

Mathematical Model for the Equilibrium Flash Vaporization of the Nile Blend Crude Oil

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ABSTRACT

Equilibrium Flash Vaporization (EFV) for the crude oil distillation is considered to be one of the crucial basis to simulate the true distillation operation in the distillation column. Classical procedures have been used to determine EFV of the crude oil, such as Maxwell and Edmister methods. Such methods are multi-graphical methods which are tedious and time consuming. Based on Maxwell graphical procedure, this paper is attempting to develop a new EFV mathematical model using experimental data from the Nile Blend crude oil. The developed model allows the process engineer to swiftly obtain the flash zone temperature of the Crude Distillation Unit (CDU) avoiding the tedious process of the graphical methods. Although the experimental data were taken from the Nile Blend oil, the same procedure could be followed to develop an EFV mathematical model for any other crude oil.

Keyword: Crude oil, TBP curve, Maxwell graphs, EFV

INTRODUCTION

Crude oil is naturally found in brown to black flammable liquid. The crude oils are mainly constituted of hydrocarbons mixed with variable amount of sulphur, nitrogen and oxygen compounds (*Sami, 2000*). It is well known that the crude oil stocks are usually evaluated using the True Boiling Point curves (TBP). TBP curves are quite sufficient for the properties of crude oil stocks but not for the design purposes. Recently, it has been stated that the EFV curves could be used instead of TBP curves. EFV distillation provides better results because it simulates the operation of a true distillation column, (*Dokhkan, 2006*).

Vapor-Liquid Equilibrium for Crude Oil

Two methods are used to calculate the vapor – liquid equilibrium of crude oil and its products. The first category uses the concept of pseudo-component in which the calculus of vapor – liquid equilibrium is based on their physical properties. The second method uses the Edmister – Okamoto or Maxwell methods which are based on experimental graphics correlations, (*Cristain and Catalin, 2009*) and (*David and Peter, 2006*).

Edmister method locates a key point (the temperature corresponding to 50% distillate volume), then estimates the EFV curve as a function of TBP using data from diagrams (*Edmister and Okamoto, 1959*). The EFV curve is obtained according to Edmister by processing all increments (multiples of 10% distillate volume). The use of intense diagrams is considered to be the greatest weakness of the Edmister method, (*David and Peter, 2006*).

Beside Edmister method, David and Peter have also explained the Maxwell method which uses straight Maxwell auxiliary cuts from TBP curve between 10% and 70% of the distillate volume. The overall Maxwell cuts within the nominated range of volume distillates are almost shown to be linear representation and called the Distillation Reference Line (DRL). The DRL is considered as a reference line for the prediction of other charts shown in Figures (2, 3 and 4) to estimate the EFV curve manually point by point (*David and Peter, 2006*).

Development of Crude Oil Distillation Curves (TBP, ASTM D86, EFV)

The True boiling point (TBP) distillation is widely used in a traditional batch distillation process to characterize the crude oils for the sake of marketing and refining purposes. The TBP curve is obtained by plotting the cumulative mass or volume distillation fractions against temperature.

The shape of this curve depends on the volatility of crude oil (*Behrenbruch and Dedigama, 2007*).

According to *Riazi*, the quality and value of crude oils are significantly depending on their TBP curves. However, the experimental determination of TBP curves is quite expensive and time consuming. Therefore, it is impractical to use the classical/ experimental TBP method as a tool for the routine monitoring of Crude Distillation Units (CDUs). This critique calls for the development of TBP calculation method having sufficient precision with minimum experimental work and omits the tedious manner of the classical procedure. During the last two decades, *Riazi* has developed a three-parameters distribution model that is widely used to estimate TBP in addition to other properties of above C7 fractions of petroleum fluids (*Riazi, 1989 and 1997*). *Riazi* model could

precisely predict the TBP distributions even if the distillation data are not available, where instead only three crude oil properties have to be known such as molecular mass, density and refractive index. Moreover and according to *Argirov, Riazi* model could be used for the prediction of the rest of the distillation curves needed in petroleum processing "ASTM D 86, EFV, CD, ..., etc.", (*Argirov, et al.*, 2012).

