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Hydrogen donor and acceptor abilities of pitches from coal and petroleum evaluated by gas chromatography¹

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Abstract

Among the characteristics of coal-tar and petroleum pitches, the thermal reactivity of their constituents is one of the most important because it determines the development of mesophase and, consequently, the structure of graphitizable carbons (cokes). At the early stages of the carbonization process the hydrogen transfer reactions and the availability of donatable hydrogen are crucial to give high fluidity/low viscosity systems. In such conditions, aromatic molecular systems have enough mobility to stack parallel to each other resulting in a more ordered coke structure. A chemical procedure for estimating the reactivity of a pitch to supply and consume hydrogen from the reaction system is the co-carbonization with anthracene and 9,10-dihydroanthracene (DHA) as hydrogen acceptor and donor agents, respectively. A series of pitches including impregnation and binder coal-tar pitches, petroleum pitches and pitch-like residues from the by-products coking plants was studied. Carbon disulphide extracts from the co-carbonization systems (pitch+anthracene and pitch+DHA) were analyzed by capillary gas chromatography. Results indicate that pitches with the highest hydrogen donor ability favour the formation of 1,2,3,4-tetrahydroanthracene in the reaction system. The relation between the amount of volatile matter released in the temperature range of 400–500°C and the hydrogen donor and acceptor ability of the pitches can be considered as important factors in the development of coke structure. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: Coal-tar pitch; Petroleum; Anthracene; Dihydroanthracene; Tetrahydroanthracene

1. Introduction

Graphitizable carbons are formed from parent materials, e.g., coal-tar and petroleum pitches, which pass through a fluid stage during carbonization. The fluidity of the reaction system facilitates the appropriate mobility of the aromatic molecules in the system, resulting in intermolecular dehydrogenative

polymerization reactions to create aromatic, lamellar molecules. These aromatic molecules ‘associate’ to create an intermediate anisotropic nematic liquid crystal phase—mesophase—in the isotropic fluid matrix at a temperature between 350 and 500°C [1,2]. A fluid phase is the requirement for the production of graphitizable carbons. The stages following the formation of the anisotropic mesophase spheres within the carbonizing system are the growth and coalescence of the mesophase spheres to give an anisotropic carbon material. It is generally accepted that the role of inter- and intramolecular hydrogen transfer reactions and the availability of transferable

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hydrogen in terms of the stabilization of reactive free radicals in mesophase development are crucial factors in the formation of anisotropic cokes (graphitizable carbons) [3–6]. During the carbonization process thermal cleavage of C–C and C–H bonds in reactive components of starting materials gives free radicals. When these thermally induced radicals are not stabilized by transferable hydrogen from the system, they may rapidly recombine with other species present in the high viscous system to form isotropic carbon and small-sized anisotropic carbon structures. However, when the radicals are stabilized by hydrogen transfer reaction, the growth of aromatic molecules occurs and, consequently, the growth and coalescence of mesophase takes place under low viscosity/high fluidity conditions and more ordered anisotropic carbon structure is formed. The formation and the effective stabilization of radicals by hydrogen transfer depend upon the chemical composition of pitch and the reactivity of its components. While physical methods are widely used to obtain structural information and to relate structural parameters to the thermal behaviour of pitch during mesophase formation, chemical methods such as the evaluation of hydrogen transfer ability can be also useful in this respect [7–12]. The amount of transferable hydrogen is closely related to the hydrogen donor (HDa) and acceptor abilities (HAa) of pitch. Hydrogen donor ability of a pitch is strongly influenced by the hydroaromatic structures since they provide the hydrogen radical to stabilize thermally induced radicals, to give rise to low molecular species and to improve the fluidity of the reaction system. The fluidity of the system allows carbon network layers to stack parallel to each other resulting in larger and more ordered optical texture of the resultant carbon material. That means that hydrogen donor ability (HDa) of a pitch reflects the modifying ability of the reaction system while the hydrogen acceptor ability (HAa) is an indication of the transformation of the pitch itself. The HDa can be measured by the formation of 9,10-dihydroanthracene (DHA) from anthracene (hydrogen acceptor) at 400°C and a heating rate of 5 K/min, while hydrogen acceptor ability can be estimated by the formation of anthracene (ANT) from 9,10-dihydroanthracene (hydrogen donor). The evaluation of DHA and ANT has been carried out by proton

NMR [7–11]. Alternative techniques for the evaluation of DHA and ANT such as gas chromatography (GC) was also used [13]. The authors claim that GC analysis of reaction samples is simpler and faster than proton-NMR analysis, especially for detecting and evaluating the existence of consecutive hydrogen transfer reactions to form 1,2,3,4-tetrahydroanthracene (THA) which needs to be considered in the total HDa and HAa determinations [13].

