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THERMOANALYTICAL STUDIES OF PITCH PYROLYSIS
Comparison with polycyclic aromatic hydrocarbons

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Characterization of pitches by thermal analysis techniques is highly relevant to the practical use of these materials, as they undergo heat treatments in all of their utilization processes. The aim of this work was to improve the interpretation of the complex DTA curves of pitches by comparison with model compounds. For this, TG/DTG/DTA was used to study under identical conditions the pyrolysis of a petroleum pitch and a coal tar pitch as well as a number of polycyclic aromatic hydrocarbons. Results were interpreted as a function of the molecular structure, pyrolysis reactivity and graphitizability of cokes from the hydrocarbons. It is concluded that condensation and polymerization, which are the most likely exothermal reactions predominant in petroleum pitches, indicate the presence therein of reactive molecules. Alternatively, endothermal phenomena such as distillation, depolymerization and cracking, predominant in coal tar pitches, suggest the presence of light, little reactive aromatic molecules.

Keywords: pitch pyrolysis, polycyclic aromatic hydrocarbons

Introduction

Pitches are highly complex mixtures of polycyclic aromatic and heterocyclic compounds. Commercial pitches are produced by thermal treatment of coal- and petroleum-derived tars. Pitches are, in turn, subjected to the action of heat in most of their utilization processes, e.g., when used as binder material in electrodes or as precursors for carbon fibres and carbon-carbon composites. Consequently, thermal analysis methods should provide essential data in connection with the practical uses of pitches. However, whereas TG has been quite often used to study pitch pyrolysis [1–16], the application of DTA [1, 3, 4, 10, 14–18] and DSC [12, 19–21] has been scarce, and only limited information has been obtained from the two latter techniques. The main reason may be the complex composition of pitches, which results in DTA curves with multiple peaks difficult to interpret, since in the most cases they are due to the overlapping of exo

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and endothermal phenomena. In some instances, it was even concluded that 'no useful results were obtained by DTA' [3] as concerns pitches.

In a previous work [14] we used combined TG/DTG/DTA to study the pyrolysis behaviour of a number of coal tar and petroleum pitches and their fractions. The essential aim of the current paper is to get some additional insights into the DTA behaviour of pitches. For this, we compare the thermal characteristics of two representative pitches with those of a number of model polycyclic aromatic hydrocarbons (PAH), most of them being typical constituents of tars and pitches [22–24]. The various PAH studied were selected taking into account different factors, such as molecular structure, pyrolysis reactivity, and graphitizability of their cokes.

Experimental

Materials

Two typical commercial binder pitches were studied, namely a petroleum pitch, PP (92.0 wt% C (daf), 6.0 wt% H (daf), 0.5 wt% quinoline insolubles), and a coal tar pitch, CTP (92.9 wt% C (daf), 4.8 wt% H (daf), 90.8°C Krämer Sarnow softening point, 6.5 wt% toluene insolubles, 14.2 wt% quinoline insolubles). Polycyclic aromatic hydrocarbons studied included: acenaphtene (BDH, Laboratory Reagent grade); acenaphtylene (Fluka AG, 97% pure); benzo (g,h,i) perylene (Janssen Chimica, >98% pure); coronene (Fluka AG, 97% pure); decacyclene (Janssen Chimica, 95% pure); 1, 2, 5, 6-dibenzoanthracene (Janssen Chimica, 97% pure); 9, 10-dimethylanthracene (Janssen Chimica, 97% pure); fluorene (Schuchardt, 99% pure); pentacene (Fluka AG, 97% pure); and rubrene (5, 6, 11, 12-tetraphenylnaphtacene) (Janssen Chimica, purity degree not specified).

Methods

Simultaneous TG/DTA measurements were performed in a Stanton-Redcroft STA-781 apparatus provided with a CETA computer system for data acquisition and processing. Additional details are given elsewhere [25]. Experiments were carried out under identical conditions for all the materials studied. Pitch or PAH samples ground to <0.212 mm and weighing 15–17 mg were used. Pyrolysis runs were carried out under 99.995% pure argon at a flow rate of 50 ml/min, using a heating rate of 10 deg/min over the 20°–950°C interval. This relatively high heating rate was selected to enhance the DTA signals despite the foreseeable decrease in carbon yields and graphitizability of the residues.

