

EVAPORATION RATE OF SPILLS OF HYDROCARBONS AND PETROLEUM MIXTURES

by

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ABSTRACT

For assessing the behavior of oil spills in Arctic regions it is essential to have the capability of calculating the oil's evaporation rate. In this report procedures are described for quantifying the rate of environmental evaporation of liquid mixtures such as crude oils and petroleum products under a variety of environmental conditions. Equations are derived from mass transfer theory which relate the fraction evaporated to an evaporative exposure and a Henry's Law Constant. The dimensionless evaporative exposure characterizes the exposure conditions of atmospheric turbulence, spill volume and area. The dimensionless Henry's Law Constant is a function of the liquid composition, temperature and of the fraction of liquid which has evaporated. Experimental procedures are described for measuring evaporation characteristics of a liquid mixture and for producing samples of partially evaporated material.

Note: A paper based on this work has been submitted to Environmental Science and Technology for publication.

Résumé

Pour évaluer le comportement des nappes d'hydrocarbures dans les régions arctiques, il faut pouvoir en calculer la vitesse d'évaporation. Le présent rapport décrit comment mesurer la vitesse d'évaporation de mélanges liquides, tels que les bruts et les produits pétroliers, dans diverses conditions. Les équations s'obtiennent de la théorie de transfert des masses et établissent une relation entre la fraction évaporée et un terme, sans dimension, qui caractérise les conditions d'exposition (turbulence atmosphérique, volume et superficie de la nappe) ainsi qu'une constante de la loi de Henry. Cette constante, elle aussi sans dimension, y est une fonction de la composition du liquide, de sa température et de la fraction du liquide qui s'est évaporée. Le rapport décrit les manipulations qui permettent de mesurer les caractéristiques d'évaporation d'un mélange liquide et d'obtenir des échantillons de matière partiellement évaporée.

Remarque: Une communication basée sur le présent travail a été soumise à
Environmental Science and Technology.

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CONCLUSIONS AND RECOMMENDATIONS

The theoretical background for quantifying evaporation rates of crude oils has been developed and related to three experimental techniques, tray evaporation, gas stripping and distillation. The concept of a dimensionless evaporative exposure has been devised. The evaporative exposures provides characterization of environmental or laboratory exposure conditions. It incorporates the oils' area and volume, the prevailing wind speed and the time of exposure. Experimental procedures to obtain fraction evaporated as a function of evaporative exposure have been discussed. A synthetic oil was used to verify the evaporative behaviour of these experiments. Crude oils were studied and a correlation was developed to predict the oil's evaporation curve from its distillation curve. The gas stripping and tray evaporation techniques are ideal for measuring the evaporation rates of crude oils and for producing weathered samples of crude oil. The distillation technique can be used for the prediction of the evaporation curve only, in general it should not be used for producing samples.

It is recommended that several Arctic oils be subjected to evaporative behavior determination as described in this report. It may also be useful to extend this work to evaporation of chemical spills.

Acknowledgements

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INTRODUCTION

When crude oils are spilled on land or water, evaporation is often a significant process of mass loss from the spill. Thus, a knowledge of the evaporation rate can be useful in several respects. For example, the evaporation rate controls the atmospheric vapor concentration and hence the threat of toxic exposure to those in the vicinity. Evaporation may modify the physical, chemical and toxicological properties of the liquid, notably density, viscosity and the fraction of lower molecular weight substances.

There have been several reports describing the evaporation behavior of spills. Reviews have been compiled by, for example, NAS (1), Malins (2), and Jordan and Payne (3) and attempts have been made to develop expressions quantifying evaporation rates, notably those of Yang and Wang (4), Butler (5), Sivadier and Mikolaj (6), Mackay and Leinonen (7), Mackay and Matsugu (8), Mackay et al (9, 10), Reijnhart and Rose (11), Payne et al. (12), Drivas (13) and Feigley (14). None of these approaches is completely satisfactory in enabling evaporation rates to be calculated from easily measured experimental properties and being applicable to a wide variety of oils and environmental conditions.

This paper reviews the thermodynamic and kinetic parameters which influence oil evaporation rates. Experimental procedures are presented which can be used to determine evaporation properties, thus providing a basis for calculating evaporation rates under a variety of environmental conditions. The work starts with the simple case of describing the evaporation characteristics of a pure liquid, and then extending the description to include evaporation of multi-component systems. In doing so, the concept of a dimensionless

"evaporative exposure" is introduced as a criterion for determining extent of evaporation.

The difficulty with multi-component systems is primarily that of expressing the liquid's vapor pressure as a function of its changing composition. As a liquid evaporates the more volatile materials are lost preferentially and the mixture's total vapor pressure falls. There are two approaches for calculating the changing vapor pressure:- the pseudo-component approach used by Yang and Wang (4), Mackay and Leinonen (7), Reijnders and Rose (11) and Payne et al. (12); or an analytical expression in which the vapor pressure is expressed as a function of fraction evaporated, as used by Mackay et al. (9). In the pseudo-component approach, a number of real or pseudo-components are selected with relative quantities such that they reproduce the oil's evaporation or distillation characteristics. The amounts can be obtained by trial and error; however, guidance can be obtained from gas chromatographic analysis. A disadvantage of the pseudo-component approach is that while calculating evaporation rates, it is essential to compute and store the change in composition. The analytical approach, on the other hand, permits easier calculations; however, this may be at the expense of less accuracy. This work investigates the analytical approach.

It is first useful to review the experimental methods which can be used to obtain information about volatility.

EXPERIMENTAL CONFIGURATIONS

The evaporation characteristics for a mixture may be obtained under two limiting experimental conditions, isothermal, non-isobaric conditions, and isobaric, non-isothermal conditions. Figure 1 illustrates the configurations.

In isothermal systems, there are two limiting cases depending on how the oil is exposed to evaporation and how the evaporated vapors are removed. Surface or tray evaporation in, for example, a constant temperature wind tunnel is controlled by the mass transfer rate limitation at the liquid surface and the air leaving the system is far from saturated with oil vapor. A typical evaporation rate curve is illustrated in Figure 1. An alternative is equilibrium control in which the liquid is contacted with a slow flow of air, such that the air leaving the system is fully saturated with oil vapor, by for example bubbling air through a column of the oil. The evaporation rate is then controlled entirely by the flowrate of air through the system and mass transfer rates are unimportant. A curve similar to Figure 1 is obtained.

An example of isobaric system is the familiar boiling point versus fraction distilled curve shown in Figure 1. As the mixture evaporates the temperature rises to the "bubble point" temperature at which it exerts a constant vapor pressure, normally atmospheric pressure. Kinetic considerations are irrelevant in this system since the rate of composition change is determined by the rate of heat supply, and the temperatures achieved are dependent on composition and independent of time.

A primary objective in this work is to establish theoretical links between the data obtained from the distillation, tray evaporation and air bubbling configurations and show how data can be used to calculate environmental evaporation rates.