In this study, GC–flame ionization detection (FID) was used for the evaluation of DHA, THA and ANT to assess: the parameters HDa and HAa (partial and total) and the amount of compounds formed by secondary reactions such as ring-opening reactions. This work constitutes an attempt to widen the knowledge of hydrogen transfer reactions in pitches of different origin (petroleum and coal-tar) and different industrial applications and to assess their influence on the critical carbonization stage in the temperature range between 400 and 500°C.

2. Experimental

The series of nine pitches used in this study includes: two residues from the distillation column of benzol of the by-product coking plants (pitch-like residue, RP1 and RP2), four commercial pitches derived from coal tar with different characteristics and industrial applications (one impregnation pitch (BI1) and three binder coal-tar pitches (CTP) and three petroleum pitches (PP)). The main characteristics of these materials are shown in Table 1.

To evaluate hydrogen donor and acceptor abilities (HDa and HAa, respectively), anthracene (ANT) was used as a hydrogen acceptor compound while 9,10-dihydroanthracene (DHA) was assessed as a hydrogen donor agent. Heat treatment of mixtures of ANT or DHA and pitch (1:1, w/w, total amount 0.4 g) at 400°C was carried out in sealed pyrex–glass tubes in the absence of air at a heating rate of 5°C/min with no soaking time [8,13,14]. After the reaction, the sealed tubes were cooled to room temperature and then stored in the refrigerator until the subsequent GC analysis were carried out. To prevent oxidation of anthracene derivatives, the reaction tubes were opened and the residues immediately extracted with CS₂ and then the extracts analyzed by capillary GC.

Table 1
Origin and main characteristics of pitches

Pitch	C/H ^a	N+S+O ^b	SP (°C) ^c	QI (wt%) ^d	TI (wt%) ^d	CS ₂ -I (wt%) ^d	VM400–500 (wt%) ^e	CY (wt%) ^e	LWMC (%) ^f
Pitch-like residues									
RP1	1.59	5.7	53	1.0	21.8	30.0	8.9	30.8	1.1
RP2	1.55	6.0	75	1.7	32.2	37.9	14.0	35.2	5.7
Impregnation pitch									
BI1	1.58	1.9	50	9.8	30.0	26.9	20.1	38.0	5.0
Binder coal-tar pitch									
CTP1	1.98	1.9	98	17.3	38.1	37.0	35.4	44.8	2.1
CTP2	1.87	1.5	85	9.4	29.4	29.5	33.3	41.8	0.6
CTP3	1.75	1.8	93	2.9	27.4	33.9	30.5	42.4	<0.1
Petroleum pitch									
PP1	1.29	0.2	110	0.6	17.0	15.0	29.4	45.1	2.6
PP2	1.42	0.5	123	0.0	29.0	22.0	32.7	50.8	1.4
PP3	1.42	0.1	140	5.0	29.0	17.5	36.0	50.4	1.3

^aCarbon:hydrogen atomic ratio from elemental analysis.

^bNitrogen, sulphur and oxygen content from elemental analysis.

^cSoftening point by Kraemer–Sarnow method.

^dQI, quinoline insoluble; TI, toluene insoluble; CS₂-I, carbon disulphide insoluble

^eVM400–500: the amount of volatile matter released between 400 and 500°C; and CY: coke yield determined at 1000°C in a termbalance. Data taken from reference [16].

^fLWMC, percentage in the CS₂ extract of pitches of low-molecular-weight components (alkyl substituted and no substituted aromatic compounds containing from one to three rings).

The GC analyses were achieved on a Hewlett-Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph equipped with FID and a Hewlett-Packard Vectra ES/12 computer for storing the chromatograms. Separations were performed using a fused-silica capillary column (25 m×0.25 mm I.D.) coated with SE-54 (McReynolds polarity=337) with temperature programmed from 100 to 190°C at 4°C/min, hydrogen as carrier gas (flow-rate, 2 ml min⁻¹), splitter ratio of 1:80, injector and detector temperature of 300 and 350°C, respectively. For chromatographic quantification, fluorene was used as an internal standard [13–15]. The reaction of pitches with ANT gave two major hydrogenated products, DHA and THA, which were identified by comparison of retention time with those of standard compounds and confirmed by GC–MS analysis. The HDA of pitches was calculated from the amount of DHA and THA formed from anthracene and expressed as milligrams of hydrogen per gram of pitch. With the assumption that THA was produced from DHA, the HAA was estimated as the difference between the amount of ANT and the THA formed after heating. The HAA is also expressed as milli-

grams of hydrogen per gram. The data are the average of at least three chromatographic determinations.

