Design and qualification of a bench-scale model for municipal waste-to-energy combustion

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ABSTRACT
This paper reports the design and qualification of the first purpose-built, bench-scale reactor system to model the municipal waste-to-energy combustion of fluorinated polymers. Using the principle of similarity, the gas-phase combustion zone of a typical municipal waste-to-energy plant has been scaled down to the bench with a focus on chemical similarity. Chemical similarity is achieved in large part through the use of methanol as a surrogate for municipal solid waste (MSW). Review of prior research shows that methanol is one of the major volatile products expected during MSW thermal conversion in the fuel bed of waste-to-energy plants. Like full-scale waste-energy plants, the design of the bench-scale model includes a flame zone and a post-flame zone. Maintaining steady methanol vapor flow premixed with air to the model reactor system ensures stable combustion resulting in bench-scale CO emission levels comparable to those of full-scale waste-to-energy plants. Since investigation of fluorinated polymer combustion includes trace analysis of exhaust gas for perfluorooctanoic acid (PFOA), qualification testing focused on PFOA collection efficiency. High PFOA collection efficiency (>90%) demonstrated the capability of the reactor system in transporting and absorbing PFOA that may be generated during high-temperature combustion testing of fluorinated polymers. Overall, the bench-scale system is qualified for its intended use to investigate potential generation of PFOA from combustion of fluorinated polymers under conditions representative of waste-to-energy combustion.

Implications: Decision-makers depend on environmental researchers to provide reliable predictions of pollutant emissions from waste combustion of polymers at end of product life. Reliable predictions are especially important with regard to questions about potential PFOA emissions from municipal waste combustion of fluorinated polymers. Results from qualification testing confirm that the novel bench-scale model reactor system is capable of representing gas-phase municipal waste combustion behavior upstream of air pollution control and generating representative exhaust gas samples for off-line trace-level analysis of PFOA.

Introduction

Environmental professionals are often asked how to reliably predict pollutant emissions generated by burning some particular material in a modern waste combustion system. If the question concerns emission of carbon dioxide (CO₂), it is readily answered once the carbon content of the material has been determined. If the focus is on emission of an organic compound present in the material, the question is typically straightforward to answer by first checking where the compound stands on the thermal stability-based incinerability index (Carroll et al. 1992; Dellinger, Taylor, and Lee 1993; Taylor, Dellinger, and Lee 1990) and then comparing that ranking to the furnace operating temperature. For conventional pollutants, the U.S. Environmental Protection Agency’s Compilation of Air Pollutant Emission Factors (AP-42) (EPA 1995) provides the answer. And for emission of other pollutants such as certain hydrocarbons (Curran 2019a) and small halocarbons (Tsang, Burgess, and Babushok 1998), computer simulation can fill the data gap. But when it comes to predicting waste combustion emissions for the myriad polymers and synthetic materials in the modern household that can wind up in the trash, the only way to answer the question is to measure empirically. The challenge is to make the measurements in a way that isolates the fate of the specific material and that realistically represents what happens during combustion in a municipal waste-to-energy plant. Simultaneously achieving these two objectives generally requires making initial measurements in the laboratory. Indeed, working in the laboratory allows
evaluating the emission impact of the specific material in isolation without the influence of variable process conditions (e.g., municipal waste feed composition) encountered at full scale (Carnes and Dellinger 1987; Wikström and Marklund 1998). Laboratory-scale thermal reactors also permit economically generating decomposition data from small quantities of test material (Rubey 1980), precise control of operating parameters for reproducible conditions (Fängmark et al. 1991; Lin, Wu, and Liu 1997; Rubey and Carnes 1985), easy cleaning between replicate runs (Fängmark et al. 1991; Marklund et al. 1990), and routine access to the test system (Winter 2009). While existing laboratory-scale systems generally have these attributes in common, their use has involved different approaches to representing full-scale behavior and revealed unexpected challenges when studying the high-temperature combustion of fluorinated polymers (as defined by Buck et al. (2011)).

### Representing full-scale gas-phase behavior

Examination of the design features and combustion performance of the reactors used in four recent studies illustrates differences in modeling full-scale gas-phase behavior in the laboratory; see Table 1. Unlike the vast literature on pyrolysis of fluorinated polymers reviewed in 2014 (Puts, Crouse, and Ameduri 2014), these four works investigated the high-temperature combustion characteristic of waste-to-energy plants in the U.S. and municipal waste incinerators in Europe. As with full-scale facilities, the design of the laboratory reactors in these studies can be assessed in terms of the 3 Ts of combustion: time, temperature, and turbulence (Meissner 1961), where turbulence refers to the mixing of oxygen with volatiles evolved from the solids in the fuel bed (Corey et al. 1953). Review of Table 1 indicates that the reactors in these studies were designed to operate at temperatures and gas residence times generally consistent with the ranges observed at full-scale waste-to-energy plants in the U.S. or Europe (Giraud, Taylor, and Huang 2021).

Comparison of combustion performance brings out differences in how the reactor designs deal with mixing. The bench-scale thermal degradation reactor used by Yamada et al. (2005) pyrolyzed the polymer and associated material cocurrent with air without provision for gas mixing as evidenced by the relatively high carbon monoxide (CO) concentration (321 ppmv) resulting in combustion efficiency below 99%. The bench-scale reactor employed by García, Viciano, and Font (2007) was partly packed with Raschig rings to facilitate mixing between air and the gases evolved during polymer pyrolysis. The resulting low combustion efficiencies (≤73%) seem to reflect the focus of García et al. on substoichiometric fuel-rich conditions because earlier exploration of polyvinyl chloride combustion with the same reactor (Aracil, Font, and Conesa 2005) yielded 100% combustion efficiency at 1000°C, demonstrating the effectiveness of their mixing approach. Similarly, the pilot-scale

### Table 1. Reactor systems used to investigate high-temperature combustion of fluorinated polymers.

| Reactor configuration | Temperature control | Polymer test material | Associated material | Mass of polymer per run (g) | Temperature (°C) | Gas residence time (second) | Oxygen (%) | Carbon monoxide (ppmv) | Carbon dioxide (ppmv) | Combustion efficiency (%) |
|-----------------------|---------------------|-----------------------|---------------------|----------------------------|------------------|--------------------------|-------------|-----------------------|------------------------|--------------------------|
| bench-scale reactor   | electric furnace    | polyester/nylon fabric| none                | 6.5                        | 100              | 2                        | 10          | 321 ppmv              | 10,326 ppmv            | 96.7                     |
| bench-scale reactor   | Raschig rings       | polytetrafluoroethylene (PTFE) |          | 50.6 mg                    | 850              | 2 to 6                   | 13.6%       | 3.0 ppmv              | 36.8 ppmv              | 73.0                     |
| pilot-scale reactor   | pilot-scale reactor | pilot-scale reactor    | pilot-scale reactor | 1.03 g                     | 1000             | 2 to 3                   | 2.7         | 2 ppmv                | 6.5%                   | >99.9                    |
| pilot-scale reactor   | pilot-scale reactor | pilot-scale reactor    | pilot-scale reactor | 1.03 g                     | 1000             | 2 to 3                   | 2.7         | 2 ppmv                | 6.5%                   | >99.9                    |

Notes:

- aDry basis
- bCombustion efficiency (%) = CO_2/(CO_2 + CO) x 100 (Wikström, Tysklind, and Marklund 1999)
systems of Lemieux et al. (2007) and Aleksandrov et al. (2019) exhibited very high (≥99.8%) combustion efficiencies and low carbon monoxide (CO) concentrations (<100 ppmv), signaling the same sort of turbulent mixing of oxygen with volatiles observed at full-scale (Ryu, Shin, and Choi 2002).

Comparison of temperature control approaches indicate differences in reaction atmosphere. Electric furnaces were used to control temperature in the two bench-scale systems. Such external heating was required for the non-flame reactor used by Yamada et al. (Graham, Berman, and Dellinger 1993; Yamada et al. 2005). Lee (Lee et al. 1987) criticized the use of bench-scale non-flame reactor results to represent full-scale waste combustion in part because there are no free radicals generated in the flame to be available in the post-flame zone. In contrast, the two pilot-scale systems were heated by burning a hydrocarbon polymer/cellulose blend and wood pellets, respectively, along with natural gas. Hydrocarbon polymers, cellulose, and wood are major components of municipal solid waste (MSW) (Zhou et al. 2014). Hence, the reaction atmospheres above the rotary kiln-based fuel beds in these pilot-scale systems are expected to be comparable to the gas composition above the fuel bed of a municipal waste-to-energy plant.

Comparison between the pilot-scale systems and the bench-scale systems highlights the importance of designing a model reactor configured to operate with (1) sufficient control over temperature and gas residence time, (2) an effective surrogate for MSW, (3) adequate air-volatile mixing, and (4) a flame zone prior to the post-flame zone.