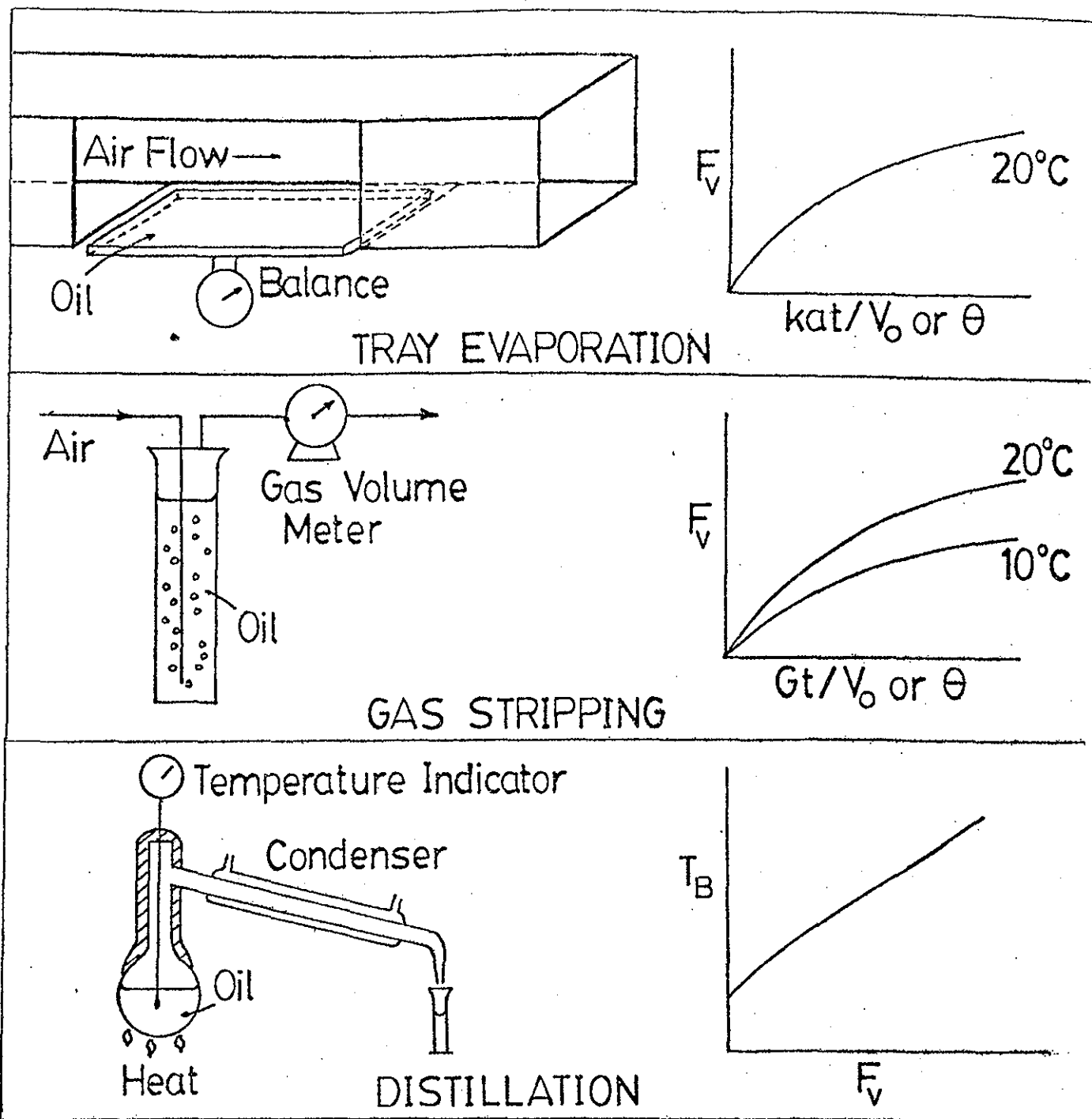


Figure 1. Evaporation configurations

THEORETICAL

Surface Evaporation

If a liquid, of vapor pressure $P(\text{Pa})$, is spilled over an area of $a (\text{m}^2)$, the rate of evaporation is given by:-

$$N = kaP/RT \quad (1)$$

where N is the molar flux (mol/s), k is the mass transfer coefficient under the prevailing wind conditions (m/s), R is the gas constant ($8.314 \text{ Pa}\cdot\text{m}^3/\text{mol}\cdot\text{K}$) and T is the environmental temperature (K). Equation (1) can be arranged to give:-

$$dF_v/dt = kaPv/V_oRT \quad (2)$$

Where F_v is the volume fraction evaporated, t is time(s), v is the liquid's molar volume (m^3/mol) and V_o is the initial volume of spilled liquid (m^3). Rearranging gives

$$dF_v = (Pv/RT) (kadt/V_o) \quad (3)$$

$$\text{or } dF_v = H \cdot d\theta \quad (4)$$

The right hand side of equation (3) has been separated into two dimensionless groups. The group (kat/V_o) , is termed the "evaporative exposure" and is denoted as θ . The evaporative exposure is a function of time, the spill area and volume (or thickness) and the mass transfer coefficient (which is dependent on the wind speed). The evaporative exposure can be viewed as the ratio of exposed vapor volume to the initial liquid volume.

The group (Pv/RT) or H is a dimensionless Henry's Law constant or ratio of the equilibrium concentration of the substance in the vapor phase (P/RT) to that in the liquid ($1/v$). It is a function of temperature but not of other environmental conditions.

The product θH is thus the ratio of the amount which has evaporated (oil concentration in vapor times vapor volume) to the amount originally present.

If the liquid is pure, H is independent of F_v and equation (4) can be integrated directly to give

$$F_v = H\theta \quad (5)$$

If k , a and temperature are constant, the evaporation rate is constant and evaporation is complete (F_v is unity) when θ achieves a value of $(1/H)$.

If the liquid is a mixture, H depends on F_v and equation 4 can only be integrated if H is expressed as a function of F_v , i.e. the principal variable of vapor pressure is expressed as a function of composition. The evaporation rate slows as evaporation proceeds in such cases.

Stripping

The second approach is to use a gas stripping technique with an exit gas rate $G(\text{m}^3/\text{s})$. If the exit gas is saturated, the evaporation rate will be (GP/RT) mol/s and

$$dF_v/dt = (GP/RT)(v/V_o) \quad (6)$$

$$\text{or } dF_v = H d\theta \quad (7)$$

The evaporative exposure θ is now defined as Gt/V_o and is the actual ratio of vapor volume to liquid volume.

The identical nature of Equations 4 and 7 suggest that if surface (tray) and stripping experimental data are plotted as F_v versus θ the points should lie on a common line, θ being defined either as kat/V_o or Gt/V_o . This is later verified experimentally.

Distillation

In principle, if enthalpy of vaporization (Δh) data are available it is possible to convert a boiling point to a vapor pressure at a lower temperature. Thus a plot of boiling point T_B as a function of F_v could be converted into a plot of vapor pressure P as a function of F_v . This would permit the calculation of H versus F_v and hence preparation of a plot of F_v versus θ . Unfortunately Δh is not always known and it varies with temperature and composition. There is also doubt about the changing molar volume. These difficulties require the use of an empirical expression relating H to T_B . The form of this expression is suggested by the Clapeyron-Clausius relationship and Trouton's Rule, which in combination give

$$\ln(P/P_A) = 10.6 (1 - T_B/T) \quad (8)$$

where P_A is atmospheric pressure (101325 Pa) at which the boiling point is measured, and P is the vapor pressure at the environmental temperature T (K). It follows that H (which equals Pv/RT) can be expressed as

$$\ln H = \ln(P_A v/RT) + 10.6 - 10.6 T_B/T \quad (9)$$

$$= A - BT_B/T \quad (10)$$

where A and B are dimensionless constants which can be obtained by fitting experimental data.

Now, the distillation data yields an equation relating F_v to T_B which in its simplest form could be

$$T_B = T_0 + T_G F_v \quad (11)$$

where T_0 is the initial boiling point at F_v of zero, and T_G is the gradient of the T_B, F_v line. Other more complex equations could be fitted but only this simple equation is considered here. Combining equations 7, 10 and 11 gives

$$dF_v = \exp [A - B(T_0 + T_G F_v)/T] d\theta \quad (12)$$

which can be integrated to give

$$F_v = \ln[1 + B(T_G/T)\theta \exp(A - B T_0/T)] [T/BT_G] \quad (13)$$

This equation can be used to calculate the F_v versus θ curve from the distillation curve, if estimates of A and B are available.

In summary, the key characterization of a liquid's evaporative behavior is a plot of F_v versus θ , different lines applying at different temperatures, because of the dependence of P , and hence H , on temperature. These curves may be obtained from wind tunnel or gas stripping experiments or (if A and B are known) from the boiling point curve. If environmental estimates are available for the mass transfer coefficient k and the spill initial thickness (V_0/a) it is then possible to calculate θ at any time and thus estimate F_v . If the spill thickness or k change with time it is necessary to calculate F_v by analytical or numerical integration. For oil spill models in which other processes are occurring simultaneously it is normally preferable to use a finite difference form of equation, namely.

$$\Delta F_v = \exp[A - B(T_0 + T_G F_v)/T] (ka\Delta t/V_0) \quad (14)$$

$$= H ka\Delta t/V_0 \quad (15)$$

It may be desirable to obtain an equation to fit the experimentally determined $F_v - \theta$ evaporation curve. The form of this curve fit is suggested by the distillation expression (Equation 13).

$$F_v = (T/K_1) \ln(1 + K_1\theta/T) \exp(k_2 - k_3/T) \quad (16)$$

A value for K_1 can be obtained from the slope of the F_v versus $\log \theta$ curve. For θ greater than $10^4 K_1$ is approximately $2.3T$ divided by the slope. The expression $\exp(k_2 - k_3/T)$ can then be calculated and K_2 and K_3 may be determined individually from evaporation curves at two different temperatures.

EXPERIMENTAL

The evaporation characteristics of five crude oils and one synthetic oil were studied. The crude oils used were Norman Wells, La Rosa, Murban, Lago Medio and Prudhoe Bay. The synthetic oil was a mixture of n-alkanes, the mole fraction composition being pentane 0.130, hexane 0.087, heptane 0.104, octane 0.071, decane 0.084, undecane 0.045, dodecane 0.086, tridecane 0.042, tetradecane 0.108, hexadecane 0.107, octadecane 0.048 and eicosane 0.050.

The procedures for weathering the crude and synthetic oils were the same, however, during the synthetic oil runs frequent samples were taken for analysis by gas chromatography.

Samples (0.5 μ L) were analysed using a Hewlett-Packard Model-700 gas chromatograph. The column was 3m long, 0.125 inch O.D stainless steel, coated with 10% SE-30 ultraphase on chromosorb P, A/W, DMCS, mesh 60/80. The injection port temperature was 300°C. The oven started at 50°C and was temperature programmed at 7.5°C/min to a maximum temperature of 280°C. A Shimadzu Model C-RIA integrating recorder was used.

