STUDY ON PYROLYSIS OF CARBONACEOUS ADDITIVES IN GREEN SAND FOUNDRIES

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Abstract

This research evaluated the hydrocarbon emission characteristics during pyrolysis of four carbonaceous additives that can be used in green sand foundries. These included a highly volatile bituminous coal, anthracite, lignite and cellulose. The samples were flash pyrolyzed in a Curie-point pyrolyzer at 920 ^{o}C with a heating rate of about 3000 ^{o}C/sec. This simulated the fast heating conditions that the carbonaceous additives would experience at the metal-mold interface when molten metal is poured into green sand molds. The samples were also pyrolyzed in a thermogravimetric analyzer (TGA) from ambient temperature to 1000 ^{o}C with a heating rate of 20 ^{o}C/min; and this simulated the slow heating conditions that the carbonaceous additives would experience within the bulk of green sand molds that is further away from the metal-mold interface. Hydrocarbon emissions from flash pyrolysis were analyzed with GC-FID, while those from TGA pyrolysis were monitored with mass spectroscopy and GC-FID. The anthracite exhibited very low volatile hydrocarbons during both flash pyrolysis and TGA pyrolysis. The cellulose released less hydrocarbons than bituminous coal or lignite in TGA pyrolysis, but more hydrocarbons than those two during flash pyrolysis. This means that cellulose can release sufficient volatile hydrocarbons at the intensely heated molten metal-mold interface where they are most desired for ensuring casting quality, but much less within the bulk of the mold where they are undesirable. This characteristic of cellulose offers an important opportunity for green sand foundries to diminish their hazardous air pollutant (HAP, defined herein as the 189 compounds that are categorized in Title III: Hazardous Air Pollutants of the 1990 Clean Air Act Amendments.) emissions.

Introduction

Hazardous air pollutant (HAP) emissions from green sand foundries pose considerable hazards to the environment and human health. Among the 189 HAPs listed in the 1990 Clean Air Act Amendment (CAAA), some 40 compounds have been identified in the air emissions from the foundries; and over 90% of the foundry HAPs are organics (Technikon, 2000; Glowacki et al., 2003; Fox et al., 2002). One of the major sources of the organic HAPs is the pyrolysis of carbonaceous additives that are added into the green sand mold to improve casting quality (Fox et al., 2002; Allen et al., 1991; Mckinley, et al., 1993). These HAPs are released during metal pouring, mold cooling, and casting shakeout when the carbonaceous additives are exposed to the casting heat.

Carbonaceous additives are used in nearly all green sand iron foundries. Although there are many different theories and rules of thumb regarding the role of carbonaceous additives in the iron casting process, most functions pertain to their volatile hydrocarbons released during pyrolysis at the metal-mold interface (Wang et al., 1973; Green et al., 1980; Dempsey et al., 1997). The volatile hydrocarbons are particularly important for ensuring the casting quality because (a) they form a gaseous blanket between the molten metal and the sand, and thus keep the sand grains from sticking to the casting surface (Green et al., 1980); (b) these volatile hydrocarbons could be further pyrolyzed to deposit a shiny graphitic carbon film (characterized as lustrous carbon in foundries) at the metal-mold interface. This lustrous carbon film prevents the molten metal from penetrating the mold surface during the pouring, and also prevents the formation of iron silicate (Wang et al., 1973; Dempsey et al., 1997); (c) they provide a reducing atmosphere at the metal-mold interface, and the carbon reacts with oxygen to prevent the oxidation of the hot casting surface (Green et al., 1980). From many years' experience, foundry personnel have perceived that a certain amount of volatile hydrocarbons from the carbonaceous additives must be present at the metal-mold interface in order to produce quality castings. For example, when there are insufficient volatile hydrocarbons at the metal-mold interface, the extent of sand adherence to the casting surface increases (Wang et al., 1973; LaFay et al., 1998a; Volkmar, et al., 2000), while too much volatile hydrocarbons may generate wrinkles at the casting surface due to the piling up of lustrous carbon films (Naro, 2002).

