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An Iteratively Refined Distillation Line Method

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The focus of this article is distillation design feasibility. It is shown that existing methods for determining feasibility can give incorrect results or produce feasible designs that waste energy due to over-specification and mass balance errors. An iterative refinement procedure based on direct substitution is proposed within the distillation line method of Lucia et al. that automatically adjusts one product composition to determine feasibility. Direct substitution equations are presented in detail and 14 literature examples are used to illustrate the efficacy of iterative refinement. Numerical results show that iterative refinement can find feasible designs that other methods cannot find, often resulting in significant reductions in energy requirements, and that it is all product compositions, not just trace compositions that affect most shortcut methods for distillation design. Iterative refinement can also find minimum energy requirements and identify sets of specifications that give infeasible designs. © 2010 American Institute of Chemical Engineers *AIChE J,* 57: 2164–2173, 2011
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Introduction

Distillation line methods[1,5] are shortcut design methods used in the early stages of synthesis and design of separation processes and are based on generating liquid composition trajectories for a given set of desired product specifications.

Boundary Value Design Procedure

In the boundary value design procedure (BVDP) described in the study of Levy et al.,[1] a reflux ratio is selected and a rectifying trajectory is generated starting from the given distillate composition moving down from the top of the column. A boil-up ratio is then computed directly from the selected reflux ratio and the calculated boil-up ratio and bottoms composition are used to generate a stripping trajectory from the bottom up. If the rectifying and stripping trajectories intersect, then the column design is considered feasible. Otherwise the design is infeasible, a new value of the reflux ratio is selected and the procedure is repeated (see Ref. 2).

When applied to mixtures with four or more components, the BVDP easily fails to find feasible designs when they exist. To see this, consider the following motivating example.

Motivating example

Consider the following simple example in which it is desired to separate a saturated liquid feed of *n*-pentane (1), *n*-hexane (2), *n*-heptane (3), and *n*-octane (4) at 1 atm into a high purity distillate product of 99 mol % or better of *n*-pentane and a bottoms product that is essentially an equimolar mixture of hexane, heptane, and octane. The exact specifications for the feed and bottoms compositions, as well as the distillate composition assumed for the purpose of applying the BVDP are shown in Table 1. The reader should not confuse this assumed distillate composition with the distillate specification of 99 mol % or better of *n*-pentane. The phase models used in this example was Raoult's law. Extended Antoine constants can be found in Appendix Table A1.

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Table 1. Simple Motivating Example

Component	Feed Composition*	Distillate Composition	Bottoms Composition
Pentane	0.25	0.9900	0.0010
Hexane	0.25	0.0097	0.3309
Heptane	0.25	0.00026	0.3340
Octane	0.25	0.00004	0.3341

*Feed is saturated liquid.

Figure 1 shows the rectifying and stripping liquid composition profiles for the boundary value design procedure (or distillation line approach) of Fidkowski et al. (distillate to rectifying pinch point curve, bottoms to stripping pinch point curve) for a specified boil-up ratio, $s = 1.0$ and calculated reflux ratio, $r = 1.972$.

As we show later, this design is feasible. However, for the specifications given in Table 1 and a value of $s = 1.0$ ($r = 1.972$), the approach used by Fidkowski et al.[2] yields rectifying and stripping profiles for this four-component example that do not intersect. Thus the boundary value design procedure gives the false result that the design is infeasible! This is a serious concern because even an experienced design engineer would instinctively either increase the boil-up or reflux ratio or try to adjust nonkey compositions in an effort to find a feasible design for this separation. However, this often leads to a column that is operating with a higher boil-up ratio and wasting energy as it is difficult to adjust product compositions and it is well known that distillation line methods are sensitive to product compositions (see Refs. 3 and 4). The difficulty with BVDP is that it over-specifies the synthesis and/or design problem by fixing all feed conditions, the boil-up ratio (or reflux ratio), and all component compositions in both products. This also gives rise to mass balance errors at the feed stage.

Distillation Line Method of Lucia et al.

In the more recent distillation line strategy proposed by Lucia et al.,[5] mass balance errors at the feed stage are completely avoided by performing the calculations in a complete bottom up (or top down) manner. In this approach, the calculations proceed from product to product and the switch from difference equations in one section of the column to difference equations in the other section of the column is made based on the existence of pinch point curves or some other criterion. Feasibility is determined using conditions at the opposite end of the column from which the calculations proceed. For example, in a bottom up approach, the column is considered feasible if some given distillate specification is satisfied (e.g., $\| y_D^{(spec)} - y_D^{(calc)} \| < \zeta$ for some small value of ζ, say $\zeta = 0.05$). However, this approach leads to mass balance errors of a different kind. Specifically, overall component mass balances for the column will be in error because $y_D^{(calc)}$ is rarely exactly equal to $y_D^{(spec)}$, and therefore small overall component mass balance errors are common.

Consider the motivating example again where the bottom up approach of Lucia et al.[5] is used and the distillation column design is considered feasible if both $y_D^{(calc)}$ for pentane ≥ 0.99 and the component mass balances for the column are tightly converged. Using $s = 1.0$, again the calculated reflux ratio is 1.972. We set the number of stripping and rectifying stages to 300. The calculated distillate composition is $y_D^{(calc)} = 0.9596$ and the conclusion is that the original bottom up approach of Lucia et al. gives an infeasible design. No other choice of number of stripping and rectifying stages gives a feasible design. This clearly illustrates that one set of bottom up (or top down) distillation line computations can lead to an incorrect design decision.

