

Characterization of medium-temperature Sasol-Lurgi gasifier coal tar pitch

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Abstract

Medium-temperature gasifier pitch (MTP) is only partly soluble in acetonitrile, methanol and ethanol. Single-stage pitch extraction with a large quantity of methanol yielded two liquid phases containing 76 wt. % and 27 wt. % pitch respectively. The pitch fractions recovered from these two phases featured similar aromaticity indices. However, the pitch from the pitch-rich phase had a higher average molar mass and gave an improved carbon yield at 1000 °C. Analysis of the methanol-insoluble pitch fraction showed that methanol extraction at reflux temperatures effectively removed boronic acid model compounds from pitch samples spiked with the same.

Keywords: Medium temperature gasifier pitch; solvent extraction; boron; characterization

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1. Introduction

Coal tar and petroleum pitches are important raw materials for carbon-based artefacts [1]. These products find application in aluminium and steel production, in construction, in the automotive industry, and in nuclear reactors [2]. Medium-temperature gasifier pitch (MTP) is a by-product of the Sasol-Lurgi coal gasification process. It is graphitisable [3] and as such a potential precursor for nuclear grade materials used in graphite-moderated reactors [2].

Pitches contain a myriad of different compounds [4] and differ with respect to their molecular weight distributions. Solvent extraction tests can provide information about the complex structure of pitches [5-7]. The solubility of pitches in organic solvents such as toluene and quinoline are considered important indicators for industrial applications [4, 5]. Guillén *et al.* [5] investigated the extractive ability of 27 organic solvents and concluded that coal tar pitches were most soluble in quinoline and 1-methyl-2-pyrrolidinone. They concluded that no simple relationship exists between the solubility of pitch and the solvent parameters commonly used for correlation purposes [8]. Solvent extraction has also been employed to make superior carbon precursors from coal tar pitch [9]. A key focus of this investigation was to improve the carbon yield of MTP through targeted solvent extraction.

Thermal neutrons are responsible for sustaining the fission processes in nuclear reactors [2]. Carbons for nuclear applications must meet stringent specifications with respect to neutron absorbing impurities such as boron [10]. Owing to boron's high neutron cross section [11], nuclear graphite should contain less than 1 ppm [12]. Boron is a common impurity element present in most carbonaceous materials [13]. It occurs in various forms [14, 15] but it is more likely to be associated with the organic part of the carbonaceous material than the mineral matter [14]. MTP would be a good nuclear grade carbon precursor were it not for its high boron content of up to 14 ppm.

Boron atoms are incorporated into the carbon lattice on coking and graphitization. A portion can still be removed by high temperature purification of the graphite in the presence of halogens. However, boron removal by solvent extraction at the pitch stage is a more practical proposition. Ideally the pitch should be insoluble or at most partially soluble while all the boron-containing compounds should concentrate in the extraction solvent. Consequently this study focused on the chemical and physical characterization of MTP including extractions with a range of different solvents. It investigated the feasibility of using methanol as the extractive solvent to improve the carbon yield and to remove boron from MTP laced with selected boron model compounds.

2. Experimental

2.1. Materials

Sasol supplied the medium-temperature gasifier pitch. The properties of this pitch are presented in Table 1. High purity organic solvents were purchased from Merck. The solvents used include formamide, *n*-hexane, cyclohexane in addition to those indicated in Fig. 1. Boronic acid model compounds, listed in Table 2, were acquired from Sigma Aldrich. They were selected based on their varying aromatic character.

2.2 Pitch extraction experiments

2.2.1 MTP room temperature extractions

Exploratory MTP solvent extractions were conducted at ambient temperature (25 ± 5 °C). These batch experiments were performed using 100 mL solvent aliquots placed in 500 mL propylene bottles. To these were added tarry pitch quantities of 5, 10, 20, 30, 40 and 50 g.

