

# ACCESS AND UTILIZATION OF THE DIPPR PHYSICAL PROPERTY DATABASE IN CH. E. EDUCATION

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## Introduction

Physical property data are essential for problem solving in chemical engineering and other related fields such as environmental and biochemical engineering. Physical property data may be required for large number of compounds over wide ranges of temperatures, pressures and compositions in chemical process design and optimization as well as environmental impact assessment.

In the not very distant past, property data was often very difficult to find. This can be demonstrated with reference to the “semi-batch steam distillation” problem that will be discussed in the next section. This problem was originally suggested by Prenosil in 1976. At that time he had to collect the data required for solving the steam distillation problem from various sources.

He provided the details of these sources, as follows: “The constants of the Antoine equations for the vapor pressures of *n*-octane and *n*-decane were taken from The Handbook of Chemistry and Physics (1970) and for water they were obtained by non-linear regression from steam tables (Perry, 1963). The  $C_p$  values of the liquid components were also found in Perry (1963) and their temperature dependence was neglected. The  $C_p$  data for the vapor components were calculated as functions of temperature from the equation  $C_p = A + BT + CT^2$  with the constants taken from Balshiser et al. (1972). The latent heats of evaporation for the organic material came from Cox and Pilcher (1970) and that of water from Landolt-Börnstein (1960). The Handbook of Chemistry and Physics (1970) also served as a source of critical data. The molar volume at 95 °C was only found for *n*-octane in Timmermans (1965). The molar volume of *n*-decane was obtained by extrapolation from the data tabulated at lower temperatures and our own measurements up to a temperature of 70 °C.”

Finding the necessary data in that era represented a “small research project.” There was usually a need to make some assumptions (such as neglecting the temperature dependence of the  $C_p$  values), or to extrapolate the data with no basis to evaluate the validity of the assumptions and the reliability of the extrapolated values. Also converting the data and correlations collected from difference sources to the same consistent set of units represented a challenge and often may have introduced errors into the mathematical model of the process.

Currently, most of the needed properties can be found in available databases. The database we have been using is the DIPPR<sup>®</sup> database, (<http://dippr.byu.edu/>, Rowley et al., 2006). The DIPPR database developers have invested considerable efforts to provide complete sets of constant pure component properties. Additionally temperature dependent correlations for the compounds are provided, even if some of the properties must be predicted. Estimations for the uncertainty of the measured or predicted values are also supplied. The completeness of the datasets as well as the availability of the uncertainty estimations has great value in both chemical engineering education and industrial practice. The provision of only

experimental data, as several data bases do, puts the burden on the user to predict the property data which is essential for solving particular problems.

Unfortunately, the use of physical property databases in engineering education and practice is not as widespread as might be desired. Firstly, property databases are rarely mentioned in current textbooks, so that even the instructors are unaware of their potential educational benefits. Students who use property data provided by the instructor or from limited lists appearing in the appendices of the textbooks do not acquire the habit of obtaining all property data from one reliable source. Consequently they may not use databases in their graduate research or engineering practice. Secondly, many of the current property databases do not efficiently enable the transfer of property and correlation data from the databases to computer codes, and the transfer can be a cumbersome, complex and error prone process. The name of the property, its units, value, uncertainty and additional information are usually stored in separate cells in the database. This typically requires considerable copying, pasting and manual manipulation so that important information can be introduced and documented in the computer code. For temperature dependent properties, the name of the property, its units, the coefficients of the correlations, the range of validity of the correlation, the uncertainty of the calculated values and some additional information are all stored separately. Here, also, after copying the data, manual introduction into the respective equations and the computer code is required. Shacham et al. (2009) have shown that careless rounding of coefficients while copying from the database to various software packages may cause significant errors.

In order to simplify the transfer of the data from the database to computer code and thus minimize the probability of the introduction of errors during the process, we have developed a "DIPPR to Code" interface. This interface enables searching the database for a particular compound, marking the desired properties and obtaining as output the necessary data and correlations in a format that can be copied and pasted directly into a computer code. The formats that are currently supported are for Polymath Software™ (a product of Polymath Software, <http://www.polymath-software.com>) and MATLAB® (a product of The Math Works, Inc. <http://www.mathworks.com>). The Polymath package is a user-friendly, easy-to-learn package which is widely used for problem solving in engineering. MATLAB can be considered as an advanced computer language that is widely used in graduate engineering and scientific education and research. Property correlation equations coded in MATLAB format can be introduced into programs written in various computer languages with very minimal changes.

The Polymath package is also capable of exporting equations to Excel® (a product of Microsoft Corporation, <http://www.microsoft.com>) by provision of automatic conversion of the DIPPR correlation equations to Excel formulas. This is very important as practically all engineers use Excel for their computational tasks. Thus the "DIPPR to Code" interface enables exporting DIPPR data and equations to many of the widely used software packages.

The use of the DIPPR database, the interface program and their potential benefits will be demonstrated by modeling and simulating a semi-batch steam distillation process.

### **Semi-Batch Steam Distillation of a Binary Organic Mixture – Problem Definition**

A typical example of a process model that includes a large amount of constant and temperature dependent data is steam distillation of an organic mixture. Such an example is provided by Prenosil (1976). This illustrative example involves semi-batch steam distillation of an *n*-octane (comp. 1) and *n*-decane (comp. 2) mixture. A simplified version of this problem appears in the textbook of Ingham et al. (2007) and this version will be presented here.

