A New Method for Estimating the EFV Distillation Curve

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Abstract: This work presents a new method to estimate the equilibrium flash vaporization (EFV) distillation curve from standard laboratory analytical assay procedures. In this method, experimental data are utilized by a chemical process simulator to obtain the EFV curve. Any simulator able to model petroleum can be used for this task. To evaluate the performance of the proposed method, several types of petroleum were analyzed experimentally in this work. The obtained curves were compared with those produced by other methods showing a good match. The main advantage of the proposed method is its non-dependence on experimental data.

Keywords: CHEMCAD, distillation, EFV, HYSYS, simulation

INTRODUCTION

To model a process containing crude oil, the properties of the oil must be known or at least estimated. Determining the exact composition of crude oils is not feasible because of the enormous number of components comprising these mixtures. Instead, a boiling curve analysis is usually performed by measuring the temperature of the distillate fraction at specific cumulative volume percentages. These boiling-point measurements are then related to the physical properties of the oil using correlations developed by the industry. The correlations estimate properties, such as specific gravity, molecular weight, viscosity, critical temperature and pressure, etc., based on the crude oil analysis. In this way, a crude oil mixture may be modelled as a group

of hypothetical components whose properties are estimated from different portions of the boiling curve. Other properties, such as molecular weight, specific gravity, or viscosity, may also be determined at specific cumulative volume percentages. More commonly, molecular weight and specific gravity are supplied as "bulk properties," which are measured for the overall oil sample. These additional curves and bulk properties help to improve the petroleum characterization.

On the other hand, light ends are low-molecular-weight organic compounds, such as methane, ethane, propane, etc., which can be included as components in the oil. Light ends can be generated from the boiling curve data, supplied from a separate analysis, or no light ends can be specified. If generated or supplied, the amount of each light-end component represents the amount of the oil mixture that has an average boiling point equal to the specified light end. (i.e., the basis for a light end's amount is the same as the original assay data basis).

This work presents a new method to estimate the equilibrium flash vaporization (EFV) distillation curve from standard laboratory analytical assay procedures, such as true boiling-point distillation (TBP), ASTM D86, and D1160 distillation (separately or combined), D2887 simulated distillation curve generated from chromatography analysis (Watkins, 1981), and others. By definition, an EFV curve is generated by a series of experiments conducted at constant pressure (usually at 1 atm). The results relate the equilibrium temperature versus volume percent of distilled liquid, where the total vapor is in equilibrium with the unvaporized liquid. This curve is broadly used to design industrial equipment (Cerutti, 2002). However, since the experimental procedure required to obtain the EFV curve is rather difficult and laborious, this curve is generally estimated from other experimental curves that demand more simple procedures. A number of methods to estimate the EFV curve were developed, the Edmister and the Maxwell methods being the most utilized (Maxwell, 1950; Nelson, 1958; Edmister and Okamoto, 1959; Edmister, 1961). Both methods perform the estimation by using graphical techniques combined with data from tables and diagrams, which is a complex and error-prone practice.

To solve those problems, this work introduces a new method to estimate the EFV curve by utilizing chemical process simulators. The method is presented by using the simulators HYSYS and CHEMCAD; but it can be implemented in any other simulator able to model petroleum. To evaluate the performance of the proposed method, several types of petroleum were analyzed, and the obtained EFV curves were compared with those produced by the Edmister and Maxwell methods. In all tested cases, the EFV curves produced by the proposed method were located between the other two curves. Finally, a big advantage of this procedure is that it does not depend on the type of laboratory data available; thus, the EFV curve can be estimated following the same procedure regardless of the type of distillation curves entered into the simulator for petroleum characterization.

PETROLEUM CHARACTERIZATION

Laboratory standard methods for distillation of petroleum and fractions are of great value in refining and formulating fuels. Three of the most important assays are (Wuithier, 1971; Speight, 1998; Cohen, 2003) ASTM (considered the universal, normalized method), TBP (whose results are difficult to reproduce), and Flash (instantaneous vaporization).