Table 1: Properties of MTP and its methanol, benzene and toluene insoluble fractions

| Property | Units | Parent pitch (MTP) | Insoluble fractions* | | | |
|---------------------------------------------------------|--------|--------------------------|----------------------|----------|----------|------|
| | | | Methanol | Toluene | Benzene | |
| Solvent extraction residue | wt. % | - | 54.7±2.3 | 3.0±0.01 | 3.3±0.01 | |
| Softening point | °C | 38.5 | 59.6 | nd | nd | |
| FTIR absorbance ratio A_{3040}/A_{2920} | - | 0.20 | 0.20 | nd | nd | |
| ^{13}C n.m.r. aromaticity index (f_a)** | % | 78 | 77 | 85 | 85 | |
| Number average molar mass (M_n) | a.m.u. | 327 | 359 | 432 | 420 | |
| Weight average molar mass (M_w) | a.m.u. | 403 | 437 | 543 | 553 | |
| Polydispersity index (M_w/M_n) | - | 1.23 | 1.22 | 1.26 | 1.32 | |
| Carbon yield @ 1000°C | wt. % | 8.25 | 25.3 | 53.5 | 50.8 | |
| Elemental Analysis | C | wt. % | 85.3 | 87.1 | 84.1 | 83.2 |
| | H | wt. % | 6.39 | 6.34 | 5.43 | 4.96 |
| | N | wt. % | 1.95 | 1.82 | 2.91 | 2.83 |
| | S | wt. % | 0.51 | 0.53 | 0.33 | 0.31 |
| | O | wt. % | 5.83 | 4.24 | 7.19 | 8.67 |
| | C/H | - | 1.12 | 1.15 | 1.3 | 1.4 |

*Extractions based on 2 g pitch in 100 mL solvent. **Aromaticity index determined from ^{13}C n.m.r. spectra

Table 2: Properties of the boron model compounds

| Boron model compound [CAS No.] | Formula | B, wt. % |
|--------------------------------------------------------|-----------------------------------------------------------------------------|----------|
| Methyl boronic acid (MBA) [13061-96-6] | $\text{CH}_3\text{B}(\text{OH})_2$ | 18.06 |
| Boric acid (BA) [10043-35-3] | H_3BO_3 | 17.48 |
| 2-(Benzyloxy)phenylboronic acid (BPA) [190661-29-1] | $\text{C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_4\text{B}(\text{OH})_2$ | 4.74 |
| 4-Dibenzofuranboronic acid (DBA) [100124-06-9] | $\text{C}_{12}\text{H}_9\text{BO}_3$ | 5.10 |
| 2-Phenoxyphenylboronic acid (PBA) [108238-09-1] | $\text{C}_6\text{H}_5\text{OC}_6\text{H}_4\text{B}(\text{OH})_2$ | 5.05 |
| p-Tolylboronic acid (TBA) [5720-05-8] | $\text{CH}_3\text{C}_6\text{H}_4\text{B}(\text{OH})_2$ | 7.95 |
| Phenylboronic acid (PLA) [98-80-6] | $\text{C}_6\text{H}_5\text{B}(\text{OH})_2$ | 8.87 |

Each sample bottle was kept for thirty days and shaken intermittently. Thereafter the