Results and discussion

Figure 1 shows TG, DTG and DTA curves obtained during the pyrolysis of PP and CTP pitches. These two samples are representative for the thermal behaviour of a number of petroleum and coal tar commercial binder pitches, respectively [14]. A clear parallelism between their TG curves may be observed. Weight loss occurs in both cases as a single step over the approximate temperature intervals 232°–554°C (PP) and 206°–539°C (CTP), followed by a small, continuous weight loss. No plateau in TG is attained even at the maximum temperature of the experiments (950°C). The magnitude of weight loss is similar for both pitches [e.g. 25.0 wt% (PP) and 29.0 wt% (CTP) at 400°C; 64.2 wt% (PP) and 60.2 wt% (CTP) at 900°C]. DTG traces exhibit a main peak (456°C for PP, 392°C for CTP) with various small shoulders at higher and lower temperatures.

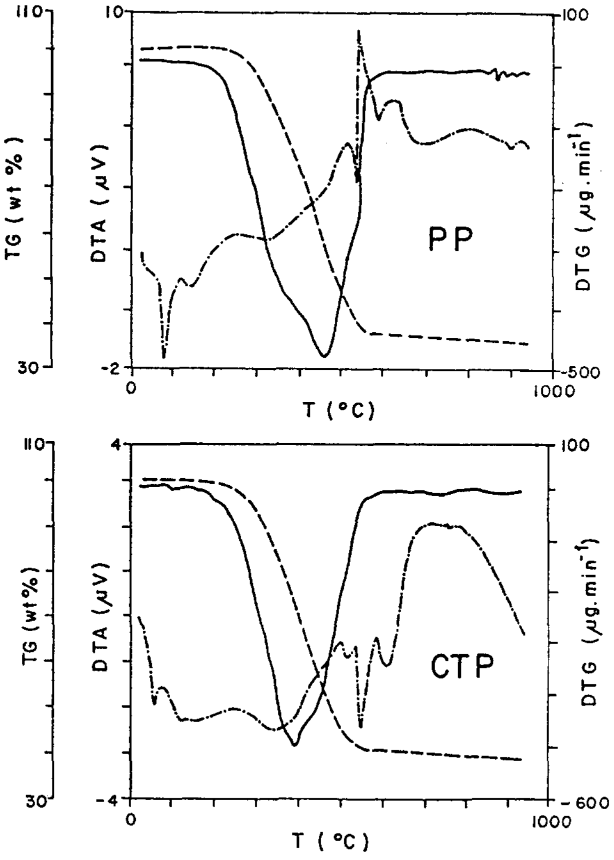

Fig. 1 TG, DTG and DTA curves for pitches

In contrast to the TG behaviour, DTA curves of PP and CTP pitches (Fig. 1) reveal clear differences between both samples, but the interpretation of the various DTA peaks is not unambiguous. Endothermal peaks appearing below 150°C can be ascribed to the glass transition and softening temperatures of pitches in analogy with DSC endothermal peaks at the same temperature range which have been used to determine pitch properties related to the glassy transformation (glass transition point, specific heat, enthalpy of relaxation) [12, 19–21]. From 150° to 600°C, exothermal effects are clearly predominant for the petroleum pitch whereas endothermal effects are comparatively more intense for the coal tar pitch. This temperature range is important since it includes the fluid interval with mesophase formation which defines the degree of preorder and further graphitization of residue. In fact, further exothermal effects detected for both pitches above 600°C (Fig. 1) can be mainly ascribed to hydrogen loss with formation of planar aromatic structures, what justified the small weight loss in the 600°–950°C temperature interval.

