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Effect of pressure on the coking yields of coal tar pitches

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Pyrolysis of five coal tar pitches with wide ranging characteristics, made from the same coal tar precursor, has been studied under nitrogen pressures of 10^5, 50×10^5, 90×10^5 and 160×10^5 Pa, at a temperature of 550 °C. The residues were further heat-treated to 900 °C to obtain the ultimate normal (10^5 Pa) and pressure coking yields of these pitches. The literature states that for pitches with relatively lower softening points the carbonization pressure not only increases the coking yield but also lowers the temperature at which the pyrolysis is complete. This is seen to hold true for the present set of pitches, having a much wider range of softening points. Further, one of the pitches, earlier reported by us to be a good preforming pitch for carbon–carbon composites, gave an ultimate coking yield of 88% on subjection to a nitrogen pressure of 160×10^5 Pa at 550 °C followed by ambient pressure carbonization to 900 °C. It thus appears that a carbonization pressure of 160×10^5 Pa for a suitable preforming pitch can act as a reasonably good alternative to the expensive hot isostatic pressure impregnation carbonization technique employed in the production of carbon–carbon composites.

1. Introduction

Pyrolysis of coal tar and petroleum pitches under nitrogen gas pressure has been studied by a number of researchers. Such studies are useful in the development of speciality carbons like high-performance carbon–carbon composites for aerospace, defence and other advanced applications. The aim behind these studies has been to obtain a higher coke yield of the pitch materials undergoing carbonization. Fitzer and Terewiesh [1] studied the effect of nitrogen gas pressure upto 10^7 Pa on the coke yield of conventional pitches, and found that maximum coke yields are achieved at pressures of approximately 10^7 Pa maintained upto 550 °C. Huttinger and Rosenblatt [2, 3] later reported that increasing the pressure does not only affect the increase in the coke yield, but also lowers the temperature at which the pyrolysis is completed. They further observed that the microstructure of the pitch pyrolysed under pressure becomes coarser and isotropic.

The improvement in the coking yield of commercial pitches as a result of pressure has, in fact, become the basis of a process called "hot isostatic pressure impregnation carbonization" (HIPIC), which is carried out in a specially modified and expensive hot isostatic pressure equipment [4–8]. It has been found that the HIPIC process is able to give a carbon–carbon composite with a density of about $2.0\,\mathrm{g\,cm^{-3}}$ as against a value $1.65\,\mathrm{g\,cm^{-3}}$ obtained using atmospheric pressure carbonization. The present authors have recently reported on the preparation procedure and the characteristics of a special coal tar pitch having a high softening point, a high coking value and a high content of beta-resins, which on field trials involving atmospheric pressure carbonization, led to carbon–carbon composites with a density of $1.8\,\mathrm{g\,cm^{-3}}$ [9–14].

Though substantial work has been done on the carbonization pressure of relatively lower softening point coal tars and petroleum pitches, nothing in this direction seems to have been reported on the above-said type of high softening point coal tar pitches. In view of this, an attempt was made to study the effect of pressure upto 160×10^5 Pa on the carbonization yields of five different coal tar pitches including the one possessing the characteristics suitable for making high density carbon–carbon composites reported by the present authors [14]. The present paper gives an account of this attempt and the results obtained therefrom.

2. Experimental procedure

A suitable crude coal tar was subjected to increasingly severe thermal treatments involving distillation, condensation and polymerization, in the temperature range of 350–400 °C and under a partial pressure of 10–20 cm Hg, to obtain five coal tar pitches numbered 1 to 5. These were characterized with respect to softening point (SP) by the Ring and Ball method, quinoline (QI) and toluene (TI) insolubles contents, beta-resins content, coking value (CV), carbon (C), hydrogen (H) and Nitrogen (N) contents, and atomic C/H ratio, as per the standard procedures. However, the

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TABLE I Characteristics of the various coal tar pitches

