SOLVING L-L EXTRACTION PROBLEMS WITH EXCEL SPREADSHEET

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Liquid-liquid (L-L) extraction, sometimes called solvent extraction, is the separation of the components of a liquid solution by contact with another insoluble liquid. One method used to solve this problem is the equilibrium stage concept.[1] Most L-L extraction processes concern only one component transferred between phases and nearly all L-L equilibrium data are presented in tabular form or as a graphical diagram, either triangular or with ordinary y-x coordinates. So it is not surprising, as a consequence, that it is convenient to solve these problems graphically. However, there are disadvantages to the graphical method.[2] These lead chemical engineers to seek other modern methods/tools for computation.

Nowadays, personal computers or notebooks are widely used and have become an indispensable tool. Several commercial software packages such as Mathcad and Matlab, etc., are available and referred to by some chemical engineering textbooks.[3-5] However, such software must be purchased separately and is not available in all companies. On the other hand, Microsoft Excel is part of Microsoft Office, which is commonly installed in most computers. Excel is a powerful spreadsheet application that can be used to solve scientific problems. The advantages of using Microsoft Excel are that not only are calculations effectively performed, but also that the graphical presentation of solutions can be simultaneously displayed.[6,7] This enables students or engineers to clearly understand the calculation procedures, just as the graphical method does. Moreover, with some add-in tools and Visual Basic for Applications (VBA) more complex problems can be conveniently solved.[8-10]

At the King Mongkut's University of Technology Thonburi, separation processes are studied by third-year chemical engineering students. The course has been taught by the author for many years, and the use of Excel spreadsheets to solve these problems has been developed in parallel. Since nearly all students have a notebook computer with Microsoft Office installed including Excel, it was worthwhile to teach them to use spreadsheets.

As most chemical engineering students are familiar with the graphical method, it is preferable to perform spreadsheet calculations based on the same principle. With an Excel spreadsheet there is no need to draw any graphical diagrams. But in some circumstances, it is advantageous to display the spreadsheet solution obtained in a graphical form similar to a graphical solution. In this manner, both calculation results can be compared and checked with each other. Moreover, understanding how to construct a line or curve enables one to create a worksheet more easily.

The objective of this paper is to explain the use of Microsoft Excel with simple functions for solving L-L extraction problems. The spreadsheets are designed to require student interaction step-by-step, which prevents the spreadsheet from becoming a black box.

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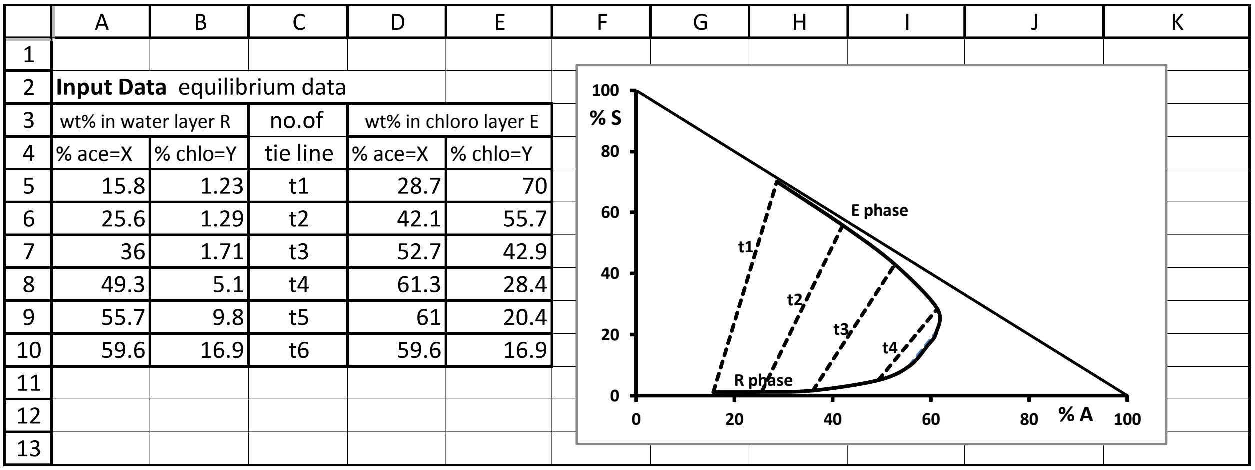
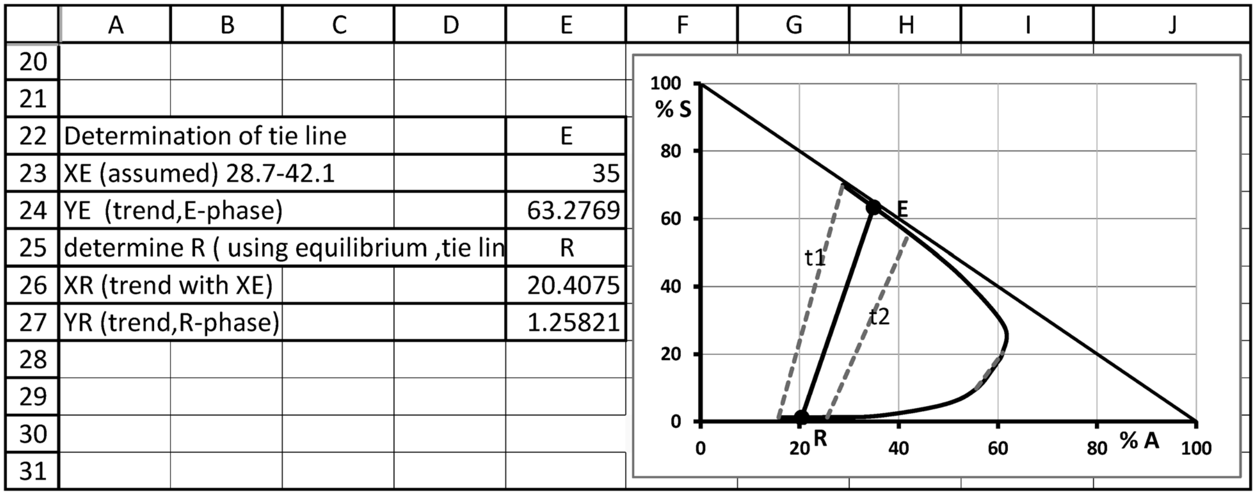


