

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/24261905>

Characterization of Pyrolysis Products from a Biodiesel Phenolic Urethane Binder

ARTICLE *in* ENVIRONMENTAL SCIENCE AND TECHNOLOGY · APRIL 2009

Impact Factor: 5.33 · DOI: 10.1021/es8024929 · Source: PubMed

CITATIONS

14

READS

31

5 AUTHORS, INCLUDING:



Yujue Wang

Tsinghua University

60 PUBLICATIONS 459 CITATIONS

SEE PROFILE

Characterization of Pyrolysis Products from a Biodiesel Phenolic Urethane Binder

YUJUE WANG,^{†,‡} FRED S. CANNON,^{*,†} MAGDA SALAMA,[§] DANIA A. FONSECA,^{||} AND SCOTT GIESE[⊥]

Department of Civil and Environmental Engineering, Material Research Institute, and Energy Institute, The Pennsylvania State University, University Park, Pennsylvania 16802, Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China, and Department of Industrial Technology, The University of Northern Iowa, Cedar Falls, Iowa 50614

Received September 3, 2008. Revised manuscript received December 14, 2008. Accepted December 22, 2008.

Analytical pyrolysis was conducted to identify and quantify the major pyrolysis products of a biodiesel phenolic urethane binder as a function of temperature. This biodiesel binder has been used in U.S. foundries recently to replace conventional phenolic urethane binders for making sand cores. Flash pyrolysis and thermogravimetric analytical (TGA) slow pyrolysis were conducted for the core samples to simulate some key features of the heating conditions that the core binders would experience during metal casting. Pyrolysis products from flash and TGA pyrolysis were analyzed with gas chromatography–mass spectrometry/flame ionization detection/thermal conductivity detection. The evolution profiles of the pyrolysis products during TGA slow pyrolysis were also monitored via thermogravimetry–mass spectrometry (TG-MS). The combination of TG-MS and TGA pyrolysis emission data facilitated a quantification of gaseous pyrolysis products of the biodiesel binder as a function of temperature. The major monitored carbonaceous pyrolysis products of the biodiesel binder included CO, CO₂, CH₄, and a variety of methyl esters such as dimethyl glutarate, dimethyl adipate, and methyl oleate. These latter species were the components of the biodiesel binder's solvent. Pyrolysis of the biodiesel binder also generated a variety of hazardous air pollutants listed by the U.S. EPA, with benzene, toluene, xylene, phenol, and cresols being the prominent species. A considerable fraction of the binder's released mass did not appear as exhausted volatile carbonaceous species, but rather recondensed before they exhausted from the TGA. This represented mass that could likewise recondense within a green sand molding system during full-scale operations, as an environmentally favorable containment of air emissions.

Introduction

The metal casting industry represents an important manufacturing component in the United States. Each year, U.S. foundries produce millions of tons of casting products that are important for everyday life (1). However, volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions from the foundries may pose hazards to the environment and human health (2, 3). Indeed, previous research has shown that more than 40 HAPs listed by the U.S. EPA are identified in the air emissions from foundries (4). One of the major sources of the foundry VOC and HAP emissions is the pyrolysis of core binders (e.g., organic resins) during the casting process (2–6).

Phenolic urethanes are currently the most widely used core binder in the foundry industry due to several favorable operation-related characteristics and well-entrenched precedent. More than 100 millions pounds of phenolic urethanes are consumed annually in U.S. foundries, and they account for the largest market share of the no-bake systems (over 45%) or cold-box systems (more than 85%) in use (7). Essentially, all phenolic urethane systems are comprised of three parts that include phenolic resin (part I), polymeric isocyanate (part II), and tertiary amine catalyst (part III). The phenolic resin and polymeric isocyanate have been traditionally dissolved in organic solvents, because of their very high viscosity. The proper choice of the solvents is important for achieving complete reaction and curing of the binder, as well as the speed of cure. The conventional solvents contain high percentages of high boiling aromatic hydrocarbons (e.g., heavy aromatic solvent naphtha). It has been found that the heavy aromatics contributed considerable fractions of the HAP emissions when the core binder was pyrolyzed during the casting process (7, 8). To help foundries to diminish their HAP emissions and meet the ever more stringent environmental regulations, researchers recently developed a new solvent system that was free of the heavy aromatics and based on methyl esters of vegetable oils (7, 9). The biodiesel phenolic urethane binder system was developed in the late 1990s, and it has recently been applied in full-scale foundry operations to replace the conventional naphtha phenolic urethane systems. There is continuing value in foundries evaluating the emission characteristic of the new biodiesel product as a part of adopting it in full-scale production. The identification and quantification of pyrolysis products from the biodiesel-solvent binder systems are important because (a) the pyrolysis products may in part represent what the foundry workers and nearby neighbors may be exposed to, and (b) these species may be sorbed or condense in waste molding sand, and then be leached out from the waste molding sand when the sand is reused as agricultural soil blends or as landfill hydraulic barrier materials (10–12).

