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Solvent Screening Based on Energy Requirements Using UNIFAC

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Abstract

A computational method is suggested for the selection of the best solvent for the extraction of aromatics from hydrocarbons using the UNIFAC method. The method is applied for the separation of benzene from hexane using 21 solvents. The application of such a method requires knowledge of the functional groups present in the feed and the interaction parameters between these groups and the solvents.

INTRODUCTION

Aromatics are the backbone of the petrochemical industries and becoming increasingly important. They are derived mainly from reformed naphtha cuts. These cuts also contain nonaromatic hydrocarbons which have the same boiling point range as the aromatics, so separation by distillation is difficult. Liquid-liquid extraction has been widely used commercially. The success of a liquid-liquid extraction process is strongly dependent on the selection of the most appropriate solvent. Selection of such a solvent will be a compromise between its selectivity, capacity, system physical properties, and the complexity of the downstream process for solvent recovery.

A literature survey shows that a variety of properties has been used for solvent selection. The criteria for solvent choice can be classified into three main groups (*1*):

A. Criteria relating to separability where solubility, density, interfacial tension, chemical reactivity, stability, and viscosity are considered.
B. Criteria based on performance, which is the ability of a proposed solvent to extract the solute from the feed solution, where selectivity, capacity, and distribution coefficient are considered.
C. Criteria affecting acceptability of the entire system, which is related to the cost of the operation. Corrosiveness, flammability, toxicity, and recoverability of solvent are also considered here.

Rawat et al. (*2*) identified the basic considerations in the solvent selection into chemical and physical properties. On a theoretical basis it was shown that solvents with high concentrations of nonhydrogen bonded polar groups, such as oxygen in ketones and sulfones, nitrogen in nitriles, and alkylated or cyclic amides or amines, possess high selectivity. The cyclic structure of five- or six-membered rings also appears to impart a favorable selectivity factor.

Hampe (*3*) discussed the selection of solvents in liquid–liquid extraction based on physicochemical aspects. It was shown that high selectivity and capacity are important but do not represent the only considerations in the selection of suitable solvents. A list of physical properties of solvents used in liquid–liquid extraction was discussed by Hampe (*3*).

Yorulmaz and Karpuzcu (*4*) studied the recovery of aromatics from catalytically reformed naphthas using diethylene glycol, which was compared with sulfolane both in terms of yield and selectivity. Experiments were performed for the two solvents at different temperatures, solvent-to-feed ratios, feed compositions, and water addition on solvent capacity and selectivity. Solvent capacity was found to increase with increasing temperature, solvent-to-feed ratio, and decreasing dilution, whereas selectivity increases with lowering temperature and feed concentration. It was concluded in this study that sulfolane is more advantageous in view of temperature, solvent-to-feed ratios, and solvent recovery.

Medina et al. (*5*) used activity coefficients at infinite dilution as a useful tool for solvent selection in extractive distillation processes. The merits of group contribution models such as UNIFAC and ASOG were assessed by comparing experimental and predicted values of activity coefficients and selectivities. Solvents such as phenol, dimethylformamide, *N*-methylpyrrolidone, aniline, furfural, and ethylene glycol were used.

Ratkorics and Dallos (*6*) used UNIFAC as a method for solvent selection. Capacity and selectivity were calculated by using activity coefficients by UNIFAC. Ease of solvent recovery was shown qualitatively by the prediction of vapor-liquid equilibria using UNIFAC.

Up to this point, the main aspects considered in solvent screening are capacity, selectivity, and solvent recovery. All methods of calculation depend either on liquid-liquid equilibria in the extraction process or vapor-liquid equilibria in the distillation process. No attempts were made to calculate energy requirements in both the extraction and solvent recovery stages although energy calculations were contained in principle phase equilibria calculations where capacity and selectivity of the solvent were considered. Energy requirements indicate the acceptability of the entire process in terms of its cost.

In this work the entire separation process, consisting of extraction followed by solvent recovery by distillation, will be studied. The UNIFAC model will be used to estimate liquid-liquid equilibria in extraction and vapor-liquid equilibria in distillation. Finally, by using the calculated compositions and activity coefficients, the total energy required for extraction and distillation will be calculated per unit mass of product. This will be taken as the only criterion for solvent selection.

