TAILORING PITCH PYROLYSIS THROUGH THE USE OF ENVIRONMENTALLY BENIGH ADDITIVES

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Introduction

Coal tar pitches are widely used as binders during the manufacture of carbon artifacts. However due to the emission of hazardous and carcinogenic polyaromatic hydrocarbons (PAHs) during baking of carbon artifacts, coal tar pitches are facing strong environmental and commercial challenges(1) . The industry has addressed these challenges by using additives, mainly sulfur based, that are routinely placed into the paste mixture of carbon artifacts to promote the polymerization of coal tar binder pitches and therefore achieve high carbon yields upon baking or pyrolysis. However, the emission of sulfur species during baking of the carbon artifacts is becoming a major concern for the carbon artifact industry. Accordingly, this study has analyzed a traditional coal tar pitch and investigated the effect of alternative additives that can reduce PAHs emissions.

Experimental

Two environmentally benign additives, A1 and A2 were used in the present study to improve the pitch pyrolysis yield. Thermogravimetical analyses (TGA) were carried out on a Perkin Elmer TGA-7 with a heating rate of 5^{o}C/min from ambient up to 900^{o}C, using about 10 mg of sample under a flow of nitrogen. The pyrolysis GC/MS were conducted on a Hewlett-Packard 5890 Series 2 GC coupled with an HP 5971A MS detector, where about 0.25mg of sample was placed in a quartz tube. The quartz tube was placed horizontally into the heating coil and heated at 10^{o}C/s to 610^{o}C and held for 10 seconds.

After adding a given concentration of additive to the pitch, the green carbon pellets were produced by mixing calcined coke with the pitch, then heated to ~130^{o}C and press into pellets. The green carbon bodies were then baked in a horizontal tube furnace (maximum temperature 1000^{o}C), using Argon to carry the volatiles out of the tube and preventing them from condensing inside the furnace. The baking program consisted of three segments as follows: (1) 25-500^{o}C at 1^{o}C/min; (2) 150-500^{o}C at 0.5^{o}C/min; and (3) 500-800^{o}C or 500-1000^{o}C at 1^{o}C/min, providing an overall length of around 24 hours for a completed baking cycle.

Results and discussion

The authors have previously conducted extensive studies on the role of the toluene soluble (TS) fraction of coal tar pitch as a binder pitch, since a good binder pitch has typically ~60-70wt% of TS. The TS fraction consists of small polyaromatic (PAH) units with ~4-5 condensed aromatic rings where around 6-10 such units are linked together in an oligomeric network. It was shown that the weight loss during baking of carbon artifacts is particularly dependent on the TS content(2). Upon baking or pyrolysis, these PAH units can either volatilized off or fuse with a neighboring unit. Therefore, the key to future design will be to optimize this fraction in terms of low viscosity but high coking yield by using additives that promote the formation of condensed networks by cross-linking reactions. Accordingly, the present paper focus on tailoring pitch pyrolysis behavior with non-sulfur environmentally benign additives.

Thermal gravimetric analysis. The thermal weight loss, as determined by TGA, for the pitch alone and with different concentrations of additive A1 are shown in Figure 1. For the pitch alone(PB), as expected and similar to other pitches previously investigated(2), the weight loss started at temperatures above 150^{o}C and get around 62% during its carbonization at temperature up to 850^{o}C. However, with additive A1, the weight loss at 850^{o}C was reduced, indicating an improvement in the solid yield. Furthermore, the pitch/additive mixture with the highest concentration of additive A1 (10wt% vs. 3.7%) shows the highest carbon yield (47wt% vs. 41wt%). In addition, the pitch/additive mixtures seem to start losing weight at temperatures lower that the pitch alone (120^{o}C vs. 150^{o}C) and also present a larger weight loss than the pitch alone in the temperature range 120-300^{o}C. This can be attributed to the weight loss directly associated with the additive A1, as also indicated by the fact that the mixture with the highest additive content stars losing weight at lower temperature (120^{o}C for the mixture pitch/10% A1 vs. 140^{o}C for the mixture pitch/3.7%A1).

