

A METHOD TO MEASURE BENZENE PRODUCTION DURING PYROLYSIS; RESULTS FROM TESTING OF CARBONACEOUS ADDITIVES IN FOUNDRY SANDS

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ABSTRACT

Carbonaceous additives that are blended with clays in foundry sands and sand cores are recognized as a source of benzene emissions in the foundry industry. Impending legislation will possibly mandate substantial reductions in benzene emissions in this sector despite the fact that, with current technology, carbonaceous additives are essential for the production of quality castings. However, it may be possible to identify substitutes that provide acceptable casting performance while generating less benzene. As a first step, a method has been developed to measure the production of benzene during pyrolysis of carbonaceous materials. The method entails pyrolysis of carbonaceous samples in a thermogravimetric analyzer, absorption of the pyrolysis products onto activated charcoal, extraction of the charcoal with CS₂ containing p-cymene, and gas chromatographic quantitation of benzene. Results are presented for several potential sand-mold additives including a series of coals of varying rank, gilsonite, asphaltic suspensions, and metallurgical coke.

INTRODUCTION

It has been estimated that about 90% of all durable goods produced in the U.S. contain at least some metal castings.¹ During 1994, over 13 million metric tons of metal, ~85% of which were iron or steel, were processed by ~3,100 foundries in the U.S.² In 1996, the number of persons directly employed in the U.S. foundry industry numbered just over 220,000³ which does not include the estimated hundreds of thousands of others that supply products to or sell finished goods from this sector. It is, therefore, clear that the foundry industry is a critical segment of the overall domestic economy, one that cannot be substantially curtailed without severe economic repercussions.

From 1971-1991, the domestic foundry industry declined by 32%, due in part to the implementation of increasingly stringent environmental protection regulations including the Clean Air Act (1970) and the Clean Air Act Amendments (1977 and 1990).⁴ The most recent amendment calls for development and implementation of maximum achievable control technology (MACT) standards for the iron foundry categories by November, 2000. Meanwhile, some states are planning to implement their own regulations which set limits separate from those federally mandated. In Wisconsin, for example, sites that exceed such limits must either demonstrate emission controls that provide the lowest achievable emission rates (LAER) through technological advances or other options or show why they should be granted a variance.⁵ In an effort to address the mandates of BACT and/or LAER, one of the options being examined by the foundry industry in that state is reformulation of the molding sand.

Though the carbonaceous materials added to sand molds and cores are believed partially responsible for unwanted emissions, they are essential in providing a reducing atmosphere during pouring which suppresses reaction between the casting sand and metal surfaces.⁶ They also seal the voids between the sand grains thereby suppressing penetration of the molten metal into the sand mold.⁷ The material most widely used to alleviate such casting defects is bituminous coal, commonly referred to in the foundry industry as seacoal. However, when subjected to high temperatures in a reducing atmosphere, i.e., pyrolysis, such coals generate one- and two-ring aromatics, both directly and via secondary reactions.⁸ Of the aromatic components, benzene is of greatest concern due to its relatively high production and proven carcinogenicity. Numerous materials including petroleum resins, cellulosic flours, rosin and petroleum pitch, asphaltic emulsions, asphaltene chips, graphite, fuel oil, gilsonite, coal tar, and even sugar, starch, and molasses were developed as replacements for seacoal.⁹ However, total displacement of seacoal by these additives was not realized for various reasons including uncertainties in availability and inferior performance. Today, the use of these replacements has either been discontinued or they are used as seacoal supplements, typically comprising 20-40 wt% of the carbonaceous additive. This latter trend of blending carbonaceous materials is believed to hold the most promise for reducing the release of hazardous pollutants. Accordingly, the work reported here represents an initial effort aimed at identifying potential additives that emit less benzene during casting yet meet the commercial criteria of low cost, acceptable performance, and availability.

EXPERIMENTAL

Briefly, measurement of the benzene-emitting potential entailed pyrolysis of carbonaceous additives by TGA, collection of evolved volatiles on activated charcoal, extraction of the charcoal with CS₂, and chromatographic quantitation of benzene. With the exception of the pyrolysis step, the method was modified from OSHA protocols for the measurement of benzene vapors in the workplace.¹⁰

Study Samples. A listing of the samples examined along with a brief description is given in Table I. All samples were solid materials with the exception of two proprietary aqueous asphaltic suspensions (AE-1 and AE-2). Several of these materials are currently used in commercially prepared green-sand blends including the bituminous coals, gilsonite, lignite, and the asphaltic emulsions. The solids were pulverized to the particle range as utilized in molding sands ranging from ~75% pass 40 mesh for the lignite to >90% pass 100 mesh for the gilsonite.