Tray Evaporation

A volume of oil was weighed and placed on to a tray (area 0.082 m²) to obtain a slick thickness of 1 to 5mm. The tray was then placed into a wind tunnel, and subjected to wind speeds between 4 and 12 m/s. The mass transfer coefficient for the various wind speeds was measured separately by toluene evaporation. The mass of the toluene or oil was measured as a function of time using an in situ top loading balance. The length of the experiments varied from six hours to two weeks. During the synthetic oil runs the samples

taken were used for density measurement by pycnometer as well as for GC analysis.

Thin-Film Tray Evaporation

A small volume (1mL) of weathered oil was pipetted onto a small circular tray (area 64cm²). This oil was then spread over the tray using a spatula to obtain a uniform thin-film. The spatula was weighed before and after to account for the oil sticking to its surface. The tray was then clamped into the wind tunnel and subjected to wind speeds of between 4 and 12 m/s. The mass of the tray was measured as a function of time, but in this case a separate analytical balance was used. The runs lasted approximately 7 days.

Gas Stripping

The apparatus is shown in Figure 2. Either a 250 mL or a 1L graduated cylinder was used. The gas trap was loosely packed with 3M sorbent and placed in an ice bath. A integrating wet test meter was used to measure the cumulative air flow. For experiments at other than room temperature a water bath ($\pm 2C^{\circ}$) was used for both the graduated cylinder and the air feed.

The graduated cylinder was filled with the oil. The mass of the cylinder before and after as well as the volume of the oil were recorded. Air was then bubbled through the oil taking care to prevent liquid entrainment. Periodically, the air flow was stopped and measurements made of the mass and volume of oil as well as the volume of air passed through the oil. Before recording the volume of oil sufficient time was taken to allow all the air

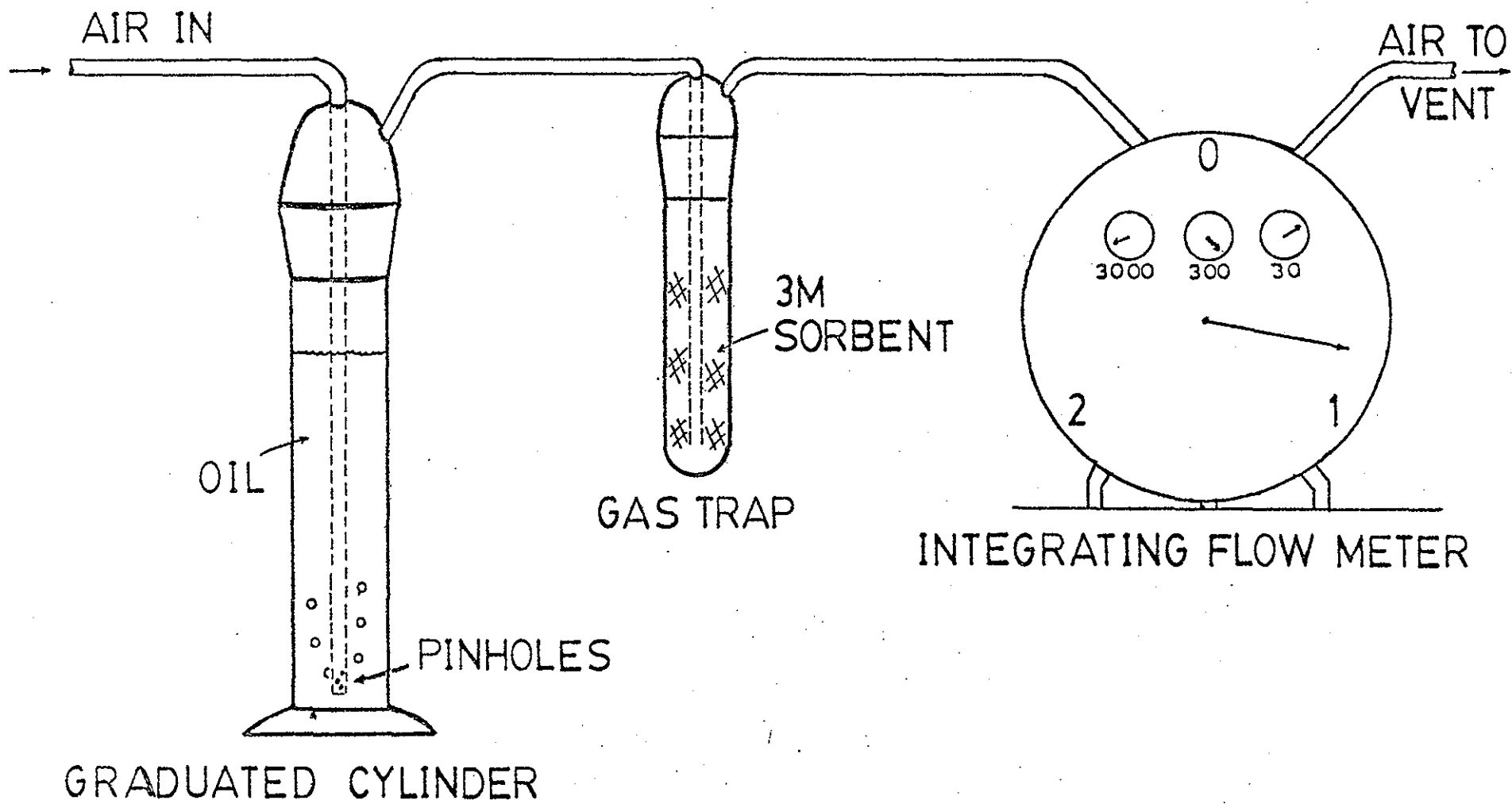


Figure 2. Gas Stripping apparatus

bubbles to escape from the oil. The evaporation curve was thus obtained on both a mass and volume fraction basis.

Distillation

The distillation apparatus consisted of standard laboratory equipment. A known volume (usually between 150 and 200 mL) was poured into the 500 mL flat bottom distilling flask. Small (1-2 mm dia.) glass beads were added to reduce bumping. The oil was stirred with a teflon-coated magnetic bar on a hot-plate stirrer. The flask was partly insulated as shown to minimize heat losses and give more consistent results. The oil was heated slowly with the heat input increased slowly to give a uniform boiling rate in the flask. The condensate was collected in 10 mL graduated cylinders (gradations 0.1 mL). The liquid temperature was measured using a thermocouple. The volume distilled was recorded as a function of liquid boiling temperature.

RESULTS AND DISCUSSION

Wind Tunnel Mass Transfer Coefficient

The mass transfer coefficient for the wind tunnel experiments was measured by the evaporation of toluene. The experimental procedure was the same as that for the synthetic and crude oils. The mass transfer coefficient k was calculated from equation 1 using literature values for the vapor pressure of toluene. The resulting mass transfer coefficient characterizes the gas phase resistance only since a pure liquid has been used. It is well established that k depends also on the Schmidt number of the evaporating component. No correction was made here because its magnitude is not large and because an oil is made up of many components thus there is doubt about the appropriate Schmidt number. Several runs were performed giving a relation for the mass transfer coefficient as a function of the air velocity as measured by a pitot tube in the wind tunnel. Relations are available in the literature for mass transfer coefficients in environmental situations, e.g. Mackay & Matsugu(8) and Mackay and Yuen (15).

Synthetic Oil

The synthetic oil was used to test the equivalence of the three evaporation techniques. Equivalence implies that the experimental techniques give the same evaporation rates on a evaporative exposure basis, and the same compositional changes. In addition, the experimental results were compared with those which can be computed from reported vapor pressures (Zwolinski 16).

