad (5)$$

While integrating Eq. (5) may be possible, the final solution would be based on the specific vapor pressure equation that was used to represent p_i for the temperature range involved. The Antoine equation is one of many models that are used for estimating solvent vapor pressure as a function of vapor pressure.

Numerical Integration Approach (Trapezoidal Rule)

Numerical Integration using computers is a common approach for integrating complex functions, which do not have convenient solutions. Many numerical techniques exist for approximating the integral value of Eq. (5) between the initial and final temperature. One integration method is known as the Trapezoidal Rule [3] shown in Eq. (6).

$$y_1 = y_o + \frac{n}{2}(f_o + f_1) + O(h^3) \qquad (6)$$

where y_1 is the integral of function f at x_1, y_o is the integral of function f at x_o, f_o and f_1 are functional evaluations of f at x_o and x_1, and $O(h^3)$ is the integration error for this approximation method.

In applying this computer technique, one normally integrates the function f between two limits by setting the step size h to a small value and iterates from x_0 to the x_n by summing the incremental integration values for y_n. Note that the integration error term $O(h^3)$ is a function of h and that a small step size will result in a smaller overall integration error. In applying the Trapezoidal Rule to our heating problem, y_o would be set to zero because it represents the amount of toluene vapors that have exited the vessel prior to the initial temperature T_0. By performing the integration in a single step and substituting n_{nc} for h, $p_{i,1}/p_{nc,1}$ for f_o, and $p_{i,2}/p_{nc,2}$ for f_1 Eq. (6) becomes:

$$n_i = n_{nc} \frac{1}{2}\left(\frac{p_{i,1}}{p_{nc,1}} + \frac{p_{i,2}}{p_{nc,2}}\right) + O(h^3) \qquad (7)$$

where n_i are the moles of volatile component (or toluene in

this discussion) and n_{nc} are the moles of noncondensable (or nitrogen) component exiting the vessel through the vent between conditions 1 and 2. $p_{i,1}$ and $p_{i,2}$ are partial pressures of the volatile component and temperature 1 and 2. $p_{nc,1}$ and $p_{nc,2}$ are the partial pressures of the noncondensable component at T_1 and T_2.

If we were to ignore the error of integration term and remove it from the numerical expression, we could obtain the following simplified expression:

$$n_i = n_{nc} \frac{1}{2}\left(\frac{p_{i,1}}{p_{nc,1}} + \frac{p_{i,2}}{p_{nc,2}}\right) \qquad (8)$$

Note that Eq. (8) is identical to the standard equation for calculating VOC emission losses from heating in the EPA literature [1]. The resulting accuracy from using Eq. (8) to calculate the amount of solvent vapor emitted during heating decreases as the final temperature approaches the solvent boiling point. Note that, as T_2 approaches the solvent boiling point $p_{i,2}/p_{nc,2}$ approaches ∞.

Alternative Approach to Estimating Solvent Vent Losses (Proposed New Model)

During the basic heating process, the solvent vapor content of the vessel headspace increases because of the elevating solvent vapor pressure. At the same time the increasing temperature reduces the vessel headspace capacity for gas through the Ideal Gas Law (PV=nRT).

If one ignores the effect of temperature on the vessel headspace molar volume then the heating problem can be approached in a similar manner as the Empty Vessel Purge model [1]. The Empty Vessel Purge model is used for estimating solvent vapor emissions when a vessel has been recently emptied of process material and air
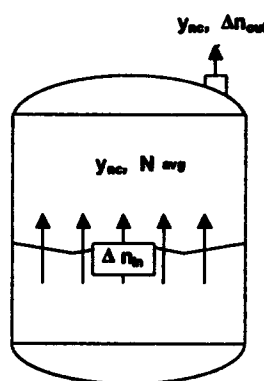

or nitrogen is introduced to sweep the residual vapors out of the vessel. In the case of the Heating Model, rising vapors from the vessel liquid contents displace the non-condensable gas components from the headspace through the process vent. Ultimately, all of the air or nitrogen will be purged from the vapor space as the liquid mixture reaches the boiling point.

