PROPERTIES OF GAS SPARGED COAL TAR PITCHES

S.F. Myram, J.W. Patrick and M. Turpin
Dept of Chemical Engineering, University of Loughborough
Loughborough, Leics, LE11 3TU, UK

Introduction

Various pretreatments of coal tar pitches are used in the formulation of matrix precursors for carbon-carbon composites, in particular air blowing or gas sparging has been widely employed to produce pitches of increased softening point. The observed hardening may involve a number of mechanisms. Volatilisation of low molecular weight species, molecular growth in the residuum and oxidative cross-linking are all considered likely. There is a particular need for clarification of the role of oxygen in gas sparging, it is unclear to what extent, if any, oxidation of the pitch influences hardening.

Experimental

The aim of the study was to compare pitches that have been gas sparged using process gases with a nominally oxidising or reducing nature. The oxidising gas was 1% oxygen in nitrogen whilst the reducing gas was 5% hydrogen in nitrogen. Both sparge gases were employed at 400°C for 1, 2 or 4 hours, using a custom build gas sparging unit. Two precursor pitches were used; pitch A had a softening point 86°C, pitch B had a softening point of 111°C. The methods used to characterise the pitches and sparge products were the softening point (SP), the carbon yield (CY) from thermogravimetric analysis, the pentane, toluene and quinoline insolubles (PI, TI and QI respectively) and optical microscopy. In addition the yield of pitch residuum obtained after gas blowing has been recorded as SY

Results and Discussion

The results for pitch analysis are presented in Table 1. The results for the oxygen-sparged pitches are in agreement with previous work on oxidative gas blowing of pitch [1], in that the softening point is increased, the carbon yield is increased and solubility is decreased as sparging progresses. Data from the hydrogen blowing experiments have shown that the pitches produced are broadly similar to those from oxygen blowing.

In a number of instances it is clear that the datum obtained after a 2 hour process time is anomalous in that the pitch may be softer than that obtained after 1 hour. The reason for this phenomenon lies in the relatively poor control that is intrinsic in all gas sparging processes. The lack of fine control over the process leads to the large batch to batch variability recorded at the foot of Table 1.

Analysis of the measured data requires a postulate as to the mechanism by which pitch is hardened in the gas sparging process. The simplest model is one in which the pitch consists of two fractions, one of which comprises molecules which produce carbon on pyrolysis, the other being molecules which are volatile and evaporate during pyrolysis.

Let W_c be the weight fraction of carbon producing molecules and W_v the weight fraction of volatile molecules. Let the carbon yield, expressed as a weight fraction, obtained on pyrolysis of the raw pitch be C, and that of the gas sparged pitch be C'.

Relatively straightforward treatment of the model system yields:-

$$C = \frac{\upsilon_c \cdot W_c}{W_c + W_v} = \upsilon_c \cdot W_c \qquad (1)$$

Where V_c is the weight fraction of the carbon obtained from the carbon-producing phase.

For the gas sparged pitch

$$C' = \frac{\upsilon_c \cdot W_c}{W_c + W_v - W_l} = \frac{\upsilon_c \cdot W_c}{1 - W_l} \qquad (2)$$

Where W_l is the fraction weight loss of the pitch during sparging. i.e. $1\text{-}W_l$ is the sparge yield, SY.

Substitution of 1 into 2 yields by rearrangement:-

$$\frac{1}{1 - W_l} = \frac{C'}{C} \qquad (3)$$

A plot therefore of the reciprocal sparge yield vs. the carbon yield of the gas sparged pitches should yield a straight line of gradient 1/C. Moreover, both the hydrogen and oxygen treated pitches should fall upon the same line, since in this simple model we have assumed that the process gas is non-reactive.

Conducting this exercise for Pitch A yields the data in Figure 1. It is clear that both sets of data do indeed fall upon the same line which has a correlation coefficient (r^2) of 0.97. The carbon yield for the raw pitch is estimated from the gradient at 28.3 % which is a tolerable agreement with the observed TGA value of

36.3%. The fact that the observed value of the raw pitch carbon yield is higher than the apparent value, determined from the plot, is satisfactory, since the observed value is obtained from TGA under quiescent conditions and should be higher than that observed if the pyrolysis was conducted in a gas sparged system.
Conducting the same exercise with pitch B gives markedly different results. It is clear from Figure 2 that for this pitch the results of sparging with hydrogen and oxygen containing gases are different. The hydrogen sparge data gives an apparent carbon yield for the raw pitch of 31% (correlation 0.977) which again is somewhat lower than the value observed in the quiescent TGA experiment. Once again it would seem that the carbon producing phase in pitch B is unchanged by the passage of hydrogen.
For the oxygen data it is apparent that much higher carbon yields are obtained than would be expected. The apparent carbon yield, obtained from the slope of the graph is 45% (correlation 0.995), somewhat higher than the value obtained experimentally. The higher apparent yield from the gas sparging experiment, relative to the quiescent TGA experiment, is difficult to explain by physical means. The conclusion that may be drawn from this is that the oxygen containing process gas has chemically altered the pitch, to increase the quantity of the carbon-producing phase at the expense of the volatile matter.

