Journal of Thermal Analysis, Vol. 32 (1987) 1843–1854

AN INVESTIGATION OF THE EFFECTS OF PRESSURE AND TEMPERATURE ON THE VAPOURIZATION CHARACTERISTICS OF CRUDE OIL USING FIRST APPROXIMATION THERMAL ANALYSIS

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(Received September 3, 1986; in revised form April 16, 1987)

This study investigates the effect of pressure and temperature on crude oil vaporization using first approximation thermal analysis. Developed here is a technique for quantifying the vaporization of fractions of a crude oil using an experimentally obtained thermogravimetric (TG) curve of the crude.

The initial data utilized is the weight loss versus temperature values at atmospheric pressure, together with physical property data and equilibrium constant, k values.

The results of this study allow the estimation of the volume of oil distilled underground when steam is injected into oil reservoirs at varying pressures and temperatures to recover crude oil.

Crude oil vaporization has been the subject of only a few research investigations despite its importance to a number of phenomena occurring in the displacement of oil by thermal recovery techniques. The work of William et al. [1] and Rhee and Doscher [2] showed that crude oil vaporization functions as an important recovery mechanism within a zone occupied by steam during displacement of oil. In the method of William for determining the areal advancement of the steam zone during continuous steam injection, the quantity of distillable products being displaced by steam must be known before an overall oil recovery factor can be determined.

The model presented by Satter and Parrish [3] describes two-dimensional heat loss in the steam zone and a phase change of steam, however, the model has omitted the important phenomena of the change of phase of the oil when contacted by steam at varying temperature and pressures.

Numerous other authors [4–7] have emphasized the important role played by crude oil vaporization and have indicated the need for incorporating the phenomena into mathematical models used for predicting oil recovery by steam injection.

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Akadémiai Kiadó, Budapest

However, although a need for quantifying crude oil vaporization as a function of temperature and pressure has been identified, obtaining such data should be accomplished with regard for speed, reliability and reproducibility of data thereof.

This study presents a method of obtaining vaporization characteristics of crude oil which satisfies these conditions and in addition, presents the information in a form which may be incorporated into any mathematical simulator or model which requires a numerical value of crude oil vaporized under varying steam and reservoir conditions.

The first approximation thermal analysis presents a general but useful technique of pseudo components to quantify vaporization characteristics at atmospheric conditions. The use of equilibrium constants for hydrocarbons up to C_{20} additionally shows the value of first approximation of pseudo components in obtaining vaporization data at simulated steam conditions in the reservoir.

Equipment used for analysis

Equipment used in this study consisted of a DuPont 951 Thermogravimetric Analyser (TGA) controlled by 1090B Programmer and a Hewlett Packard 7470A Plotter.

The 951 TGA unit is capable of constantly measuring the amount and rate of weight change of material, either as a function of increasing temperature or time or isothermally as a function of time. Used with the 1090B Programmer, it has a temperature range from ambient to 1500° at selected heating rates in multiples of 1, 2 and 5, starting from 0.2 deg per minute.

In this system the desired gas can be purged through the cell chamber (not through the sample).

Development of analytical methods

The sample size of approximately 20 mg was prepared and transferred to the sample pan. To maintain equilibrium conditions between the vapour and the liquid present on the sample pan during heating, an inert atmosphere of nitrogen was used and which remained stagnant during the analysis. The mouth of the TG chamber which contained the sample pan with sample was opened to the atmosphere, however, nitrogen was kept circulated at this location to prevent air re-entering the chamber and possibly contaminating the sample causing oxidation. A very low heating rate of 1 deg per minute was employed to heat from ambient to maximum steam temperatures used in reservoirs of about 300°. This low heating rate allowed minimum temperature gradients to be set up in the sample being analyzed. In this way vaporization data was obtained from a sample at thermal equilibrium.

Effect of nitrogen on TG curves

Figure 1 illustrates the effect of nitrogen on the crude oil thermal curve. The appearance of two peaks in the derivative curve on this figure is an indication of two different mechanisms causing loss of mass when crude oil is heated in the presence of stagnant nitrogen. The first peak of ambient to around 400° is primarily distillation and the second peak between 400 to 500° is a combination of distillation and thermal cracking. A small residue of around 6 per cent remained in the pan even after heating to above 600°.