METHOD OF CALCULATION

A general flow diagram of a typical extraction followed by solvent recovery is shown in Fig. 1. A feed of 50% solvent plus 25% aromatics and 25% nonaromatics (benzene-hexane-solvent system) is introduced to a single extraction stage. After extraction, each phase, extract and raffinate, goes to the distillation column for extractive distillation and separates hexane from benzene and solvent (Dist 1 and Dist 3). Then solvent recovery takes place in Dist 2 and Dist 4, with benzene of 98% quality as the product in the upper stream. A detailed discussion of the calculations in each stage is given below.

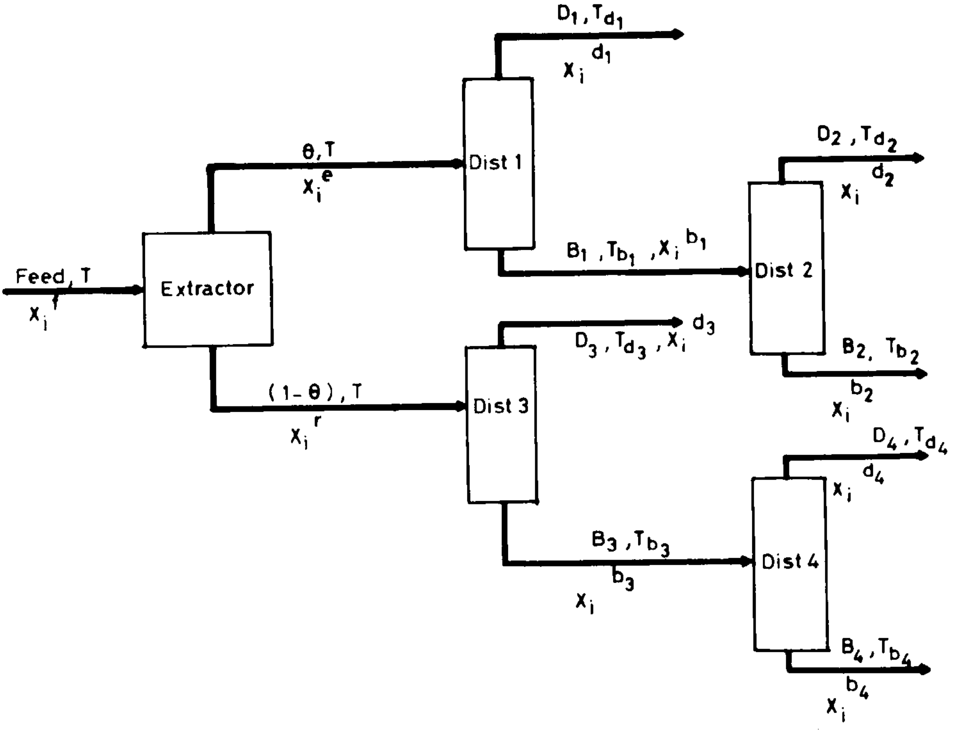

FIG. 1. Schematic diagram of extraction followed by solvent recovery.

(A) Extraction (*7*)

For computation of the liquid–liquid equilibrium phase compositions, Eq. (1) along with the material balance Eqs. (2)–(4), shown below, are simultaneously solved for a particular feed composition by using an iterative procedure based on the Newton-Raphson search technique, as described in Fig. 2.