A schematic plot of the steam distillation apparatus is shown in Figure 1. The organic mixture is charged into the still initially and steam is bubbled through continuously until the desired degree of separation has been reached. There are two different periods in the operation of the still: the heating period, until the boiling point temperature of the organic mixture is reached, and the distillation period. A brief description of the mathematical models for the two periods follows.

### Heating Period

A simple mass balance on the water phase yields

$$\frac{dm_w}{dt} = W_s \quad (1)$$

where  $W_s$  is the steam flow-rate and  $m_w$  is the mass of water in the still. It is assumed that all the steam condenses in the distillation vessel and that the organic phase masses remain constant during the heating period.

An energy balance on the still provides the equation for the change of the temperature ( $T$ )

$$\frac{dT}{dt} = \frac{W_s(H_s - H_{Lw}) + Q}{m_w c_{pLw} + m(x_1 c_{pL1} + x_2 c_{pL2})} \quad (2)$$

where  $H_s$  is the enthalpy of the steam,  $H_{Lw}$  is the enthalpy of liquid water,  $Q$  is the rate of heat transfer to the surrounding,  $c_{pLw}$  is the molar specific heat of the water,  $m$  is the mass of the organic phase in the still,  $x_1$  and  $x_2$  are the mole fractions and  $c_{pL1}$  and  $c_{pL2}$  are the molar specific heats of  $n$ -octane and  $n$ -decane, respectively. The heat transfer rate to the surrounding is calculated from Eq. 3

$$Q = UA(T_E - T) \quad (3)$$

where  $U$  is the overall heat transfer coefficient,  $A$  is the contact area with the surrounding and  $T_E$  is the ambient temperature.

Assuming ideal liquid behavior, Rault's law can be used to calculate the vapor mole fraction of the components in the organic phase. Thus

$$y_1 = \frac{x_1 P_1}{P} \quad y_2 = \frac{x_2 P_2}{P} \quad (4)$$

where  $P$  is the total pressure and  $P_1$  and  $P_2$  are the vapor pressures of the organic compounds. The mole fraction of the water which is immiscible in the organic phase is given by  $y_w = P_w / P$ . The heating period continues until the sum of vapor pressures of the organic compounds and the water is equal to the total pressure. Thus, the following "bubble point" equation has to be satisfied.

$$f(T) = 1 - (y_1 + y_2 + y_w) = 0 \quad (5)$$

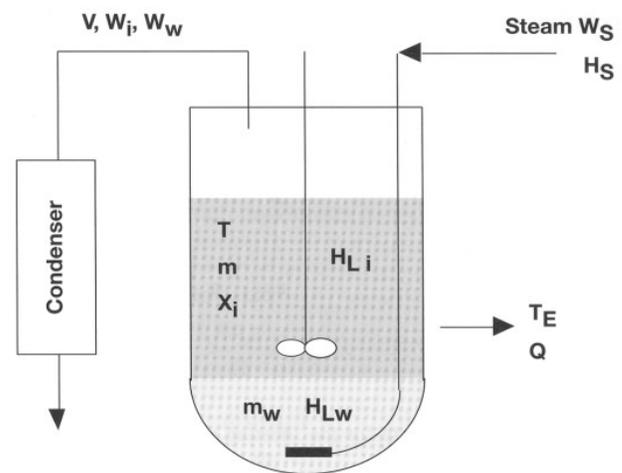


Figure 1 – Schematic plot of steam distillation

## Distillation Period

During the distillation period, there is output of water vapor from the still. Thus Eq. 1 must be modified to

$$\frac{dm_w}{dt} = W_s - Vy_w \quad (6)$$

where  $V$  is the outlet vapor flow rate. Material balances on the two organic compounds yield two additional differential equations

$$\frac{d(mx_1)}{dt} = -Vy_1 \quad \frac{d(mx_2)}{dt} = -Vy_2 \quad (7)$$

The organic mass in the still at any time is given by:  $m = mx_1 + mx_2$ . The temperature in the still changes in a manner so that the bubble point equation (Eq. 5) is satisfied. The energy balance at a particular temperature yields the momentary vapor flow rate

$$V = \frac{W_s(H_s - H_{Lw}) + Q}{H_v - [y_w h_{Lw} + (y_1 h_{L1} + y_2 h_{L2})]} \quad (8)$$

where  $H_v$  is the molar enthalpy of the vapor phase,  $h_{Lw}$ ,  $h_{L1}$  and  $h_{L2}$  are the liquid phase molar enthalpies of water,  $n$ -octane and  $n$ -decane respectively. Material balances on the water and organic phases in the still can provide the amount and the mole fractions of the various components in the distillate.

A typical assignment in using this semi-batch distillation apparatus may involve the calculation of the distillation time when a pre-specified separation can be reached. Various initial organic phase compositions can be investigated.

## Solution Algorithm for the Semi-Batch Steam Distillation Problem

Two separate models can be used for solving this problem. In the solution of the “heating period model,” the special challenge is to determine the time when the function of Eq. 5 approaches close enough to zero. For one or a few sets of data, this can be done by some kind of “trial and error” procedure. However, for larger sets of input data it is preferable to find the most appropriate time by solving a “two-point boundary value problem” as demonstrated, for example, in Prob. 6.4 of the Cutlip and Shacham (2008) textbook. When the boiling point is first achieved, the temperature and mole fraction values must be passed to the “distillation period” model, as initial values.

