REMOVAL OF BORON FROM MEDIUM TEMPERATURE GASIFIER PITCH

Gedion J. Papole, Brian Rand and Walter W. Focke

SARChI Chair in Carbon Technology and Materials, Institute of Applied Materials, Department of Chemistry, University of Pretoria, Pretoria, 0002, South Africa.
Corresponding author: walter.focke@up.ac.za

Introduction

Sasol medium temperature gasifier pitch (MTP) is a potential precursor for graphitizable carbons [1, 2]. The actual boron content of MTP is low (< 10 ppm) and this makes accurate determinations difficult. Nevertheless, the boron content is too high for nuclear moderator applications which require graphites containing less than one ppm B [3]. Solvent extraction at the pitch stage is an attractive boron removal option. Ideally the pitch should be insoluble in the extraction solvent that selectively dissolves all boron-containing compounds. This preliminary study reports on extraction experiments conducted with MTP artificially laced with different boronic acids.

Experimental

High purity organic solvents were purchased from Merck. The solubility of MTP was determined via extraction experiments conducted at ambient conditions. MTP samples (5 - 50 g) were placed in polypropylene bottles containing 100 mL solvent. The bottles were tightly closed and intermittently shaken over a period of five days. Then the samples were suction filtered through Whatmann filter paper (8 µm pore size) and the mass of a dry residue (MTP rich phase) was recorded.

Boron was purposefully added to MTP to make extraction experiments easier. Table 1 lists the boron-containing compounds in the order of increasing aromatic character. MTP samples, laced with the equivalent of 1000 ppm B, were refluxed with methanol for 2 h. This ensured that both phases were in the liquid state to facilitate partitioning. On cooling, the mixture formed a methanol-rich layer on top and a semi-solid pitch phase at the bottom. The methanol phase was recovered by decantation and the pitch fraction collected from the bottom of the flask. The boron content of the pitch residue was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES).

FTIR spectra were recorded on a Perkin Elmer machine equipped with an attenuated total reflectance (ATR) cell. The pyrolytic carbon yield was determined as the mass loss recorded at 1000 °C in a nitrogen atmosphere on a Mettler Toledo A851 simultaneous TG/DTG machine.

Results and Discussion

The solvent extraction results are presented in Fig. 1 and in Fig. 2. DMF, morpholine and quinoline were good solvents dissolving more than 200 g/L pitch. The pitch proved virtually insoluble in water and in formamide. The solubility of the pitch in methanol was less than 80 g/L.

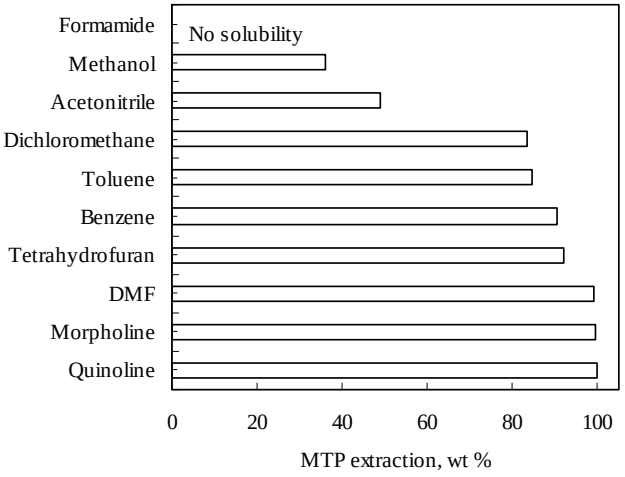

Fig. 1 Pitch extracted into various solvents at ambient temperature. The pitch concentration was 50 g/L solvent.

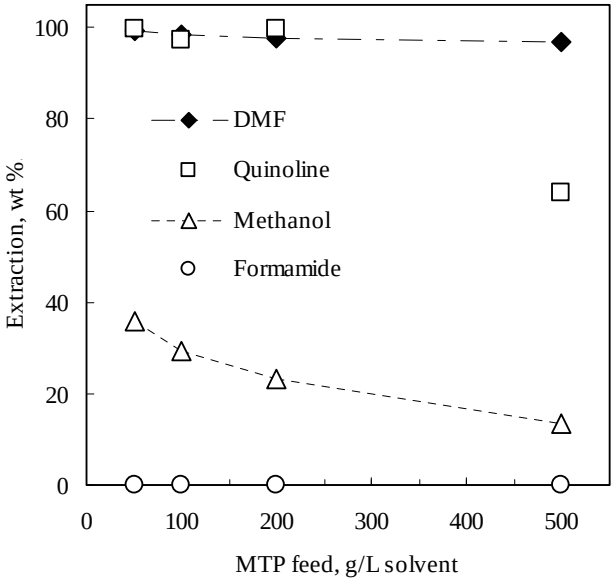

Fig. 2 The effect of the pitch:solvent ratio on the extent of extraction.