Laboratory analytical pyrolysis that simulates key features of the thermal conditions of metal casting has been shown to be a useful tool to study the pyrolysis behavior and emission characteristics of carbonaceous additives and organic binders that are used in foundries (13–20). TGA slow pyrolysis and flash pyrolysis techniques have been used to measure the “emission potentials” (14, 16, 19, 20) of the carbonaceous additives and core binders to release air pollutants when they are pyrolyzed. Usually, the “emission potentials” measured by analytical pyrolysis have been higher than the actual emission levels observed in full-scale operations, because of several events that could occur in full-scale operations. For example, a fraction of the air pollutants (i.e., VOCs and HAPs) could be burned with residue oxygen in

* Corresponding author e-mail: fcannon@engr.psu.edu; address: 212 Sackett Building, The Pennsylvania State University, University Park, PA 16802.

[†] Department of Civil and Environmental Engineering, The Pennsylvania State University.

[‡] Tsinghua University.

[§] Material Research Institute, The Pennsylvania State University.

^{||} Energy Institute, The Pennsylvania State University.

[⊥] The University of Northern Iowa.

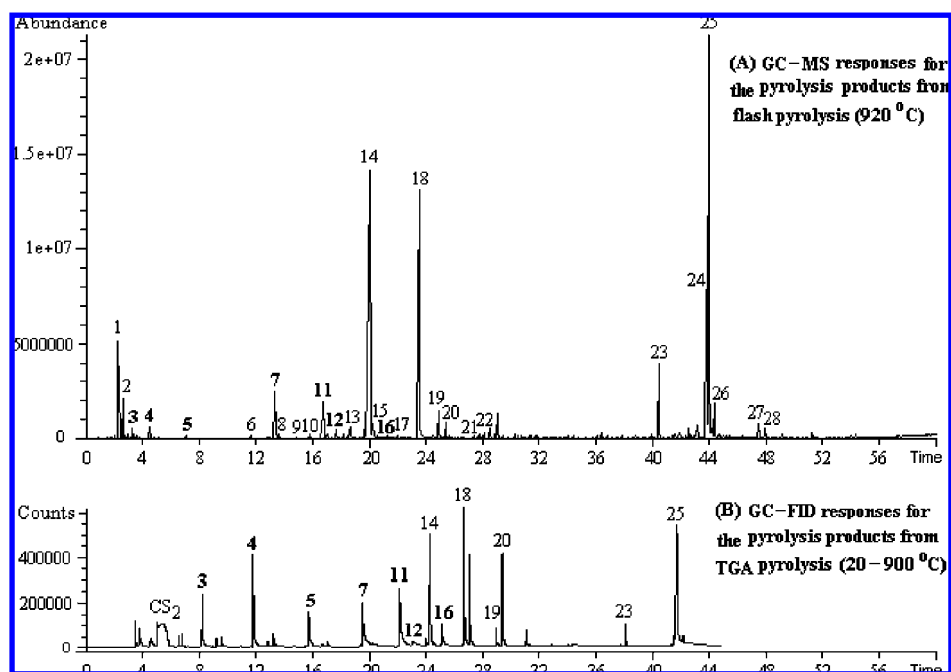


FIGURE 1. (A) GC-MS responses for the pyrolysis products of the biodiesel phenolic urethane core samples during flash pyrolysis, MS monitored species with molecular weight of 40–650; (B) GC-FID responses to the GAC captured hydrocarbon emissions of the biodiesel phenolic urethane core samples during TGA pyrolysis (20–900 °C). Hazardous air pollutants listed in Title III of the 1990 Clean Air Act Amendment have been indicated by lettering with bold font. Refer to Table 1 for the names.

TABLE 1. Pyrolysis Products of the Biodiesel Phenolic Urethane Core Samples during Flash Pyrolysis (hazardous air pollutants listed in the Title III of 1990 Clean Air Act Amendment have been indicated by the numbers with *italics*)

