Experimental K-value Prediction

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Abstract

The Equilibrium ratios (K-values) depend on temperature, pressure and the overall composition of the reservoir fluid. Several correlations are being used and are considered accurate enough. But on close examining these correlations provide accurate results only at lower pressures. This is because at lower pressure the K-values are primarily dependent on pressure and temperature. The compositional dependence which is more complicated to model happens at higher pressures. The compositional dependence is believed to be only a function of convergence pressure. When we consider that predicting convergence pressure in itself is dependent on the correlations, we can fathom the cause of inaccurate prediction of K-values. We believe that there is not enough data available to generate accurate correlations. The inaccuracy of correlations in prediction of the K-values will be shown in this paper by comparison with the experimental data.

Introduction

Phase behavior data is one of the most important tools used to evolve reservoir development strategy. Knowledge of Vapor–Liquid-Equilibrium (VLE) data is essential for understanding the separation processes in the reservoir as well as in the surface equipment. This information helps in selection of equipment for flash separation at the well head, distillation columns and even for design of pipeline and unit operations. The thermodynamic equilibrium between vapor and liquid phases depend on equality of temperature, pressure, and fugacity of each component in both phases.

In most simplistic format this thermodynamic equilibrium between vapor and liquid phase can be represented as;

$$K_i = \frac{y_i}{x_i} \qquad (1)$$

Equation (1) forms the foundation of vapor-liquid equilibrium calculations. In this equation; K_i is called the equilibrium ratio or K-value, and y_i and x_i are vapor and liquid mole fraction respectively of component "i" in the system. For volatile components the equilibrium ratio is usually greater than one and for less volatile components it is less that one.

Even though experimental measurement are expensive and time consuming they still are more desirable, because of their accuracy. Several approaches are available for determination of K-values depending on the system under study. One such method (Danesh, 1998) uses Raoult's law; which assumes an ideal gas conditions for vapor phase and ideal solution conditions for the liquid phase.

For an ideal gas;

$$f_i^{\,v} = y_i P \qquad \text{and} \qquad f_i^{\,l} = x_i P^{sat}$$

Hence

$$\frac{y_i}{x_i} = K_i = \frac{P^{sat}}{P} \qquad (2)$$

But the assumptions of ideal gas and ideal solution limit the usage of this method as these assumptions can only be valid at low pressure and temperature conditions. Several K-value charts are also used for estimation of vapor liquid equilibrium. The earliest of these charts was for light hydrocarbons (Natural Gasoline Supply Men's Association, 1941). In these charts K-values are plotted against temperature and are available for a pressure range of 10 to 1000 psia and the temperature range of from 40 to 500 ºF.

Later high pressure experiments showed that if K-values are plotted against pressure the K-values of all components converged toward a common value of unity at some high enough pressure. This "Convergence Pressure" of the system formed the basis for use as a correlation parameter and thus resulted in generalized K-values charts. This paved the way for plotting (Engineering Data Book, 1998) of K-values as a function of pressure and temperature and convergence pressure as parameters. The convergence pressure can be determined by the correlation (Standing, 1981). Natural gas association of America (Equilibrium Ratio data for Computers, 1958) curve fitted these K-value charts with the help of industrial experts and academia.

Equation of State approach to find K-values require computer programming and are most difficult (Prausnitz, 1999). The correlations method is relatively easy and scientists and petroleum engineers have developed many correlations using polynomial and exponential curve fitting techniques. Wilson's correlation (Wilson, 1968) is one such correlation widely in use. It should be mentioned here that these correlations are only applicable for limited pressure and temperature conditions or specific to certain fluid systems.

$$K_i = \frac{P_{ci}}{P} \exp[5.37(1-\varpi_i)(1-\frac{T_{ci}}{T})] \qquad (3)$$

Where;

T_{ci} =   critical temperature, in ºR
P_{ci}, =   critical pressure
ω_i =   acentric factor,
P =   system pressure
T =   system temperature

This correlation is applicable for low pressures.

The PVT and compositional data are usually obtained either experimentally or using correlations. The correlations are routinely used because of their relative ease and being less time consuming but they lack in accuracy. Even best of the models, need some tuning from one sample to another. Since every reservoir fluid have unique composition, physical properties and PVT behavior; experimental analysis to some extent is inevitable.

