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A relationship for the evaluation of coking values of coal tar pitches from their physical characteristics

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A relationship has been proposed to evaluate the coking values of coal tar pitches from the knowledge of their three other characteristics, namely, softening point, benzene insolubles content and quinoline insolubles content. It has been tried on 44 self-prepared coal tar pitches and 18 others obtained from the literature, possessing widely-ranging characteristics, and is found to give coking values comparable to those obtained experimentally. The coefficients of correlation between the theoretical (obtained using the relationship) and experimentally determined coking values for the two lots of pitches have been calculated to be 0.98 and 0.94 respectively, which indicate an excellent validity of the proposed relationship for the evaluation of coking values of coal tar pitches.

1. Introduction

Coal tar pitch is the second most important raw material used in the manufacture of conventional carbon and graphite products, where it is used as a binder [1-3]. The same coal tar pitch, but possessing lower softening point and lower contents of quinoline and benzene insolubles, is used as an impregnating pitch for the densification of these carbon products. Recently the authors [4-5] have found that a coal tar pitch of higher softening point than that of a conventional binder pitch, and possessing higher coking value and β-resins serves as a good preforming pitch for the development of high density carbon-carbon composites. For all these applications of coal tar pitch, its important properties are softening point (SP), benzene or toluene insolubles (BI), quinoline insolubles (QI), β-resins (BI-QI) and coking value (CV). The other characteristics such as specific gravity, apparent viscosity, molecular weight, C/H atomic ratio etc. are essentially taken care of by the properties stated above. Reasonably accurate, reproducible and fast methods covered under ASTM Standards exist for the determination of each of these important characteristics of a coal tar pitch. However, regarding the coking value determination, the authors have found from their studies [6] that the coking value of a pitch determined in N_2 atmosphere by heating the pitch to a temperature of 900° C in a 5 h cycle comes close to that found by the Conradson Carbon Residue Method. This is in agreement with the observations of Martin and Nelson [7] that by reducing the heating cycle from 40 h to 10 h in their Great Lakes method of CV determination at 1000° C in N_2 atmosphere, the CV of a pitch decreased and approached (though still higher) the value obtained by the Conradson method.

Tanaka *et al.* [8] tried to determine the relationship between the fixed carbon (FC) contents of pitches, derived from petroleum residues and the fixed carbon contents of their component parts (solvent fractions obtained using benzene and n-heptane), and found the necessity of a correction factor to obtain the coking value of a whole pitch from its components. A similar work has been carried out by the present authors wherein the aim has been to derive a relationship for evaluating the coking value of a coal tar pitch from the knowledge of its softening point, BI, QI and β-resins content. An equation has been found and applied to 44 self-prepared coal tar pitches having widely ranging characteristics, as well as to 18 others, the data of which were taken from the literature [9-11]. The details of the results obtained are described and discussed in this paper.

2. Theory

The theoretical evaluation of the CV of a coal tar pitch has been based on the law of mixture, i.e. the CV of a pitch is the sum total of the contributions towards the CV of its three components, namely, QI, β-resins (BI-QI) and BS obtained by solvent fractionization as shown in Fig. 1. It is reported [12, 13] that the coking values of the QI and β-resin (BI-QI) fractions of a coal tar pitch are almost constant and independent of the origin of the pitch. Further, it is known [14] that the coking values of the QI and β-resin (BI-QI) fractions vary around 95 to 97% and 87% respectively. In the present investigation, the authors have assumed the coking values of QI and β-resin (BI-QI) fractions at 95% and 85% respectively. However, the CV of BS fraction has been supposed to vary from 30 to 55% depending upon the softening point of the pitch. This is reasonable since the higher the softening point of a coal tar pitch, the higher will be average molecular weight of its BS fraction and consequently higher will be the contribution of this fraction towards the CV of

TABLE I Coking values, experimental as well as theoretical, along with other characteristics of 20 self-prepared coal tar pitches