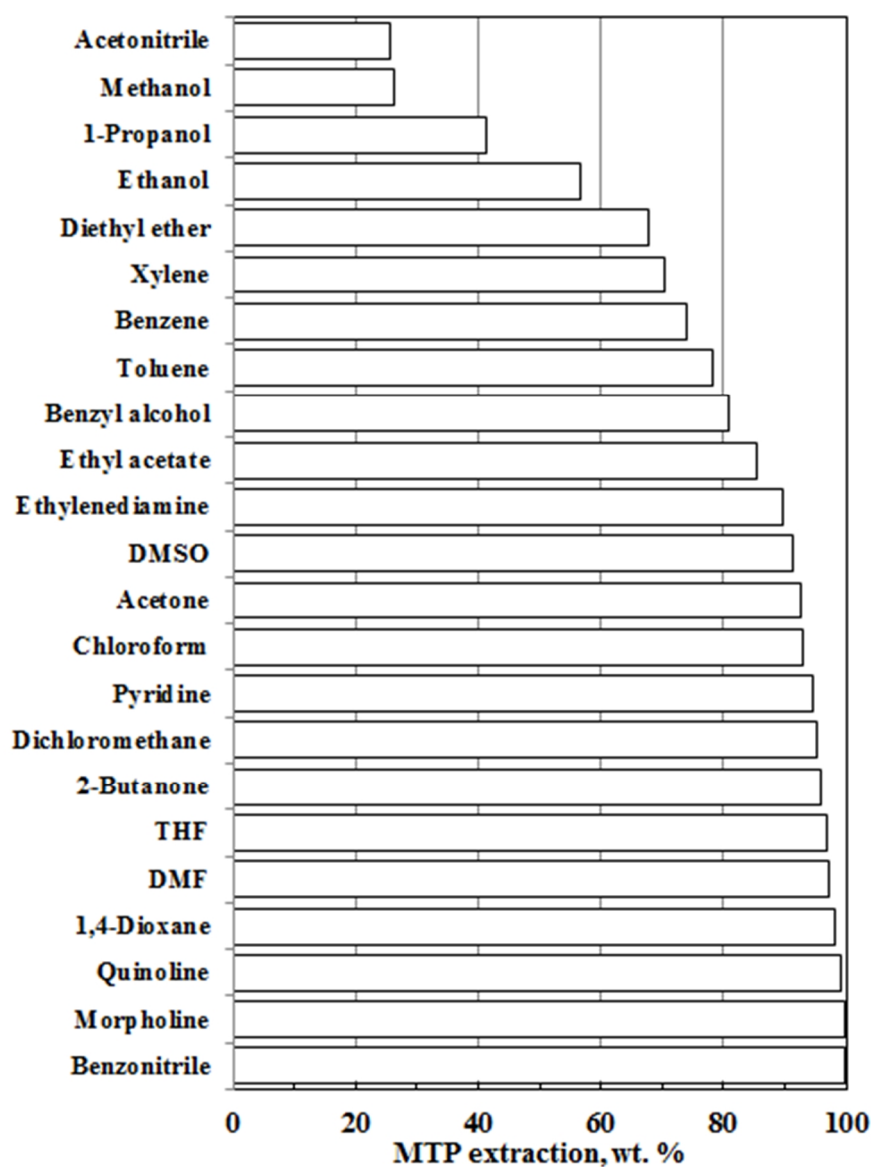


Fig. 1 Solvent extraction results obtained at ambient temperature on contacting 20 g MTP pitch with 100 mL solvent for 30 days.

insoluble residues were recovered on 8 μm pore size No. 2 Whatmann[®] filter paper using vacuum filtration. The residues were dried at 80 °C in a convection oven to constant mass.

2.2.2 Reflux extractions

MTP reflux extractions were performed using methanol, toluene and benzene. This method utilized 2 g MTP that was transferred into a 250 mL round bottom flask to which 100 mL solvent was added. The solution mixture was heated and maintained under reflux for 30 minutes. Residue was again filtered under vacuum using an 8 μm pore size No. 2 Whatmann[®] filter paper. The residue was subsequently washed with hot portions of the corresponding solvent until the filtrate was clear. This was done to ensure that the residue was free of all soluble fractions.

2.2.3 Simulated boron extractions

Pitch samples were spiked with 1000 ppm boron as follows. The calculated amount of the model compound was added to the MTP previously placed in a round bottom flask. The mixture was heated gently using a heating mantle. It was swirled when the pitch started to melt to aid dispersion and dissolution of the boron model compound. Initially the model compounds were visible as small white specks dispersed in the dark black and viscous pitch phase. Heating and swirling was continued until the mixture appeared uniform on visual inspection. After forming a uniform mixture, the flask was removed from the heating mantle and cooled to ambient temperature.

Both neat and boron-spiked MTP samples were reflux-extracted with methanol as follows. Boron extractions were conducted using a pitch: methanol mass ratio of 1:1.564. However, this ratio was varied down to 1:1.32 for neat pitch extractions. The predetermined quantity of methanol was added to the round bottom flask. The mixture was reflux-extracted for 2 h and then left to cool to ambient temperature. Two layers formed upon cooling. The top layer was a methanol-rich phase and it was separated from the pitch-rich phase by decanting. The pitch content of both phases was determined by placing them in 100 mL Petri

dishes. Most of the solvent was allowed to evaporate before the samples were dried at 80 °C in a convection oven. The boron contents of the pitch-rich residue phases were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) based on ASTM D 5158-02.

2.3 Pitch characterization

2.3.1 Elemental analysis

Determination of carbon, hydrogen, nitrogen and sulphur contents of parent MTP and its insoluble fractions was carried out using a Carlo Erba NA 1500 C/N/S Analyser.

2.3.2 Softening point

The softening point of MTP pitch was determined using a TA Q400 V22.1 thermomechanical analyser (TMA) fitted with a penetration probe. A force of 0.05 N was applied, the nitrogen flow rate was 50 mL.min⁻¹ and the temperature was scanned at 2 °C.min⁻¹.