Historically, early foundries selected carbonaceous additives primarily based on their performance, with less emphasis on environmental effects. The most commonly used carbonaceous additive is a highly volatile bituminous coal (traditionally identified as seacoal by foundry personnel) due to its high release of volatile hydrocarbons during pyrolysis. However, these volatiles include HAPs. Roughly 80% of the HAPs are benzene, toluene, xylene (BTX) compounds (Glowack, et al., 2003). As a response to the ever more stringent regulations on air emissions, some foundries may consider alternative carbonaceous additives that could replace the bituminous coal in the green sand. Among many bituminous coal

replacements that have been tested, anthracite, lignite, and cellulose have shown some promising results for producing casting with acceptable quality (LaFay et al., 2004; Thiel, et al., 2005). However, only a limited number of emission data sets are available regarding the HAP emission characteristics of these materials. Full-scale stack testing is expensive, and fraught with considerable variability and statistical uncertainty that reflects true variations in foundry operation conditions (LaFay et al., 2004; Thiel, et al., 2005; Land et al., 2004). In comparison, laboratory analytical pyrolysis can be readily conducted and analyzed under strictly controlled conditions that simulate key features of the thermal conditions that carbonaceous additives experience in the green sand mold (Bachmann, et al., 1982; LaFay et al., 2000; Wang et al., 2004 and 2005).

It is noted that carbonaceous additives are heated via quite different means at various locations within a green sand mold (Zeng et al., 1985; Chen et al., 1990; Shih, et al., 1996; Hsiau, et al., 1998; Wang et al., 2004). At the metal-mold interface, green sand is heated to about 1400 ^{o}C instantly after the metal is poured into the mold. The temperature ramping rates right at this interface could be thousands ^{o}C/sec. Then during the casting solidification and mold cooling, as the heat dissipates outwards through the green sand mold, green sand further away from the metal-mold interface is progressively heated, but at lower heating rates of several ^{o}C/min to hundreds ^{o}C/min, as dictated by the distance from the metal-mold interface. The peak temperatures also decrease approximately exponentially as the distances from the metal-mold interface increase. The huge difference in the heating conditions profoundly affects the volatile yields and distributions of the carbonaceous additives. Particularly, previous studies on cellulose pyrolysis have shown that the percent of gaseous products increased dramatically as the heating rate increased. In contrast, lower heating rates yield more cellulose tars. The prominent composition of cellulose tar is levoglucosan (1,6-anhydro-β-D-glucopyranose) that has a melting point of 182 ^{o}C and boiling point of 280 ^{o}C (Fisher et al, 2002; Li et al., 2001; Fushimi et al., 2003; Banyasz et al, 2001; Maekawa et al., 1998). The authors herein perceived that this characteristic of cellulose would offer the foundries a great opportunity to diminish their HAP emissions, as discussed below.

In this light, the **objectives** of this research were (a) to compare the hydrocarbon emission characteristics of bituminous coal and the potential substitute carbonaceous additives in bench scale pyrolysis experiments, (b) specifically, characterize the emissions released during the abrupt thermal shock of flash pyrolysis which simulates green sand conditions at the molten metal-mold interface, (c) compare these to the emissions released during gradual heating in a thermogravimetric analyzer, which simulates bulk green sand conditions away from the metal-mold interface, and (d) test the hypothesis that cellulose was a good potential carbonaceous additive that could provide a suitable hydrocarbon blanket at the metal-mold interface while minimizing HAP emissions in the green sand mold.

Materials and Methods

The highly volatile bituminous coal used in this research was shipped from a full-scale foundry (Neenah Foundry, WI). The anthracite was from Jeddo Coal Company (Wilkes-Baree, PA). The lignite was from Mississippi Lignite Mining Company (Red Hills Mine, Ackerman, MS). The cellulose was from Spilltech ltd. (Alpharetta, GA). The bituminous coal, anthracite, and lignite were crushed to pass through a 75 μm sieve. Cellulose with a particle size of about 100 μm was used in the test. All the samples were dried at 105 ^{o}C overnight and stored in a desiccator prior to use. The elemental analysis of these samples is shown in Table 1.

Table 1. Elemental Analysis (dry ash free) of the Carbonaceous Additives and amount remaining following: (a) burning at 600 ^{o}C (ash), (b) TGA under N_2 to 1000 ^{o}C, (c) Curie-point flash pyrolysis under helium at 920 ^{o}C

Sample	C%	H%	N%	O% (by diff.)	Ash%	Remain after TGA %	Remain after Curie-point pyrolysis %
Anthracite	94.3	2.25	0.89	2.59	12.8	90.4	89.5
Bituminous coal	86.4	5.74	1.68	6.22	10.9	62.0	56.3
Lignite	68.3	5.25	1.10	25.4	25.3	58.6	47.2
Cellulose	48.3	6.07	0	45.6	8.56	22.9	7.8

