

**Using CHEMCAD to Solve EPA Air Emission Problems:
Estimating Emissions While Charging Solvents to an Empty Vessel**

By

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Abstract

Methods are presented to show how CHEMCAD can be used to solve the two example problems for charging liquid to an empty vessel given in **EIIP Document Chapter 16: Methods for Estimating Emissions from Chemical Manufacturing Facilities, August, 2007(1)**.

The first example involves the charging of a single component, hexane, to an empty vessel filled with nitrogen. In addition to showing the solution to the EPA example for emission rate from a vessel, the effect of adding vent condensers is demonstrated. A CHEMCAD sensitivity analysis is described to show the effect of process-side vent condenser outlet temperature on hexane emission rate. Finally, it is shown how CHEMCAD can be used to calculate the maximum hexane feed rate to the vessel that does not exceed an emission rate that may be set for the plant by a regulatory agency.

The second example involves the charging of a two-component mixture, 50-50 by volume heptane-toluene, to an empty vessel filled with nitrogen. Again the effect of the presence of vent condensers is demonstrated. The effect of the choice of VLE models on emission rate is investigated. It is shown that the VLE model, Raoult's Law, used in Chapter 16 underestimates the true emission rate by about 10% because the system is non-ideal.

Introduction

In August, 2007 the EPA published Volume II: Chapter 16 of its Emission Inventory Improvement Program (EIIP) (1). It is entitled: **Methods for Estimating Air Emissions from Chemical Manufacturing Facilities**.

The purpose of this publication, as stated in its introduction, is as follows:

"The purpose of this guideline document is to describe emission estimation techniques for point sources in an organized manner and to provide concise example calculations to aid in the preparation of emission inventories. While emissions estimates are not provided, the information presented in this document may be used to select an emission estimation technique best suited to a particular application. This chapter describes the procedures and recommended approaches for estimating emissions from batch chemical manufacturing operations and is intended to assist industry as well as regulatory agency personnel.

As EPA has indicated in this and other EIIIP documents, the choice of methods to be used to estimate emissions depends on how the estimate will be used and the degree of accuracy required, and methods using site-specific data are preferred over other methods. Because this document provides non-binding guidance and is not a rule, EPA, the States, and others retain the discretion to employ or require other approaches that meet the specific requirements of the applicable regulations in individual circumstances.”(1)

The purpose of this series of CHEMCAD white papers is to demonstrate how these emission calculations can be made easily and accurately with CHEMCAD. The CHEMCAD files used to make these calculations are provided as templates that can be downloaded from the Chemstations web site (www.chemstations.com/Support/Technical_Articles). They can be adapted to anyone’s needs, simply by changing the component list and operating conditions for the particular case of interest.

This paper describes how two examples in Chapter 16 can be calculated using CHEMCAD. These are: (1) charging a pure solvent to an empty vessel, and (2) charging a solvent mixture to an empty vessel. The more interesting case of charging solvents to a vessel already containing the same or different solvents will be discussed in the next paper in this series.

EPA Illustration 3-1: Charging a Pure Solvent to an Empty Vessel

The EPA example, **Illustration 3-1, Charging a Pure Solvent to an Empty Vessel**, is described as follows:

“A 5,000-gallon reactor is filled at ambient conditions (25 °C and 1 atm) with 3,600 gallons of hexane in one hour. The empty vessel was previously made inert with nitrogen, and the vessel is vented to atmosphere. Calculate the vapor emissions from this process.”(1)

Let’s look at how to set up a CHEMCAD flowsheet to solve this problem.

CHEMCAD Flowsheet for Charging a Pure Solvent to an Empty Vessel

Although the problem statement asks us to calculate the emissions over a one-hour time period—a dynamic situation—the problem is solved in steady-state in EPA Chapter 16. The problem can be solved this way because the hexane hourly flow rate is fixed throughout the time period.

The CHEMCAD file used for this problem can be downloaded from the Chemstations web site:

ChargingAnEmptyVesselEPAHexaneExample

It is recommended that the reader download, open, and refer to referenced CHEMCAD files while reading about the approaches to solving the various problems discussed in this paper.

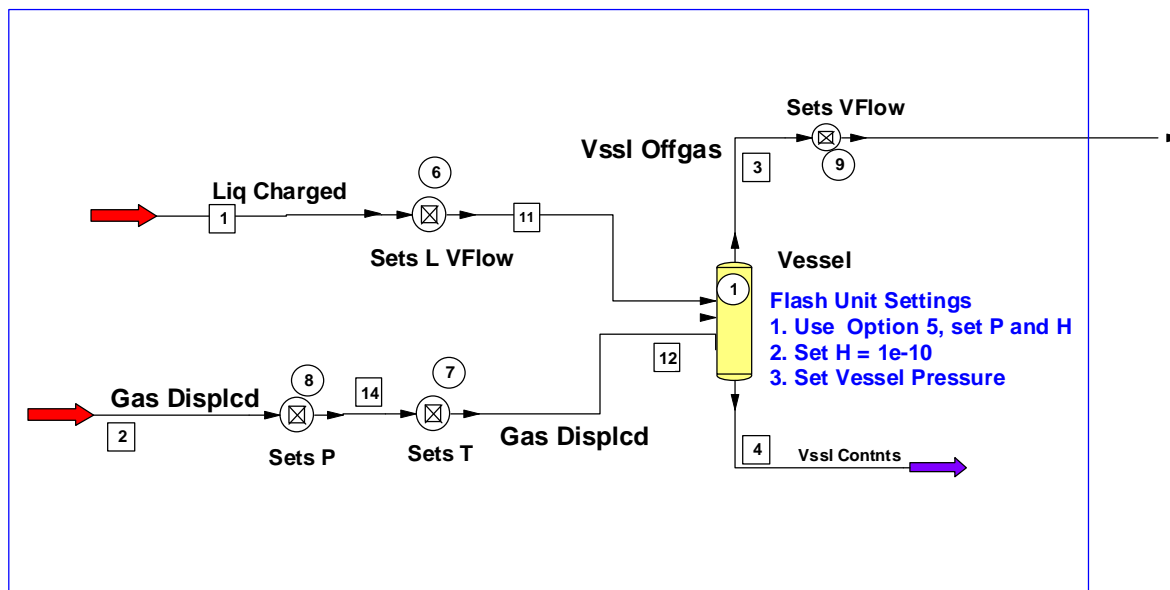


Figure 1 – The problem as solved in EPA Chapter 16

Figure 1 shows the CHEMCAD flowsheet for the steady-state EPA solution. It is contained within the blue box. Guidelines for selecting thermodynamic options are provided in the CHEMCAD file in a text box.

There are two feed streams: the hexane feed, stream 1, and a nitrogen stream, stream 2. Note that the liquid flow rate for the flowsheet is set in gph. To set these units, select **Format > Engineering Units** and then choose **Liquid Vol. Rate**.

The mass flow rate of hexane is adjusted by **Controller 6** so that the flow is the required 3600 gph. To access the settings for **Controller 6**, double-click the controller icon on the flowsheet. These settings are shown in **Figure 2**.

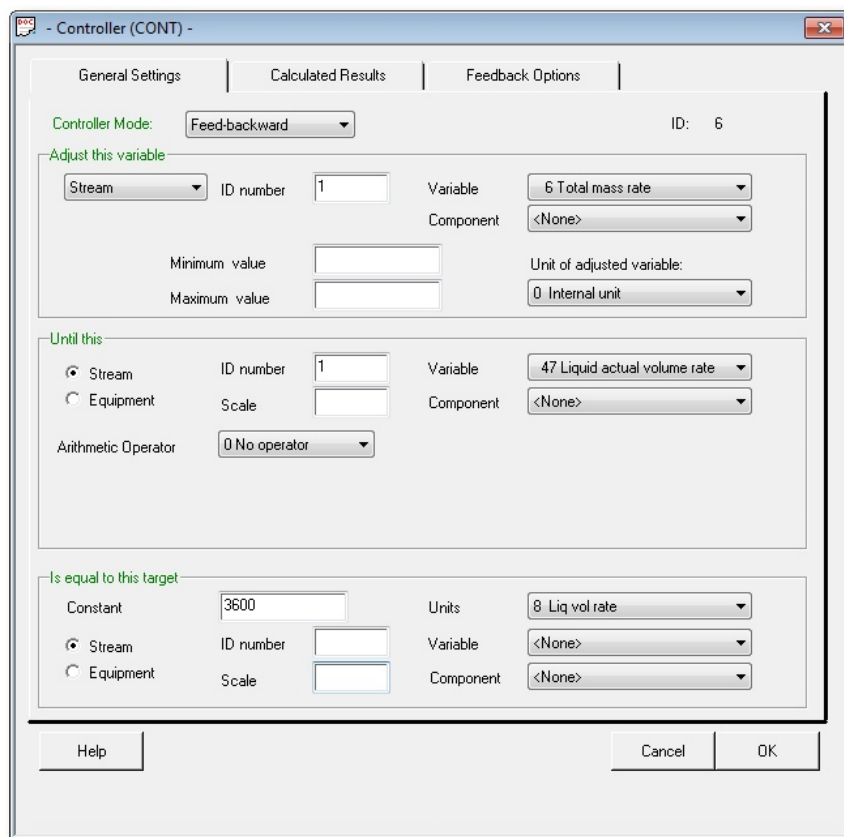


Figure 2 - Specifying Controller 6 to achieve the desired hexane flow

The nitrogen stream flow rate must be equal to the rate of displaced nitrogen from the tank due to the addition of liquid hexane. If 3600 gallons of hexane are added to the tank, they displace 3600 gallons of the vapor space of the tank, sending that vapor to the atmosphere or to an air pollution control device. The vapor will contain a mixture of hexane and nitrogen. This flowsheet calculates the amount of pure nitrogen displaced using **Controller 9**.

Controller 9 adjusts the nitrogen flow of stream 2 so the volume of total vapor displaced in stream 3 is equal to the volume of liquid hexane added. As with the previous controller, simply double-click the flowsheet icon for **Controller 9** to access its settings.

It is assumed that the hexane feed temperature, the nitrogen temperature in the tank, and the temperature of the tank are identical. This assumption is not necessarily true under all circumstances. For example, the hexane could be added hot to the vessel, where it will be cooled or further heated after other components are added to the tank. This is a surprisingly complex problem because of the thermal effects of the tank; such a scenario is outside the scope and intent of this white paper.

Controller 7 sets the nitrogen temperature equal to the hexane temperature. **Controller 8** sets the pressure of the displaced nitrogen in stream 2 equal to the vessel pressure set in the Vessel by Flash Unit 1. The feedback options for controllers 7 and 8 are identical.