Pitch	Softening point (°C)	Quinoline insolubles (%)	Toluene insolubles (%)	Beta resins (%)	Coking value (%)	Carbon content (%)	Hydrogen content (%)	Nitrogen content (%)	Atomic C/H ratio
1	72	6.0	19.6	13.6	44.0	92.56	4.57	1.13	1.700
2	96	7.6	25.8	18.2	51.7	92.58	4.39	0.67	1.770
3	121	9.2	31.9	22.7	58.4	93.23	4.24	1.31	1.845
4	151	13.7	47.0	33.3	64.9	93.96	4.07	1.00	1.939
5	194	28.5	60.8	40.3	76.8	93.46	3.73	0.95	2.103

TABLE II Coking yields of the various coal tar pitches under different conditions of temperature and pressure. The figures in parentheses denote the pressure coking yields (in %) at 550 °C (intermediate values)

Pitch	Normal coking yield (coking value) (%)	Coking yields (%) (Ultimate values, HTT = 900 °C) of pitch samples pressure-coked at 550 °C under pressure ($\times 10^5$ Pa)			Ratios of pressure coking yields at 900 °C (Ultimate values) to the pressure coking yields at 550 °C (intermediate values) under pressure ($\times 10^5$ Pa)		
		50	90	160	50	90	160
1	44.0	46.2 (48.6)	47.0 (49.1)	47.3 (49.3)	95.0	95.7	95.9
2	51.7	54.8 (57.1)	56.6 (58.4)	61.4 (63.8)	96.0	96.9	96.2
3	58.4	63.0 (65.3)	68.1 (70.5)	75.0 (77.4)	96.5	96.6	96.9
4	64.9	72.4 (75.0)	78.0 (80.5)	88.0 (90.7)	96.6	96.9	97.0
5	76.8	84.0 (86.9)	87.2 (90.0)	92.4 (94.8)	96.7	96.9	97.5

The figures in parentheses denote the pressure coking yields (in %) at 550 °C (intermediate values).

CV was determined by heating the pitch to a temperature of 900 °C in a nitrogen atmosphere in a 5 h cycle [15]. The details of the characteristics of these five coal tar pitches are given in Table I.

All the five pitches were pyrolysed in a laboratory autoclave at a temperature of 550 °C under a constant nitrogen pressure of 50×10^5, 90×10^5 and 160×10^5 Pa in three separate experiments. The samples of pitches for these experiments were taken in covered cylindrical quartz crucibles. The temperature was raised at the rate of 3 °C min^{-1} and the final temperature of 550°C was maintained for 15 min. Then the pyrolysed samples were cooled and finally taken out of the autoclave and weighed. All these pressure pyrolysed samples were subsequently carbonized to 900 °C at ambient pressure, in an atmosphere of high-purity nitrogen, to determine their ultimate coking yields.

The data of the pressure coking yields of the five pitches carried out at 550 °C under the three different nitrogen pressures, along with the ultimate coking yields of these pitches (HTT = 900 °C, 1×10^5 Pa) has been compiled in Table II. This data has been used to plot the variations of pressure coking yields as well as the percentage increases in the normal coking yields by way of pressure carbonization, against the applied pressure and also against the normal coking yields (coking values), as shown in Figs 1–4.