TGA pyrolysis -mass spectroscopy (MS) analysis

About 20 mg of the samples were placed in a TGA 2050 (TA Instruments, Newcastle, DE) and pyrolyzed from ambient temperature to 1000 ^{o}C with a heating rate of 20 ^{o}C/min under an argon atmosphere. This simulated the slow heating conditions away from the metal-mold interface. The gaseous effluent from the TGA flowed to a downstream mass spectroscopy (Thermostar GSD 301T, Pfeiffer Vacuum Inc., Nashua, NH) for emission kinetics analysis. Duplicates of TGA-MS were conducted for cellulose: the intensities for the specific hydrocarbons were within 10% of each other, and the temperatures corresponding to highest peaks were within 5% of each other.

TGA pyrolysis-GAC capture-solvent extraction-GC-FID analysis

In a second round of TGA tests that quantified overall net hydrocarbon emissions, about 20 mg of the samples were pyrolyzed in a TGA (Cahn TG-131, Thermo Electron Inc., CA) with a heating rate of 20 ^{o}C/min from ambient temperature to 1000 ^{o}C under N_2. During the heating, granular activated carbon tubes (Supelco, ORBO^{TM} 32, Bellefonte, PA) captured the TGA emissions in the TGA effluent. Then the emissions were extracted from the activated carbon with carbon disulfide solvent for 24 hrs. The solvent with analytes was then analyzed for hydrocarbons by a gas chromatography-flame ionization detector (GC-FID) (Hewlett-Packard 5890 Series II, packed column inlet with a 100% dimethyl polysiloxane colume). Duplicates were conducted for each carbonaceous additive, and Table 2 lists the average concentrations and standard deviations.

Flash pyrolysis-GC-FID analysis

About 1.5 mg sample was tightly wrapped in a ferromagnetic foil that was then placed in a small quartz reactor (4.0 mm i.d.) in the Curie-point pyrolyzer (Japan Analytic Ind., JHP-22). The foil rapidly heated to its specific Curie-point temperature of 920 ^{o}C in a helium atmosphere. The heating rate was about 3000 ^{o}C/sec. This simulated the fast heating conditions at the metal-mold interface. The 920 ^{o}C was held for three seconds so as to achieve complete pyrolysis of the carbonaceous additives. The gases emitted were carried through a heated (200 ^{o}C) transporting tube to the GC-FID (Hewlett-Packard 5890 Series II, packed column inlet with a 100% dimethyl polysiloxane colume) for hydrocarbon emission analysis. Four replicates of flash pyrolysis were conducted for each carbonaceous additive, and Table 2 lists the average concentrations and standard deviations.