The thermogravimetric measurements of the pitches were carried out using a Perkin-Elmer TGA7 thermobalance. Briefly, samples (100 mg) were heated to 1000°C at a rate of 3°C/min, at a nitrogen flow-rate of 95 ml/min [16,17]. The coke yield (CY) defined as the weight percent of residue after heat treatment at 1000°C and the percentage of the volatile matter between 400 and 500°C (VM400–500) were chosen as parameters reflecting the thermal behaviour of pitches [14–17].

3. Results and discussion

The GC analysis of CS₂ extracts of the residue from heating anthracene (ANT) alone showed that no detectable amount of products from self disproportionation reactions occur under the tested conditions (Fig. 1a).

When anthracene (hydrogen acceptor) was carbonized with pitch under the same conditions, two major

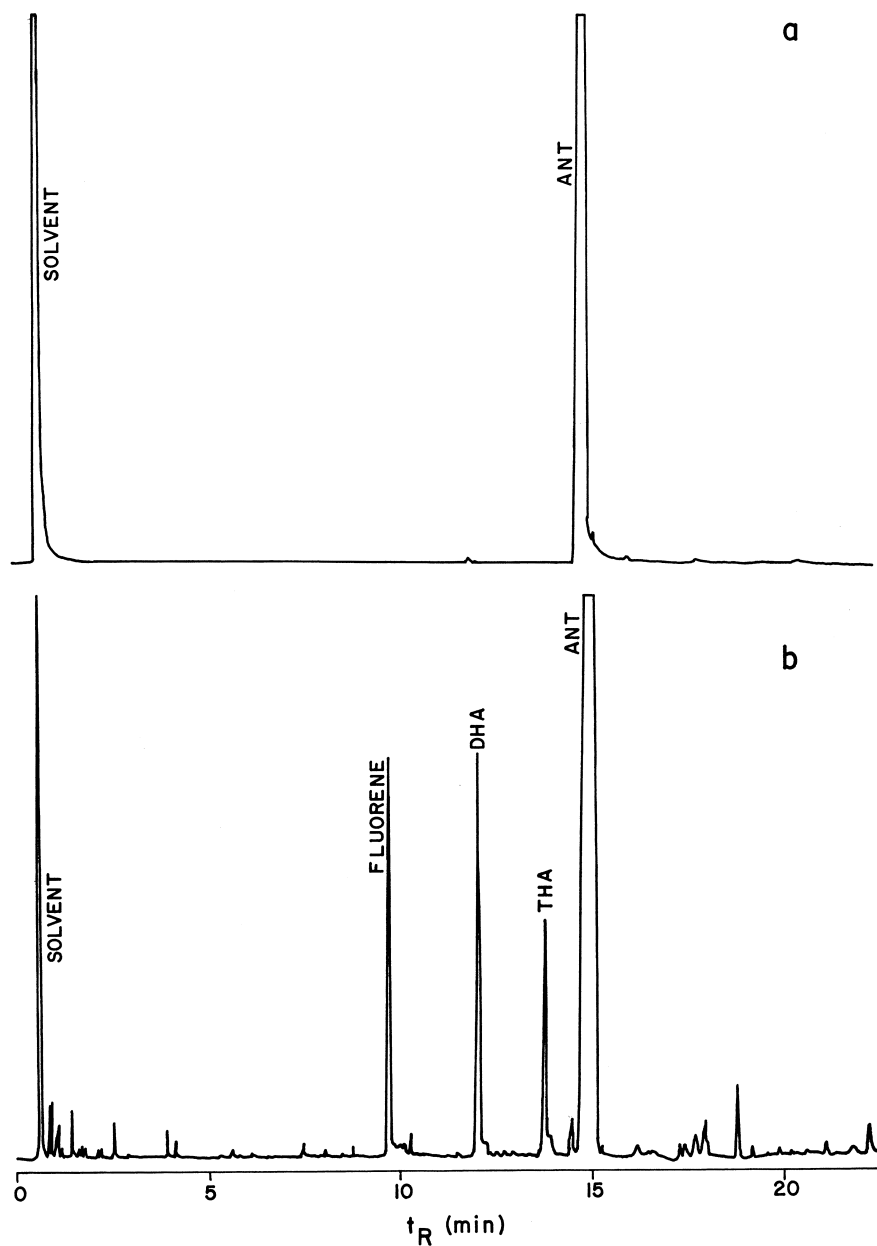


Fig. 1. Capillary gas chromatograms of the CS_2 extracts from the reaction of (a) single anthracene at 400°C ; and (b) petroleum pitch PP2+anthracene at 400°C . ANT, anthracene; DHA, 9,10-dihydroanthracene; THA, 1,2,3,4-tetrahydroanthracene.

hydrogenated products, DHA and THA, were generated (Fig. 1b). The initial step of the thermal reaction of anthracene in the presence of a source of transferable hydrogen appears to be the formation of DHA which is formed via hydrogen transfer at the central

carbon atoms in anthracene (the 9- and 10-positions). The values of the free valence by simple molecular orbital theory for the different carbon positions in anthracene [18–20] show that the formation of DHA (the maximum free valence indices at the 9- and

10-positions, 0.520) should be the dominant reaction [18–20]. As the free valence index can be considered to be an approximate indication of free radical activity [18–20], the 1- and 2-positions in anthracene (0.459 and 0.408, respectively) are expected to be less reactive [18]. However, as can be deduced from Fig. 1b, the formation of DHA is not fully selective and THA is also produced.

Although the chemistry for the formation of THA in liquid and gaseous phases is not clear, two possible types of reaction can be considered. The first type of reaction involves that, on further transferable hydrogen, the two *meso*-hydrogen atoms in DHA can migrate to one of the site rings via radical formation [21] and, then, THA will be formed. This reaction consumes transferable hydrogen from the reaction system and/or an amount of the DHA formed. The second one proceeds, in addition to DHA formation from anthracene, via direct hydrogen transfer at the end of the anthracene molecule to give THA. This means that less positional selectivity occurs. As in the previous reaction, it consumes donatable hydrogen from the pitch or from the DHA formed. A combination of the two types of reaction is also not excluded. Although the main features of the thermal chemistry of anthracene in liquid phase are well established [21], very little information on mechanistic details of THA formation is available and further clarification is required.