A specific challenge in the solution for the distillation period is the need to follow the bubble point temperature curve (Eq. 5) during the time of the integration. This requires solving a nonlinear algebraic equation for each and every integration step. (This is basically a differential-algebraic or DAE problem.) A simple method that we recommend using for this purpose is the “controlled integration” technique of Shacham and Brauner (1997). Using this method Eq. 5 is rewritten

$$\varepsilon = 1 - (y_1 + y_2 + y_w) \quad (5A)$$

and a “proportional controller” is added to the system of equations for changing the temperature:

$$\frac{dT}{dt} = K_c \varepsilon \quad (9)$$

The proportional gain,  $K_c$ , is selected large enough so as to keep  $\varepsilon$  below a pre-specified tolerance. Setting  $K_c$  at a large positive value will often lead to a “stiff” system of differential equations which has to be solved using specific stiff algorithms.

Thus, the semi-batch steam distillation problem can be considered a Multiple-Model, Multiple-Algorithm (MMMA) problem. There are two different models for the heating and the distillation periods and two different integration algorithms (non-stiff for the heating period, stiff for the distillation period) are used. The solution of MMMA problems has been discussed in detail recently by Cutlip et al. (2009).

## Physical Property Needs and Sources

In addition to the mathematical models, pure component physical property data is required for all three compounds involved in the steam distillation process. Most of the data is needed in the form of equations (correlations) that enable calculation of a particular pure component property as function of the temperature. Correlations are needed for liquid vapor pressure, liquid heat capacity and enthalpy, ideal gas heat capacity and enthalpy. For calculating the ideal gas enthalpy, the heat of vaporization at a reference temperature is also needed. The volume of the liquid in the still need to be determined (for preventing overflow of liquid at any stage of the distillation, for example), and thus correlations for liquid densities are required.

The information that is provided by the interface program in the Polymath format is demonstrated in Table 1 for the needed properties of *n*-octane that are required for the steam distillation problem. This table shows the exact information as provided by the “DIPPR to Code” interface when the Polymath format is specified.

Table 1. Physical properties of *n*-octane as obtained from the DIPPR database by the “DIPPR to Code” interface for use in Polymath

No.	Equation/ # Comment
1	# Liquid Vapor Pressure of <i>n</i> -OCTANE (C8H18)
2	# Error: < 1%; Data Type: Experimental; Source Type: Unevaluated; Source Detail: Primary; Error Source: Staff
3	# Min_T=216.38, Max_T=568.7, Min_Val=2.1083, Max_Val=2467300
4	VP_C8H18 = exp(96.084 - 7900.2 / T - 11.003 * ln(T) + 7.1802E-06 * T ^ 2) # Pa
5	# Liquid heat Capacity (at 1 atm below normal boiling point, saturation pressure at and above) of <i>n</i> -OCTANE (C8H18)
6	# Error: < 1%; Data Type: Smoothed; Source Type: Evaluated; Source Detail: Evaluated; Error Source: Staff
7	# Min_T=216.38, Max_T=460, Min_Val=229340, Max_Val=341890
8	LCP_C8H18 = 0 - 186.63 * T + 0.95891 * T ^ 2 + 224830 # J/kmol*K
9	# Ideal Gas Heat Capacity of <i>n</i> -OCTANE (C8H18)
10	# Error: < 1%; Data Type: Predicted; Source Type: Evaluated; Source Detail: Evaluated; Error Source: Staff
11	# Min_T=200, Max_T=1500, Min_Val=145290, Max_Val=497640
12	#HIG_C8H18 = 135540*T + 443100 *1635.6* (coth(1635.6 / T)) - 305400 *746.4* (tanh(746.4 / T))+Hcon # J/kmol
13	ICP_C8H18 = 135540 + 443100 * (1635.6 / T / sinh(1635.6 / T)) ^ 2 + 305400 * (746.4 / T / cosh(746.4 / T)) ^ 2 # J
14	# Liquid Density (at 1 atm below normal boiling point, saturation pressure at and above) of <i>n</i> -OCTANE (C8H18)
15	# Error: < 1%; Data Type: Smoothed; Source Type: Evaluated; Source Detail: Evaluated; Error Source: Staff
16	# Min_T=216.38, Max_T=568.7, Min_Val=6.705, Max_Val=2.05
17	LDN_C8H18 = 0.5266 / 0.25693 ^ (1 + (1 - T / 568.7) ^ 0.28571) # kmol/m^3
18	# Heat of Vaporization of <i>n</i> -OCTANE (C8H18)
19	# Error: < 1%; Data Type: Experimental; Source Type: Unevaluated; Error Source: Staff
20	# Min_T=216.38, Max_T=568.7, Min_Val=45898000, Max_Val=0, Error:< 1%
21	HVP_C8H18_273 = 4.2902E+07 # J/kmol (T=273.15)

The code that is generated by the interface program includes correlation equations, definition of constant values and comments (text that starts with the “#” sign and ends with the end of the line). The row numbers shown in Table 1 are not part of the output generated by the interface program; they were added as references for the explanations that follow. Lines 1-17 can be generated at once by selecting the desired “property equations” and the “basic” log level. The “log level” determines the amount of information that is to be included as comments. The data for the heat of vaporization at 273.15 K (lines 18 to 21) have to be generated separately as it is not an equation but rather a point value of the property.