2.3.3 Fourier transform infrared spectroscopy (FTIR)

FTIR spectra were collected with A Perkin Elmer Spectrum RX IFT-IR system equipped with MIRacle™ attenuated total reflectance (ATR) cell from Pike Technologies. The instrument's resolution was 2 cm⁻¹. The spectra were recorded in the range 4000-600 cm⁻¹ and represent the averaging of 32 scans collected at intervals of 1 cm⁻¹.

2.3.4 Solid-state ¹³C n.m.r.

Solid-state nuclear magnetic resonance (n.m.r.) spectra were collected on a Varian VNMRS 500 MHz two-channel spectrometer fitted with a Chemagnetics™ T3 HX MAS probe comprising four 4 mm zirconia rotors. Cross-polarization (CP) spectra were recorded at

ambient temperature with proton decoupling, a 2.9 μs 90° pulse, and a recycle delay time of 2 s. The power parameters were optimized for the Hartmann-Hahn match; the radio frequency fields were $\gamma_{\text{C}}B_{1\text{C}} = \gamma_{\text{H}}B_{1\text{H}} \approx 56$ kHz. The contact time for cross-polarization was 1.0 ms after optimization with a variable contact time experiment. One-pulse spectra were recorded at ambient temperature with proton decoupling, a 2.9 μs 90° pulse, and a recycle delay time of 80 s. The free induction decay had 1787 complex points Fourier transformed with 20 Hz line broadening. Magic-angle-spinning (MAS) was performed at 9 kHz. Adamantane was used as an external chemical shift standard where the downfield peak was referenced to 38.3 ppm.

2.3.5 MALDI-TOF

An Applied Biosystems Voyager-DE STR matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) spectrometer was used in the reflector mode. The target plate was positively charged and set to 20 kV. The mass range was scanned from 20 to 1000 m/z. Each sample was dissolved in 1 mL chloroform and spotted onto the plate without the matrix. After spotting, the samples were allowed to dry before being analysed. α -Cyano-4-hydroxycinnamic acid was used as the matrix. The operating parameters included a delayed extraction mode, an extraction delay time of 500 ns, a manual acquisition control, and a grid voltage of 70%.

2.3.6 Thermogravimetric analysis (TGA)

The pyrolysis behaviour of MTP and its soluble and insoluble fractions was determined using a Mettler Toledo TGA/SDTA A851 thermal analyser. Approximately 20 mg of each sample was heated in a 70 μl alumina pan from 25 to 1000 °C at a heating rate of 10 °C min^{-1} in nitrogen flowing at 50 mL min^{-1} .

3. Results and Discussion

3.1. Solvent extractions

Fig. 1 reports the fraction of pitch extracted by contacting 20 g pitch with 100 mL of solvent for 30 days at ambient temperature. Quinoline, morpholine, 1,4-dioxane, dimethylformamide (DMF), tetrahydrofuran (THF) and 2-butanone and benzonitrile were the most effective extraction solvents. All of them solubilized more than 95 % of the pitch. Cyclohexane, *n*-hexane and formamide (not shown in Fig.1) extracted less than 1 % of the pitch. Blanco and Guillén [16] previously observed the very low solubility of coal tar pitch in formamide.

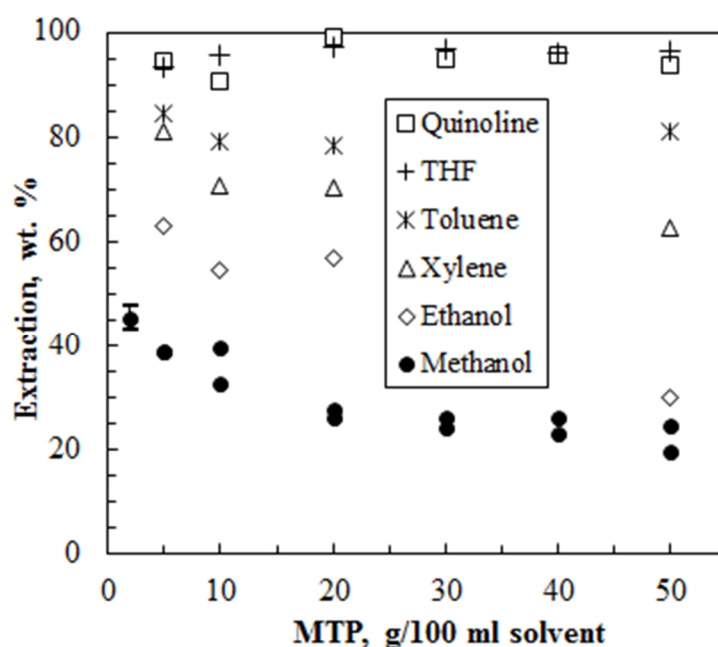


Fig. 2 Effect of the pitch to solvent ratio on the MTP extraction yield for selected organic solvents.