ASTM Curve

The ASTM distillation employs a batch fractionation apparatus, and it is conducted using nonrefluxed Engler flasks, which possess standard dimensions. The heat flow is adjusted to produce 5 cm^3 of distillate per minute. The temperature is registered when the first drop of distillate falls and then every time 10% of distillate is collected. The maximum temperature is 370°C; therefore, it is a soft distillation where there is no division.

TBP Curve

A TBP analysis is performed using a multistage batch fractionation apparatus operated at relatively high reflux ratios (15–100 theoretical stages with reflux ratios of 5:1 or greater). TBP distillations are conducted at either atmospheric or vacuum conditions. The petroleum fluid's bubble point is a multicomponent equilibrium condition such that there is an incipient vapor phase forming. This would, in effect, be a single stage of fractionation as opposed to the highly refluxed operation of a TBP analysis.

The TBP distillation is not standardized. The distillate is obtained from the division into fractions of the load components. A getter device for petroleum and its derived products is used, which is loaded with 1,000 to 5,000 cm^3 of liquid. The fractioning column is surrounded by a heater that compensates the lost heat. A condenser at the top produces the vapor condensation, and the condensate descends; when it makes contact with the vapor, the separation takes place. The temperature of the first drop, as well as for each 10% of distillate, is registered.

EFV Curve

An EFV curve is generated by a series of experiments conducted at constant pressure (1 atm). The results relate the temperature versus volume percentage of liquid distilled, where the total vapor is in equilibrium with the unvaporized liquid. Figure 1 shows a flash laboratory equipment simplified in order to make the simulation easier; however, this simplification does not affect the exactness of results. The tank T-1 contains the petroleum to be analyzed at
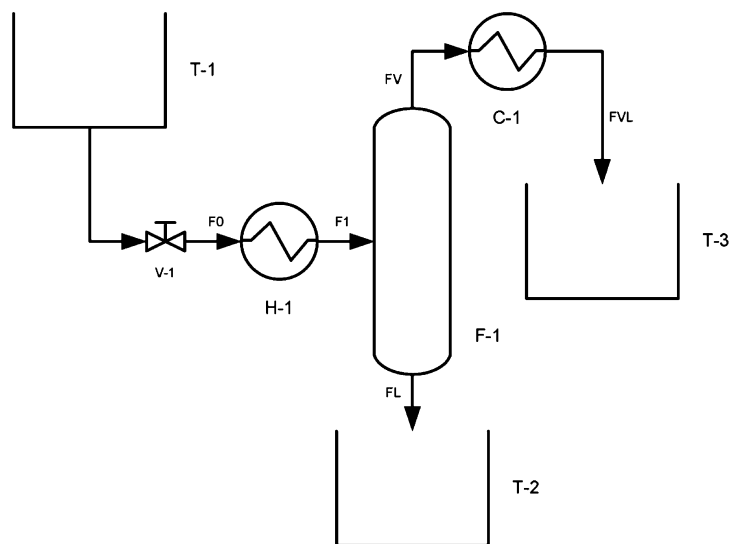
Figure 1. Flash laboratory equipment.

standard conditions (15°C, 1 atm). It flows through the heater H-1 to reach the desired temperature of equilibrium. The liquid–vapor separation occurs in the tower F-1, whose pressure is 1 atm. The liquid is deposited in the tank T-2, whereas the vapor is condensed and cooled down to 15°C by the cooler C-1 and finally collected in the tank T-3. The volume percent of liquid distilled can be obtained by $100 \times$ (liquid volume in T-3 at the end)/(liquid volume in T-1 at the beginning), or, which is better, $100 \times$ (FVL flow)/(F0 flow). This way, by repeating the experiment for several temperatures of equilibrium and plotting the corresponding percentage of distillate volume, the EFV curve is created.

EFV CURVE ESTIMATION

Knowledge of vapor–liquid phase equilibrium conditions of petroleum fractions is essential for the design of most petroleum process equipment. This information can be obtained experimentally by determining the EFV curve. However, this procedure generally requires a considerable amount of time and money. For this reason, empirical correlations have been widely used for predicting the EFV curve from the simpler ASTM or TBP distillations.