From CDUs, the preprocessed data are used for product properties prediction. Consequently, the temperatures of top distillate, side-stripper draw plate and flash zone are corrected for partial pressure of hydrocarbons. Eventually, this will represent the EFV temperatures of the same products, (*Shrikant et al.*, 2003).

New method has been developed by *Enrique et al* to estimate the EFV for petroleum fractions based on modeling and simulation. The developed model was fitted using several distillation curves and simple experimental work. The method has been applied using commercial simulators. Several advantages have been recorded for such method compared to Edmister's and Maxwell's methods (*Enrique et al.*, 2008).

Later, *Kowang* has utilized thermodynamics using the Vapor-Liquid Equilibrium (VLE) model to investigate and estimate the accuracy of the often used EFV calculation in petroleum. The method has been conducted for the crude oil fractions and vacuum residue at high temperature (*Kowang*, 2011).

Nile Blend Crude as a Case Study for the Proposed EFV Model

Nile Blend is a trade mark for the Sudanese crude oil which is partially refined in Khartoum Refining Company (KRC). Nile Blend is considered to be sweet and light crude oil having a gravity of 33°API and low sulphur content of 0.045% (*Imad*, 2010). Nile Blend crude is fractionated in KRC into product-cuts such as light-end hydrocarbons, naphtha, kerosene, diesel and atmospheric residue.

For the current study, samples have been taken from the Nile Blend crude oil to run some experiments related to the EFV development. Prior investigations were conducted for the bulk properties such as: density, relative density and API gravity. Moreover, using the TBP pilot plant the experimental TBP curve was obtained where the true boiling temperature has been determined for each volume percentage of the distillate product. Table (1) and Fig (1) show the bulk properties and experimental TBP for Nile blend.

Table (1) Bulk Property Characterization of Nile Blend Crude Oil

| Item | Result |
|------------------------------------------------|----------------|
| Density (15°C), kg/m ³ , ASTM D4052 | 861.4 |
| API° gravity, ASTM D1298 | 32.76 |
| TBP, ASTM D2892 | |
| | Volume% |
| | Temperature, K |
| | 0 |
| | 10 |
| | 20 |
| | 30 |
| | 40 |
| | 50 |
| Distillation of crude petroleum | 60 |
| | 70 |
| | 80 |
| | 90 |
| | 100 |

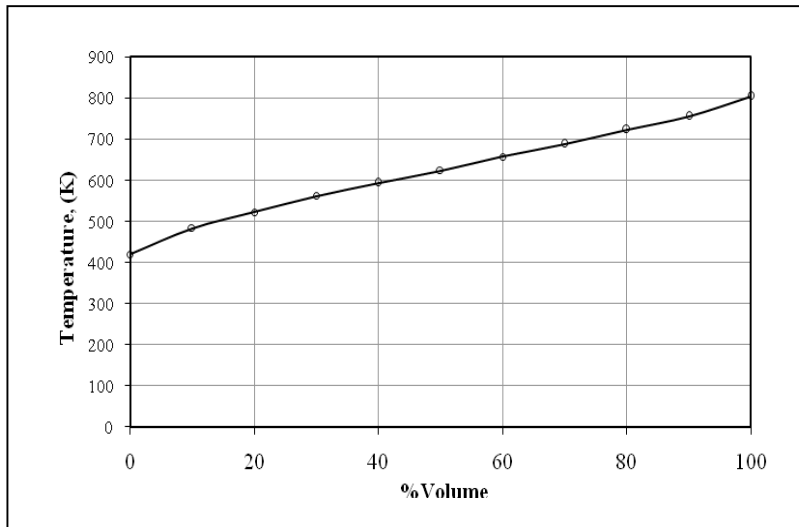


Figure 1: The True Boiling Point (TBP) Curve.

Model Development

This paper is to investigate the possibility of shaping a mathematical model for vapor – liquid equilibrium for the complex systems of hydrocarbons in the crude oil by using TBP to estimate the EFV graphic correlations – Maxwell method. Then to develop this method by building a mathematical equation of vapor – liquid equilibrium (EFV) curve by using MS Excel or any

other regression package. So that, this method can be used for different crude oils to estimate an equation for the EFV curve.