peak	compd name	peak	compd name
1	CO ₂	15	isomers of dimethyl phenol
2	ethanamine, <i>N,N</i> -dimethyl	16	naphthalene
3	benzene	17	isomers of trimethyl phenol
4	toluene	18	hexanedioic acid, dimethyl ester (dimethyl adipate)
5	xylene	19	2-methyl-naphthalene
6	benzene, isocyanato-	20	1-methyl-naphthalene
7	phenol	21	ethyl-naphthalene
8	Benzofuran	22	isomers of dimethyl naphthalene
9	6-heptenoic acid, methyl ester	23	hexadecanoic acid, methyl ester (methyl palmitate)
10	benzaldehyde, 2-hydroxy	24	9,12-octadecadienoic acid (<i>z,z</i>)-, methyl
11	<i>o</i> -cresol	25	9-octadecenoic acid, methyl ester (methyl oleate)
12	<i>m</i> -cresol, <i>p</i> -cresol	26	octadecanoic acid, methyl ester
13	2,3-dimethyl phenol	27	11-eicosenoic acid, methyl ester
14	pentanedioic acid, dimethyl ester (dimethyl glutarate)	28	eicosanoic acid, methyl ester

sand molds, or recondense within the sand system rather than be released as emissions. Nevertheless, previous studies have shown that the emission potentials measured by analytical pyrolysis were able to reflect the relative emission trends that were observed in full-scale foundries, although not quantitatively correspondent (8, 14, 19–21). Thus, it holds promise that with proper adjustments that take account of such effects as the VOC burning and recondensation, the emission potentials determined by analytical pyrolysis could be applied as a first step toward full-scale operation emission modeling.

It is also noted that carbonaceous additives or core binders are heated under quite different conditions (e.g., heating rates and peak temperatures) at various locations within a sand mold or core (22–24). The difference in heating conditions could considerably affect the emission yields and compositions from the carbonaceous additives and core binders at the various locations (8, 14). Thus, the emission potentials determined under certain conditions of analytical pyrolysis can not be indiscriminately applied to the entire sand mold or core for emission modeling. It is noticed that

TG-MS has shown to be a useful tool for characterizing the gaseous pyrolysis products that can be released from different materials (25–28). Further, the TGA heating programs can be adjustable, and thus allow the monitoring of evolution profiles of emissions under variable conditions (e.g., different heating rates, peak temperatures and gas environment). These may be related to the emissions that these materials could release in full-scale molding operations. Nevertheless, quantifying emissions by TG-MS itself is difficult. Thus, we proposed that by coupling TG-MS and other analytical pyrolysis techniques that quantify emissions under certain conditions, it is possible to shed light on emission potentials as a function of heating conditions.

In this light, the main objectives of this research were (a) to identify the major pyrolysis products of the biodiesel binder system by analytical pyrolysis techniques, and (b) to explore suitable analytical pyrolysis methodologies to determine the upper bound of the “emission potential” in a way that they could be usefully incorporated (by others) into computer modeling programs for modeling the emissions from the sand molds or cores. It is noted that some pyrolysis products

TABLE 2. TGA (20–900 °C) pyrolysis products quantified in TGA-Tedlar air sampling bag-GC-FID/TC and TGA-GAC-GC-FID tests (duplicate samples)

Pyrolysis Product (mg/g core binder)		
	average	SD
Greenhouse Gas ^a		
CH ₄	18.64	1.66
CO	22.00	0.74
CO ₂	82.90	7.27
Representative HAPs ^b		
hexane	0.269	0.009
benzene	1.258	0.148
toluene	2.009	0.092
xylene	1.117	0.009
phenol	3.220	0.380
Cresols	2.310	0.316
Other Emissions ^b		
methyl-naphthalene	1.449	0.098
methyl oleate	9.000	1.332
other species ^c (normalized as methyl oleate)	14.395	1.958
sum of quantified pyrolysis products in gas-phase exhaust (mg/g core binder)	158.6	7.4
mass loss of core binder during pyrolysis (mg/g core binder)	766.7	8.0

^a Bag-GC-FID/TC tests. ^b TGA-GAC-GC-FID tests. ^c Peaks with retention time of 24–40 min, methyl-naphthalene excluded. Based on equivalent response that methyl oleate generated.

will either burn or recondense during full-scale operations as described above, and the extent of these would be site-specific and beyond the scope herein. Therefore, we refer herein to “pyrolysis products” and “emission potentials”, rather than “simulated emissions.”

Materials and Methods

Core Sample Preparation. The biodiesel binder tested herein was from HA International Inc. (Westmont, IL). The main compositions of the three parts of the biodiesel binder are listed in Table S1 of the Supporting Information. The sand was a high silica round grain sand (IC55) from Unimin Corporation (New Canaan, CT). The core samples were prepared according to the procedure described by foundry personnel (refer to the Supporting Information), and they contained 1.5% (by weight) core binder.