$$(\gamma_i X_i)^e = (\gamma_i X_i)^r \tag{1}$$

$$X_i^f = \theta X_i^e + (1 - \theta)X_i^r \tag{2}$$

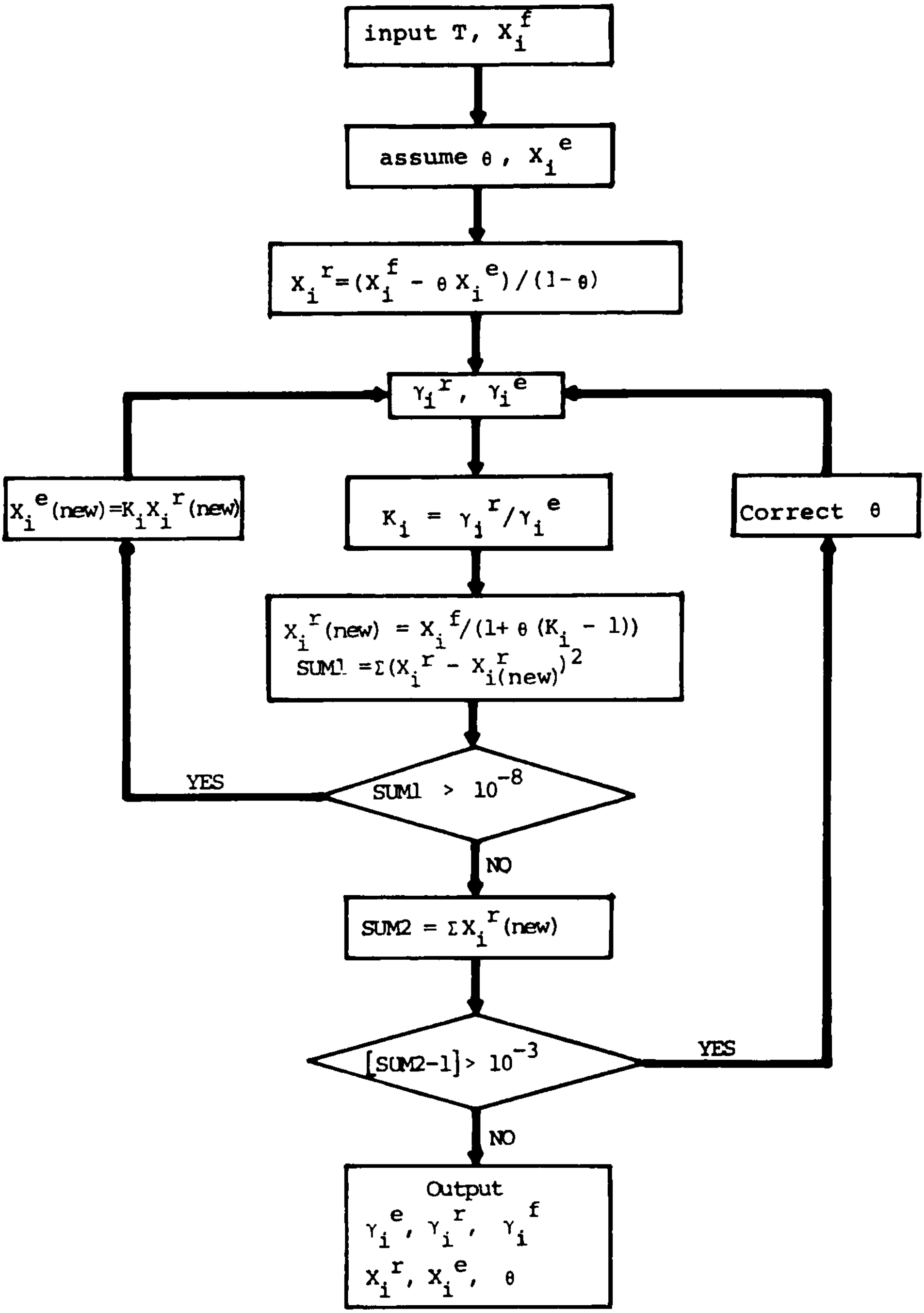

FIG. 2. Algorithm for computation of liquid–liquid equilibrium compositions.

For the extract phase:

$$\sum_{i}^{N} X_i^e = 1.0 \tag{3}$$

and for the raffinate phase:

$$\sum_{i}^{N} X_i^r = 1.0 \tag{4}$$

This method essentially consists of starting with an initial estimate for θ and X_i^e and improving this assumption by successive iterations until Eq. (1) is satisfied. Assuming an initial set of values for X_i^e and θ, estimated values of X_i^r are calculated by Eq. (2). The X_i^e and X_i^r values are next calculated using the compositions just obtained from the UNIFAC model where liquid–liquid equilibrium interaction parameters are used (*8*). New values of X_i^r and X_i^e are then calculated from Eqs. (5) and (6):

$$X_i^r(\text{new}) = \frac{X_i^f}{1 + (K_i - 1)} \tag{5}$$

$$X_i^e(\text{new}) = K_i X_i^r(\text{new}) \tag{6}$$

where

$$\begin{aligned} K_i &= X_i^e / X_i^r \\ &= \gamma_i^r / \gamma_i^e \end{aligned} \tag{7}$$

These values of X_i^r, X_i^e, and θ are improved upon in successive iterations until the following convergence criteria for X_i^r and K_i are satisfied:

$$\sum (X_i^r - X_i^r(\text{new}))^2 < 10^{-8} \tag{8}$$

and

$$\left| \sum X_i^r(\text{new}) - 1.0 \right| < 10^{-3} \tag{9}$$

The outputs of this algorithm are X_i^r, X_i^e, and activity coefficients with the corrected θ value.