Fig. 2 shows the effect of the pitch to solvent ratio on the degree of MTP extraction for the solvents tested at room temperature. No significant variation was found for DMF, quinoline, THF, toluene and pyridine. This suggests that the solubility limit of MTP in these solvents was not reached and it should therefore exceed 50 g/100 mL solvent. The degree of MTP extraction decreased with pitch to solvent ratio for xylene, ethanol, and methanol. This

indicates that the solubility limit of the pitch in these solvents had been reached. The degree of extraction with methanol as solvent decreased from about 45 wt. % at 2 g MTP/100 mL solvent to less than 25 wt. % at 50 g MTP/100 mL methanol.

Methanol was chosen for boron extraction experiments on the basis that the pitch showed a lower solubility in this solvent. Furthermore, it is likely that organic boron in the pitch could be present as compounds with a boronic acid functionality. Boronic acids and boric acid have a distinct affinity to alcohols and may even react with them to form the corresponding esters [17]. Such esters are usually significantly less polar and they are consequently more volatile. This could facilitate their removal when the methanol solvent is stripped from the pitch. Hydroxyl compounds have been used to remove boron from fresh waters [18]. Ideally, the extractive solvent must not dissolve the pitch at all, except those compounds containing boron.

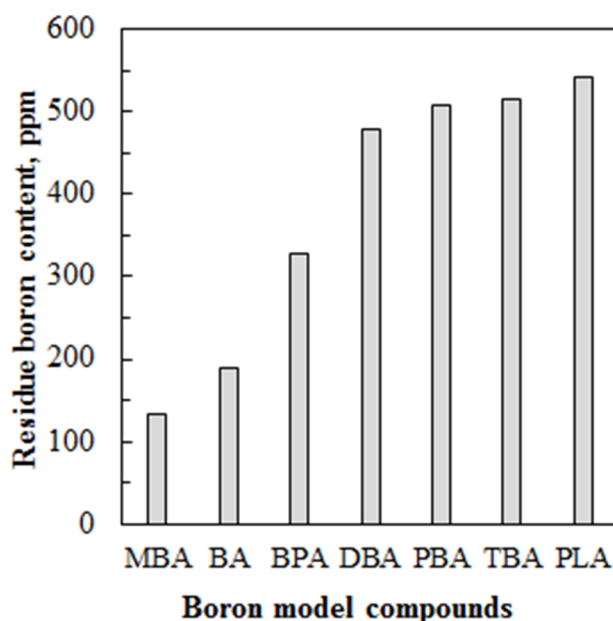


Fig. 3 Apparent partition coefficients and boron content of MTP residues after 2 h reflux extraction with methanol. The pitch samples were initially spiked with 1000 ppm boron by adding the model compounds listed in Table 2.

Fig. 3 shows the boron content of MTP residues recovered after 2 h reflux-extraction with methanol. The pitch samples were spiked with 1000 ppm boron. The pitch to methanol ratio was set at 50.5 g pitch/100 mL methanol, i.e. a mass ratio of 1:1.56. Fig. 3 shows that methanol extraction effectively reduced the boron content to values ranging from 133 ppm (methyl boronic acid) and 542 ppm (phenyl boronic acid). The former compound and also boric acid were removed most effectively and this is attributed to the formation of highly volatile methyl esters. It is likely that some of the other boron compounds were also stripped from the pitch residues as volatile boronic acid esters when the methanol was distilled off.

3.2 Characterization of pitch fractions from reflux extractions

The properties of the MTP and the residues, obtained following reflux solvent extractions with 2 g pitch/100 mL solvent, are presented in Table 1. After extraction the pitch content of the pitch-rich and methanol-rich phases were 76 ± 2 wt. % and 27 ± 1 wt. % respectively. The pitch residue remaining after extraction was 54.7 ± 2.3 wt. %. Thus more than half the pitch was methanol insoluble but almost all of it was extracted by toluene and benzene. The softening point of the parent pitch was 38.5 °C and that of the methanol insoluble fraction was 59.6 °C. As expected, the MTP elemental composition was dominated by the carbon and hydrogen content. As previously observed by Sima *et al.* [3], the oxygen content of MTP pitch exceeds the nitrogen and sulphur levels. The latter authors attributed the high oxygen concentration of MTP to the presence of significant quantities of phenolic compounds.