Flash Pyrolysis Emission Analysis. About 10 mg of the core sample was flash pyrolyzed in a CDS Analytical Pyroprobe 1000 at 920 °C for 10 s. The heating rate was 5000 °C/s, and this rate simulated the abrupt temperature ramping at the metal-core interface after metal pouring. The pyrolyzed gas products were swept into a gas chromatograph–mass spectrometer (Hewlett-Packard 5890 Series II fitted with a 5971A MSD) by helium carrier gas for analysis, refer to the Supporting Information for details.

TGA Slow Pyrolysis Emission Analysis. Fifteen grams of core sample was pyrolyzed in a thermogravimetric analyzer (TGA) (Cahn TG-131, Thermo Electron Inc., CA) with a heating rate of 10 °C/min from ambient temperature to an array of peak temperatures (up to 900 °C) under 60 mL/min N₂; with 60 mL/min He sparge. This TGA protocol simulated some key features of the slow heating conditions that the core experienced at distances that were further away from the metal–core interface. During the heating, either granular activated carbon (GAC) tubes (ORBO 32, Supelco, Bellefonte, PA) or Tedlar air sampling bags (Supelco, Bellefonte, PA) (but not both simultaneously) were used to collect the TGA

emissions in the TGA effluent. A Tygon tube (0.5 m long; 0.5 cm dia, which could not be heated) connected the TGA to the GAC or Tedlar bag.

The GAC captured emissions were extracted by CS₂ solvent, and then analyzed by a gas chromatography–flame ionization detector (GC-FID) (Hewlett-Packard 5890 Series II), following the EPA method 18 that measures gaseous organic compound emissions (refer to SI).

The Tedlar bag collected all exhaust gases from the TGA. The CO, CO₂, and gaseous hydrocarbons C1–C5 (i.e., from methane to pentane) in the Tedlar bags were analyzed by a GC (Shimadzu GC-17A) that was combined with a FID for hydrocarbon analysis and a thermal conductivity detector (TCD) for CO and CO₂ analysis, refer to SI.

TGA Slow Pyrolysis-Mass Spectrometer Analysis. About 400 mg of core sample was placed in a TGA 2050 (TA Instruments, Newcastle, DE) and pyrolyzed from ambient temperature to 1000 °C with a heating rate of 10 °C/min under an argon atmosphere. The gaseous effluent from the TGA flowed to a downstream mass spectrometer (Thermostar GSD 301T, Pfeiffer Vacuum Inc., Nashua, NH) for emission kinetics analysis. For species identification, the mass spectra were compared to those in the NIST Mass Spectral Library (Chem SW, Version 2.0, Fairfield, CA). An ³⁸Ar isotope of the carrier argon gas served as an inner standard. The MS intensities were normalized to the intensities of the ³⁸Ar isotope to account for changes in ion current caused by a shift in the MS sensitivity, and these were then normalized by the mass of the core samples.

Results

Flash Pyrolysis Emission Analysis. The major products from flash pyrolysis of the core sample were as shown in Figure 1A and Table 1. These species were likely similar to those generated at the metal-core interface, where the core is abruptly heated after metal pouring. As shown, the predominant pyrolysis products of the biodiesel binder were methyl esters (dimethyl glutarate, dimethyl adipate and methyl oleate etc that were peak 14, 18, and 23–28 in Figure 1). Also, there were smaller amounts of a variety of aromatic hydrocarbons. These ester pyrolysis products were consistent with the ingredients of the binder solvent (see Table S1 in the Supporting Information). The major HAP emissions identified in flash pyrolysis included phenol, *o*-cresol, benzene, toluene, xylenes (BTX), and naphthalene.

TGA Slow Pyrolysis Emission Analysis via GAC and Tedlar Bag Capturing. Table 2 summarized the quantification results for the CO, CO₂, and hydrocarbon emissions of the biodiesel binder during TGA slow pyrolysis. The major HAP releases identified during TGA pyrolysis (Figure 1B) were the same as those identified in flash pyrolysis (Figure 1A), and they include BTX, phenol, and *o*-cresol. Methane accounted for about 90–95% of the alkane (C1–C5) emissions, followed by small amounts of ethane, and propane, etc.

During TGA slow pyrolysis, some of the high boiling temperature hydrocarbons, for example, naphthalene, methyl-naphthalene, and the various methyl esters, were released from the core samples that were suspended from the TGA. However, because of their high boiling temperatures (see Table S2 in the Supporting Information), a portion of these compounds could inherently recondense in the cool regions of the TGA or in the transporting Tygon tubing from the TGA to GAC tube. Indeed, considerable amounts of liquid pyrolysis products were found at the bottom of the TGA reactor after TGA pyrolysis of the core sample. Consequently, the yields of the methyl esters observed in TGA slow pyrolysis (Figure 1B) were inherently lower than those observed in flash pyrolysis (Figure 1A). We note that this protocol usefully reflects full-scale behavior, in that similar recondensation into core sand and green sand will occur during full-scale