Rectification Body Method

The rectification body method (RBM) has been developed by Marquardt and co-workers and is primarily a tool for determining minimum energy demands (reflux ratio; Ref. 3) The key ideas of RBM are to generate relevant parts of pinch point curves and a manifold of possible profiles from pinch point information and eigen decompositions at various nodes. Rectification bodies, which represent an envelope or manifold of possible solutions, are generated using convex approximations by linearly connecting product compositions to feasible pinch points on the appropriate pinch point curves. Minimum energy requirements are indicated by rectification bodies that just touch. However, because the RBM is not intended to be used to determine feasibility, it is not considered any further in this article.

Consequences of Mass Balance Errors

All distillation line methods to date lead to mass balance errors and, in our opinion, this is bothersome. These methods are noniterative methods in the sense that they simply generate trajectories once and make decisions based on this single simulation. Moreover, these decisions can be very wrong! In some cases, a design engineer will conclude that the separation is feasible when it does not really meet the desired product specifications (e.g., in the bottom up approach of Lucia et al.[5]) and in other cases a design engineer will

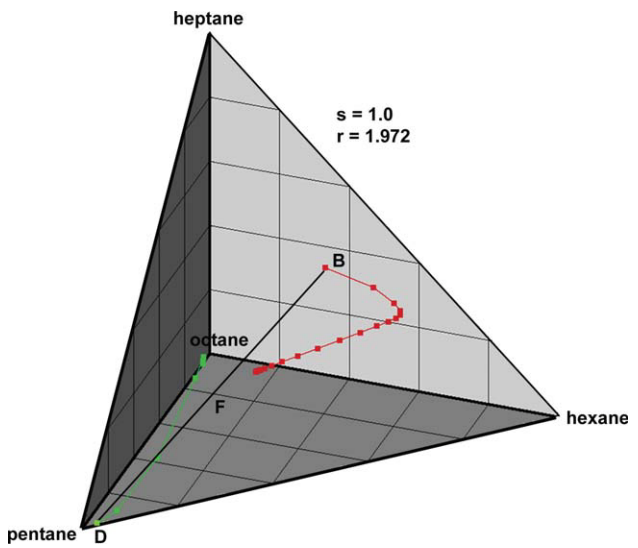

Figure 1. False infeasible design using the boundary value design procedure.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

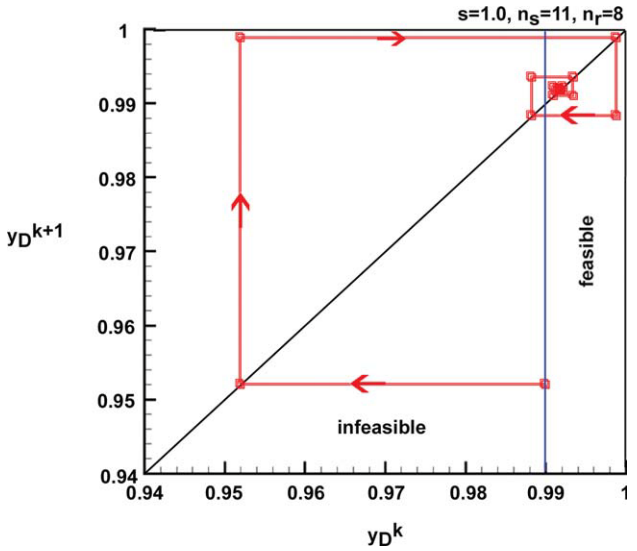

Figure 2. Direct substitution for pentane/hexane/heptane/octane distillation.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

conclude the separation in infeasible when it is really feasible (e.g., using the boundary value approach)! These difficulties in making correct decisions regarding feasibility and operating conditions rest largely with the fact that it is often difficult to accurately estimate product compositions consistent with both mass balance and phase equilibrium.

In this article, we propose an iteratively refined distillation line method to circumvent all of the difficulties associated with existing distillation line methods. Accordingly, an iteratively refined approach to distillation design feasibility based on direct substitution is described. This is followed by supporting numerical results for 14 example problems from the open literature. The article ends with a summary of the novel ideas contained in this work and some ideas for advancing the concept of iterative refinement in distillation line methods.

An Iteratively Refined Distillation Line Method

The bottom up (or top down) approach of Lucia et al.[5] is ideally suited for iterative refinement. For example, given desired product compositions x_B and x_D (or y_D) and starting from the bottom of the column, one selects a boil-up ratio and generates a liquid composition profile using the usual difference equations for modeling the stripping section.

$$x_{j+1} = x_j + [s/(s+1)]y_j - x_j + [1/(s+1)]x_B = [s/(s+1)]y_j + [1/(s+1)]x_B \qquad j = 1, \cdots, N_s \quad (1)$$

where j denotes a stage number, N_s is the total number of stripping stages, y_j is the vapor composition in equilibrium with the liquid composition x_j, and $x_1 = x_B$. Next the reflux ratio is calculated using the expression

$$r = (s - q + 1)[(y_D - x_F)/(x_F - x_B)] + q \quad (2)$$

for some designated key component in the mixture. This is followed by the generation of a rectifying trajectory using the equation

$$x_{j+1} = x_j + [(r+1)/r)]y_j - x_j - (1/r)x_D = [(r+1)/r]y_j - (1/r)x_D \qquad j = N_s, \cdots, N \quad (3)$$

where N is the total number of stages, $x_D = x_N$ and y_D is the vapor in equilibrium with x_D.

$$y_D = K_N x_D \quad (4)$$

Finally, x_D (or y_D) is compared to some specified condition for x_D (or y_D) and a determination of feasibility is made based on that comparison. However, as noted in the Introduction section, rarely does $y_D^{(calc)} = y_D^{(spec)}$.