Many correlations relating the three distillations (ASTM, TBP, and EFV at atmospheric pressure) have been presented in the literature. However,

none of these methods is sufficiently complete to enable phase equilibrium calculation for all operating ranges of temperature and pressure existing in the petroleum distillation. Moreover, the methods developed to estimate the EFV curve are rather complicated and laborious. Two of the most applied examples are outlined below.

Maxwell Method

The Maxwell method uses an auxiliary straight line that cuts the TBP curve in 10% and 70% of the distillate volume; this straight line is called the distillation reference line (DRL). Then, the flash reference line (FRL) is defined in function of the former line by using data obtained from several ad hoc diagrams. Finally, the EFV curve is obtained from the FRL and additional diagrams (Maxwell, 1950). Due to the intense use of diagrams, this method becomes too complex and inaccurate.

Edmister Method

The Edmister method locates a key point (the temperature corresponding to 50% of vaporized fraction). It then estimates the increments of the EFV on function of the increments of the TBP curve by using ad hoc diagrams (Edmister and Okamoto, 1959; Edmister, 1961). Finally, the EFV curve is obtained by processing all its increments. Once again, the intense use of diagrams is the main weakness of the method.

Correction for Pressure

The obtained EFV curve, corresponding to 1 atm, can be used to estimate a new EFV curve for another pressure. This can be done by plotting a parallel line whose position is determined by the Cox diagram and the desired pressure.

EFV CURVE ESTIMATION BY SIMULATION

The applications of chemical simulators are in continual expansion, and they can also be used to estimate the EFV curve with several advantages. In the following section, the simulation of the flash laboratory equipment presented in Figure 1 is outlined. The model utilized to perform that simulation is then used to introduce another model, which is easier to implement but conceptually more complex. HYSYS can handle the second model, but the first one can be handled by any simulator, such as CHEMCAD.
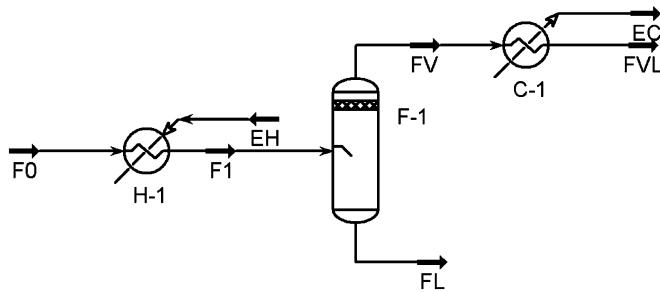
Figure 2. Flash laboratory equipment simulated with HYSYS.

Equipment Simulation with HYSYS

Figure 2 shows the HYSYS PFD (Process Flow Diagram) corresponding to the experimental equipment of Figure 1. Only the part that begins in stream F0 is simulated. The Peng Robinson fluid package is recommended. Table 1 shows the objects and inputs required for the simulation. The temperature variation can be carried out by using the *Case Studies* tool. The necessary steps to provide the petroleum composition to the simulator are given in the following section, where the complete PFD of Figure 2 is replaced by only one material stream called FT.

Material Stream Simulation with HYSYS

Although the preceding simulation is correct, the same results can be achieved by using a simpler model that utilizes special HYSYS features. Indeed, this

Table 1. Unit operations and streams for HYSYS

Name	Object type	Inputs
H-1	Heater	*Delta P* = 0
F-1	Separator	*Delta P* = 0
C-1	Cooler	*Delta P* = 0
EH	Energy stream	
EC	Energy stream	
F0	Material stream	Petroleum composition, $T = 15°C$, $P = 1$ atm, *Liq Vol Flow @Std Cond (m^3/h)* = 100
F1	Material stream	T = Desired temperature of equilibrium
FV	Material stream	
FL	Material stream	
FVL	Material stream	$T = 15°C$

new model is formed by only one material stream. The complete procedure to build the EFV curve with this model follows:

1. Create a new case in HYSYS.
2. In the PFD, insert a material stream called FT with the petroleum composition. To do so, carry out the following steps:
    2.1. In the *Fluid Pkgs* tab, select the Pen Robinson fluid package, and add the components that constitute the light ends.
    2.2. In the *Oil Manager* tab, click the *Enter Oil Environment* button.
    2.3. In the *Assay* tab, click the *Add* button to define a new *Assay*. In the *Input Data* tab, enter the available experimental data, which can be a TBP curve, an ASTM curve, or any type of curve accepted by HYSYS. Any additional data (e.g., *Bulk properties*) can be specified there, too. Click the *Calculate* button to determine the corresponding *Working Curves*. Close the *Assay* window.
    2.4. In the *Cut/Blend* tab, click the *Add* button to define a new *Blend*. In the *Data* tab, select the above defined assay. At this moment, several types of distillation curves, except the EFV one, can be generated in the *Property plot* tab. Besides, the cut distribution can be obtained in the *Distribution plot* tab. Close the *Blend* window.
    2.5. Finally, in the *Install Oil* tab, install a material stream, and call it FT. Click the *Return Basic Environment* button.
    2.6. Click the *Enter Simulation Environment* button.
3. In the stream FT, specify the following conditions: $P = 1$ atm, $T =$ the beginning temperature of the *Assay* curve, *Liq Vol Flow@Std Cond* = 100 m^3/h (the basis of calculation). At this moment, HYSYS can solve the stream, and it becomes blue.
4. To generate the EFV curve automatically, use the *Databook* tool. To do so, carry out the following steps:
    4.1. In the *Variables* tab, insert the variables *Temperature* and the *Phase Liquid Volume Flow STD (Vapour Phase)* belonging to FT.
    4.2. In the *Case Studies* tab, add a new case called "EFV curve." Select *Temperature* as the independent variable and *Phase Liquid Volume Flow STD (Vapor Phase)* as the dependent variable.
    4.3. Click the *View* button. In the *Independent Variables Setup*, specify the *Low Bound*, the *High Bound*, and the *Step Size* for *Temperature*. The following values are suggested: the bubble point temperature (HYSYS calculates this temperature when the *Vapor Fraction* of FT is set at 0) for *Low Bound*, the dew point temperature (HYSYS calculates this temperature when the *Vapour Fraction* of FT is set at 1) for *High Bound*, and (*High Bound–Low Bound*)/24 for *Step Size*.
    4.4. Click the *Start* button.

4.5. Once the calculation is completed, click the *Results* button and select *Table*. Copy the table (select it, and press Ctrl+C), or select *File/Print* to generate a text file.
5. Paste or import the data into a spreadsheet application (e.g., Microsoft Excel).
6. Plot the EFV curve.

Simulation with CHEMCAD

The complete procedure to create the EFV curve with CHEMCAD follows.

1. Start a new job.
2. Create a flowsheet as is shown in Figure 3. To do so, use the data provided in Table 2 and Table 3.
3. In the *Component List*, select the components that constitute the light ends.
4. Select *Peng-Robinson* both for *K-value* and *Enthalpy* options.
5. Define the stream 1 by entering the available distillation curve as follows:
    5.1. In the *ThermoPhysical* option, select *Distillation Curve*. The program will display a screen prompting *ID* numbers of streams to be characterized. Enter 1 to define the stream 1.
    5.2. Select the correlations to use for characterizing the distillation curve and for estimating the pseudocomponents properties. Select *Chemstations* for both *Molecular Weight Method* and *ASTM D86-TBP Interconversion Method*, and select *Lee Kesler* for *Critical Properties Method*.
    5.3. The next form will ask the *Curve Temperature Cut Range*. The range of the cut and the number of cuts determine the "width" of the boiling range for each pseudocomponent. For the first row, enter the beginning and ending temperature of the available curve, and 50 for *No_of_points*.
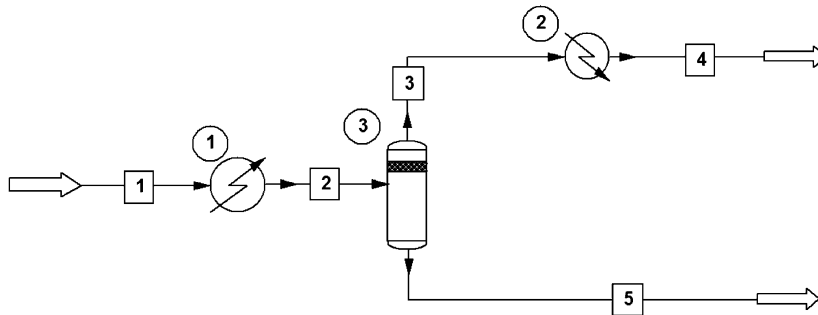