The tray evaporation results are shown in Figure 3 as a plot of volume fraction evaporated (F_v) versus evaporative exposure (θ). Note the linear and

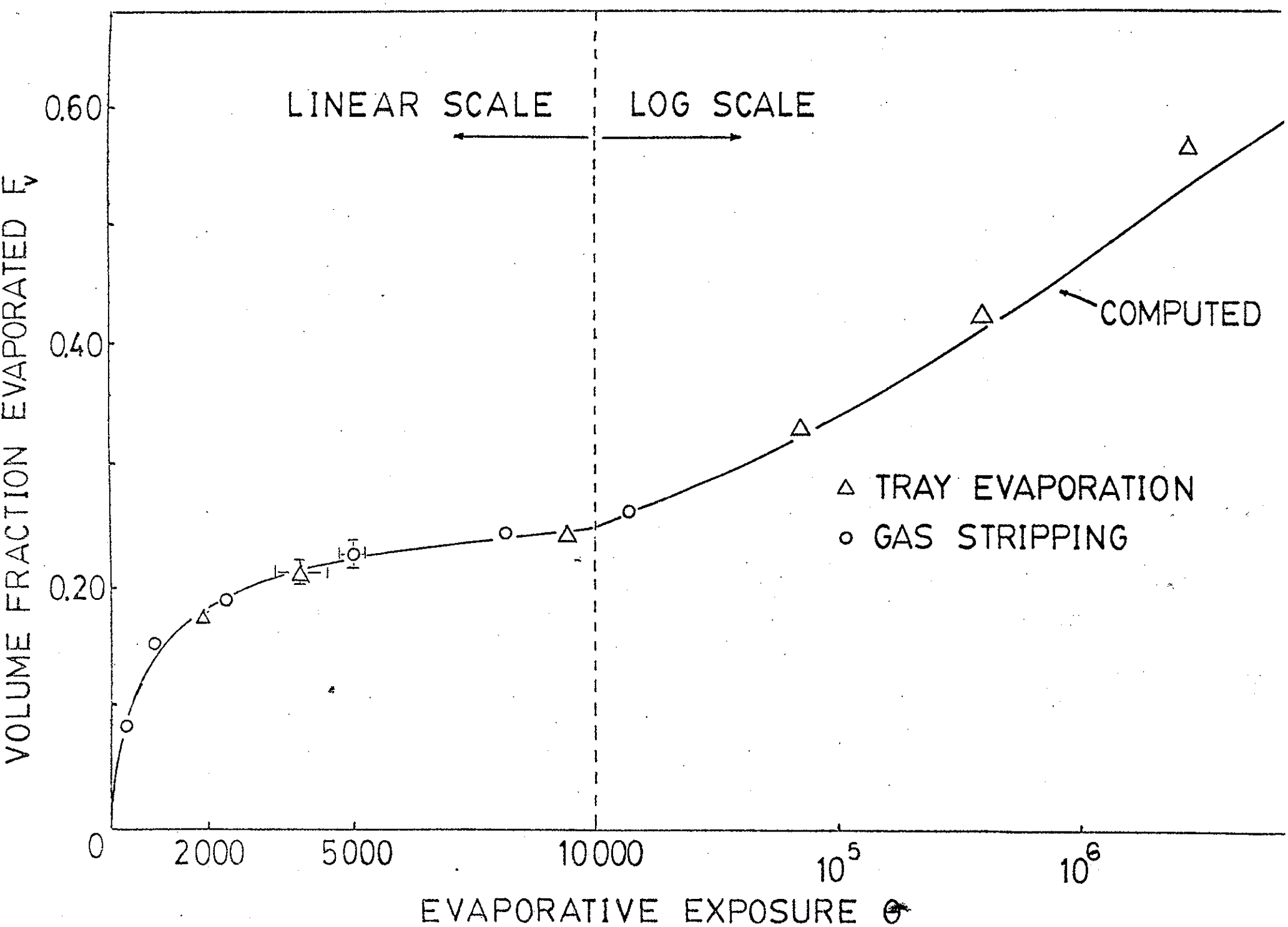


Figure 3. Plot of volume fraction evaporated versus evaporative exposure for the synthetic oil.

logarithmic scales. The evaporative exposure was calculated from the time of exposure based on a mass transfer coefficient of 1.4×10^{-2} m/s and an initial slick thickness (V_o/a) of 2.5 mm. Measurements in the tray evaporation experiments were on a mass basis. From the initial and final densities (ρ_o and ρ_F) the mass fraction F_m can be converted to a volume fraction F_v using,

$$(1 - F_v) = (1 - F_m)(\rho_o/\rho_F) \quad (17)$$

The gas stripping results and the computed evaporation curve based on vapor pressures from Zwolinski (16) are also shown in Figure 3. The coincidence of the curves verifies the evaporation rates as measured by the two experimental techniques when expressed in terms of θ . Error bars estimates are given for the gas stripping and tray evaporation curves. The gas stripping technique is believed to be more accurate.

The gas flowrate (G) in the gas stripping experiments was 1.3×10^{-5} m³/s (300 mL/min) and the initial oil volume (V_o) was 240 mL giving a rate of exposure (G/V_o) or $d\theta/dt$ of 3.2 per min. The rate of exposure for the tray evaporation technique (ka/V_o) was 340 per min. The slower rate of gas stripping exposure is one reason for its greater accuracy. Interestingly, under typical environmental oil spill situations the rate of exposure is approximately 600 per min or 1 million per day (k of 0.01 m/s, V_o/a of 1 mm). Thus, to achieve a wide time range of evaporation data a three regime approach is useful. For θ from 0 to 50000, gas stripping is ideal. Tray evaporation is suitable for θ from 50000 to 10^7 . For exposures greater than 10^7 a thin-film ($V_o/a \sim 0.1$ mm) technique is best.

The distillation curve for the synthetic oil is given in Figure 4. A correction was applied for the volume of uncondensed vapor in the system. The theoretical batch distillation curve, assuming one theoretical stage separation, is also shown. A considerable temperature difference of some 20C°

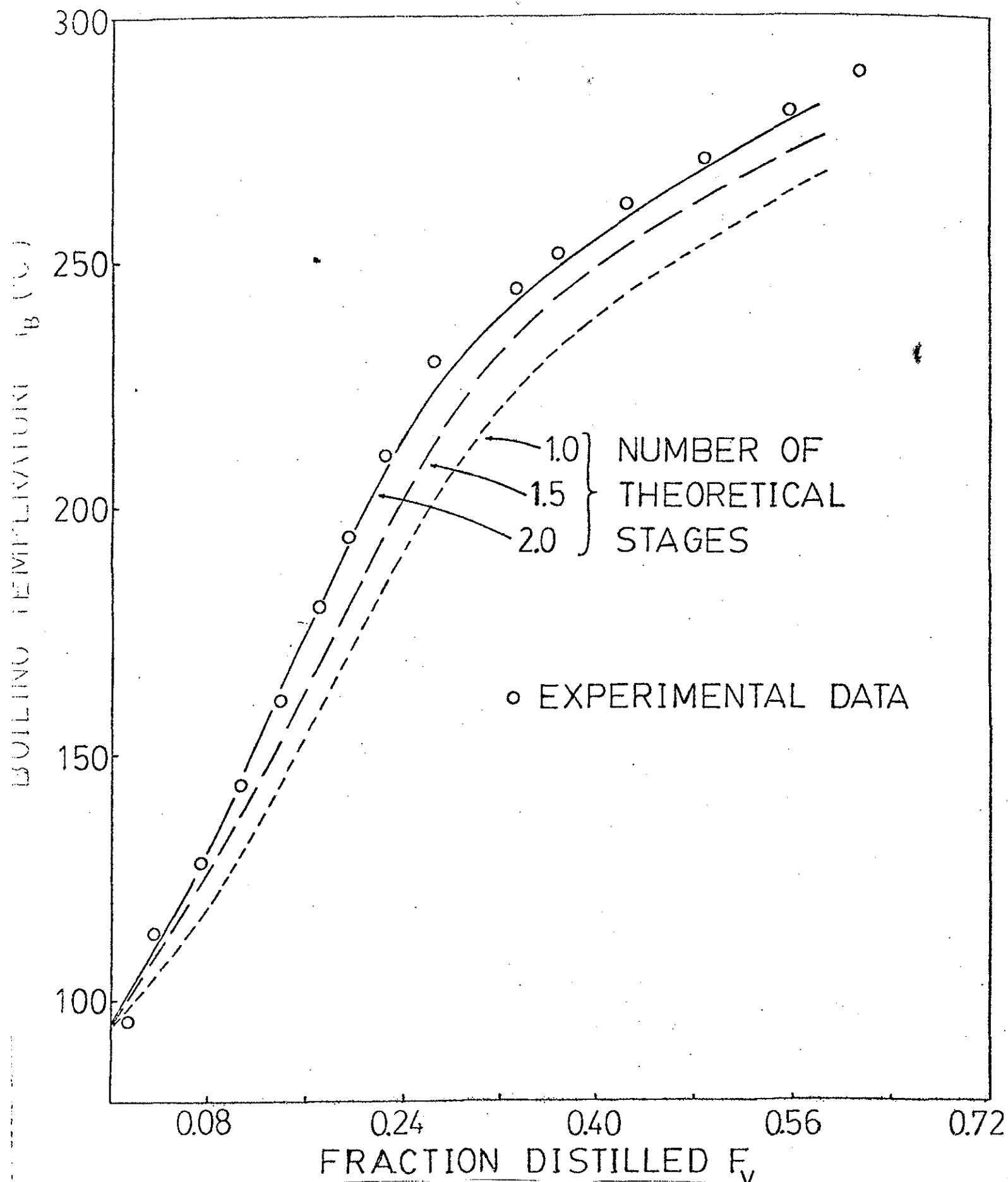


Figure 4. Distillation curves for the synthetic oil showing computed curves assuming 1.0, 1.5 and 2.0 theoretical stages.

exists between the theoretical and experimental curves, the experimental temperatures being higher.