Pyrolysis. 20-90 mg samples were pyrolyzed in triplicate in a TA model 2950 thermo-gravimetric analyzer (TGA) under flowing Argon (60 mL/min). Following a 1 minute equilibration, the furnace was ramped from ambient to 800 °C at 100 °C/min and held for 5 minute. A fast heating rate was selected to more closely simulate the conditions within a sand mold during casting. The heating profile used for the aqueous emulsions was similar except that a 3-minute hold at 100 °C was substituted for the initial 1-minute hold. This modification was necessitated by the high water content of these samples which otherwise resulted in sample *splattering* from the pan. Weight loss from room temperature to ~200 °C was assigned to H₂O while losses above ~200 °C assigned to volatile matter.

Collection of volatiles. Glass tubes (~100 x 5 mm-i.d.) containing 20/40 mesh activated coconut charcoal (ORBO™-32) were used to collect the volatile matter generated during each TGA run. These tubes were partitioned into two in-series chambers; a primary containing 400 mg and secondary containing 200 mg of charcoal. The primary chamber, positioned nearest to the furnace exit, served to absorb the volatile matter as it evolved (including benzene) during the TGA run. The secondary chamber was used to ensure that benzene did not saturate and break through the primary. One end of the tube was loosely connected to the TGA-furnace exit while the other was connected to house vacuum. The vacuum was regulated such that roughly 200 cm³/min gas flow was pulled through the tube. Thus, all carrier and pyrolysis gases exiting the TGA furnace were pulled into the charcoal tube without significantly affecting the furnace pressure.

Benzene quantitation. Prior to the extraction, benzene that is present in commercial-grade CS₂ was removed by passing the CS₂ through molecular sieve 13x, refluxing overnight with H₂SO₄/HNO₃ then again passing through molecular sieve. Chromatographic analysis of the processed CS₂ indicated complete removal of the benzene contaminants.

The charcoal from the primary chamber of each absorbent tube was transferred to a 4-mL, teflon-capped vial to which 2.00 mL of CS₂ spiked with *p*-cymene (10.24 ppm) was added. The vial was capped, shaken, and allowed to equilibrate at least 30 min at room temperature prior to analysis. Duplicate 1-2 µl injections of the extract were made into a HP5990 gas chromatograph equipped with a FID, a 10'x1/8" 20% SP2100/0.1% CW1500 column, and a HP-3390A integrator. Benzene was quantitated by comparison of the benzene/cymene ratios from the sample extract to a similar ratios from benzene/cymene standards, also prepared in CS₂. Due to interference with the cymene internal standard, benzene quantitation for gilsonite was achieved via an external standard technique.

RESULTS

Volatile Release Profile. TGA plots for the lignite, gilsonite, anthracite, and one of the bituminous coals (D4) are shown in Figure 1. Bituminous coal provides beneficial volatile matter release characteristics as evidenced by its common commercial usage in green-sand blends. The volatile release curve for gilsonite, also often used in commercial blends, is similar in that volatiles evolve over a relatively narrow temperature range, typically from 450-500 °C. This is in contrast to the weight loss curves for lignite and anthracite which are broader and occur at lower and/or higher temperatures. The weight loss curves for the asphaltic emulsions were reasonably similar to the D4 plot whereas weight loss for metallurgical coke was more similar to that from the anthracite.

It must be noted that the presence of carbonaceous materials in the sand mold is not of itself sufficient to assure good castings. Rather, it is the volatile component released during pyrolysis that plays the most significant role in creating a reducing atmosphere thereby minimizing oxidation.¹¹ Further, it has been shown that both the composition and temperature of release of the volatile matter governs the amount of *lustrous* or pyrolytic carbon formed (coke deposited onto the molten metal and adjacent sand).¹² Compelling evidence has also shown that only additives that are prone to lustrous carbon formation are of benefit in preventing burn-on.¹³ Thus, the difference in volatile release profiles exhibited by the various materials in Figure 1 is likely an indicator of casting performance.