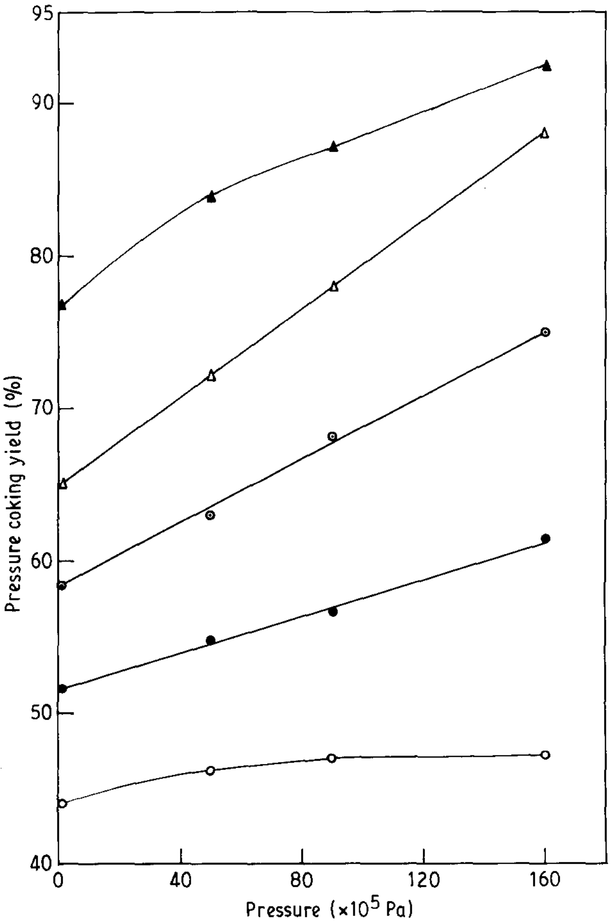

Figure 1 Pressure coking yield of the various coal tar pitches as a function of the applied pressure. (○) Pitch 1; (●) Pitch 2; (⊙) Pitch 3; (△) Pitch 4 and (▲) Pitch 5.

3. Results and discussion

Table I shows the characteristics of the five coal tar pitches 1 to 5, obtained from the coal tar precursor. It is observed that by increasing the severity of the heat-treatment conditions of the coal tar, one obtains increasingly higher values of the softening point, beta-resins content, aromaticity and coking value of the resultant pitches. This is quite obvious, as increasing severity of the thermal treatment will cause an increasing removal of the low molecular weight species from

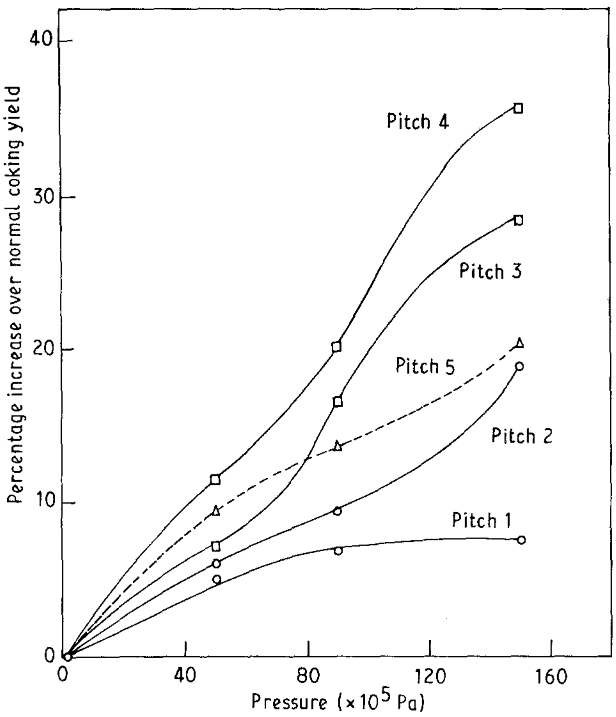

Figure 2 Percentage increase over the normal coking yield of the various coal tar pitches as a function of the applied pressure.