<p align="center">Results</p>

TGA pyrolysis-MS analysis

The mass loss and derivative thermogravimetric (DTG) profiles during TGA-MS tests are shown for the four samples in Figure 1. The anthracite lost the least mass (9.6%) and its mass loss was above 400 ^{o}C, while the bituminous coal lost mass mainly at 400-600 ^{o}C, and the lignite lost mass over a broader temperature range. The cellulose lost more than 60% of its mass at 200-400 ^{o}C.
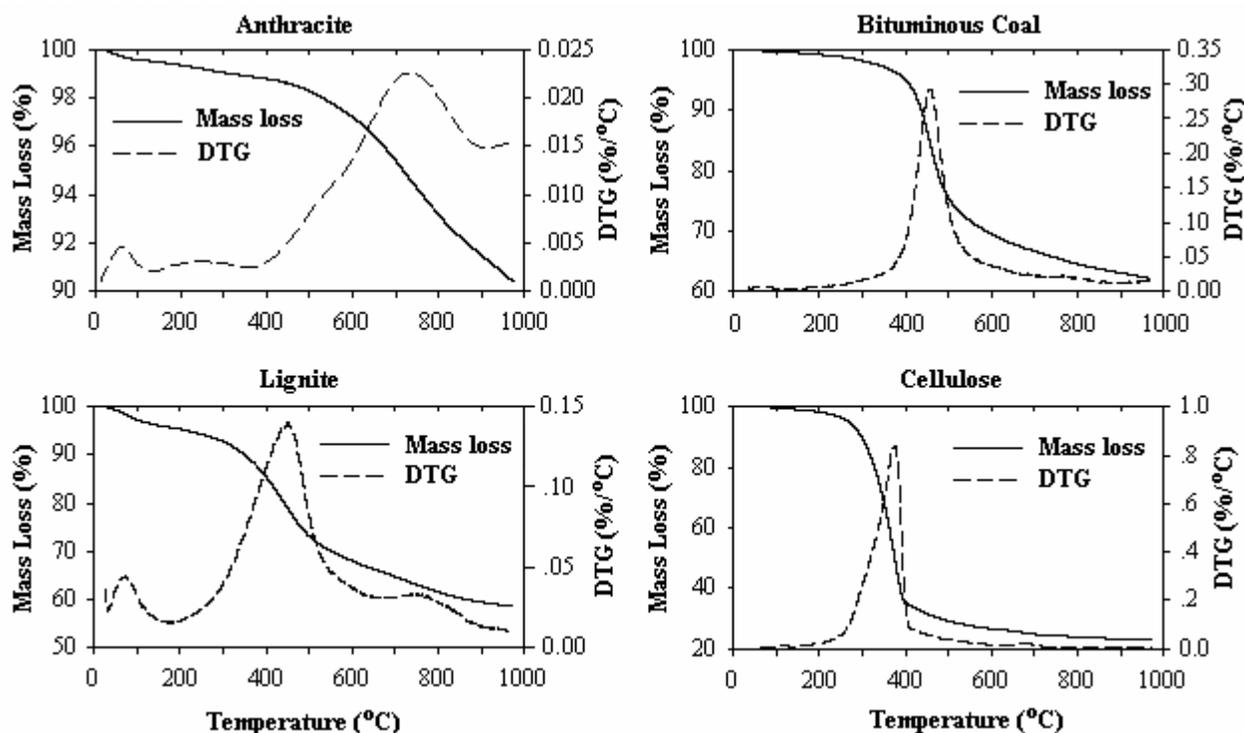

Figure 1. TGA and derivative thermogravimetric (DTG) profiles of the carbonaceous additives in an argon gas environment (20 ^{o}C/min).

TGA-mass spectroscopy (MS) plots revealed the temperature ranges where the major gas products were released from the carbonaceous additives during TGA slow heating (see Figure 2). The anthracite MS responses were less than those for the other materials. The bituminous coal released most of the hydrocarbon gases (e.g. methane (m/z=15)) and major HAPs (e.g. benzene (m/z=78), toluene (m/z=92), and xylene (m/z=106)) in the temperature range of 350-700 ^oC. The lignite commenced release of methane and BTX compounds at a lower temperature (about 300 ^oC). The cellulose released methane starting at 250 ^oC, and it released BTX compounds over 300-700 ^oC.

TGA pyrolysis-GAC capture-solvent extraction-GC-FID analysis

The emission analysis results from the TGA-GC-FID tests have been summarized in Table 2. The hydrocarbons of C1-C5 were the sum of hydrocarbons that were detected between methane (C1) and pentane (C5) by the GC-FID, while the C6-C16 were the sum of hydrocarbons that were detected between hexane (C6) and hexadecane (C16). In Table 2, the C1-C5 were normalized to the standard of methane, and the C6-C16 were normalized to the standard of benzene. The C6-C16 have been often taken as a measure for the volatile organic compound (VOC) emissions from American foundries (Glowacki et al., 2003; Goudzwaard, et al, 2003). As shown, the bituminous coal exhibited the highest volatile hydrocarbon yields in slow TGA heating situation, followed by the lignite, cellulose and anthracite.

Table 2. Hydrocarbon emissions of the carbonaceous additives during TGA pyrolysis and Curie-point flash pyrolysis

Sample		Hydrocarbon (mg/g)[*]				Representative HAPs (mg/g)					
		C1-C5		C6-C16		Benzene		Toluene		Xylene	
		mean	SD	mean	SD	mean	SD	mean	SD	Mean	SD
TGA pyrolysis-extracted GC-FID	Anthracite	0.11	0.04	0.37	0.10	0.072	0.027	0.021	0.007	0.005	0.002
	Bituminous Coal	10.09	0.09	8.50	0.75	0.406	0.021	0.783	0.065	0.384	0.059
	Lignite	5.27	0.62	4.57	0.18	0.351	0.002	0.413	0.006	0.160	0.004
	Cellulose	3.84	0.47	2.60	0.30	0.213	0.015	0.298	0.038	0.077	0.009
Flash pyrolysis	Anthracite	2.25	0.18	0.81	0.02	0.14	0.01	0.11	0	0.04	0
	Bituminous Coal	58.33	2.54	27.27	1.23	1.49	0.13	1.33	0.05	0.65	0.01
	Lignite	36.98	3.37	17.36	1.84	2.11	0.15	1.25	0.11	0.47	0.05
	Cellulose	80.66	14.94	37.56	2.76	4.45	0.62	1.38	0.06	0.22	0.02
Ratios of 100×TGA versus Flash pyrolysis	Anthracite	4.9		45.6		51.4		19.1		12.5	
	Bituminous Coal	17.3		31.2		27.2		58.9		59.1	
	Lignite	14.3		26.3		16.6		33.0		34.0	
	Cellulose	4.8		6.9		4.8		21.6		35.0	