**Experimental challenges**

During three of the four studies in Table 1, experimental challenges with the reactor systems were encountered when investigating the potential high-temperature transformation of fluorinated polymers into perfluoroalkyl substances such as perfluorooctanoic acid (PFOA). The bench-scale system used by Yamada et al. (2005) included a quartz wool packed cold trap in the reactor exhaust line to collect volatiles for in-line determination via gas chromatography/mass spectrometry (GC/MS) consistent with prior work on chlorinated organics in the same research group (Graham, Berman, and Dellinger 1993; Rubey and Grant 1988). This reliance on GC/MS limited the sensitivity of PFOA detection to 0.35 ppmv (5.85 mg dscm⁻¹ where STP = 25°C, 1 atmosphere). But for trace-level analysis of ionic perfluoroalkyl substances, liquid chromatography with tandem mass spectrometry (LC/MS/MS) is the preferred technique (Larsen and Kaiser 2007) because LC/MS/MS offers orders of magnitude lower quantitation than GC/MS (Jahnke and Berger 2009). Attempts by Yamada et al. (2005) to attain more sensitive detection were thwarted by poor PFOA absorption in their custom bubblers during collection of aqueous samples for off-line LC/MS/MS analysis. Their measurement of PFOA transport across the reactor system yielded collection efficiencies of 15–21% when using aqueous sampling and LC/MS/MS analysis for PFOA as perfluorooctanoate (PFO) anion. Measured high collection efficiency (>70%) is necessary to confirm the ability of the reactor system to capture any PFOA that may result from polymer combustion. Determination via in-line GC/MS yielded a collection efficiency of 74%, and the authors suggested PFOA condensation in an unheated transport line as a potential cause for the shortfall. Since PFOA adheres to glass (Sundström et al. 2012), adsorption to the quartz wool packing in the cold trap was also a likely cause.

The two pilot-scale systems (Aleksandrov et al. 2019; Lemieux et al. 2007) suffered sampling problems of a different sort. PFOA background contamination was experienced in both studies. Lemieux et al. (2007) were not able to distinguish between emissions from burning natural gas and from burning carpet spikes with long-chain side-chain-fluorinated acrylate polymer due to extensive past use of fluorinated polymer tubing for gas sampling or to laboratory artifacts. Aleksandrov et al. (2019) raised their LC/MS/MS-based PFOA limit of quantitation to 300 ng dscm⁻¹ (where STP = 0°C, 1 atmosphere) due to contamination of the solvent used during recovery of the gas sampling train. While the solvent contamination problems faced by Aleksandrov et al. could be overcome on a going-forward basis, the need for large quantities (300 g per run) of high-cost fluoropolymer (Zhang et al. 2016) presents another challenge in pursuit of reliable emission predictions. When the number of experimental runs and the mass of polymer consumed by preparatory material characterization are considered, the amount of fluorinated polymer required for pilot-scale emission testing becomes cost-prohibitive.

The challenges encountered during research with these reactor systems highlight the need to ensure collection of representative gas samples for off-line trace-level analysis that are free from external contamination. Additionally, cost-based quantity constraints on the test material favor bench-scale over pilot-scale combustion.

**Purpose**

In light of the advantages and challenges posed by prior reactor systems, the purpose of this project was to design and qualify a bench-scale reactor system capable of (a)
representing municipal waste combustion gas-phase behavior above the fuel bed and (b) collecting representative exhaust gas samples for off-line trace-level analysis of PFOA. Important attributes for the design (Weekman 1974) included: (1) compatibility with very small available quantities of test material, (2) tight control over reactor system temperature and gas residence time, (3) an effective surrogate for MSW, (4) adequate air-volatile mixing, (5) a flame zone prior to the post-flame zone, and (6) preventing the influence of external PFOA contamination. This paper reports the first purpose-built reactor system to model the municipal waste-to-energy combustion of fluorinated polymers at bench scale.

**Approach**

Designing a bench-scale model reactor involves scaling down key aspects of the commercial unit being simulated (Carberry 1964). In theory, the principle of similarity (Johnstone and Thring 1957) can guide scale-down of the combustion zone of a typical full-scale waste-to-energy plant to the bench to allow study of trace combustion products. However, since complete similarity between bench scale and full scale is essentially impossible (Froment 1981; Spalding et al. 1963), simplifications are needed to apply similarity to the complexities of combustion process scaling (Leckner, Szentannai, and Winter 2011). For example, Wochele and Stucki (1999) have demonstrated how to effectively employ similarity in the design of a bench-scale, batch-fed tubular reactor as a model of a continuous, grate-fired municipal waste incinerator to study the emission behavior of heavy metals. Consistent with Leckner, Szentannai, and Winter (2011), Wochele and Stucki omit consideration of fluid dynamic similarity in their scale down. Like Winter (2009), they focus more on chemical similarity. Following these precedents, the scale down in this project concentrated mainly on chemical similarity.

This paper describes the design and qualification of the bench-scale model of municipal waste-to-energy combustion of fluorinated polymers in five subsequent sections. First, key aspects of waste-to-energy combustion technology affecting chemical transformation are characterized to provide the design basis for the bench-scale model. The design of the model system is then presented, highlighting similarity to full-scale municipal waste combustion. Next, the experimental methodology to qualify the bench-scale model for use is summarized before presenting the results and discussion of this qualification testing, followed by conclusions.

**Municipal waste combustion as design basis**

In practice, full-scale waste-to-energy plants have the following components: waste supply, thermal conversion, gas-phase combustion, energy recovery, air pollution control, and management of ash and other residues (Leckner 2015). An additional plant component is gas monitoring for process control and compliance with emission standards on pollutants such as CO (Kedrowski and Chromec 2013). Thermal conversion and gas-phase combustion dominate the chemical transformations. MSW is thermally converted to gases and vapors via pyrolysis and gasification in the first stage, and then the gas is combusted in the second stage. Figure 1 conceptually illustrates the main components of a waste-to-energy plant in a block flow diagram.

The potential to emit compounds as gas-phase products of incomplete combustion (PICs) depends not only on the design and operation of the combustion process but also on the characteristics of the waste feed (Brunner 1985). Hence, waste characterization is discussed next prior to turning to thermal conversion and gas-phase combustion in later subsections.

**MSW Characterization**

For the waste-to-energy process, the feedstock is a complex mixture of materials differing in physical and chemical characteristics, namely MSW (Matsakas et al. 2017). As part of their tracking of MSW composition, the U.S. Environmental Protection Agency (EPA) characterizes waste processed via municipal waste combustion. The main MSW source categories in 2017 were food waste (22.0%), plastics (16.4%), paper and paperboard (13.2%), textiles (9.3%), metals (8.6%), wood (8.4%), rubber (6.7%), yard waste (6.2%), glass (4.3%), other (4.3%), and leather (0.6%) (EPA 2019a, 2019b). The “other” category includes wood pulp and other disposable diaper residues (EPA 2019b).

Reallocating these source categories to high-level material classes facilitates an understanding of the effect of waste inputs on reaction atmosphere above the fuel bed of full-scale waste-to-energy facilities. Figure 2 provides a Sankey diagram (Lupton and Allwood 2017) to summarize the material characterization of MSW into plant-based materials, synthetic polymers, inorganics, and animal products as presented in section S1 of the Supplemental Material.

As shown in Table S1 in the Supplemental Material, MSW can be characterized into the following high-level material classes: 49% plant-based materials, 25% synthetic polymers, 13% inorganics, and 13% animal products. These values are on a wet (as is) basis.
Accounting for roughly half of the annual feed to U.S. waste-to-energy plants, plant-based biomass consists of water, carbohydrates, lignin, lipid, proteins, ash precursors, and extractable compounds (Speight 2008). Of these fractions, water is generally the most abundant, typically accounting for 70% of food waste, 6% of waste paper, 10% of textile waste, 20% of waste wood, and 60% of yard waste (Tchobanoglous, Theisen, and Vigil 1993). Plant carbohydrates can be divided into monosaccharides (e.g., glucose), disaccharides (e.g., sucrose), and polysaccharides (Sawyer and McCarty 1978). The polysaccharides include cellulose, hemicellulose, and starch (e.g., pectin).

The rich diversity of plant-based biomass can be seen in the varying carbohydrate composition of plants and plant-based products on a dry basis. Raw peeled potatoes contain 85% starch (Quadram Institute 2019). U.S. newsprint (part of paper and paperboard category) contains 48.5% cellulose, 9% hemicellulose, and 24% lignin (Eleazer et al. 1997). On the other hand, office paper contains 80% cellulose, 10% hemicellulose, and 0% lignin (Castaldi et al. 2020). Bond paper and some paperboard contain 2% to 4% starch (Hofreiter 1980) as an additional constituent. Cotton (the major component in the textile subcategory) contains over 95% cellulose (Castaldi et al. 2020). Across wood species, carbohydrate composition varies. Poplar is on the high end of cellulose content at 50% cellulose, 25% hemicellulose, and 18% lignin (Davison et al. 2013). Pine bark is on the low end with 34% cellulose, 16% hemicellulose, and 34% lignin (Prakash and Karunanithi 2008). While the grass clippings part of yard waste contains 25–27% cellulose, 10–15% hemicellulose, and 22–28% lignin, leaves contain 15% cellulose, 11% hemicellulose, and 44% lignin (Eleazer et al. 1997). Collectively, cellulose, hemicellulose, lignin, and starch account for the bulk of dry plant-based biomass. Consistent with the prevalence of cellulose and lignin, this plant-based biomass is often referred to as lignocellulose or lignocellulosic materials (Balat 2011; Speight 2008). The observation that lignocellulosic materials account for 49% of MSW combusted in the U.S. indicates a decrease from the almost 65% noted by Helt
and his coworkers in 1989 (Ahmed, Kumar, and Helt 1989). This decrease makes sense in light of the fraction of paper and paperboard combusted decreasing from 30% in 1990 to 13.2% in 2017 (EPA 2019b).