Fig. 2 depicts the effect of the MTP:solvent ratio on the fraction pitch solubilized. Based on these results, methanol was chosen for boron extraction studies. The -OH functional group was expected to interact favorably with the B-OH functional group present in all the boron model compounds.

Fig. 3 compares the FTIR spectrum of the MTP methanol insoluble fraction with that of parent pitch. The main differences were in the intensities of the various C-H bands.

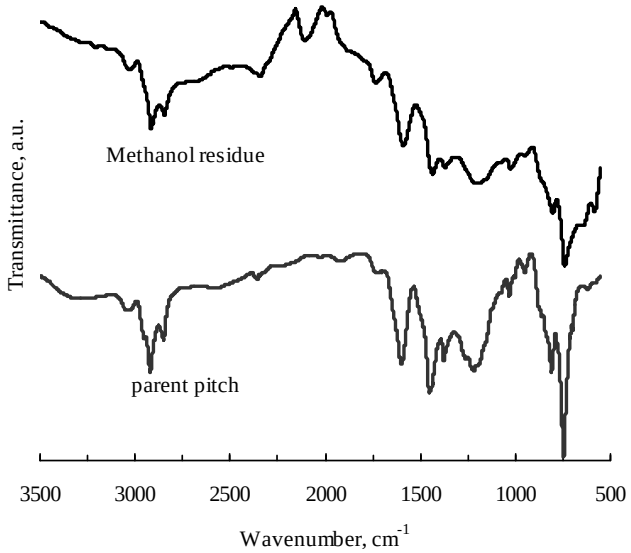

Fig. 3 Attenuated total reflectance (ATR) spectra of MTP and the residue following methanol extraction.

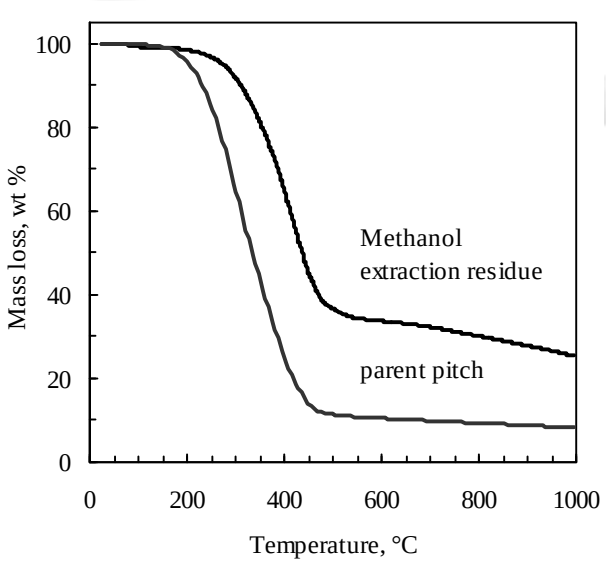

Fig. 4 TG curves of medium temperature gasifier pitch and its methanol insoluble fraction in N_2.

Table 1. Boron Content of MTP Initially Laced with 1000 ppm B after a Single Methanol Extraction.

Name	B (ppm)
Methylboronic acid	163
p-Tolylboronic acid	204
2-(Benzyloxy) phenylboronic acid	211
9-Anthraceneboronic acid	229

The aliphatic C-H stretching band at 2915 cm^{-1} is less pronounced in the methanol insoluble fraction. The aromaticity index [4] for MTP (34%) is lower than that of the methanol insoluble fraction (41%). These observations suggest that methanol preferentially dissolved compounds with aliphatic substituents. The bands in the region 900-700 cm^{-1} are due to out-of-plane vibrations of aromatic C-H bonds. The band at 750 cm^{-1} is attributed to ortho-substituted aromatic rings. For these bands the absorbance is higher in the parent pitch than in the methanol extraction residue.

Table 1 lists the boron content of MTP initially containing 1000 ppm B following methanol extraction. The boron content was significantly reduced by methanol extraction. As expected, the boron content of the pitch residue scaled with the aromatic content of the compound added. The partition coefficient is defined by $K = X_{methanol}/X_{pitch}$, where X_s is the mass fraction of boron present in phase *s*. *K* varied from 5.1 for methyl boronic acid to 3.4 for the highly aromatic anthraceneboronic acid.

The TG traces in Fig. 4 revealed that the pitch residue from the methanol extraction had a higher carbon yield (25 wt %) than the parent pitch (8 wt %). The residue also had a higher pyrolytic thermal stability.

Conclusions

Sasol medium temperature pitch is highly soluble in DMF and morpholine and virtually insoluble in formamide. It has a relatively low solubility in methanol. FTIR results suggest that methanol preferentially extracts compounds with a high aliphatic content from the pitch. This is consistent with a higher carbon yield for the residue compared to the parent pitch. Preliminary solvent extraction results showed that methanol also selectively removed substituted boronic acids dissolved in the pitch. The methanol-pitch partition coefficient *K* ranged from 5.1 for methyl boronic acid to 3.4 for the highly aromatic anthraceneboronic acid.

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References

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