To predict K-values at reservoir like conditions we need to measure phase behavior properties and phase compositions experimentally at high temperature and pressure. The usual experimental techniques employed for phase behavior analysis can be termed as reliable for phase volume measurements, but for compositional analysis equilibrium of the system is violated and other assumptions are required to arrive at the ultimate composition. Very scarce data is available even to test the accuracy of the correlations. The more and more experimental data is needed to develop better correlations. We will try to highlight this need for more experimental data by showing the ineffectiveness of the correlation to predict the K-values at lower pressures.

Methodology

As mentioned earlier, there is very little data available to even test the correlations. Separator data was used for the K-value calculation. The total composition and composition of the gas phase is available and the liquid phase composition will be calculated using the material balance method. The method was used to predict the compositions and hence the K-values for one, two and three stage separation systems.

The bottom-hole composition, separator GOR, separator vapor phase composition, and stock tank API are the known quantities. To estimate the Liquid phase composition we developed the spread-sheet solution technique where the Molecular weight of the liquid phase, vapor phase fraction, liquid phase fraction and compositions are calculated simultaneously. The material balance is based on moles.

$$z_i = f_v y_i + f_l x_i \qquad (4)$$

Where;

f_v and f_l are vapor and liquid phase fractions respectively and are calculated based on number of moles of liquid and vapor phase present for each STB basis. First of all moles in liquid and vapor phases are calculated based on one STB liquid. While the vapor moles calculation is easy for calculation of liquid phase moles we have to assume a molecular weight.

$$M_l = \frac{5.615 * \gamma_o * 62.4}{MW} \qquad (5)$$

Where:

M_l is moles of liquid /STB

MW is liquid molecular weight, assumed value for first approximation.

γ_o is stock tank oil specific gravity

Vapor and liquid phase fractions f_v and f_l are calculated based on total moles in liquid and vapor.

$$f_v = \frac{M_v}{M_v + M_l} \qquad (6)$$

$$f_l = \frac{M_l}{M_v + M_l} \qquad (7)$$

Using equation (4) the liquid phase compositions are calculated. New liquid molecular weight for the liquid phase is calculated and compared with the assumed molecular weight. If this molecular weight is different then the new moles of liquid are calculated using equation (5) and the new liquid molecular weight. The rest of the process is repeated until the convergence of assumed and calculated molecular weight is achieved.

Results

The liquid phase compositions for single to three stage separators were calculated and based on these calculated values the equilibrium K-values were estimated.

Single Stage Separator

Table-1 gives the composition of the bottom-hole sample and gas phase composition from the separator. The separator conditions are 15 psia and 100 ºF. The separator GOR is 100 SCF/STB. Stock tank API is 29.6.

Components	Bottom-hole Composition	Density	API	M. Wt.	Separator Vapor Phase Composition
Nitrogen	0.33			28.02	1.32
Carbon dioxide	0.86			44.01	4.37
Hydrogen sulfide	0.73			34.08	2.51
Methane	5.62			16.04	27.62
Ethane	4.77			30.07	22.20
Propane	6.79			44.09	24.11
i-Butane	1.55			58.12	3.68
n-Butane	5.33			58.12	9.16
i-Pentane	2.38			72.15	1.98
n-Pentane	3.66			72.15	2.11
Hexanes	3.94			86.17	0.81
Heptanes & heavier	64.04	0.8991	25.9	287.00	0.13

Table-1 Bottom-hole composition and separator vapor phase composition for the single stage separator case.

Table-2 gives the vapor phase composition, calculated liquid phase composition and calculated K-values for the single stage separator case.

Components	y_i	x_i	K_i
Nitrogen	1.32	0.13	10.0565
Carbon dioxide	4.37	0.16	28.1264
Hydrogen sulfide	2.51	0.37	6.7353
Methane	27.62	1.20	22.9494
Ethane	22.20	1.27	17.4674
Propane	24.11	3.31	7.2773
i-Butane	3.68	1.12	3.2787
n-Butane	9.16	4.56	2.0083
i-Pentane	1.98	2.46	0.8048
n-Pentane	2.11	3.97	0.5313
Hexanes	0.81	4.57	0.1773
Heptanes & heavier	0.13	76.87	0.0017

Table-2 Liquid and vapor phase composition and equilibrium K-value for the single stage separator case.