Sample No.	SP (R&B) (°C)	BI (%)	QI (%)	β-resins (BI-QI) (%)	BS (%)	K	CV_{Exp} (%)	CV_{Th} (%)	Percentage deviation (%)
1	50	15.4	4.2	11.2	84.6	0.30	39.9	38.9	−2.5
2	72	19.6	6.0	13.6	80.4	0.35	44.0	45.4	+3.2
3	80	19.5	1.0	18.5	80.5	0.35	43.7	44.9	+2.6
4	80	20.3	6.5	13.8	79.7	0.35	47.4	45.8	−3.4
5	89	15.9	0.9	15.0	84.1	0.35	44.8	43.0	+4.0
6	96	25.7	7.6	18.2	74.3	0.40	51.7	52.4	+1.4
7	98	21.0	0.0	21.0	79.0	0.40	49.3	49.5	+0.4
8	105	28.8	4.3	24.5	71.2	0.40	55.9	53.4	−4.5
9	121	31.9	9.2	22.7	68.1	0.45	58.4	58.7	+0.5
10	122	33.6	10.0	23.6	66.4	0.45	62.7	59.4	−5.3
11	144	42.7	18.3	24.4	57.3	0.45	65.4	63.9	−2.4
12	145	42.6	8.2	34.4	57.4	0.45	63.5	62.9	−0.9
13	149	39.0	13.3	25.7	61.0	0.45	61.9	61.9	0.0
14	151	47.0	13.7	33.3	53.0	0.50	64.9	67.8	+4.5
15	152	46.1	13.6	32.5	53.9	0.50	65.9	67.5	+2.4
16	157	44.8	14.7	30.1	55.2	0.50	70.5	67.2	−4.7
17	159	36.4	13.2	23.2	63.6	0.50	61.5	64.0	+4.2
18	191	53.4	18.3	35.1	46.6	0.55	75.9	72.9	−4.0
19	192	63.2	8.2	55.0	36.8	0.55	78.1	74.8	−4.2
20	210	54.7	25.2	29.5	47.3	0.55	74.8	73.9	−1.2

the pitch. The proposed relationship for the CV of a coal tar pitch can thus be written as

$$(CV)_{Th} = QI \times 0.95 + (BI\text{-}QI) \times 0.85 + BS \times K$$

where, $0.30 \leqslant K \leqslant 0.55$, such that

$$K = 0.30 \text{ for } 50°C \leqslant SP \leqslant 70°C$$
$$K = 0.35 \text{ for } 70°C < SP \leqslant 90°C$$
$$K = 0.40 \text{ for } 90°C < SP \leqslant 120°C$$
$$K = 0.45 \text{ for } 120°C < SP \leqslant 150°C$$
$$K = 0.50 \text{ for } 150°C < SP \leqslant 180°C$$
$$K = 0.55 \text{ for } 180°C < SP \leqslant 220°C$$

It may be mentioned here that any possible effect of the mutual interaction between the three component fractions towards the CV, such as the surface induced carbonization effect in the BS fraction, due to the presence of QI, has been accounted for by selecting the value of K to be higher by about 0.05 than the fractional coking value of the isolated BS fraction.

3. Experimental procedure

44 coal tar pitches with widely ranging characteristics were prepared from two different crude coal tars by the techniques of distillation, condensation and polymerization at temperatures up to 420° C under partial vacuum and/or inert atmosphere of N_2. These were characterized with respect to SP, BI, QI and CV. The SP, BI and QI were determined as per the ASTM Standards nos. D 36-70 (Ring and Ball method), D 2317-76 and D 2318-76, respectively. However, the CV was determined by heating the pitch to a temperature of 900° C in N_2 atmosphere in a 5 h cycle.

Knowing the characteristics of the 44 self-prepared coal tar pitches, and those of 18 others chosen from the literature [9–11], the coking values were calculated

TABLE II Coking values, experimental as well as theoretical, along with other characteristics of 18 coal tar pitches selected from literature

Sample No.	SP (R&B) (°C)	BI (%)	QI (%)	β-resins (BI-QI) (%)	BS (%)	K	CV_{Exp} (%)	CV_{Th} (%)	Percentage deviation (%)	Ref.
1	93	30.3	4.5	25.8	69.7	0.4	54.1	54.1	0.0	[9]
2	98	23.9	4.6	19.3	76.1	0.4	53.3	51.2	−3.9	[9]
3	95	36.0	7.4	28.6	64.0	0.4	54.5	56.9	+4.4	[9]
4	102	28.1	5.8	22.3	71.9	0.4	54.7	53.2	−2.7	[9]
5	96	29.3	5.1	24.2	70.7	0.4	52.7	53.7	+1.9	[9]
6	98	21.8	3.5	18.3	78.2	0.4	50.4	50.2	−0.4	[9]
7	102	31.3	8.8	22.5	68.7	0.4	57.4	55.0	−3.8	[9]
8	103	37.0	13.6	23.4	63.0	0.4	59.1	58.0	−1.9	[9]
9	106	34.0	13.9	20.1	66.0	0.4	57.0	56.7	−0.5	[10]
10	107	36.8	12.0	24.8	63.2	0.4	55.0	57.8	+5.1	[10]
11	108	36.9	16.5	20.4	63.1	0.4	58.4	58.3	−0.2	[10]
12	102	37.7	14.1	23.6	62.3	0.4	57.5	58.4	+1.6	[10]
13	109	40.9	16.7	24.2	59.1	0.4	60.3	60.1	−0.3	[10]
14	114	42.2	16.0	26.2	57.8	0.4	61.0	60.6	−0.7	[10]
15	120	45.8	18.6	27.2	54.2	0.4	62.7	62.5	−0.3	[10]
16	110	32.7	13.2	19.5	67.3	0.4	58.0	56.0	−3.4	[11]
17	173	42.7	16.1	26.6	57.3	0.5	71.5	66.6	−6.9	[11]
18	174	49.0	16.7	32.3	51.0	0.5	67.7	68.8	+1.6	[11]