It is assumed that the hexane is saturated in the nitrogen at the temperature and pressure of the vessel. The calculation at saturation is the result **always** returned by the **Flash Unit**, which is **UnitOp 1** in the flowsheet. This unit performs the vapor-liquid equilibrium calculation using the selected thermodynamic options. It performs mass and energy balance calculations and returns the liquid and vapor composition, as well as the mass of each phase.

The settings for **Flash Unit 1**, representing the vessel, are shown in **Figure 3**.

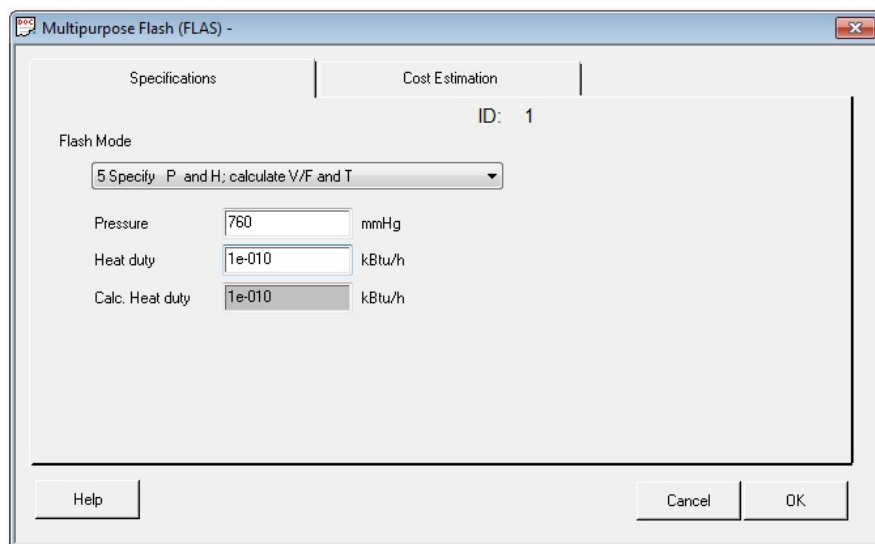


Figure 3 – Specifying Flash UnitOp 1

Flash Mode 5 is selected. The vessel pressure is the first parameter. It is assumed that the vessel is well insulated and is adiabatic. So the second parameter sets the heat loss or gain at $1e-10$ But/hr. Rather than set parameters like this equal to zero, I set them to a very low number so I am confident my intentions are satisfied.

The Flash unit simulates the final conditions in the vessel after one hour of feeding hexane to it. The hexane stream and the correctly sized displaced nitrogen stream are combined and separated according to the VLE option selected, in this case UNIFAC, and the Flash unit parameters, fixed vessel pressure and adiabaticity. The feed streams separate into the accumulated displaced vapor overhead stream and the accumulated liquid added to the vessel as the bottoms stream, after one hour.

A word should be said here about the thermodynamic option chosen, in this case UNIFAC. Since this particular problem involves a single liquid component and an inert gas, any standard thermodynamic option can be chosen, e.g., Raoult's Law, NRTL, UNIQUAC, Wilson, or UNIFAC. However, as you'll see in the second example described in this paper that involves a liquid mixture of two components, the choice of VLE options requires some consideration.

Running the EPA Problem

The EPA problem within the blue box is now ready to run. Follow these steps:

1. On the toolbar, select **Specifications > Feed Streams** to enter the flow rate of each component, and the pressure and temperature of streams 1 and 2 as shown in **Figure 4**. Before entering the T and P, delete the value in the Vapor Fraction field and leave it blank. You are only permitted to enter two of these three parameters. Before leaving this screen, flash both streams. When you click **Flash**, CHEMCAD calculates the vapor fraction and displays the results in the dialog box. Click **OK** to continue.

Stream No.	1	2
Stream Name	Liq Charged	Gas Displcd
Temp C	25	25
Pres mmHg	760	759.995
Vapor Fraction	0	1
Enthalpy kBtu/h	-19846.8	7.31418e-007
Total flow	20000	50
Total flow unit	lb/h	lb/h
Comp unit	lb/h	lb/h
N-Hexane	20000	0
Nitrogen	0	50

Figure 4 - Entering data in the Edit Streams dialog box

2. On the toolbar, select **Run > Convergence** to enter the convergence parameters shown in **Figure 5**.

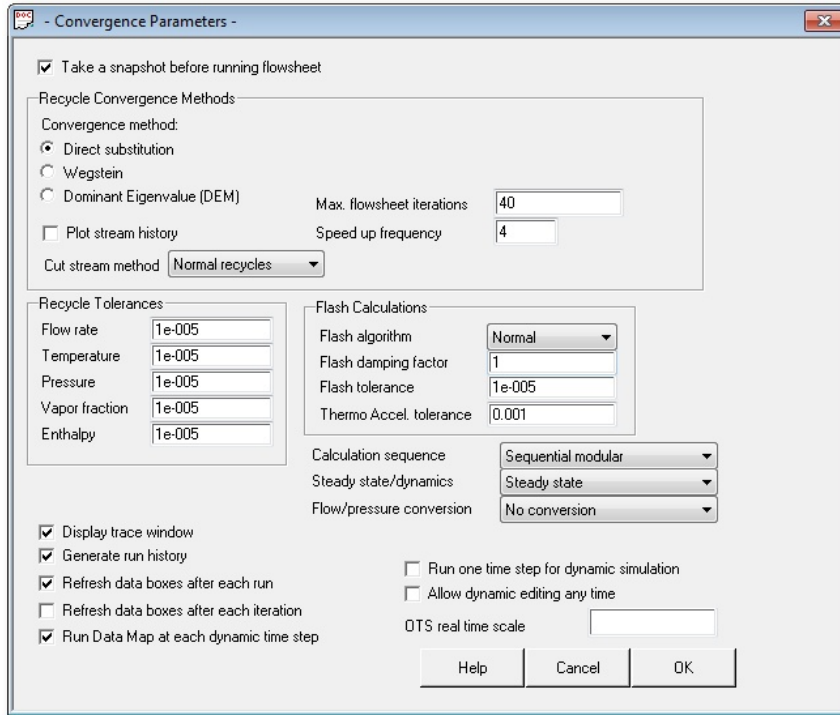


Figure 5 – Setting convergence parameters

The problem is simple and straightforward without recycle streams, so selecting the CHEMCAD default values on this page is fine. I changed the recycle tolerances to 1e-5, as is my habit. In this case, the results are unaffected.

Select **Sequential Modular** as the calculation sequence and make sure that **Steady state** is selected. Select **Display trace window** in the lower left part of the dialog box. This will provide the results of the calculations in real time as CHEMCAD is solving the problem. Select **Generate run history**, to provide a printable summary of the calculations made during the run. For debugging more complicated problems that are not converging, this is a very useful tool for determining the origin of the difficulty. Click **OK** to continue.

3. On the toolbar, select **Run > Run > Run Selected UnitOps**. A pop-up screen will appear. Rather than typing in UnitOp numbers, you can simply click on the UnitOps on the flowsheet, in the order you want to run them. The numbers will appear in the Select UnitOps screen as you click, as shown in **Figure 6**. Click **OK** to run the selected UnitOps.

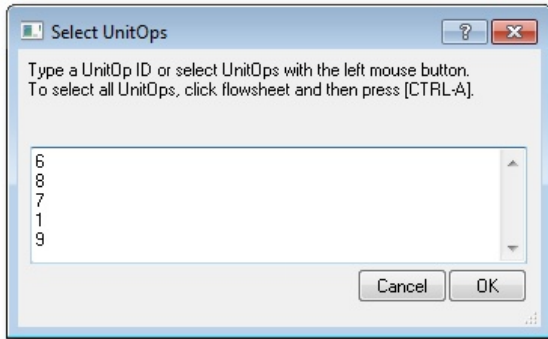


Figure 6 - Determining run order by clicking UnitOps on the flowsheet

4. The CHEMCAD Trace Window opens. Click **Go**. A series of controller calculation results will appear in the window. If you scroll down to the bottom of calculation results, you will see that the controller errors are all very small. The controller error is the difference between the CHEMCAD calculated value of the controller set point and the actual set point value you entered in the various controller dialog boxes. Above the **Go** button in the trace window is a message: *Run finished*.
5. Click **Close**. The run history now appears on your screen. To close it and return to the flowsheet, look for a tab at the bottom of the screen labeled **RunInfo**, and click the red **x** to the right of the tab name.

Simulation Results

It's good practice to check the results for each controller, to confirm that it converged and did what you asked it to do. You should also check the inlet and outlet streams for each unit operation, and for the entire flowsheet, to confirm that the results make sense and that the UnitOp settings are indeed what you wanted.

To obtain the inlet and outlet streams for a given UnitOp, simply right-click the unit and select **View Stream Composition**. Results for any and all streams are obtained by selecting **Report > Stream Compositions** and then making a stream selection. Stream physical properties can be obtained in a similar manner, by selecting **Stream Properties** instead of **Stream Compositions**.

Now let's examine the simulation results and compare them to the values given in EPA Chapter 16.

If you right-click **Stream 3, Vssl Offgas**, and select **View Composition**, you'll see the total vapor mass of hexane and nitrogen that leaves the vessel in one hour. EPA Chapter 16 results are 21.03 lb/hr hexane and 27.56 lb/hr nitrogen. CHEMCAD calculated values are 21.18 and 27.67, respectively. Note that the temperature is slightly lower than 25 °C. This is due to evaporative cooling of the hexane.

Off Gas Composition

The composition of the off gas is important, since there may be regulatory limitations. On the toolbar, select **Report > Set Flow Units**, then choose **Mole Fractions** and click **OK**. Now review the stream composition. The stream is almost 20% hexane by volume. This concentration and the hexane mass rate may both be too high to meet the plant's regulatory requirements. So some air pollution control may be necessary.

In the CHEMCAD flowsheet I have added two vent condensers; the first uses chilled water, and the second uses a refrigerant. The heat exchanger design details are not important for this example. In the first condenser, the off gas is cooled to 10 °C. The dialog box for the chilled water condenser is given in **Figure 7**.

Simple Heat Exchanger (HTXR) - ID: 2

Specifications | Utility Rating | Cost Estimations

Pressure drop: 2.5857 mmHg

For design mode, enter only ONE of the following:

Temperature of stream 5	10	C
Vapor fraction of stream 5		
Subcooling for stream 5		C
Superheat for stream 5		C
Heat Duty		kBtu/h
Delta T stream 5 - stream 15		C

Backcalc Mode (for Autocalc):
0 No back calculation

Calculated Heat Duty	-2.2718	kBtu/h
LMTD (End points)		C
LMTD Corr Factor	1	
Utility Flow rate (see Rating Case)		lb/h

Help | Cancel | OK

Figure 7 – Specifications for chilled water condenser

The dialog box for the refrigerated condenser is shown in **Figure 8**.