Synthetic polymers make up the other major fraction of municipal combustion feedstock. In descending order, the top three contributors to this category are the hydrocarbon plastics: polyethylene (high and low density), polypropylene, and polyester (i.e., polyethylene terephthalate or PET) (EPA 2019b). In this category, other components include polystyrene, polyisoprene, and polyvinyl chloride.

Overall, 74% of the MSW feed to waste-to-energy plants in the U.S. is composed of wet plant-based biomass and synthetic polymers. In simplest terms, the bulk of this MSW feed can be thought of as a wet mixture of lignocellulosic materials and synthetic polymers. Their thermal conversion in the fuel bed drives the composition of gases available for gas-phase combustion.

**Thermal conversion**

In over 90% of municipal waste-to-energy facilities globally, thermal conversion of the MSW takes place in a waste fuel bed on a mechanical grate (Castaldi and Themelis 2010). (The other major type of MSW combustion technology relies on a fluidized bed for this conversion (Leckner and Lind 2020/05).) As MSW moves along the grate, it is exposed to primary combustion air from below and radiation from above via the flame and walls (Leckner 2015). Consequently, thermal conversion proceeds through a series of four major steps: drying, devolatilization, char gasification, and char burning (Asthana et al. 2010/08; Switchenbank and Sharifi 2013). The main final products of this step-wise conversion are volatiles (i.e., vapors and gases) for combustion as well as bottom ash. Other than the heterogenous oxidation of carbonaceous char particles in the bed, combustion involves the homogeneous oxidation of volatiles evolved from the bed in the flame zone above the bed and continuing up into the furnace (Leckner 2015; Switchenbank and Sharifi 2013).

From a fuel perspective, MSW consists of water, volatile matter, fixed carbon, and non-combustibles (i.e., inorganics) (Tchobanoglous, Theisen, and Eliassen 1977). The first three undergo transformation in the fuel bed of a waste-to-energy plant. Water evaporates into steam. Beginning at about 260°C, volatile matter (primarily lignocellulosic materials and synthetic polymers) undergoes devolatilization, evolving gases (e.g., CO, CO₂, H₂) and hydrocarbon (CₘHₙOₙ) vapors (Yang et al. 2003/12). Concurrently, MSW solids undergo further radiative heating, ignite, burn vigorously, consume locally available oxygen, and form char (Goh et al. 1998, 2000/07). Consistent with the ignition temperature for paper (Williams 2003), Goh et al. (1998) estimate MSW ignition temperature at roughly 320°C. In practice, MSW solids ignite over a range of temperatures because they are made up on different materials (Yang et al. 2004/05), and ignition temperature varies with moisture content and combustion air preheat temperature (van Blijderveen, Bramer, and Brem 2013/06). The devolatilized char undergoes gasification and combustion (Goh et al. 2000/07). Fixed carbon in the MSW and the residual char report to bottom ash with heavy non-combustibles. The unburned carbon content of bottom ash from modern MSW combustion is generally less than 2% (Splaethoff 2010). The remaining non-combustibles travel with the gases for later removal as fly ash. During devolatilization, heat-driven reactions release volatiles in both the presence and absence of oxygen (Fritsky, Miller, and Cernansky 1994/09). Pyrolysis occurs in localized areas where oxygen has been consumed. Hence, the process of devolatilization involves gasification, pyrolysis, and oxidation. Hydrogen is generated through the pyrolysis and gasification of lignocellulosic materials (Demirbas 2006/09; Hajaligol et al. 1982/07) and hydrocarbon plastics (Kaminsky 1985/04; Williams and Williams 1997) in MSW. Thermal conversion is shown schematically in Figure 3.

**Measurements above the fuel bed**

Gaining a quantitative understanding of the vapors and gases generated during thermal conversion starts with review of waste-to-energy plant data. Sampling and analysis of grate-fired commercial facilities has characterized gaseous species in the vicinity of the fuel bed. Over-bed measurements at a conventional 168 Mg day⁻¹ reciprocating grate plant near Linköping, Sweden (Dos Santos and Collin 1992) included characterization of the 700–1000°C segment of the grate. Here, fuel bed devolatilization (3–4 m from inlet) results in dry-basis gas concentrations of 15–18% CO₂, 10–18% CO, 6–16% H₂, 1.8–2.2% methane (CH₄), 0.7–1% ethylene (C₂H₄), and 0.5–1% O₂ within 0.5 m above the bed. Dos Santos and Collin (1992) observe that these high CO₂ and low O₂ concentrations reflect oxidative conditions in the bed and note the influence of the water-gas shift reaction (equation 1) on the high observed H₂ concentrations.

\[
CO + H₂O \rightleftharpoons H₂ + CO₂ \tag{1}
\]

Measurements at a conventional 240 Mg day⁻¹ reciprocating grate plant in Frankfurt, Germany (Waldner et al. 2013/02) indicate that the first half of the grate is dominated by drying and pyrolysis and that the second half is an air-rich zone for carbon burnout. Accordingly, the gases observed above the bed in the first half contain up
to 40% H2O, 10% CO, and 5% H2 as well as CO2 and hydrocarbons. While molar composition values are not reported for CO2 and hydrocarbons, Gehrmann and his colleagues (Waldner et al. 2013/02) do note the absence of O2 in the gases above this drying and pyrolysis zone. Related modeling results (Simsek et al. 2009/08) suggest these concentrations correspond to above-bed temperatures between 500°C and 900°C and a gas concentration of 1% to 3% CH4.

Testing above the fuel bed of a 330 Mg day−1 reverse-reciprocating grate gasification-combustion plant in Tulsa, Oklahoma (Lusardi et al. 2014) indicates gasification stage dry-basis concentrations of 12.8% H2, 11.4% CO, and 3.7% CH4 along the centerline. Castaldi and his coworkers (Lusardi et al. 2014) attribute 2% O2 and 7% CO2 in the synthesis gas leaving the substoichiometric gasification zone to air bypassing along the walls. They also note that the gas temperature for this stage is 677°C or greater. Although not reported in these three studies, rapid heating rates on the order of 10⁴–10⁶°C min⁻¹ are expected close to the reaction front in grate combustion of MSW (Mätzing et al. 2018/08). With an understanding of the relevant ranges for temperature (500–1000°C) and heating rates, prior studies on pyrolysis of the dominant lignocellulose fraction of MSW provide important information on the products of thermal conversion.

**Lignocellulose pyrolysis and gasification**

The products of lignocellulose pyrolysis and gasification have been extensively characterized. Rapid heating during primary pyrolysis favors the generation of volatiles, which may be converted further by secondary gas-phase reactions (Collard and Blin 2014/10). Including these secondary reactions, the most abundant volatile products of lignocellulose pyrolysis are CO, H2O, CH4, CO2, and H2 (Ranzi, Faravelli, and Manenti 2016). The three primary pyrolysis pathways are char formation, depolymerization, and fragmentation (Collard and Blin 2014/10). While CO, CH4, and H2 are the main volatile products of char formation reactions above 500°C, fragmentation of cellulose, hemicellulose, and lignin forms CO and CO2 as well. Levoglucosan is the main product of cellulose depolymerization and one of the main products of hemicellulose depolymerization (Collard and Blin 2014/10). At 600°C and a heating rate of 70°C/min, secondary reactions of levoglucosan yield 2% formaldehyde (CH2O) and 0.5% CH4 under an N2 atmosphere (Fukutome, Kawamoto, and Saka 2016). At the same temperature, increasing O2 concentration from 0% to 7% results in the methanol (CH3OH) yield increasing to 2% (an increase of 40 times relative to N2 atmosphere), surpassing the yields to CH2O and CH4. In the same study, CH4 yields from both levoglucosan and cellulose exceeded 9% in N2 at 900°C. Lignin fragmentation also produces CH2O and CH3OH among the main volatile products, and CH3OH is one of the main volatile products of hemicellulose fragmentation (Collard and Blin 2014/10). Formation of methanol via lignocellulose pyrolysis is not surprising because pyrolytic “destructive distillation” of wood was how methanol, also known as wood alcohol, was commercially produced in the early part of the 20th century (Frolich, Spalding, and Bacon 1928; Stiles 1977). Depending on temperature, fragmentation of methoxy (−OCH3) groups in lignin is seen as the common source of both CH3OH and CH4 (Collard and Blin 2014/10). The −OCH3 group on the 4-O-methylgluronic acid unit is also considered the precursor of the greater than 1% yield to methanol from hemicellulose between 510°C
and 690°C (Shen, Gu, and Bridgwater 2010/03). Jegers and Klein (1985) suggest that the methyl (−CH₂OH) side groups in lignin are significant in methanol formation. The prevalence of −CH₂OH side groups in cellulose (Speight 2008), hemicellulose (Ebringerová, Hromádková, and Heinzé 2005), and starch (Sawyer and McCarty 1978) helps explain methanol formation more broadly.