When pitch is present in the reaction system, the GC analysis indicates that other types of reaction, such as ring-opening reactions, took place in the reaction system leading to naphthalene derivatives with short chains. This fact is clearly observed from the chromatogram corresponding to petroleum pitch PP2 in Fig. 1b. Compounds with smaller retention time than fluorene (internal standard) were identified by GC–MS as naphthalene (m/z 128), methyl-, dimethyl- and trimethyl naphthalenes (m/z 142, 156, 170), diphenylmethane (m/z 168) and methyldiphenylmethane (m/z 182). Although these compounds are present in the CS₂ extracts of the starting pitches without thermal treatment at 400°C, the GC analysis reveals that the total amount of aromatic compounds containing one to three rings with or without alkyl substitution is always lower than 5.7% (Table 1). This is in agreement with previous results corresponding to pitches of different

origin and properties [22,23]. The recovery of the products (unreacted ANT, DHA and THA) was always higher than 90%, except for three pitches RP1, BI1 and PP2. The highest values correspond to the commercial binders CTP1 and CTP2 (more than 96%) indicating that ring-opening reactions do not occur to a significant extent (Table 2).

The transferred hydrogen from the pitch to anthracene can be monitored by the extent of formation of DHA and THA (HDa–DHA and HDa–THA, respectively). Different parameters were estimated which reflect the amount of hydrogen transferred from ANT to DHA (HDa–DHA); the amount of hydrogen donated from the pitch to form THA (HDa–THA). Taking into account the above considerations on the THA formation and those findings in previous studies [13], the third parameter was defined as the total amount of transferable hydrogen involved in the formation of both, DHA and THA (HDa). Table 2 shows the partial and total hydrogen donor ability values of the pitches. As expected, all the pitches studied have the ability to donate hydrogen to anthracene, the highest being for petroleum pitches. Due to their origin, petroleum pitches are rich in alkyl substituents and naphthenic and hydroaromatic systems. This is reflected by the lower atomic C/H ratio from elemental analysis (Table 1). However, the distribution of the above components in the different petroleum pitches is certainly not constant and its variation broadly modifies the ability of the pitch to donate hydrogen to anthracene. As