Method Reproducibility. Various aspects of the reproducibility of the method are shown by the data in Table II, obtained from replicate runs with the Birmingham seacoal. Columns 3 and 4 indicate the scatter in the moisture and volatile matter values from TGA was <5% rsd ($\sigma-1$) for this particular set of runs. Likewise, columns 6 and 7 indicate the range in peak integration reproducibility from duplicate injections was typically <10% relative to the mean. Finally, the last two columns indicate the overall reproducibility of the method was just over 1% rsd ($\sigma-1$) for this sample. This level of reproducibility was the best of the samples examined. However, the relative standard deviation was less than 5% rsd for most samples and less than 10% (Table III) for all samples with the exception of the anthracite and metallurgical coke from which benzene generation was very low.

Relative benzene generation. Benzene production, moisture content, and volatile matter release are shown for all samples in Table III. Benzene production ranged approximately two orders of magnitude from a low of <0.02 mg/g coal for the anthracite to approximately 2 mg/g for gilsonite. Benzene production is plotted versus volatile matter release in Figure 2. Not surprisingly, this plot shows that increased levels of volatile matter release results in a proportional increase in benzene generation. This implies that foundry-sand blends capable of generating the required levels of volatile matter during casting must obviously contain relatively greater quantities of those additives that generate less volatile matter (and less benzene) suggesting a near constant level of benzene production regardless of the additive. However, note that there are substantial differences in the ratio of benzene production to volatile matter release as shown in the last column of Table III. In general, those samples that generated less volatile matter during pyrolysis produced even less benzene on a relative basis. Thus, a 25 mg sample of lignite, for instance, would generate as much volatile matter on an absolute basis, as 10 mg of gilsonite while generating less than half as much benzene. The data in the final column of Figure 2 would, therefore, favor the use of anthracite, metallurgical coke, or lignite instead of bituminous coal or gilsonite in foundry sands. While this may well be true in terms of benzene generation, as discussed previously, suitable volatile release characteristics are critical for producing acceptable metal castings. In other words, it is not simply the quantity of volatile matter generated but the composition and temperature of release that are most important. In this respect, neither lignite nor metallurgical coke may be suitable as total replacements for bituminous coals (Figure 1) but may yet prove to be effective as partial replacements.

SUMMARY

A TGA pyrolysis/charcoal absorption method has been developed as a means to estimate the benzene-generating potential of carbonaceous additives in foundry sands. The method was shown to provide excellent reproducibility on samples ranging in size from 20 to 90 mg. Application of the method to a series of potential or currently used carbonaceous foundry-sand additives indicated substantial differences in the relative production of benzene during pyrolysis suggesting potentially fruitful areas for future work.

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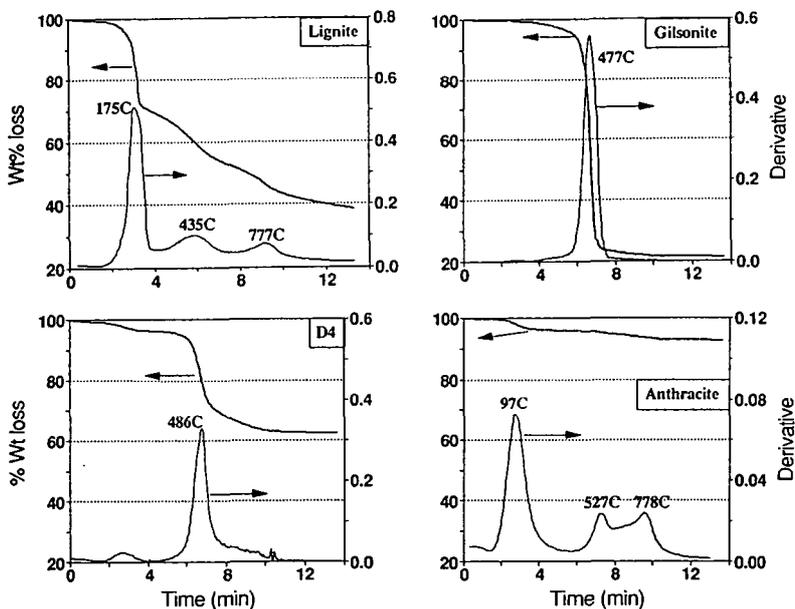


Figure 1. TGA plots showing weight loss and 1st derivative curves for lignite, Gilsonite, an asphaltic emulsion (AE-1), the D4 bituminous coal, and anthracite.