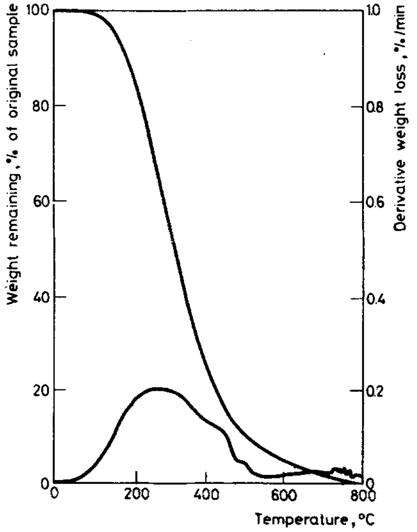

Fig. 1 TG/DTG curve for crude oil. Heating rate 1 deg/min

These phenomena were verified by the technique of gas-liquid chromatography. The effluent of the TG cell was connected to the GLC so that some knowledge may be had of the distillable components. The analysis of the chromatograph indicated a continual increase in hydrocarbon number in the effluent components with an increase in temperature up to approximately 350°. After this temperature it was noticed that there was a significant increase in the effluent components having relatively low carbon numbers and a corresponding reduction in the components having carbon numbers of C_5 and higher. This led to the conclusion that the change in trend of the DTG curve of Figure 1 at 360° was in fact due to the completion of the distillation regime and the onset of the cracking of heavier non-distillable hydrocarbons into lighter hydrocarbons.

Analysis and synthesis of laboratory data

Further study of Figure 1 indicates that 70 percent of total crude sample represents 100 per cent of the total vaporizable components at atmospheric pressure. Figure 1 also shows that vaporization is essentially complete at 370°.

Table 1 shows the normalized values of weight of crude oil distilled which were determined from the value of weight distilled from Figure 1 up to a temperature of 370°. Normalization was important, as a distillation curve had to be the starting

Table 1 Normalized weight loss

Temperature, °C	Actual weight vapourized, %	Normalized weight vapourized, %
50	0	0
100	1.5	2.1
150	5.3	7.5
200	18.0	25.7
250	35.5	50.7
300	51.3	73.2
350	65.6	93.7
370	70.0	100.0

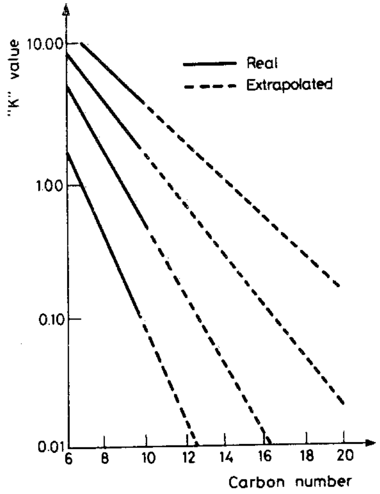

Fig. 2 Extrapolated "*K*" values at atmospheric pressure.

point of this technique which is to be used as the first approximation to the number of components contained in the crude oil sample and which can be distilled.

Crude oils may be categorized within three basic types: paraffinic, naphthenic and asphaltenic. The results of DSC experiments in Table 2 indicated that there was no significant variations in heats of distillation for the three classes of crude oils. A statistical variability analysis conducted on heats of distillation of oil samples showed that there was no evidence to conclude that crude oils of paraffinic composition will not distil in a similar manner to crude oils of any other composition.

Table 2 Heats of distillation of various crude types

Heat of distillation, J/g	Type of crude oil
441	Paraffinic
446	Paraffinic
448	Paraffinic
439	Paraffinic
447	Naphthenic
438	Naphthenic
450	Naphthenic
440	Naphthenic
441	Naphthenic
437	Asphaltenic
445	Asphaltenic
441	Asphaltenic
448	Asphaltenic

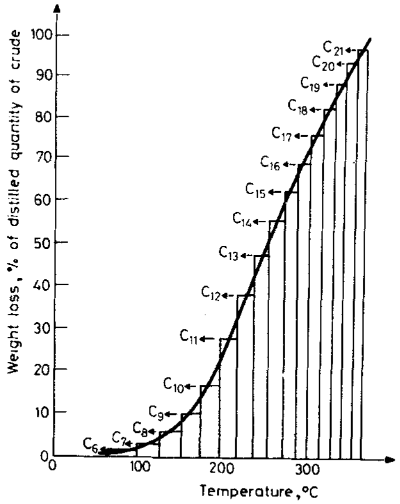

Fig. 3 Normalized weight loss curve and estimate of pseudocomponents

The 'k' values for paraffins are more widely published than its counterparts and thus were used in preference to the 'k' values of other classes of hydrocarbons.