In order to understand the reasons for this discrepancy some simple binary distillations were performed using a mixture of dodecane and hexadecane. The experimental distillation temperature curve was again higher than expected. Compositional analysis of samples of the residual mixture indicated that greater separation was occurring than would be expected from a single stage. The distillation curve and the compositional changes were in agreement with approximately a 1.8 stage separation. This increased separation capacity of the apparatus may be caused by some refluxing in the neck of the flask.

Returning to Figure 4 and the distillation curve for the synthetic oil, the predicted curves for 1.5 and 2.0 equilibrium stages are shown. The experimentally attained curve is in agreement with approximately a 2.0 stage separation.

Gas chromatographic analysis of the residual oil verified this two stage separation. Figure 5 is a plot of per cent n-decane remaining versus the fraction distilled. The computed results based on 1.0, 1.5 and 2.0 theoretical stage separations are plotted along with the experimental results. The experimental compositions indicate a 1.8 equilibrium stage separation.

Compositional comparison of the three experimental techniques are shown in Figure 6. It is evident that the tray evaporation and gas stripping techniques are giving the same compositional changes but that the distillation gives different compositions. The effect of the apparent 2 stage separation and the higher temperature in the distillation experiments will alter the relative volatilization rates of the various classes of components present in a crude oil. The distillation technique is believed to be less accurate for

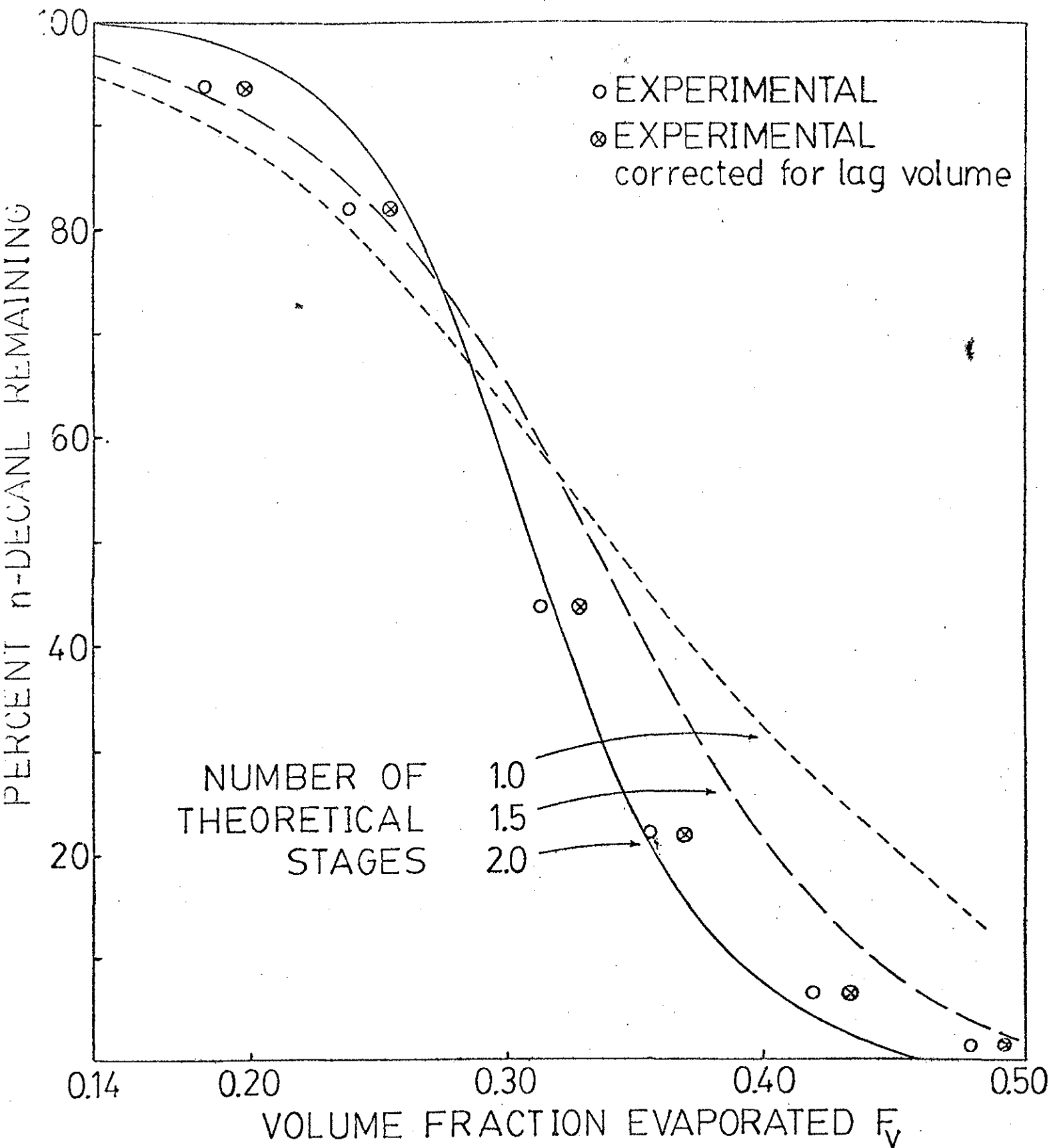


Figure 5. Experimental and computed fractions of n-decane as a function of F_v for the distillation technique.

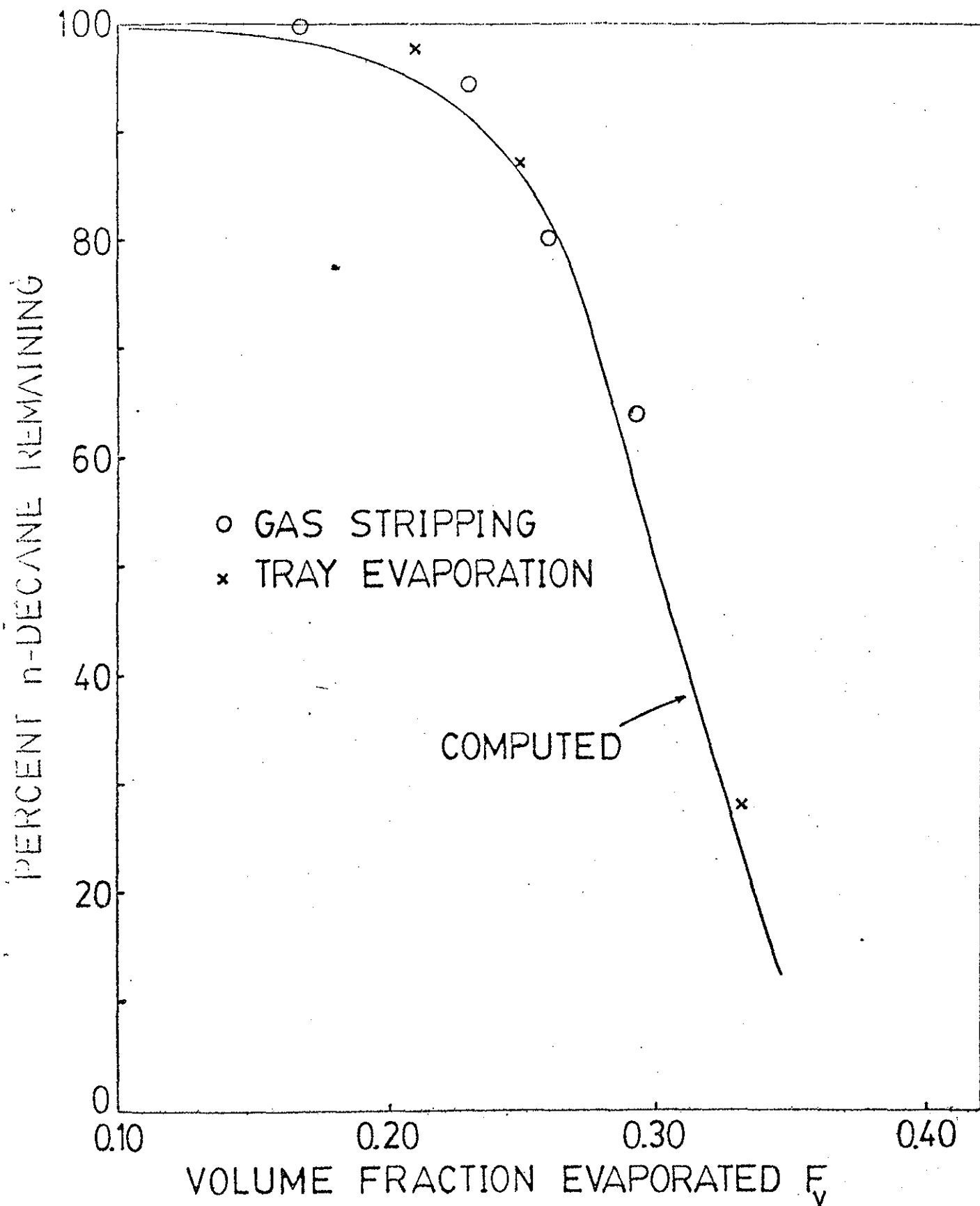


Figure 6. Experimental and computed fractions of n-decane a function of F_v for the gas stripping and tray evaporation.

predicting evaporation rates than stripping ^{or} tray evaporation but it can provide the data rapidly.