The TG/DTG/DTA behaviour of a number of PAH was studied to faciliate the interpretation of the various DTA peaks found for the pitches. Figure 2 shows the thermoanalytical curves obtained for various PAH with low pyrolysis reactivity (i.e., undergoing thermal decomposition at temperatures near or higher that their boiling point). Fluorene represents the simplest case. An endothermal peak at 119°C corresponds to melting, whereas another endothermal minimum at 243°C should be associated with vaporization. Accordingly, the latter peak coincides with the only weight loss step observed. It is thus evident that fluorene reaches complete evaporation before starting to pyrolyze at atmospheric pressure. Fluorene is little reactive [1] under its boiling point despite the presence therein of a methylene bridge, which could lead to fission of the bridge bonds, with formation of higher molecular weight aromatics by chemical condensation of previously formed free radicals.

The behaviour of both acenaphtene and 1, 2, 5, 6-dibenzoanthracene (results not shown) is much similar to that of fluorene, with two endothermal DTA peaks merely due to physical changes of state, and a single DTG peak coincident with the higher-temperature DTA peak (vaporization). It is interesting to note that 1, 2, 5, 6-dibenzoanthracene behaves in this way despite its comparatively high boiling point (524°C).

9, 10-dimethylanthracene (Fig. 2) exhibits a slightly more complex thermal behaviour. This PAH was selected because of the very high graphitizing ability of its coke [26] whereas the hydrocarbon has a low boiling point. After the melting (DTA endothermal peak at 185°C), a small DTA exothermal peak appears at 254°C that may be associated with condensation reactions. This is to be expected for this PAH, since chemical condensation is more likely to occur for