Development of EFV Mathematical Model Correlation

Based on the Maxwell method, the EFV correlation could be developed systematically. The EFV curve together with correlation for the Nile Blend crude at atmospheric pressure is determined by the following steps based on Maxwell:

1. From the crude TBP, the slope of the curve (S_{TBP} as $K/\%volume$) is calculated according to equation (1) for the volume percentage between 10 and 70. Within this region the equation represents a linear correlation and hence could be used directly for Distillation Reference Line (DRL).

$$S_{TBP} = \frac{t^{\circ}K \text{ at } 70\% - t^{\circ}K \text{ at } 10\%}{60} \quad (1)$$

2. From Maxwell curve (Dived, 2006); data is extracted manually as in Table (2). The data is re-plotted for fitting as shown in Figure (2) to accurately determine the predicted Flash Reference Line. The slope of Flash Reference Line is (S_{FRL} in $K/volume\%$) and correlated as per the following equation:

$$S_{FRL} = -0.0054S_{TBP}^3 + 0.115S_{TBP}^2 + 0.208852S_{TBP} - 0.0101 \quad (2)$$

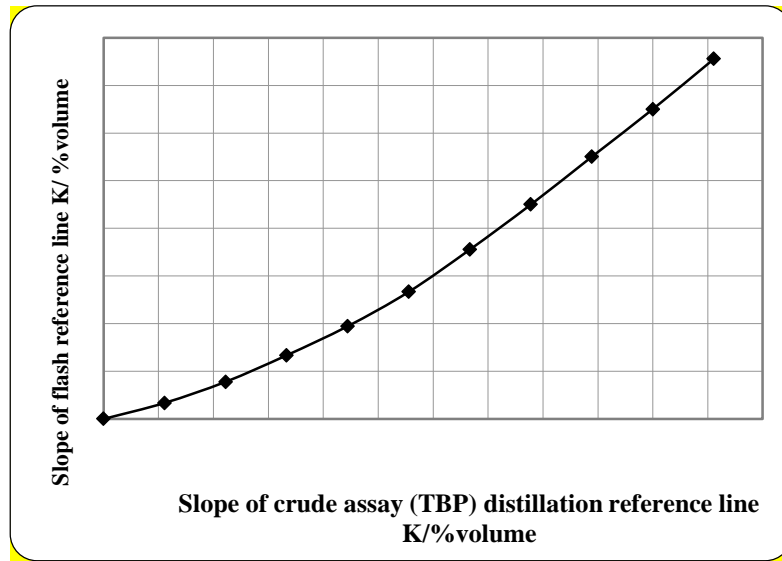


Figure 2: Prediction of Flash Reference Line (FRL) from Distillation Reference Line (DRL).

Table (2) Actual data of FRL from DRL and Result from Fitting Curve of Slope FRL K%

| Actual, S_{TBP} | Actual, S_{FRL} | Result from fitting curve, S_{FRL} | Deviation from actual |
|-------------------|-------------------|--------------------------------------|-----------------------|
| 0.0 | 0.00 | 0.01 | -0.01 |
| 0.6 | 0.17 | 0.16 | 0.01 |
| 1.1 | 0.39 | 0.38 | 0.01 |
| 1.7 | 0.67 | 0.65 | 0.01 |
| 2.2 | 0.97 | 0.98 | -0.01 |
| 2.8 | 1.33 | 1.36 | -0.03 |
| 3.3 | 1.78 | 1.78 | -0.01 |
| 3.9 | 2.25 | 2.24 | 0.01 |
| 4.4 | 2.75 | 2.74 | 0.01 |
| 5.0 | 3.25 | 3.25 | 0.00 |
| 5.6 | 3.78 | 3.79 | -0.02 |