Table 2
Recovery from the hydrogen donor ability tests and partial (HDa–DHA and HDa–THA) and total (HDa) hydrogen donor ability of pitches determined from GC analysis

Pitch	Recovery (%) ^a	HDa–DHA	HDa–THA	HDa
RP1	86.8	0.295	0.111	0.406
RP2	92.7	0.288	0.140	0.428
BI1	88.1	0.402	0.169	0.571
CTP1	97.2	0.387	0.191	0.578
CTP2	96.4	0.400	0.159	0.559
CTP3	92.4	0.254	0.075	0.329
PP1	92.7	0.646	0.667	1.313
PP2	89.1	0.743	0.740	1.483
PP3	91.2	0.881	1.095	1.976

^aRecovery of unreacted anthracene and 9,10-dihydroanthracene (DHA) and 1,2,3,4-tetrahydroanthracene (THA) which are formed in the pitch/anthracene system.

only naphthenic and hydroaromatic systems are considered to be the pitch constituents contributing to HDa, no correlation between atomic C/H ratio and HDa can be expected.

On the contrary, the commercial binder CTP3 has the lowest value, suggesting that the modifying ability of this pitch is very limited. For pitches derived from coal tars and those generated in the by-product plants as a residue, the contribution of HDa–DHA to the total HDa values accounts for more than 67%, while for the petroleum pitches studied it always represents $\leq 50\%$. This means that, in general, pitches with a great source of transferable hydrogen such as petroleum pitches promotes the formation of THA. In this case, the reaction between anthracene and pitch is less selective. Fig. 2 shows the relationship between the total HDa and partial HDa–DHA and HDa–THA values. The intercept of the two curves representing the same contribution of transferred hydrogen to generate DHA and THA gives a total HDa value of 1.553. For pitches with higher HDa values, there is a relevant contribution of HDa–THA to HDa values. Inclusion of additional data corresponding to petroleum cokes with a low HDa [14,15] shows the lower contribution of the formation of THA to the total HDa (Fig. 2). This

finding, again, suggests that the THA formation may be associated with donor–sample interactions.

On the contrary to anthracene, when heating 9,10-dihydroanthracene (DHA) alone to 400°C , one of the most typical hydrogen donor hydrocarbons, the GC analysis of the CS_2 extracts shows that the reaction proceeds mainly via hydrogen donation from DHA to form ANT (27%) and probably via hydrogen transfer across 9,10-positions in DHA to give THA (7%). If so, the reactions taking place in the self-disproportionation of DHA imply a consumption of the DHA available in the system. However, no secondary reactions such as ring-opening reactions can be drawn from the GC analysis (Fig. 3a).

As in the case of the evaluation of hydrogen donor ability, the presence of pitch induces ring-opening reactions (Fig. 3b, Table 3) which probably proceed via hydroaromatic intermediates forming free radicals [21]. The recovery of unreacted DHA and ANT and THA formed in each run is quite similar to that found in the evaluation of hydrogen donor ability. That is, in both tests, the extent of secondary reactions to give ring-opened products is quite similar, with the exception of petroleum pitch PP1.

The total hydrogen acceptor ability (HAa) is higher for pitch-like residues RP1 and RP2 (Table

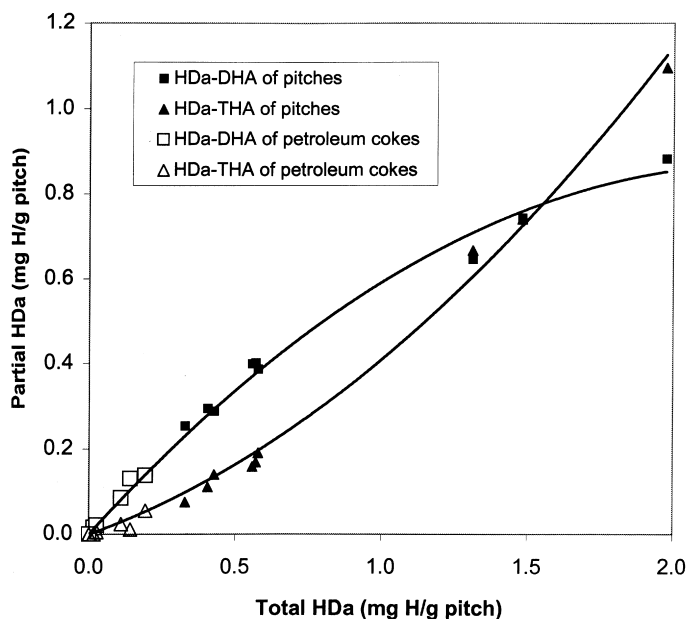


Fig. 2. Relation between the total (HDa) and partial (HDa–DHA and HDa–THA) hydrogen donor abilities of pitches and petroleum cokes.

