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VOLATILITY CHARACTERISTICS OF PETROLEUM FRACTIONS BY DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The volatility characteristics of commercial petroleum fractions (gasoline (petrol), kerosine (paraffin) and gas oil) are studied by evaporation using open pans, closed pans with very narrow orifices in their lids and a differential scanning calorimetry (DSC) unit. The effect of varying the pan orifice size, the rate of DSC sensor heating and the flow rate of the purge gas (N_2) has been investigated. Integration of the DSC thermograms obtained for evaporation of the fractions, in terms of percentage fraction evaporated vs. temperature, gives curves that can be correlated with standard distillation curves. The data obtained for the evaporation of petroleum fractions in closed pans with a minute orifice under specified conditions can be used as a simple test of the volatility characteristics of the fractions.

INTRODUCTION

The partial pressure p_i of a volatile component (i) is related to the vapour pressure of the pure component P_i and its mole fraction in solution x_i at equilibrium (Raoult's law) [1]. The p_i value is also related to the mole fraction of the component in the vapour y_i and the total pressure of the system P at the same temperature (Dalton's law) [2],

$$p_i = x_i P_i \tag{1}$$

$$p_i = y_i P \tag{2}$$

By combining eqns. (1) and (2), eqn. (3) is obtained:

$$\frac{y_i}{x_i} = \frac{P_i}{P} = K_i \tag{3}$$

Where K_i is the phase equilibrium constant. Hence, the distribution of a component between vapour and liquid may be expressed as a function of temperature and pressure because eqn. (3) is applicable for ideal systems, where K_i is constant at a specified temperature and pressure.

For non-ideal solutions, the selection of semi-empirical correlations applicable to the system depends on the computing facilities available and their

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accuracy [1]. In a differential scanning calorimeter (DSC) pan the vaporization is acting upon a non-ideal system because the vapour → liquid transition is controlled by changeable pressure. Barrall [2] has considered, in general terms, the estimation of melting and boiling points by both DSC and differential thermal analysis (DTA).

In the present work, the vaporization of some petroleum distillates and blends has been investigated by DSC using open pans and closed pans pierced with a small orifice in the centre of the lid, making use of the DSC programmed temperature increase.

EXPERIMENTAL

Petroleum distillates

Commercial petroleum fractions

These include gasoline (boiling range (b.r.) 50–200 °C), kerosine (b.r. 140–245 °C) and light gas oil (b.r. 180–340 °C) collected by fractional distillation from an Arabian crude oil.

Petroleum ethers

Two petroleum ethers (AnalaR grade, BDH) with specified b.r. values of 100–120 °C and 120–160 °C were used.

DSC measurements

A DSC-30 unit of the thermo-analytical system TA-3000 (Mettler) was used. Two sets of DSC runs were carried out using standard aluminium pans; one set with open (uncovered) pans and the other with pans covered with lids containing a very narrow orifice in the centre. The orifice diameter was about 20 μm as inspected under a microscope. For the first set of runs, the reference pan was also an uncovered one, whereas in the second set, the reference pan was a covered one with a pierced lid. The pan rims and lids were hermetically sealed by cold welding using the pan sealing press. The following conditions were used: start temperature, 35 °C; heating rate, 10 K min^{-1} (except where otherwise specified); final temperature, 350 °C; full-scale range, 25 mW; purge gas and its flow rate, N_2 at 50 $\text{cm}^3\ \text{min}^{-1}$ (except where otherwise specified). Integral plots of the DSC thermograms were computed in terms of per cent evaporated vs. temperature such that evaporation terminated at 100% evaporation. In all DSC measurements, samples of weight 20 mg were used.

RESULTS AND DISCUSSION

In an open system, the solid → liquid transition is sharp and independent of pressure, whereas the liquid → vapour change is controlled by pressure which depends on mass transfer from the liquid surface to the vapour phase. Consequently, the DSC peak shape depends on the rate of evaporation which is a function of the temperature and of the rate at which vapour is removed. The surface area of the liquid and the size of orifice through which the vapour escapes to the surroundings are therefore important factors [3].