Performing a material balance around the vessel headspace for the non-condensable component (air, nitrogen, etc.) results in the following differential expression:

$$d(y_{nc}N_{avg}) = y_{nc,in}dn_{in}$$
$$-y_{nc}dn_{out} \qquad (9)$$

where y_{nc} is the noncondensable component mole fraction of the vessel headspace moles N_{avg} and of the exiting vent gas dn_{out}. The noncondensable mole fraction of the incoming vapors dn_{in} is $y_{nc,in}$.

N_{avg} represents the average molar volume of the vessel headspace during the heating process. Temperature changes near the liquid mixture boiling point have a much smaller effect on the head-

space molar volume due to the Ideal Gas Law than they do on the incoming volatile component due to increases in vapor pressure of the liquid component. This comparison enables the assumption to be made that the average molar headspace volume remains constant relative to changes in the molar composition of the vessel headspace. $y_{nc,in}$ is zero since the incoming vapors do not contain any noncondensables. Also dn_{out} is equal to dn_{in} since the moles of gas entering the vessel are equal to the moles leaving. Adjusting for these changes, Eq. (9) may be simplified:

$$N_{avg} dy_{nc} = -y_{nc} dn_{in} \qquad (10)$$

$$\frac{dy_{nc}}{y_{nc}} = -\frac{1}{N_{avg}} dn_{in} \qquad (11)$$

Additionally, y_{nc} is equal to p_{nc}/P_{sys} so that Eq. (11) finally becomes:

$$\frac{dp_{nc}}{p_{nc}} = \frac{1}{N_{avg}} dn_{in} \qquad (12)$$

When integrated this results in:

$$\ln\left(\frac{p_{nc,1}}{p_{nc,2}}\right) = \frac{n_{in}}{N_{avg}} \qquad (13)$$

By rearranging Eq. (13), an expression can be developed that relates the amount of volatilizing component entering the vessel headspace from the solvent to the solvent vapor pressure.

$$n_{in} = N_{avg} \ln\left(\frac{p_{nc,1}}{p_{nc,2}}\right) \qquad (14)$$

$n_{i,in}$ represents the total number of moles of vapor entering the vessel headspace from the volatilizing liquid and equals n_{in} since it is free of any noncondensable component. Performing a material balance on component i at any temperature during the heating results in the following expression for the moles of i being emitted from the vessel.

$$n_{i,out} = n_{in} - \left(n_{i,2} - n_{i,1}\right)_{vessel} \qquad (15)$$

Substituting Eq. (14) into Eq. (15) and simplifying the expression further, a final expression can be obtained for calculating the moles of i (or volatilizing component) emitted from the vessel from the overall heating operation.

$$n_{i,out} = N_{avg} \ln\left(\frac{p_{nc,1}}{p_{nc,2}}\right) - \left(n_{i,2} - n_{i,1}\right)_{vessel} \qquad (16)$$

where $n_{i,out}$ are the moles of volatile component i leaving the vessel process vent. N_{avg} is the average gas space molar volume during the heating process, while $p_{nc,1}$ and $p_{nc,2}$ are the partial pressures of air (or nitrogen) in the vessel headspace at temperature T_1 and T_2. $n_{i,1}$ and $n_{i,2}$ are the moles of volatile component in the vessel headspace at T_1 and T_2. For this problem, the liquid consisted of a single solvent compoient i. For cases involving two or more volatile components Eq. (16) can be further revised to include the individual volatile components.

$$n_{voc,out} = N_{avg} \ln\left(\frac{p_{nc,1}}{p_{nc,2}}\right) - \left(n_{voc,2} - n_{voc,1}\right)_{vessel} \qquad (16a)$$

$$n_{i,out} = \left(\frac{p_{i,avg}}{\sum_{i=1}^{J} p_{i,avg}}\right) n_{voc,out} \qquad (16b)$$

$$p_{i,avg} = \frac{1}{2}\left(p_{i,1} + p_{i,2}\right) \qquad (16c)$$

and J is the total number of volatile solvent components.