	A	B	C	D	E
1					
2	**Input Data** equilibrium data				
3	wt% in water layer R		no.of	wt% in chloro layer E	
4	% ace=X	% chlo=Y	tie line	% ace=X	% chlo=Y
5	15.8	1.23	t1	28.7	70
6	25.6	1.29	t2	42.1	55.7
7	36	1.71	t3	52.7	42.9
8	49.3	5.1	t4	61.3	28.4
9	55.7	9.8	t5	61	20.4
10	59.6	16.9	t6	59.6	16.9
11					
12					
13					

Figure 1. Worksheet data of tie lines for the system acetone-water-chloroform. Note: Figures 1, 2, and 3 are all part of a single spreadsheet that can be used to pattern the method of finding tie lines and doing mass balances with Excel.



	A–D	E
20		
21		
22	Determination of tie line	E
23	XE (assumed) 28.7-42.1	35
24	YE (trend,E-phase)	63.2769
25	determine R (using equilibrium ,tie lin	R
26	XR (trend with XE)	20.4075
27	YR (trend,R-phase)	1.25821
28		
29		
30		
31		

Figure 2. Resulting composition of new tie line.

CONVERSION FROM GRAPHICAL PROCEDURES TO SPREADSHEETS

Excel can plot only rectangular coordinates; therefore, describing ternary equilibrium on a right triangular diagram is considered here. Only two compositions are used to locate each location on the diagram. The remainder is calculated by difference. In this paper the abscissa (x-axis) represents the mass fraction of solute (A) and the ordinate (y-axis) represents mass fraction of solvent (S). It is convenient to use Y to refer to the mass fraction of solvent S in the mixture, whereas X is the mass fraction of A in the same mixture. Subscripts identify the solution to which the concentration refers and stages are identified by number. For example, X_M = mass fraction of solute A in mixture M and Y_{E1} = mass fraction of solvent S in mixture E leaving stage 1. Use of the upper cases here is to provide convenience when typing in the Excel worksheet. Figure 1 shows the tie line data and equilibrium diagram for the system acetone-water-chloroform at 298 K and 1 atm (adapted from Example 7.1, Benitez[3]).

According to the phase rule, for a ternary system with two phases in equilibrium, the number of degrees of freedom is equal to 3.[1] There are six variables: temperature, pressure, and four concentrations. If the pressure and temperature are specified, then only one concentration can be arbitrarily chosen. The other three concentrations must be determined from the phase equilibrium. For example, consider the equilibrium data in Figure 1, where the temperature and pressure are fixed (298 K and 1 atm.). Then choose, for example, the concentration of A in extract phase on tie line t_3, $X_E = 52.70\%$. Since three variables have been completely specified, the three remaining concentrations can be determined from equilibrium. That is, the concentration of S in the extract phase, $Y_E = 42.90\%$, is determined as $Y_E = f_E(X_E)$ where f_E represents the function for the extract portion of the solubility envelope.

The raffinate concentration $X_R = 36.00\%$ is determined as $X_R = f_{EQ}(X_E)$, where f_{EQ} is the function represented by the tie line data. When plotted on a X-Y diagram f_{EQ} is the equilibrium distribution curve. Finally, $Y_R = 1.71\%$ as $Y_R = f_R(X_R)$ represents the function for the raffinate part of the solubility envelope. The three functions f_E, f_{EQ}, and f_R permit determination of a tie line from a single mass fraction.