Figures 1 and 2 show the DSC thermograms obtained for the evaporation of the three commercial petroleum fractions; gasoline, kerosine and gas oil in uncovered DSC pans (Fig. 1) and in closed pans with a very narrow orifice in their lids (Fig. 2). For a single petroleum fraction, the pan type used causes large differences in the peak maximum temperature as well as in the evaporation termination temperature appearing in the thermograms. So, in open pan runs (Fig. 1) the thermograms show peak maxima at 80, 124 and 213° C for gasoline, kerosine and gas oil, respectively; while in closed pans with narrow holes the evaporation thermograms of these fractions show these maxima at 119, 207 and 305° C, respectively (Fig. 2). Also, the evaporation termination for these fractions appear at 135, 160 and 245° C in open pan runs and at 204, 245 and 340° C in closed pan runs, respectively.

Figure 3 shows the integrated version of the DSC thermograms given in Figs. 1 and 2. It should be noted that open pan evaporation gives smooth

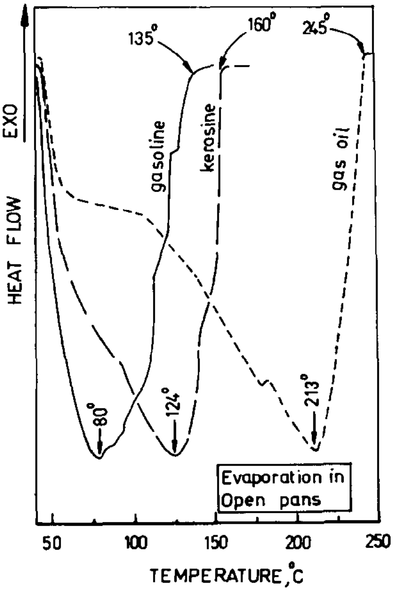

Fig. 1. DSC thermograms for gasoline, kerosine and gas oil evaporation in open pans.

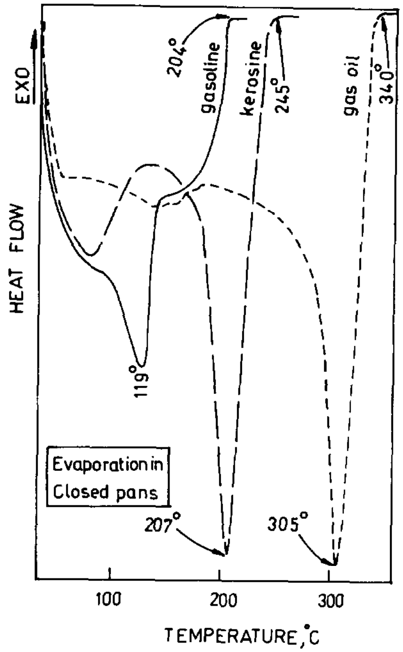

Fig. 2. DSC thermograms for gasoline, kerosine and gas oil evaporation in closed pans with a very narrow orifice in their lids.

curves, whereas closed pan evaporation results in segmented curves suggesting better resolution of the fractional composition with different volatility ranges. Such behaviour of integral curves may occur because of the blending of respective fractions collected from different sources, i.e. different crude

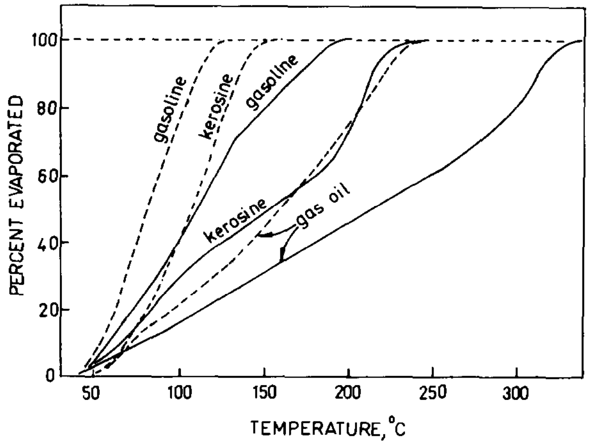

Fig. 3. Integrated thermograms in terms of per cent evaporated vs. temperature for gasoline, kerosine and gas oil: - - - - - -, in open pans; ———, in closed pans with a very narrow orifice in their lids.

