

PYROLYSIS OF A BORON DOPED PETROLEUM RESIDUE

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Introduction

Polyaromatic mesophase can be used as a precursor material to produce high performance carbon products such as high density isotropic graphite and fine grain high strength sintered carbons [1]. Introduction of heteroatoms in polyaromatic mesophase maybe interesting to further improve its properties and to develop new applications in the future. In this way, the presence of boron in carbonaceous materials catalyses graphitization and inhibits oxidation [2, 3].

Doped carbons have been traditionally obtained by chemical vapour deposition, CVD [4], but recently, co-pyrolysis of mixtures of pitch and a heteroatom precursor has been reported as a suitable substitutive method [5], more advantageous than CVD from the operational and economic point of view.

In this work, the synthesis of a boron-doped material via co-pyrolysis of an aromatic petroleum residue and a boron source (pyridine-borane complex, PB) is reported. Reactivity of the borane and the effects upon the molecular growth during the pyrolysis are studied.

Experimental

Mixtures of an aromatic petroleum residue, R1 [6] and PB, with a boron content ranging from 0 to 1 wt%, were pyrolysed in a laboratory-sized pilot plant as previously described [6, 7]. Pyrolysis was performed under a nitrogen pressure of 1.0 MPa, at different soaking times (1.5, 3, 6 h) and temperatures (400, 420 and 440 °C). Release of pressure to 0.1 MPa occurred at the end of the pyrolysis experiment, at the temperature of reaction, causing a second distillation. Yields, insolubility in toluene (TI) and polarized optical microscopy were analysed. Boron content was determined by totally ashing 2-3 g samples at 1200 °C during 3 hours, a colourless ash of B₂O₃, as determined by XPS, remains in the crucible.

Solid products were sequentially extracted with heptane (H), toluene (T) and 1-methyl-2-pyrrolidinone (NMP) to separate them in three soluble fractions (HS, TS, NMPS) and one insoluble fraction (NMPI) [7]. Boron content of the fractions was also determined as described above.

Results and discussion

Table 1 shows the evolution of yields, TI and amount of mesophase for the different conditions studied. In the early stage of pyrolysis (400 °C, 1.5 and 3 h), solid yield decrease (2-3 wt%) with the addition of PB. When pyrolysis is more developed, yields do not change with PB, except the case of 0.4 wt % B and strong pyrolysis conditions (440 °C, 3 and 6h), when the yields slightly (2-4 %) decrease.

Table 1. Solid yield; solid yield on the basis of the petroleum residue and BH₃ added, assuming pyridine distillation; TI and mesophase content of solid pyrolysis products.

T (°C)	soak time	wt% B	Ysolid (wt%)	Ysolid pyr (wt%)	TI (wt%)	Mesoph (%)
400	1.5	0	50	50	8	..
		0.4	48	50	24	6
		1.0	48	54	43	10
	3	0	50	50	14	..
		0.4	47	49	31	17
		1.0	47	51	49	47
	6	0	48	48	21	..
		0.4	46	47	41	42
		1.0	48	53	53	51
440	1.5	0	42	42	37	14
		0.4	42	43	63	58
		1.0	43	47	76	82
	3	0	43	43	49	52
		0.4	41	42	80	78
		1.0	43	47	89	84
	6	0	44	44	65	44
		0.4	40	42	84	81
		1.0	44	49	95	100

When a heteroatom precursor is introduced in the system, a diluting effect should be expected due to the addition of a low molecular weight compound (heteroatom precursor) into the high molecular weight system of the petroleum residue, specially in the early stages, when the reactivity of the precursor is low. This effect would be observed by an

enhancement or a reduction of pyrolysis yields, depending on the compound being retained in the solid or distilled; and a reduction of TI respect to the undoped residue.

However, in the co-pyrolysis with PB, carbonization yields are almost constant and the analysis of TI (Table 1) shows that, opposite to what was observed with other heteroatoms [8], even in the early stages of pyrolysis, insoluble content strongly increases with boron addition. Formation of mesophase is also enhanced (Table 1), and, as observed by optical microscopy, the structure of mesophase has smaller size than the undoped one, indicating an increase of the nucleation sites and a hindrance of the spheres to coalesce.

These results indicate that, rather than diluting, the presence of the borane catalyses molecular growth. What is more, the constant yield observed is probably due to almost a total distillation of pyridine [5]. So, when yields are related to the total mass of the mixture after deducing the pyridine content (Table 1), an increase of the solid yield with the boron content has been observed. The presence of pyridine in the liquid distillates has been confirmed by H-NMR.