Unfortunately, most of the solubility data is available in tabular form, which is convenient for graphical solution, but is not convenient for numerical solution with a spreadsheet. This is one of the main reasons why L-L extraction analysis is usually performed on a graphical diagram. Hence, to solve the problem numerically, it is necessary to establish a mathematical relationship of equilibrium compositions. Users of Excel will be tempted to establish a correlation by using "Trendline" from the chart menu. Due to the complexity of L-L solubility, the equations provided in Excel are not sufficiently accurate to represent solubility data in the range of interest. Hence, this method must be discarded.

A second, more useful approach is to interpolate by using the "TREND" worksheet function to perform interpolation in a table of data. Excel can do cubic interpolation in which four points are used for interpolation, and linear interpolation which requires only two adjacent points.[11] The latter is equivalent to manual interpolation on a graphical diagram that is familiar to most chemical engineering students. Furthermore, the syntax of this type is simple and easy for students to use. For example, to construct a new tie line located between tie lines t_1 and t_2, we choose X_E=35% and use TREND to find the other corresponding values as shown in Figure 2, a portion of the spreadsheet. The function is listed as TREND (known y's, known x's, new x's) and returns a new y value. To find the tie line between t_1 and t_2 cell E24 is =TREND(E5:E6,D5:D6,E23).

SAMPLE CALCULATIONS

In order to compare the results obtained from spreadsheet calculations with those from graphical solutions, example problems solved by graphical methods and/or commercial software mentioned in textbooks have been selected.

Single Stage Extraction

Consider a feed solution F mixed with solvent S to form a mixture M. Then M is separated into mixtures E and R which are in equilibrium. If the coordinates of R, M, and E are (X_R,Y_R), (X_M,Y_M) and (X_E,Y_E), respectively, from mass balances one obtains the relations,

$$M = F + S,\ X_M = [FX_F + SX_S]/M,\ Y_M = [FY_F + SY_S]/M \qquad (1a,b,c)$$

$$[Y_E - Y_M]/[Y_E - Y_R] = [X_E - X_M]/[X_E - X_R] = R/M \qquad (2a,b)$$

In compact form Eq. (2a) is,

$$\Delta Y \text{ ratio} = \Delta X \text{ ratio} \qquad (3)$$

Since the coordinates of M (X_M,Y_M) are easily determined from mass balances, and the coordinates of E (X_E,Y_E) and R (X_R,Y_R) depend on only the abscissa value in the E phase (X_E), students determine this value by manually using the "Goal Seek" function to find the value of X_E that satisfies Eq. (3). In this manner the tie line passing through any fixed point can be determined.

Example 1. *Consider Example 7.2, Benitez.*[3] The box in Figure 3 (next page) lists the input conditions for a single stage extraction of acetone A from water using chloroform solvent S. After entering the mass rates and compositions of feed F and solvent S, the composition and flow rates of mixture M can be calculated from mass balances, Eq. (1).

Mixture M then separates into streams E and R that are in equilibrium. Then the tie line passing through point M can be determined as described above. Once the compositions of E and R are determined, their flow rates can be found from mass balance Eq. (3) and E = M – R. The results of the spreadsheet calculation are shown in Figure 3.