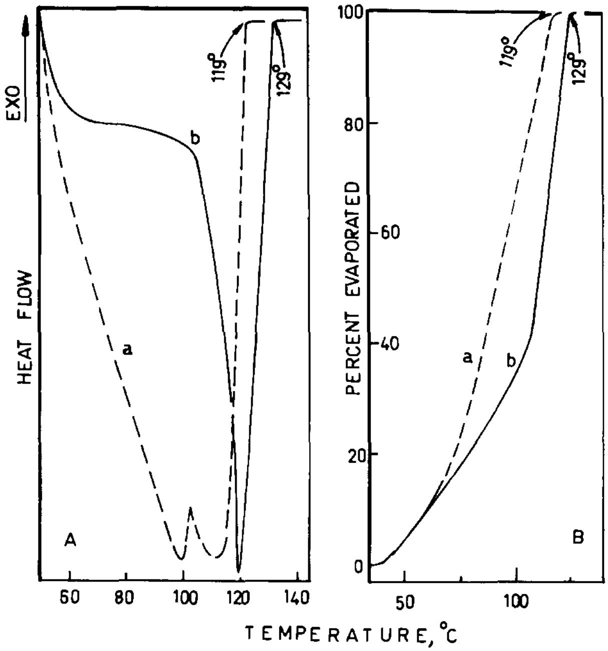

Fig. 4. DSC testing of petroleum ether evaporation. A, DSC thermograms; B, integrated thermograms. a (------), Petroleum ether, b.r. 120–160 ° C (open pan); b (———), petroleum ether, b.r. 100–120 ° C (closed pan with very narrow orifice in the lid).

oils or differently processed distillates. It is also notable that the blending nature is more recognizable in the integral curves of gasoline and kerosine than in the gas oil curve. Correlation of the temperature ranges of the curves in Fig. 3 shows to what extent evaporation can be retarded by using closed pans with a narrow orifice; for instance, the kerosine closed-pan evaporation curve overlaps, in various positions, the gas oil open-pan evaporation curve. Furthermore, the extent of evaporation retardation in closed pans with an orifice compared with open pans is more clearly illustrated by the curves in Fig. 4. The figure shows curves for two petroleum ethers with strict boiling ranges (AnalaR grade, B.D.H.); a petroleum ether with a b.r. of 100–120 ° C which has been evaporated in a closed pan with a very narrow hole, and a 120–160 ° C petroleum ether which has been evaporated in an open pan. The DSC thermograms (Fig. 4A) and their integrated versions (Fig. 4B) show that the heavier ether evaporates in an open pan over a much lower temperature range than the lighter ether evaporated in a pierced closed pan.

The integrated curves, see also Fig. 3, can be easily correlated with the standard American Society for Testing Materials (ASTM) distillation curves which are widely used in quality control petroleum laboratories to check the volatility characteristics of the distillate fractions produced.

It has previously been shown [3] that the evaporation of a drop of water in an open DSC pan gives a thermogram similar to a plot of vapour pressure

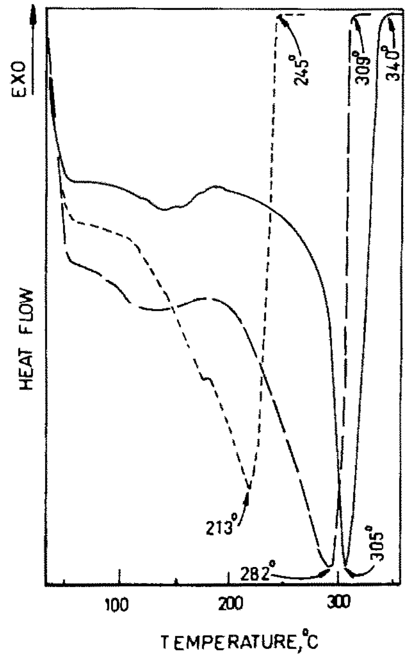

Fig. 5. DSC thermograms for gas oil evaporation: - - - - - -, in an open pan; — — —, in a closed pan with a 50 μm orifice; ———, in a closed pan with a 20 μm orifice.