In iterative refinement, Eqs. 2–4 are used to construct a natural direct substitution. That is, we define

$$r^k = (s - q + 1)[(y_D^k - x_F)/(x_F - x_B)] + q \quad (5)$$

where k denotes an iteration number. Iterative values of y_D^k are computed using Eqs. 3 and 4 in the form

$$x_{j+1} = [(r^k + 1)/r^k]y_j - x_j - (1/r^k)y_D^k \qquad j = N_s, \cdots, N^k \quad (6)$$

$$y_D^{k+1} = K_{Nk} x_{Nk} \quad (7)$$

The new calculated value, $y_D^{(calc)} = y_D^{k+1}$, is then used again in Eq. 5 to compute a new reflux ratio, r^k, and the process is repeated until there is no change in the successive values of y_D. Specifically, iterative refinement continues until $\| y_D^{k+1} - y_D^k \| \le \varepsilon = 10^{-5}$.

In an earlier paper by Fidkowski et al. (Ref. 6, page 1771) the authors propose an iterative procedure using the product compositions of the nonkey component and a direct substitution procedure. This idea differs from the proposed method of iterative refinement in three key ways:

(1) Our procedure adjusts all compositions in the distillate.

(2) The Fidkowski et al.'s procedure does not resolve the issue of mass balance errors.

(3) The method suggested by Fidkowski et al.[6] is not applicable to sloppy splits.

In contrast, the iterative refinement procedure that we propose adjusts all distillate (or bottoms) compositions simultaneously, makes no assumptions about the separation being performed, and satisfies all overall component mass balances to the specified tolerance (usually 10^{-5}).

Motivating example revisited

Consider the motivating example again, only this time we will use iterative refinement to automatically adjust the reflux ratio, r, and all distillate compositions y_D. Figure 2 shows direct substitution iterations for $y_D(C_5)$ using a fixed boil-up ratio of $s = 1.0$ for which the initial reflux ratio calculated from Eq. 5 was $r = 1.97218$. The initial distillate composition, y_D, for the iterative refinement process was set equal to the distillate composition in Table 1.

There are two important observations that can be gleaned from Figure 2. First, as pointed out before, the first iteration

Table 2. Specifications for Distillation Design Problem Definitions

Problem	Mixture	Phase Models (L–V)	x_F	x_B	s	$y_D^{(spec)}$
1	Acetic acid (HK)–ethyl acetate (LK)–water	*UNIQUAC–HOC	(0.5000, 0.3150, 0.1850)	($0.9999, 5 \times 10^{-5}, 5 \times 10^{-5}$)	3.4204	$y_{D1} \leq 1 \times 10^{-4}$, $y_{D2} \leq 0.6300$
2	Acetic acid–water (LK)–acrylic acid (HK)	UNIQUAC–HOC	(0.0495, 0.5000, 0.4505)	($0.1000, 1 \times 10^{-10}$, 0.9000)	4.4333	$y_D(W) \geq 0.99$
3	Chloroform–acetone (LK)–benzene (HK)	UNIQUAC–ideal	(0.1100, 0.1700, 0.7200)	($0.13266, 1 \times 10^{-10}$, 0.86734)	1.2204	$y_D(A) \geq 0.99$
4	Chloroform (LK)–acetone–benzene (HK)	UNIQUAC–ideal	(0.4395, 0.0330, 0.5275)	(0.3297, 0.0330, 0.6373)	2.5860	$y_D(C) \geq 0.945$
5	Formic acid–acetic acid (HK)–water (LK)	UNIQUAC–HOC	(0.05377, 0.6600, 0.2862)	(0.0717, 0.8800, 0.0483)	6.9790	$y_D(W) \geq 0.9990$
6	Formic acid (LK)–acetic acid–water (HK)	UNIQUAC–HOC	(0.7000, 0.1216, 0.1784)	(0.5050, 0.2000, 0.2950)	3.9419	$y_D(FA) \geq 0.9900$
7	Acetic acid (HK)–ethanol–ethyl acetate (LK)–water	UNIQUAC–HOC	(0.5000, 0.0697, 0.2800, 0.1527)	($0.9950, 0.00025, 0.0030, 1.75 \times 10^{-3}$)	5.8022	$\|\|y_D^{(spec)} - y_D^{(calc)}\|\| \leq 0.1$
8	Carbon tetrachloride–chloroform (LK)–acetone–benzene (HK)	UNIQUAC–ideal	(0.0928, 0.6713, 0.0921, 0.1438)	(0.1400, 0.5000, 0.1400, 0.2200)	4.5849	$y_D(C) \geq 0.99$
9	*n*-Butane–*i*-pentane (LK)–*n*-pentane (HK)–*n*-hexane	K-Wilson–K-Wilson	(0.25, 0.30, 0.20, 0.25)	(9.1×10^{-21}, 0.01228, 0.38544, 0.60227)	10.4216	$\|\|y_D^{(spec)} - y_D^{(calc)}\|\| \leq 0.06$
10	*n*-Pentane (LK)–*n*-hexane–*n*-heptane–*n*-octane (HK)	Ideal–ideal	(0.25, 0.25, 0.25, 0.25)	(0.001, 0.3309, 0.3340, 0.3341)	1.0000	$y_D(C_5) \geq 0.99$
11	Methanol (LK)–acetic acid (HK)–ethanol–ethyl acetate–water	UNIQUAC–HOC	(0.4150, 0.3538, 0.0117, 0.1873, 0.0322)	(0.05134, 0.8217, 0.0251, 0.0383, 0.06355)	4.3952	$\|\|y_D^{(spec)} - y_D^{(calc)}\|\| \leq 0.02$
12	Propane (LK)–*n*-butane–*i*-butane–*i*-pentane–*n*-pentane–*n*-octane (HK)	K-Wilson–K-Wilson	(0.15, 0.20, 0.15, 0.20, 0.15, 0.15)	(1×10^{-10}, 0.2352, 0.1764, 0.2352, 0.1764, 0.1768)	0.7243	$y_D(C_3) > 0.9890$
Problem	Mixture	Phase Models (L–V)	x_F	y_D	r	$x_B^{(spec)}$
13	Acetic acid–water (LK)–acrylic acid (HK)	UNIQUAC–HOC	(0.0495, 0.5000, 0.4505)	(1×10^{-11}, 0.9900, 0.0100)	1.3460	$x_B(AcrA) \geq 0.99$
14	Methanol (LK)–ethanol–*n*-propanol (HK)	Constant relative volatility	(0.30, 0.25, 0.45)	(0.55, 0.44, 0.01)	1.4825	$x_B(P) \geq 0.99$