*: C1-C5 normalized to the standard of methane; C6-C16 normalized to the standard of benzene

Flash pyrolysis-GC-FID analysis

With regard to hydrocarbon emissions created by Curie-point pyrolysis, the nature of generated species was similar for the four carbonaceous additives (see Figure 3 and Table 3 list), but not of the same magnitudes (see Table 2). Methane comprised the prominent hydrocarbon emission; while benzene, toluene, and xylene (BTX) were the major specific HAP compounds. As shown in Table 2, during flash pyrolysis, the cellulose yielded the highest mass of volatile hydrocarbons per mass of additive. This was followed in order by the bituminous coal, lignite and anthracite.
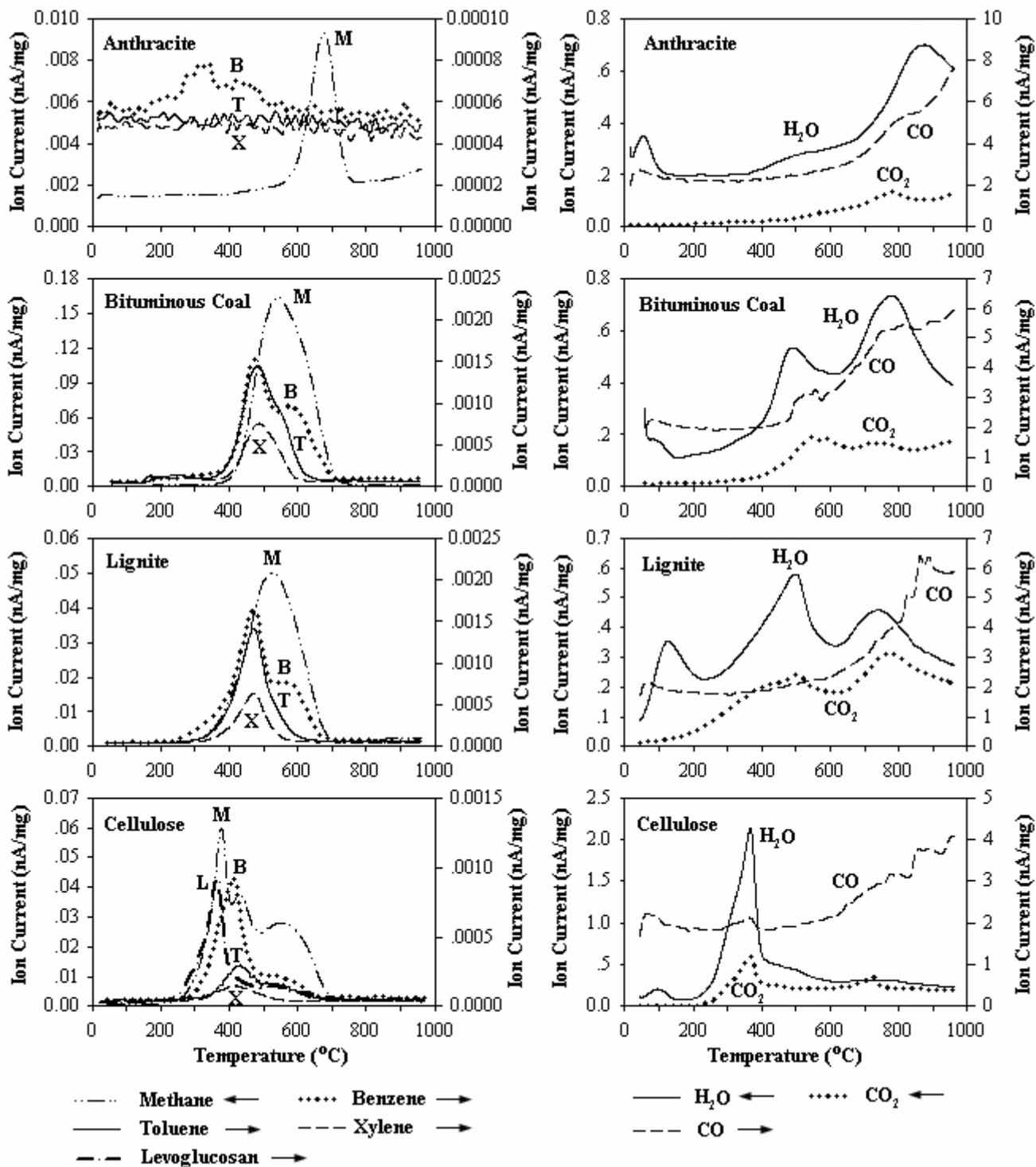