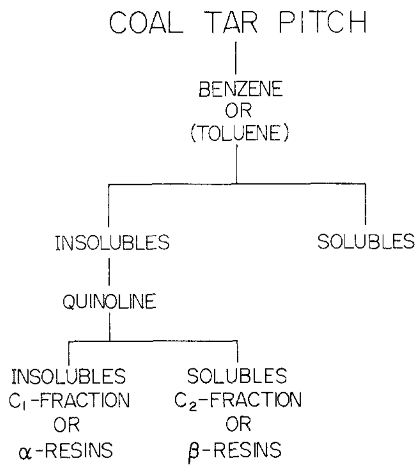

Figure 1 Solvent fractionation of a coal tar pitch.

by the presently devised relationship. The values so obtained were compared with the experimentally obtained coking values and the percentage deviation of these calculated coking values is computed in all the cases. The data of the coking values, experimental and theoretical both, along with the other characteristics of 20 coal tar pitches (a representative portion of 44 self-prepared pitches) and 18 others have been given in Tables I and II respectively. The deviations obtained in the various cases, have been divided into 3 groups as shown in Tables III and IV. The theoretically obtained coking values have been plotted against the experimentally obtained CV's for all the pitches as shown in Figs 2 and 3.

4. Results and discussion

Table I shows the characteristics of 20 pitches, as representative cases out of the lot of 44 self-prepared coal tar pitches, along with the coking values obtained using the proposed equation and the percentage deviations of these values from the experimentally determined coking values. However, the data on the distribution of these deviations have been given for all the 44 cases in Table III. It is seen from this table that in 50% of the cases, coking values estimated by the proposed equation vary within only 3% of the experimentally determined values. This observation refers to a very good workability of the equation. Further, in more than 45% cases the deviations vary in the range of 3 to 5%, which corresponds to reasonably good validity of the equation. It is only in less than 5% cases that the deviations are more than 5%. These observations are shown in the form of a graph between the theoretical CV (CV_{Th}) and the experimental CV (CV_{Exp}) in Fig. 2. It is seen in this figure that most of the points lie in a very narrow band around a line having a slope of 1. This is in agreement with the value of the correlation coefficient between CV_{Exp} and CV_{Th} which has been found to be 0.98. It can, therefore, be concluded that the proposed equation works very well for the given lot of 44 pitches.

TABLE III Distribution of percentage deviation in coking values in 44 coal tar pitches (self-prepared)

Group	Percentage deviation range	Number of cases (and their percentage)
1	0–3	22 (50.0)
2	3–5	20 (45.5)
3	5	2 (4.5)

Table II shows the data, collected from the literature, on the characteristics of 18 coal tar pitches, along with the coking values calculated using the proposed equation as well as their percentage deviations from the experimental values. However, the