* UNIQUAC is Universal Quasi-Chemical; HOC is Hayden-O'Connell.

Table 3. Initial Values for Distillation Design Feasibility Problems

Problem	s	r	N_s	N_r	$y_D^{(initial)}$
1	3.4204	2.4204	300	300	(1×10^{-4}, 0.6300, 0.3699)
2	4.4333	3.3447	300	300	(1×10^{-11}, 0.9900, 0.0100)
3	1.2204	4.8868	300	300	(6.666×10^{-4}, 0.9900, 0.0093)
4	2.5860	10.9293	300	300	(0.9450, 0.0330, 0.0210)
5	6.9790	19.9214	300	300	(0.0005, 0.0005, 0.9990)
6	3.9419	4.8625	300	300	(0.9900, 0.0050, 0.0050)
7	5.8022	4.8327	300	300	(1×10^{-10}, 0.13511, 0.5546, 0.3103)
8	4.5849	7.5302	300	300	(0.005, 0.990, 0.003, 0.002)
9	10.4216	6.3960	300	300	(0.4274, 0.5042, 0.0684, 1×10^{-10})
10	1.0000	1.9722	300	300	(0.99, 0.0097, 0.00026, 0.00004)
11	4.3952	2.3237	300	300	(0.6900, 1×10^{-10}, 0.0015, 0.3000, 0.0085)
12	0.7243	3.0489	300	300	(0.9890, 0.0031, 0.0023, 0.0031, 0.0023, 0.0002)
Problem	s	r	N_s	N_r	$x_B^{(initial)}$
13	2.3939	1.3460	300	300	(0.100, 1×10^{-10}, 0.9000)
14	2.9904	1.4919	300	300	(5×10^{-11}, 0.022, 0.9780)

yields an infeasible design. Second, even though the first and third direct substitution iterations are infeasible, all subsequent iterations are feasible and iterative refinement converges in 13 iterations to a feasible design with 11 stripping stages, eight rectifying stages, and final values of reflux ratio and distillate compositions of $r = 1.97265$ and $y_D = (0.9915, 0.0086, 1.3335 \times 10^{-6}, 2.856 \times 10^{-10})$, respectively. The exact bottoms composition is shown in Table 1. Moreover, note that the calculated reflux ratio changes very little from a initial value of 1.97218 to a final value of 1.97265; it is the changes in distillate composition, even the ones in trace amount, that are more significant in determining feasibility.

Iterative Refinement and the BVDP

In our opinion, it is not possible to use iterative refinement with the original boundary value design method.[1] This is because both product compositions are specified and profiles are generated from distillate to rectifying pinch point and bottoms to stripping pinch point.

However, the overall mass balance line for the column is drawn through the product composition that is completely specified and the feed, which is given. For a ternary mixture, drawing the overall mass balance line fixes the one "missing" composition in the bottoms or distillate product so that liquid composition profiles from both products can be generated. Unfortunately, the decision to fix the overall mass balance around the column (i.e., both product compositions), while reasonable, precludes the use of iterative refinement.

Numerical Results

In this section, numerical results for the proposed iteratively refined distillation line method for 14 different distillation problems available in the open literature are presented. While several ternary mixtures are included in this problem set, in our opinion, the examples with four or more components represent the more interesting examples. All calculations were performed on a Pentium IV equipped with a Lahey-Fijitsu LF95 compiler in double precision arithmetic. Binary interaction parameters for the UNIQUAC equation and critical properties, acentric factors, and relative volatilities can be found in the Appendix. Light and heavy key components are denoted by LK and HK, respectively. Convergence is based on two criteria: (1) satisfaction of component mass balances around the entire column to an accuracy of 10^{-4} and (2) $\| y_D^{k+1} - y_D^k \| \leq \varepsilon = 10^{-5}$ for the iterative refinement process.

Problem Definitions

Tables 2 and 3 give problem specifications and initial values for the 14 problems, which include ideal, nonideal, and azeotropic mixtures.

Explanation of Tables 2 and 3

Specifications for all problems are shown in Table 2 whereas initial values for iteratively refined variables are shown in Table 3. For the bottom up calculations, all problems used a saturated liquid feed (i.e., $q = 1$) and fixed boilup ratio, s. Also x_F and x_B were specified whereas y_D, r, N_r, and N_s were calculated using the distillation line method described in the study of Lucia et al.[5] The value $y_D^{(initial)}$ is y_D^0 or the initial distillate composition for iterative refinement. Given this value, the initial reflux ratio, r^0, was calculated from Eq. 2. Note that the value $y_D^{(spec)}$ does not necessarily uniquely determine the initial value of y_D. For example, the inequality in problem 2 does not uniquely define the distillate composition. The initial values of N_s and N_r for all problems were 300. Iterative values of N_s were determined by simply locating the smallest stage number in the stripping section for which the column remained pinched (i.e., the smallest value of N_s for which $\|x_{j+1} - x_i\| \leq 10^{-4}$; see Eq. 1). The number of rectifying trays, N_r, was then determined as the first stage in the rectifying section for which the distillate specification was met, unless the rectifying trajectory resulted in one or more compositions outside the range 0–1, in which case the iterative design was deemed infeasible. For the top down calculations, reverse the roles of y_D and x_B, s and r, and N_s and N_r.