Table I. Listing and brief description of the samples examined.

Sample	Description
Anthracite	Mammoth coal bed, Schuylkill Co., PA
Met Coke	Commercial metallurgical coke
Lignite	Causticized lignite from North Dakota
Coal-Gran	Bituminous coal blended with 15% granulated sugar
D4 SC	Bituminous coal from West Virginia (washed)
Birm coal	Bituminous coal from West Virginia (washed)
Coal-liquid	Bituminous coal w/15% high fructose corn syrup
AE-1	asphaltic emulsion
AE-2	asphaltic emulsion
Gilsonite	gilsonite from Bonanze, Utah

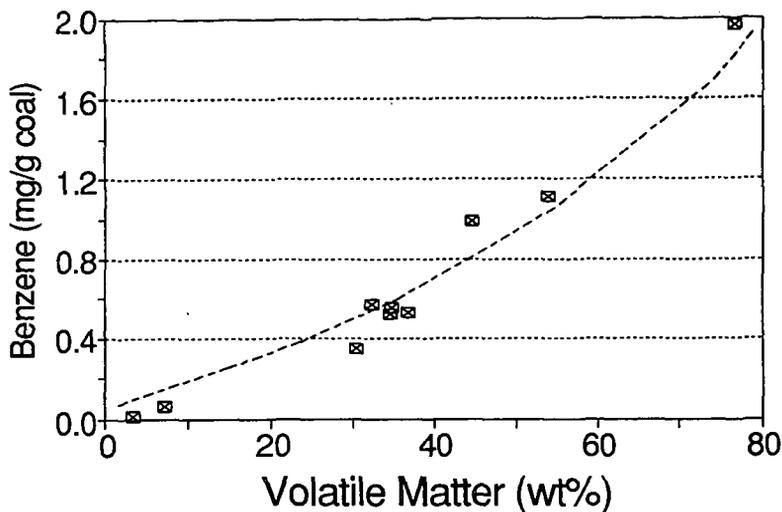


Figure 2. Benzene production as a function of volatile matter release during pyrolysis.

Table II. Method reproducibility as illustrated by replicate values from four TGA runs and duplicate GC injections (Birmingham coal sample).

TGA Run#	Sample Weight (mg)	Moisture by TGA (wt%)	Volatile matter (wt%)	GC Inj. #	Integrated Benz/cymene ratio	Total Benzene (ug)	Measured Benzene (mg/g coal)	Benzene Average (mg/g coal)
23	48.211	3.99	34.68	1st	1.408	26.26	0.545	0.549
				2nd	1.428	26.64	0.553	
24	42.883	3.90	35.46	1st	1.219	22.73	0.530	0.558
				2nd	1.349	25.16	0.587	
25	43.786	3.60	34.18	1st	1.302	24.29	0.555	0.553
				2nd	1.293	24.12	0.551	
26	34.140	3.73	34.47	1st	1.027	19.16	0.561	0.542
				2nd	0.958	17.86	0.523	
Mean		3.81	34.70				0.554	0.551
Std dev		0.151	0.475				0.016	0.007
rsd (%)		3.96	1.37				2.89	1.24

Table III. Benzene production (GC), moisture, and volatile matter (TGA) for all study samples.

Sample	# TGA runs	Moisture (wt%)	Vol matter (wt%)	Benzene (mg/g coal)	rsd (%) (sigma-1)	Benz/VM Ratio
Anthracite	4	3.88	3.45	0.019	22.5	0.006
Met Coke	4	0.92	7.32	0.065	35.2	0.009
Lignite	6	27.7	30.3	0.350	6.1	0.012
Coal-Gran	4	2.47	36.8	0.527	5.5	0.014
D4 SC	4	3.35	34.6	0.520	2.8	0.015
Birm coal	4	3.81	34.7	0.551	1.2	0.016
Coal-liquid	4	4.71	32.4	0.567	2.7	0.018
AE-1	5	35.8	53.9	1.117	8.9	0.021
AE-2	3	43.1	44.7	0.991	2.6	0.022
Gilsonite	3	0.88	76.6	1.972	2.9	0.026