The K-values were calculated for the hydrocarbons from methane to hexane for the separator temperature and pressure conditions using Wilson's correlation. Table-3 compares these K-values obtained experimentally and obtained from the Wilson's correlation. It is worth noting that the Wilson's correlation over predicts k-value at even such a low pressure and temperature. Also more volatile the component greater is the difference between correlation and experimental values. Figure-1 compares these equilibrium K-values graphically for the volatile components and the comparison for less volatile components is shown in Figure-2.

Components	Ki Calculated	Ki Wilson's Correlation
Methane	22.9494	362.4155
Ethane	17.4674	52.2304
Propane	7.2773	12.6685
i-Butane	3.2787	4.8205
n-Butane	2.0083	3.4288
i-Pentane	0.8048	1.3658
n-Pentane	0.5313	1.0481
Hexanes	0.1773	0.3526

Table-3 Comparison of equilibrium K-values calculated from experimental data and Wilson's correlation.
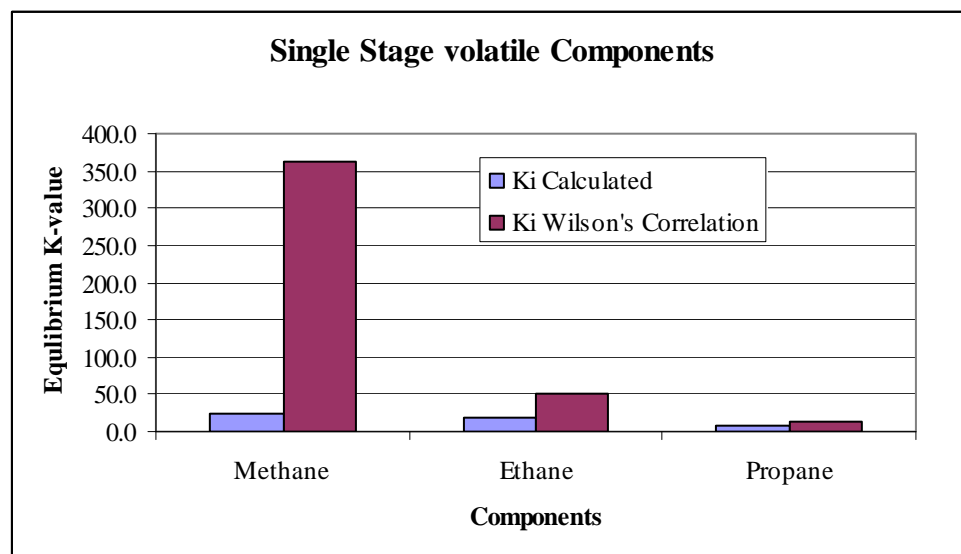

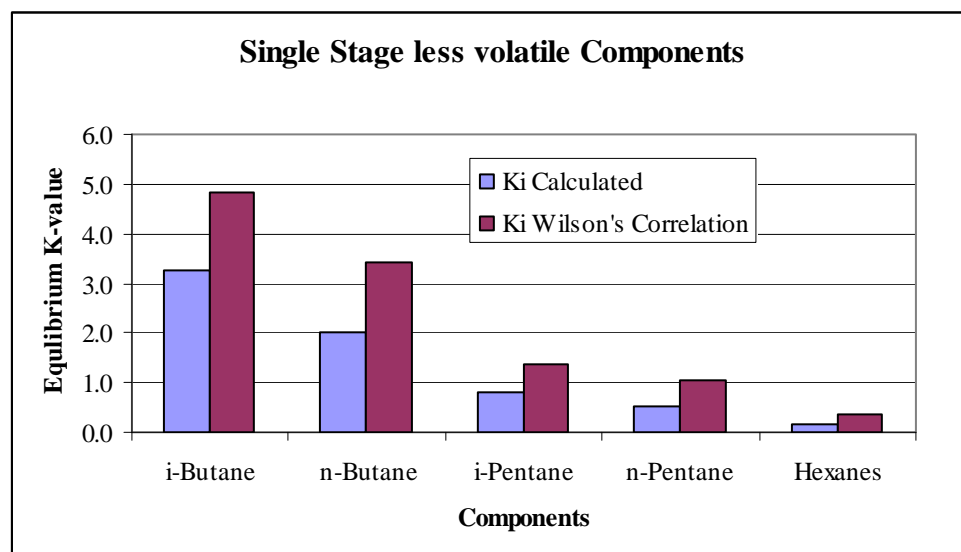**Figure-1** Comparison of equilibrium K-value for volatile components.