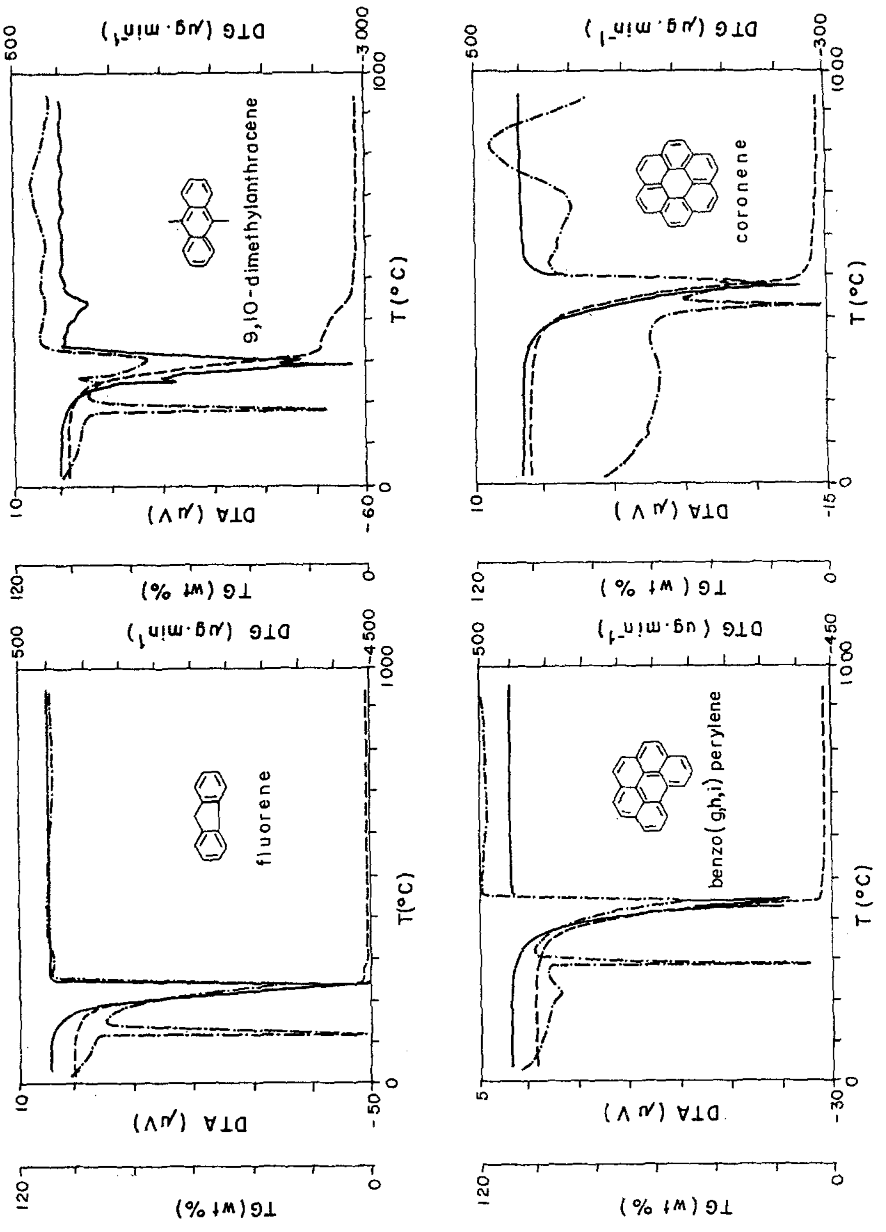

Fig. 2 TG, DTG and DTA curves for some little reactive PAH

alkyl aromatics than for unsubstituted ones, as a direct ring condensation is rarely found [1]. Interestingly, this DTA peak coincides with a small DTG peak at 254°C. The ensuing DTA/DTG peaks (302°C) are undoubtedly due to vaporization, but the DTA endotherm is little sharp (compare with fluorene, Fig. 2), indicating overlapping with an exothermal process, probably simultaneous condensation. On the other hand, a new TG step takes place between 325° and 454°C as for acenaphtylene (see below, Fig. 3).

Results obtained with benzo (g,h,i) perylene and coronene (Fig. 2) emphasize the role of competition between distillation and pyrolysis. Both PAH have similar molecular structures, the main difference lying in the presence in the former of various possible locations of primary bond rupture, so that this is expected to give a less graphitizable coke than that from coronene. However, at the same time there is a large difference in boiling point the result being that benzo(g,h,i)perylene behaves much like fluorene (the only qualitative difference being a weak endothermal DTA peak at 217°C, possibly due to some impurity). Coronene coke is known to undergo a surprisingly low degree of graphitization, and this was attributed to Edstrom and Lewis [26] to the fact that this large symmetrical structure may be sufficiently refractory to resist thermal reaction until the temperature is so high that reaction takes place simultaneously in different molecular sites. The result would be rapid but limited growth at many sites, so that these structures may not yield the mobile reactive species presumed necessary for growth and rearrangement to large planar graphite structures. This interpretation agrees with results from Fig. 2, taking into account the small temperature difference between the two DTA endotherms at 428° and 475°C, involving a narrow fluid interval. Nevertheless, note that the DTA peak at 428°C cannot be exclusively attributed to melting, since weight loss begins at significantly lower temperatures (ca. 330°C). A further remarkable feature is the strong DTA exotherm at 809°C due to ring condensation in the char from coronene.

Figure 3 shows thermoanalytical curves corresponding to PAH with higher reactivity in pyrolysis. Rubrene and pentacene show some analogies, especially the overlapping between strong exo and endothermal effects. In the case of rubrene, exothermal condensation is superimposed on melting (DTA minimum at 313°C and subsequent maximum at 331°C). Unlike this behaviour, it has been reported [22] that at atmospheric pressure pentacene does not melt but decomposes above 300°C with formation of dihydropen- tacene and a carbonaceous residue. Nevertheless, results obtained with pentacene (Fig. 3) indicate that exothermal condensation occurs (406°C) just after the beginning of the endothermal decomposition (399°C). As indicated above, direct ring condensation is rarely found, however, acene systems (i.e., structures formed by direct annellation of benzene rings) are well known for their high reactivity [22]. This may justify the