Different mixtures of pitch and additive A1 were prepared at various concentrations of additives to assess whether the pitch yield is proportional to the amount of additive present (Figure 2). The results indicate that the pitch yield seems to increase proportionally with the amount of additive at concentrations up to 10% addition of A1. However, the pitch yields seem to level off at additive concentrations above 10%, indicating that there is a crucial level for the additive investigated. A further increase in the concentration of this additive did not improve the solid yields. Nevertheless, all the pitch/A1 mixtures present higher solid yields than the pitch alone, where the yields are as high as 47% compared to only 38% for the pitch alone at 850°C.

A preliminary assessment of a second additive candidate, A2, was also conducted, as shown in Figure 3. When the pitch was mixed with only 1wt% of the additive A2, the weight loss at 850°C was reduced, indicating an improvement in the solid yield, compared to that of the pitch alone. Similarly to the additive A1, the pitch /additive mixture starts losing weight at temperatures lower than the pitch alone (120°C vs. 150°C) and also presents a larger weight loss than the pitch alone at temperatures below 400°C. It should be noted that the two additives investigated have boiling points ~120°C and therefore, the earlier weight losses for the pitch/additive mixtures can be attributed to the weight loss directly associated with the additive itself.

The preliminary assessment conducted thus far on A2 indicates that this additive could be superior to the previously examined A1, where lower concentrations of additive A2 produce similar pitch yields to those observed at higher concentrations of additive A1. In fact, the pitch yield was improved from 38% to the pitch alone up to 41% with the addition of 3.7% of A1. However, it was only required to add 1wt% of additive A2 to obtain pitch yield of 42%. Further investigations are being conducted to ascertain the different role that these two additives play in the polymerization of binder pitches and also their cost-effectiveness.

Study of PAHs emissions: Pyrolysis GC/MS. The pyrolysis GC/MS spectra of the pitch alone (bottom) and that of the pitch mixed with 1% A2 is shown in Figure 4. As expected, the volatile part from the pitch consists mostly of aromatic compounds with 3-6 aromatic rings. The most dominant compounds are 4 member rings, similar to those reported previously by solid state ^{13}C NMR measurements on the TS fractions [(2)]. Upon the addition of the additive, A2, the signal intensity of the aromatic compounds decreased with a factor of about 3. Keeping the signal of the dibenzo[dfg,nmo]chrysene at 64 minutes retention time as a reference, the main reduction appears in the region of the 3 to 4 aromatic ring system. The reduced signal intensity is also related to the retention of 32±2% of the pitch in the pyrolysis GC/MS sample holder (an average of two runs) for the pitch with A2 compared to only 7±2% for the pitch alone. This indicates that additive A2 is reacting with the low molecular weight compounds in the pitch and enhances the pyrolysis yield through their polymerization.

Study of the carbon bodies. Green carbon bodies were produced by mixing calcined coke and the coal tar pitch alone (CB) and with the additive A1 (CB-A1). The concentration of A1 was around 10wt% of the pitch (i.e. 2.5wt% A1, 22.5wt% pitch and 75wt% petroleum coke), and the green bodies were baked to 800°C and 1000°C. The results were listed in Table 1. The apparent densities of both green carbon bodies are very similar (1.753g/ml and 1.755g/ml for CB and CB-A1, respectively), indicating that the additive did not have any impact in the density of the carbon body produced. After baking, as expected, the pitch yield was lower for the carbon bodies baked at 1000°C than those baked at 800°C. The pitch yields of the baked carbon bodies containing the additive A1 (CB-A1-800 and CB-A1-1000) were higher than their counterparts without the additive (CB- 800 and CB-1000). Furthermore, the apparent densities of the carbon bodies with the additive A1 were higher than their counterparts with the additive (1.398g/ml and 1.413g/ml for CB-A1-800 and CB-A1-1000, respectively, vs. 1.385g/ml and 1.409g/ml for CB-800 and CB-1000, respectively), due to their higher pitch yields. However, these densities are lower than those those desired by industry, due to both the open baking system vs. closed system and the fast baking program used (24 hr vs. ~1 week).

Conclusions

1. The polymerization additives A1 and A2 can increase the pitch yields, where values as high as 47wt% for the pitch/additive mixtures were obtained compared to only 38wt% for the pitch alone.
2. Pyrolysis GC/MS studies indicates that the additive reacts with the low molecular weight compounds present in the pitch.
3. The apparent densities of green carbon bodies prepared with additive A1 are very similar to those prepared without additive. Furthermore, the pitch yields and apparent densities of the baked carbon bodies containing the additive A1 are higher than their counterparts without the additive.