Figure 3 demonstrates the process by which the distillation curve was used to determine the pseudocomponents of the crude oil distillate. The abscissa represents a temperature scale which has been sub-divided into the boiling regions of paraffinic pseudocomponents varying from C_6 to C_{22}. The ordinate represents the percentage by weight of each pseudocomponent which has been distilled within the boiling region of each component.

Table 3 gives the pseudocomponents and their respective percentages by weight which have been vaporized based on this present technique. It has been assumed that each component will distill between its boiling point and the boiling point of the next component in the paraffinic homologous series.

Table 3 Pseudocomponents estimate of crude oil

Component	Cumulative. weight loss, %	Component weight loss, %	Component mole fraction, %
C_6	1.4	1.4	3.1
C_7	3.1	1.7	3.2
C_8	7.2	4.1	6.9
C_9	9-7	2.5	3.7
C_{10}	16.6	6.9	9.3
C_{11}	28.0	11.4	14.0
C_{12}	39.0	11.0	12.4
C_{13}	48.0	9.0	9.3
C_{14}	56.0	8.0	7.7
C_{15}	63.5	7.5	6.8
C_{16}	70.0	6.5	5.4
C_{17}	76.5	6.5	5.1
C_{18}	83.0	7.5	4.8
C_{19}	89.0	6.0	3.4
C_{20}	94.0	5.0	2.7
C_{21}	98.0	4.9	2.1
C_{22}	100.0	2.0	0.1

Determination of distillation from equilibrium *k* values and pseudocomponents

Mole percent of component in crude oil

The k values used in this study was taken from the NGPA Charts published by Gas Process Association, Tulsa (1957). These k values are only given for C_1 to C_{10}, however, because the technique required pseudocomponents up to C_{22}, k values were required for the C_1 to C_{22} fractions. A semilog plot was made of k values versus carbon number (C_n) for all the temperatures and pressures being considered. Therefore, subsequent extrapolation of the k versus C_n curves yielded approximate k values for the paraffinic pseudocomponents C_{11}–C_{22}.

A total of forty-two sets of 'k' values were obtained by extrapolation which are too numerous to be presented in this study. However, Figure 2 shows a sample extrapolation of those values for atmospheric pressure.

Table 3 shows the mole percentage of each pseudocomponent in crude oil which was determined by the use of Figure 3. In subsequent calculations, for simplification, one mole of starting crude oil will be used as a basis.

Mole percent of each pseudocomponent in liquid and vapour phases

For pressures at which vaporization of an oil sample occurs, both liquid and vapour are present in finite quantities. The determination of the composition of the liquid and the vapor in such a multicomponent system is complex and involves iterative flash calculations for each i^{th} component.

$$z_i M_s = X_i M_1 + Y_i M_v \tag{1}$$

Applying Raoult's Law and Dalton'w Law to the i^{th} pseudocomponents and employing a necessary empirical correction for non-ideal solution, Equation (2) is obtained

$$Y_i = k_i X_i \tag{2}$$

A combination of Equations (1) and (2) gives Equations (3) and (4) from which the composition of the liquid and the vapour in a non-ideal multicomponent system may be determined by an iterative process.

For this iterative process, values of M_1 and M_v are assumed and the required summation of molar values at the temperature and pressure in question is carried out. If the summation value does not equal unity, then a second value M_1 and M_v is assumed and the computation repeated until a value of unity is obtained.

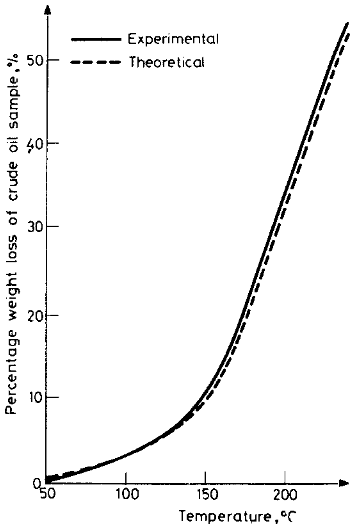

Fig. 4 Comparison of experimental & theoretical TG curves at atmospheric pressure.