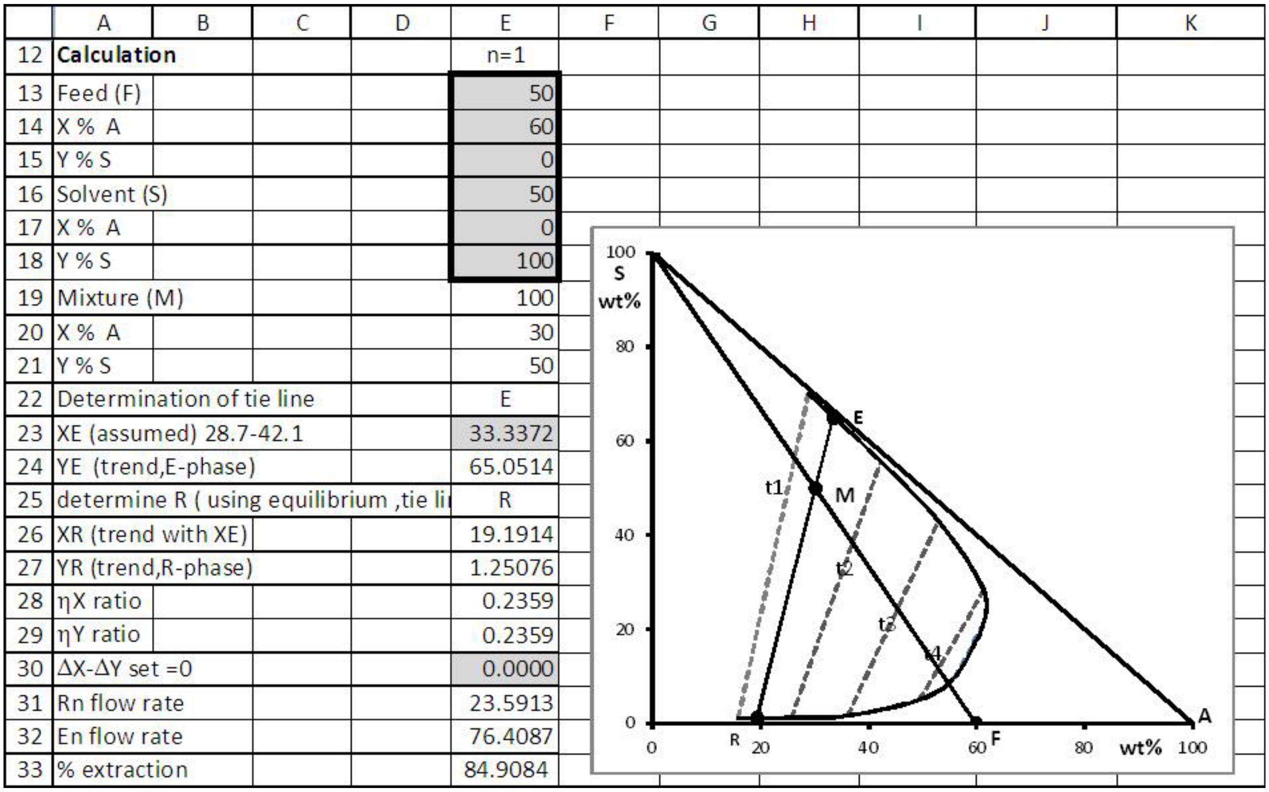
These results are in good agreement with the results from commercial software Mathcad.[3] Slight discrepancies may be noticed, but these are not significant. Mathcad also employs interpolation along with an initial guess value, as does Excel. However, students find the Excel spreadsheet calculation to be simpler, more straightforward, and more easily understood.

The worksheet in Figure 3 can be extended to multistage crosscurrent extraction by transferring mass flow rate and composition of raffinate R to the feed for the next stage and repeating the calculation.

In the preceding example, point M is intentionally chosen to be located between tie lines t_1 and t_2 for simplicity to demonstrate the calculation. Generally, the location of point M is not yet known, hence, a pair of tie lines, or in other words a range of X_E to be interpolated, cannot be selected beforehand. Since students are interacting with the spreadsheet, they can apply TREND over several tie lines (*e.g.*, TREND(E5:E8,D5:D8,E23) to obtain an initial solution. This solution will indicate the appropriate tie lines to use for a more accurate interpolation.

Multistage countercurrent extraction

According to Seader and Henley,[2] the problem specifications for the cascade of L-L extraction can be classified into six sets. Only set 1 is to be considered in this paper (for Excel calculation for other types of specifications, see Teppaitoon[12]). In this type of problem the flow rates and compositions of the feed and solvent as well as the desired raffinate composition are specified and it is desired to determine the number of stages required. The calculation is analogous to the graphical method of Hunter and Nash.[2] From the parameters given we can compute the flow rates and compositions of mixing point M with Eq. (1). Since raffinate product mass fraction of the solute is specified, the solute and product point mass fractions of extract (E_1) can be determined from the equilibrium data using



	A	E
12	**Calculation**	n=1
13	Feed (F)	50
14	X % A	60
15	Y % S	0
16	Solvent (S)	50
17	X % A	0
18	Y % S	100
19	Mixture (M)	100
20	X % A	30
21	Y % S	50
22	Determination of tie line	E
23	XE (assumed) 28.7-42.1	33.3372
24	YE (trend,E-phase)	65.0514
25	determine R (using equilibrium ,tie li	R
26	XR (trend with XE)	19.1914
27	YR (trend,R-phase)	1.25076
28	ηX ratio	0.2359
29	ηY ratio	0.2359
30	ΔX-ΔY set =0	0.0000
31	Rn flow rate	23.5913
32	En flow rate	76.4087
33	% extraction	84.9084

Figure 3. *Problem statement and results returned for Example 1.*

the TREND function. If we modify Eq. (2) for the countercurrent system to

$$[Y_{E1}-Y_{M}]/[Y_{E1}-Y_{RN}]=[X_{E1}-X_{M}]/[X_{E1}-X_{RN}]=R_{N}/M \qquad (4a,b)$$

we can determine R_N and then $E_1 = M - R_N$. The difference (or delta) or operating point P with coordinates (X_P, Y_P) and flow rate P can be determined,

$$P=S-R_{N}\,,\ X_{P}=[SX_{S}-R_{N}X_{RN}]/P,\ Y_{P}=[SY_{S}-R_{N}Y_{RN}]/P \qquad (5a,b,c)$$

The operating point, which can be treated in material balances as a stream, will be used to determine the operating lines.