Rapid pyrolysis experiments confirm the relative abundance of methanol produced by lignocellulose pyrolysis under conditions relevant to grate-fired waste-to-energy plants. At a heating rate of 1.8 × 10⁴ °C min⁻¹, Funazukuri, Hudgins, and Silverston (1987/01) reported a CH₃OH yield from cellulose at 600°C on par with that of CH₄. More recently, Norinaga and his coworkers found CH₃OH yield from cellulose within a factor of 2 of those of CH₄ and CO₂ between 700°C and 800°C (Norinaga et al. 2013/01). Hajaligol et al. (1982/07) detected the same trend for CH₃OH and CH₄ yields from cellulose between 800 and 1000°C with a heating rate of 6 × 10⁴°C min⁻¹ and found that the CH₃OH yield plateaued at 800°C, 200°C lower than the plateau for CH₄ yield. Using the same experimental rig and heating rate, Nunn et al. (1985/07) reported CH₃OH yield from milled wood lignin within a factor of 2 relative to CH₄ and CO₂ between 727°C and 927°C, with the CH₃OH yield from lignin being higher than that of CH₄ at 527°C. Caballero et al. (1993/12) observed the same trends during pyrolysis of Klason lignin (from almond shells) between 600°C and 800°C with heating rates greater than 1.2 × 10⁶°C min⁻¹. Norinaga and his coworkers generally confirmed these results, finding CH₃OH yields from lignin within a factor of 5 of those to CH₄ and CO₂ between 650°C and 750°C (Yang et al. 2015/07). Across these prior studies, yields to CO were much higher; and yields to H₂ were comparable to or lower than the yield to CH₃OH where reported. These studies also demonstrate that CH₃OH is a major volatile product of lignocellulose pyrolysis under conditions expected during MSW thermal conversion along the grate.

**Thermal conversion products**

Adding to steam generated during drying and volatiles produced from pyrolysis and gasification of lignocellulose, devolatilization of synthetic polymers in MSW contributes significant levels of hydrocarbons. For example, Conesa et al. (1994/11) reported CH₄ and C₂H₂ yields from pyrolysis of high-density polyethylene (HDPE) of 3.1% and 15.1%, respectively, at 700°C with heating rates in the range of 1.2 × 10⁵°C min⁻¹ to 1.6 × 10⁵°C min⁻¹. When the pyrolysis temperature was increased to 800°C and secondary reactions were also considered, the same research group (Font et al. 1995/04) observed CH₄ and C₂H₄ yields from HDPE increased to 19.45% and 37.02%, respectively. During pyrolysis and gasification, further increases in temperature lead to higher H₂ levels and lower levels of C₂H₂ and CH₂=CH₂ (Wu and Williams 2014). Hydrogen is generated by high-temperature thermal decomposition of C₂H₂ (Westbrook, Dryer, and Schug 1982/01) and steam reforming of CH₂=CH₂ (Wu and Williams 2014), as shown in equation 2 (Pinto et al. 2003). As described in equations 3 and 4, char gasification produces additional CO and H₂ (Asthana et al. 2010/08). Char burning generates CO₂ and CO according to equations 5 and 6, respectively (Mätzing et al. 2018/08).

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO} + 3\text{H}_2
\]

(2)

\[
\text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2
\]

(3)

\[
\text{C} + \text{CO}_2 \rightarrow 2\text{CO}
\]

(4)

\[
\text{C} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}
\]

(5)

In light of (a) these transformations, (b) full-scale measurements, and (c) the products of lignocellulose pyrolysis, the major vapor-phase products of MSW thermal conversion are expected to be H₂O, CO₂, CO, H₂, CH₂=CH₂, C₂H₄, and CH₃OH in generally descending order. Except for H₂ (not reported), García, Font, and Marcilla (1992/05) confirmed this trend in their study of MSW pyrolysis with a heating rate of 2.5 × 10⁴°C min⁻¹. Like the results of Yang et al. (2015/07) for lignin pyrolysis, they observed a CH₃OH yield from MSW at 700°C within a factor of 5 of the yield to CH₄. The major volatile products above constitute the bulk of the reaction atmosphere for gas-phase combustion of minor species in MSW.

**Gas-phase combustion**

Gases and vapors that evolve from thermal conversion mix with secondary combustion air and burn in the gas phase above the fuel bed of a municipal waste-to-energy plant. In the gas-phase combustion zone (see Figure 1), the gas residence time is typically over 2 seconds at temperatures above 1000°C in excess air (Giraud, Taylor, and Huang 2021), and excess air levels can range from 50% to 200% (Chandler et al. 1997). At such elevated temperatures, hydrocarbons undergo high-temperature combustion (Warnatz 1984), organic molecules break down via chain-induced decomposition, carbon atoms bond to oxygen, and more free radicals
are formed as the reactions proceed to completion (Tsang 1990/11). Recognizing molecular and radical species common to the oxidation of all hydrocarbons (e.g., H•, •OH), extensive kinetic models have been systematically developed, incorporating a wide range of species (e.g., H2, CH4, CH3OH, C2H4) (Westbrook and Dryer 1984/01). For methane (the most abundant hydrocarbon of the thermal conversion products), high-temperature combustion involves four interlinked chain reactions for oxidation of H2, CH4, CH3O, and CO (Lissianski, Zamansky, and Gardiner 2000). Overall, methane combustion proceeds through the sequence (Basevich 1987/01; Lissianski, Zamansky, and Gardiner 2000) depicted in Figure S1, where free radical species are framed by dashed lines.

These reactions begin in the free radical-rich flame zone above the bed and continue in the post-flame zone where flame-heated oxidative decomposition takes place (Lee and Huffman 1989). Lee and Huffman (1987/01) found that in-flame hydrocarbon conversion is responsible for ≥90% of organic destruction with the post-flame zone accounting for the remainder. After hydrocarbons rapidly oxidize to CO in the flame zone, gas residence time in the post-flame zone allows the much slower oxidation of CO to CO2 to proceed to completion (Howard, Williams, and Fine 1973/01; Niessen 2010). Consequently, CO concentration is used as an indicator of combustion control for trace organic emissions (Kilgro et al. 1990/11) and as a regulatory emission standard in the U.S. The CO emission standard for large grated-fired plants is 100 parts per million by volume (ppmv) corrected to 7% oxygen, dry basis (EPA 2006). As the plot of typical performance of a 363 Mg day−1 reciprocating grate plant in Spokane, WA in Figure 4 indicates, full-scale waste-to-energy plants generally operate at low levels well below the emission standard.

The flames and product gases in the combustion zone above the bed radiate heat to the furnace walls, which in turn allows energy recovery in the form of steam (Zhang, Li, and Zhou 2016) and radiative heating of the fuel bed surface (Goh et al. 1998). As such, radiation is the predominant mode of heat transfer in full-scale combustion systems (Niessen 2010). The furnace shell enclosing combustion is made largely of silica-alumina refractory materials (Niessen 2010) and corrosion-resistant metals such as chromium-silicon-iron-nickel alloy tubing (Lee, Themelis, and Castaldi 2007/03). Following energy recovery and air pollution control, the combustion exhaust gas is continuously monitored prior to discharge to the atmosphere.

![Figure 4. Typical CO emission performance for grate-fired waste-to-energy plant.](source)

Source: Plotted using full-scale waste-to-energy plant CO emission performance data provided by Kelle Vigeland of the City of Spokane.

**Gas monitoring**

Continuous emission monitoring assures ongoing compliance with design and emission standards (Kilgro et al. 1990/11). For example, furnace exit gas on-line monitoring has been a longstanding approach to measure O2 levels (Visalli 1987/12) used to control addition of secondary combustion air (El Asri and Baxter 2004). Oxygen is typically monitored with paramagnetic analyzers (Lee, Huffman, and Oberacker 1986/08). Emissions are monitored for CO to ensure compliance with applicable environmental regulations (EPA 2006, 2000). Continuous emission monitors (CEMs) are also used to track CO2 emissions for greenhouse gas reporting at large waste-to-energy plants (EPA 2009). For both CO and CO2, the standard approach is to monitor with nondispersive infrared (NDIR) photometers (Lee, Huffman, and Oberacker 1986/08). In each case, extractive sampling is generally used to convey the gas sample to the relevant emission analyzer (White 1991).

Produced by ABB, one of the leading suppliers of CEM technology globally (Bogue 2006), the Model EL 3020 EasyLine continuous gas analyzer (CGA) is a typical example of an extractive, rack-mounted CEM used at solid fuel combustion facilities. For example, common configurations for the EL 3020 either pair a paramagnetic analyzer for oxygen with an NDIR photometer for CO (Kristensen, Kristensen, and Rodrigues 2017) or with an NDIR photometer for CO2 (Ndibe et al. 2015/09/09). In either configuration (or with all three detectors combined), ABB (ABB 2005) notes that the EL 3020 is designed to operate with a gas flow of 30–90 L hr−1 (0.5–1.5 L min−1).
Design of model system

To represent full-scale waste-to-energy plant gas-phase behavior above the fuel bed, the design of the bench-scale model reactor focuses on the same four elements of a full-scale system described in the design basis section: feedstock, thermal conversion, gas-phase combustion, and gas monitoring. To ensure collection of representative exhaust gas samples for off-line trace analysis, the design also addresses a fifth element: exhaust gas sampling. Figure 5 conceptually illustrates the main components of the bench-scale model reactor system. The point of this design is to capture the essential chemistry affecting transformations in the combustion zone above the bed. This section presents each of the five design elements in turn. (Introduction of test material is described in the thermal conversion subsection).