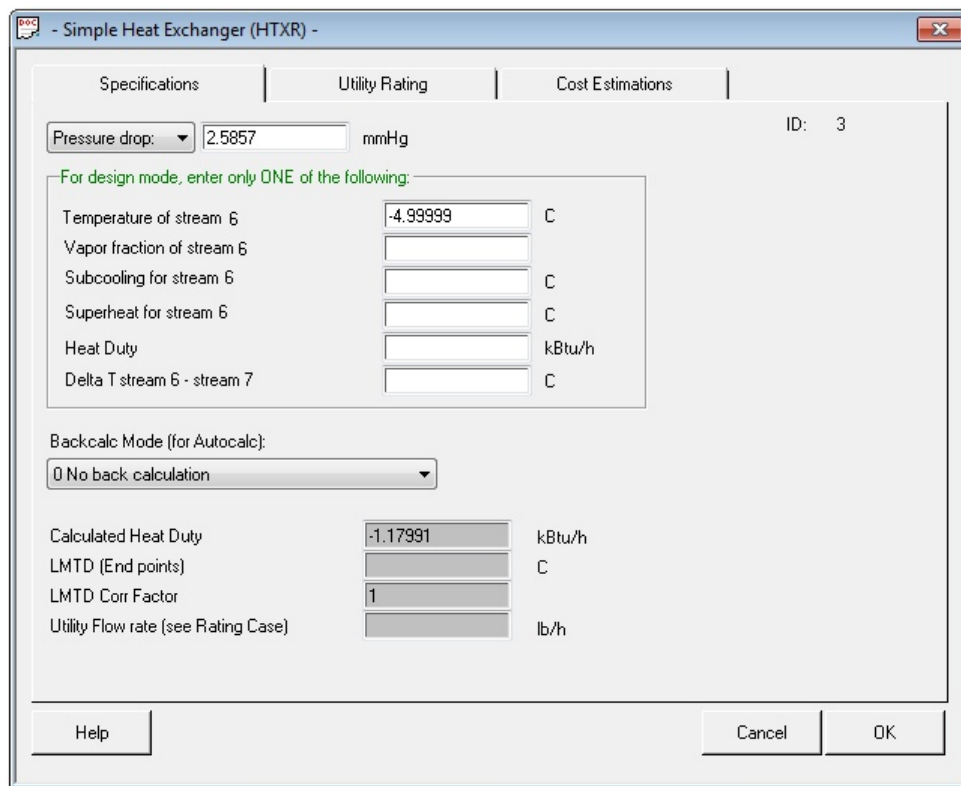


Figure 8 – Specifications for refrigerated condenser

The process stream is cooled to -5 °C. To add some realism to the situation, a process-side pressure drop of 0.05 psi is assigned to each condenser. To open these dialog boxes, simply double-click the appropriate heat exchanger icon on the flowsheet.

The flash units following each vent condenser act as liquid-vapor separators, removing the condensate from the vapor stream that goes forward in the process. The settings are identical. Again, open the dialog box for flash unit settings by double-clicking the appropriate flowsheet icon.

The flash unit instruction is to maintain the feed stream temperature and pressure for the two product streams. Consequently with no heat added or removed and no change in pressure or temperature, there is no production or condensation of vapor. The only thing the flash unit can do, with these settings, is to separate the liquid and vapor in the two-phase feed.

What is the effect on hexane vapor effluent of adding vent condensers? An examination of the chilled water condenser off gas, stream 7, shows that the hexane flow rate has been cut by 55%, from 21.18 lb/hr to 9.55 lb/hr, and the composition from 20 mole % to 10 mole %. Adding the refrigerated condenser cuts the hexane emission to 4.1 lb/hr and 4.59 mole %.

Hexane emissions at these lower levels may in fact be required in a particular plant. So a simple simulation of this type can be valuable in demonstrating to what extent air pollution devices may be

necessary. If a refrigerated condenser is not adequate in reducing the hexane emitted to a sufficiently low level, installation of a scrubber might be necessary. This additional control device can also be simulated in CHEMCAD to determine operating conditions and sizing of the equipment. This, however, is outside the scope of this paper.

Sensitivity Study

The Sensitivity Study tool is a very useful feature of CHEMCAD. It enables you to vary an input parameter in the flowsheet to determine the effect on output parameters of the system. To demonstrate this feature, you will vary the first vent condenser outlet temperature to determine the effect on vent condenser heat duty, hexane emission rate, and composition.

To start, select **Run > Sensitivity Study > New Analysis**. This opens a dialog box that asks you to name the analysis. Let's call it **Effect Condenser T**. When you click **OK**, a new dialog box opens to enter the independent parameters of interest under the Adjusting tab. **Figure 9** shows the completed dialog box. Choose the first vent condenser outlet temperature as the independent variable that you will vary from 25 °C, the temperature of the tank, down to -5 °C in one-degree intervals.

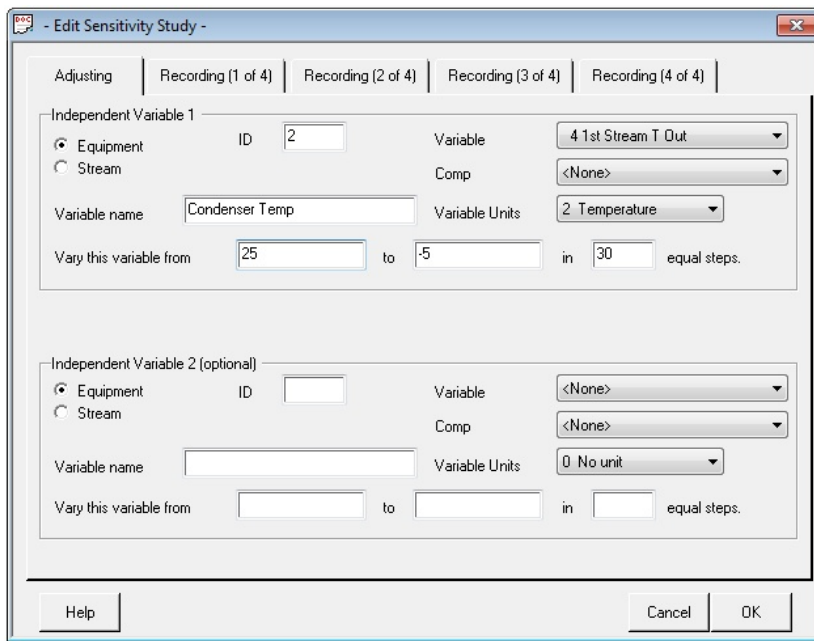


Figure 9 – Creating a new sensitivity analysis: the Adjusting tab

A second parameter is permitted in CHEMCAD. This could be condenser pressure drop, for example. In this case, no second independent variable is chosen.

Selecting the second tab, **Recording (1 of 4)**, enables you to enter the output variables you want to examine. Select condenser duty, hexane mass rate in the off gas (stream 7), and hexane mole fraction in the off gas. These settings are shown in **Figure 10**.

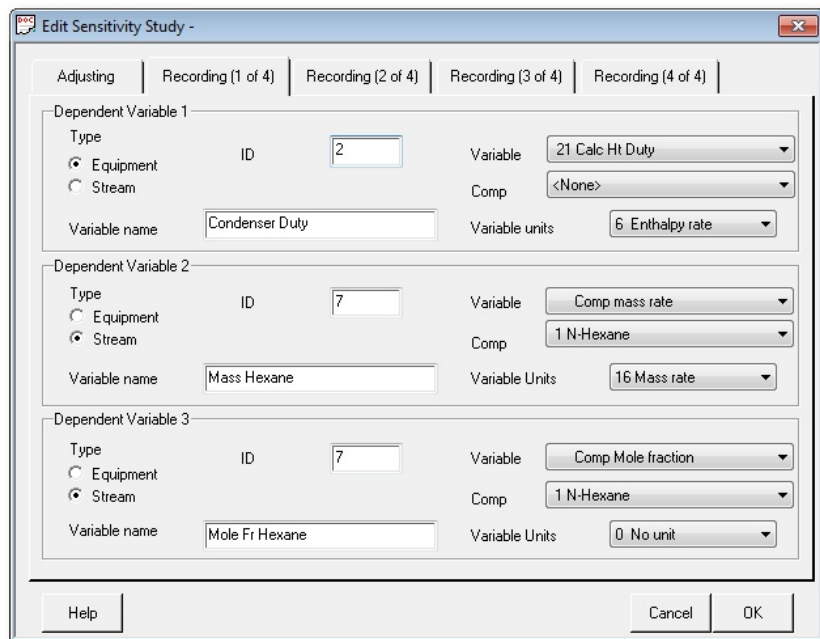


Figure 10 - Setting up dependent variables

Up to 12 dependent variables can be selected if all of the recording tabs are used. Click **OK** to save these settings and close the dialog box.

Before running the sensitivity study, select **Run > Convergence** and make sure that **Generate Run History** is **unchecked**. If you check this box, a run history will be generated for every temperature increment.

To run the sensitivity study that you just created, select **Run > Sensitivity Study > Effect Condenser T > Run Selected**. You don't need to run the entire flowsheet using the **Run All** command, because you're only interested in the flowsheet through the first L-V separator. Instead, use the **Run Selected** command, and choose the UnitOps you want to run. You can either enter UnitOp ID numbers by hand in the order you want them to run, or simply click on them from the flowsheet. Set up the UnitOps to run in the order shown in **Figure 11**.