Conclusions

The two pitches studied behave quite differently when sparged with hydrogen and oxygen containing gases. Pitch A sparge products appear to be independent of the sparge gas used whilst for pitch B the use of an oxygen containing sparge gas results in a markedly harder product pitch.

Table 1. Properties of the gas sparged pitches

Pitch	Treatment	SY/%	SP/°C ±6°C	CY/% ±0.7%	PI /% ±1%	TI /% ±4%	QI /% ±0.3%
A	-		84	36.3	84	22	0.1
AH1	H_2 /1 hour	56.7	218	56.5	97	43	0.5
AH2	H_2 /2 hours	65.7	210	51.1	98	41	0.9
AH4	H_2 /4 hours	50.2	255	62.4	97	54	1.0
AO1	O_2 /1 hour	66.4	192	50.4	93	36	1.0
AO2	O_2 /2 hours	64.5	185	48.3	94	38	1.3
AO4	O_2 /4 hours	54.5	237	61.2	96	57	1.3
B	-		111	37.9	90	28	2.1
BH1	H_2 /1 hour	74.7	178	48.8	96	42	3.2
BH2	H_2 /2 hours	62.1	206	54.4	96	51	5.0
BH4	H_2 /4 hours	59.0	245	60.4	100	58	4.8
BO1	O_2 /1 hour	73.3	189	55.1	94	46	2.6
BO2	O_2 /2 hours	72.4	188	56.5	96	47	3.1
BO4	O_2 /4 hours	63.1	233	63.9	98	60	4.9
Batch Errors			±23	±14	±1	±7	n/d

The fact that two relatively soft coal tar pitches behave so differently is an important finding, which perhaps helps to explain the often contrary results which have been reported in the literature.

Acknowledgement

The authors would like to thank the European Coal and Steel Community for financial assistance under research programme 7220-EC767

References

1. Fernandez JJ, Figueiras A, Granda M, Bermejo J and Menendez R. Carbon 1995; 33:295.

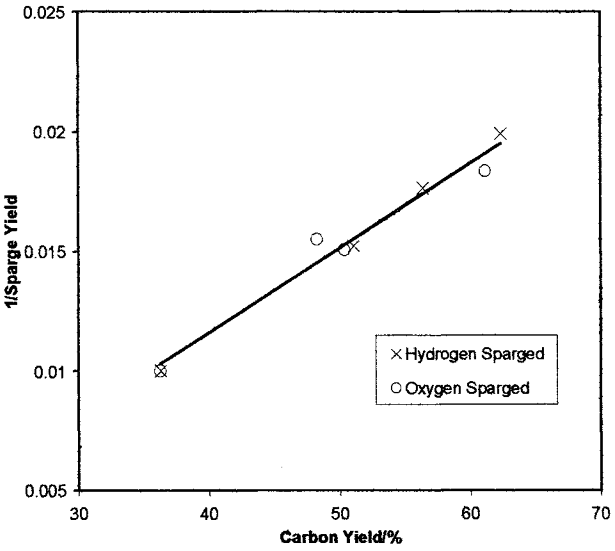

Figure 1. Reciprocal SY vs CY for pitch A

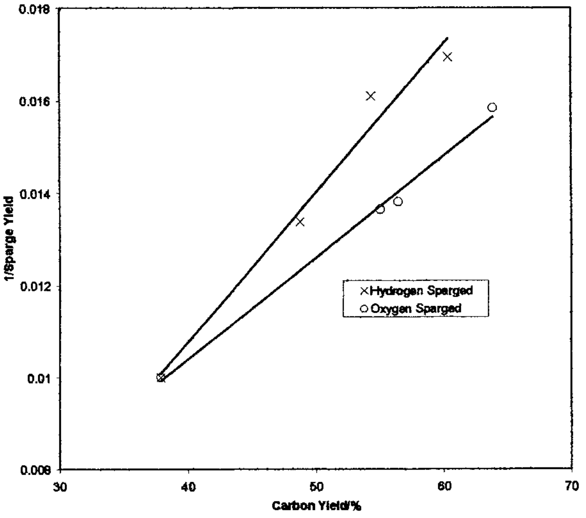

Figure 2. Reciprocal SY vs CY for pitch B