Aspen Plus Validations

Feasible designs for all problems defined in Table 1 are shown in Table 4 and have been validated using the RADFRAC block in the Aspen Plus simulator. Detailed

Table 4. Final Calculated Numerical Results for Distillation Design Feasibility Problems

Problem	N_S	N_R	Iterations (Time*)	Final $y_D^{(calc)}$	Final r
1	33	9	10 (0.31)	$(1.203 \times 10^{-10}, 0.627, 0.372)$	2.4211
2	22	8	51 (1.18)	(0.00296, 0.9904, 0.0065)	3.3489
3	100	23	12 (0.44)	$(1.8731 \times 10^{-4}, 0.9907, 0.0090)$	4.8888
4	29	11	216 (4.35)	(0.9685, 0.0278, 0.0035)	11.3406
5	31	18	5 (0.30)	$(2.5565 \times 10^{-8}, 8.4703 \times 10^{-4}, 0.9991)$	19.9101
6	25	16	27 (2.98)	$(0.9910, 4.3041 \times 10^{-9}, 0.0089)$	4.8836
7	14	2	8 (0.25)	(0.0011, 0.1022, 0.6465, 0.2501)	4.8198
8	54	24	8 (0.36)	$(0.0082, 0.9915, 2.0752 \times 10^{-4}, 2.3130 \times 10^{-7})$	7.5710
9	65	6	1 (0.03)	$(0.4136, 0.4752, 0.1104, 6.5615 \times 10^{-4})$	6.3960
10	11	8	13 (0.05)	$(0.9914, 0.0086, 1.3335 \times 10^{-6}, 2.856 \times 10^{-10})$	1.9726
11	14	4	31 (0.86)	$(0.6702, 4.1844 \times 10^{-7}, 0.0029, 0.3181, 0.0086)$	2.0856
12	76	14	64 (3.32)	$(0.9929, 1.9166 \times 10^{-4}, 0.0068, 2.6340 \times 10^{-9}, 1.0860 \times 10^{-10}, 1.8480 \times 10^{-18})$	3.0543
Problem	N_S	N_R	Iterations (Time*)	Final $x_B^{(calc)}$	Final s
13	4	31	8 (0.52)	$(3.3296 \times 10^{-7}, 0.0033, 0.9966)$	2.3776
14	19	16	119 (2.66)	$(3.4069 \times 10^{-7}, 0.0077, 0.9923)$	3.0596

*Computer time in seconds.

calculations for iterative refinement designs and RADFRAC validations are available on request from the authors.

Table 3 gives initial values for all examples in Table 2. Results for both bottom up (problems 1–12) and top down (problems 13 and 14) calculations are presented in Table 4.

Detailed Examples

In this section, two examples with four or more components are presented to illustrate the power of the proposed iteratively refined distillation line method.

Example 1

Consider the separation of a saturated liquid feed mixture of carbon tetrachloride, chloroform, acetone, and benzene at atmospheric pressure. The liquid phase was modeled by the UNIQUAC equation of Prausnitz et al.[7] while the vapor phase was assumed to be ideal. The separation is considered feasible if the chloroform composition of the distillate stream $y_D(C) \geq 0.99$. The specifications for this problem (problem 8) can be found in Table 2, was studied by Amale and Lucia[4], and has both a pinched and a nonpinched minimum energy design. Initial values for all distillation line variables [N_s, N_r, r, $y_D^{(initial)}$] can be found in Table 3.

Figure 3 shows the direct substitution iterative refinement for a specified boil-up ratio of $s = 4.585$; the corresponding initial distillate composition and reflux ratio are $y_D^{(initial)} = (0.005, 0.990, 0.003, 0.002)$ and $r = 7.5302$, respectively. Note that the first iteration yields an infeasible design and creates all of the same difficulties described in the Motivating Example section. That is, going no further the design engineer will be faced with choice that either requires him/her to increase boil-up or adjust product compositions. However, using the iterative refinement process, the distillate composition and reflux ratio are effectively and automatically adjusted and the calculations converge in eight iterations to a feasible design with 54 stripping stages, 24 rectifying stages, and a final distillate composition of $y_D = (0.00827, 0.991521, 2.0752 \times 10^{-4}, 2.3130 \times 10^{-7})$, which is slightly better than the specified composition of chloroform in the distillate. The final calculated reflux ratio was $r = 7.5710$ and only slightly different than the initial reflux ratio (see Tables 3 and 4 for comparisons). Again, this points to the fact that it is the adjustment of the distillate composition that has a more significant impact on feasibility. The computer time required for iterative refinement for this example was, in our opinion, not very demanding (0.36 s on a Pentium IV personal computer).