Figure 3. Flash laboratory equipment simulated with CHEMCAD.

Table 2. Unit operations for CHEMCAD

Name	Object type	Inputs
1	Heater	*Delta P* = 0
		Temperature of stream 2 = Desired temperature of equilibrium
2	Cooler	*Delta P* = 0
		Temperature of stream 4 = 15°C
3	Separator	

5.4. Select *Edit Curve Data* to enter the bulk properties for the whole material. Select *0) User specified* for *Distillation Curve*, and select the corresponding type for the original distillation curve (e.g., TBP, ASTM, etc.). If the density curve is not known, enter the corresponding *Bulk gravity*. Select *4) m³/hr* for *Selected total flow units*, and enter 100 for *Total flow rate* (the basis of calculation). A dialog box is now displayed for entering the experimental distillation curve. The next dialog box is for entering gravity versus volume percentage. If the bulk gravity is entered, the gravity curve is optional; however, if both the bulk gravity and gravity curve are provided, the program will adjust the gravity curve to match the bulk gravity.

5.5. Click on *Save and Exit* to start calculations.

6. In stream 1, specify the following conditions: $P = 1$ atm, $T = 15$°C. At this point, CHEMCAD can solve the stream. To do so, click the *Flash* button.

7. For the heater 1, enter the beginning temperature of the available curve for *Temperature of stream 2*.

8. For cooler 2, enter 15°C for *Temperature of stream 4*.

9. Verify the model by solving it (click *Run all*).

10. To generate all the points of the EFV curve automatically, use the *Sensitivity Study* tool. To do so, carry out the following steps:

Table 3. Streams for CHEMCAD

Name	Object type	Inputs
1	Material stream	Petroleum composition, $T = 15$°C, $P = 1$ atm, *Liq Vol Flow @Std Cond (m³/h)* = 100
2	Material stream	$T = $ Desired temperature of equilibrium
3	Material stream	
4	Material stream	$T = 15$°C
5	Material stream	

10.1. Select the *Sensitivity Study* option from the *Run* menu.

10.2. Select the *New Analysis* option.

10.3. Enter name "EFV curve" for the sensitivity analysis.

10.4. Click *Edit Independent Variable*, select *Equipment* option, specify 1 for *ID*, select *4 T Out Str 1* for *Variable*, type "Teq" for *Variable name*, and enter the beginning and ending temperature for *Vary this variable from/to*, and 24 for *equal steps*. As was suggested in the previous section, the bubble point temperature of stream 1 should be the beginning temperature, whereas its dew point temperature should be the ending temperature.

10.5. Click *Edit Recorded Variables*, select *Stream*, specify 4 for *ID*, select *7 Total std liq.* for *Variable*, type "Vol %" for *Variable name*, and select *29 Actual liq vol rate* for *Variable units*.

10.6. Click *Run All*. CHEMCAD generates the complete EFV curve.

10.7. To plot the EFV curve, click *Plot Results*, select "Teq" for the *Y axis*, and "Vol %" for the *X axis*.

11. Paste or import the data into a spreadsheet application (e.g., Microsoft Excel).

12. Plot the EFV curve again.

CASE STUDIES

Several types of petroleum were studied to evaluate the proposed method. Table 4 presents the characteristics for all the studied samples. A wide range of petroleum composition was selected for this evaluation. For the first three cases, the TBP curve was used to characterize the petroleum; while for the last two, the ASTM D86 was utilized. For all the cases, for enabling validation, the EFV curves were estimated by applying the Edmister and the Maxwell methods. Afterward, HYSYS and CHEMCAD were used to estimate the EFV curves by simulation. Figures 4 to 8 show the obtained curves for the samples of Table 4. For all the case, both for TBP and ASTM D86 curves, the EFV curves built by simulation are between those obtained by the Edmister and the Maxwell methods. However, in Sample 2, where crude oil is heavier than the others, the CHEMCAD curve shows a downward deviation, regarding