Figure-2 Comparison of equilibrium K-value for less volatile components.

Two-Stage Separator

Next the calculation of equilibrium K-values were done for a two-stage separation system. Table-4, give the composition of the bottom-hole sample and gas phase compositions from the two separator stages. Pressures, temperatures and GOR for the two stage separator are listed in Table-5.

Components	Bottom-hole Composition	Density	API	M. Wt.	Separator Vapor Phase Composition Stage 1	Separator Vapor Phase Composition Stage 2
Nitrogen	0.22			28.02	5.22	0.36
Carbon dioxide	0.62			44.01	7.12	5.53
Hydrogen sulfide	0.00			34.08	0.00	0.00
Methane	3.21			16.04	52.98	19.23
Ethane	1.87			30.07	13.68	18.62
Propane	3.85			44.09	11.75	28.26
i-Butane	1.24			58.12	1.97	5.82
n-Butane	3.86			58.12	4.08	12.73
i-Pentane	2.20			72.15	1.07	3.49
n-Pentane	3.50			72.15	1.16	3.61
Hexanes	5.61			86.17	0.75	1.91
Heptanes & heavier	73.82	0.94	18.20	343.00	0.18	0.39

Table-4 Bottom-hole composition and separator vapor phase compositions for the two stage separator case.

	stage1	stage2
P (psia)	60	15
Temp (F)	120	110
GOR SCF/STB	21	20

Table-5 Pressures, temperatures and GOR

For calculation of the stock tank oil composition, the gas composition is combined on GOR weighted basis.

$$y_{ic} = \frac{y_1 * GOR_1 + y_2 * GOR_2}{GOR_1 + GOR_2} \qquad (8)$$

Where; y_{ic} is the combined composition.
The rest of the procedure for calculation of the liquid phase composition of the last stage is same as was for the single stage case. The preceding stage's liquid composition will be calculated by combining the liquid and vapor composition of the subsequent stage based on moles.

$$x_{i1} = \frac{y_{i2} * M_{v2} + x_{i2} * M_{l2}}{M_{v2} + M_{l2}} \qquad (9)$$

Where;

M_{v2} is the number of moles in vapor phase in stage 2 and M_{l2} is the number of moles in liquid phase in stage 2.

The liquid phase composition of the second stage was calculated using equation (4) and applying the same convergence of calculated and assumed liquid molecular weight. The results are tabulated in Table-6.

Components	yi	xi
Nitrogen	2.85	-0.03
Carbon dioxide	6.34	0.07
Hydrogen sulfide	0.00	0.00
Methane	36.52	-0.01
Ethane	16.09	0.50
Propane	19.80	2.31
i-Butane	3.85	0.99
n-Butane	8.30	3.43
i-Pentane	2.25	2.20
n-Pentane	2.36	3.61
Hexanes	1.32	6.03
Heptanes & heavier	0.33	80.92

Table-6 Liquid and combined vapor phase composition for second stage.

We see that the liquid phase composition for nitrogen and methane show negative values. This must have been because of some experimental error either in vapor phase composition measurement or in GOR calculations. Since the error is small we assume that all of these gases have been produced in the gas phases and the composition for them in liquid phase is zero. The corrected and normalized compositions are given in Table-7.

Components	yi	Corrected xi
Nitrogen	2.85	0.00
Carbon dioxide	6.34	0.07
Hydrogen sulfide	0.00	0.00
Methane	36.52	0.00
Ethane	16.09	0.50
Propane	19.80	2.31
i-Butane	3.85	0.99
n-Butane	8.30	3.43
i-Pentane	2.25	2.19
n-Pentane	2.36	3.61
Hexanes	1.32	6.02
Heptanes & heavier	0.33	80.89

Table-7 Corrected liquid composition and combined vapor phase composition for second stage.

The equilibrium K-values were calculated for the second stage from experimental data and with Wilson's correlation. These K-values are compared in Table-8.

Components	Ki Calculated	Ki Correlation
Ethane	37.6023	57.9725
Propane	12.2509	14.4757
i-Butane	5.8940	5.6099
n-Butane	3.7121	4.0243
i-Pentane	1.5906	1.6317
n-Pentane	1.0003	1.2611
Hexanes	0.3171	0.4340

Table-8 Comparison of equilibrium K-values calculated from experimental data and Wilson's correlation second stage.