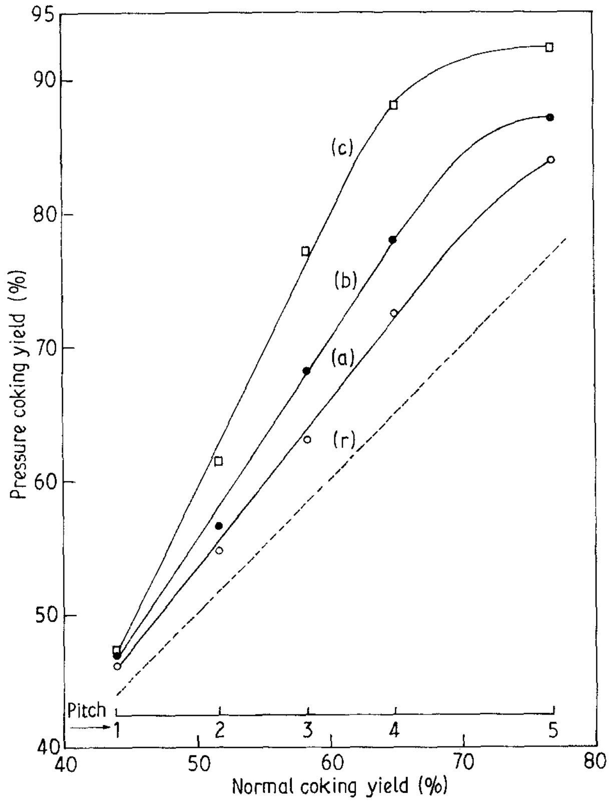

Figure 3 Pressure coking yield of the various coal tar pitches at different applied pressure as a function of the normal coking yield. (a) 50×10^5 Pa; (b) 90×10^5 Pa; (c) 160×10^5 Pa; (r) reference line with slope 1.

the tar, besides an increasing probability of condensation and polymerization reactions among the various molecular species.

Further, it is seen from Fig. 1 that the coking yields of all the pitches increase almost linearly, in general, as the pressure is increased from 1×10^5 to 160×10^5 Pa. Also, the slopes of the pressure coking yield versus pressure curves increase, as one goes from pitch 1 to pitch 4, having increasing values of the softening point, beta-resins content, aromaticity and coking value (normal coking yield). For the pitch 5, however, the slope of such curve is almost same as that for the pitch 4 upto a pressure of 50×10^5 Pa, beyond which it decreases. The increasing enhancement in the coking yield by the increasing pressure for a pitch may be attributed to the increasing suppression of the otherwise volatile components in the pitch by the increasing pressure. The increase in the slope of the pressure coking yield versus pressure curves, as one goes from pitch 1 to 5, may be due to the presence of decreasing amounts of low molecular weight components in the pitches, as is evident from their increasing softening points signifying their average molecular weights. The lowest value of this slope for pitch 1 (as seen in Fig. 1) may thus be attributed to the presence of the largest amount of the low molecular weight species present in this pitch, which may be difficult to coke even under pressure. The decrease in the slope of the curve for pitch 5 above a pressure of 50×10^5 Pa may be referring to the already high degree of aromaticity in this pitch, having relatively fewer volatile components capable of getting coked under pressure.

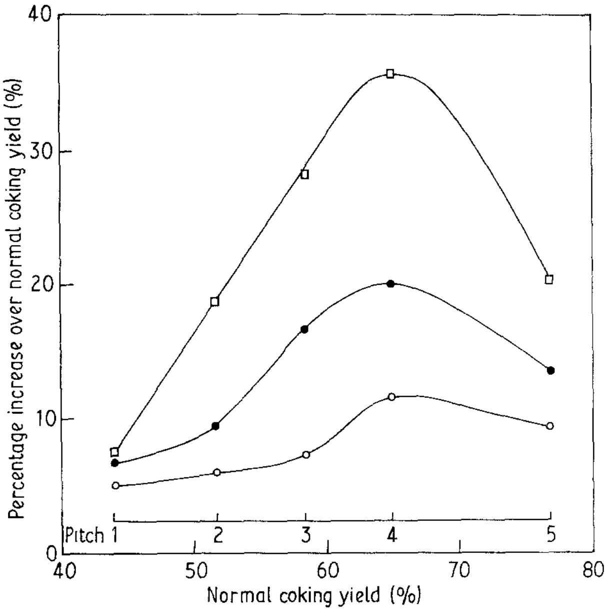

Figure 4 Percentage increase over the normal coking yield of the various coal tar pitches at different applied pressure as a function of the normal coking yield. (○) 50×10^5 Pa; (●) 90×10^5 Pa; (□) 160×10^5 Pa.