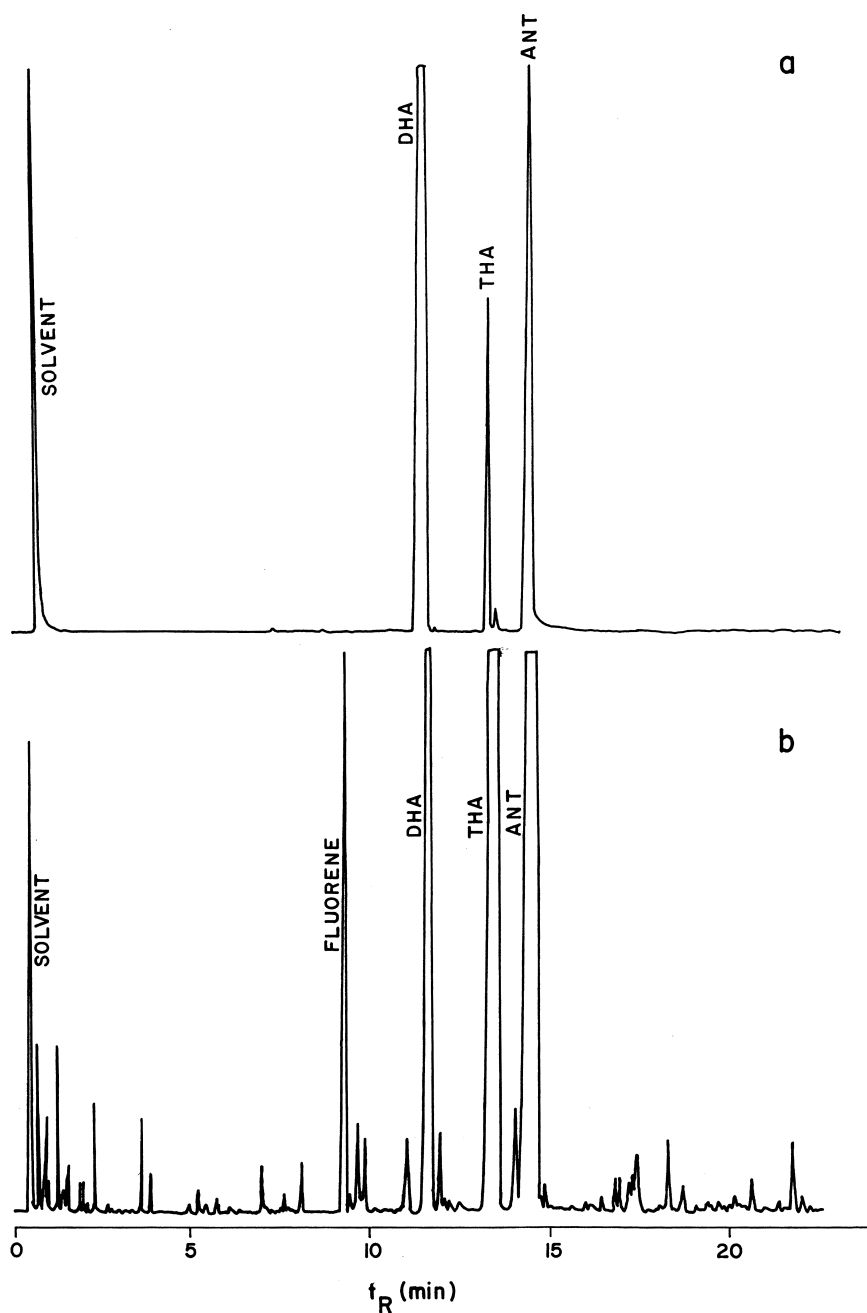


Fig. 3. Capillary gas chromatograms of the CS_2 extracts from the reaction of (a) single 9,10-dihydroanthracene at 400°C ; and (b) petroleum pitch PP2+9,10-dihydroanthracene at 400°C . ANT, anthracene; DHA, 9,10-dihydroanthracene; THA, 1,2,3,4-tetrahydroanthracene.