Lines 1 through 4 contain the information related to the vapor pressure of *n*-octane. In line 1 the full name of the property, the full name of the compound and its formula are shown (as a comment). In line 2, information concerning the reliability of the vapor pressure correlation, as determined by the DIPPR staff is shown. The uncertainty (error) in the predicted vapor pressure is < 1% and the correlation is based on experimental data. There are additional details given in this line regarding the reliability of the data source. In line 3, the range of validity of the correlation equation is shown. “Min\_T” is the lower temperature limit of the range of validity, “Max\_T” is the upper temperature limit, “Min\_Val” is the property (vapor pressure, in this case) value at the lower temperature limit and “Max\_Val” is the property value at the upper temperature limit.

In line 4, the property correlation is shown. The variable into which the calculated value of the vapor pressure is entered made up from the symbol of the property (VP in this case) and the chemical formula of the compound involved. The Riedel equation is used to model the change of the vapor pressure with the temperature. The units of the property (vapor pressure in this case) are included in a “comment” in the same line with the equation. The units of the temperature are not given explicitly as the only units used are K.

Similar information is provided for liquid heat capacity (lines 5 through 8) and liquid density (lines 14 through 17). The point value of the heat of vaporization of *n*-Octane is provided in lines 18 through 21. The variable name in which the point property is stored (see line 21) includes the property symbol (HVP), the formula of the compound (C8H18) and the integer digits of the temperature (273). The comment provides the units of the property and the exact temperature value.

The ideal gas heat capacity (lines 9 – 13) deserves special discussion. DIPPR provides the coefficients for the Aly and Lee (1981) equation for this property. The integrated form of this equation, for calculating ideal gas enthalpy is considerably different than the heat capacity equation. For the benefit of the users, whenever the ideal gas heat capacity is requested by the user, the equation for ideal gas enthalpy is also included, as a comment (see line 12). Note that the enthalpy equation includes an integration constant *Hcon*. This constant depends on the standard state selected for the enthalpy calculation. For example, selecting as standard state pure liquid component at 0 °C (273.15 K) yields *Hcon* as ideal gas enthalpy at 273.15 K subtracted from the heat of vaporization of the component at the same temperature. The equations for calculating *Hcon* for *n*-octane are shown in Table 2. This set of equations yields: *Hcon* = -4.928E+08 J/kmol.

Table 2. Calculation of *Hcon* for *n*-Octane (reference state for enthalpy: pure liquid at 273.15 K)

No. Equation/ # Comment

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1	$T_0 = 273.15$ #K
2	$HIG\_C8H18 = 135540 * T_0 + 443100 * 1635.6 * (\coth(1635.6 / T_0)) - 305400 * 746.4 * (\tanh(746.4 / T_0))$ # J/kmol
3	$HVP\_C8H18\_273 = 4.2902E+07$ # J/kmol (T=273.15)
4	$Hcon\_C8H18 = HVP\_C8H18\_273 - HIG\_C8H18$ # J/kmol

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## Heating Period Model for the Steam Distillation Example

The Polymath program for modeling the heating period of the semi-batch distiller is shown in Table 3. In lines 1 and 2 the principal equations of the model (Eqs. 1 and 2) presented. The numerical data for the problem, as provided by Ingham et al. (2007) are included in lines 3 through 12. The auxiliary equations (3), (4) and (5A) are in lines 13 through 17. All the physical property equations necessary are shown in lines 18 through 26. These include the Riedel equations for calculating the vapor pressure of the three compounds, the equations for calculating the heat capacity of the individual compounds as well as the heat capacity of the liquid phase (in line 23). The enthalpy of the steam and the enthalpy of the water (required in Eq. 1) are calculated in lines 25 and 26 respectively. In lines 27 through 30, the initial values of the dependent variables  $T$  and  $m_W$  and the initial and final values of the time:  $t$  (s) are shown.

Table 3. Polymath program for simulating the “heating period” in the steam distiller