3. Referring to Maxwell (DRL – FRL), again the data has been extracted and tabulated in Table (3) to re-plot and fit the predicted Flash Reference Line (FRL) at 50% volume. Two polynomial correlations were obtained as described in equations (3) and (4):

$$\Delta t_{50,(DRL-FRL)} = -0.0546FRL^6 + 0.9667FRL^5 - 6.304FRL^4 + 17.828FRL^3 - 18.752FRL^2 + 5.9476FRL - 4.4353 \quad (3)$$

$$\Delta t_{50,(DRL-FRL)} = -0.0795S_{DRL}^6 + 1.3689S_{DRL}^5 - 8.6297S_{DRL}^4 + 23.398S_{DRL}^3 - 23.139S_{DRL}^2 + 6.9121S_{DRL} - 0.1319 \quad (4)$$

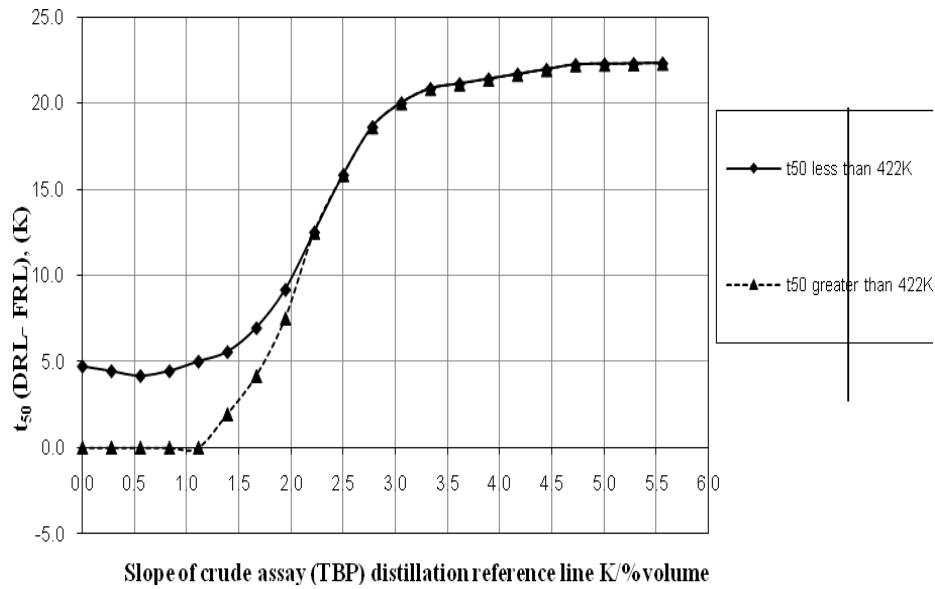


Figure 3: Prediction of FRL 50% volume

Table (3) The Actual Data of FRL 50% Point and Result from Fitting Curve Deviation:

| Slope of crude assay (TBP) – DRL K% | t ₅₀ (DRL-FRL) at less than 422K | | | t ₅₀ (DRL-FRL) at greater than 422K | | |
|-------------------------------------|---------------------------------------------|--------------------|-----------|------------------------------------------------|--------------------|-----------|
| | From curve | From fitting curve | Deviation | From curve | From fitting curve | Deviation |
| 0.0 | 4.7 | 4.4 | 0.3 | 0.0 | -0.13 | 0.13 |
| 0.3 | 4.4 | 5.0 | -0.5 | 0.0 | 0.46 | -0.46 |
| 0.6 | 4.2 | 4.5 | -0.3 | 0.0 | -0.17 | 0.17 |
| 0.8 | 4.4 | 4.0 | 0.4 | 0.0 | -0.54 | 0.54 |
| 1.1 | 5.0 | 4.3 | 0.7 | 0.0 | 0.09 | -0.09 |
| 1.4 | 5.6 | 5.4 | 0.1 | 1.9 | 1.91 | 0.03 |
| 1.7 | 6.9 | 7.4 | -0.5 | 4.2 | 4.75 | -0.58 |
| 1.9 | 9.2 | 10.0 | -0.8 | 7.5 | 8.23 | -0.73 |
| 2.2 | 12.5 | 12.8 | -0.3 | 12.5 | 11.89 | 0.61 |
| 2.5 | 15.8 | 15.5 | 0.3 | 15.8 | 15.30 | 0.54 |
| 2.8 | 18.6 | 17.8 | 0.8 | 18.6 | 18.11 | 0.50 |
| 3.1 | 20.0 | 19.7 | 0.3 | 20.0 | 20.11 | -0.11 |
| 3.3 | 20.8 | 20.9 | 0.0 | 20.8 | 21.29 | -0.45 |
| 3.6 | 21.1 | 21.5 | -0.4 | 21.1 | 21.74 | -0.63 |
| 3.9 | 21.4 | 21.6 | -0.2 | 21.4 | 21.74 | -0.35 |
| 4.2 | 21.7 | 21.6 | 0.1 | 21.7 | 21.60 | 0.06 |
| 4.4 | 21.9 | 21.5 | 0.5 | 21.9 | 21.64 | 0.30 |
| 4.7 | 22.2 | 21.5 | 0.7 | 22.2 | 22.05 | 0.17 |
| 5.0 | 22.3 | 21.7 | 0.6 | 22.3 | 22.77 | -0.52 |
| 5.3 | 22.3 | 21.8 | 0.5 | 22.3 | 23.31 | -1.03 |
| 5.6 | 22.3 | 21.1 | 1.2 | 22.3 | 22.58 | -0.28 |