3). No clear relation was found between the total and partial HAa. On the other hand, the total hydrogen acceptor abilities of pitches are always larger than

HDa, except for PP3 (Tables 2 and 3). Considering all the pitches studied no relationship was found between HDa and HAa. However, attending to the

Table 3

Recovery from the hydrogen acceptor ability tests and partial (HAa-ANT and HAa-THA) and total (HAa) hydrogen acceptor ability of pitches determined from GC analysis

Pitch	Recovery (%) ^a	HAa-ANT	HAa-THA	HAa
RP1	85.9	6.025	1.351	4.674
RP2	90.1	4.168	0.931	3.237
BI1	87.8	4.344	2.361	1.983
CTP1	97.1	4.441	2.628	1.813
CTP2	96.1	4.565	2.501	2.064
CTP3	91.3	5.579	3.154	2.425
PP1	86.7	5.374	2.890	2.484
PP2	89.5	5.906	3.612	2.294
PP3	91.7	5.271	3.579	1.692

^aRecovery of unreacted 9,10-dihydroanthracene (DHA) and anthracene (ANT) and 1,2,3,4-tetrahydroanthracene (THA) which are formed in the pitch/DHA system.

different origin of the pitches, they can be clearly differentiated by their ability to donate and consume transferable hydrogen during carbonization. Fig. 4 displays the relation between VM400–500 and the hydrogen donor and acceptor abilities of the pitches studied. In previous studies, the parameter VM400–500 has been successfully used in the characterization of delayed petroleum cokes [14,15] and tars and pitches [16,17] to evaluate the degree of chemical activity in the fluid stage of co-carbonizing systems. It reflects the amount of volatile matter released in the temperature range between 400 and 500°C and can be taken as an indication of the modifying ability of the material during thermal treatment. The molecular species evolved in this temperature range should act as reactive components providing paths for chemical reactions such as hydrogen shuttling or stabilizing free radicals [3,5]. In the case of petroleum cokes, a good correlation has been observed between VM400–500 and the ability to supply transferable hydrogen to the reaction system. Higher hydrogen donor ability of petroleum coke in terms of hydrogen transfer to anthracene (HDa) was associated to a higher amount of volatile matter released between 400 and 500°C [14,15].

In this study, lower HDa and higher HAa values characterize the two residual pitches, containing no significant amount of quinoline-insoluble material (Table 1). Higher values of the hydrogen acceptor ability (HAa) correspond with lower hydrogen donor ability (HDa) of the pitch. With less donatable

hydrogen available in the carbonizing system, intermediate free radicals may decompose into gaseous products and condense into coke. In such conditions, reactive free radicals can moderately be stabilized by the hydrogen donor compounds present in the pitch and the condensation of aromatic molecules is accelerated because pitch can not satisfy the demand of transferable hydrogen. This results in a high amount of volatile matter released during the first stages of carbonization, less effective volatile matter in the critical stage of the process (VM400–500) and a low yield in coke (Table 1). The lower volatile matter involved in the critical stage of carbonization (VM400–500) and the great number of heteroatoms contained in these pitches (Table 1) may be the reasons to weaken its HDa and to exhibit its high degree of transformation (HAa). From Fig. 4a, there appears that petroleum pitches, containing no quinoline insoluble material (Table 1), belong to the same family with intermediate values for the impregnation pitch BI1. The petroleum pitches, however, exhibit highest hydrogen donor ability and less or more moderate hydrogen acceptor ability (Fig. 4). It can be due to the lower proportion of polar compounds which is reflected in the content of heteroatoms (N, S and O) (Table 1), together with the higher concentration in naphthenic and hydroaromatic compounds expected for this type of pitch. Opposite to residual pitches, hydrogen transfer is expected to take place efficiently to stabilize free radicals. Then, the higher amount of volatile matter evolved in the temperature range between 400 and 500°C maintains the carbonizing system at relatively low viscosity/high fluidity. In such conditions, the growth and coalescence of mesophase is facilitated and, then, a higher coke yield and a more ordered coke structure will be obtained. Another different group corresponds to binder coal-tar pitches that are characterized by a moderate ability to supply and consume hydrogen in the carbonization process. The great difference with the petroleum pitches is the lower hydrogen donor ability. However, in terms of the consumption of hydrogen (HAa) which is provided to the system by DHA, the coal-tar pitches have equivalent values to the petroleum pitches studied and they fall in the same region (Fig. 4b). In general, there appears to be a link between the ability to donate hydrogen to anthracene and to accept