Comparing Results Between the Standard EPA (1994) Heating Model and the Proposed Heating Model
Standard EPA (1994) Heating Model

The EPA literature [1] documents a worked example for the Heating Model as EPA Example #3 where a vessel containing toluene is heated from 20°C to 70°C. In this example

T_i	= 20°C	= 298.15°K	(Initial temperature)
T_f	= 70°C	= 343.15°K	(Final temperature)
P_T	= 1.0 atm	= 760 mm Hg	(Total system pressure)
V_{gas}	= 500 gallons	= 66.843 ft³	(Gas space volume)

$$P_{toluene,20°C} = \exp\left(16.0137 - \frac{3096.52}{293.15 - 53.67}\right) \qquad (17)$$

$$= \exp(3.0835) = 21.84 mmHg$$

$$P_{toluene,70°C} = \exp\left(16.0137 - \frac{3096.52}{343.15 - 53.67}\right) \qquad (18)$$

$$= \exp(5.317) = 203.74 mmHg$$

Universal Gas Constant:

$$R = 998.9\left[\frac{mmHg \cdot ft^3}{lb - mole \cdot °K}\right]$$

Gas Law:

$$n = \frac{PV}{RT}, \text{ also } n_i = \frac{p_i V}{RT}$$

for a single component, i, in the gas space.

Moles of nitrogen displaced by heating:

$$n_{nitrogen} = \left(\frac{p_{i,1}V}{RT_1}\right) - \left(\frac{p_{i,2}V}{RT_2}\right)$$

$$= \left(\frac{V}{R}\right)\left[\left(\frac{p_{i,1}}{T_1}\right) - \left(\frac{p_{i,2}}{T_2}\right)\right] \qquad (19)$$

Table 1. Toluene Emission Comparisons
(Heating From 20°C to 70°C)

Toluene Emissions (EPA 1994 Model)	Toluene Emissions (Proposed New Model)	Toluene Emissions Trapezoidal Rule (n=10, b=50°C)	Toluene emissions Trapezoidal Rule (n=50, b=1°C)
1.095 lb	0.995 lb	0.871 lb	0.868 lb

Table 2. Toluene Emission Comparisons
(Heating from from 20°C to 100°C)

Toluene Emissions (EPA 1994 Model)	Toluene Emissions (Proposed New Model)	Toluene Emissions Trapezoidal Rule (n=10, b=50°C)	Toluene emissions Trapezoidal Rule (n=80, b=1°C)
16.78lb	9.64 lb	8.46 lb	8.33 lb

Table 3. Toluene Emission Comparisons
(Heating from from 20°C to 110°C)

Toluene Emissions (EPA 1994 Model)	Toluene Emissions (Proposed New Model)	Toluene Emissions Trapezoidal Rule (n=18, b=50°C)	Toluene emissions Trapezoidal Rule (n=90, b=1°C)
425.9 lb	45.0 lb	65.1 lb	41.2 lb

$$n_{nitrogen} = \left(\frac{66.84}{998.9}\right)\left[\frac{(760-21.84)}{293.15} - \frac{(760-203.84)}{343.15}\right] \quad (20)$$

$$= (0.0669)[2.518 - 1.621] \quad (21)$$

$$n_{nitrogen} = 0.0600lb - moles$$

$$wt_{nitrogen}$$
$$= (0.0600lb - moles)(28.0134lb / lb - mole) \quad (22)$$
$$= 1.68lbs$$

The number of moles of toluene displaced from the vessel is equal to the moles of nitrogen which are displaced from the vessel during the heating operation multiplied by the average molar ratio.