Stage-to-stage calculation

Just as in other stagewise processes, stage-to-stage calculation in L-L extraction alternates between the equilibrium relationship (tie line) and the operating line equation. The calculation can start from either end of the cascades, but it is customary to start with stage 1. For stage 1, streams F and E_1 are specified, and streams R_1 and E_2 are to be determined. Since we assume equilibrium stages, E_1 and R_1 are in equilibrium; one can then estimate the composition of stream R_1 (X_{R1} and Y_{R1}) from X_{E1} using TREND with the phase equilibrium data as described earlier.

The equilibrium relationship gives the composition of the R_1 phase, but it does not give the mass flow rate. Although mass flow rate can be determined in the graphical method, it is not required. By contrast, for numerical stage-to-stage calculation it is necessary to know both the flow rate and composition of each stream for further calculation. The equation obtained from the material balances, after rearrangement, yields the useful equalities:

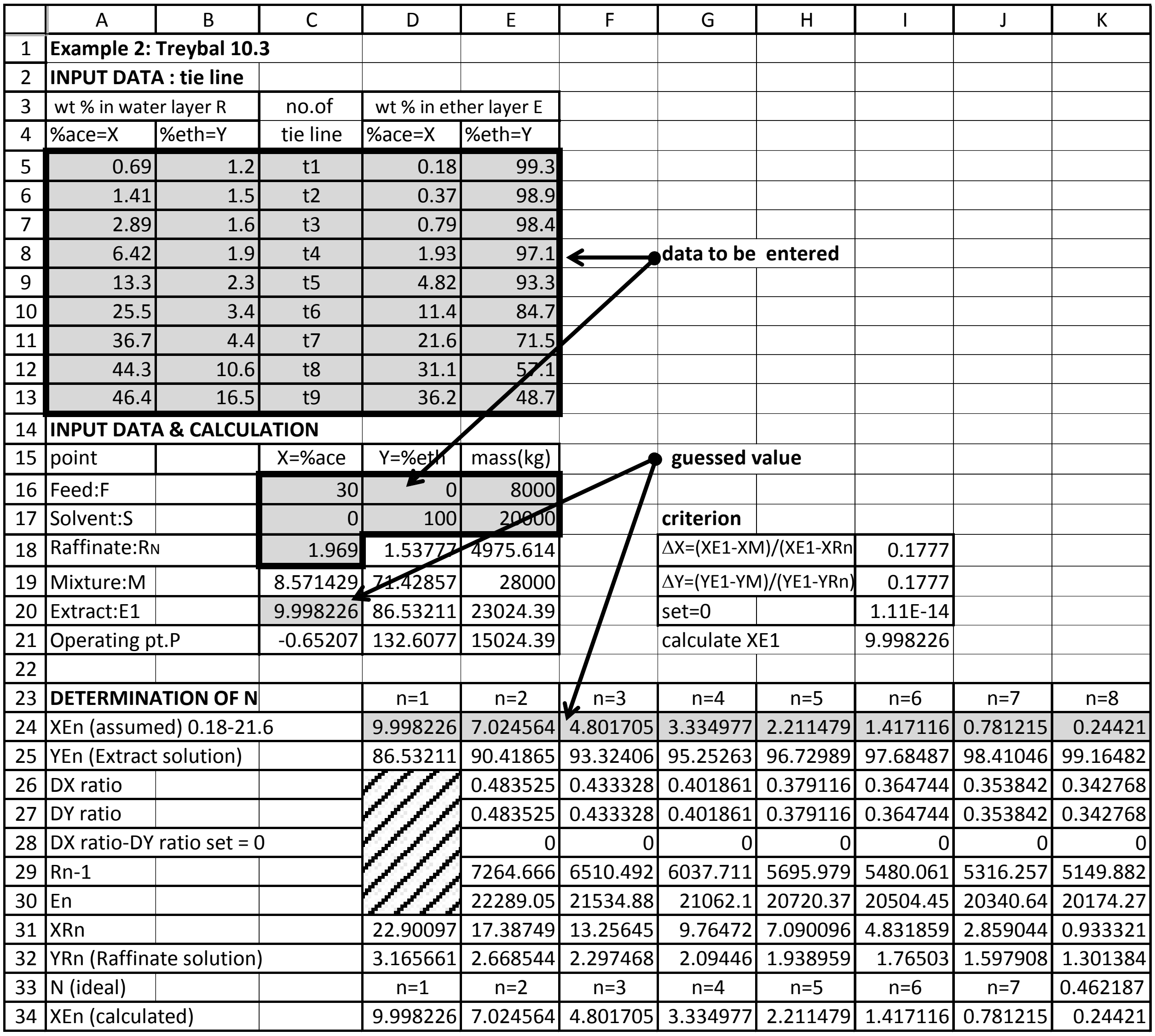
$$[X_{P}-X_{EN}]/[X_{EN}-X_{Rn-1}]=[Y_{P}-Y_{En}]/[Y_{En}-Y_{Rn-1}]=R_{n-1}/P \qquad (6a,b)$$