Figure 2. Mass spectroscopy responses to the gas emissions during TGA-MS pyrolysis under argon atmosphere. Left column shows methane (left y-axis); benzene, toluene, xylene and levoglucosan (right y-axis). Right column shows H_2O, CO_2 (left y-axis); and CO (right y-axis).
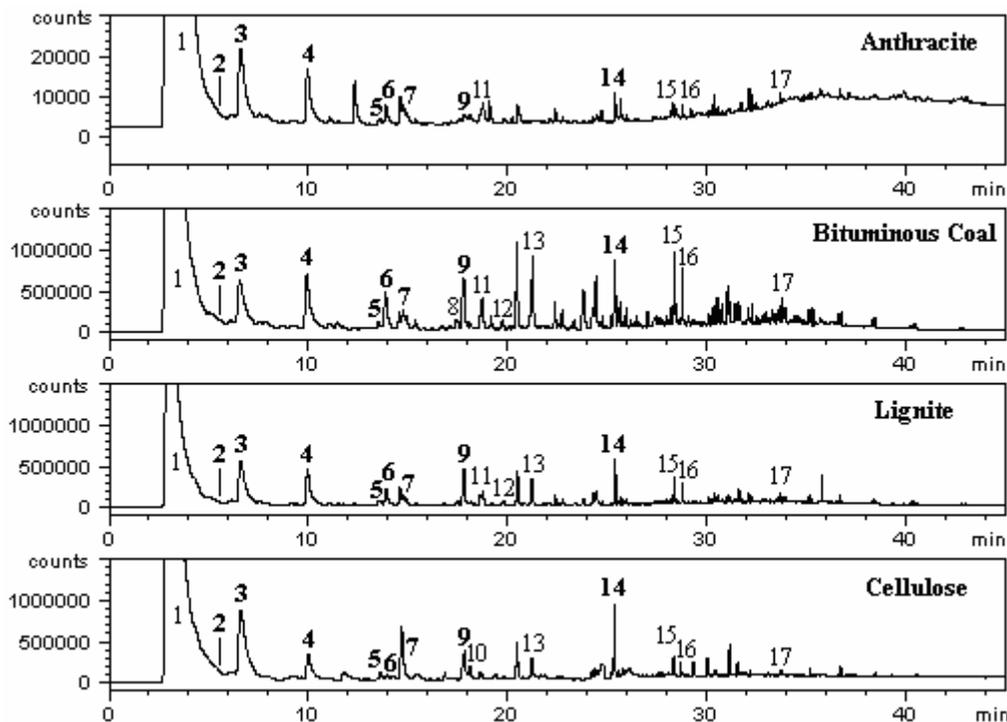
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Figure 3. GC-FID responses to the hydrocarbon emissions of the carbonaceous additives during the flash pyrolysis (Peak 1 truncated to fit the figure).

Table 3. Major hydrocarbon compounds identified by GC-FID in flash pyrolysis products of anthracite, bituminous coal, lignite and cellulose. Hazardous air pollutants that are categorized in Title III of 1990 Clean Air Act Amendment are shown in bold font.