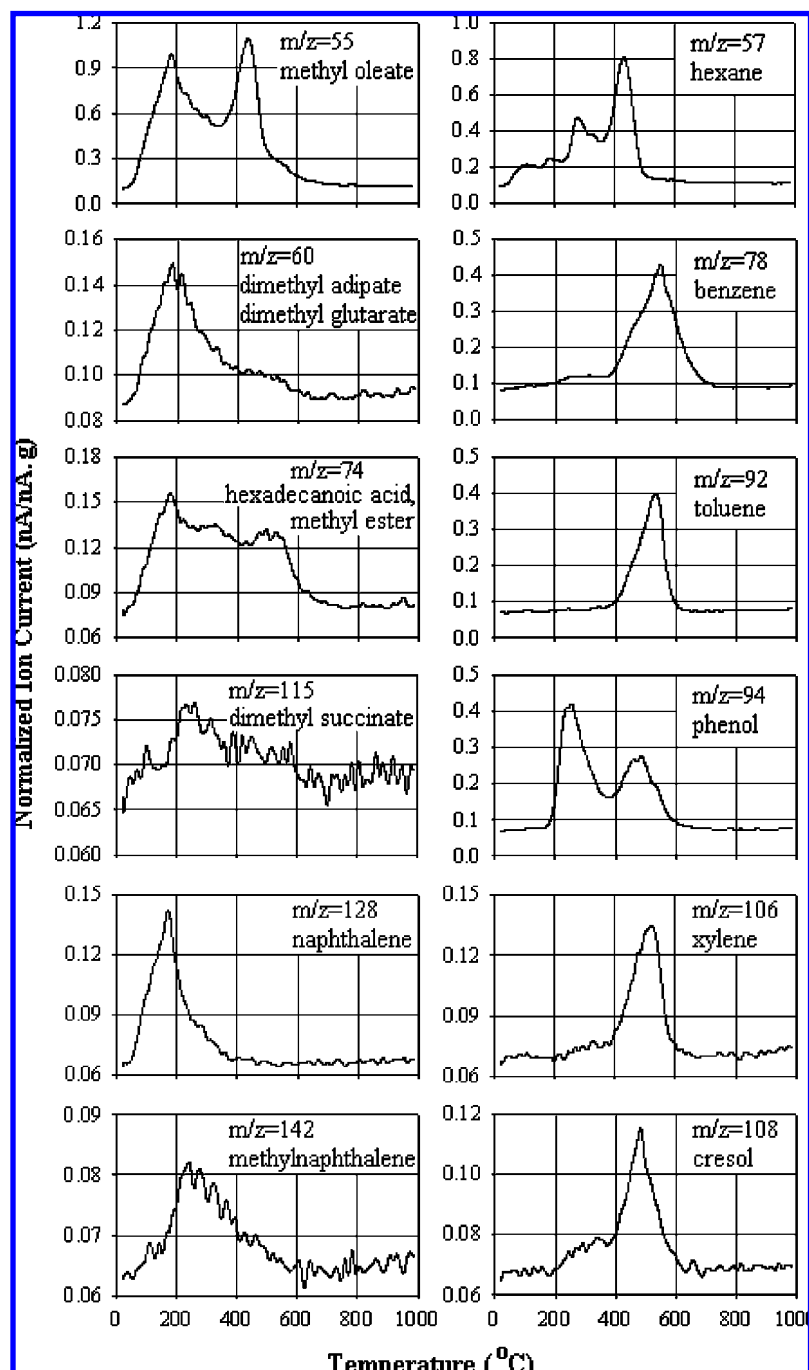


FIGURE 2. Mass spectrometry responses to the gas emissions during TGA-MS pyrolysis (heating rate 10 °C/min) under an argon atmosphere.

molding operations. These recondensed hydrocarbons could serve as carbon sources for green sand when the used core sand is used to make green sand molds for next casting cycles (refer to the Supporting Information). This reflects an environmentally favorable containment of volatiles, as discussed below.

As shown in Table 2, the core sample released about 75% of the mass of the core binder when slowly heated to 900 °C. The quantified GAC and Tedlar bag captured pyrolysis products accounted for roughly 20% of the released mass, whereas the balancing 80% of released mass mainly represented the high boiling compounds that recondensed before they exhausted from the TGA as gaseous products. Moreover, the decomposition of the core binder could generate certain amounts of water (refer to Figure S3 in the Supporting

Information and ref 16) that had not been quantified herein, but would account for a fraction of the total mass loss.

