A CORRELATION FOR ESTIMATING THE VAPOUR PHASE FRACTION OF A MULTICOMPONENT MIXTURE TO PERFORM FLASH EQUILIBRIUM CALCULATIONS

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ABSTRACT

An approximate analytical solution of the flash equilibrium equations is presented. A correlation to provide an accurate initial guess of vapor phase fraction (V/F) for starting the numerical solution of flash equilibrium calculations is then derived. In some cases the predicted results obtained by using the presented correlation are accurate enough such that no further numerical improvements are necessary. Generally, the predicted initial estimate of V/F by using the proposed correlation is in the vicinity of its exact value. Applications of the proposed correlation for flash equilibrium calculations of different hydrocarbon mixtures are also presented. The proposed correlation is a reliable tool for many practical situations when multiphase equilibrium calculations are needed.

<u>Keywords</u>: flash calculation, correlation, multicomponent mixture, equilibrium.

INTRODUCTION

The equilibrium flash of multi-component mixtures is very widely utilized in petroleum refineries, petrochemical complexes and natural gas processing plants. Flash calculations constitute the predictive method used in establishing the phase fractions and compositions of the two contiguous phases, vapor and liquid, in a state of equilibrium [1]. For simulation and design of multi-stage fractionation units and two phase flow pipelines it is necessary to carry out several trial-and-error flash calculations in a typical run. Unfortunately the exact analytical solution of flash equilibrium equation is not yet available such that the numerical methods are used. Since these calculations are usually based on an iterative procedure, an accurate initial guess is required to ensure the convergence to the final solu-

tion [1,2]. Having such an accurate initial estimation is especially important when the bubble point or dew point regions of a multicomponent mixture are approached. In this work an approximate analytical solution of flash equilibrium formulation is obtained and a correlation for predicting an accurate initial guess to start the numerical calculations is presented.

THEORETICAL

Schematic diagram of an equilibrium flash unit is shown in Fig. 1. The feed stream is denoted as F consisting of N components. The vapor and liquid streams leaving the flash unit are V and L and the mole fractions of ith species in the vapor and liquid streams are y_i and x_i, respectively. Since the flash unit is assumed to be an equilibrium stage, the temperature (T)

and pressure (P) of outlet streams are the same as those for the flash unit. According to these nomenclatures, the overall mass balance can be written:

$$F = L + V \tag{1}$$

For each species we can write a material balance over the unit:

$$Fz_i = Lx_i + Vy_i \tag{2}$$

The mole fraction constraints for the individual streams can be written:

$$\sum_{i=1}^{N} z_i = \sum_{i=1}^{N} x_i = \sum_{i=1}^{N} y_i = 1 \tag{3}$$

Since the phases are in equilibrium, we have the following thermodynamic relation

$$y_i = K_i x_i \tag{4}$$

where K_i is the K-value for species i. Writing $R = L/F$ and combining the above equations, we have:

$$\sum_{i=1}^{N} \frac{z_i}{K_i(1-R)+R} = \sum_{i=1}^{N} x_i \tag{5}$$

The left side of Eq. (5) can be written:

$$\sum_{i=1}^{N} \frac{z_i}{K_i(1-R)+R} = \sum_{i=1}^{N} \frac{2z_i/(K_i+1)}{1-(K_i-1)(2R-1)/(K_i+1)} \tag{6}$$

Combination of Eqs (5) and (6) gives:

$$\sum_{i=1}^{N} \frac{z_i}{1-(K_i-1)(2R-1)/(K_i+1)} = \sum_{i=1}^{N} \frac{K_i x_i + x_i}{2} \tag{7}$$

The right side of Eq. (7) can be written:

$$\sum_{i=1}^{N} \frac{K_i x_i + x_i}{2} = \frac{\sum_{i=1}^{N} y_i + \sum_{i=1}^{N} x_i}{2} = 1 \tag{8}$$