Defining the left-hand side and right-hand side Eq. (6a) as the DX ratio and DY ratio, respectively, one obtains an equation in compact form as

$$\text{DX ratio} = \text{DY ratio} \qquad (7)$$

Eq. (7) is used to determine the composition of stream E_2 by a trial-and-error procedure that is very similar to the procedure used to find equilibrium tie lines. We will use Goal Seek to find the value of X_{E2} that forces Eq. (7) to be valid. To do this, after assuming a value for X_{E2}, we calculate $Y_{E2} = f_E(X_{E2})$ from the equilibrium data. Since (X_P, Y_P) and (X_{R1}, Y_{R1}) are already known, we calculate the DX ratio and DY ratio, then compare these ratios (Eq. 7). If they are not equal, Goal Seek will find the value of X_{E2} that makes them equal. Once X_{E2} and Y_{E2} are known, Eq. (6b) can be used to determine the mass flow rate of R_1 (set n = 2). The mass flow rate of $E_2 = R_1 + E_1 - F$. Now, move to the next stage and repeat the calculation until X_{Rn} is less than X_{RN}, the specified value.

Example 2. *Consider Illustration 10.3 from Treybal.*[13] The first box in Figure 4 presents the tie line data, and the lower box lists the specified variables. The worksheet is divided into three parts: input data, calculation, and graphical diagram. The stage-by-stage procedure is done in rows 24 to 32.



	A	B	C	D	E	F	G	H	I	J	K
1	**Example 2: Treybal 10.3**										
2	**INPUT DATA : tie line**										
3	wt % in water layer R		no.of	wt % in ether layer E							
4	%ace=X	%eth=Y	tie line	%ace=X	%eth=Y						
5	0.69	1.2	t1	0.18	99.3						
6	1.41	1.5	t2	0.37	98.9						
7	2.89	1.6	t3	0.79	98.4						
8	6.42	1.9	t4	1.93	97.1						
9	13.3	2.3	t5	4.82	93.3						
10	25.5	3.4	t6	11.4	84.7						
11	36.7	4.4	t7	21.6	71.5						
12	44.3	10.6	t8	31.1	57.1						
13	46.4	16.5	t9	36.2	48.7						
14	**INPUT DATA & CALCULATION**										
15	point		X=%ace	Y=%eth	mass(kg)						
16	Feed:F		30	0	8000						
17	Solvent:S		0	100	20000		**criterion**				
18	Raffinate:RN		1.969	1.53777	4975.614		ΔX=(XE1-XM)/(XE1-XRn		0.1777		
19	Mixture:M		8.571429	71.42857	28000		ΔY=(YE1-YM)/(YE1-YRn)		0.1777		
20	Extract:E1		9.998226	86.53211	23024.39		set=0		1.11E-14		
21	Operating pt.P		-0.65207	132.6077	15024.39		calculate XE1		9.998226		
22											
23	**DETERMINATION OF N**			n=1	n=2	n=3	n=4	n=5	n=6	n=7	n=8
24	XEn (assumed) 0.18-21.6			9.998226	7.024564	4.801705	3.334977	2.211479	1.417116	0.781215	0.24421
25	YEn (Extract solution)			86.53211	90.41865	93.32406	95.25263	96.72989	97.68487	98.41046	99.16482
26	DX ratio			▨	0.483525	0.433328	0.401861	0.379116	0.364744	0.353842	0.342768
27	DY ratio			▨	0.483525	0.433328	0.401861	0.379116	0.364744	0.353842	0.342768
28	DX ratio-DY ratio set = 0			▨	0	0	0	0	0	0	0
29	Rn-1			▨	7264.666	6510.492	6037.711	5695.979	5480.061	5316.257	5149.882
30	En			▨	22289.05	21534.88	21062.1	20720.37	20504.45	20340.64	20174.27
31	XRn			22.90097	17.38749	13.25645	9.76472	7.090096	4.831859	2.859044	0.933321
32	YRn (Raffinate solution)			3.165661	2.668544	2.297468	2.09446	1.938959	1.76503	1.597908	1.301384
33	N (ideal)			n=1	n=2	n=3	n=4	n=5	n=6	n=7	0.462187
34	XEn (calculated)			9.998226	7.024564	4.801705	3.334977	2.211479	1.417116	0.781215	0.24421

Figure 4. *A portion of the worksheet for solving Example 2.*

For any stage n the combination of the equilibrium calculation [$Y_{En} = f_E(X_{En})$] plus operating line calculation [force DX ratio = DY ratio with Goal Seek] and Eq. (6b) to find R_{n-1} and mass balances to find $E_n = R_{n-1} + E_1 - F$ will determine the values of unknowns X_{En}, Y_{En}, R_{n-1}, and E_n. The TREND function can be used to determine $X_{Rn} = f_{EQ}(X_{En})$ and $Y_{Rn} = f_R(X_{Rn})$. The results returned are shown in Figure 4. This layout permits us to extend the calculation to any number of stages desired by using "Copy and Paste" for additional columns and applying Goal Seek at each stage.