TG-MS Analysis. The TG-MS revealed the temperature regimes where the major pyrolysis products were released from the core sample. As shown in Figure 2, the ingredients of the biodiesel binder (e.g., the methyl ester solvents and phenol) began to release from the core samples once the cores were heated. The evolution rates reached the maximums at about 180–250 °C. In contrast, most of the HAPs (e.g., BTX and cresol) were released at temperatures above 400 °C (Figure 2, right column). It appeared that these compounds were more likely generated as the cross-linked polymer structures of the core binders became thermally destructed, and temperatures above 400 °C were required for this active thermal decomposition of the biodiesel binder

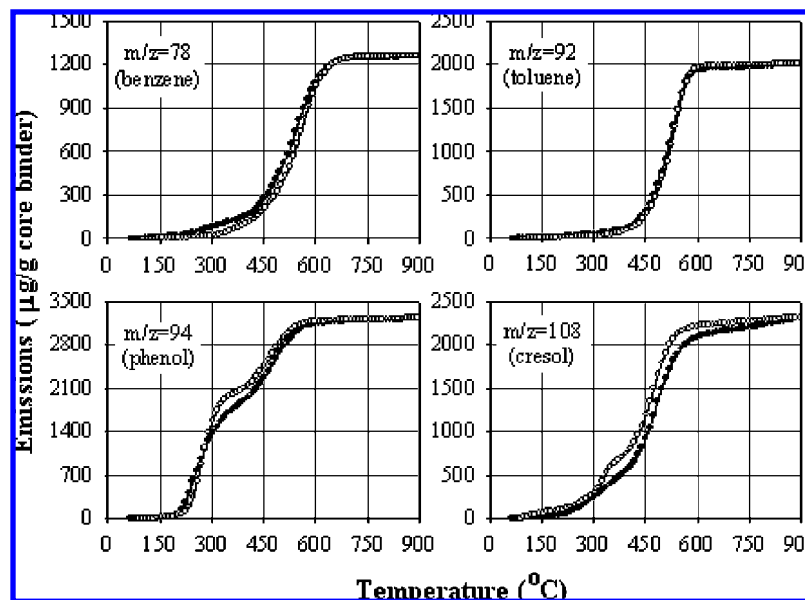


FIGURE 3. Emission potential factors as a function of temperatures (duplicate samples).

to occur. This result was consistent with the TGA emissions measured by the TGA-GAC capturing protocol: holding the core samples at 400 °C for yet another 45 min generated very little more BTX release (see Figure S1 in the Supporting Information).

Discussion

Comparison of Pyrolysis Products from the Conventional Phenolic Urethane and Biodiesel Phenolic Urethane.

Dungan et al. (17) have studied the pyrolysis products of a conventional phenolic urethane using a similar flash pyrolysis-GC-MS protocol as that adopted herein. It was found that most of the esters identified herein were not present in the pyrolysis products of the conventional phenolic urethane (17). Conversely, the conventional phenolic urethane generated many methyl-, ethyl-, and propyl-substituted benzenes or phenols (17) that were not identified in this study. The above trends were with the exception of methyl oleate (peak 25), which was found in the pyrolysis products of both binder systems. Moreover, in a previous study that compared the emissions from a conventional phenolic urethane binder and the biodiesel binder by Curie-point pyrolysis (8), we have also found that the conventional binder released much higher levels of polyaromatic hydrocarbons (PAHs) than the biodiesel binder. We herein interpret that the distinctions in the emission characteristics of the biodiesel binder versus the conventional binder can be attributed to the higher-boiling solvents that were used in the biodiesel system. Specifically, the biodiesel binder used the methyl esters of vegetable oils as the solvent, whereas the conventional binder used the heavy aromatic solvent naphtha.

From the perspective of environmental concerns, the conventional binder may pose a higher level of regulated HAPs to the environment and foundry workers than does the biodiesel binder. The predominance of the pyrolysis products of the conventional resin are aromatics that are easily volatilized, and thus are more prone to release from the sand system as emissions. In contrast, the predominant pyrolysis products of the biodiesel binder are high boiling methyl esters (e.g., dimethyl glutarate and methyl oleate) that favor condensation within the sand system. For air emission control, there may be an air-regulatory preference that the hydrocarbons be recondensed within the sand system (and then to serve as carbon sources for green sand) rather than released as emissions. Specifically, some of the gaseous

aromatics that were present in the pyrolysis products of conventional resin have been noted as HAPs by the U.S. EPA, whereas the methyl esters have not been.