Example 2

The purpose of this second example, problem 12 in Table 2, is twofold. First it shows that iterative refinement can require a number of direct substitutions and, in the process, can alternate between feasible and infeasible designs before converging to a feasible design. Second it shows that the use of traditional distillation line methods can cause significant over-design with regard to energy requirements. Therefore, consider the separation of a six-component mixture of light paraffins at 400 psi (27.229 bar), in which both

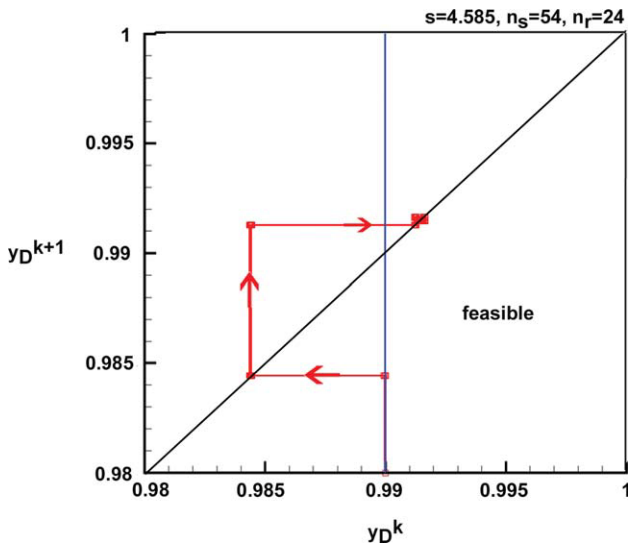

Figure 3. Direct substitution for carbon tetrachloride/chloroform/acetone/benzene distillation.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary. com.]

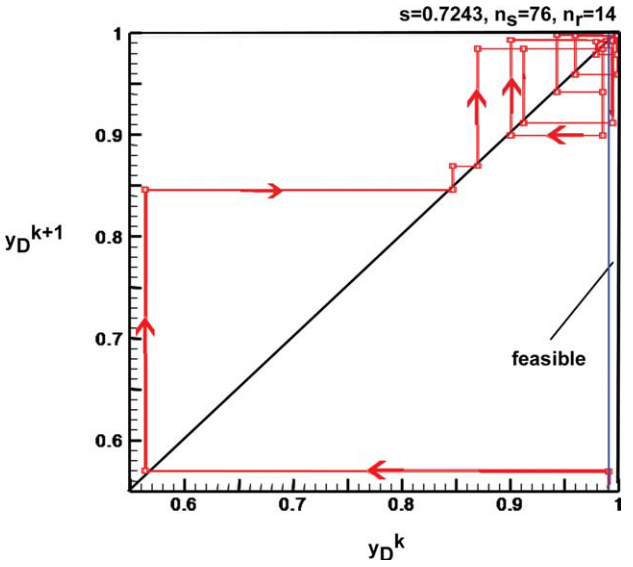

Figure 4. Direct substitution for C_3/n-C_4/i-C_4/n-C_5/i-C_5/n-C_8 distillation.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the liquid and vapor phases are modeled using the K-Wilson model (see Ref. [8]). The feed is a saturated liquid mixture of propane (nC_3), *n*-butane (nC_4), *i*-butane (iC_4), *i*-pentane (iC_5), *n*-pentane (nC_5), and *n*-octane (nC_8). Problem specifications and initial values for the bottom up distillation line computations can be found in Tables 2 and 3.

This example was studied by Lucia et al.[2] who report a minimum energy design with a boil-up ratio of $s_{min} = 3.1032$ for a stripping pinched column for the desired separation. The calculated distillate product for this direct split reported by Lucia et al. was computed using the feasibility specification $\| y_D^{(spec)} - y_D^{(calc)} \| \leq 0.01$ for the distillate product. The actual calculated value of y_D was $y_D = (0.98444, 0.004875, 0.010266, 0.0003078, 0.0001108, 3.5 \times 10^{-7})$. However, Table 3 shows that using iterative refinement a much better solution can be found in 64 direct substitution iterations. Note that the design reported in Table 3 has 76 stripping stages, 14 rectifying stages and operates with a boil-up ratio of $s = 0.7243$, which is roughly 75% lower than the boil-up ratio of $s_{min} = 3.1032$ reported in Lucia et al. Moreover, the distillate product is purer in *n*-propane (0.992948 when compared with 0.98444).

Figure 4 shows the direct substitution iterations for $y_D(nC_3)$ for this example, which alternate between feasible and infeasible design for many iterations (45) before converging to a feasible design. Again, comparisons of the initial and final distillate composition and reflux ratio shown in Tables 3 and 4 clearly show that it is the distillate composition that more significantly affects feasibility. The reflux ratio changes very little in this example, from an initial value of $r = 3.0489$ to a final value of $r = 3.0543$.

Robustness

Clearly Example 2 illustrates the robustness of the iterative refinement procedure. Note that the first iterate has a composition of $y_D(nC_3) = 0.5765$, which is considerably different than the desired composition of $y_D(nC_3) \geq 0.99$. However, to further illustrate that the proposed procedure is robust we use the motivating example and significantly change the initial estimate of the distillate composition. Here we use an initial distillate composition of $y_D^{(initial)} = (0.60, 0.20, 0.13, 0.07)$ instead of the value $y_D^{(initial)} = (0.99, 0.0097, 0.00026, 0.00004)$ and simply set $N_s = 11$ and $N_r = 8$. Using this initial value of y_D, the corresponding initial reflux ratio, $r = 1.140309$, is below the minimum reflux ratio. Thus the starting point for this example is very poor with a poor value of $y_D^{(initial)}$ and a reflux ratio below minimum. Nevertheless, our iterative refinement procedure easily handles this poor starting point and converges in 15 iterations and 0.05 s to a feasible design with the final calculated values of $y_D = (0.9914, 0.0086, 1.3335 \times 10^{-6}, 2.856 \times 10^{-10})$ and $r = 1.97265$, which are exactly the same values shown in Table 4.