Peak	Compounds
1	C1-C5, methane is the predominant species, followed by ethane, propane, etc.
2	**Hexane** (Start point for C6-C16 integration)
3	**Benzene**
4	**Toluene**
5	**Ethylbenzene**
6	**m-xylene, p-xylene** (peaks overlap)
7	**o-xylene**
8	3-ethyltoluene, 4-ethyltoluene (peaks overlap)
9	**Phenol**
10	2-ethyltoluene
11	1,2,4-trimethylbenzene, Tert-butylbenzene (peaks overlap)
12	1,2,3-trimethylbenzene, p-cymene (peaks overlap)
13	1,2-diethylbenzene and some unidentified compounds
14	**Naphthalene**
15	2-methylnaphthalene
16	1-methylnaphthalene
17	Hexadecane (End point for C6-C16 integration)

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Discussion

Previous study showed that lustrous carbon film is formed at the metal-mold interface instantly as the molten metal is poured into the green sand mold (Naro, 2002). And rationally, the role of the volatiles and lustrous carbon film in preventing sand grains from sticking to the casting surface and from the iron becoming oxidized is most effective before the casting develops a solid skin; and this usually takes less than one minute after metal pouring (Shih et al, 1996; Hsiau, et al, 1998). Thus, the authors herein proposed that only the hydrocarbons that are released from flash pyrolysis of carbonaceous additives at the very vicinity of the metal-mold interface are of great importance in developing the gaseous blanket and lustrous carbon film. The hydrocarbons released from the slow heating of carbonaceous additives that are further away from the metal-mold interface do not help develop the lustrous carbon film and prevent sand adherence to the casting surface. For example, it has been shown that it took about 3 and 10 minutes respectively for the green sand that was 1.0 cm and 1.5 cm away from the metal-mold interface to be heated to 400 ^{o}C after the metal pouring, and thus to release volatile hydrocarbons (Shih et al, 1996; Hsiau, et al, 1998). But by 3-10 minutes, the metal skin has become solidified and the hydrocarbon blanket is less needed.

Based on these two notions that a certain amount of volatile hydrocarbons is needed at the metal-mold interface to ensure the casting quality, and these hydrocarbons are released from flash pyrolysis of carbonaceous additives that are at the very vicinity of the interface, the usage of the carbonaceous additives in the green sand can be strategically adjusted according to their unit capacity to release hydrocarbons during flash pyrolysis. From the perspective of this function, the anthracite seems not an ideal carbonaceous additive since it offers very low volatile hydrocarbons during flash pyrolysis unless very large (and costly) amounts of anthracite are used. Thus, the anthracite is excluded for further discussion herein.

It could be seen from Figure 2 that HAP emissions from the other three carbonaceous additives mainly occur above 300-350 ^{o}C when slowly heated. In casting practice, green sand molds are usually kept intact for about 45-120 min for casting solidification and mold cooling after the molten metal is poured into the mold. During this period, as the casting heat dissipates from the metal-mold interface outwards through the green sand mold, a considerable fraction of the green sand mold (as dictated by casting size, metal-sand-ratio, cooling time, etc) can be gradually heated to temperatures above 300 ^{o}C, and thus release hydrocarbons (Dempsey et al., 1997; Wang et al., 2006; LaFay et al, 1998b). These volatile hydrocarbons are detrimental because they contain significant amounts of HAPs that can become released from the green sand mold during mold cooling and shake-out.

Thus, from the combined perspective of optimizing both performance and environmental friendliness, the ideal carbonaceous additives would be ones that could release sufficient volatile hydrocarbons during flash pyrolysis at the metal-mold interface, while concurrently releasing the least amount of volatile hydrocarbons during slow heating throughout the bulk volume of the green sand mold. Of the carbonaceous additives tested herein, the cellulose performs the closest to this technical ideal.

To appraise this, the authors compared the ratios of TGA pyrolysis volatile hydrocarbons to Curie-point flash pyrolysis volatile hydrocarbons. As shown in Table 2, the volatile hydrocarbons generated by slow TGA pyrolysis were much lower than those generated by flash pyrolysis for all the samples tested herein; and the ratio was specifically the lowest for cellulose. When considering the larger molecular hydrocarbons (C6-C16) that contain most of the identified HAP compounds, cellulose volatile hydrocarbons for TGA pyrolysis were 7% of those for flash pyrolysis, and these compared to ratios of 46% for anthracite, and 26-31% for lignite and bituminous coal.