Therefore the Eqs. (7) and (8) are combined to give:

$$\sum_{i=1}^{N} \frac{z_i}{1-(K_i-1)(2R-1)/(K_i+1)} = 1 \tag{9}$$

Here, we define the following change of variables:

$$G_i = \frac{K_i-1}{K_i+1} \tag{10}$$

$$H = 2R - 1 \tag{11}$$

Since $|G_i| < 1$ and $|H| < 1$, we always have $|G_i H| < 1$. Therefore it is possible to write each term of the left side of Eq. (9) as a convergent series in terms of $G_i H$ as follows:

$$\sum_{i=1}^{N} \frac{z_i}{1-G_i H} = \sum_{i=1}^{N} z_i + \sum_{i=1}^{N} z_i G_i H +$$

$$+ \sum_{i=1}^{N} z_i (G_i H)^2 + \sum_{i=1}^{N} z_i (G_i H)^3 + \ldots\ldots\ldots \tag{12}$$

We can neglect the fourth and higher terms of the above convergent series. Combination of Eqs (3) and (12) yields:

$$\sum_{i=1}^{N} z_i G_i H + \sum_{i=1}^{N} z_i (G_i H)^2 = 0 \tag{13}$$

Employing Eqs. (1), (10), (11) and (13), we have:

$$\frac{V}{F} = 0.5(1 + \frac{\sum_{i=1}^{N} z_i[(K_i-1)/(K_i+1)]}{\sum_{i=1}^{N} z_i[(K_i-1)/(K_i+1)]^2}) \tag{14}$$

At a fixed T and P, a good initial estimation of V/F for using in a numerical procedure can by obtained from Eq. (14). In the usual flash calculation routines the computation starts with the initial value of $V/F = 0.5$. However Eq. (14) gives a much better initial estimation.

RESULTS AND DISCUSSION

Eq. (14) gives a good initial estimation very close to the final converged solution of the problem. In this section we compare the initial estimate given by Eq. (14) with the final solution obtained by using the Newton-Raphson iterative method [1-4].

The combination of Eqs. (1) - (4) in terms of vapor phase fraction leads to the Rachford-Rice objective function [1]:
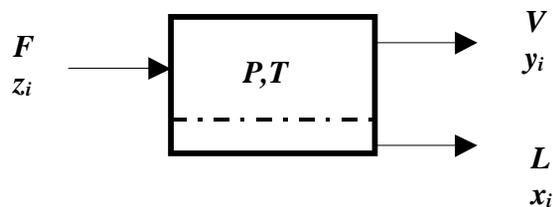
Fig. 1. Schematic diagram of an equilibrium flash unit.

Table 1. Results of flash calculation at T = 4.4°C and P = 2.4 bar.

Comp.	z_i	K_i	L_i	x_i	V_i	y_i
C_1	0.33960	61.000	0.0059	0.0114	0.3337	0.6966
C_2	0.06460	9.0000	0.0070	0.0134	0.0576	0.1203
C_3	0.09870	2.2000	0.0327	0.0627	0.0660	0.1379
iC_4	0.01736	0.7700	0.0102	0.0195	0.0072	0.0150
nC_4	0.02604	0.5200	0.0176	0.0338	0.0084	0.0176
iC_5	0.01530	0.1800	0.0131	0.0252	0.0022	0.0045
nC_5	0.01670	0.1300	0.0149	0.0286	0.0018	0.0037
nC_6	0.03000	0.0350	0.0291	0.0558	0.0009	0.0020
C_7^+	0.39170	0.0032	0.3906	0.7496	0.0011	0.0024

Initial estimation of (V/F) from Eq.14 = 0.479
Final converged value of (V/F) by Newton-Raphson procedure = 0.479

Table 2. Results of flash calculation at T = 100°C and P = 40 bar.