$$n_{toluene} = \left(n_{nitrogen}\right)\left(\frac{p_{toluene}}{p_{nitrogen}}\right)_{average} \quad (23)$$

$$= (0.060)(0.1979) = 0.011874lb - moles$$

$$wt_{toluene} \quad (24)$$
$$= (0.011874lb - moles)(92.13lb / lb - mo\iota$$
$$= 1.09lbs$$

Calculations using the Proposed New Model

As shown earlier, the proposed new model is based on the average molar volume of the vessel headspace, the initial and final partial pressures of the noncondensable component (air, nitrogen, ...) in the vessel headspace, and the initial and final partial pressures of the volatile vapor component in the vessel headspace. In our example problem the non-condensable component is nitrogen and the volatile component is toluene vapor.

The average molar volume of the vessel headspace becomes:

$$n_{avg,sys} = \frac{1}{2}\left[\left(\frac{PV}{RT}\right)_1 + \left(\frac{PV}{RT}\right)_2\right]$$

$$= \frac{760 * 66.843}{2 * 998.9}\left(\frac{1}{293.15} + \frac{1}{343.15}\right) \quad (25)$$

$$n_{avg,sys} = 0.1608lb - moles \quad (26)$$

The initial and final partial pressures of the nitrogen component become:

$$p_{nc,1} = 760 - p_{toluene,1} = 760 - 21.84$$
$$= 738.16mmHg \quad (27)$$

$$p_{nc,2} = 760 = p_{toluene,2} = 760 - 203.74$$
$$= 556.26mmHg \quad (28)$$

The initial and final number of moles of toluene vapor in the vessel headspace are:

$$n_{toluene,1} = \left(\frac{p_{toluene,1}V}{RT} \right) = \frac{21.84 * 66.843}{998.9 * 293.15}$$
$$= 0.00499 moles \qquad (29)$$

$$n_{toluene,2} = \left(\frac{p_{toluene,2}V}{RT} \right) = \frac{203.74 * 66.843}{998.9 * 343.15} \qquad (30)$$
$$= 0.0397 \ moles$$

Substituting these values into Eq. (10) the toluene emission for the heating process becomes:

$$n_{i,out} = n_{avg,sys} \ln \frac{p_{nc,1}}{p_{nc,2}} - \left(n_{i,2} - n_{i,1} \right) \qquad (16)$$

$$n_{toluene,out} = 0.1608 \ \ln\left(\frac{738.16}{556.26} \right)$$
$$-(0.0397 - 0.00499) \qquad (31)$$

$$n_{toluene,out} = 0.0108 lb - moles \qquad (32)$$

$$wt_{toluene,out} = 0.0108 * 92.13$$
$$= 0.995 lbs \qquad (33)$$

Comparing the Results Between the Two Models

The 9% overestimation of toluene emissions (1.09 pounds based on the EPA 1994 model and 1.00 pound based on new model) is due largely to the error of integration $O(b^3)$ term, which was eliminated from the Trapezoidal Rule in Eq. (7). The error of integration $O(b^3)$ would have been lower if the Trapezoidal Rule integration technique had been applied using smaller incremental integration steps. Table 1 shows the effect that the integration step size (or number of integration steps)

has on the resulting toluene emissions using the Trapezoidal Rule.

The calculated difference between the EPA and the proposed model becomes more significant when the final temperature is increased to levels that are closer to the boiling point of the solvent. In the case of toluene, the liquid boiling point is 110.63°C. The calculated results when T2 is set to 100°C are shown in Table 2. For this final temperature, the proposed new model yields a toluene emission which is 57% as much as those obtained from the 1994 EPA model and only slightly more than the 8.33 pounds obtained from the Trapezoidal Rule with a 1°C iteration step size.

Table 3 presents the calculations for the case where T_2 is 110°C. The calculated results for the proposed model amounts to only 10.6% of the calculated results from the 1994 EPA model and is much more comparable to the results obtained from the Trapezoidal Rule with a 1°C iteration step size.

LITERATURE CITED

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