There is no K-value for methane as we had to assume that all the methane has been removed in the vapor phase. But the comparison is significantly better than the single stage case, as can be seen from Figure-3.
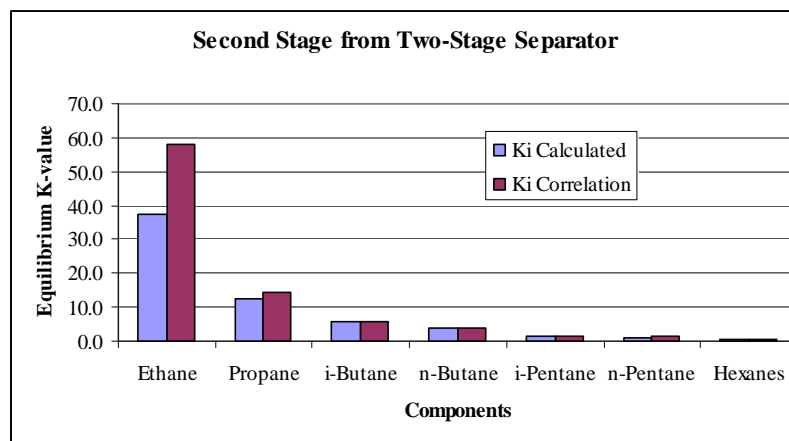

Figure-3 Comparison of equilibrium K-values for second stage of a two-stage separator.

The liquid phase composition for the first stage is calculated as suggested in equation (9). The liquid and vapor phase compositions of the first stage are tabulated in Table-9.

Components	Vapor Composition	Liquid Composition
Nitrogen	5.22	0.02
Carbon dioxide	7.12	0.31
Hydrogen sulfide	0.00	0.00
Methane	52.98	0.87
Ethane	13.68	1.31
Propane	11.75	3.48
i-Butane	1.97	1.21
n-Butane	4.08	3.85
i-Pentane	1.07	2.25
n-Pentane	1.16	3.61
Hexanes	0.75	5.84
Heptanes & heavier	0.18	77.27

Table-9 Liquid and vapor phase for first stage.

The equilibrium K-values are compared in Table-10 and Figures 4 and 5.

Components	Ki Calculated	Ki Correlation
Methane	61.18	101.63
Ethane	10.43	15.95
Propane	3.38	4.08
i-Butane	1.63	1.61
n-Butane	1.06	1.16
i-Pentane	0.48	0.48
n-Pentane	0.32	0.37
Hexanes	0.13	0.13

Table-10 Comparison of equilibrium K-values calculated from experimental data and Wilson's correlation first stage.
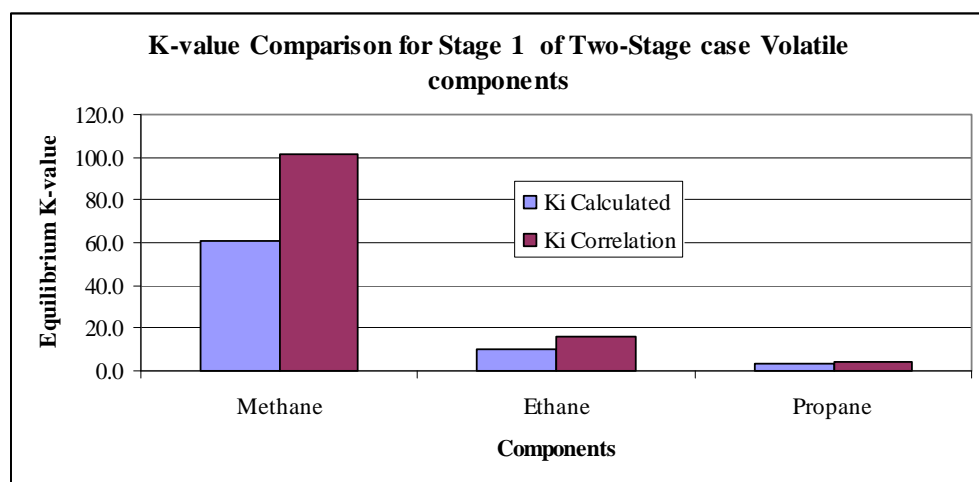