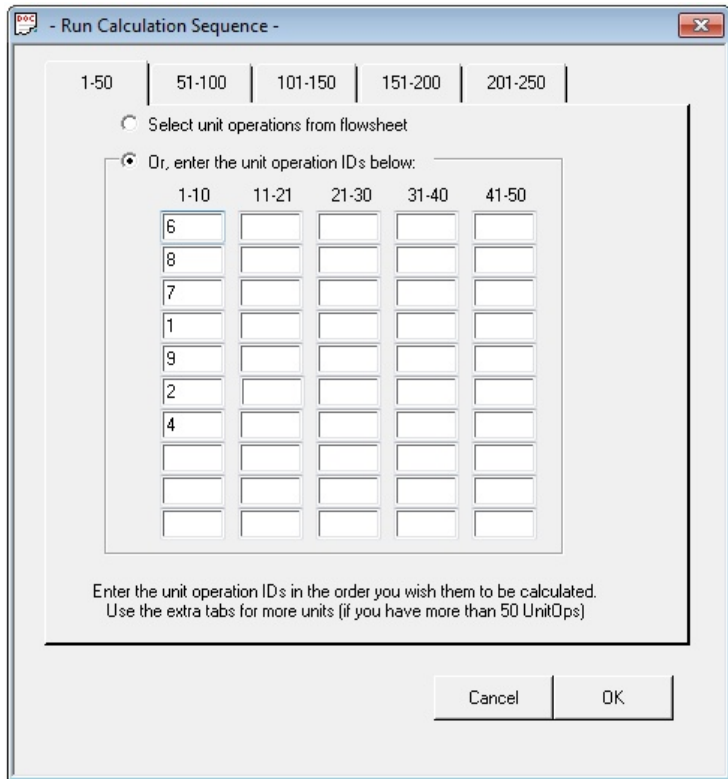


Figure 11 - Setting up the run order for the sensitivity study

Click **OK** to run the sensitivity study. The CHEMCAD Trace Window will open. Click **OK** and the calculations will scroll through the box. When you close the trace window, a pop-up dialog appears, asking: **Do you wish to reset the process data to the original state?** The choice is yours; the results of the sensitivity study are unaffected. In this case let's choose **Yes**. The dialog box closes.

To see the results of the sensitivity study, select **Run > Sensitivity Study > Effect Condenser T > Report Results**. A table appears, giving the results of the sensitivity study.

This table can be shown as an Excel spreadsheet if you choose; indeed, any CHEMCAD report can be provided in Excel format. To switch to Excel report output, click **Tools > Options > Preferences** and select **Report Viewer**. Under **Default Report Destination**, select **Excel**, then click **OK**. The next time you obtain the report results as above, an Excel window will launch and display the results of your sensitivity study.

Graphical results of the sensitivity study can also be generated directly from CHEMCAD. Select **Run > Sensitivity Study > Effect Condenser T > Plot Results**. This opens the Sensitivity Plot dialog box. You can choose the variables you want to examine on the X-Y axis, label the Y axis, and give the plot a name.

Choose **Mass Hexane** as the Y axis option and **Condenser Temp** as the X axis option. Click **OK** to obtain a table of the plotted points in whatever format you chose under **Report Default Destination**, as described above. When you close this screen, the plot appears, as shown in **Figure 12**.

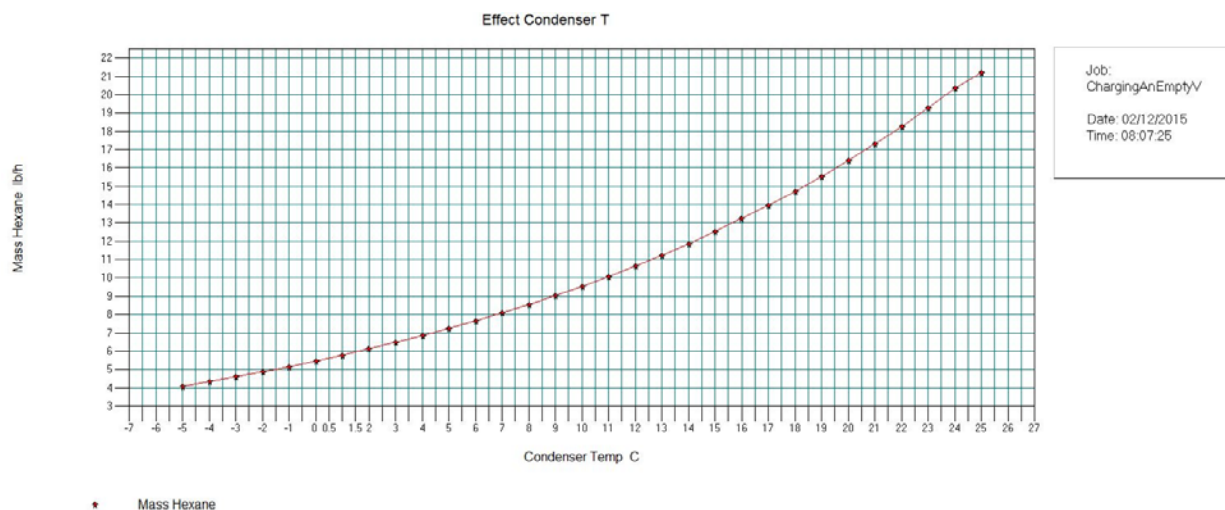


Figure 12 – Plot showing hexane flow as a function of condenser temperature

Non-Uniform Hexane Flow

If the hexane flow varies in some non-uniform way, but the total flow of hexane remains the same at 3600 gallons, this method would provide the cumulative hexane emission over the one-hour time period, but not the instantaneous emission rate at any time during the one-hour time period. It is important to know the instantaneous emission rate, because regulatory agencies often set instantaneous emission rate limits at chemical plants for designated compounds, as well as total accumulated component emission mass over a one-year period.

Calculate Maximum Hexane Charge Rate

If we know the maximum permitted instantaneous emission rate for hexane, we can use CHEMCAD to back-calculate the maximum permissible hexane charge rate. Let's assume that the maximum emission rate is 5 lb/hr. This will be demonstrated in the CHEMCAD file called:

ChargingAnEmptyVesselEPAHexaneExample - Max Fd Rate

The flowsheet is shown in **Figure 13**.

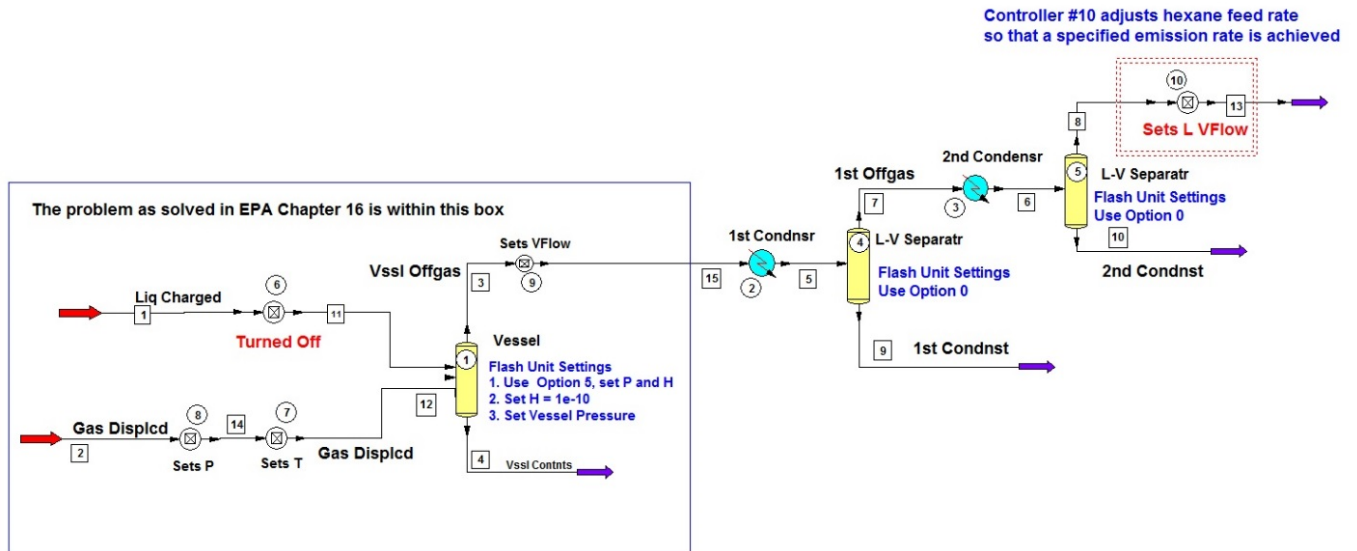


Figure 13 – CHEMCAD simulation used to calculate maximum hexane charge rate

When you open the file, you'll notice that in this flowsheet an additional controller, **Controller 10**, is added after the **L-V Separator, Unit Op 5**, at stream 8. This controller adjusts the flow rate of hexane, stream 1, so that the emission rate at stream 8 is equal to 5 lb/hr. To access the settings for **Controller 10**, double-click the controller on the flowsheet.

Controller 6, which sets the flow of hexane to exactly 3600 gpm in the previous example, **must** be turned off because it conflicts with the new controller. To access the new settings for **Controller 6**, double-click the controller.

When you run the simulation, you will find that the maximum hexane feed rate is 4392.7 gph, using the air pollution control devices, the vent condensers, shown on the flowsheet.

EPA Illustration 3-2: Charging a Solvent Mixture to An Empty Vessel

The second EPA example, **Illustration 3-2, Charging a Solvent Mixture to an Empty Vessel**, is described as follows:

“A 50-50 volume percent solvent mixture of heptane and toluene is charged to a surge tank at a rate of 50 gal/min. A total of 1500 gallons of mixed solvent is charged at 20 °C. Calculate the vapor emissions from this process.”(1)

Let’s see how we can set up a CHEMCAD flowsheet to solve this problem.

CHEMCAD Flowsheet for Charging a Solvent Mixture to an Empty Vessel

Figure 14 shows the CHEMCAD flowsheet for the steady-state EPA solution. It is contained within the blue box. Guidelines for selecting thermodynamic options are provided in a text box on the flowsheet.