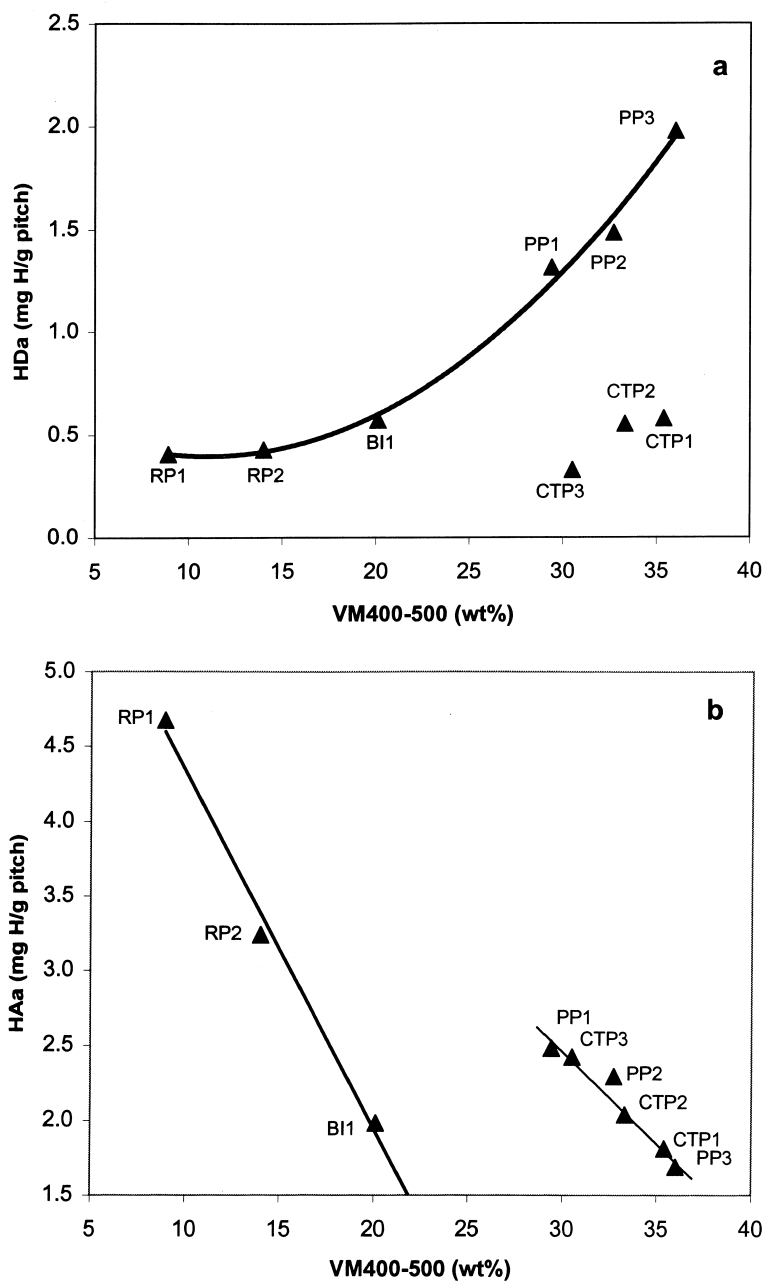


Fig. 4. Relation between the volatile matter released in the temperature range of 400 and 500°C (VM400–500) and: (a) the total hydrogen donor ability (HDa); (b) hydrogen acceptor ability (HAa) of pitches.

hydrogen from DHA for pitches of the same origin. The greater the donor reactivity of the pitch, the lower the facility to accept hydrogen from donating molecules within the system.

4. Conclusions

GC analysis is a simple and rapid method for evaluating the hydrogen donor and acceptor ability

of pitch and for monitoring the extent of ring-opened compounds formed during the co-carbonization. It can be established that the contribution of the formation of 1,2,3,4-tetrahydroanthracene to the total HDa is greater than 50% for pitches with a great source of donatable hydrogen. The hydrogen donor and acceptor abilities of pitches can be associated with the amount of volatile matter released between 400 and 500°C in the carbonization process.

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