The gas stripping and tray evaporation techniques are preferred for producing "typical" samples of weathered oil, but distillation may be used if samples are required rapidly.

Crude Oils

The tray and gas stripping evaporation curves for Norman Wells and Kuwait crude oils are shown in Figures 7 and 8. The tray evaporation curve lags slightly behind the gas stripping curve for the Kuwait crude, as was the case for the other three oils studied. It is possible that this is caused by a liquid phase resistance. For example, Yang and Wang (4) observed the formation of a thin waxy film on the oil surface significantly reducing their measured evaporation rates. Other factors which may be contributing to the lag are evaporative cooling or a diffusivity (Schmidt Number) effect on the mass transfer coefficient. In any event the lag is small and it is concluded that the tray and stripping techniques also give consistent results for crude oils. Ignoring liquid phase resistance may result in errors for highly viscous oils.

The distillation curves for the two crude oils are given in Figure 9. To convert these distillation curves into evaporation curves it is necessary to determine the constants A and B for equation 10. From the $F_v - \theta$ curves, the mean slopes (H) were measured at selected F_v points. The corresponding boiling points were read off the distillation curves. Figure 10 was then compiled of $\ln H$ versus T_B , a linear relationship being expected (Equation 10). The correlation coefficient was 0.96 for the linear regression, fitting A and B to

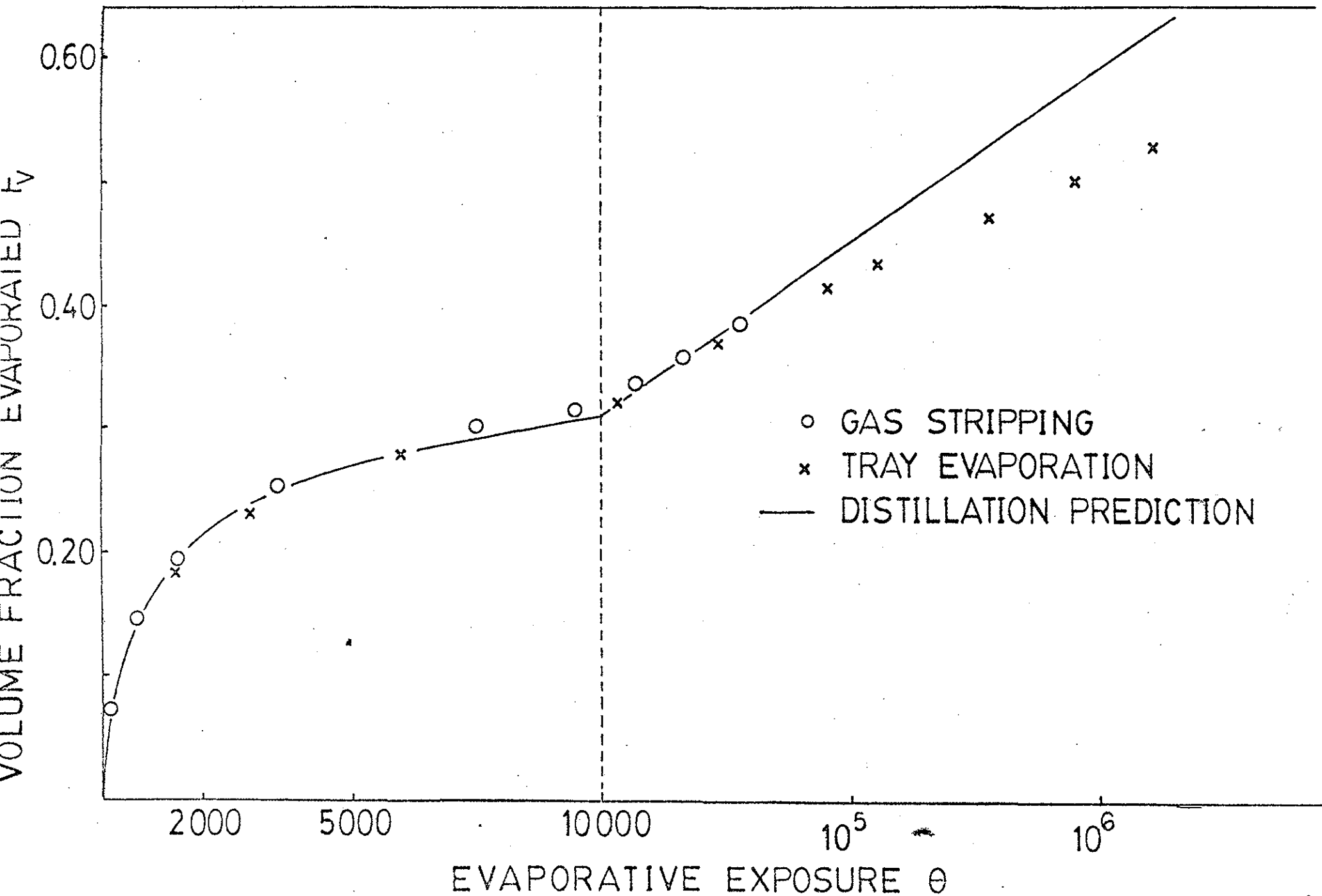


Figure 7. Evaporation curves for Norman Wells crude oil at 22°C.

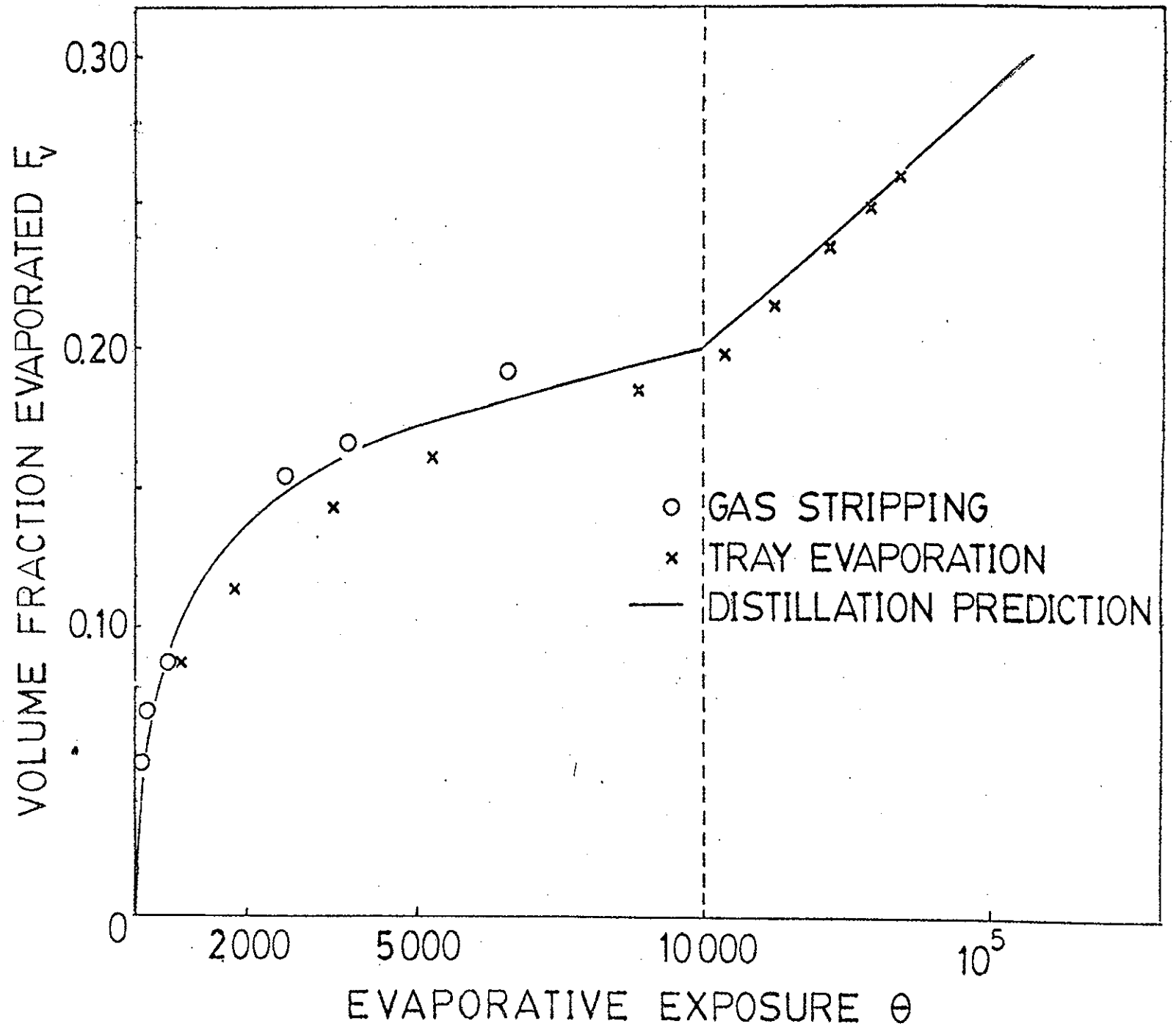


Figure 8. Evaporation curves for Kuwait crude oil at 22°C.