For the coals, flash pyrolysis caused more extensive thermal fragmentation of coal molecules, and thus produced more volatiles (especially lower molecular weight hydrocarbons) than did slow TGA heating (Berkowitz, 1985; Speight, 1994). In comparison, flash pyrolysis dramatically enhanced cellulose's hydrocarbon gas production via a distinct mechanism. Unlike the coals, the cellulose pyrolysis consisted of two stages. The first stage (200-400 ^{o}C) primarily yielded H_2O, CO_2 and tar (e.g. levoglucosan) (see Figure 2). The hydrocarbon gases are primarily generated from the secondary thermolysis of the tar at higher temperatures (>400 ^{o}C) (Fisher et al., 2002; Li et al., 2001; Fushimi et al., 2003; Banyasz et al., 2001). However, cellulose's tar is easily volatilized below 400 ^{o}C. For example, the prominent composition of cellulose tar, levoglucosan (mp 182 ^{o}C, bp 280 ^{o}C) is known to sublimate over 200 ^{o}C (Maekawa et al., 1998). Thus, when the cellulose was slowly heated, as in TGA pyrolysis, the tar was volatilized and escaped from the TGA reactor more quickly than the temperature rose (Fushimi et al., 2003). This prevented the tar from further pyrolyzing to form the C1-C16 volatile hydrocarbons tested herein. In contrast, when the cellulose was flash pyrolyzed, the tar could decompose into hydrocarbon gases before it escaped from the reactor due to the very rapid heating rate. This characteristic of the cellulose makes it an ideal carbonaceous additive for diminishing HAP emissions from the foundry, while also provides sufficient volatile hydrocarbons at the metal-mold interface.

As mentioned before, during the casting solidification and mold cooling, a considerable fraction of the green sand mold can be slowly heated to temperatures above 300 ^{o}C, and thus release HAPs. However, when the cellulose is used, the slow heating would allow the tar released from the cellulose at 200-400 ^{o}C to volatilize and move outwards before the

temperature rises above 400 $^{\circ}$C in the region where the tar is generated. The cellulose tar would then progressively move away from the hot regions and then re-condense in the cool regions further away from the metal-mold interface, just as the water vapor does in a green sand mold (Shih et al., 1996; Marek, 1963). This would prevent the cellulose tar from further pyrolysis (that occurs above 400 $^{\circ}$C) to form HAPs. In contrast, the bituminous coal and lignite generate tar and hydrocarbon gases simultaneously when slowly heated to above 350 $^{\circ}$C; and the coal tars are much less volatile compared with the cellulose tar. For example, it has been shown that about 50% of coal tar had boiling points >450 $^{\circ}$C (Berkowitz, 1985). So the tar of bituminous coal and lignite stays in the hot region and is further pyrolyzed to form volatiles (and HAPs) as the temperature goes up. In practice, this means that HAP emissions from the bulk volume of the green sand mold that is slowly heated would be greatly reduced when the cellulose is used instead of the other carbonaceous additives tested herein.

To appraise this concept, the authors compiled Figure 4, which shows the ratio of BTX and hexane released during slow TGA heating, as compared to the total volatile hydrocarbons (C1-C16) released during flash pyrolysis. As shown, when all the carbonaceous additives release the same amount of volatile hydrocarbons during flash pyrolysis (that are needed at the metal-mold interface for ensuring casting quality), the cellulose releases only about 10-50% as much BTX and hexane as do other carbonaceous additives during slow pyrolysis (that occurs at the bulk of the green sand mold). Thus, cellulose offers a technically sound opportunity for the foundry to cut down on HAP emissions.
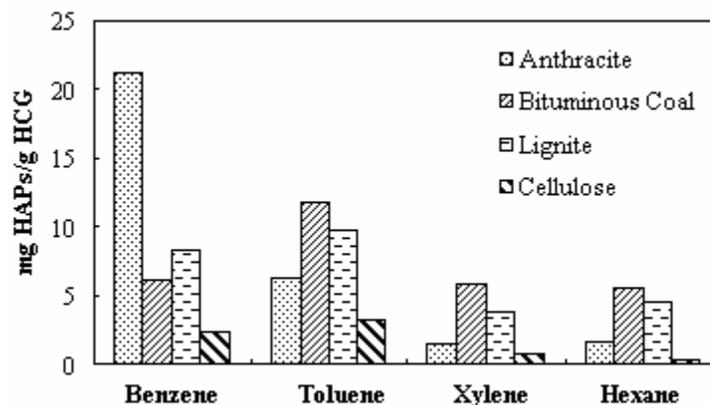

Figure 4. Ratios of BTX and hexane yields during gradual TGA Pyrolysis to the total volatile hydrocarbon gas (HCG) yields (C1-C16 as benzene) during flash pyrolysis

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