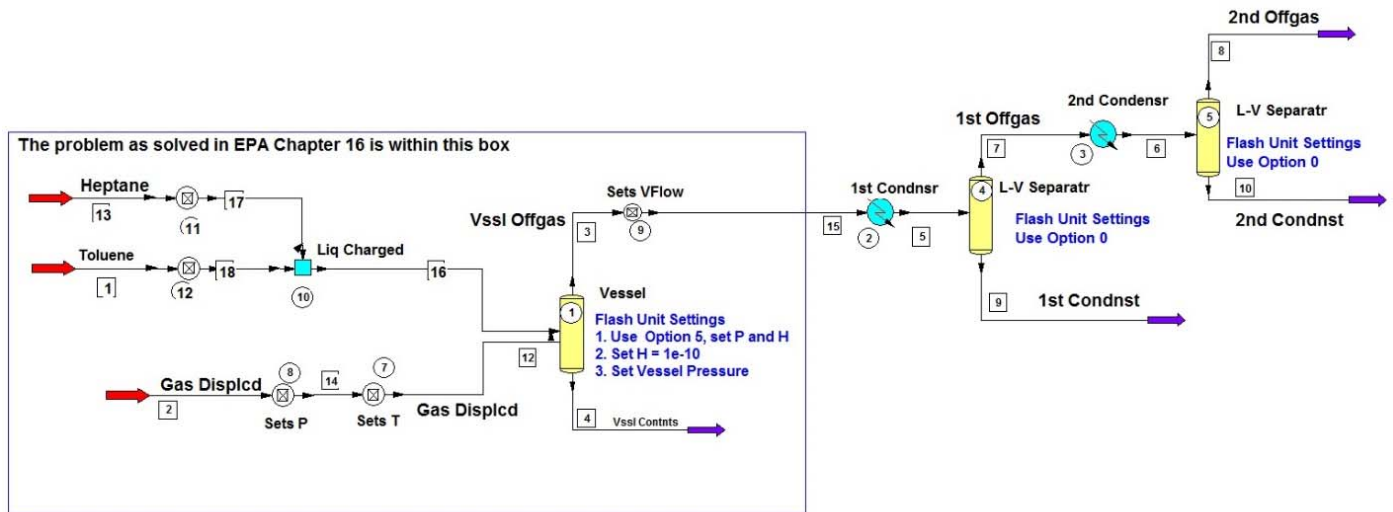


Figure 14 - CHEMCAD simulation used to calculate vapor emissions of 50-50 heptane-toluene mixture charged at 20 °C

The CHEMCAD file for this flowsheet is called:

ChargingAnEmptyVesselEPAHeptane-TolueneExampleIdeal

There are three feed streams: heptane, toluene, and nitrogen, respectively. To achieve the required 50-50 mixture by volume, the volumetric flow rates of heptane and toluene are each set to 25 gpm at 20 °C and 1 atm pressure. This is accomplished by **Controller 11** for heptane and **Controller 12** for toluene. To access the settings for these controllers, double-click their icons on the flowsheet.

Controller 7 sets the gas temperature equal to the temperature of the mixed stream, **Stream 16**. Again, to access this controller’s settings, simply double-click the controller on the flowsheet.

The rest of the flowsheet is identical to the hexane flowsheet, except for a slight change in **Controller 9** settings. The referenced stream for liquid flow in the controller is the mixture charged, **Stream 16**. Check the controller settings to confirm this, by double-clicking the controller on the flowsheet.

To simulate EPA illustration 3-2 (Chapter 16, page 16.3-3), it is necessary to set the VLE option to ideal system, or Raoult's Law. To make this setting, select **Thermophysical > Thermodynamic Settings** and then choose **Ideal Vapor Pressure (Raoult's Law)** under **Global K-value Model**. Click **OK**.

Simulation Results

Run the simulation by using the **Run** menu (select **Run > Run All**), or by clicking the green **Run All** button on the toolbar. Then check the composition of Stream 3, the vapor leaving the surge tank. Simply double-click Stream 3 to see this information. The CHEMCAD results are 2.03 lb/hr for heptane and 1.60 lb/hr for toluene. The results in EPA Chapter 16 are 2.04 lb/hr and 1.60 lb/hr, respectively.

Wow! The agreement is nearly perfect.

The only problem with these results is that they are wrong. Making the assumption that the heptane-toluene binary is an ideal system is incorrect. This is a decidedly non-ideal system, as we shall see.

Nearly every real binary system is at least a little bit non-ideal; this is true even for systems we were taught are ideal, like benzene-toluene. Some systems have very significant deviations from ideality: they form homogeneous azeotropes, like acetonitrile-water; heterogeneous azeotropes, like n-butanol-water; or irregular X-Y diagrams, like acetone-water. Many non-ideal systems involve an organic compound and water, but this is not always the case.

Let's examine the moderately non-ideal heptane-toluene system more closely, so we can see what effect not accounting for this non-ideality has on emission rates.

First, here's a little theory to set up the discussion.

Calculating Liquid-Vapor Compositions of Binary Systems

The equation governing the vapor-liquid equilibrium for binary systems is the following:

$$P_T = \gamma_1 X_1 P_1^0 + \gamma_2 X_2 P_2^0 \quad (1)$$

where:

P_T = the total pressure of the system

X_1, X_2 = liquid phase mole fraction of component 1 and 2, respectively

γ_1, γ_2 = the liquid phase activity coefficient for component 1 and 2, respectively

P_1^0, P_2^0 = the pure component vapor pressure for component 1 and 2, respectively

The pure component vapor pressures are temperature-dependent, and the data usually can be correlated with the classic Antoine equation given in the examples in EPA Chapter 16 (1), or the industry standard fitting equation developed by the Design Institute for Physical Properties (DIPPR), given in the

CHEMCAD Help file (2). The CHEMCAD physical property database contains DIPPR-certified vapor pressure equations for all of the more than 2200 compounds in the DIPPR database.

The liquid phase activity coefficients are equal to unity for an ideal system, greater than unity for systems with positive deviations from ideality, and less than unity for systems with negative deviation from ideality. Most, but not all, systems exhibit positive deviation from ideality. The liquid phase activity coefficients can be thought of as correction terms for the ideal system. They are functions of the liquid composition and the system temperature.

For the EPA problem under consideration, the temperature is fixed at 20 °C and the liquid composition is known to be 50-50 by volume. This simplifies the solution of equation (1) considerably. All of the terms on the right side of the equation are known. Solving this equation gives the total vapor pressure of the liquid mixture at 20 °C.

If the system pressure were equal to this total vapor pressure, the liquid would boil. In other words, equation (1) calculates the system pressure corresponding to a 20 °C bubble point for the heptane-toluene mixture. However, the system pressure in the EPA problem is 760 mm Hg. So the nitrogen in the vessel makes up the difference to maintain the system pressure at atmospheric and it does not boil.

The total vapor pressure of the liquid components is significant, because this value is directly proportional to the number of moles of organic saturated in the nitrogen that is displaced from the surge tank by the incoming heptane-toluene mixture. The higher the total vapor pressure becomes, the higher the total organic emissions will be.

Liquid Phase Activity Coefficient Models

There are four main models for the liquid phase activity coefficient: NRTL (3), UNIQUAC (4), Wilson (5), and UNIFAC (6). These differ from the two older models, Van Laar and Margules. The latter two models are strictly curve fitting equation forms with two adjustable constants that fit the data for many binary systems. As such, they are quite adequate, since they are relatively simple equation forms. However, their application is limited to systems of no more than three components, using six adjustable constants. Additionally, these models are not functions of temperature, so strictly speaking, they are only applicable for the temperature and pressure conditions of the data that were regressed.

Wilson, NRTL, and UNIQUAC are all based on thermodynamic principles related to molecular structure; they permit their respective equations to be expanded to, at least theoretically, an unlimited number of components. This is accomplished by permitting the entire system to be defined in terms of each binary pair of the system, rather than all of the components simultaneously. Components can be added to or removed from the system without the need to re-correlate the data.

This is an extremely powerful feature that permits large and complex systems to be accurately analyzed. However, the activity coefficient equations are quite complex, even for small systems, and equation (1) must be solved by numerical analysis for each liquid composition if the system is at constant pressure rather than constant temperature. CHEMCAD automatically performs this regression analysis easily and

effortlessly. Additionally, the models are functions of temperature, so the VLE can be estimated over a wide range of temperatures and pressures. The equations for these models are given in the CHEMCAD Help file (2).

UNIFAC (**UNIQUAC Functional-group Activity Coefficients**) is a predictive activity coefficient model that is widely used for systems for which there are no data. UNIFAC uses interaction coefficients between the functional groups that compose the molecules that make up the liquid mixture to calculate activity coefficients. The interaction coefficients are determined by back-calculating from regression analysis of real data for binary systems of full compounds. CHEMCAD maintains an up-to-date library of UNIFAC information, since Chemstations is a contributing member of the consortium of chemical companies that supports this ongoing research and the maintenance of a library of VLE data.

Researchers for this group, **The Dortmund Data Bank Group (DDBG)**, correlate all of the binary data in the library using the models described above, and publish the results for use by their supporters. The CHEMCAD physical property library contains interaction parameters for these activity coefficient models for all of the binary systems regressed by the DDBG, including heptane-toluene.

Let's now see this how this system looks when these non-ideal activity coefficient models are used.

Comparing VLE Results of Activity Coefficient Models

To make this comparison, I have copied the ideal system CHEMCAD file we just worked with to four new CHEMCAD files that you can download. These files have the following names:

ChargingAnEmptyVesselEPAHeptane-TolueneExampleNRTL

ChargingAnEmptyVesselEPAHeptane-TolueneExampleUNIQUAC

ChargingAnEmptyVesselEPAHeptane-TolueneExampleWilson

ChargingAnEmptyVesselEPAHeptane-TolueneExampleUNIFAC

Each file's name reflects the thermodynamic option used in the simulation. The XY diagram, the TXY or PXY diagram, and the graph of activity coefficients can be plotted for each model.

Open one of these simulations, and click **Plot > TPXY** to open the dialog box shown in **Figure 15**.

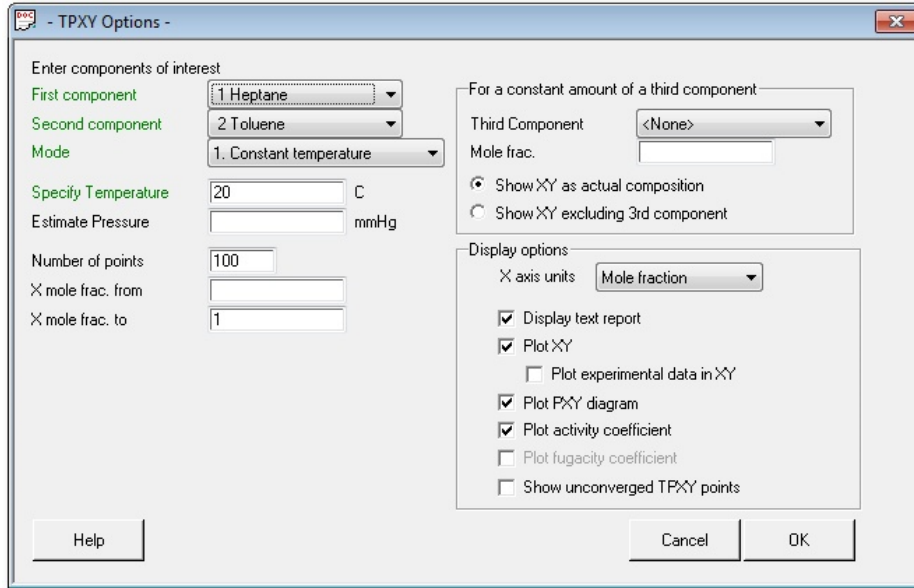


Figure 15 – TPXY Options dialog for the UNIFAC model example

When you click **OK**, a table of TPXY and activity coefficient values displays. When you close this window, the XY diagram is shown. Closing that window gives you the TXY or PXY diagram, depending on the choice of constant pressure or constant temperature. And, finally, closing that window gives you a plot of activity coefficients. Examples of these three curves for NRTL are given in **Figures 16, 17, and 18**.