Figure-4 Comparison of equilibrium K-values for first stage of a two-stage separator, volatile components.
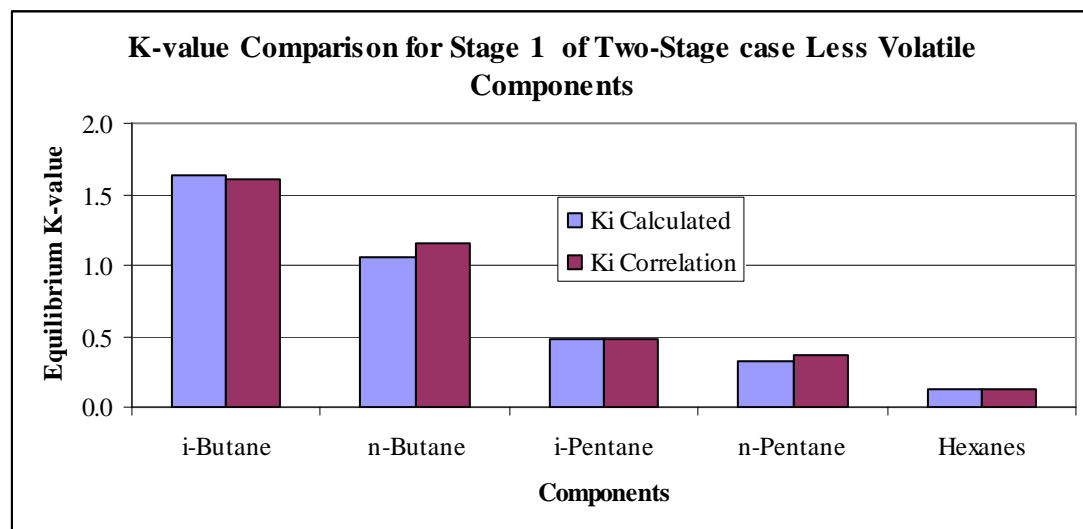

Figure-5 Comparison of equilibrium K-values for first stage of a two-stage separator, less volatile components.

The comparison here is reasonably good, especially in case of less volatile components.

Three-Stage Separator

Calculation of equilibrium K-values for three-stage separator case followed the same pattern as two-stage case. Table-11 and Table-12 show the compositions and other parameters for the separator stages.

Components	Bottom Hole Composition	Density	API	M. Wt.	Separator stages		
					stage1	stage2	stage3
Nitrogen	0.07			28.02	0.74	0.72	0.72
Carbon dioxide	1.85			44.01	19.53	21.13	18.16
Hydrogen sulfide	0.25			34.08	0.35	1.03	2.57
Methane	3.07			16.04	53.44	40.08	16.15
Ethane	1.66			30.07	9.47	12.7	16.68
Propane	2.92			44.09	8.14	12.24	22.43
i-Butane	1.36			58.12	1.5	2.26	4.48
n-Butane	4.02			58.12	3.25	4.81	9.51
i-Pentane	2.57			72.15	0.95	1.39	2.65
n-Pentane	3.27			72.15	1.04	1.51	2.83
Hexanes	6.01			86.17	0.73	1.11	1.98
Heptanes & heavier	72.95	0.9429	18.4	362.57	0.86	1.02	1.84

Table-11 Compositions for three-stage separator case

	stage1	stage2	stage3
P (psia)	115	55	15
Temp (F)	117	100	80
GOR SCF/STB	10.3	13.3	19.4

Table-12 Pressures, temperatures and GOR for three-stage separator case

Table-13 to Table-15 show the comparison of experimentally determined K-values and values obtained at separator temperature and pressure condition for third, second and first stage respectively. Figure-6 to Figure-8 similarly graphically depicts the comparison.

Components	Ki Calculated	Ki Correlation
Ethane	45.6236	42.2653
Propane	14.6551	9.6872
i-Butane	3.8156	3.5570
n-Butane	2.5405	2.4885
i-Pentane	1.0024	0.9577
n-Pentane	0.8316	0.7247
Hexanes	0.3048	0.2332