MSW surrogate

To elucidate the effect of the test material, it is essential to feed a consistent fuel with steady composition throughout the entire study as a surrogate for MSW (Marklund et al. 1990). In the 1990s, the common approach to preparing an MSW surrogate was to match the surrogate’s composition to the elemental (Wochele and Stucki 1999) or material (Wikström and Marklund 1998) composition of the relevant country’s MSW. More recently, biomass thermochemical conversion researchers (Mettler et al. 2012) have inspired focus on a surrogate that generates pyrolysis products relevant to the solids of interest. Since hydrocarbon plastics generally complete decomposition at higher temperatures than lignocellulose (Garcia, Marcilla, and Font 1995/04; Williams and Besler 1992), pyrolyzing the polymer test material in the presence of a volatile product of lignocellulose pyrolysis would subject it to the same sort of reaction atmosphere experienced by synthetic polymers in full-scale waste-to-energy plants. As described in the design basis section, these volatiles include methane and methanol.

Methanol vapor is an effective surrogate for the volatiles produced by thermal conversion of the dominant lignocellulosic fraction of MSW. Methanol is one of the major volatile products of lignocellulose pyrolysis. Like the most abundant volatile hydrocarbon product (methane), methanol has a hydrogen to carbon ratio of 4:1. Moreover, high-temperature combustion of methanol follows the same conversion pathway as methane depicted in Figure S1 except that •CH₂OH is the principal intermediate en route to CH₃O rather than •CH₃ (Liao et al. 2011; Lissianski, Zamansky, and Gardiner 2000). Importantly, using methanol maintains the focus on gas-phase combustion behavior because methanol flames do not form soot (McEnally and Pfefferle 2011/03). For an academic environmental engineering laboratory that relies on cylinders for gas supply, methanol is inherently safer (Bollinger et al. 1996) to work with than methane because the amount of methanol liquid needed during a set of experiments can be readily minimized. Delivery of methanol vapor is a key part of the thermal conversion component of the model reactor system.

Thermal conversion

In the bench-scale reactor system, thermal conversion is represented by pyrolysis and gasification of the test material in the presence of vaporized methanol premixed with air.

Delivery of methanol vapor

Assuring a representative reaction atmosphere starts with steady introduction of methanol vapor. In turn, maintaining a consistent flow of methanol vapor requires (1) a steady flow of liquid methanol and (2) reproducible, effective vaporization of the liquid.

As the piping and instrument diagram for the model system in Figure 6 shows, a syringe pump is used to supply methanol liquid. Specifically, a Model 100DX high-pressure Isco syringe pump with an ultra-high molecular weight polyethylene seal (Teledyne Isco, Lincoln, NE) is used to supply methanol liquid. This type of pump can provide steady flow free of pulsation (Simpson, Wei, and Sundaresan 1996; Woitalka, Kuhn, and Jensen 2014/09).

Under excess air levels typical of full-scale waste-to-energy plants (see design basis section) and a total gas flow rate in the range of the commercial-scale

---

Figure 5. Bench-scale model reactor system block flow diagram.
extractive CEM (0.5–1.5 L min⁻¹), the required methanol flow rate to the system is less than 100 µL min⁻¹. Achieving such low methanol flow rates requires insulation and control of the pump cylinder head temperature to minimize temperature fluctuations that would interfere with pump performance at such low liquid flow rates (Teledyne Isco 2006). Accordingly, the methanol supply pump (Model 100DX) is outfitted with an Isco insulating cover and cooled to a fixed temperature (24°C) with a NESLAB RTE-7 D1 115/60 circulating water chiller (ThermoFisher, Newington, NH). Using anhydrous methanol (DriSolv® 100 mL bottle with septum cap, EMD Chemicals, Gibbstown, NJ), a steady flow of 61.71 µL min⁻¹ has been attained by running in pressure control mode at 2400 psig (165.5 bar) through a 12.5 feet (3.81 m) length of 0.0025 inch (65 µm) ID PEEK™ capillary tubing.

Recognizing that vaporization rate is proportional to droplet size (Diemer et al. 1995), pneumatic atomization can be used to break the liquid up into fine droplets (Niessen 2010). Due to the low flows in this system, combustion air is used to effect atomization (instead of the independent atomization air used for liquid burners at full scale). This approach facilitates methanol-air mixing concurrent with methanol vaporization. Moreover, the low liquid flow rate requirement calls for the sort of nebulizer used to introduce samples to an inductively coupled plasma mass spectrometer (ICP-MS) for metals analysis (Montaser et al. 1998) rather than a traditional liquid fuel atomizer. However, even ICP-MS nebulizers are generally designed for liquid flow rates above 250 µL min⁻¹ (Beauchemin 2020). Therefore, the model system employs a custom nebulizer. Borrowing from another part of analytical chemistry (liquid chromatography) (Woolf 1993), a commercial stainless steel post-column reaction mixing tee (Part # TCEF411C, Valco Instruments, Houston, TX) provides the body for the custom nebulizer. As Figure S2 illustrates, the post-column reaction tee has been modified to pass a partly sleeved length of 0.005 inch (130 µm) ID x 0.1 inch (2.54 mm) stainless steel capillary tubing through the throat for liquid flow and to create an annulus for air flow. This configuration resembles Golitizine’s nozzle design as depicted by Gretzinger and Marshall (1961) in their study characterizing pneumatic atomization.

**Figure 6.** Piping & instrument diagram for bench-scale model reactor system.
As Table S2 indicates, the nebulizer body is temperature controlled by Heat Zone 5 with heating tape (target 40°C). With a steady flow of liquid less than 100 µL min⁻¹, atomization via this custom nebulizer with preheated air provides a steady flow of methanol vapor pre-mixed with air.

Also noted in Table S2, the air heater exit temperature is controlled by Heat Zone 4 with two band heaters (target 35°C) surrounding a length of split cylindrical stock that fits around the process tubing, and the nebulizer exit mixture flows through tubing that is temperature-controlled in the same way by Heat Zone 1 (target 100°C). Consistent with industrial laboratory reactor practice, heat transfer to small diameter tubing is facilitated through the use of metal (e.g., aluminum) stock clamped by band heaters around the tubing (Hickman 2020).

To further assure delivery of a well-mixed vapor/air mixture to the tubular reactor, the low flow rate (laminar flow) mixture next passes through a helical-element static mixer (Myers, Bakker, and Ryan 1997; Patterson et al. 2004), electrically heated to effectively function as a heater-mixer. The mixer is a Kenics ½ inch (6.35 mm) O.D. stainless steel tube mixer with 27 elements (Chemineer, North Andover, MA), and its temperature is controlled by Heat Zone 2 (target 100°C). Upstream of the inlet to the tubular reactor, vapor/gas temperatures are maintained below the lower flammability limit for the target concentration of methanol in air.

The resulting methanol vapor/air mixture flows toward the tubular reactor, sweeping the products of test material pyrolysis and gasification into the reactor.

**Pyrolysis and gasification of test material**

Just like the thermal conversion process taking place in full-scale waste-to-energy plants, pyrolysis and gasification transform the test material into vapor to undergo gas-phase combustion in the model reactor system. To accomplish this, an analytical pyrolyzer with a resistive heating coil heats up a sample of the solid test material according to pre-set temperature programming (Moldoveanu 2019; Wampler 2006). Specifically, the sample solids in a small quartz tube are placed into the coil and then heated and gasified with a 1/4 -inch (6.35 mm) diameter CDS-2000 pyroprobe (CDS Analytical, Oxford, PA). Although traditionally connected by a low volume interface to a GC/MS with helium as sweep gas (Funazukuri, Hudgins, and Silveston 1986; Moldoveanu 2019), the pyroprobe in the model system introduces vapor into a tubular reactor akin to how Caballero, Font, and Marcilla (1996/12) connected a CDS-1000 pyroprobe with a tubular laminar flow reactor for further pyrolysis. However, the methanol/air mixture sweeps the pyrolysis vapors into the inlet of the tubular reactor rather than helium so that the tubular laminar flow reactor in this system performs gas-phase combustion.

Funazukuri, Hudgins, and Silveston (1986), Garcia, Font, and Marcilla (1992/05), and more recent studies, e.g., (Biagini, Lippi, and Tognotti 2006/12) have found significant discrepancies between the pyroprobe nominal heating rate and the measured actual heating. To minimize the impact of such discrepancies, use of this reactor system has included three provisions. First, sample tubes (cartridges) are the same length as the heating coil and open on both ends (without quartz wool). Second, test material pyrolysis is continued to a higher temperature than predicted by thermogravimetric analysis (TGA) or held for several minutes at the temperature corresponding to the final TGA weight loss asymptote. Third, the empty cartridge after pyrolysis is weighed after the experiment to confirm the absence of residue and thereby verify complete gasification.

Moldoveanu (2010) reports very good reproducibility for CDS pyroprobes, especially when used to pyrolyze synthetic polymers (the planned use for the bench-scale model). Sablier and his coworkers (Ji et al. 2009/04) have confirmed that use of a CDS-2000 pyrolyzer can provide reproducible results when sample quantity and sampling loading technique are consistent. The procedures for use of this reactor system have been set accordingly to assure pyroprobe performance for one experiment is comparable to another.