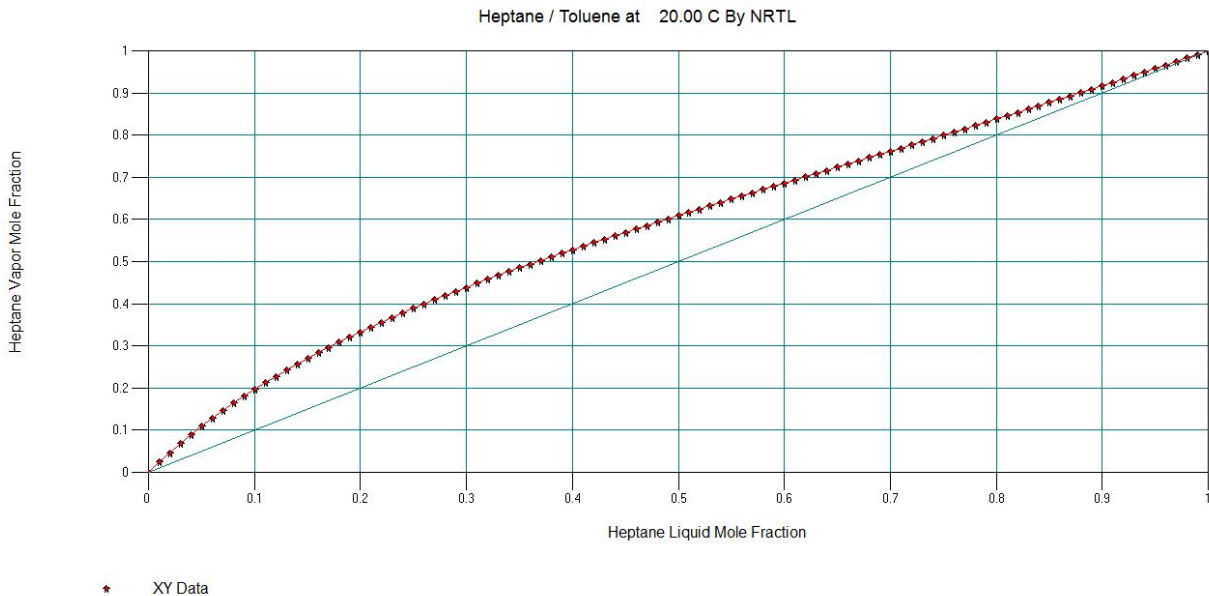


Figure 16 - XY diagram for NRTL model example

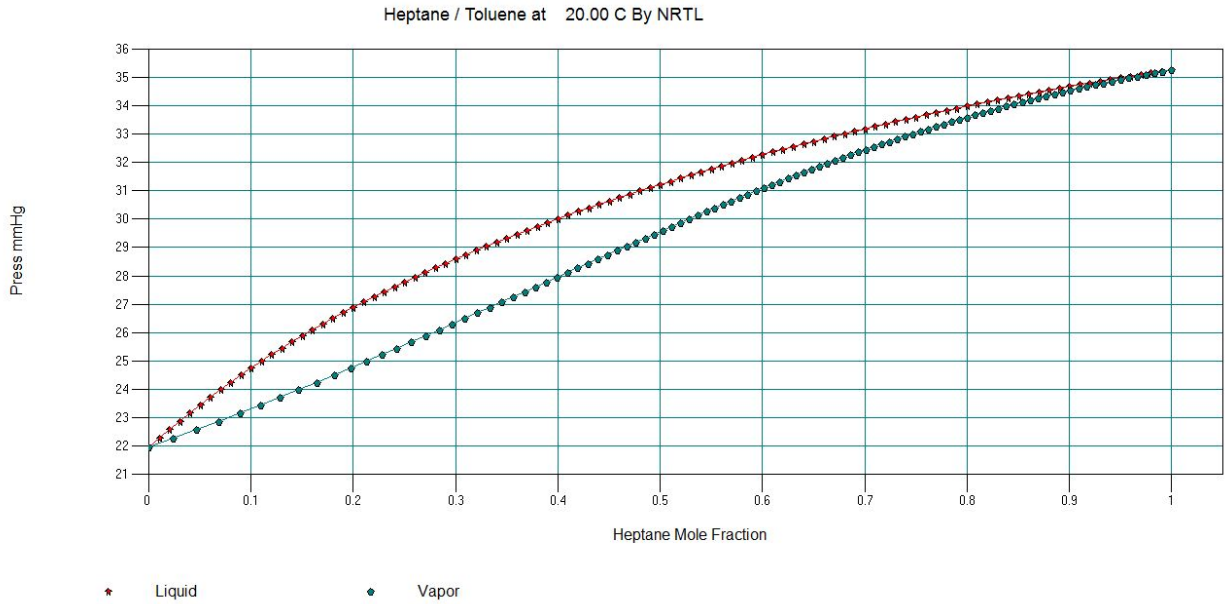


Figure 17 - PXY diagram for NRTL model example

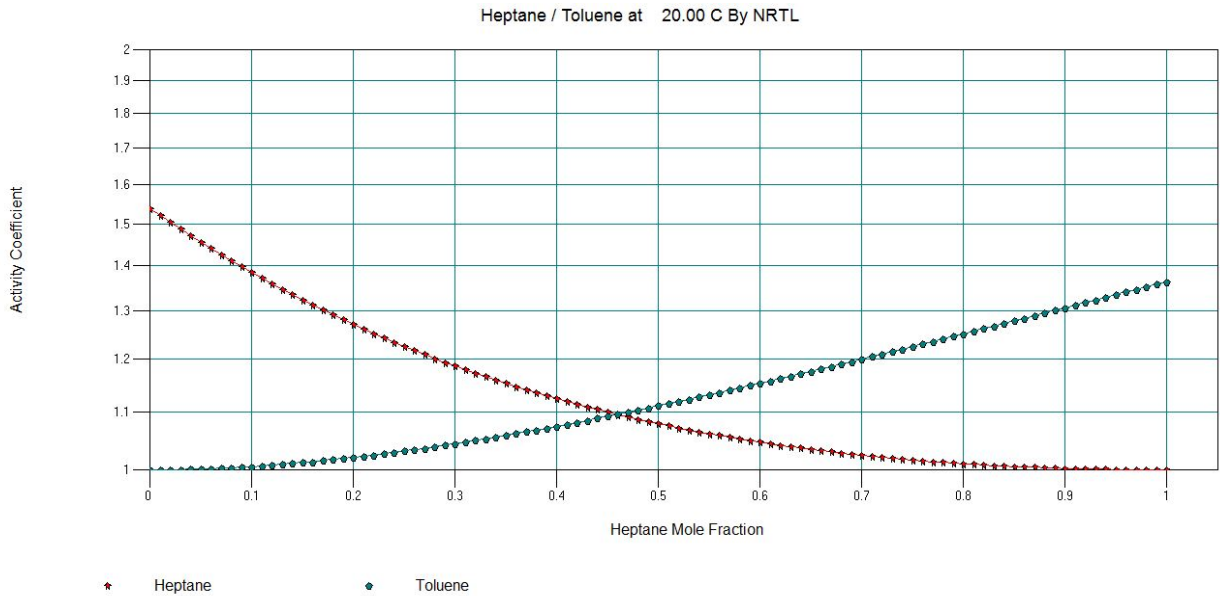


Figure 18 - Activity coefficient plot for NRTL model example

Constant temperature at 20 °C was specified in the TPXY dialog box to reflect the conditions of the EPA problem.

It should be noted that the regression analyses made by the DDGB for the NRTL, UNIQUAC, and Wilson models used the same raw heptane-toluene VLE data. These analyses produced the two fitting

constants for each model that give the best least squares fit of the raw VLE data. These constants are contained in the CHEMCAD physical properties database and are automatically used in a simulation.

To view the constants for each model, select **Thermophysical > Thermodynamics Settings** and then click **OK**; they are also displayed in the tabular printout of TPXY values before the plots appear.

Total Organic Emission Rate

A glance at the activity coefficient plots for all models in **Figure 19** shows just how non-ideal this system is.

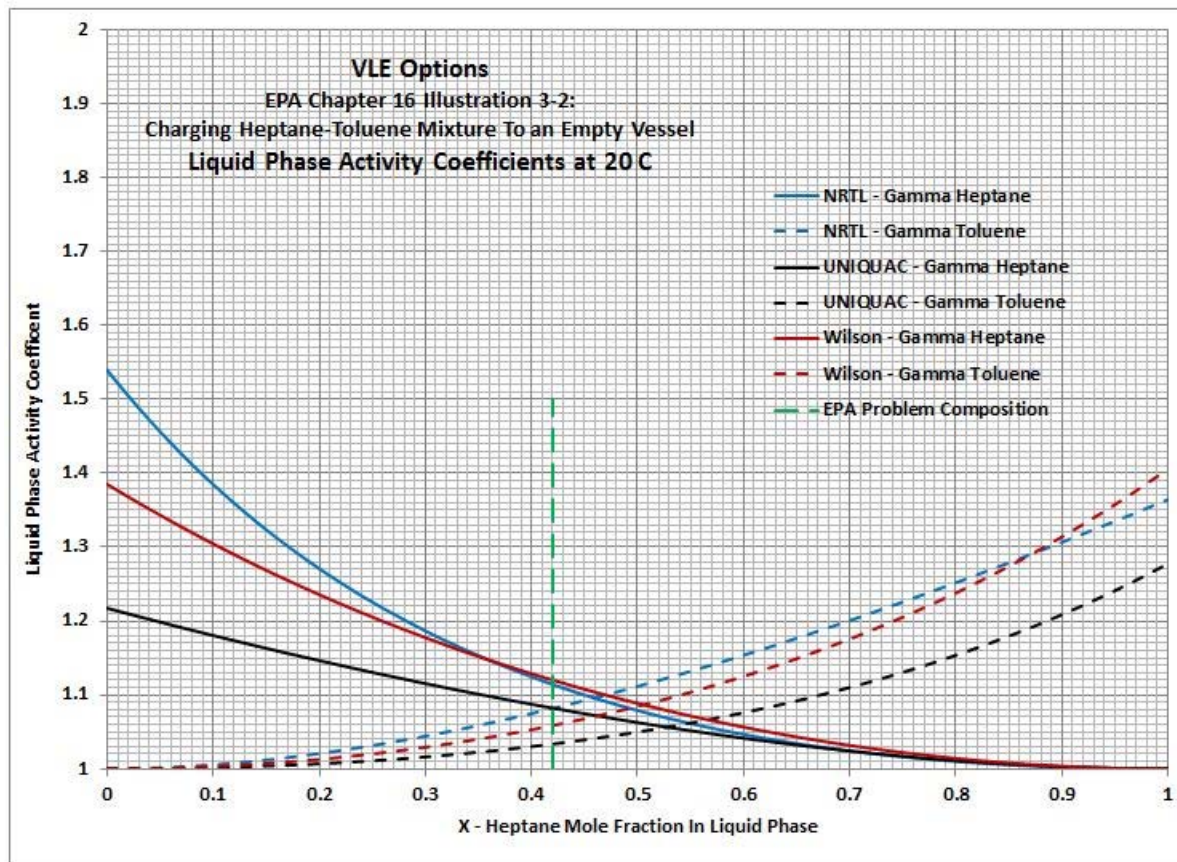


Figure 19 - Activity coefficient plots for all models

The activity coefficients are all greater than unity, so the system exhibits positive deviation from the ideal system of Raoult's Law. From equation (1) it is clear that at a fixed temperature, the total vapor pressure for this non-ideal system is greater than that for the ideal system. Thus, for any composition, the moles of organic in the displaced vapor will be larger than for an ideal system. **The assumption of ideality will underestimate the emission rate and produce an incorrect result.**

Figure 20 shows the total vapor pressure curve for each model.