### No. Equation/ # Comment

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1	$d(\text{Temp})/d(t) = (\text{MS} * (\text{HS} - \text{HL\_H2O}) + \text{Q}) / \text{CpL}$	# Still temperature from heat balance
2	$d(\text{MW})/d(t) = \text{MS}$	# Mass of water in the still (mol) from mass balance
3	$\text{TK} = \text{Temp} + 273.15$	# Absolute temperature (K)
4	$\text{T0} = 273.15$	
5	$\text{TSK} = 99.2 + 273.15$	# Steam temperature (K)
6	$\text{P} = 9.839\text{E}+04$	# Ambient Pressure (Pa)
7	$\text{MS} = 3.85\text{e}-5$	# Steam flow rate (kmol/s)
8	$\text{U} = 1.05$	# Heat transfer coeff (J/s-K)
9	$\text{Ta} = 25$	# Ambient temperature (deg C)
10	$\text{x1} = 0.725$	# Mole Fraction of n-octane
11	$\text{x2} = 1 - \text{x1}$	# Mole Fraction of n-decane
12	$\text{M} = 0.015$	# Initial amount of organics, kmol
13	$\text{Q} = \text{U} * (\text{Ta} - \text{Temp})$	# Heat removed from the still (J/s)
14	$\text{Y1} = \text{VP\_C8H18} * \text{x1} / \text{P}$	# n-octane vapor mole fraction
15	$\text{Y2} = \text{VP\_C10H22} * \text{x2} / \text{P}$	# n-decane vapor mole fraction
16	$\text{YW} = \text{VP\_H2O} / \text{P}$	# Water vapor mole fraction
17	$\text{err} = 1 - (\text{Y1} + \text{Y2} + \text{YW})$	# Error used for bubble point determination
18	$\text{VP\_C8H18} = \exp(96.084 - 7900.2 / \text{TK} - 11.003 * \ln(\text{TK}) + 7.1802\text{E}-06 * \text{TK}^2)$	# Pa
19	$\text{VP\_C10H22} = \exp(112.73 - 9749.6 / \text{TK} - 13.245 * \ln(\text{TK}) + 7.1266\text{E}-06 * \text{TK}^2)$	# Pa
20	$\text{VP\_H2O} = \exp(73.649 - 7258.2 / \text{TK} - 7.3037 * \ln(\text{TK}) + 4.1653\text{E}-06 * \text{TK}^2)$	# Pa
21	$\text{LCP\_C8H18} = (0 - 186.63 * \text{TK} + 0.95891 * \text{TK}^2 + 224830)$	# J/kmol*K
22	$\text{LCP\_C10H22} = (0 - 197.91 * \text{TK} + 1.0737 * \text{TK}^2 + 278620)$	# J/kmol*K
23	$\text{LCP\_H2O} = (276370 - 2090.1 * \text{TK} + 8.125 * \text{TK}^2 - 0.014116 * \text{TK}^3 + 9.3701\text{E}-06 * \text{TK}^4)$	# J/kmol*K
24	$\text{CpL} = \text{MW} * \text{LCP\_H2O} + \text{M} * (\text{x1} * \text{LCP\_C8H18} + \text{x2} * \text{LCP\_C10H22})$	# Heat capacity of the liquid J/kmol*K
25	$\text{HS} = (33363 * \text{TSK} + 26790 * 2610.5 * (\coth(2610.5 / \text{TSK}))^2 + 8896 * 1169 * (\tanh(1169 / \text{TSK})) - 4.471\text{E}+07)$	# Steam Enthalpy (J/kmol)
26	$\text{HL\_H2O} = (276370 * (\text{TK} - \text{T0}) - 2090.1 * ((\text{TK}^2 - \text{T0}^2) / 2 + 8.125 * (\text{TK}^3 - \text{T0}^3) / 3 - 0.014116 * (\text{TK}^4 - \text{T0}^4) / 4 + 9.3701\text{E}-06 * (\text{TK}^5 - \text{T0}^5) / 5))$	# J/kmol
27	$\text{Temp}(0) = 25$	# Temperature in the still (deg. C)
28	$\text{MW}(0) = 0$	# Mass of water in the still (kmol)
29	$\text{t}(0) = 0$	
30	$\text{t}(f) = 181.7$	# s

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Note that Polymath automatically reorders the equations, as needed, before starting the computations. Thus initially the equations can be arranged so as to provide clear and concise documentation of the model if desired. The comments related to the range of applicability and

the uncertainty of the physical property correlations, that were shown in Table 1, have been removed for brevity; however, it is recommended that these comments be retained in the final program to provide more detailed documentation.

The completion time of the heating period (in line 30 of Table 3), that brings  $f(T)$  of Eq. 5 close to zero, was found by trial and error to be:  $t_f = 181.7$  s. At this point the temperature in the still is  $T = 90.65$  °C and the mass of water in the still is  $m_W = 0.07$  kmol. These values are transferred to the distillation period model as initial values.

### Distillation Period Model for the Steam Distillation Example

Part of the Polymath program for modeling the distillation period of the semi-batch distiller is shown in Table 4. Only the lines that were not included in Table 3 are shown in this table.

Table 4. Polymath program for simulating the “distillation period” in the steam distiller