As Figure 6 illustrates, the pyroprobe inserts into the reactor inlet through a ball valve. The ball valve permits steady-state methanol combustion to be demonstrated prior to introduction of the gasified test material, and this arrangement is designed to minimize disruption to methanol combustion upon pyroprobe insertion.

**Gas-phase combustion**

Like the gases above the fuel bed in grate-fired waste-to-energy plants, the vapor/air mixture entering the tubular reactor is radiatively heated. Reactor heating is provided by a horizontally oriented, bench-top, split-tube furnace (ThermCraft, Inc., Winston Salem, NC) described in Table S2. While this furnace can accommodate a larger diameter reactor tube as needed for a specific project, here it heats a 14 mm I.D. x 997 mm long quartz reactor tube with 2 mm thick walls (H.S. Martin, Vineland, NJ). Quartz is known to stand up to temperatures above 1100°C (Rubey and Carnes 1985) and to minimize activity toward potential surface reactions at the wall (Rasmussen et al. 2008; Sudholt, Cai, and Pittsch 2019/
LFL and UFL. By LFL, Coward (1995/05) and Bawn (1956). As such, the reactor walls resemble the enclosures of full-scale furnaces described in the design basis section. The temperature controller for each furnace zone operates on feedback from an imbedded thermocouple integral to the furnace. Due to the gap between the inside diameter of the furnace and the exterior of the reactor tube, specifying temperature controller setpoints requires correlating the controller readings with reactor tube temperature measurements; see the experimental section. Extending beyond the side walls of the furnace are the ½ inch (12.7 mm) O.D. ground quartz ends of the reactor. These ends are connected to the inlet and exit process tubing via Ultra-Torr fittings (Swagelok, Solon, OH), equipped with S310 VMQ (silicone) O-rings (Freudenberg-NOK, Plymouth, MI) rated for 70 hours of continuous service at 260°C (Simrit 2007) to facilitate reactor tube change-out. Although the first and last 3 inch (7.62 cm) long sections inside the furnace are insulated and not radiatively heated, each is heated by conduction along the quartz tube. Conduction along the quartz tube also affects the temperature at the inlet and exit ground quartz ends of the tube as well as the metal tubing used for inlet and exit transfer lines (Heat Zones 6 and 7). A ceramic conduction shield inserted between Heat Zone 6 (100°C < target < 240°C) and Heat Zone 3 (target 100°C) reduces the temperature influence of the split tube furnace on upstream process tubing, minimizing the potential for methanol oxidation upstream of the reactor.

As the vapor/air mixture proceeds into the radiation-driven, conductively heated inlet of the reactor tube, it enters into the flammability region due to its rise in temperature and begins to react. While Lange’s Handbook (Lange and Dean 1979) reports the lower flammability limit (LFL) and upper flammability limit (UFL) for methanol in air at 25°C as 6.7 and 50%, respectively, these limits are influenced by temperature (Coward and Jones 1952). Observing an 8% decrease in LFL and an 8% increase in UFL as temperature increases each 100°C across a wide range of hydrocarbons, Bodurtha (1980) provides equations 7 and 8 to show how the flammability limits (as volume %) change with temperature (T).

\[
\text{LFL}_T = \text{LFL}_{25^\circ} - (0.8\text{LFL}_{25^\circ} \times 10^{-3})(T - 25) \tag{7}
\]

\[
\text{UFL}_T = \text{UFL}_{25^\circ} + (0.8\text{UFL}_{25^\circ} \times 10^{-3})(T - 25) \tag{8}
\]

By 300°C (temperature at inlet to reactor), the LFL drops to 5.2%, indicating that a mixture containing 5.2% methanol in air is flammable. This concentration corresponds to 155% excess air for the target methanol injection rate noted previously, which is within the 50–200% range for full-scale waste-to-energy plants (see design basis section). The flow of the methanol/air mixture entering the reactor is laminar because it has a Reynolds number (Re) of 26. Between 320°C and 390°C, methanol begins to partially oxidize at atmospheric pressure, initially producing CH₂O and CO (Bone and Gardner 1936). Initiation of the chain-induced decomposition of methanol under preflame conditions produces •HO₂ radicals that go on to propagate the chain reaction (Aniolek and Wilk 1995/05; Bell, Tipper, and Bawn 1956).

Further heating of the flammable mixture brings on ignition and high-temperature combustion. At a temperature between 385°C (Zabetakis 1965) and 433.1 ± 8.7°C (Chen et al. 2010), the mixture ignites spontaneously in the absence of a spark or supplemental flame. As in the ASTM test method (ASTM 2015), ignition in the reactor tube occurs upon externally heating the premixed vapor/air to this autoignition temperature. In effect, radiation from the electrical furnace enclosing the reactor tube causes ignition, thereby simulating radiation above the fuel bed in full-scale plants (Mätzing et al. 2018/08). In the flame, ignition occurs at least than the autoignition temperature due to diffusion of free radicals upstream from the flame (Borman and Ragland 1998). The characteristic length of this laminar premixed flame is known as the flame thickness (δ), which can be estimated from the laminar flame velocity (S_L) and thermal diffusivity (α) (Glassman, Yetter, and Glumac 2015; Williams 1985) using equation 9.

\[
\delta \sim \alpha / S_L \tag{9}
\]

where \( \delta \) = \( \lambda / \rho C_p \)

\[
\lambda = \text{thermal conductivity of unburned gas at } T_{\text{avg}} \quad \text{W} \text{ (m K)}^{-1}
\]

\[
\rho = \text{density of unburned gas at } T_{\text{avg}} \text{, kg m}^{-3}
\]

\[
C_p = \text{heat capacity of unburned gas at } T_{\text{avg}} \text{, } \text{kJ} \text{ (kg K)}^{-1}
\]

Evaluating properties for combustion air as the unburned gas properties (Borman and Ragland 1998), the length of the flame zone in the reactor is estimated as flame thickness in Table S3. The calculated thickness (5 mm) is in the same range of flame thicknesses predicted by Westbrook and Dryer via detailed modeling with a methanol combustion mechanism involving 84 elementary reactions and 26 chemical species (Westbrook and Dryer 1979, 1980/01). The balance of the reactor serves as the post-flame zone. Overall, gas-phase combustion of methanol is described by equation 10.
\[
\text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}.
\] (10)

During combustion in laminar flow, mixing is limited to molecular diffusion (Hottel and Hawthorne 1948/01). Specifically, the volatiles emanating from the pyroprobe are mixed with premixed methanol vapor/air via radial diffusion. The extent of such diffusion can be assessed by comparing the diffusion distance \(x\) in equation 11 (Crank 1979) to the radial distance outward from the pyroprobe (\(r = 0.3175\) cm) to the reactor wall (\(r = 0.70\) cm).

\[
x \sim \sqrt{Dt}
\] (11)

where

\[
D = \text{diffusivity (cm}^2\text{ sec}^{-1})
\]

\[
t = \text{time (sec)}
\]

Diffusivity between two species \(A\) and \(B\) can be computed from Chapman-Enskog theory and the Lennard-Jones 12–6 potential via equation 12 (Reid, Prausnitz, and Sherwood 1977; Sherwood, Pigford, and Wilke 1975).

\[
D = 1.858 \times 10^{-3}T^{1.5} \left(1/M_A + 1/M_B\right)^{0.5} / (\text{P} \sigma_{AB}^2 \Omega_D)
\] (12)

where

\[
T = \text{temperature (°K)}
\]

\[
M_A = \text{molecular weight of species } A
\]

\[
M_B = \text{molecular weight of species } B
\]

\[
\text{P} = \text{pressure (atm)}
\]

\[
\sigma = \text{Lennard-Jones characteristic length (Å)}
\]

\[
\Omega_D = \text{collision integral, dimensionless}
\]

Pyrolysis of the common fluorinated polymer PTFE yields gaseous difluorocarbene (Puts, Crouse, and Ameduri 2014) with a molecular weight of 50.01 g/mole. The diffusivity between difluorocarbene and air can be estimated by calculating the diffusivity between \(\text{CO}_2\) (molecular weight of 44.01 g/mole) and air based on their comparable molecular weights. Using the procedures and data compiled by Reid, Prausnitz, and Sherwood (1977), the diffusivity between \(\text{CO}_2\) and air is calculated via equation 12 to be 1.867 cm\(^2\) sec\(^{-1}\) at 1000°C. This value can be used to estimate the diffusivity between difluorocarbene pyrolysis gas and premixed methanol/air undergoing combustion. Solving equation 11 for time indicates that radial diffusion from the outer radius of the pyroprobe to the outer radius of the reactor tube (\(r_1 - r_2 = 0.3825\) cm) occurs in less than 0.08 seconds. Since this is equivalent to less than 4% of a 2 second gas residence time at 1000°C, molecular diffusion is sufficient to provide radial mixing of the pyrolysis gas and the reacting premixed methanol/air. The combination of radial mixing and premixing assures adequate air-volatile mixing in this reactor system. Under these conditions, the organofluorine content of the PTFE pyrolysis gas is expected to transform to hydrogen fluoride (HF) consistent prior observation of HF as a thermodynamic end product of fluorocarbon combustion (Manion and Tsang 1997).