References

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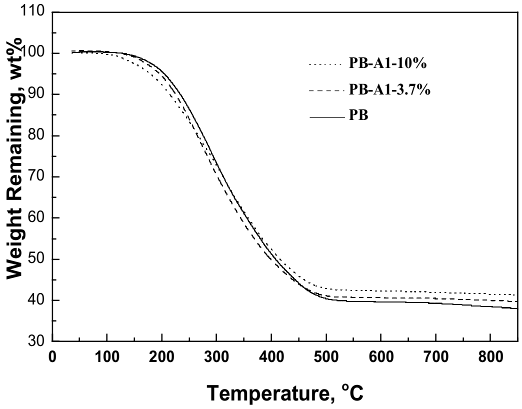


Figure 1. Comparison of the TGA traces for the pitch alone and mixed with additive A1.

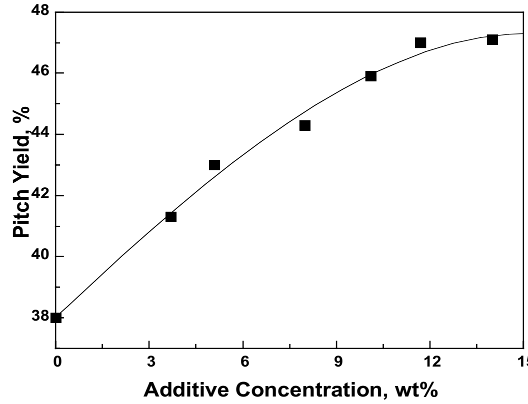


Figure 2. Variation of pitch yield for the pitch with additive A1.

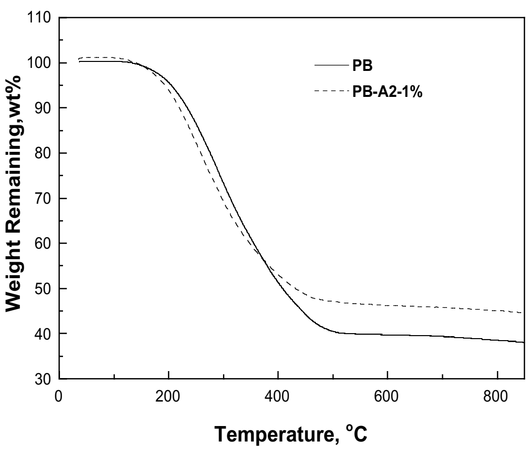
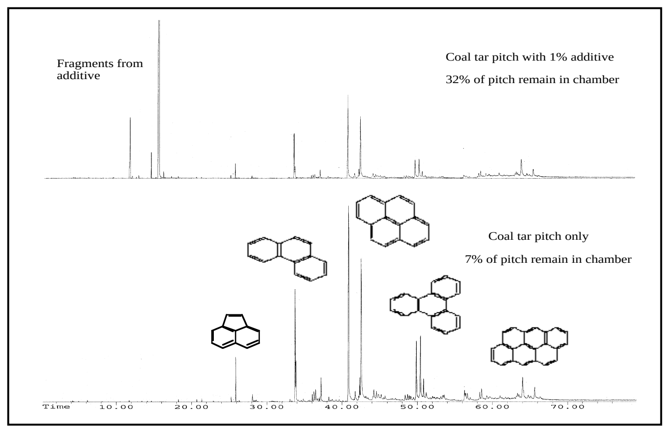


Figure 3. Comparison of the TGA races for the pitch alone and mixed with additive A2.



gure 4. The pyrolysis GC/MS spectra of the pitch alone (bottom) and that of mixture pitch/1wt% A2

Table 1. The properties of carbon bodies before and after baking.

I.D.	Formulation, %			Baking Temperature	Pitch yield	Apparent density, g/ml	
	Pet. Coke	Pitch	A1	^{o}C	%	Green	Baked
CB	75	25	0	800	52.0	1.753	1.385
				1000	58.7		1.398
CB-A1	75	22.5	2.5	800	50.8	1.755	1.409
				1000	56.5		1.413