Equation (3) is only valid for temperature less than 422K whereas equation (4) which is applied for Nile Blend crude oil is valid for temperature greater than 422K.

4. As explained earlier, the DRL is straight line located in the range of volume percentage between 10 and 70 on the TBP curve. Consequently, the linear equation describing this line for 50% volume which represents the average temperature of DRL could be stated as follows:

$$t_{50,DRL} = 3.4V_{50} + 450 \quad (5)$$

5. Based on the $t_{50,DRL}$ obtained above, determination of the flash reference line at average temperature $t_{50,FRL}$ could be explained as in the following equation:

$$t_{50,FRL} = t_{50,DRL} - t_{50(DRL-FRL)} \quad (6)$$

6. The ratio of flash and crude assay is a temperature difference (Δt^l) ratio which is described as a departure of the actual flash and distillation curves from their respective reference line as shown in Table (4) and Figure (4). Δt^l might be either (+ve) or (-ve) but the ratio is always positive (Devid, 2006). In figure, the ratio is shown to be constant through 30 to 100 % volume which is approximately 0.37. However for the volume percentage between 0 and 30, the values for Δt^l ratio are 0.2, 0.4 and 0.38 and for this region the polynomial equation will not be feasible and accordingly constant values for the ratio will be used. The temperature difference ratio could be explained mathematically using the equations from (7) to (10) as shown below:

$$\Delta t^l_{ratio} = \frac{\Delta t^l_{flash}}{\Delta t^l_{assay}} \quad (7)$$

$$\left. \begin{aligned} \Delta t^l_{flash} &= t_{actual,flash} - t_{FRL} \\ t_{actual,flash} &= \Delta t^l_{flash} + t_{FRL} \end{aligned} \right\} \quad (8)$$

$$t_{FRL} = S_{FRL}(V - V_{50}) + t_{50,FRL} \quad (9)$$

$$\Delta t^l_{assay} = t_{TBP} - t_{DRL} \quad (10)$$

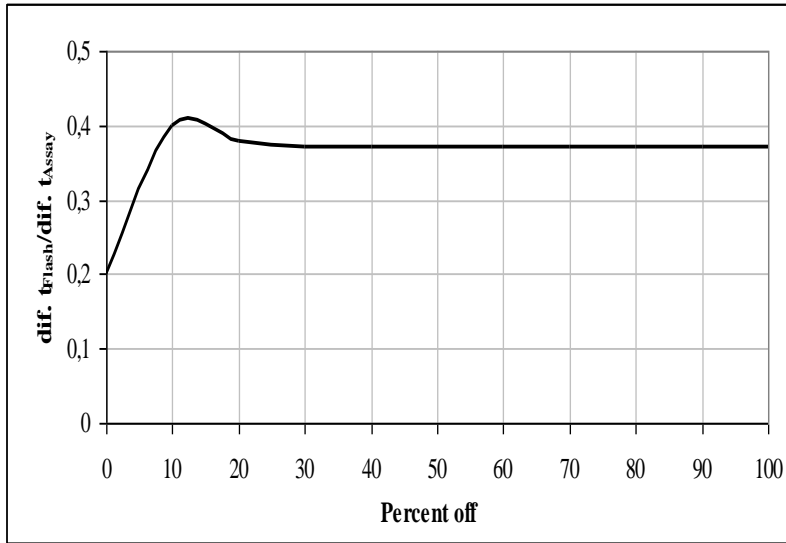


Figure 4: The prediction of flash curve from its reference.