Solvent capacity and solvent selectivity can be calculated by using X_i^r and X_i^e as follows:

$$\text{Capacity} = X_2^e/X_2^r \tag{10}$$

$$\text{Selectivity} = \frac{X_2^e/X_2^r}{X_1^e/X_1^r} = \frac{(X_2/X_1)^e}{(X_2/X_1)^r} \tag{11}$$

For the separation of the hexane/benzene system, X_2 is the mole fraction of benzene which is the target component to be separated, and X_1 is the mole fraction of hexane.

Solvent capacity is considered as a measure for the tendency of the solute to concentrate in the solvent. The solvent selectivity, on the other hand, measures the ability of the solvent to extract the solute in preference to the feed solvent. As benzene comes out with solvent in the extract phase, then capacity and selectivity can be described as shown in Eqs. (10) and (11). Thus solvent selectivity measures the purity of product while solvent capacity quantifies the yield of the extraction process.

(B) Distillation

The distillation program used here is a modified version of the UNIDIST program developed by Anderson (*9*). The column equations are solved by Newton-Raphson iteration by applying analytical derivatives of the equilibrium ratio with respect to liquid molar flows of each component and temperature.

The UNIDIST program uses the UNIFAC group contribution method for describing liquid phase nonidealities; the vapor phase is assumed to be ideal. The output results of the UNIDIST program are given for each stage for temperature, liquid flow rate, vapor flow rate of each component, and actual number of stages. Top and bottom products plus feed temperature are used to calculate the energy requirement, as shown later. The number of stages in the distillation columns will be a criterion for the best solvent choice.

The UNIDIST program also checks if the system has an azeotrope. It makes calculations to get products before or after the azeotrope, depending on feed composition and temperature. The only required parameters needed to execute UNIDIST are feed composition and Antoine constants, which are shown in Table 1.

TABLE 1
Antoine Constants[a] (*15*)

Component	A	B	C
Hexane	3.9805	1162.4	223.3
Benzene	4.0248	1211.03	220.79
Diethylene glycol	4.509	1790.38	150.65
Nitromethane	4.50288	1504.30	232.76
H_2O	5.06836	1657.46	227.02
Dimethylformamide	6.91386	3497.99	292.67
Dimethylsulfoxide	5.36	2089.88	203.94
Furfural	5.08638	2023.20	235.58
Sulfolane	5.1938	2441.663	185.11
NMP	6.35709	2805.69	262.72
Acetonitrile	4.44928	1477.44	250.14
Methylformamide	5.2753	2296.55	217.44
t-Methylene sulfone	1.53348	1298.86	252.58
Monoethylene glycol	5.9065	2615.4	244.9
Phenol	4.2524	1515.8	174.56
Aniline	4.3596	1674.99	200.0
Methyl ethyl ketone	4.3265	1367.96	236.5
Acetone	4.349	1276.79	237.22
Pyridine	4.106	1343.9	212.0
Propionitrile	4.048	1276.97	218.0
Nitrobenzene	4.2717	1762.72	202.0
Methanol	5.19	1574.71	238.85
Ethanol	5.33	1651.75	231.47

[a] Based on Antoine equation $\log_{10} P = A - B/(T + C)$, where P is in atm and T is in °C.

(C) Energy Computations

Consider the extraction stage shown in Fig. 1. The minimum rate of work in terms of compositions and activity coefficients at pressure near ambient is shown by (*10*)

$$-W_{\min} = RT\{\theta \sum X_i^e \ln X_i^e + (1-\theta)\sum X_i^r \ln X_i^r - \sum X_i^f \ln X_i^f\}$$
$$+ RT\{\theta \sum X_i^e \ln \gamma_i^e + (1-\theta)\sum X_i^r \ln \gamma_i^r - \sum X_i^f \ln \gamma_i^f\} \qquad (12)$$

where X_i^e, X_i^r, and the activity coefficients are calculated by using the algorithm shown in Fig. 2, as discussed earlier.