The attenuated total reflection Fourier transform infrared (ATR-FTIR) spectrum of the MTP methanol insoluble fraction in Fig. 4 differed only slightly from those of parent MTP. The bands in the region $900\text{-}700$ cm^{-1} are due to out-of-plane vibrations of aromatic C-H bonds [19]. All spectra featured characteristic aromatic and aliphatic C-H stretching bands located just above 3000 cm^{-1} and near 2920 cm^{-1} respectively [19]. The ratio of the

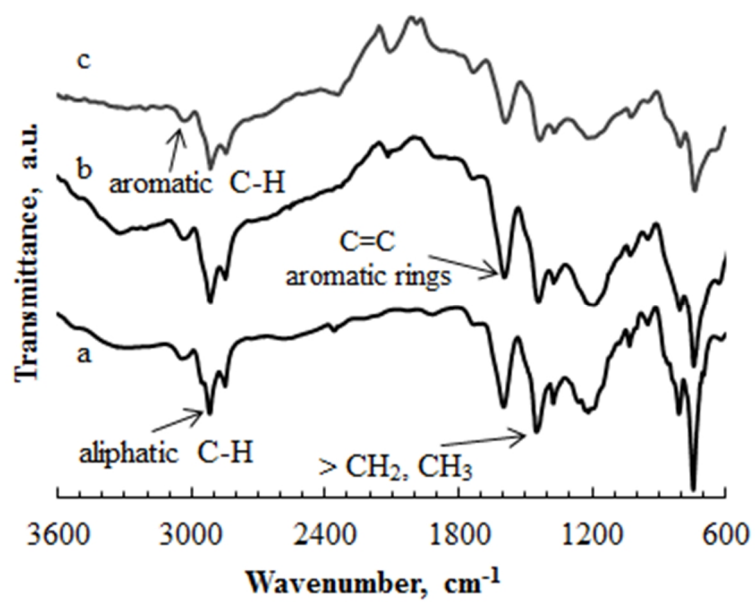


Fig. 4 ATR-FTIR spectra of (a) neat MTP; (b) methanol soluble, and (c) the methanol insoluble fractions.

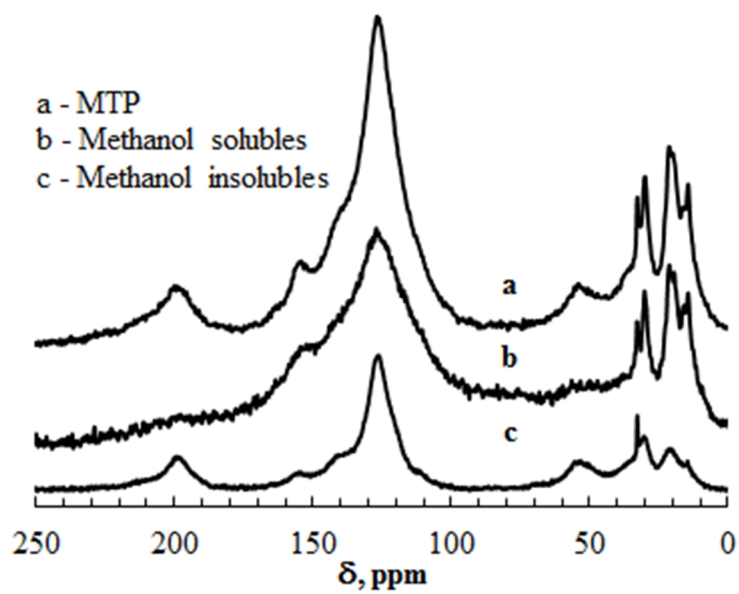


Fig. 5 Solid-state ¹³C n.m.r. CP MAS spectra of MTP and its methanol soluble and insoluble fractions.