Comp.	z_i	K_i	L_i	x_i	V_i	y_i
CO_2	0.0125	4.050	0.0012	0.0040	0.0113	0.0163
H_2S	0.0050	1.740	0.0010	0.0033	0.0040	0.0058
C_1	0.1836	5.950	0.0128	0.0415	0.1708	0.2468
C_2	0.3478	2.160	0.0594	0.1929	0.2884	0.4167
C_3	0.1021	1.030	0.0308	0.1000	0.0713	0.1030
iC_4	0.0738	0.600	0.0314	0.1021	0.0424	0.0612
nC_4	0.1184	0.490	0.0563	0.1830	0.0621	0.0897
iC_5	0.0363	0.280	0.0223	0.0724	0.014	0.0203
nC_5	0.0501	0.240	0.0325	0.1057	0.0176	0.0254
nC_6	0.0390	0.120	0.0307	0.0998	0.0083	0.0120
C_7^+	0.0314	0.031	0.0294	0.0953	0.0020	0.0030

Initial estimation of (V/F) from Eq.14 = 0.700
Final converged value of (V/F) by Newton-Raphson procedure = 0.693

$$W(V/F) = \sum_{i=1}^{N} \frac{z_i(K_i - 1)}{(V/F)(K_i - 1) + 1} = 0 \qquad (15)$$

According to Newton-Raphson algorithm, we have:

$$(V/F)_{n+1} = (V/F)_n - \frac{W(V/F)_n}{W'(V/F)_n} \qquad (16)$$

where:

$$W'(V/F) = -\sum_{i=1}^{N} \frac{z_i(K_i - 1)^2}{[(V/F)(K_i - 1) + 1]^2} \qquad (17)$$

The calculation starts with an initial estimate of (V/F) in Eq. (16) and iterations continue until the condition of $W(V/F)_n = 0$ is satisfied and a converged solution is obtained. During the calculations, the constraint of $0 \le (V/F)_{n+1} \le 1$ should be always satisfied [2].

In Table 1 the final results of flash calculation for a sweet gas mixture entering a flash unit with the flowing rate of 1 kg mol /s at 4.4°C and 2.4 bar are given. As indicated at the bottom this Table, the estimated (V/F) from Eq. (14) is exactly equal to the final converged solution obtained by Newton-Raphson iterative method.

The final results of flash calculation for a sour gas mixture entering a flash drum with the flow rate of 1 kg mol s⁻¹ at 100°C and 40 bar are displayed in Table 2. The estimated (V/F) from Eq. (14) is 0.700, while the exact numerical solution is 0.693 which is very close to the estimated value. As we approach to the bubble point or dew point regions the flash calculations are tedious and time consuming. For these cases Eq. (14) can also be used to estimate how close we are near to the boundaries of a phase envelope. In these extreme cases, the initial estimates of Eq. (14) can strongly speed up the convergence to a right solution.

CONCLUSIONS

The presented correlation, Eq. (14), is an efficient and reliable tool for using as an initial guess for starting the numerical solution of equilibrium flash calculations. In some cases the predicted results by using this correlation are accurate enough such that no fur-

ther numerical refinement is necessary. The predicted initial estimated *V/F* value by using Eq. (14) is always in the vicinity of its exact value. Having such an accurate initial estimation is very important, especially when the bubble point or dew point regions of a multicomponent mixture are encountered.

NOMENCLATURE

F - feed flow rate to flash equilibrium unit, kg mol s⁻¹
L - liquid flow rate from flash equilibrium unit, kg mol s⁻¹
V - vapor flow rate from flash equilibrium unit, kg mol s⁻¹
K_i K-value of a component
N - number of chemical components
P - pressure, bar
T - temperature, °C
R - liquid fraction of a mixture
G_i - Function defined in Eq. (10)
H - Function defined in Eq. (11)
W - function defined in Eq. (15)
W' - derivative function defined in Eq. (17)
z_i - mole fraction of component in the feed
x_i - mole fraction of a component in the liquid phase
y_i - mole fraction of a component in the vapor phase
i - index of a chemical species
n - iteration number.

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