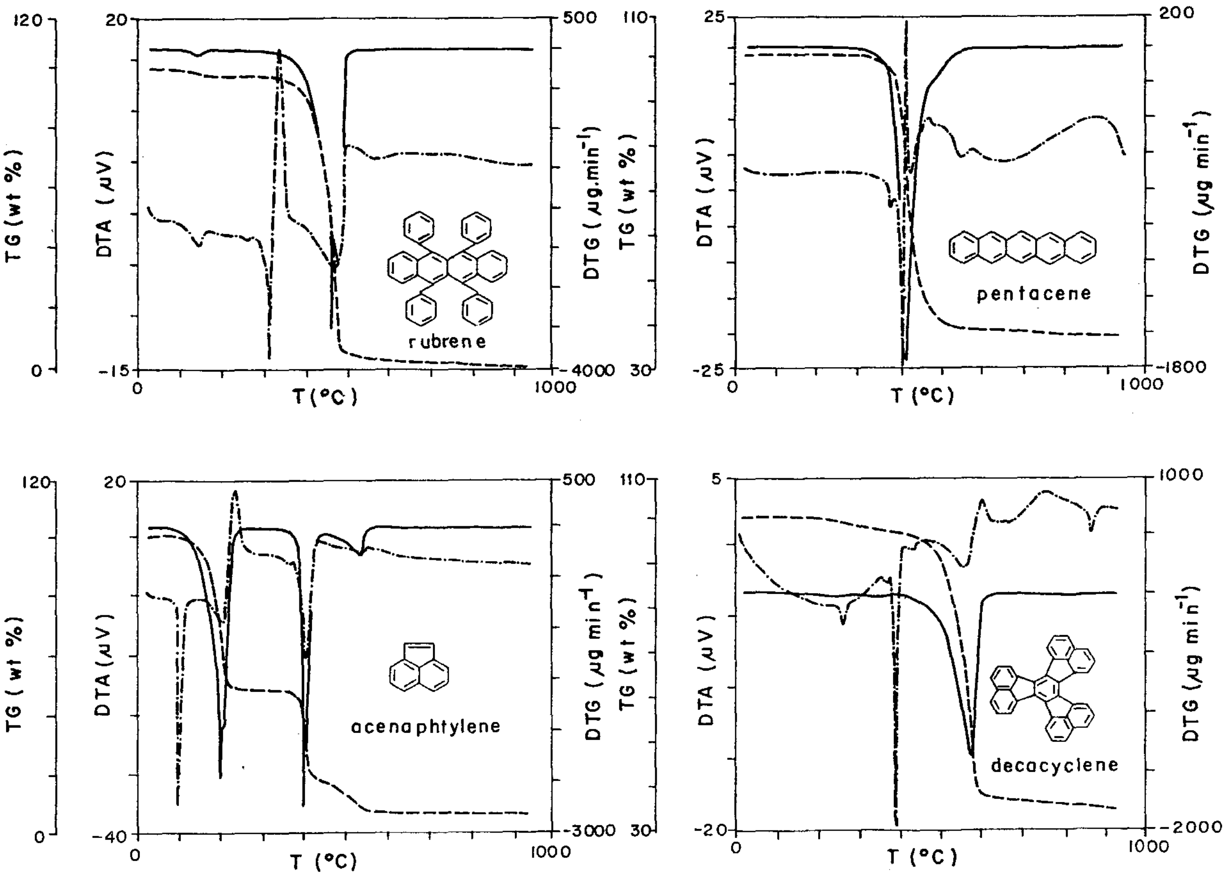

Fig. 3 TG, DTG and DTA curves for some highly reactive PAH

high tendency to condensation and subsequent strong graphitizing behaviour shown by rubrene and pentacene. In this respect, rubrene behaves much like naphtacene, suggesting that rupture of benzylic bonds occurs prior to condensation.