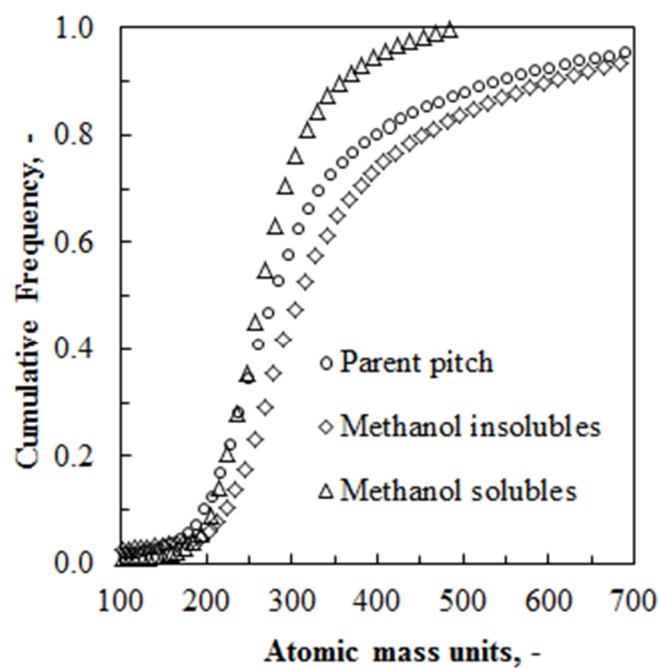


Fig. 6 Cumulative frequency distributions from the MALDI mass spectra of the MTP parent pitch, its methanol insoluble and soluble fractions.

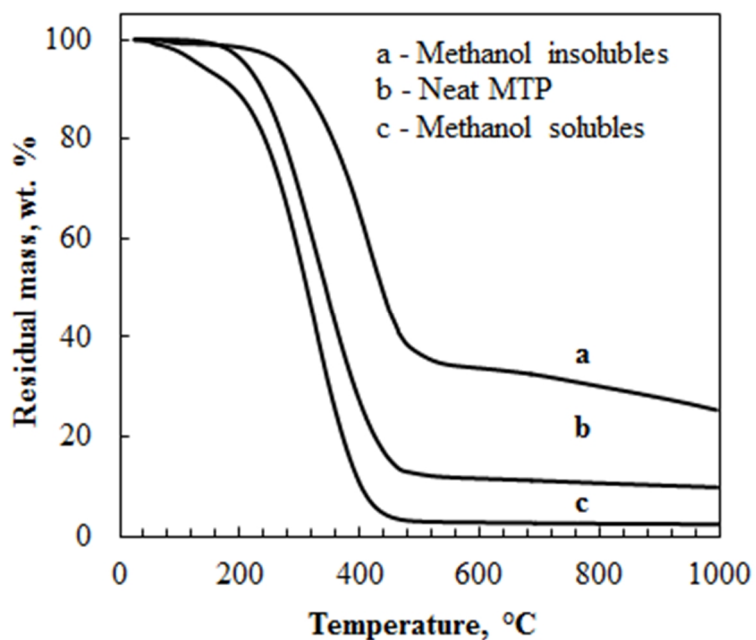


Fig. 7 TG curves of MTP and its methanol soluble and insoluble fractions obtained in a nitrogen atmosphere. Temperature was scanned at $10\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to $1000\text{ }^{\circ}\text{C}$.

absorbance maxima corresponding to these bands also provides an indication of the aromaticity of the pitches [20]. The FTIR spectra for the neat pitch and its methanol fractions all yielded the same value of $A_{3050}/A_{2920} \approx 0.20$. This implies that the aromaticity of the methanol soluble and insoluble fractions were rather similar.

Fig. 5 shows the solid-state ^{13}C n.m.r. CP MAS spectra of MTP and its solvent fractions. The asymmetric peak in the region of 127 ppm shift indicates the presence of aromatic carbons [21]. The peaks in the region 0-50 ppm are due to the presence of aliphatic carbons. The peaks located at 200 ppm and 55 ppm represent spinning sidebands for the aromatic carbons and the aliphatic carbons respectively. The aromaticity index (f_a) values reported in Table 1 were estimated from the ^{13}C n.m.r. spectra using the technique proposed by Mokoena *et al.* [22] that corrects for the influence of these spinning sidebands. This index provides a semi-quantitative measure of the aromaticity of pitches [22, 23] suitable for comparing trends. Compared to the parent pitch, the benzene and toluene insoluble fractions featured higher f_a values and lower sulphur contents. The higher C/H ratios found for these residues are consistent with higher aromaticity indices. However, the benzene and toluene extractions yielded lower residue values as the pitch was almost completely soluble in these solvents. In contrast, the methanol extraction residue featured a slightly lower aromaticity index and somewhat higher sulphur content than the parent pitch. The C/H ratio of the methanol insoluble fraction was only slightly higher than that of the parent pitch.