Table 4. Samples characteristics

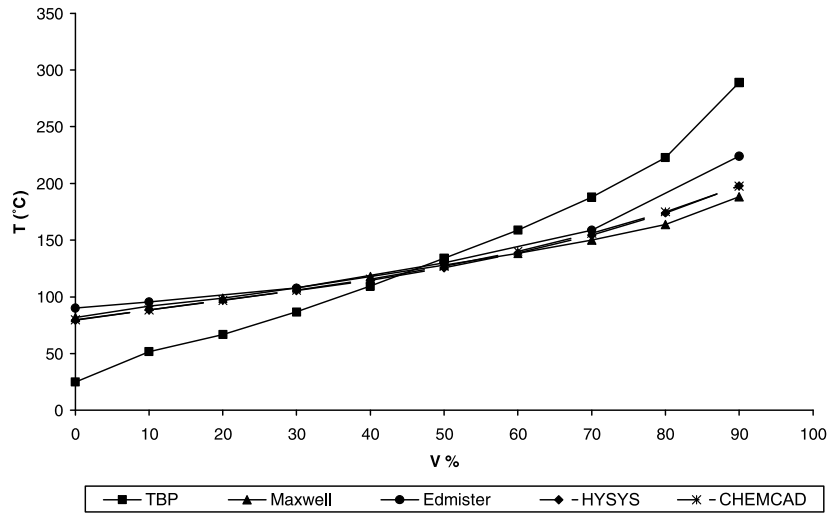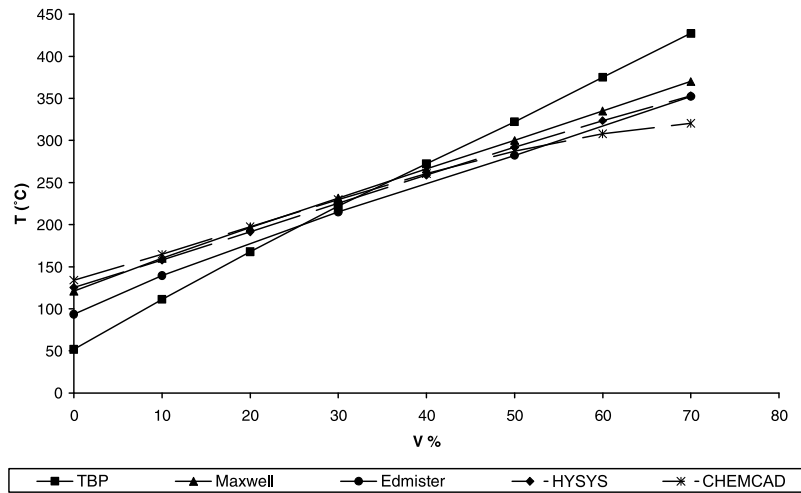| Sample	Experimental curve	Temperature range (°C)	$\rho^{15/15}$	Comment
1	TBP	25–289	0.80	Crude oil
2	TBP	61–461	0.84	Crude oil
3	TBP	58–88	0.76	Naphtha
4	ASTM D86	71–256	0.75	Crude oil
5	ASTM D86	56–358	0.75	Crude oil