Table-13 Comparison of equilibrium K-values calculated from experimental data and Wilson's correlation third stage of a three-stage separator.
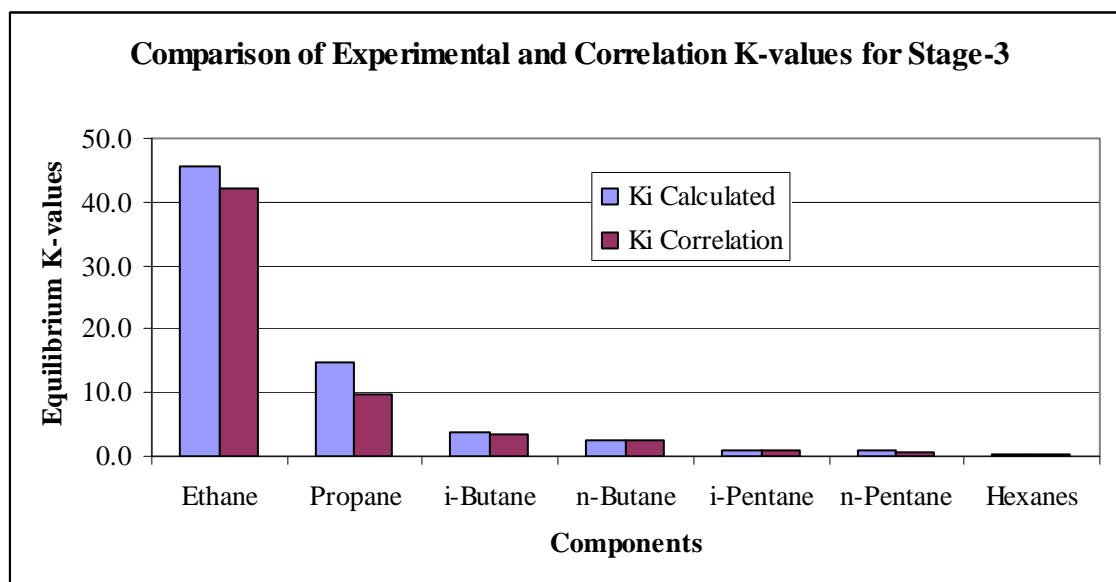
Comparison of Experimental and Correlation K-values for Stage-3

Figure-6 Comparison of equilibrium K-values for third stage of a three-stage separator

Components	Ki Calculated	Ki Correlation
Methane	53.76	98.88
Ethane	11.35	14.28
Propane	4.91	3.47
i-Butane	1.70	1.32
n-Butane	1.20	0.94
i-Pentane	0.53	0.37
n-Pentane	0.45	0.29
Hexanes	0.18	0.10

Table-14 Comparison of equilibrium K-values calculated from experimental data and Wilson's correlation second stage of a three-stage separator.
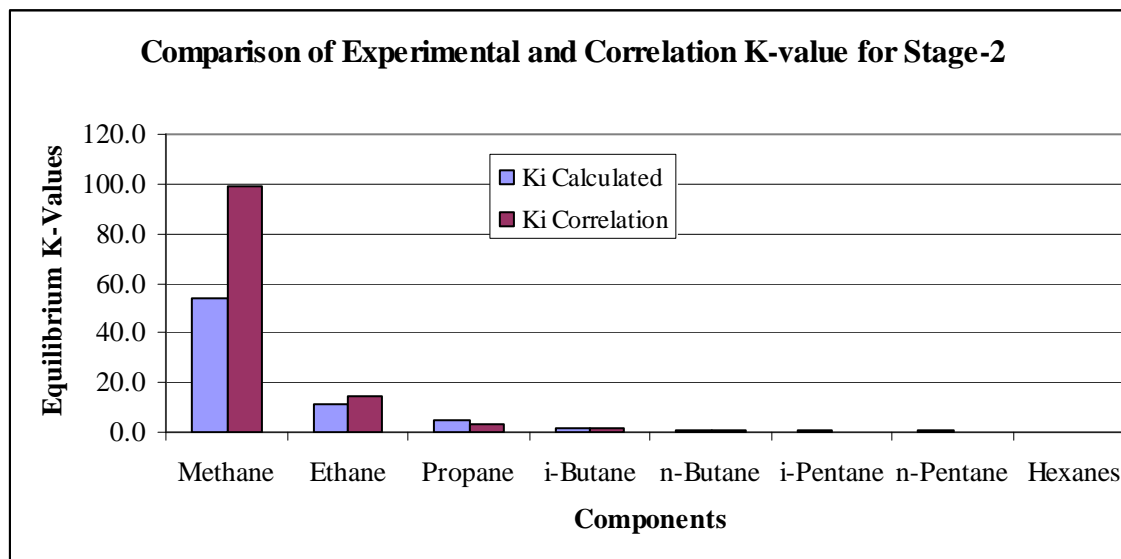
Figure-7 Comparison of equilibrium K-values for second stage of a three-stage separator