For the distillation column, n, the minimum rate of work will be calculated as follows (*11*):

$$-W_{\min} = RT_{\mathrm{ave}}\{D_n \sum X_i^{d_n} \ln X_i^{d_n} + B_n \sum X_i^{b_n} \ln X_i^{b_n} - \theta \sum X_i^{e} \ln X_i^{e}\} \qquad (13)$$

where T_{ave} is the average column temperature. $X_i^{d_n}$, $X_i^{b_n}$, D_n, B_n, and the temperatures are calculated by using the UNIDIST program. These calculations are repeated for each column.

The summation of these work values gives us the total energy needed in the extraction and solvent recovery stages, which gives us the best solvent, i.e., the solvent requiring the minimum total energy expressed in kJ/mol product (0.98 benzene).

DISCUSSION OF RESULTS

Solvent selection is discussed here on the assumption that these solvents have been screened for their physical properties. The only three factors which will affect the final screening are capacity, selectivity, and ease of solvent recovery expressed as energy requirements.

1. Selection Based on Selectivity and Capacity

The capacity of a solvent is defined as the aromatics concentration ratio of the extract phase to the raffinate phase. Selectivity is defined by the ratio of the distribution factor of the aromatics to the distribution factor of the nonaromatics.

For a comparison of solvents, the data of selectivity and capacity are plotted on a diagram where selectivity is the ordinate and capacity is the abscissa. Such a diagram is presented in Fig. 3 for the system hexane–benzene–solvent. UNIFAC was used to compute the phase compositions required for capacity and selectivity calculations.

It is obvious that some solvents have high capacity but low selectivity and vice versa. An ideal solvent for extraction should have both high capacity and high selectivity. For the evaluation of the best solvent, it is important to know where the economic balance between selectivity and capacity lies. Figure 3 suggests that dimethylsulfoxide could be the best solvent for the hexane–benzene system, but according to the above discussion, more information besides selectivity and capacity must be obtained for the final choice.

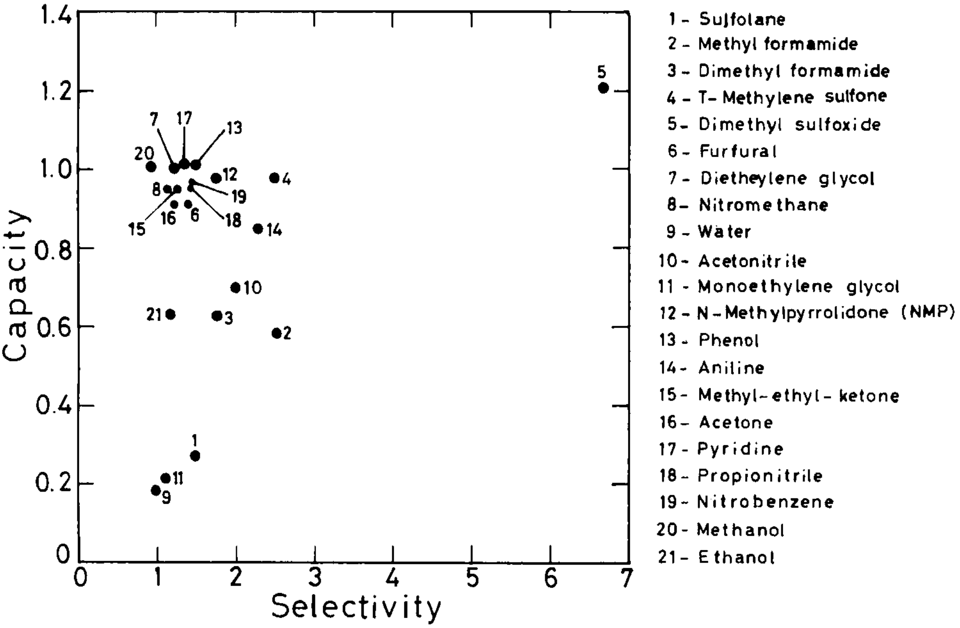

FIG. 3. Capacity vs selectivity of solvents used.