From Figure 4, the flow rates and compositions in both phases passing through each stage can be clearly seen. The number of ideal stages required is 7.46. Compared with the graphical method (the McCabe-Thiele diagram), which yields the number of theoretical stages of 7.6,[13] both results are in agreement with each other. The results can be displayed not only in a triangular diagram but also in the form of a McCabe-Thiele diagram, as illustrated in Figure 5 (next page).

The worksheet created can be applied to other conditions/systems of interest for the same type of problem so that the students can explore the effect of pertinent parameters on extraction performance.

Example 3. *Determine* $(S/F)_{min}$ *for Example 2.* A simple method (maybe *the* simplest method) to find $(S/F)_{min}$ is a trial-and-error procedure with the help of the Excel spreadsheet by reducing the value of S continuously and computing a difference of X_E in any pair of adjacent stages, for instance $\Delta X_E = X_{E4} - X_{E3}$ for each value of S. As S is decreasing ΔX_E is diminished until it exhibits a change in sign. Once this condition is met, $(S/F)_{min} = 1.563$ will be found. Compared to the graphical method,[13] the $(S/F)_{min}$ is 1.63. With the same principle, the Excel spreadsheet gives the result 1.563.[12]

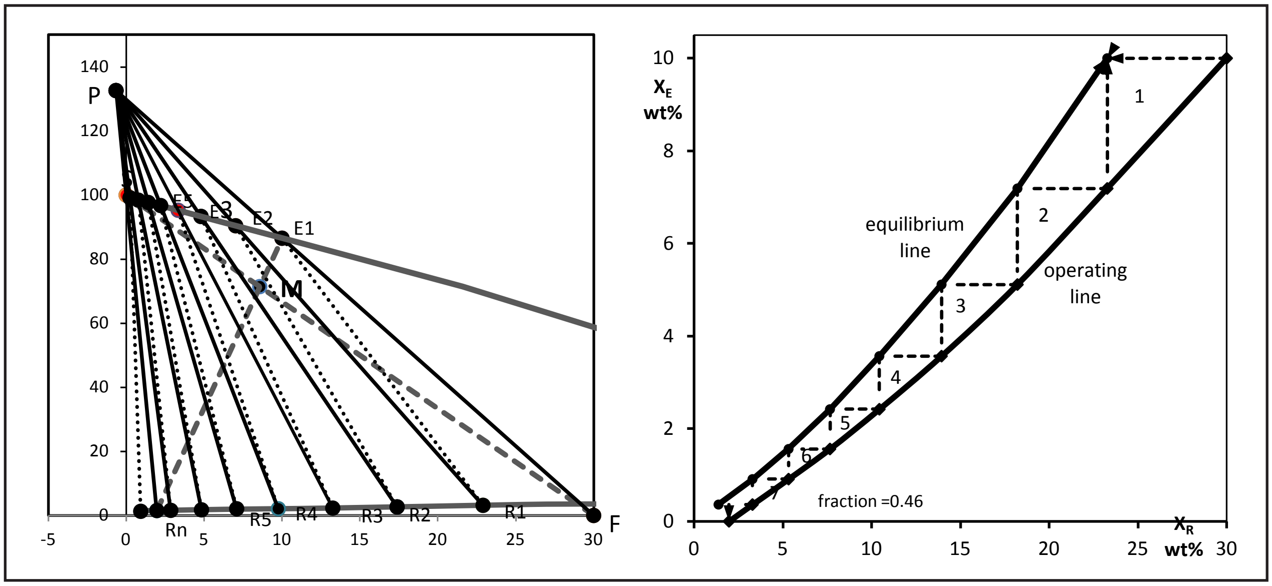


Figure 5. *Graphical output for Example 2 (produced from Excel spreadsheet).*

The difference may result from the lesser accuracy of the graph drawn, which yields values of X_{E1} and X_M equal to 0.143 and 0.114, respectively, whereas the values from Excel are 0.148597 and 0.117082, respectively. Had the former values been substituted by the latter, the $(S/F)_{min}$ value of 1.5624 would have been obtained.