vs. temperature, whereas in a closed pan with an orifice in its lid, the water boiling point determined corresponds closely to the intersection of the extrapolated baseline and the leading edge of the DSC peak (within ±1°C). However, the petroleum fractions under study are composed of huge numbers of hydrocarbon components of different structural groups and their DSC curves (Figs. 1 and 2) and, hence, their integral versions (Fig. 3) show that the start of evaporation in both open and closed pans takes place at temperatures much lower than the initial boiling points of the fractions determined by ASTM distillation. For hydrocarbon fractions the integral curves are largely similar to the vapour pressure vs. temperature relationships [3]. Nevertheless, the final boiling points given by the ASTM distillation plots are found to be very close to the evaporation termination temperatures determined by DSC using closed pans with a very narrow orifice in their lids (see Experimental section and Fig. 3).

Figure 5 gives more insight to how important the size of the orifice in the lid of the DSC pan is; It correlates the thermograms of gas oil evaporation in an open pan, a closed pan with a very narrow orifice (20 μm) and in a closed pan with a wider orifice (50 μm). The DSC peak temperatures and evaporation termination temperatures are significantly decreased by increasing the size of the orifice in the pan lid.

Figure 6 shows the importance of the rate at which the DSC sensor is heated and hence, the rate of sample evaporation. Lower heating rates are

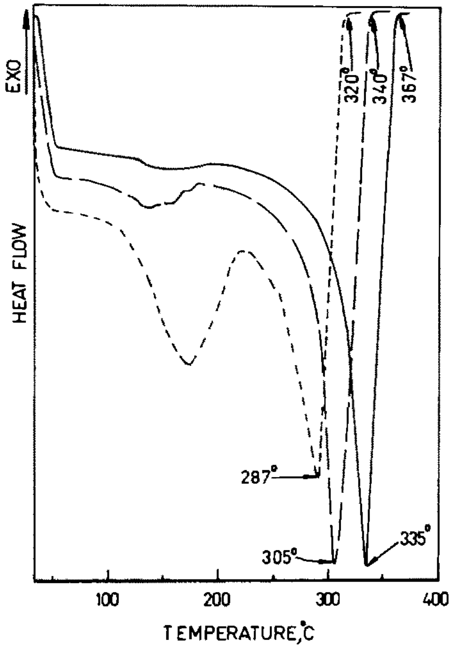

Fig. 6. Effect of heating rate on gas oil evaporation in closed pans with a very narrow orifice in their lids: ------, 5 K min^{-1}; — — —, 10 K min^{-1}; ———, 20 K min^{-1}.

evidently giving thermograms with peak maxima and evaporation termination at lower temperatures. This is because of the longer sample heating period needed to reach a certain temperature. So, a temperature of 300 °C is reached after 60 min at a heating rate of 5 K min^{-1}, whereas it is reached after only 15 min at a heating rate of 20 K min^{-1}.

Another variable that appears to play an important role in the DSC measurements of the evaporation of petroleum fractions is the flow rate of the purge gas. In this study nitrogen is used to prevent possible oxidation. It has been found that flow rates between 30 and 60 cm^3 min^{-1} do not result in significant variation in thermograms obtained from evaporation measurements using closed pans with a minute orifice. However, although no measurements have been carried out to study the effect of purge gas flow rate when using open pans (a rate of 50 cm^3 min^{-1} only was used), it is assumed that higher rates would accelerate the rate of distillate evaporation and lower the temperatures obtained for peak maxima and evaporation termination.

If the manufacturer of the DSC standard pans produces lids with a precisely pierced orifice, highly reproducible thermograms and integral curves can be obtained and the DSC evaporation measurements can be used as a simple test of the volatility characteristics of petroleum fractions. Moreover, the evaporation termination temperature of petroleum fractions, as a substitute for the final boiling point (determined by the ASTM distillation), is of great importance when producing gasolines to be used as motor fuels, kerosines to be used as jet turbine fuels and gas oils to be used as diesel fuels. Moreover, the test requires a very small sample weight.

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