Process monitoring allows automatic control of the reactor. As noted in Table S3, the combustion air feed to the reactor is synthetic air composed of 79% nitrogen and 21% oxygen in cylinders (Airgas, Royal Oak, MI). A steady flow of synthetic air is measured and controlled by a Brooks Model 5850S mass flow controller with Buna-N seals (Brooks Instrument, Hatfield, PA) that reads out in standard cubic centimeters per minute (sccm) with standard conditions set at 21.1°C and 1 atmosphere. Flow measurement is accomplished by a thermal mass flow sensor (Kim, Han, and Kim 2007) integral to the mass flow controller. Five 1/8 inch (3.175 mm) O.D. Type K thermocouples of varying length (KQXL-18 U, Omega Engineering, Stamford, CT) are placed along the length of the reactor tube. As noted in Figure 6, these thermocouples are designated T23, T24, T3, T25, and T30. T23 monitors the furnace temperature at the beginning of the first 6-inch (15.24 cm) long heated zone, 7.62 cm from the inlet of the furnace. T24 monitors the exterior wall temperature of the reactor tube at the midpoint of the inlet-end heated zone, 15.24 cm from the inlet of the furnace. T3 monitors the exterior wall temperature of the reactor tube at the midpoint of the 18-inch (45.72 cm) long middle heated zone (midpoint of the reactor), 45.72 cm from the inlet of the furnace. T25 monitors the exterior wall temperature of the reactor tube at the midpoint of the exit-end 15.24 cm long heated zone, 76.2 cm from the inlet of the furnace. T30 monitors the furnace temperature near the end of the exit-end heated zone, 81.28 cm from the inlet of the furnace. For the three thermocouples along the wall of the reactor tube (T24, T3, and T25), wire secures the thermocouple shielded by a ceramic protection tube (Omega Engineering, Stamford, CT) at the prescribed location. T23 and T30 were held in place by the 3 inches (7.62 cm) of insulation on the inlet- and exit-ends of the furnace, respectively. LabVIEW data acquisition equipment and software (National Instruments, Austin, TX) are used to continuously record flow rate and temperature data during each run. Additionally, a Florite (Valencia, CA) Model 990 M2C2 Universal Flow Controller is used to set and read gas flow rate values.
Gas monitoring

The exhaust gas exits the reactor through the heated Silcosteel® (Restek, Bellefonte, PA) outlet transfer line (Heat Zone 7, 200°C < target < 250°C), where the exit flow is split at a Silcosteel® reducing tee. The vast majority of the ~700 sccm exhaust gas flows out a stub slanted approximately 45 degrees downward, connected to flexible white silicone tubing (Part # 06411–71, Cole Parmer, Vernon Hills, IL) en route to the gas sampling apparatus described in the next section. Upon leaving the sampling apparatus, the gas flows to the CGA through flexible tubing with three tee fittings along the way. The first tee connects a thermocouple to monitor gas temperature exit the gas sampling apparatus. The second and third tees in series connect a needle valve (SS-1RS4, Swagelok®, Solon, OH) and a Magnehelic® standard low-pressure differential gauge (0–50 in. W.C., Dwyer Instruments, Michigan City, IN) for manual control to prevent pressure buildup downstream of the sampling apparatus by venting excess flow. The gas between the sampling apparatus and the first tee flows through white silicone tubing (Cole Parmer). Between the first tee and the barbed stainless steel fitting on the CGA, the gas flows through clear Tygon® tubing (Saint-Gobain, Malvern, PA) or amber latex rubber tubing (VWR, Radnor, PA) to maintain gas-tight connections. The lesser part of the split is a nominal flow of 1 sccm. This portion passes through a fused silica capillary through Heat Zone 8 (target 201°C) and into the GC oven set at 201°C (Tmax = 400°C, Model 5890, Hewlett-Packard, Inc., Palo Alto, CA) without chromatographic separation and into the mass selective detector (Model 5970B, Hewlett-Packard, Inc., Palo Alto, CA). As configured, the mass selective detector provides real-time monitoring of H2O, conceptually consistent with Curran’s measurement of H2O as a combustion diagnostic (Curran 2019b) and observes O2, CO2, and N2. Monitoring for these gases did not include a quartz wool packed cold trap. The target temperatures for Heat Zones 7 and 8 were set to prevent PFOA condensation in the exit transfer lines.

Primary real-time monitoring of exhaust gas composition relied on technology described in the design basis section, namely NDIR photometers for CO and CO2 and a paramagnetic analyzer for O2. In fact, this monitor was the same model CGA (EL 3020, ABB, Frankfurt, Germany) described previously, yet with the option to combine CO and CO2 measurement along with O2 monitoring in one instrument. ABB’s Uras26 modules measured CO and CO2, and Magnos206 module measured O2 (ABB 2005). Consistent with commercial practice at waste-to-energy plants, the exhaust gas was dried prior to the CGA (McCurdy 2001). Moisture was selectively removed from the exhaust gas just upstream of the instrument via a Ballston coalescing filter (Parker Hannifin, Lancaster, NY) and a Nafion® membrane dryer (Model DM-110-24, Perma Pure LLC, Toms River, NJ) commonly used for sample conditioning at full-scale plants (Clarke 1998a).

LabVIEW data acquisition equipment and software are used to continuously record CGA concentrations during each run. ChemStation (Agilent Technologies, Santa Clara, CA) software is used to record mass selective detector monitoring.

Gas sampling

Gas sampling design for pollutants of interest starts with an understanding of the available analytical methods (Ostaszewski 2019). Therefore, the gas sampling component of the model system was designed to capture PFOA into water because of the availability of trace-level LC/MS/MS analysis for PFOA anion in this matrix (Larsen and Kaiser 2007; Risha et al. 2005/03). With the exception of the nominal 1 sccm flow to the mass selective detector noted previously, the entire exhaust gas flow from the reactor is routed to a set of glass impingers. The impingers are 30 mL midget impingers, commercially scaled down from larger Greenburg-Smith impingers (US Public Health Service 1944). They are like the ones used in EPA Method 26 (EPA) non-isokinetic HF emission sampling at full-scale plants. While Method 26 notes a gas flow rate of 2 liters min−1, EPA has also demonstrated the suitability of midget impingers to sample hydrogen halides at gas flow rates between 0.5 and 1.0 L min−1 (Stern et al. 1984). Supplied by Kimble-Kontes (Vineland, NJ, Part 737550–0000), these graduated midget impingers feature a 1 mm orifice at the bottom of the dip tube (US Public Health Service 1944). The gas sampling apparatus consists of three midget impingers in series connected by flexible white silicone tubing (Cole Parmer). The first and second contain HPLC-grade water, consistent with the type of water used for solution makeup for trace analysis of PFOA (Berger et al. 2011/06). The third impinger is empty to capture any liquid carried over from the first two. While the bulk of the impinger solution is assigned to PFOA analysis, a small portion of high-temperature combustion testing impinger solution is set aside for fluoride ion analysis to determine the other main pollutant of interest, HF. Due to the potential effect of hydroxide on PFOA recovery (Zhang et al. 2013/06) and the lack of available method development studies to explore
such effects, hydroxide is not added to the HPLC-water in the impingers. Nevertheless, water has been successfully used as an effective HF absorbent in industrial emission control (Kohl and Riesenfeld 1979) and in stack gas sampling (Clarke 1998b; Jacobson and Heifer 1976/11). In stack gas sampling, water-containing Greenburg-Smith impinger trains have been found to have high HF collection efficiencies (Jacobson and Heifer 1976/11), comparable to the fluoride collection efficiencies of impingers containing 0.1 N sodium hydroxide (Mitchell and Midgett 1976).

**Experimental**

Consistent with the general approach for evaluation of field instruments prior to deployment (Kerfoot et al. 1990/08), the performance of the model reactor system was characterized prior to routine use at planned experimental operating conditions. This sort of qualification testing is critical to assuring the equipment is “fit for purpose” (Burgess and Jones 1998).

**Equipment calibration**

As standardized measurements are necessary for reliable and reproducible results (Coleman et al. 2015), qualification testing began with calibration checks on key process instrumentation traceable to NIST standards at the beginning of each set of experiments. The factory calibration of the three Brooks mass flow controllers was confirmed using an ADM 2000 reference flowmeter (Agilent Technologies, Wilmington, DE). Beside the flow controller for synthetic air described previously, mass flow controllers of the same design are in place for nitrogen used for zero calibration of the CGA and the mass selective detector and for calibration gas used to span the CGA and mass selective detector. The CO₂ span gas has a nominal concentration of 5.5% CO₂ in N₂. The gas used for span calibration of the CGA CO signal is nominally 900 ppmv CO in N₂. The CGA and mass selective detector were calibrated at zero and span levels using certified cylinder gases (Airgas, Royal Oak, MI). The mass selective detector was calibrated for H₂O via water injection through the reactor system using an Isco 260D syringe pump (Teledyne Isco, Lincoln, NE). Flow checks were performed for both this water supply pump and the Isco 100DX methanol supply pump to confirm acceptable pump flow accuracy. The KQXL-18 U thermocouples used to monitor reactor wall temperature in the furnace were Omega (Stamford, CT) special limits of error thermocouples.