Figure 4. Sample 1 curves.
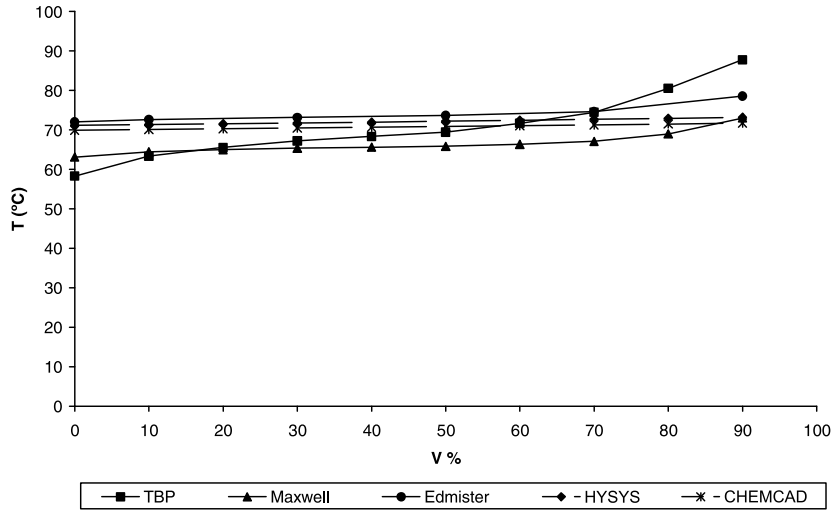

Figure 5. Sample 2 curves.

Figure 6. Sample 3 curves.
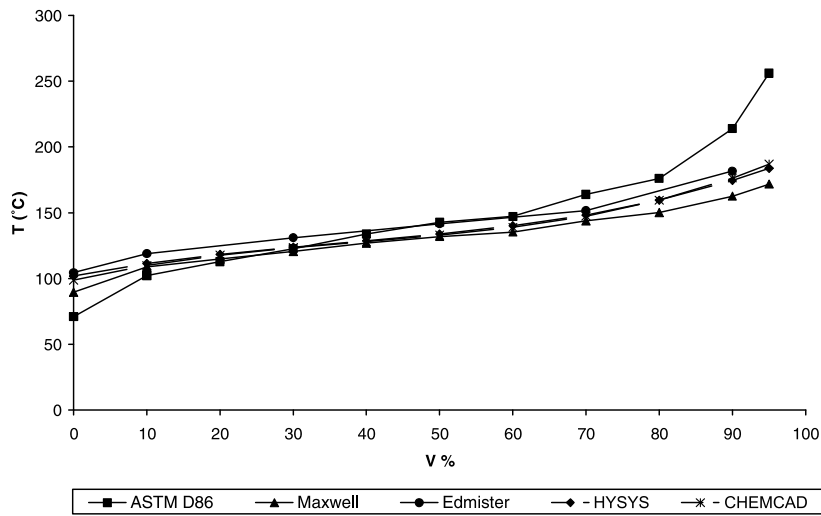

Figure 7. Sample 4 curves.