Sequential extraction of solid pyrolysis products has been carried out in order to monitor the progress of chemical transformations leading to molecular growth. Comparison of the doped and undoped samples at different temperatures (Figure 1.a-d) shows that the evolution of fractions is different in each system.

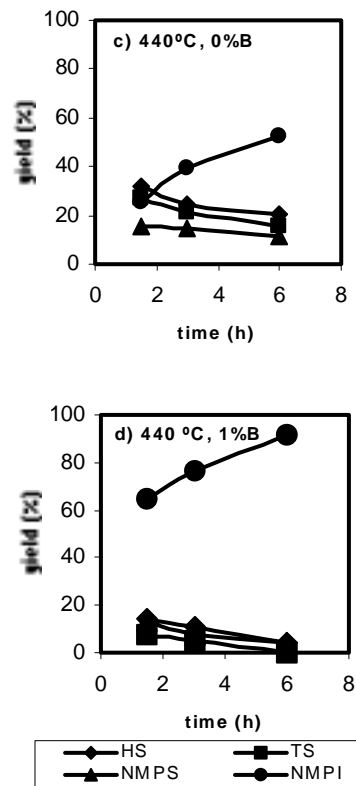
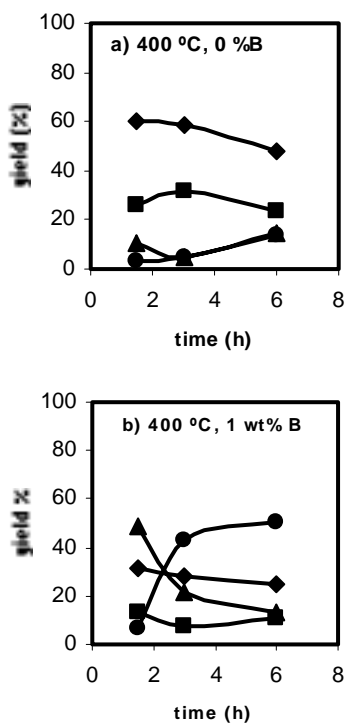


Figure 1. Evolution of yield of soluble and insoluble fractions of the pyrolysis of the petroleum residue at 400°C, a) 0 %B; b) 1.0 %B; and 440 °C, c) 0 %B; d) 1.0 %B. Symbols are explained at the bottom of figure 1.d

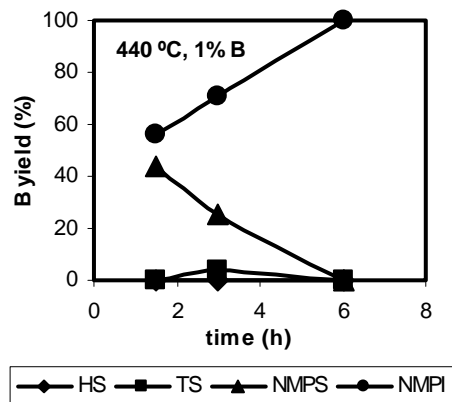
At 400 °C (Fig 1.a) and in the early stage (1.5 h), the undoped sample is mainly composed of HS fraction (about 60 wt%). After boron addition (Fig 1.b), the growth up to NMPS fraction is strongly enhanced at the same soaking time. Assuming a consecutive reaction model [8]:



At 400°C the NMPS accumulation for the doped samples points out at boron catalysing conversion from HS to NMPS, transformation from NMPS to NMPI still being slow. Longer soaking times (3 and 6 hours) are needed to allow the reaction between the NMPS molecules that yields NMPI. At higher temperature, 440 °C (Figure 1.c,d), boron reactivity increases and no accumulation of NMPS is observed. Evolution from HS to NMPI is, in this case, similar to that of the undoped sample, but occurs much faster in the presence of boron.

Yield of boron in the fractions has been determined (Figure 2) and it is observed a boron enrichment in the

high molecular weight fraction, NMPI, indicating that boron is linked to the molecules and grows with them. Since after co-pyrolysis with 1 wt% B at 440 °C, 6 h the solid is completely anisotropic (Table 1), and it contains 100 % of the boron initially added, it is deduced that boron is completely incorporated into the mesophase, in agreement with previous results on boron doping [5].



Conclusions

Boron catalyses molecular growth during pyrolysis of petroleum residues, which results in higher solid yields, larger amount of TI and a stronger mesophase development. Formation of a high molecular weight fraction, NMPI, is strongly enhanced after boron addition.

Mesophase developed after boron addition has a fine coarse structure; it has been shown that boron is incorporated into the mesophase and it is suspected to be bonded to the polyaromatic molecules. Although the nature of this bond has not been determined yet, it should cause an increase in the viscosity of the mesophase spheres that prevents them to coalesce.

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