Fig. 6 shows cumulative frequency distributions estimated from MALDI mass spectra. It reveals that, compared to other commercial coal tar pitches, the isotropic MTP comprises lower molecular mass compounds. Fig. 6 clearly shows that the methanol preferentially solubilized the lower molar mass compounds. Consequently the extraction residue featured a higher molar mass distribution. The weight average molecular mass (M_w) of the parent pitch, the methanol soluble fraction and the methanol insoluble fraction were 403, 288 and 437

a.m.u. respectively. The polydispersity index (PDI) is defined by the ratio of the weight average to the number average molar masses ($PDI = M_w/M_n$). It provides a measure of the width of the molar mass distribution. The PDI of the parent pitch and the methanol insoluble fraction were similar equalling $PDI = 1.23$ and $PDI = 1.22$ respectively. The methanol soluble pitch fraction featured a narrower molar mass distribution with $PDI = 1.06$.

Thermogravimetric analysis (TG) traces are reported in Fig. 7 for MTP and the methanol derived fractions. The carbon yield was taken as the mass residue remaining at 1000 °C and it is reported in Table 1. MTP had a low carbon yield of only 9 wt. % at 1000 °C. The low carbon yield of MTP is attributed to a high content of low molecular mass species with significant volatility [3]. Fig. 7 shows that, compared to neat MTP, mass loss for the methanol soluble and methanol insoluble fractions commenced at lower and higher temperatures respectively. The corresponding carbon yields were 2.4 wt. % and 25 wt. %. The toluene insoluble fractions had the highest carbon yield (53 wt. %) closely followed by benzene insoluble fraction with the carbon yield of 51 wt. %.

4. Discussion and conclusions

Medium-temperature pitch from the Sasol-Lurgi gasifier is a potential source for nuclear grade graphite. However, its intrinsic boron content might on occasion be too high for this application. Unfortunately the boron content of the pitch sample received for the present study was below the detection limit of the available instrumental techniques. It was therefore of interest to determine whether simple solvent extraction was able to reduce the boron content of pitch samples spiked with organic boron model compounds at 1000 ppm B. The preferred extractive solvent would have a high affinity for the boron compounds but

otherwise dissolve little or none of the pitch. Most organic solvents proved unsuitable from this perspective as the pitch was highly soluble in them. MTP was almost completely soluble in dimethylformamide, quinoline, 2-butanone, tetrahydrofuran and pyridine. The solubility limit in these solvents thus exceeded 50 g MTP/100 mL solvent. MTP was virtually insoluble in *n*-hexane, cyclohexane and formamide and but sparingly soluble in acetonitrile, methanol and ethanol.

Methanol was selected as extractive solvent instead of acetonitrile as it is more volatile and its alcohol functionality is more suited to interact and even react with the boronic acid model compounds tested. Single stage extraction tests conducted at a pitch to methanol ratio of 2 g MTP/100 mL methanol and at reflux temperatures yielded two liquid phases on cooling. The pitch concentration in the methanol-rich phase was 27 wt. % and in the pitch-rich phase it was 76 wt. %. The latter contained 54.7 wt. % of the original pitch mass. The C/H ratio determined from elemental analysis, FTIR spectroscopy and the aromaticity index estimated from ¹³C CP MAS n.m.r. indicated negligible difference in the aromaticity indices of the methanol soluble and methanol insoluble pitch fractions. However, the softening point of the latter was about 20 °C higher than the value for the neat pitch. MALDI-TOFF spectra revealed that the methanol preferentially solubilized compounds with a lower molar mass. This suggests that the higher carbon yield found for the methanol insolubles was due to a lower volatility of the higher molar mass compounds retained in this pitch fraction.

Pitch samples were spiked with 1000 ppm boron using a variety of boronic acid compounds. Following extraction at reflux temperature using a pitch to solvent ratio of 50,5 g MTP/100 mL methanol, the pitch-rich phase liquid phase was separated and the residue recovered by evaporating the methanol. These single stage extractions successfully reduced the boron content of the spiked pitch residues by a factor ranging from about 1.8 (phenyl

boronic acid) to about 7.5 (methyl boronic acid). The latter and boric acid was most easily removed. This is attributed to the formation of highly volatile methyl esters.

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