Determining Minimum Energy Requirements

Direct substitution can also be used to determine minimum energy requirements for a given desired separation by distillation. However, it is important to understand that when searching for a minimum energy design, the tolerance, ε, used to determine the number of stages (e.g., the smallest value of N_s for which $\| x_{j+1} - x_i \| \leq \varepsilon$) should be increased to machine accuracy because minimum energy designs are on the boundary between feasibility and infeasibility. Lying on the boundary between feasibility and infeasibility makes the calculations prone to approximation, rounding, and truncation errors. For illustrative purposes, we use the motivating example and consider several methods for calculating minimum energy. The product composition specifications are given in Tables 2 and 3, problem 10.

BVDP

Recall that for a boil-up ratio, $s = 1.0$ (and corresponding reflux ratio, $r = 1.97218$), the BVDP gave an infeasible design for fixed product compositions of $x_B = (0.001, 0.3309, 0.3340,$ and $0.3341)$ and $y_D = (0.99, 0.097, 0.00026,$ and 0.00004; Figure 1). To use the BVDP of Levy et al.[1] to determine minimum boil-up (or reflux) ratio, we do the following:

(1) Keep the product compositions fixed.
(2) Guess at a value of boil-up ratio, *s*.

Table 5. Iterative Refinement and Aspen Plus Minimum Energy Designs for Motivating Example

	N_r	N_s	s_{min}	r_{min}	x_B	y_D
Iterative refinement	12	300	0.7875	1.341	(0.001, 0.3309, 0.3340, 0.3341)	(0.9917, 0.0083, 8.148×10^{-9}, 1.073×10^{-14})
Aspen plus	12	300	0.79	1.46	(0, 0.33275, 0.3363, 0.3363)	(0.9917, 0.0083, 2.807×10^{-7}, 9.621×10^{-13})

Table 6. Illustration of Determination of Design Infeasibility

Iteration	Pentane Composition in Distillate
0 (initial)	0.99000
1	0.41460
2	0.96618
3	0.52913
4	0.92155
5	0.70741
6	0.98555
7	0.00635
8	0.62024
9	0.85357
10	0.93338

(3) Calculate the corresponding reflux ratio, r, from Eq. 2.

(4) Generate a liquid composition trajectory from x_B to a stripping pinch point composition.

(5) Generate a liquid composition trajectory from y_D to a rectifying pinch point composition.

(6) Check if the composition profiles intersect.

(a) If the trajectories just touch, stop. The current value of $s = s_{min}$ and $r = r_{min}$.

(b) If the trajectories intersect, reduce s and go to step 3.

(c) If the trajectories do not intersect, increase s and go to step 3.

Applying this BVDP algorithm to the motivating example gives a minimum boil-up ratio of $s_{min} = 4.495$ and a corresponding minimum reflux ratio of $r_{min} = 12.3599$, and a column with 300 stripping stages and three rectifying stages. As we show later in this section, the true minimum boil-up for this example is $s_{min} = 0.7875$. Thus the BVDP given in Levy et al.[1] and used by Fidkowski et al.[2] gives a design that uses 5.7 times the minimum energy required. In our opinion, the BVDP design wastes energy due to mass balance errors and the fact that there is no easy way to adjust product compositions.

Iterative Refinement

Straightforward application of direct substitution within an optimization algorithm that minimizes the boil-up ratio gives a minimum boil-up ratio of $s_{min} = 0.7875$, a minimum reflux ratio of $r_{min} = 1.340963$, a distillate composition of $y_D = (0.9917, 0.0083, 8.148 \times 10^{-9}, 1.073 \times 10^{-14})$, and a pinched column with 300 stripping stages and 12 rectifying stages. Moreover, our minimum energy design has been validated with the Aspen Plus simulator, as summarized in Table 5.

At the final stages of the optimization, the number of direct substitution iterations in iterative refinement usually grows. On the last iteration of the optimization calculations for this example, 1848 direct substitution iterations were required to satisfy the condition $\| y_D^{k+1} - y_D^k \| \leq \varepsilon = 10^{-5}$. However, the increase in computational effort associated with iterative refinement must be weighed against other methods that give incorrect and much higher minimum energy estimates. For example, the increase of a few seconds of computer time to generate a design by iterative refinement that reduces the minimum boil-up ratio from $s = 4.495$ by the BVDP to $s = 0.7875$ is, in our opinion, a negligible price to pay for a far superior design.

Determining Infeasibility

Using direct substitution to determine infeasibility is more challenging because direct substitution is a fixed-point method and therefore has the potential to exhibit all of the rich behavior of any fixed-point iteration: convergent, periodic, and aperiodic (or chaotic). However, in practice it is relatively easy to determine infeasibility. When the column specifications are infeasible one of the following will occur:

(1) Reflux or boil-up ratios less than zero.

(2) Repeated failure to meet product specifications.

Case 1

For very poor estimates of boil-up (or reflux) ratio, the calculated reflux (or boil-up) ratio will fall below zero. This is an indication that the overall combined mass and energy balance equations for the process (i.e., Eq. 2) cannot be satisfied. Our program automatically terminates with a clear indication of an infeasible combination of product compositions and energy input (i.e., [x_B, y_D, s (r)]).

Case 2

The more difficult case is one in which the energy input is below the minimum energy required for feasibility but the reflux and boil-up ratios are positive. In some cases, direct substitution will calculate product compositions that will not meet the product specifications and, if permitted, potentially continue indefinitely. We trap this indication of infeasibility by terminating direct substitution calculations if 10 consecutive direct substitution iterations have led to a failure in meeting desired product specifications. This is a reasonable test in our opinion as in all cases where some calculated product compositions are infeasible but iterative refinement eventually converges, the direct substitution iterates lie above and below the desired composition on the 45° line, meaning some iterates are feasible while others are not infeasible. A clear illustration of this convergent behavior can be seen in Figure 2.