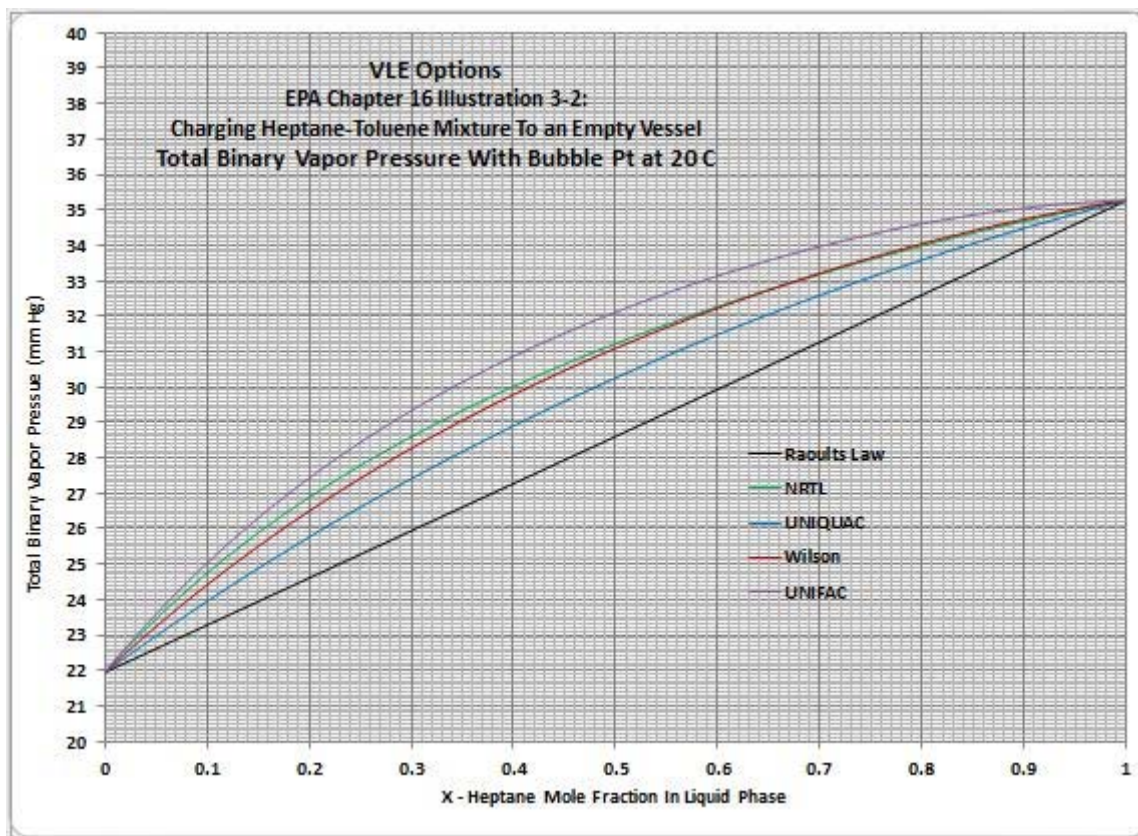


Figure 20 – Total vapor pressure curves for all models

As expected, Raoult's Law gives the lowest total vapor pressure for all liquid compositions. The predictive UNIFAC model, partially based on regression of real VLE data, consistently gives the highest total vapor pressure and the highest emission rate. The total vapor pressures for the three models based on regression of real data for the system in question (heptane-toluene) fall in between. NRTL gives the highest emission rates of the three models, with the Wilson model coinciding above about 62 mole % heptane in the liquid.

So what model should you choose?

In my opinion, the total mass rate of the organic compounds in the emission is of primary importance, since instantaneous rate and total accumulated emissions are both regulated by local and Federal agencies. My approach is to choose the model that gives the most conservative emission rate, since it would require the most conservative air pollution controls.

In this particular EPA example, would I choose UNIFAC because it gives the highest total emission rate? My answer is no, because models are available that are based on real data. I would choose NRTL, because it gives the highest total emission rate of the models that are based on real data regression. The results for Stream 3, the untreated emissions of the EPA problem, are given in **Figure 21**.

	Untreated Emissions				
FLOW SUMMARIES:	Raoult's Law	NRTL	UNIQUAC	Wilson	UNIFAC
Stream No.	3	3	3	3	3
Stream Name	Vssl Offgas	Vssl Offgas	Vssl Offgas	Vssl Offgas	Vssl Offgas
Temp C	19.9623	19.9586	19.9601	19.9589	19.9575
Pres mmHg	760	760	760	760	760
Vapor mole frac.	1	1	1	1	1
Total lbmol/h	1.0417	1.0418	1.0418	1.0418	1.0418
Total lb/h	31.7632	32.0232	31.922	32.006	32.1082
Flow rates in lb/h					
Heptane	2.0336	2.2648	2.2001	2.2769	2.3702
Toluene	1.6027	1.7338	1.6566	1.6967	1.7458
Heptane + Toluene	3.6363	3.9986	3.8567	3.9736	4.116
Nitrogen	28.127	28.0247	28.0653	28.0324	27.9923

Figure 21 - Stream 3 emission results

The emission rates for NRTL and Wilson are close, with NRTL having a higher toluene concentration and Wilson a higher heptane concentration.

In some cases, for which real VLE data are not available for regression analysis, or the data are hopelessly inconsistent, which sometimes happens, the only available choice that has some semblance to reality is UNIFAC. In the relatively few cases where UNIFAC interaction parameters are not available for all components of the compounds in the system, Raoult's Law has to be considered. CHEMCAD will, however, produce a result for the UNIFAC model, even if all interaction parameters are not available. CHEMCAD assumes these interactions are ideal. I would make a comparison between these results and the ideal case and choose the more conservative result.

Now let's look at how these models predict the vapor composition.

Vapor Composition on a Nitrogen-Free Basis

An examination of the XY diagrams in **Figure 22** reveals that each model provides different results for the vapor composition.

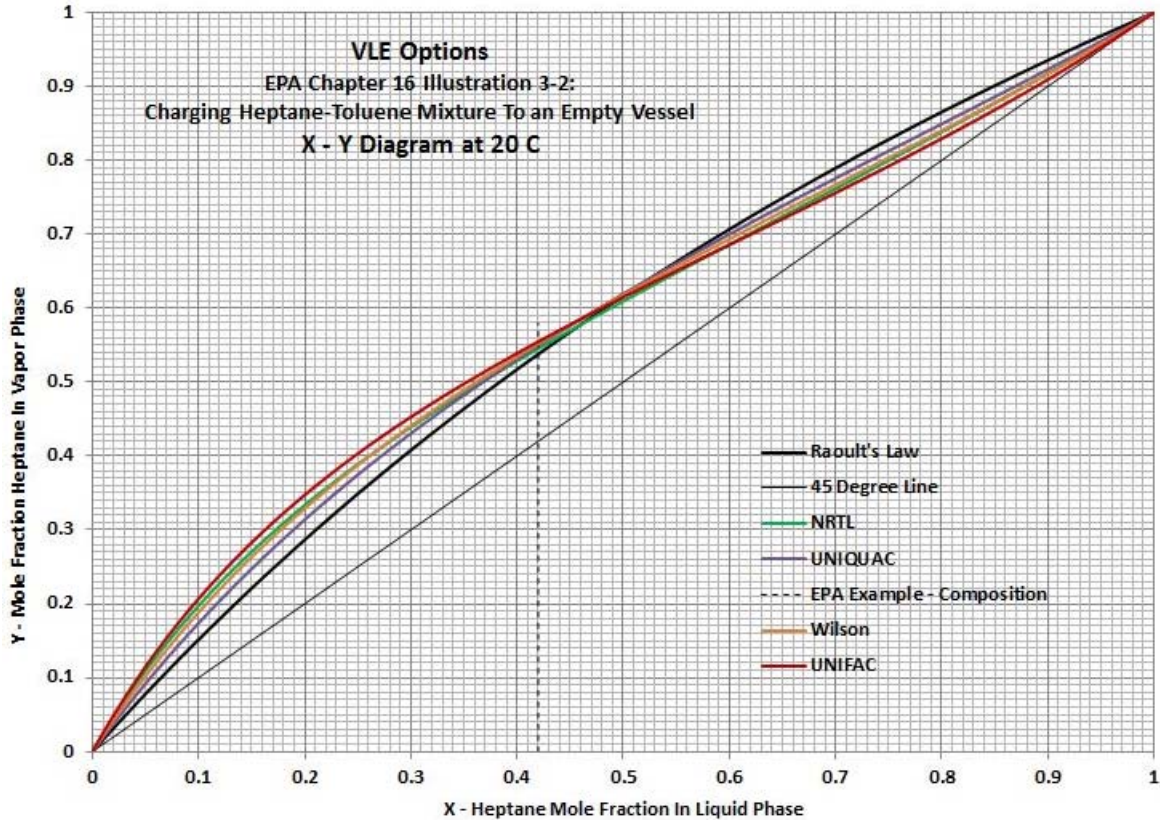


Figure 22 - Vapor composition curves for various models

All of the curves converge at about 48 mole % heptane in the liquid. Below 48 mole % heptane, all of the models that are regressed from real data show higher concentrations of heptane in the vapor phase than does the model for an ideal system. The predictive UNIFAC model, based on a group contribution approach, shows the largest concentration of heptane in the vapor below 48 mole % heptane. Above 48 mole % heptane, the situation is reversed: the ideal system shows the highest mole fractions of heptane in the vapor space. The other models show lower values in the reverse order that occurs below 48 mole % heptane. The situation for toluene is the inverse, because the mole fractions of heptane and toluene in the vapor must sum to unity. Toluene in the vapor has lower mole fractions for the non-ideal models than predicted by Raoult's Law below 48 mole % heptane in the liquid, and higher above.