No.	Equation/ # Comment
1	$d(\text{Temp})/d(t) = 1000 * \text{err}$ # Still temperature by controlled integration
2	$d(\text{Mx1})/d(t) = -V * Y1$ # Mass of n-octane in the still (kmol) from mass balance
3	$d(\text{Mx2})/d(t) = -V * Y2$ # Mass of n-decane in the still (kmol) from mass balance
4	$d(\text{MW})/d(t) = \text{MS} - V * \text{YW}$ # Mass of water in the still (kmol) from mass balance
-	lines 3-9 from Table 3
5	$x01 = 0.725$ # Initial n-octane organic liquid mole fraction
6	$x02 = 0.275$ # Initial n-decane organic liquid mole fraction
7	$M0 = 0.015$ # Initial amount of organics, kmol
8	$M = \text{Mx1} + \text{Mx2}$ # Organic mass in the still (kmol)
9	$x1 = \text{Mx1} / M$ # n-octane organic liquid mole fraction
10	$x2 = \text{Mx2} / M$ # n-decane organic liquid mole fraction
-	lines 13-17 from Table 3
11	$V = (\text{MS} * (\text{HS} - \text{HL}_{\text{H2O}}) + Q) / (\text{HV} - (\text{HL}_{\text{H2O}} * \text{YW} + (\text{Y1} * \text{HL}_{\text{C8H18}} + \text{Y2} * \text{HL}_{\text{C10H22}})))$ # Vapor flow rate (kmol/s)
12	$\text{M1dist} = M0 * x01 - \text{Mx1}$ # Mass of n-octane in the distillate (kmol)
13	$\text{M2dist} = M0 * x02 - \text{Mx2}$ # Mass of n-decane in the distillate (kmol)
14	$\text{MWdist} = \text{MS} * t - \text{MW}$ # Mass of water in the distillate (kmol)
15	$\text{Mdist} = \text{M1dist} + \text{M2dist}$ # Distilled organic phase (kmol)
16	$x1\text{dist} = \text{If} (\text{Mdist} > 0) \text{ Then} (\text{M1dist} / \text{Mdist}) \text{ Else} (0)$ # n-octane distillate mole fraction
17	$x2\text{dist} = \text{If} (\text{Mdist} > 0) \text{ Then} (\text{M2dist} / \text{Mdist}) \text{ Else} (0)$ # n-decane distillate mole fraction
-	lines 18-26 from Table 3
18	$\text{HL}_{\text{C8H18}} = (224830 * (\text{TK} - \text{T0}) - 186.63 * (\text{TK}^2 - \text{T0}^2) / 2 + 0.95891 * (\text{TK}^3 - \text{T0}^3) / 3)$ # J/kmol
19	$\text{HL}_{\text{C10H22}} = (278620 * (\text{TK} - \text{T0}) - 197.91 * (\text{TK}^2 - \text{T0}^2) / 2 + 1.0737 * (\text{TK}^3 - \text{T0}^3) / 3)$ # J/kmol
20	$\text{HL} = x1 * \text{HL}_{\text{C8H18}} + x2 * \text{HL}_{\text{C10H22}}$ # Enthalpy of the organic liquid phase (J/kmol)
21	$\text{HV1} = (135540 * \text{TK} + 443100 * 1635.6 * (\text{coth}(1635.6 / \text{TK})) - 305400 * 746.4 * (\text{tanh}(746.4 / \text{TK})) - 4.928\text{E}+08)$ # n-octane vapor enthalpy (J/kmol)
22	$\text{HV2} = (167200 * \text{TK} + 535300 * 1614.1 * (\text{coth}(1614.1 / \text{TK})) - 378200 * 742 * (\text{tanh}(742 / \text{TK})) - 5.791\text{E}+08)$ # n-decane vapor enthalpy (J/kmol)
23	$\text{HVW} = (33363 * \text{TK} + 26790 * 2610.5 * (\text{coth}(2610.5 / \text{TK}))^2 + 8896 * 1169 * (\text{tanh}(1169 / \text{TK})) - 4.471\text{E}+07)$ # Water vapor enthalpy (J/kmol)
24	$\text{HV} = \text{YW} * \text{HVW} + \text{Y1} * \text{HV1} + \text{Y2} * \text{HV2}$ # Vapor phase enthalpy (J/kmol)
25	$\text{Temp}(0) = 90.64995$ # Temperature in the still (deg. C)
26	$\text{Mx1}(0) = 0.010875$ # Mass of n-octane in the still (kmol)
27	$\text{Mx2}(0) = 0.004125$ # Mass of n-decane in the still (kmol)
28	$\text{MW}(0) = 0.006995$ # Mass of water in the still (kmol)
29	$t(0) = 181.7$
30	$t(f) = 2000$

The lines that remained the same and are included also in this program are clearly marked in Table 4. In line 1, the equation for changing the temperature using controlled integration (Eq. 9) is shown. The value of the proportional gain  $K_c$  ( $K_c = 1000$ ) was selected so that to keep the deviation of Eq. (5A) below the value of  $10^{-5}$  ( $\epsilon < 10^{-5}$ ). In lines 2 and 3, the change in the mass of the organic compounds is calculated using Eq. (7), and in line 3, the change of the mass of the water in the still is obtained from Eq. (6). The vapor flow rate is calculated using Eq. (8) in line 11 and the masses and mol fractions of the various compounds in the distillate are calculated from material balance equations in lines 12 through 17. Additional physical properties (liquid and vapor phase enthalpies) are calculated in lines 18 through 24. The initial values of the dependent variables and  $t$  (obtained as the final values of the heating period model) are shown in lines 25 through 28. The integration is continued until the amount of  $n$ -octane in the still gets below  $10^{-4}$  kmol ( $t_f = 2000$  s, line 30 in Table 4).

## Results and Discussion

The calculated temperature profile in the steam distiller is shown in Figure 2. There is a rapid increase within the first three minutes during which the temperature increases from the initial value of 25 °C to the boiling temperature of 90.65 °C. During the distillation period there is a more gradual increase of the temperature because of the depletion of the more volatile  $n$ -octane in the still. After 30 min of distillation the temperature reaches 96 °C.