Table (4) The prediction of flash curve from its reference

| Percent off | Actual, $\Delta t_{ratio}^l = \frac{\Delta t_{flash}^l}{\Delta t_{assay}^l}$ | $\Delta t_{ratio}^l = \frac{\Delta t_{flash}^l}{\Delta t_{assay}^l}$ from fitting | Deviation |
|-------------|------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-----------|
| 0 | 0.20 | 0.20 | -0.00750 |
| 10 | 0.40 | 0.41 | -0.01367 |
| 20 | 0.38 | 0.50 | -0.30942 |
| 30 | 0.37 | 0.79 | -1.13954 |
| 40 | 0.37 | 1.55 | -3.20168 |
| 50 | 0.37 | 3.07 | -7.30473 |
| 60 | 0.37 | 5.70 | -14.3941 |
| 70 | 0.37 | 9.86 | -25.6487 |
| 80 | 0.37 | 16.09 | -42.4843 |
| 90 | 0.37 | 24.97 | -66.4980 |
| 100 | 0.37 | 37.13 | -99.3554 |

7. Related to all the above equations and the obtained data in Table (5), the EFV curve could be plotted between the volume percentage and flash temperature at atmospheric pressure as shown in Figure (5). The EFV plot is found to be almost linear according to equation (11) below:

$$t_{EFV} = 1.8908V + 513.92 \quad (11)$$

Table (5) The flash curve calculated result at atmospheric pressure

| Vol. % | TBP | | | $\Delta' \text{ ratio} = \frac{(T(\text{Flash}) - T(\text{FRL}))}{(T(\text{TBP}) - T(\text{DRL}))}$ | EFV | | |
|--------|----------|----------|-----------------|-----------------------------------------------------------------------------------------------------|-------------------|----------|------------|
| | T(TBP) K | T(DRL) K | T(TBP)-T(DRL) K | | T(Flash)-T(FRL) K | T(FRL) K | T(Flash) K |
| 0 | 420 | 450 | -30 | 0.20 | -6 | 516 | 510 |
| 10 | 484 | 484 | 0 | 0.40 | 0 | 534 | 534 |
| 30 | 562 | 552 | 10 | 0.38 | 3,8 | 571 | 575 |
| 50 | 624 | 620 | 4 | 0.37 | 1,48 | 608 | 609 |
| 70 | 688 | 688 | 0 | 0.37 | 0 | 645 | 645 |
| 90 | 756 | 756 | 0 | 0.37 | 0 | 681 | 681 |
| 100 | 804 | 790 | 14 | 0.37 | 5,18 | 700 | 705 |