Having obtained the number of moles of each pseudocomponent in the liquid and vapour phases at atmospheric pressure as a function of temperature, then the theoretical TG curve may be constructed. This constructed TG curve is given in Figure 4 together with the experimental curve

$$X_i = \frac{z_i M_s}{M_1 + k_i M_v} \tag{3}$$

$$Y_i = \frac{X_i M_s}{\left(\frac{M_l}{k_i} + M_v\right)} \tag{4}$$

Generation of weight loss curves at elevated pressures

The use of Equation (4) makes it possible to determine the weight percent of crude oil in the vapour phase at any temperature and pressure since k_i is a function of both temperature and pressure. In addition, the weight fraction vaporized at any pressure and temperature is given by the use of the value of M_v. These values of M_v for specified temperatures and pressures were calculated utilizing the corresponding k values and the iterative technique in X_i and Y_i. These values of M_v were used to generate six weight loss curves for pressures of atmospheric, 3.4×10^2, 6.9×10^2, 1.4×10^3, 6.9×10^3, and 1.4×10^4 kPa.

Results and discussion of results

The generated thermal curves resulting from this study are shown in Figures 5 and 6. The family of curves in Figure 5 gives the weight of crude oil in vapor phase while those of Figure 6 gives the weight of crude oil in the liquid phase over the temperature range. These two figures demonstrate the effect of pressure on the weight loss characteristics of crude oil.

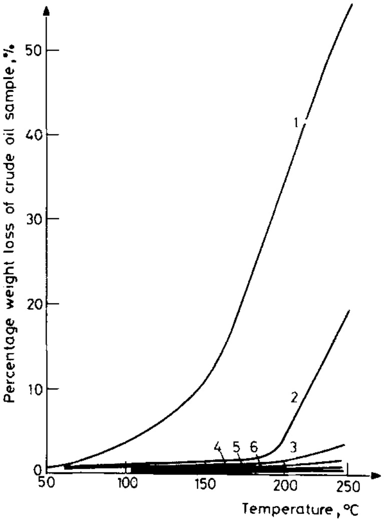

Fig. 5 Theoretical weight loss thermal curves at various pressures. 1) Atmospheric pressure, 2) 3.4×10^2 kPa, 3) 6.9×10^2 kPa, 4) 1.4×10^3 kPa, 5) 6.9×10^3 kPa, 6) 1.4×10^4 kPa

The generated percent weight loss values for atmospheric pressure compared very favourably with the experimentally determined values of the TG differing by less than 10%. This low deviation demonstrates the accuracy of this first approximation technique and subsequently ensures reliability of the procedure and of the method of generating pseudocomponents of the crude oil sample. The subsequent use of the generated pseudocomponents made it possible to derive high pressure weight loss curves with a high degree of confidence in the final results obtained.

The generated thermal curves given in Figures 5 and 6 demonstrate that an

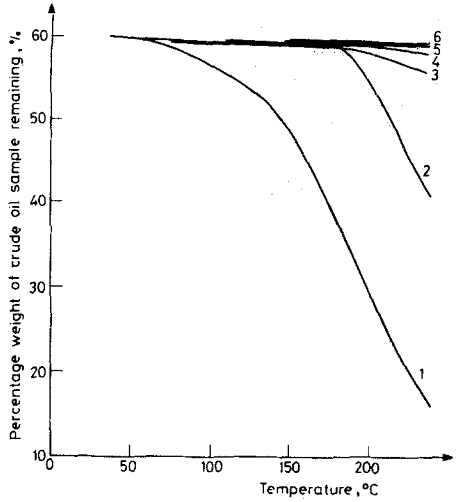

Fig. 6 Theoretical liquid remaining curves at varying pressures. 1) Atmospheric pressure, 2) 3.4×10^2 kPa, 3) $6.9 \times 10^{\ 2}$ kPa, 4) 1.4×10^3 kPa, 5) 6.9×10^3 kPa, 6) 1.4×10^4 kPa

increase in system pressure results in a decrease in the quantity of crude oil distilled. Careful scrutiny of these curves shows that an increase in pressure from atmospheric to 3.4×10^2 kPa causes a marked decrease in the quantity of oil vaporized. In addition, increases in reservoir pressure from 3.4×10^2 kPa and further to 1.4×10^3 kPa also results in decreases in vaporization, however, the decrease is less severe in each case. The curves at 1.4×10^3 and 1.4×10^4 kPa are very similar, differing by only 0.75% at a temperature of 260°.

From ambient temperature to 215° these thermal curves are visibly inseparable and represents a constant weight percentage loss of approximately 0.8%. This small quantity of vaporization which takes place at reservoir pressures above 1.4×10^3 kPa, should not be viewed as insignificant, as they may represent small fractions of some potentially large reservoir fluid contents resulting in a significant vapor pressure, solvent drive effect and therefore incremental oil production.

