

PYROLYSIS OF A SILICON DOPED PETROLEUM RESIDUE

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Introduction

Poliaromatic mesophase can be used for the production of high modulus carbon fibers and fine grain high strength carbons. Boron-doped carbons and silicon-doped carbons as substitution elements are reported to improve oxidation resistance and hardness [1]. Such carbons are commonly obtained by vapour deposition processes. Recently, several papers have been published reporting the synthesis of such carbons via co-pyrolysis of mixtures of pitch and a boron precursor [1-3]. In this work, the synthesis of a silicon doped mesophase via co-pyrolysis of an aromatic petroleum residue and a silicon source such as triphenyl silane is reported.

Experimental

An aromatic petroleum residue, R1 [4, 5], was mixed with triphenyl silane (TPS) to give mixtures of different silicon content (none, 0.4, 1 and 2 wt%). Pyrolysis of the mixtures was carried out in a laboratory-sized pilot plant as previously described [4, 5]. Pyrolysis was performed at 440°C, soak time from 1.5 to 6 h and pressure of 1 MPa. Release of pressure, 1.0 to 0.1 MPa, occurred only at the end of a pyrolysis experiment, at reaction temperature, causing a second distillation. Solids products were analysed by insolubility in toluene and 1-methyl-2-pyrrolidinone, polarized optical microscopy (O.M.) and FTIR. The silicon content of the products was determined by ashing 2 g samples at 900°C during 12 hours. Solids products were sequentially extracted with heptane (H), toluene (T) and 1-methyl-2-pyrrolidinone (NMP) to give three soluble fractions (HS, TS, NMPS) and one insoluble fraction (NMPI) [5]. Silicon content of fractions was also determined. Aromaticity of fractions was analysed by FTIR. Using the computer programme Omnic v1.0, areas of absorption corresponding to C-Har vibrations (2990-3150 cm^{-1}) and C-Hal (2800-2990 cm^{-1}) were obtained. The aromaticity parameter 'n' was calculated as the ratio of the two areas.

Results and discussion

In general terms, the addition of TPS causes an increase in solid yield, TI and aromaticity (Table 1). Solid yield is affected by the addition of TPS when the percentage of silicon is higher than 1%. This increase is due to the reduction of distillation products during depressurisation

as a result of the increase in molecular weight of the molecular constituents. The increase in TI is only evident for soak time of 6 h, TI decreasing with increasing silicon content for the rest of the samples. It is thought that TPS acts as a diluent due to its low molecular weight but it also increases reactivity by the formation of free radicals, the evolution of TI being a measure of the combination of both effects. Silicon recovery is higher than 80 % and increases with soak time.

Table 1. Solid Yields, Silicon Yield, TI and aromaticity of solid pyrolysis products.

Conditions	Solid Yield (wt%)	Silicon Yield (wt%)	TI (wt%)	n (C-Har/C-Hal)
1.5 h, 0% Si	46	--	37	0.77
3 h, 0% Si	47	--	49	0.95
6h, 0% Si	45	--	65	1.93
1.5 h, 0.4% Si	46	80	36	0.86
3 h, 0.4% Si	47	89	47	1.08
6h, 0.4% Si	46	100	66	2.00
1.5 h, 1% Si	52	98	30	0.91
3 h, 1% Si	47	86	48	1.31
6h, 1% Si	45	98	78	2.29
1.5 h, 2% Si	57	74	18	1.13
3 h, 2% Si	53	83	40	1.51
6h, 2% Si	51	100	79	2.49

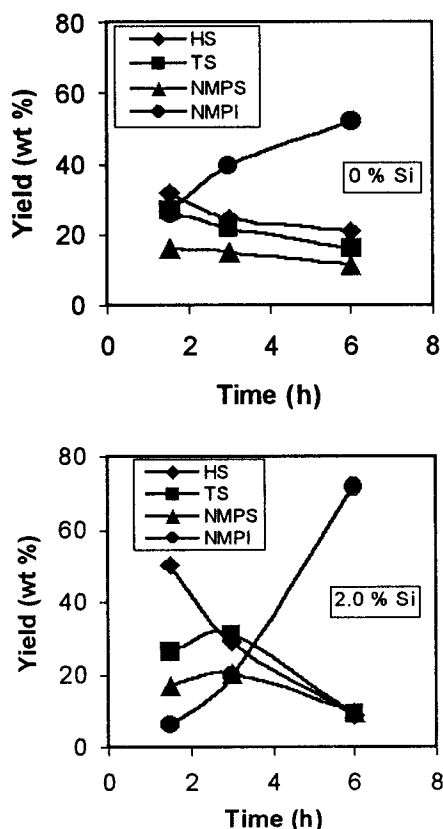
The analysis of the structure of the solids by OM shows that the addition of silicon causes a notable reduction of mesophase structures, this being more evident as silicon content increases. Solids obtained using 2% Si are almost isotropic. In this way, the addition of TPS produces a cross-linked mesophase of very high viscosity in which the obtention of planar mesophase structures is difficult.

The evolution of soluble and insoluble fraction with soak time indicates that in the first 1.5 h, the addition of TPS increases the HS fraction (Figures 1 a-b) and delays the formation of the NMPI fraction. As soak time increases, production of NMPI is faster as Si content increases. Silicon does not incorporate directly into NMPI fraction. Silicon constituents seem to transform from HS to NMPI in the same way as the rest of the molecular constituents. Figure 2 shows the evolution of silicon in fractions, for the

pyrolysis of a mixture containing 2 % Si. The shape of the Si curves (Fig. 2) is very similar to that of the evolution of fractions (Fig. 1b), indicating that molecules containing silicon follow a similar process as the rest of the molecules. As occurred with the evolution of fractions, the evolution of silicon from HS to NMPI is faster as the initial silicon content increases. The analysis of Si concentration in fractions indicates that concentration is similar in all the fractions, with some small differences: for 1.5 h soak time Si concentration is slightly higher for HS and TS fraction, but for 6h is higher for NMPS and NMPI (Table 2).

Table 2. Silicon content in the whole solid and in soluble and insoluble fractions for pyrolysis of residue R1 at 440°C, with 2% of silicon.

Soak time (h)	Si Solid (wt%)	Si HS (wt%)	Si TS (wt%)	Si NMPS (wt%)	Si NMPI (wt%)
1.5	2.5	2.5	3.1	2.2	2.0
3.0	3.0	2.6	3.7	3.2	2.8
6.0	3.9	1.9	3.0	3.6	4.0



Figures 1. Evolution of yield of soluble and insoluble fractions of the pyrolysis of residue R1 at 440°C, with 0% and 2% of silicon

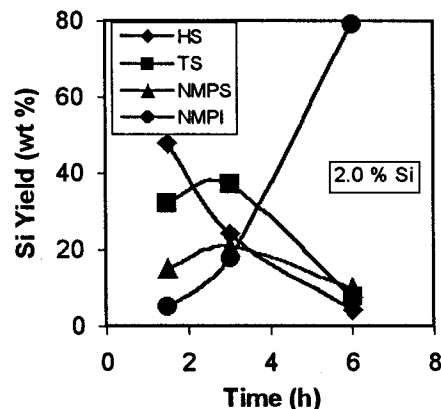


Figure 2. Evolution of yield of silicon in soluble and insoluble fractions of the pyrolysis of residue R1 at 440°C, with 2% of silicon

Acknowledgements

This work was supported by the EU (Project No. BRPRCT-97-04829)

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