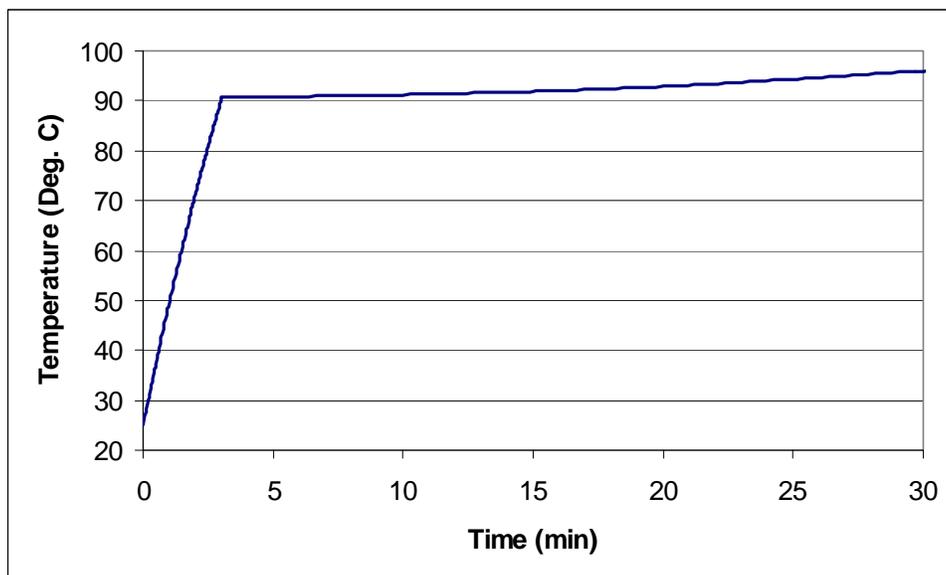


Figure 2. Temperature change during semi-batch steam distillation

The variation of the concentration of the organic compounds in the still (liquid and vapor phases) is shown in Figure 3. Starting at the beginning of the distillation period, there is a steady decrease in the liquid mole fraction of the more volatile component and steady increase in the mole fraction of the less volatile component. After 30 minutes, the concentration of  $n$ -octane reaches the value of  $x_1 = 0.085$  while the concentration of  $n$ -decane reaches:  $x_2 = 0.915$ . During the heating period there is a rapid increase in the concentration  $n$ -octane in the vapor phase however, after distillation starts the vapor phase concentration follows the same trend as the liquid phase.

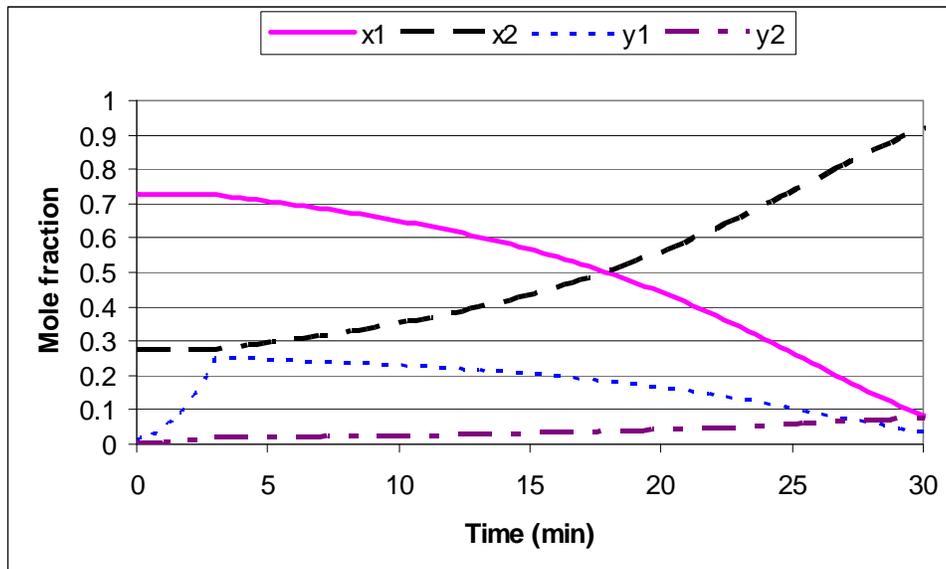


Figure 3. Change of organic phase composition during semi-batch steam distillation

Figure 4 shows the concentration of the organic compounds in the distillate. The mole fraction of the *n*-octane at the start of the distillation is  $x_{1\text{dist}} = 93\%$  and after 30 minutes it is reduced to  $x_{1\text{dist}} = 82\%$ . The distillation can be stopped when the desired level of separation is reached. For example if the desired *n*-octane concentration is  $x_{1\text{dist}} = 90\%$ , the distillation should be stopped after 18 min.

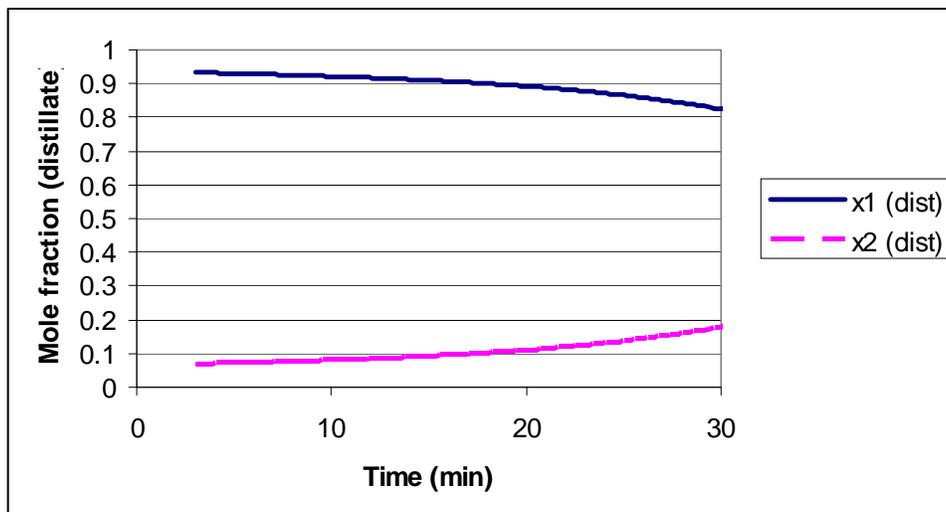


Figure 4. Change of organic phase distillate composition during semi-batch steam distillation