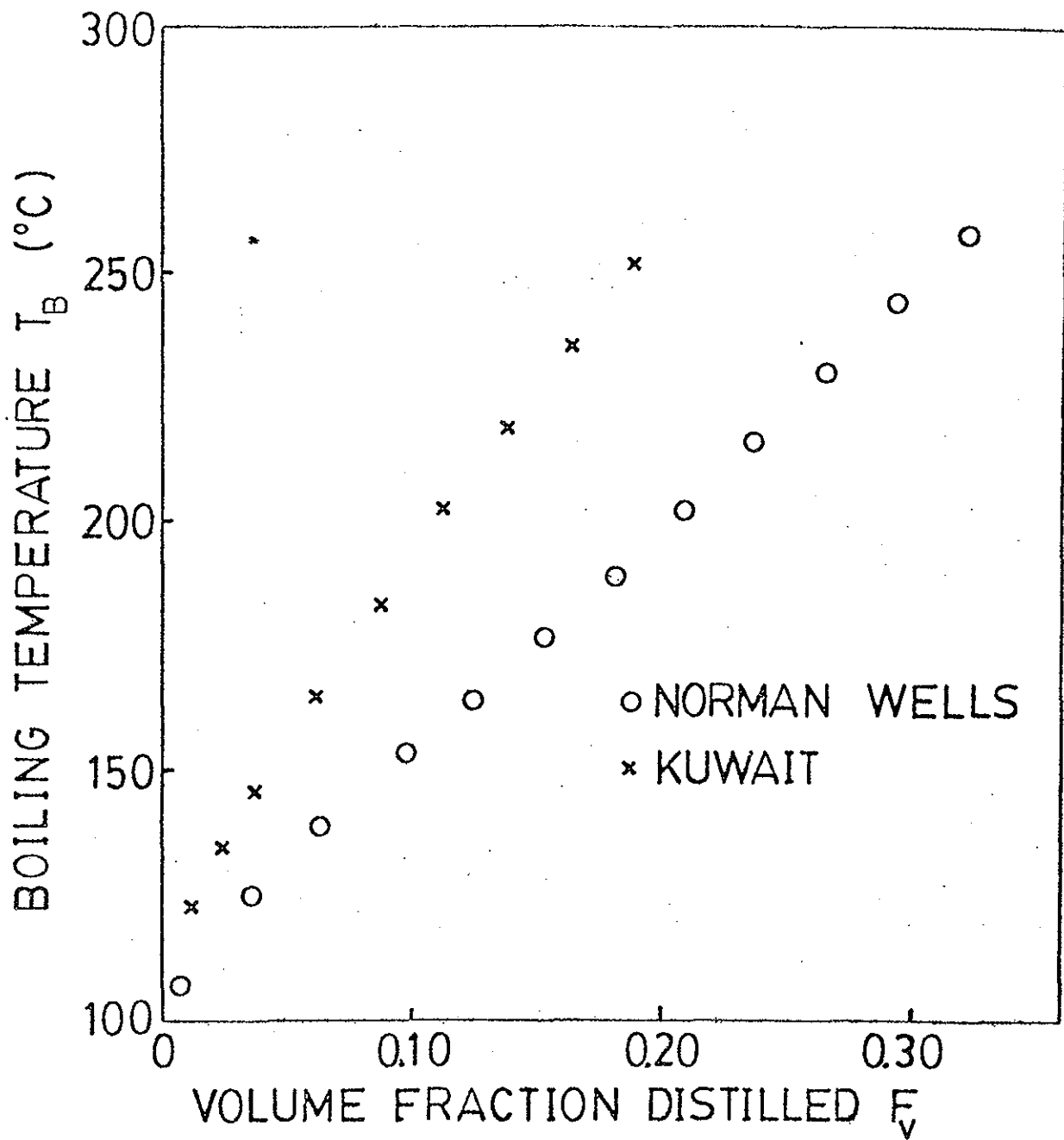


Figure 9. Atmospheric pressure distillation curves for Kuwait and Norman Wells crude oil.

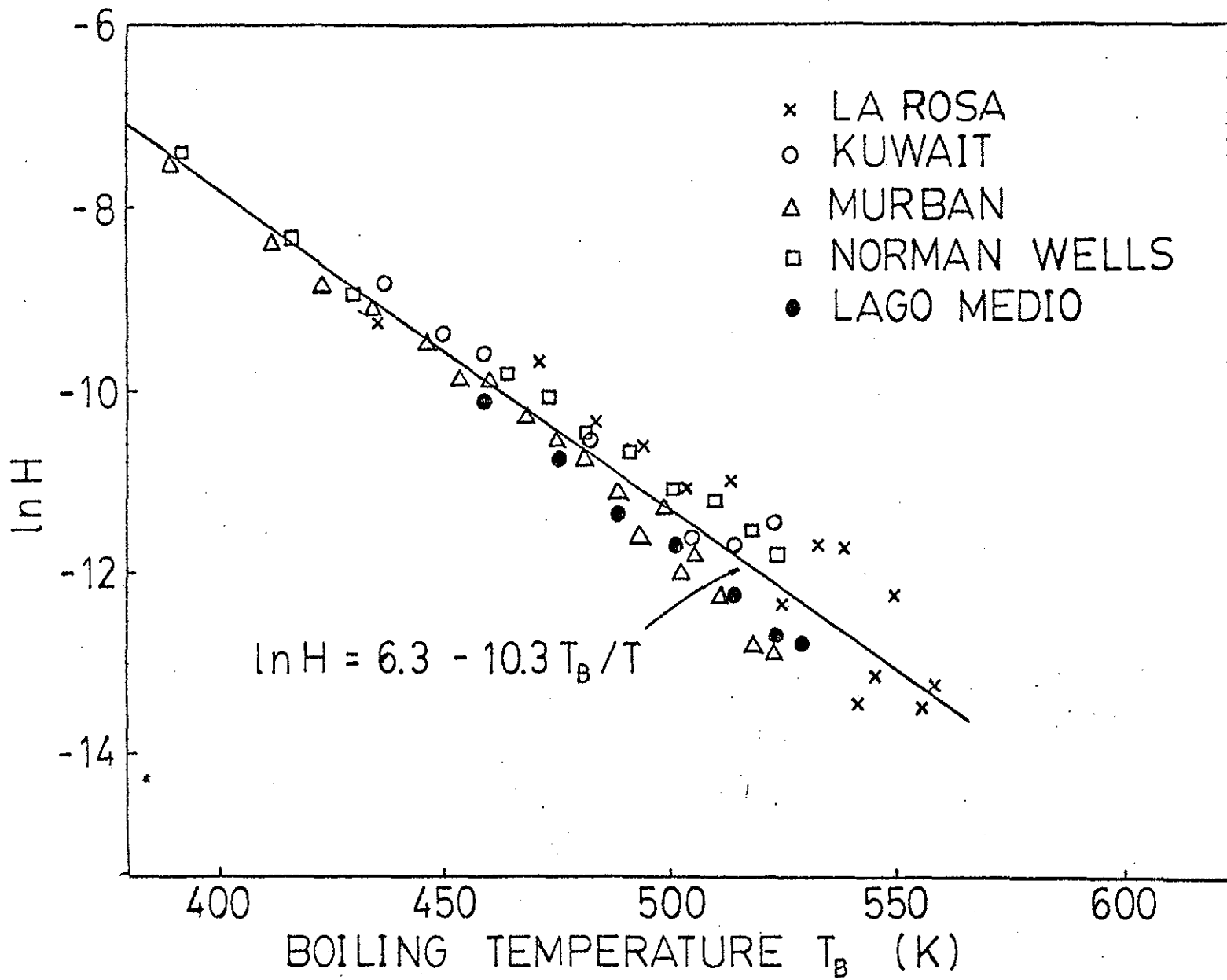


Figure 10. Plot of natural log of H at 293K versus boiling temperature (K).

give

$$\ln H = 6.3 - 10.3 T_B/T \quad (18)$$

These values of A and B were then used to predict the $F_v - \theta$ curve for all the crude oils from their boiling point curves (i.e. T_o and T_G) using equation (13). The predicted evaporation curves for Norman Wells and Kuwait are shown in Figures 7 and 8. In all cases the extent of evaporation, at a θ of 10000, was predicted correctly within 4 per cent. As shown in Figure 10 the correlation is based only up to a boiling point of 550K (280°C). Caution must be used when predicting fractions evaporated that boil above 280°C. It is believed that the correlation tends to over-predict the rate of evaporation in this region.