Components	Ki Calculated	Ki Correlation
Methane	27.37	52.16
Ethane	6.42	8.10
Propane	2.91	2.06
i-Butane	1.11	0.81
n-Butane	0.81	0.58
i-Pentane	0.36	0.24
n-Pentane	0.31	0.19
Hexanes	0.12	0.06

Table-15 Comparison of equilibrium K-values calculated from experimental data and Wilson's correlation first stage of a three-stage separator.
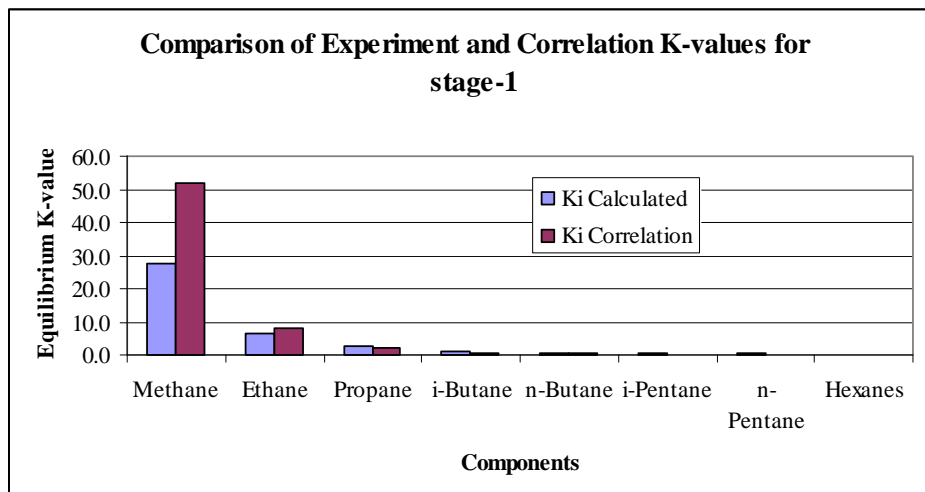

Figure-8 Comparison of equilibrium K-values for first stage of a three-stage separator

Binary System Experiment

A binary system of methane and n-pentane was tested also. The test temperature was 150 ºF and the experiment mimicking a separator test was performed at three pressures 1515, 1015, and 515 psia. Here also the phase composition of the gas was measured and the liquid compositions were calculated as was the case in separator tests to keep the uniformity of the conditions. Table-16 gives the compositional and K-value data for this binary system.

P (psia)	1515	1015	5015
	yi mix 1	yi mix 2	yi mix 3
Methane	96.72	89.67	89.70
n-Pentane	3.28	10.33	10.30
	xi mix 1	xi mix 2	xi mix 3
Methane	32.10	12.90	3.40
n-Pentane	67.90	87.10	96.60
	Ki mix 1	Ki mix 2	Ki mix 3
Methane	3.01	6.95	26.38
n-Pentane	0.05	0.12	0.11

Table-16 Vapor and liquid phase composition data and K-values calculated from the binary system experimental data.

The equilibrium K-values for these pressures and temperature conditions were calculated using Wilson's correlation. These are compared with the experimentally determined values in Table-17.

	Experimental	Wilson's Corr.
	Ki mix 1	Ki mix 1
Methane	3.013	4.715
n-Pentane	0.048	0.024
	Ki mix 2	Ki mix 2
Methane	6.951	7.030
n-Pentane	0.119	0.036
	Ki mix 3	Ki mix 3
Methane	26.382	13.800
n-Pentane	0.107	0.071

Table-17 Comparison of experimentally determined K-values and values obtained using Wilson's correlation for the binary system.

Conclusions

With detailed analysis of the data and comparison with correlations following conclusions were drawn;

- The Wilson's correlation mostly over predicts the equilibrium K-values even at relatively low pressures.
- The data from multi-stage separator match better with the correlation. This might be with more stages a better thermodynamic equilibrium is achieved.
- The difference in the experimental and correlation K-values is greater for more volatile components. This might be helped if separate correlations for more volatile and less volatile components are developed.
- The binary experiment results suggest that at higher pressure (above 1000 psia) difference in the experimental and correlation K-value was reduces. This indicates a need for separate correlations for volatile components.
- The last but not the least there is a definite need for better correlations and this can be only possible with a lot of experimental data. So there is a need for more and more experiments to understand the vapor liquid equilibrium.

Acknowledgement

Reference:

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