Quantifying Pyrolysis Product Releases versus Temperature by Coupling TG-MS and TGA-GAC. Many researchers have studied the heat transfer processes within green sand molds. Computer simulations and/or thermocouples have been used to determine the temperature profiles of the molds or cores after metal pouring (22–24). These studies revealed that core binders were heated under quite different conditions at various locations within a core, refer to the Supporting Information. As manifested by the TG-MS, TGA-GAC, and flash pyrolysis results, the compositions and yields of the emissions from the core samples changed considerably relative to these two extreme characterizations of heating rates. Thus, we expected that within a green sand mold, the difference in heating conditions would significantly affect the emission yields and compositions from the core binders at various locations within cores. Consequently, the emission potentials determined at certain conditions, for example, by flash pyrolysis at 900 °C (16) or by TGA pyrolysis at 20–900 °C as studied herein, can not be applied indiscriminately to the entire body of the core for the modeling of core emissions.

We quantified the pyrolysis product releases versus temperature by coupling the TG-MS data with the TGA-GAC and TGA-Tedlar bag data. Specifically, the TGA-GAC and TGA-Tedlar bag data offered a single quantitative measure of VOC release over the full 20–900 °C span; but it did not differentiate how much of this release occurred at any particular temperature interval within this full span. Conversely, the TG-MS data detailed measures of relative release (as ion current) at every temperature interval (refer to 25–28), but it did not offer a means of directly converting this ion current to concentrations. However, we could equate the area under the TG-MS curve to the total TGA-GAC and TGA-Tedlar bag concentrations. An example for the integration of the $m/z = 78$ curve that was assigned to benzene TG-MS emissions has been shown in Figure S4 in the Supporting Information. The fraction of area under the TG-MS curve up to a certain temperature then represented the fraction of concentration released up to that temperature. The result is curves such as presented in Figure 3 for benzene, toluene, phenol, and cresol. As shown, by the time the TGA temperature reached 900 °C, the total release for these four species

was 1200–3200 $\mu\text{g/g}$ binder. Further, the amounts of these compounds that were released at any interim temperature intervals could also be quantitatively discerned from the Figure 3 graphs. The TG-MS test was duplicated for the core samples and the reproducibility of the test was satisfactory, as shown in Figure 3.

With the help of computer modeling programs that simulate the temperature profiles of a core, others could then apply these temperature-dependent emission potentials to the core for emission modeling during full-scale operations. Nevertheless, it is important to note that when applied to emission modeling in full-scale operation, the emission potentials have to be adjusted to take account of such phenomenon as VOC combustion and recondensation within the sand system.

Acknowledgments

This study was funded by the University of Northern Iowa Center for Advanced Bio-Based Binders (CABB) through its awarded DOE Grant DE-FG36-06GO86029, and by NSF Grant BE/MUSES-GOALI 052490. We also recognize Doug Trinowski of HA International for his insights and gracious donation of materials for the project.