We have solved this problem previously with Aspen Properties<sup>®</sup> (a product of AspenTech, <http://www.aspentech.com/>) by utilizing the Aspen Properties Add-In for Excel (Shacham and Cutlip, 2004). The results using the two different property packages (Aspen Properties and DIPPR) are essentially the same.

## Exporting the Model to Excel and MATLAB

The Polymath models presented in Tables 3 and 4 can be exported from Polymath to Excel by a single key-press. The spreadsheet, which is automatically generated by Polymath, includes the Excel formulas that are equivalent to the Polymath equations. The variable names and Polymath equations are also exported to Excel as text, to provide a clear documentation for the Excel worksheet. Intrinsic functions and logical conditions are also automatically converted to Excel formulas. An ODE solver Add-Inn (provided as a separate utility along with Polymath) is available for solving the ordinary differential equations within Excel.

The Polymath models can also be exported to MATLAB in the form of MATLAB functions. Library functions for solving ODE's (such as ode45.m) can be used to solve the problem within MATLAB.

The Excel and MATLAB export options can not be demonstrated here because of lack of space; however, these options are explained in detail in chapters 4 and 5 of the Cutlip and Shacham (2008) textbook.

## Conclusions

This work demonstrates the many advantages of the use of a database, such as DIPPR, in computer-based problem solving. These advantages include:

1. Minimization of the effort for searching or predicting properties as all the necessary data are available in one source.
2. Presentation of the reliability and uncertainty of the data as all this information is available in the database.
3. Provision of the range of applicability so that correlations can be used to assure accurate results.
4. Reduction of conversion factor errors as all of the data are available in consistent units.

The use of the DIPPR data base will introduce students to an important aspect of problem solving – that good results in detailed calculations are achieved with accurate data from physical property databases. This experience will carry over database usage to their professional engineering careers.

For the instructor, the availability of database access to students can minimize the effort in making sure that needed property data are available for homework and design project assignments.

The new “DIPPR to Code” interface will enable users to have convenient export of DIPPR data and property equations to several widely used software packages, thus minimizing the required effort and reducing error introduction during this process.

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#### Appendix (Selected Screen Displays of the Polymath “DIPPR to Code” Interface)

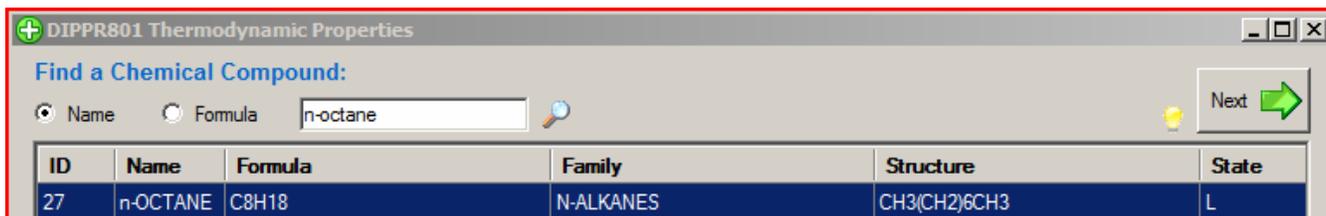


Figure A-1. Compound Search Screen

ID	Property	Description	Value	Units	Error
55874	PC	Critical Pressure	2486000	Pa	< 3%
55867	TC	Critical Temperature	568.95	K	< 0.2%

Figure A-2. List of Properties Screen

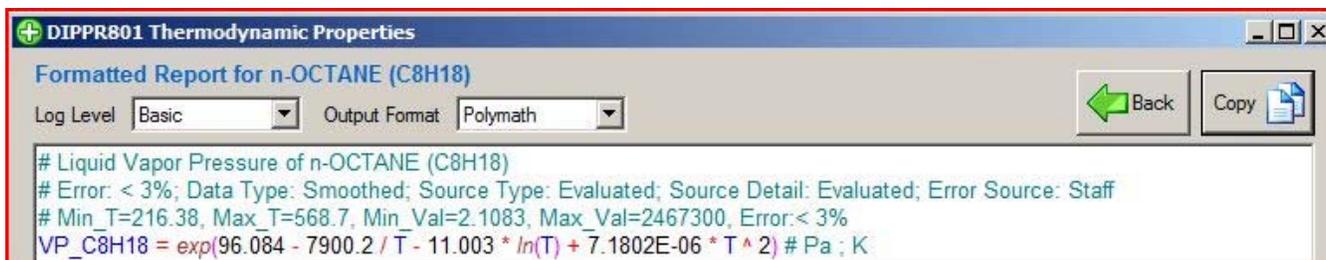


Figure A-3. Example of the Property Equation Polymath Output for n-OCTANE