2. Selection Based on Energy Requirements

Energy requirements were calculated for the extraction and distillation stages. All data needed for such calculations are derived from the UNIFAC model, which means that our choice will be completely theoretical and no experiments are required. Both the extract phase and the raffinate phase require two distillation columns to obtain a product of 98% benzene. Finally, the total energy required for the entire system, calculated per mole of benzene using several solvents, is shown in Table 2 along with the capacity, selectivity, and total number of trays in the distillation stages. As expected, when the energy requirement increases in the downstream part of the process, the number of distillation trays also increases. The number of trays calculated for different solvents ranged from 150 to 175, which is a rather limited range. For that reason, solvents are ranked here only according to the total energy required. According to the criterion of total energy required, the best nine solvents in Table 2 are sulfolane, NMP, furfural, diethylene glycol, methylformamide, *t*-methylene sulfone, dimethylformamide, phenol, and DMSO. This choice contradicts the choice based on the criteria of solvent capacity and solvent selectivity. It is obvious that the calculation of total energy per mole of product benzene takes into consideration capacity and selectivity.

The energy required in the extraction step is much less than that required in the distillation step. This result is, of course, expected, because higher temperatures are needed in the distillation step to boil off the aromatics while the extraction step is usually performed at ambient temperature.

If the final order of choice is inspected in light of the actual industrial utilization of these solvents, we find that sulfolane (*4*) and a mixed

TABLE 2
Solvent Ranking

Solvent	Capacity	Selectivity	N_{Total}	Total energy, kJ/mol of product (98% benzene)
Sulfolane	.2599	1.496	151	5.80
NMP	.985	1.736	155	6.04
Furfural	.975	1.416	160	6.30
Diethylene glycol	1.012	1.246	161	6.37
Methylformamide	.598	2.527	160	6.40
t-Methylene sulfone	1.164	2.509	155	6.47
Dimethylformamide	.768	1.758	165	6.73
Phenol	1.017	1.526	156	6.99
DMSO	1.188	6.742	170	7.39
Acetonitrile	.711	1.919	171	8.37
Aniline	.852	2.282	170	8.46
Ethylene glycol	.213	1.063	175	8.62
Methyl ethyl ketone	.954	1.194	171	9.04
Nitrobenzene	.965	1.418	165	9.39
H_2O	.182	1.002	170	9.66
Nitromethane	.94	1.143	175	10.20
Methanol	1.130	.955	165	10.21
Acetone	.910	1.261	175	10.88
Pyridine	1.128	1.323	175	11.05
Propionitrile	.955	1.441	172	11.32
Ethanol	.637	1.176	175	12.08

solvent of NMP and ethylene glycol (*12*) are used commercially in the petrochemical industry for BTX extraction. A mixed solvent of dimethylformamide and *t*-methylene sulfone has been used for aromatics extraction from paraffins (*13*). Dimethylformamide has been used in the extraction of hydrocarbons with a 10–20 carbon number (*14*). These industrial cases are supported by the conclusion achieved in this work.

CONCLUSION

When solvents are screened using physicochemical properties, they should be further examined based on the total energy required for extraction and distillation. Solvent capacity and selectivity are automatically included in such screenings because they are required in energy calculations. This method should be applied for a hydrocarbon feed under investigation for a specific solvent choice. The general rules for solvent choice can be misleading, and the procedure described in this work will avoid such a problem. The screening process described in this work could be utilized as a guide for future industrial solvent selection.

NOMENCLATURE

K_i	phase equilibrium constant
P	total pressure
T	temperature (°K)
W_{min}	minimum work (kJ/mol feed)
W_{dist}	minimum work in distillation stage (kJ/mol feed)
W_{Extr}	minimum work in extraction stage (kJ/mol feed)
X_i	mole fraction of component *i*
X_i^e	mole fraction of component *i* in extract phase
X_i^r	mole fraction of component *i* in raffinate phase
X_i^f	mole fraction of component *i* in the feed
γ_i	activity coefficient of component *i*
θ	extract-to-feed ratio
n	number of distillation columns
D_n	top product of distillation column *n*
B_n	bottom product of distillation column *n*
$X_i^{d_n}$	mole fraction of component *i* in top product of column *n*
$X_i^{b_n}$	mole fraction of component *i* in bottom product of column *n*
T_{d_n}	top temperature of column *n*

T_{b_n} bottom temperature of column n
N total number of trays

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