Further, it is clear from Fig. 2 that the percentage increase in the coking yields over the normal coking yield increases with the increasing pressure. However, this variation is different for different pitches. The percentage increase over the normal coking yield at a pressure of 160×10^5 Pa varies from a value of 7.5 for pitch 1 to a value as high as 35.6 for pitch 4, and this value decreases to 20.4 for pitch 5. This difference in the percentage increase in the coking yields could be attributed mainly to the difference in their characteristic parameters (Table I), such as the toluene and quinoline insolubles content and the C/H, atomic ratio reflecting significantly lower amounts of volatile matter in pitch 5 compared to pitch 4, and significantly higher ambient pressure (normal) coking yield of the former (pitch 5).

It may be noted from Table II, that besides the increase in the ultimate coking yields (HTT = 900 °C) of the pitches as a result of the application of pressure, the coking yields of these pitches at 550 °C also increases with the increasing pressure. It is interesting to note here that the ratio of the ultimate pressure coking yield (HTT = 900 °C) to the pressure coking yield at 550 °C for all five pitches at the three pressures varies between 95.0 and 97.5. This is confirmation of the findings of Huttinger and Rosenblatt [2, 3] that the application of pressure on low softening point pitches during carbonization causes the lowering of temperature at which the pyrolysis is completed [2, 3]. The present results thus extend the applicability of the above findings to higher softening point pitches also.

Also, it is interesting to note that as the pressure during carbonization is raised from 10^5 to 160×10^5 Pa, the coking yield of pitch 4 increases from 64.9 to 88.0%. It has been mentioned already that pitch 4 is a good preforming pitch for carbon–carbon composites [15]. So the application of 160×10^5 Pa pressure during the carbonization of an already suitable pitch is able to give a coking yield of 88%, which is what is generally achieved using a highly expensive HIPIC assembly employing a pressure of 700×10^5 Pa [7, 8].

Fig. 3 shows the pressure coking yield as a function of the normal coking yield. It is apparent that for any of the three applied pressures, the pressure coking yield increases almost linearly with the normal coking yield for the pitches 1 to 4. However, this effect tends to saturate for pitch 5. Further, it is seen from Fig. 4, depicting the curves of percentage increase over the normal coking yield versus the normal coking yield, that the percentage increase in the coking yield, over the normal coking yield, rises as one proceeds towards higher and higher normal coking yield upto a value of 64.9% referring to pitch 4, beyond which it comes down. Also, for any of the five pitches, the higher the applied pressure, the higher the percentage increase over the normal coking yield. Thus, out of all pitches, pitch 4 exhibits the highest percentage increase of 35.6 over the normal coking yield, with the application of 160×10^5 Pa pressure.

4. Conclusions

1. The finding that the carbonization pressure not only increases the coking yield but also lowers the temperature at which the pyrolysis is completed, observed on relatively lower softening point coal tars and petroleum pitches, holds true for higher softening point (upto 194 °C) coal tar pitches also.

2. The maximum percentage increase in the coking yield is observed to be 35.6 (pressure coking yield = 88%) at a pressure of 160×10^5 Pa for a pitch already reported by us to be a good preforming pitch for producing carbon–carbon composites with a density of 1.8 $\mathrm{g\,cm^{-3}}$ using ambient carbonization pressure.

3. Carbonization pressure at 160×10^5 Pa of a suitable preforming pitch, can act as a reasonably good alternative to the expensive HIPIC technique (employing a pressure of around 700×10^5 Pa) used to achieve a coking yield of the order of 88%.

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