To illustrate our procedure for determining infeasibility, consider the motivating example in which the boil-up ratio is set to $s = 0.75$, which is below $s_{min} = 0.7875$. The desired product is y_D(pentane) ≥ 0.99. Table 6 shows the product compositions calculated by the proposed iterative refinement procedure. Note that the distillate composition of pentane varies widely and remains within the composition tetrahedron. When plotted, all direct substitution iterates in Table 6 lie below the point (0.99, 0.99) on the 45° line. Thus, Table 6 shows that iterative refinement fails to find a feasible distillate composition for 10 consecutive direct substitution iterations, and our design program terminates with the correct decision that the design is infeasible. In other cases, direct substitution can converge to an infeasible vertex composition and inspection of the calculated results leads to the decision that the design is infeasible.

Conclusions

An iterative refinement approach was proposed for determining design feasibility with a distillation line framework.

The method of iterative refinement is direct substitution and was applied to the rectifying line equation in bottom up calculations or the stripping line equation in top down calculations. Thus iterative refinement automatically adjusts the composition of all components in the distillate or all components in the bottoms product, respectively. Numerical results for a wide variety of examples clearly show that in many cases iterative refinement finds feasible distillation designs whereas shortcut methods such as the BVDP fail. Additionally, our numerical results show that it is all product compositions, not just trace component product compositions as previously believed that affect the performance of distillation line methods. The proposed procedure is easily implemented on a computer and the time required to find feasible designs or determine that the design is infeasible is reasonable. For all examples studied in this article, convergence to a feasible design was achieved in less than 5 s. However, no rigorous proof of convergence of iterative refinement has been provided. Convergence analysis of iterative refinement is the subject of on-going work.

While it is possible to accelerate the direct substitution using an acceleration technique such as Broyden acceleration, we find this unnecessary. Moreover, there is always a trade-off between speed of convergence and reliability; thus we do not recommend acceleration be used.

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Appendix

Extended Antoine constants

The motivating example uses Raoult's law for the phase model, where the K values are calculated using the simple expression

Table A1. Extended Antoine Constants

Component	c_1	c_2	c_4	c_5	c_6
Pentane	69.020	−5362.5	0.0099221	−9.4897	-3.8363×10^{-5}
Hexane	−350.52	3318.3	−0.20259	68.498	8.8924×10^{-5}
Heptane	−17.613	−4669.8	−0.035093	6.9580	1.4503×10^{-5}
Octane	−13.781	−5835.0	−0.051518	7.3940	2.9243×10^{-5}

Table A2. Critical Properties and Acentric Factors for the K-Wilson correlation

Component	$P_{c,i}$ (Pa)	$T_{c,i}$ (K)	ω_i
Propane	4,249,000	369.8	0.152
n-Butane	3,797,000	425.2	0.193
i-Butane	3,648,000	408.1	0.177
i-Pentane	3,381,000	460.4	0.228
n-Pentane	3,369,000	469.7	0.249
n-Hexane	3,012,000	507.4	0.305
n-Heptane	2,736,000	540.3	0.349
n-Octane	2,486,000	568.8	0.396

Table A3. Binary Interaction Parameters for the UNIQUAC Equation

Component i	Component j	a_{ij} (K)	a_{ji} (K)
Carbon tetrachloride	Chloroform	38.19	−14.74
Carbon tetrachloride	Acetone	246.68	−92.32
Carbon tetrachloride	Benzene	−37.52	43.39
Chloroform	Acetone	93.96	−171.71
Chloroform	Benzene	4.98	−50.53
Formic acid	Acetic acid	−144.58	241.64
Formic acid	Water	1019.29	−508.85
Methanol	Acetic acid	−20.50	−25.69
Methanol	Ethanol	660.19	−292.39
Methanol	Ethyl acetate	−107.54	579.61
Methanol	Water	−50.82	148.27
Acetic acid	Ethanol	244.67	−210.53
Acetic acid	Ethyl acetate	−214.39	426.54
Acetic acid	Water	−173.64	196.41
Acetic acid	Acrylic acid	−119.22	166.65
Ethanol	Ethyl acetate	−167.61	571.73
Ethanol	Water	−64.56	380.68
Acetone	Benzene	−108.79	174.00
Ethyl acetate	Water	569.86	80.91
Water	Acrylic acid	−170.98	292.67

Table A4. Constant Relative Volatilities

Methanol	3.25
Ethanol	1.90
Propanol	1.00

$$K_i = f_i^0/p$$

where the liquid fugacity is defined by $\ln f_i^0 = c_{i,1} + c_{i,2}/(T + c_{i,3}) + c_{i,4}T + c_{i,5}\ln(T) + c_{i,6}T^2$. Values of the extended Antoine constants are given in Table A1. Note that $c_{i3} = 0$ for all components.

K-Wilson parameters

Critical properties and acentric factors for the K-Wilson method are shown in Table A2.

UNIQUAC parameters

The temperature-dependent parameters, τ_{ij}, in the UNIQUAC equation of Prausnitz et al.[7] are expressed in the form

$$t_{ij} = \exp(-a_{ij}/T)$$

where the a_{ij}s are the binary interaction parameters. The values of the UNIQUAC binary interaction parameters used in this work are shown in Table A3.

Constant relative volatilities

Constant relative volatilities are shown in Table A4.

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