Some oil spills are exposed to very rapid evaporation (high exposure θ) caused by high winds and turbulence (i.e. high k) or by the oil being spread out very thinly (i.e. low V_o/a). In these situations it is useful to know the extent of evaporation that may be attained. The thin-film technique described in the experimental section was designed to elucidate quickly the extent of evaporation that may be reached. Figure 11 shows the evaporation curve on a mass basis for Murban crude oil using the thin-film technique. The exposure of 10^8 was attained in just 4 days.

The significant effect of temperature on the evaporation rates of crude oils is illustrated in Figure 12 which gives the evaporation curves of Norman Wells at 0°C and 22°C. The extent of evaporation of the 0°C Norman Wells oil at θ of 10^4 is only 70 per cent of that for the evaporation at 22°C. Equation 13 applies and predicts the evaporation rate at 0°C accurately as shown in Figure 12.

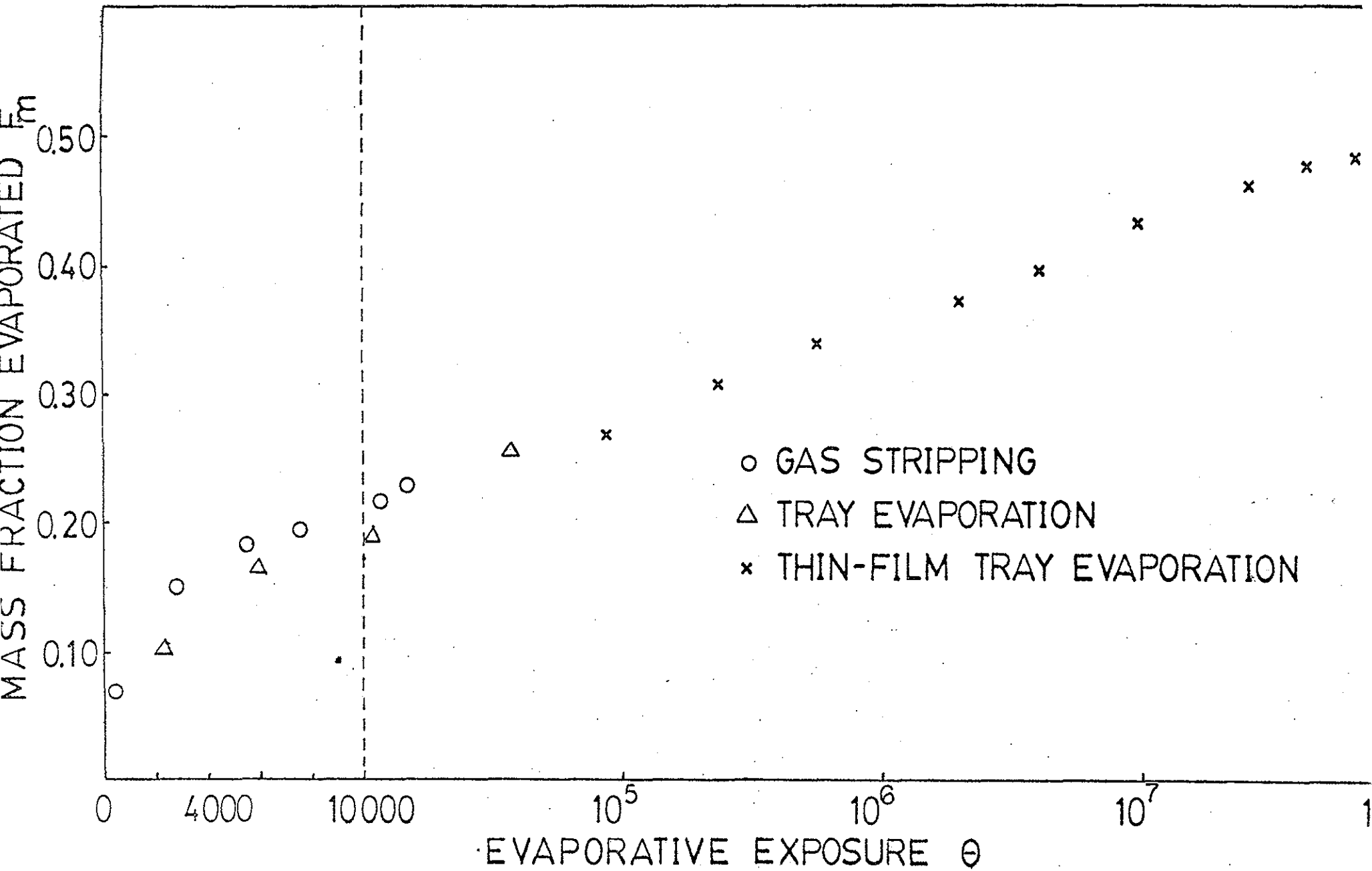


Figure 11. Extended evaporation of Murban crude oil at 22°C.

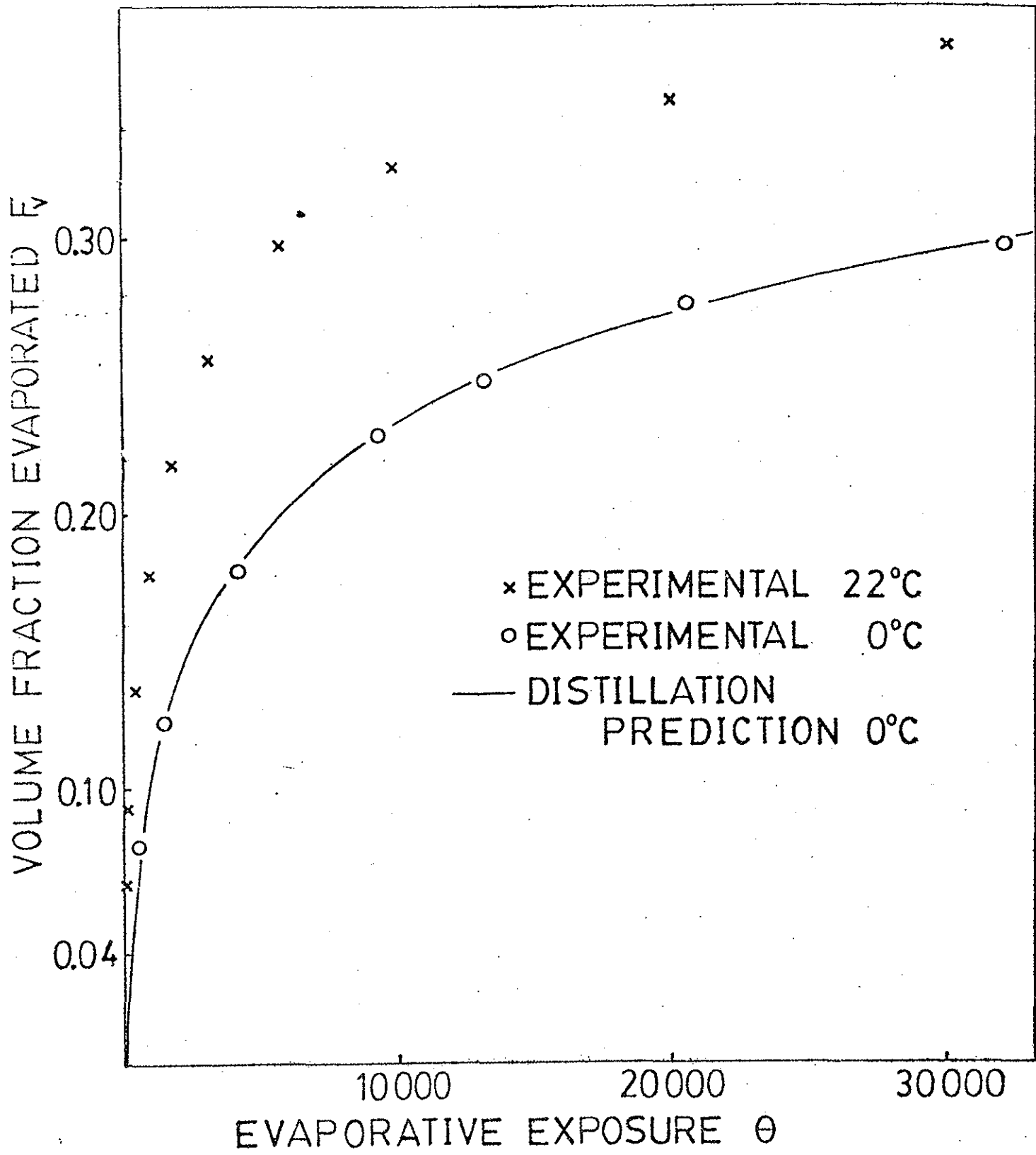


Figure 12. Evaporation curves of Norman Wells crude oil at 0°C and 22°C.

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