No one model consistently gives the most conservative results for heptane in the vapor space for all liquid compositions. Below 48 mole % heptane, UNIFAC is the most conservative. Above 48 mole %, Raoult's Law gives the most conservative results. All models have to be evaluated in any given situation.

My choice for this example would be NRTL, because of the higher overall emission rate and the higher toluene concentration.

Effect of Vent Condensers

Let's look at both NRTL and Wilson and see what effect the vent condensers have on the emission rates corresponding to streams 7 and 8 in the flowsheet, the off gas streams at 10 °C and -5 °C, respectively. This is shown in **Figure 23**, which also shows the results for Raoult's Law.

	Controlled Emissions - NRTL and Wilson Compared To Raoult's Law							
FLOW SUMMARIES:	NRTL		Wilson		Raoult's Law			
Stream No.	7	8	7	8	7	8		
Stream Name	1st Offgas	2nd Offgas	1st Offgas	2nd Offgas	1st Offgas	2nd Offgas		
Temp C	10	-5	10	-5	10	-5		
Pres mmHg	757.4143	754.8286	757.4143	754.8286	757.4143	754.8286		
Enth kBtu/h	-1.1621	-0.84037	-1.1833	-0.85605	-1.0619	-0.80639		
Vapor mole frac.	1	1	1	1	1	1		
Total lbmol/h	1.0246	1.0102	1.0248	1.0105	1.026	1.013		
Total lb/h	30.3714	28.9828	30.3733	28.9937	30.2597	29.0034		
Total std L gpm	0.0755	0.0718	0.0755	0.0719	0.0752	0.0719		
Total std V scfh	367.86	362.7	367.93	362.81	368.38	363.71		
Flow rates in lb/h								
Heptane	1.4413	0.6447	1.4603	0.6603	1.2983	0.5939		
Toluene	0.9054	0.3134	0.8806	0.3011	0.8344	0.2826		
Heptane + Toluene	2.3467	0.9581	2.3409	0.9614	2.1327	0.8765		
Nitrogen	28.0247	28.0247	28.0324	28.0323	28.1269	28.1269		

Figure 23 - Emission rates of streams 7 and 8

NRTL and Wilson give results that are quite similar, and either model would be adequate. Note that the emission rates for these non-ideal models are about 10% higher than for the ideal case.

Because the untreated emission rates for NRTL are a little higher than those for Wilson, the vent condenser designs might be more conservative. The designs will be dependent on the condensing curves generated by CHEMCAD for each model for each exchanger. I would develop condenser designs for both cases and choose the designs with the largest heat transfer areas.

Summary

Methods were presented to show how CHEMCAD can be used to solve the two example problems for charging liquid to an empty vessel given in **EIIP Document Chapter 16: Methods for Estimating Emissions from Chemical Manufacturing Facilities, August, 2007**.

The first example involved the charging of a single component, hexane, to an empty vessel filled with nitrogen. In addition to showing the solution to the EPA example for emission rate from a vessel, the effect of adding vent condensers was demonstrated. A CHEMCAD sensitivity analysis was described to show the effect of process-side vent condenser outlet temperature on hexane emission rate. Finally, it

was shown how CHEMCAD can be used to calculate the maximum hexane feed rate to the vessel that does not exceed an emission rate that may be set for the plant by a regulatory agency.

The second example involved the charging of a two-component mixture, 50-50 by volume heptane-toluene, to an empty vessel filled with nitrogen. Again the effect of the presence of vent condensers was demonstrated. The effect of the choice of VLE models on emission rate was investigated. It was shown that the VLE model, Raoult's Law, used in Chapter 16 underestimates the true emission rate by about 10% because the system is non-ideal. For proper design of air pollution control equipment, it is essential to take system non-ideality into account.

References

1. EPA, Methods for Estimating Air Emissions From Chemical Manufacturing Facilities, Volume II, Chapter 16, Section 4.2.3, EPA, Research Triangle Park, NC, 2007
2. CHEMCAD, Version 6.5.6.7502, Chemstations, Inc.
3. Renon, H., Prausnitz, J. M., "Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures", *AIChE J*, 14(1), 135-144, 1968
4. Abrams D.S., Prausnitz J.M., "Statistical Thermodynamics of Liquid Mixtures: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems", *AIChE J.*, 21(1), 116-128, 1975
5. Wilson, G.M., "Vapor-Liquid Equilibrium XI. A New Expression For The Free Energy of Mixing", *J. Am. Chem. Soc.*, 86, 127-130, 1964
6. Fredenslund, A., Jones, R.L. and Prausnitz, J.M., "Group-Contribution Estimation of Activity Coefficients in Nonideal Liquid Mixtures", *AIChE Journal*, vol. 21, 1086, 1975

Author Information

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Author's Notes

My name is Jeff Silverstein. I have a PhD in Chemical Engineering from The City College of The City University of New York, also known as CCNY. My research work was analytical, involving intensive use of the university mainframe IBM 370 computer to develop and simulate mathematical models of reactors. My thesis adviser, the late Dr. Reuel Shinnar, believed that his graduate students should work on practical problems of direct interest to the chemical industry. Accordingly, my research work involved developing design criteria for micro-fixed bed catalytic reactors so that the reactor performance in the lab would closely match the performance in the plant. In addition, I examined the integration of the design and control of plant-scale fixed bed catalytic reactors.

In those days I did my own computer programming and debugging using FORTRAN. Obviously much has changed in chemical engineering computing in the 38 years since I left CCNY to start working in the corporate engineering department of the American Cyanamid Company in Wayne, New Jersey.

I worked in the Process Analysis Section of the Process Engineering Department. This group was predominately manned and led by PhD chemical engineers. So, there was a very strong theoretical framework in all the work that we did. We were mandated by the corporation to work with R&D to provide a practical plant-oriented viewpoint from the very beginning of projects. This involved design and analysis of experiments, development of mathematical models and computer simulations. In addition, we did analysis and troubleshooting of plant problems.

Cyanamid was at the forefront of the new computer-aided approach to chemical engineering design and analysis. We developed our own in-house process simulation program, called CYSL (Cyanamid Simulation Language) that contained mathematical models for many unit operations that could be arranged to simulate an entire process. We developed both continuous (TRIDIS) and batch distillation (BATDIS) computer programs, with the capability of using liquid phase activity coefficient models so that the non-ideality of our systems could be taken into account.

In thinking back about CYSL, it was organized in a very similar way to CHEMCAD. However, there were big differences: the program was run on a mainframe computer with slow turnaround of runs, there was no graphical interface, there were no physical properties or thermodynamic databases, and the program

only calculated the material balance. The engineer had to do side calculations to estimate the splits in each unit operation. The heat balances had to be calculated by hand.

Even with these limitations, the program was a tremendous benefit to us because we could generate a plausible material balance for process analysis. It helped us to pinpoint areas of the process that needed more understanding and experimentation by R&D. It helped us to size equipment and identify cost-sensitive areas or aspects of the process that needed more scrutiny. It helped us estimate the size of recycle streams and the degree of build-up of minor components. It helped us to estimate the size and composition of solvent and waste streams and determine how to treat them. CYSL made it a snap to fill in the material balance grid on process flowsheets.

The question we had to ask ourselves at all times when using these powerful programs was, “Do the results make sense?” We had to use our technical knowledge and professional experience to test the results the computer gave us. It was, and is, very easy to get intoxicated by the computing power at our disposal and accept what the computer tells us as the truth. We had to constantly test the results from CYSL, TRIDIS, and BATDIS, programs much less sophisticated and comprehensive than CHEMCAD.

After Cytec Industries was spun off from American Cyanamid in 1994, we acquired the first-generation CHEMCAD II software package. This program was amazing. I was like a kid at Disneyland for the first time. It had a graphical interface; the results were available almost instantaneously. I could run more than one distillation column at a time, linking them with product to feed streams and with recycle streams. I explored every unit operation and ran them all. I made up fictitious cases. I ran old cases I had run on CYSL, TRIDIS, and BATDIS to see if the answers matched. CHEMCAD was better. I ran problems from my textbooks to see if CHEMCAD came up with the correct answers. I gave the program the test drive of its life and I became a believer. CHEMCAD is the real McCoy.

The thing is, however, because I had to run the old Cyanamid programs in a slightly skeptical, *I had better test the results* way, I continued to do so with CHEMCAD, and still do. Any result I get from CHEMCAD better make sense to me. If it doesn't, I need to track down the reason why. Sometimes I am wrong and the CHEMCAD answer is correct. As Sherlock Holmes would say, “When you have eliminated the impossible, what remains, however improbable, must be the truth.”

Sometimes I set up the simulation incorrectly. And yes, infrequently, there is a programming error. But—and this is a very big *but*—the Chemstations program developers jump on these issues very quickly and get them fixed. This, as a longtime user, is something I deeply appreciate.

The point is that this tool is extremely powerful, doing many things. It will give you an answer. That answer, though, is only as good as the information you give to CHEMCAD to calculate it. It's still up to you to determine whether it makes sense.

Our goal with this white paper, and those that will follow, is to provide a detailed road map for you to use CHEMCAD to do the calculations the United States EPA believes should be done to estimate air emissions from chemical plants. These papers will be written based on my technical knowledge, 38 years of experience with process analysis and mathematical simulation of chemical plants, and more than 20

years of experience using CHEMCAD on a daily basis. They will be reflective of my approach to chemical engineering: we have this powerful CHEMCAD software at our disposal, so let's turn this problem inside-out and see what we can learn about the process.

I gave a series of twelve in-plant, three-day seminars and two intranet seminars to Cytec plant engineers, describing how they can use CHEMCAD to do the kinds of calculations they require in running a chemical plant. I undertook this effort, because we found by surveys that although CHEMCAD was made available for plant engineers' use, few took advantage of it. This paper and those that will follow demonstrate how plant engineers can easily use CHEMCAD for emission estimation.

I hope that you find the papers to be useful and interesting, and that they encourage you to use CHEMCAD often in your work.