Supporting Information Available

Details of some methods, results, and discussion (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- U.S. Department of Energy. *Trends Effecting [sic] R&D in the Metalcasting Industry*; U.S. Department of Energy, Office of Industrial Technologies: Washington, D.C., March, 1996.
- Allen, G. R.; Archibald, J. J.; Keenan, T. Hazardous air pollutants: a challenge to metal casting industry. *Am. Foundry Soc. Trans.* **1991**, 99, 585–593.
- McKinley, M. D.; Jefcoat, I. A.; Herz, W. J.; Frederick, C. Air emissions from foundries: a current survey of literature, suppliers and foundrymen. *Am. Foundry Soc. Trans.* **1993**, 101, 979–990.
- Technikon Environmental Development Center. *Pre-production Air Emission Test Report*; Technikon, LLC: McClellan, CA, 2000; Parts 1–3.
- Glowacki, C. R.; Crandell, G. R.; Cannon, F. S.; Voigt, R. C.; Clobes, J. K.; Furness, J. C.; McComb, B. A.; Knight, S. M. Emissions studies at a test foundry using an advanced oxidation-clear water system. *Am. Foundry Soc. Trans.* **2003**, 111, 579–598i.
- Goudzwaard, J. E.; Kurtti, C. M.; Andrews, J. H.; Cannon, F. S.; Voigt, R. C.; Firebaugh, J. E.; Furness, J. C.; Sipple, D. L. Foundry emissions effects with an advanced oxidation blackwater system. *Am. Foundry Soc. Trans.* **2003**, 111, 1191–1211.
- Trinowski, D. M.; Ladegourdie, G.; Löchte, K. New coldbox binder system for improved productivity. *Am. Foundry Soc. Trans.* **1999**, 107, 51–57.
- Wang, Y. J.; Cannon, F. S.; Salama, M.; Goudzwaard, J.; Furness, J. C. Characterization of hydrocarbon emissions from green sand foundry core binders by analytical pyrolysis. *Environ. Sci. Technol.* **2007**, 41, 7922–7927.
- Eppley, M. C.; Laitar, R. A.; Pahr, E. R.; Roush, D. C.; Tse, R.; Zaretskiy, L. S. Improved phenolic urethane cold box foundry resin system. *Am. Foundry Soc. Trans.* **2005**, 113, 505–510.
- Abichou, T.; Benson, C. H.; Edil, T. B. Foundry green sands as hydraulic barriers: laboratory study. *J. Geotech. Geoenviron.* **2000**, 126, 1174–1183.
- Ji, S.; Wan, L.; Fan, Z. The toxic compounds and leaching characteristics of spent foundry sands. *Water Air Soil Pollut.* **2001**, 132, 347–364.
- Dungan, R. S.; Lee, B. D.; Shouse, P.; de Koff, J. P. Saturated hydraulic conductivity of soils blended with waste foundry sands. *Soil Sci.* **2007**, 172, 751–758.
- Wang, Y. J.; Cannon, F. S.; Komarneni, S.; Voigt, R. C.; Furness, J. C. Mechanisms of advanced oxidation processing on bentonite consumption reduction in foundry. *Environ. Sci. Technol.* **2005**, 39, 7712–7718.
- Wang, Y. J.; Huang, H.; Cannon, F. S.; Voigt, R. C.; Komarneni, S.; Furness, J. C. Evaluation of hydrocarbon emission characteristics of typical carbonaceous additives in green sand foundries. *Environ. Sci. Technol.* **2007**, 41, 2957–2963.
- Dungan, R. S.; Reeves, J. B. Pyrolysis of carbonaceous foundry sand additives: seacoal and gilsonite. *Thermochim. Acta* **2007**, 460, 60–66.
- Lytle, C. A.; Bertsch, W.; McKinley, M. D. Determination of thermal decomposition products from a phenolic urethane resin by pyrolysis-gas chromatography-mass spectrometry. *J. High Resolution Chromatogr.* **1998**, 21, 128–132.
- Dungan, R. S.; Reeves, J. B. Pyrolysis of foundry sand resins: a determination of organic products by mass spectrometry. *J. Environ. Sci. Health, Part A* **2005**, 40, 1557–1567.
- Wang, Y. J.; Cannon, F. S.; Voigt, R. C.; Komarneni, S.; Furness, J. C. Effects of advanced oxidation on green sand properties via iron casting into green sand molds. *Environ. Sci. Technol.* **2006**, 40, 3095–3101.
- Dempsey, T. C.; LaFay, V. S.; Neltner, S. L.; Taulbee, D. N. Understanding properties of carbonaceous additives and their potential emit benzene. *Am. Foundry Soc. Trans.* **1997**, 105, 109–117.
- LaFay, V. S.; Neltner, S. L.; Taulbee, D. N.; Wellbrock, R. J. Evaluating emission characteristics of seacoal and seacoal supplements using advanced analytical techniques. *Am. Foundry Soc. Trans.* **2000**, 108, 713–718.
- Wang, Y. J.; Cannon, F. S.; Neill, D.; Crawford, K.; Voigt, R. C.; Furness, J. C.; Glowacki, C. R. Effects of advanced oxidation treatment on green sand properties and emissions. *Am. Foundry Soc. Trans.* **2004**, 112, 635–648.
- Chen, J. H.; Tsai, H. L. An efficient and accurate numerical algorithm for multi-dimensional modeling of casting solidification, part I: control volume method. *Am. Foundry Soc. Trans.* **1990**, 98, 527–537.
- Shih, T. S.; Hsiua, S. S.; Hong, C. H. Movements of vaporization interface and temperature distributions in green sand molds. *Am. Foundry Soc. Trans.* **1996**, 104, 481–489.
- Hsiau, S. S.; Chang, W. J. Cooling analysis of castings in green sand molds. *Am. Foundry Soc. Trans.* **1998**, 106, 595–600.
- Jakab, E.; Faix, O.; Till, F. Thermal decomposition of milled lignins studied by thermogravimetry/mass spectrometry. *J. Anal. Appl. Pyrol.* **1997**, 40–41, 171–186.
- Conesa, J. A.; Marcilla, A.; Caballero, J. A. Evolution of gases from the pyrolysis of modified almond shells: effect of impregnation with CoCl_2 . *J. Anal. Appl. Pyrol.* **1997**, 43, 59–69.
- Arenillas, A.; Pevida, C.; Rubiera, F.; Pis, J. J. Comparison between the reactivity of coal and synthetic coal models. *Fuel* **2003**, 82, 2001–2006.
- Karayildirim, T.; Yanik, J.; Yuksel, M.; Bockhorn, H. Characterization of products from pyrolysis of waste sludges. *Fuel* **2006**, 82, 1498–1508.

ES8024929