Acenaphtylene has long served as a model solid organic precursor yielding a good graphitizable carbon [1, 27–31]. Its thermal decomposition is very complex, and intermediate products formed in the various steps have been characterized in detail [27, 28, 30, 31]. The relative extent of the various TG steps shown in Fig. 3 for this hydrocarbon differs from a previous report from the literature [1], this being undoubtedly due to the very different heating rate used, however, the steps are qualitatively identical and they occur in the same temperature intervals. On the other hands, we are not aware of any previous publication of DTA results for acenaphtylene. As Fig. 3 shows, after a DTA endothermal melting peak, a weight loss step takes place from this temperature to 232°C that should correspond to loss of light compounds by neutralization (initial DTA endotherm at 203°C) of radicals formed from acenaphtylene, a part of them polymerizing to polyacenaphtylene [1] near the end of weight loss (DTA exotherm at 229°C).

From 232° to 380°C the polymer does not undergo appreciable mass and energy changes (Fig. 3), although fluorocyclene and biacenaphtylidene have been proposed and intermediates formed from it in the above temperature range [1]. Starting from 380°C a new weight loss starts that extends up to 420°C yielding a DTA endotherm at 399°C. This second TG step has been attributed [1] to thermal depolymerization leading to decacyclene. Arrangement in parallel layers of the almost planar molecules of decacyclene thus formed has been proposed to explain mesophase formation from acenaphtylene above 405°C [29]. A third TG step occurs from 439° to 555°C with maximum rate of weight loss at 528°C. This should be due to decomposition of decacyclene with formation of zethrene and further condensation. The DTA signals are in this case very weak and, unfortunately, they add little information concerning this reaction step. Thermoanalytical results obtained during pyrolysis of decacyclene (Fig. 3) confirm most of the above asserts since, after a strong endotherm (394°C) corresponding to melting, a TG step appears between 419° and 599°C (DTG peak at 577°C). In the temperature interval where weight loss occurs, the DTA curve shows weak, overlapping peaks: an endothermal one (559°C) near the DTG peak, and an exothermal one at 602°C. A further exotherm at 760°C should be associated (as for other PHA and pitch samples) with hydrogen loss and aromatization (note the small, continuous weight loss from 599° and 950°C).

Concluding remarks

Thermoanalytical studies of the pyrolysis of polycyclic aromatic hydrocarbons provide clear insights into the nature of processes taking place during pitch pyrolysis.

The most probable exothermal phenomena occurring during pitch pyrolysis are condensation and polymerization reactions. Occurrence of condensation reactions suggests the presence in pitches of molecules with enhanced reactivity, e.g., bearing alkyl substituents, methylene groups, naphtenic structures, etc. Such reactive molecules are likely to be present in significant amounts in petroleum pitches (even for the binder pitch PP studied in this work) as shown by their mostly exothermal DTA behaviour.

Endothermal phenomena involved in pitch pyrolysis include most probably distillation, depolymerization, and cracking. Distillation should involve light and/or little reactive (i.e., those undergoing vaporization before thermal decomposition) molecules. Depolymerization will usually occur subsequently to polymerization, so that in this case exo- and endothermal types of reaction would take place in successive steps. Low molecular weight and little reactive compounds are likely to be main constituents of coal tar pitches, where DTA peaks are mainly endothermal.

Overlapping between exo- and endothermal phenomena are very likely to occur during pitch pyrolysis due to the extremely complex composition of pitches. Distillation and condensation are expected to overlap, the final balance being the result of the relative tendencies of the constituent molecules to vaporize and/or undergo rupture plus condensation.

DTA is a suitable method for characterizing the thermal behaviour of pitches, as it allows to differentiate samples with very similar TG/DTG features. Moreover, DTA can provide specific insights on the chemistry of this process.

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References

1 E. Fitzer, K. Mueller and W. Schaefer, Chemistry and Physics of Carbon (P. L. Walker, Jr. Ed.), Marcel Dekker, New York 1971, p. 237.
2 R. W. Wallouch, H. N. Murty and E. A. Heintz, Carbon, 10 (1972) 729.
3 Thermal Analysis of Electrode Binder Pitches, BCRA Carbonization Research Report No. 68, BCRA, Chesterfield 1979.
4 V. I. Denisenko, A. N. Chistyakov, M. V. Vinogradov and M. L. Itskov, Khim. Tverd. Topl., 18 (1984) 125.