The high pressure thermal curves generated by this present study facilitates a direct alternative to the calculation of vaporized oil in the model of Johnson et al. [7] by providing direct plots of percent oil vaporized as a function of steam temperatures and pressures. The vaporized oil can also be subsequently expressed as a percentage of the immobile oil left by the passage of the hot-water preceeding the steam zone.

Further research into the application of the generated thermal curves of Figures 5 and 6 involves the use of the quantity of vaporized oil determined by these curves to increase the reservoir vapor pressure and the subsequent increase in oil production.

Limitations of the TG first approximation technique

A major limitation of this technique is the range of temperature operation. Temperatures considered must not exceed 260° (500 °F) since extrapolation of k values above this temperatures does not ensure accuracy and reliability of the final results obtained.

The assumption of equilibrium cannot be overlooked. The conditions under which the TGA is operated allows a very small sample (20 mg) to be heated in a platinum pan contained in a chamber approximately 100 cm^3 in volume. It is difficult to ensure equilibrium of vapor with liquid when this ratio of liquid to vapor volume is of the order of that used in this study.

Finally, as the results are being used to ultimately apply to petroleum reservoirs, distillation data should be obtained from heating crude oil in a sample of the porous media representing the reservoir. As distillation rates increase with surface area some deviation of this approach with that used in the study is expected.

Conclusion

1. A technique has been developed whereby a thermogravimetric analysis carried out on a crude oil can be used to estimate the pseudocomponents content therein.
2. The theoretically obtained thermal curves indicated that an increase in pressure results in a decrease in the quantity of crude oil vaporized for a given temperature.
3. This first approximation thermal curve at atmospheric pressure may be used to generate subsequent weight loss curves at elevated pressures over the temperature range, ambient to 260°. These weight loss curves (thermograms) predicted the quantity of crude oil vaporized as functions of temperature and pressure.

References

1. E. T. William, V. V. Valleroy, C. W. Rumberg, A. J. Cornelius and L. W. Powers, J. Pet. Tech., (July 1961) 681.
2. S. W. Rhee and T. M. Doscher, SPE J., (Aug. 1980) 249.
3. A. Satter and D. R. Parrish, SPE J., (June 1971) 185.
4. Chieh Chu, SPE J., (June 1964) 85.
5. A. B. Cook, R. H. Coulter and G. B. Spencer, A Rotating Model Oil Reservoir for simulating Gas Cycling Operations, RI 5478, USMB (1959).
6. A. N. Cook, C. J. Walker and G. B. Spencer, J. Pet. Tech., (July 1969) 901.
7. F. S. Johnson, C. J. Walker and A. R. Bayazeed, J. Pet. Tech., (June 1971) 731.

Nomenclature

C — Symbol of the element, carbon
k — Equilibrium constant measuring the mole fraction of component in vapor divided by the mole fraction in liquid
M — Number of moles
X — Mole fraction in liquid
Y — Mole fraction in vapor
z — Total molar fraction

Subscripts

i — Specific component
l — Liquid
n — Number of carbon atoms
s — Sample
v — Vapor

Zusammenfassung — Diese Studie untersucht in erster Näherung mittels Thermoanalyse den Einfluß von Temperatur und Druck auf das Verdampfen von Rohöl. Es wird eine Methode zur quantitativen Bestimmung des Verdampfens von Rohölfraktionen entwickelt, die auf einer experimentell ermittelten thermogravimetrischen (TG) Kurve des Rohstoffes basiert. Als Anfangswerte werden die von der Temperatur abhängige Massenabnahme (unter Normaldruck) zusmmmen mit physikalischen Eigenschaften und der Gleichgewichtskonstante k verwendet. Die Ergebnisse dieser Untersuchung erlauben das Abschätzen des Umfanges des Öldestillationsrückstandes, insofern zur Gewinnung des Rohöls Dampf in die Ölreservoir injeziert wird.

Резюме — Используя первое приближение термического анализа, изучено влияние давления и температуры на испрание сырой нефти. Исходя из экспериментально полученной ТГ кривой сырок нефти, разработан метод количественного испарения отдельных фракций сырой нефти. Исходным данными были потеря веса при атмосферном давлении в зависимости от температуры, совместно с данными некоторых физических свойств и константой равновесия, значениями *к*. Результаты проведенного исследования позволяют определять объем очищенной подземной нефти при нагнетании пара в нефтяные скважины при различном давлении и температуре с целью извлечения сырой нефти.