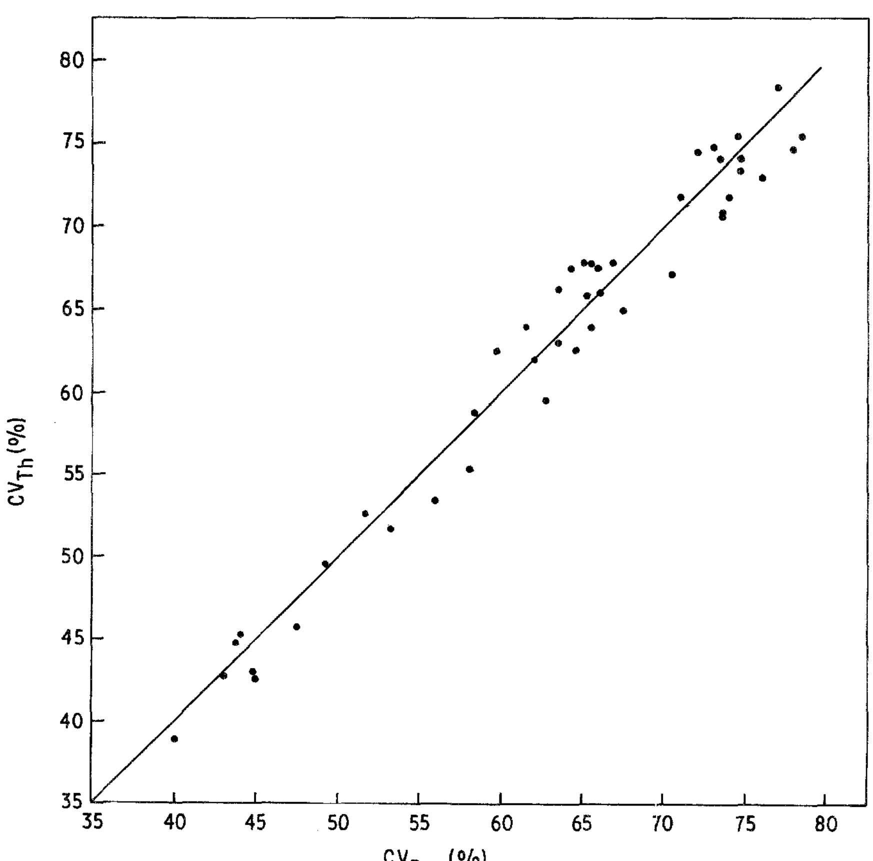

Figure 2 Relationship between the theoretical and experimental coking values for 44 self-prepared coal tar pitches.

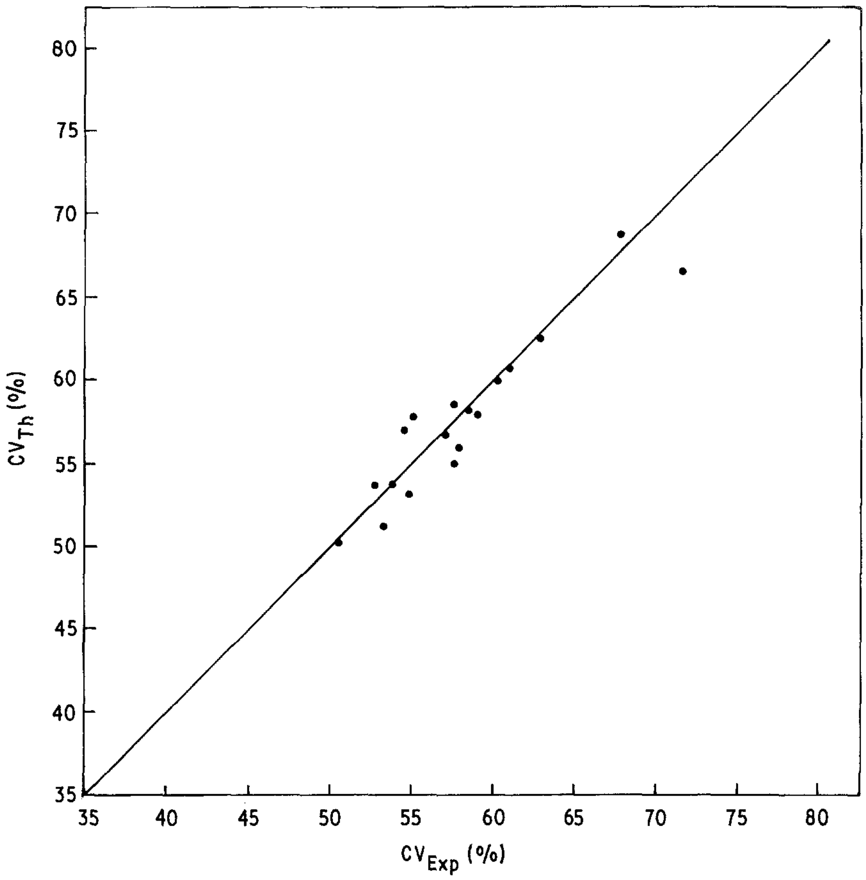

Figure 3 Relationship between the theoretical and experimental coking values for 18 coal tar pitches (data taken from literature).

break-up of these deviations into 3 groups is given in Table IV. From this table it is observed that in over 66% cases, the deviations lie within 3%; in more than 22% cases, the deviations vary in the range of 3 to 5%; and in about 11% cases, the deviations exceed a level of 5%. These observations are also evident from Fig. 3 showing a graph of the theoretical coking values versus the experimental ones, wherein again the points are seen to lie around a line with a slope of one. The correlation coefficient between CV_{Exp} and CV_{Th} in this case has been determined to be 0.94.

Thus, from the above observations, it may be concluded that the proposed relationship for the coking value of coal tar pitches works very well. The utility of this relationship lies in the fact that one could know, within a reasonable accuracy, the coking value of a coal tar pitch without actually determining it. In case the coking value has been determined experimentally, the relationship can be used to check the consistency of the different characteristics.

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TABLE IV Distribution of percentage deviation in coking values in 18 coal tar pitches (obtained from literature [9–11])

Group	Percentage deviation range	Number of cases (and their percentage)
1	0–3	12 (66.7)
2	3–5	4 (22.2)
3	5	2 (11.1)

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