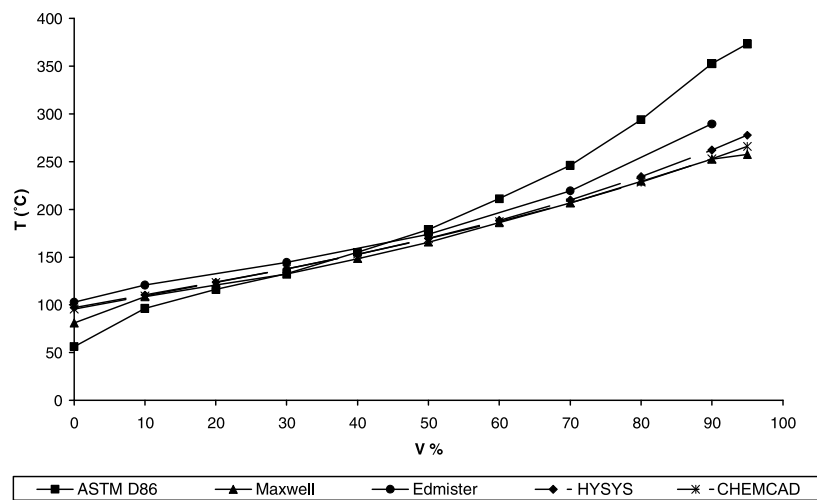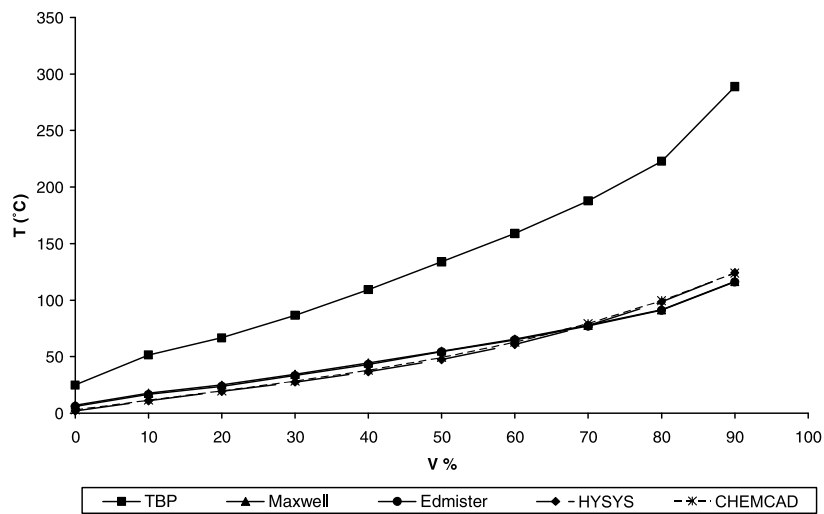***Figure 8.*** Sample 5 curves.

Figure 9. Sample 1 curves. Correction for pressure, $P = 50$ mmHg.

the other curves, for percentages of distilled liquid superior to 50%. Finally, Figure 9 shows the curves for Sample 1, for a pressure that is different from 1 atm. To obtain the curves by simulation, the new pressure value, $P = 50$ mmHg, was set into the model; no other modification was required. Again, the curves yielded by HYSYS and CHEMCAD are between those produced by Edmister and Maxwell methods corrected by pressure.

CONCLUSIONS

A new method for estimating the EFV curve by simulation was presented. HYSYS and CHEMCAD were used to implement the method, but it can be done with any other simulator. To evaluate the method performance, several types of samples were analyzed. For all of them, the EFV curves built by simulation were between those obtained by the Edmister and the Maxwell methods, two of the most used methods.

An important advantage of the proposed method is the petroleum characterization can be made with whatever type of data the simulator (e.g., TBP, ASTM D86 curves) admits; and regardless of what type of data is chosen, the estimation method remains the same. Another advantage is that the curves for different pressures can be obtained by setting the new pressure value into the model, and no further modification is required.

REFERENCES

Cerutti, A. A. (2002). La Refinación del petróleo—Tomo I. Buenos Aires, Argentina: *Ed. IAPG*.

Cohen, L. (2003). Diseño y simulación de procesos químicos (2nd ed.). Algeciras, Spain: *Editor León Cohen Mesonero* Sesur Artes Gráficas: Cádiz.

Edmister, W. C. (1961). Equilibrium flash vaporization correlations for petroleum fractions. In *Applied Hydrocarbon Thermodynamics*. Houston, TX: Editor: John J. Mckett Gulf Publishing, Vol 1., pp. 116–132.

Edmister, W. C., and Okamoto, K. K. (1959). Applied hydrocarbon thermodynamics, Part 12: Equilibrium flash vaporization correlations for petroleum fractions. *Petroleum Refiner* 8:117–129.

Maxwell, J. B. (1950). *Data Book on Hydrocarbons*. London, UK: D. van Nostrand.

Nelson, W. L. (1958). *Petroleum Refinery Engineering*. New York: McGraw-Hill.

Speight, J. G. (1998). *The Chemistry and Technology of Petroleum* (3rd ed.). New York: Marcel Dekker.

Watkins, R. N. (1981). *Petroleum Refinery Distillation* (2nd ed.). Houston, TX: Gulf Publishing.

Wuithier, P. (1971). *Refino y Tratamiento Químico: El petróleo*. Madrid, Spain: Cepsa S.A. and Marcel Dekker.