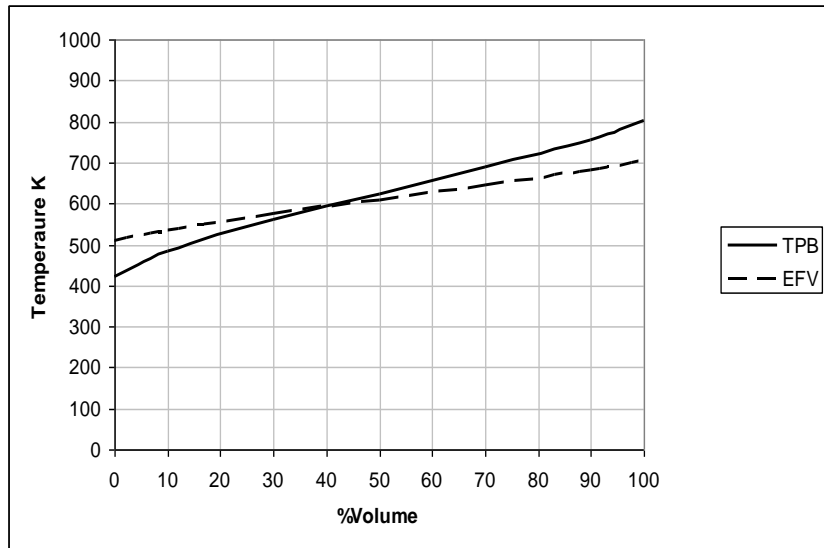


Figure 5: The TBP and EFV curves

Finally, equation (11) could be used directly to determine the flash zone temperature of the CDU at the atmospheric pressure for Nile Blend crude oil. Following the same steps from (1–7) above, equation (11) could be derived for any other crude oil.

Results and Comparison

The results of the developed model together with the actual flash zone temperature of Nile Blend crude could be summarized in Table (6).

Table (6) Results of the developed model with the actual flash zone temperatures

| Items | Value | Unit |
|---------------------------|----------|------------|
| S_{TBP} | 3.4 | K/% Volume |
| S_{FRL} | 1.837178 | K/% Volume |
| $\Delta t_{50,(DRL-FRL)}$ | 12 | K |
| $t_{50,DRL}$ | 620 | K |
| $t_{50,FRL}$ | 608 | K |
| $t_{Flash,zone,model}$ | 591 | K |
| $t_{Flash,zone,CDU}$ | 600 | K |

From the table, it is noticed that the deviation of EFV from actual CDU is almost negligible which is about 0.02733.

CONCLUSION

This paper is attempting to develop a mathematical correlation for the swift determination of EFV temperature for the crude oil at atmospheric pressure. The study was conducted for the Nile Blend crude oil and can be generalized to cover all types of crude oil. The obtained results were found to be similar to the classical cascaded graphical methods of Maxwell. The utilization of the developed correlation is expected to save engineer's times, and helps in the design of Crude Distillation Unit.

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Abbreviations

| | |
|------|----------------------------------------------|
| API | : American Petroleum Institute |
| ASTM | : American Society for Testing and Materials |
| CD | : Crude Distillation. |

Nomenclature

| | |
|---------------------------|---------------------------------------------------------|
| S_{FRL} | : Slope of Flash Reference Line |
| S_{TBP} | : Slope of True Boiling Point Curve |
| V | : Parentage volume |
| V_{50} | : Average percentage volume |
| t_{TBP} | : TBP temperature |
| t_{DRL} | : DRL temperature |
| t_{EFV} | : EFV temperature |
| Δt^l | : Ratio of flash and assay is a temperature difference. |
| $\Delta t_{50,(DRL-FRL)}$ | : Average temperature difference between DRL and FRL. |
| $\Delta t_{50,DRL}$ | : Average temperature difference of DRL |
| $\Delta t_{50,FRL}$ | : Average temperature difference of FRL |
| Δt_{Assay} | : Assay temperature difference. |
| Δt_{FRL} | : Flash temperature difference. |

الخلاصة

يعتبر منحنى اتزان درجة حرارة التبخر الوميضي (EFV) لخام البترول من أهم الأساسيات لمحاكاة عملية التقطير الحقيقية في وحدة تقطير الخام (CDU) ، وقد استخدمت طريقة تقليدية مثل طريقة (Maxwell and Edmister) وهى طريقة متعددة المعادلات والرسومات البيانية وعند استخدامها مملة ومهدرة للوقت. في هذه الورقة نحاول تطوير نموذج رياضي جديد لتقدير منحنى درجة حرارة اتزان التبخر الوميضي بإستخدام بيانات معملية لخام مزيج النيل ، حيث يُمكن المهندس الحصول بسرعة على درجة حرارة منطقة الوميض في وحدة تقطير الخام وتُجنبه عملية حسابية شاقة عند استخدام المعادلات والرسومات البيانية. ويُمكن أن نتبع نفس الإجراء لتطوير النموذج الرياضي لتقدير منحنى اتزان درجة حرارة التبخر الوميضي لأى خام بترولي آخر.