STUDENT USE

Before using Excel the illustrated examples in the textbook were solved first by the graphical method, which provided understanding to students. Then, the stage-to-stage calculation procedure was thoroughly described so students could easily perform Excel spreadsheet calculations with a computer. To achieve this purpose, the instructor and students spent more time than usual on the problems calculation. However, the result was satisfactory. Although a formal quantitative student evaluation was not conducted, it was noted that the students paid more attention to this subject, especially when performing the calculation with Excel. Instead of manually drawing the diagram on graph paper, the students preferred to use Excel to produce such a diagram, which could be changed as desired. Because the students were keen to do this, they were obliged to clearly understand stage-to-stage calculations for the process considered beforehand.

With the spreadsheet students spend less time so more types of problems can be studied. Compared with other commercial software, Excel provides additional advantages for ternary systems. Not only is the calculation simple and straightforward, but also the results obtained can be conveniently displayed as a graphical diagram. This gives students better understanding. The worksheets created, with some modifications, can be applied to other operating conditions or other systems of interest, as long as the criterion is not violated. The effects of pertinent parameters on extraction performance can conveniently be explored. Students/instructors will find that problem solving in L-L extraction processes is no longer cumbersome and instead becomes a worthwhile challenge.

SUMMARY AND CONCLUSIONS

An Excel spreadsheet numerical computation based on a firm understanding of L-L extraction that is analogous to the graphical method is developed for solving L-L extraction problems. With the simple Excel function "TREND" and criteria drawn from the mixing rule and the difference point, problem solving is effectively performed by the Excel spreadsheet, which eliminates the tedious work of drawing a graph.

Using computers cannot replace hand calculations along with graphical solutions. Good pedagogy should begin with a simple solution; however, the use of the graphical method is only to provide visualization of solving a problem. It is no longer necessary to employ graphs in an attempt to calculate accurate design solutions since there is another, more efficient tool available.

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ChE teaching tips

Humanities and Social Relevance for Chemistry and Chemical Engineering Students: The Leonardo Project

The goal of the Leonardo project is to prepare educational materials at the interface between chemical technology and society for use by chemical engineering or chemistry professors in their regular courses.

For effective practice in industry, government, or education, chemists and chemical engineers today and tomorrow must understand how technology interacts with the society that it serves. They need to understand (and be sensitive to) the culture in which they practice their profession. Because chemists and chemical engineers increasingly interact with a variety of people who often have little or no scientific background, chemical and chemical engineering education should expose students to the cultural implications (including ethical, international, legal, and political implications) of chemical science and practice.

Chemical engineering programs also need to demonstrate that students have satisfied ABET criteria 3f ("understanding of professional and ethical responsibility") and 3h ("broad education necessary to understand the impact of engineering solutions in a global, economic, environmental, and societal context").

All too often, current methods for including humanities and social studies in chemical and chemical engineering education have limited success because these subjects are taught apart from regular science and engineering courses; there is a lack of integration. In large universities, professors who teach history, philosophy, literature, etc. are rarely interested in the education of scientists and engineers. Further, special (service) courses for students outside the College of Letters and Science are often taught by part-time lecturers; these courses are frequently not taken seriously because they (and their instructors) carry little academic prestige. Regrettably, chemistry and chemical engineering faculty tend to have little interest in such courses, regarding them as a "nuisance" or, at worst, a "waste of time." Students naturally pick up on the low opinion of their professors towards these courses, and erroneously see little connection between humanities or social studies "requirements" and their professional careers.

The Leonardo Project suggests that chemistry and chemical engineering professors introduce relevant social and humanistic content directly into their existing courses. The Leonardo Project suggests that typically, twice a month, a professor may devote 10 or 15 minutes to show how a particular science or engineering topic interacts with human concerns as indicated by history, politics, ethics, or religion, etc. However, to do so, professors need help; they need case studies or examples. The purpose of the Leonardo Project is to prepare and provide a number of pertinent case studies (reports) that cover a wide range of technology-society interactions as encountered in the chemical and related industries. After careful editing, all reports are posted on the internet where anyone may use them free of charge.

For example, in a chemical kinetics course, the professor may use the report "Catalytic Converter for Automobile Emissions: A government-Supported Chemical Invention" or in an introductory course "Pain Relief for Everybody: Large Scale Production of Aspirin" or "Human Aspects of Chemistry and Chemical Practice: The Life and Work of Primo Levi." For a list of reports, see <http://www.cchem.berkeley.edu/leonardo-project/>.

Although the Leonardo Project reports do not directly provide assessments to satisfy ABET, the reports can provide the basis for assessment of criteria 3f and 3h. For example, a group of students may be asked to develop a role play based on "Love Canal: Failure of Chemical Engineering Ethics" and assess their understanding of ethical responsibility. Or, the professor may assign the detailed and lengthy Manhattan Project report to the class. After in-class discussion, students can write short analyses that can be assessed for ABET criteria 3f, 3h, and 3g (communication). ❐

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