**Confirming representative behavior**

While methanol can be fed continuously, pyrolysis and gasification via the pyroprobe is effectively a batch operation, requiring establishment of targets for test material mass and experimental run duration. Readable to 1 µg, the microbalance was capable of measuring 100 µg of test material loaded into a pyroprobe cartridge. Monitoring requirements for full-scale waste-to-energy plants (EPA 2018a) point to 15 minutes as a minimum run duration. With this as a minimum along with a typical European value for full-scale flue gas (prior to air pollution control) HF concentration of 10 mg Nm⁻³ (Kamuk 2009) in mind, a duration of 16 minutes corresponds to combustion of 100 µg of PTFE. Hence, 16 minutes was set as the run duration. With run duration set, TGA results for a test material provide the basis for pyroprobe temperature programming to assure continuous gasification of a nominal 100 µg batch of material over the course of the run.

Other high-temperature combustion test experimental conditions were based on the survey of combustion operating conditions at full-scale U.S. waste-to-energy plants (Giraud, Taylor, and Huang 2021) coupled with EPA-sponsored shutdown/startup testing at a 249.5 Mg day⁻¹ reverse-reciprocating grate furnace near Salem, OR (EPA 1988) as follows: 2 seconds gas residence time at 1000°C with 13% oxygen (dry basis) and 10% water in the exhaust. These conditions can be achieved with a methanol feed rate of 61.71 µL min⁻¹ and 155% excess air according to stoichiometric calculations for the reaction in equation 10.

Prior to beginning high-temperature experiments, the reactor was traversed with a certified, calibrated 121.92 cm long thermocouple (KQXL-18 U-48-CL5, Omega Engineering, Stamford, CT) coupled to a NIST traceable certified, calibrated thermocouple reader (CL23A, Omega Engineering) to measure gas temperature inside the reactor with synthetic air flowing at 660 sccm. Radiation-induced error in these gas temperature measurements was calculated to be less than 10°C based on the approach for thermocouple error analysis described by Carvalho and Dos Santos (1990/09). Trial and error allowed determination of the furnace zone setpoints required to achieve 1000°C ± 10°C thermocouple readings over a long section of the reactor tube that defines the effective length of the target high-temperature zone for combustion testing. This effective length is used to confirm alignment with the gas residence time target. These readings also allow the continuously measured exterior wall temperatures to be related to actual gas temperature.
High-temperature experiments evaluated system performance during methanol combustion at the target operating conditions noted earlier in this section. The reactor feeds were anhydrous methanol as described in the system design section and synthetic air as described in Table S3. While the pyroprobe was inserted and heated during this testing, its cartridge was not loaded with test material solids.

**Demonstrating PFOA collection efficiency**

Qualification testing also determined the collection efficiency for transport across the bench-scale reactor system (under conditions similar to those planned for subsequent combustion testing) and absorption of PFOA into aqueous impingers. For this collection efficiency testing, the solid test material to be gasified was 99.8% purity PFOA (Oakwood Products, West Columbia, SC) instead of polymer, and the liquid to be injected and vaporized was HPLC-grade water (Alfa Aesar, Ward Hill, MA) rather than methanol. Water injection provided the nominal 10% concentration necessary to simulate the water of combustion. To achieve the oxygen concentration expected during high-temperature combustion testing, it was necessary to feed CEM calibration gas-grade nitrogen from certified cylinders (AirGas, Royal Oak, MI) as a diluent in addition to the synthetic air. This testing required operation at a temperature much lower than the combustion test setpoint to allow quantitative determination of PFOA by minimizing degradation. Prior NMR studies indicated that PFOA is thermally stable in vacuum at 300°C (Krusic, Marchione, and Roe 2005/12). Thermogravimetric analysis of PFOA in air at 10°C min⁻¹ (Figure S3) indicates complete gasification by 150°C. Viewing these two values as bounds, the reactor midpoint temperature was set at 250°C for collection efficiency testing. The exit gas transfer line temperature was set slightly above 200°C to prevent potential loss of PFOA therein via condensation. Pyroprobe temperature programming was set to ensure complete gasification of a nominal 100 µg mass of PFOA during each experimental run across a 16-min run duration as follows: initial temperature = 100°C, heating rate = 10°C min⁻¹, and final temperature = 215°C with a holding time of 4.5 minutes.

Collection efficiency testing was conducted across three replicate tests consistent with plans for high-temperature combustion testing and standard practices for performance tests at full-scale waste-to-energy plants (EPA 2018b). Prior to each experimental run, a thermal blank run was conducted. Following each experimental run (with PFOA in a pyroprobe cartridge) was a steam cleaning run, where nitrogen was used in place of air and where 50 mL of HPLC-grade water was injected into the reactor system over a 75-min period followed by a 20-min N₂ purge. Post-run steam cleaning collected any PFOA that may have condensed in the reactor system. Except for the steam cleaning and the 250°C temperature noted above, the other conditions for collection efficiency testing (i.e., gas residence time, exhaust oxygen concentration, exhaust moisture level, and experimental run duration) were set at the levels planned for high-temperature combustion testing. During each of the three types of runs, reactor exhaust was collected in a set of three midget impingers located in a crushed ice bath. Except during steam cleaning, the first two impingers were pre-loaded with HPLC-grade water (Alfa Aesar, Ward Hill, MA). During steam cleaning, the impingers were initially empty in order to collect the condensed steam. The flexible white silicone tubing into the first impinger was rinsed with 5 mL of HPLC-grade water to collect potential condensate from this unheated line. The aqueous impinger samples from each run were weighed before and after addition of this rinsate. These aqueous samples were analyzed for PFOA by MPI Research (State College, PA) via LC/MS/MS based on the approach described by Risha and her coworkers (2005/03). The limit of quantitation (LOQ) was 25 ng L⁻¹, and the limit of detection was 5 ng L⁻¹.

**Results and discussion**

Figure 7 illustrates the temperature profile measured along the length of the reactor tube of the bench-scale system with 660 sccm synthetic air flow as well as corresponding values for the three thermocouples along the wall of the reactor tube (T24, T3, and T25). These three continuously monitored wall temperatures are within 0.5% (5°C) of interior gas temperatures. In the direction of flow, the three furnace zone setpoints required to achieve this profile were 991°C, 977°C, and 987°C. Under these conditions, a gas residence time of 2 seconds is achieved over an effective length of 66 cm for this 14 mm I.D. laminar flow reactor. The shape of the curve in Figure 7 is comparable to the temperature profile of the laminar flow reactor used by García, Viciano, and Font (2007; Esperanza, Font, and García 2000) in fuel-rich combustion experiments and approximates the “square wave” temperature profile advocated by Rubey and Carnes (1985) for precise control over gas residence time.

Figure 8 describes bench-scale reactor system performance during high-temperature methanol combustion in terms of concentrations of O₂, CO₂, and CO in the exhaust gas. Once the flow of methanol vapor had stabilized, O₂ and CO₂ levels converged on 13% and 5.7%, respectively, as expected from combustion stoichiometry at 155% excess air. At this
As Table 2 shows, the PFOA collection efficiency was greater than 90%. One-fifth of this efficiency can be attributed to the practice of steam cleaning after each experimental run. The observed efficiency represents a better than fourfold improvement in comparison to prior work (Yamada et al. 2005) and is consistent with the 70–130% general guideline for surrogate recovery in environmental analysis (Keith 1996).

Blank analysis indicates the absence of background levels of PFOA in the experimental system. The results for pretest steam cleaning and for the first thermal blank in Table 2 confirm that the reactor system as constructed did not contribute PFOA to the impinger samples. These findings demonstrate that specifying the seals on reactor system equipment (e.g., pumps and gas flow controllers) to be free of fluoropolymers prevented the sort of historical PFOA contamination associated with use of fluoropolymer parts in laboratory equipment (Martin et al. 2004). Additionally, analysis of reagent blanks (not tabulated) confirmed that the HPLC-grade water did not contain detectable PFOA.

Comparison of experimental results to waste-to-energy plant operation and design forms the basis for assessing the degree of similarity achieved in the design of model reactor system (Wochele and Stucki 1999). Thermal similarity across these two scales is supported by radiation-driven heat transfer as observed at full-scale (Niessen 2010). Use of the same gas monitoring technology for O₂, CO₂, and CO practiced at full-scale allows...
Table 2. PFOA collection efficiency.

| Sample identification | Concentration of PFOA in impingers (ng L\(^{-1}\)) | Sample volume collected (mL)\(a\) | PFOA Output Mass in Impinger Sample (µg) | PFOA Input Mass in Feed to Reactor (µg) |
|-----------------------|-----------------------------------------------|-------------------------------|------------------------------------------|----------------------------------------|
| Pretest Steam clean   | < 25\(^b\)                                     | 53.75                         | 73.21                                    | 105                                    |
| Run 1 Thermal blank   | < 5\(^c\)                                      | 69.10                         | 66.27                                    | 99                                     |
| Run 1 Experimental test run 1 | 1,160,000                           | 63.11                         | 67.15                                    | 284.95                                |
| Run 1 Steam clean     | 315,000                                       | 61.61                         | 19.84                                    | 314                                    |
| Run 2 Thermal blank   | 516                                           | 63.06                         | 8.28                                     | 0.04                                   |
| Run 2 Experimental test run 2 | 1,400,000                           | 51.78                         | 20.14                                    | 110                                    |
| Run 2 Steam clean     | 389,000                                       | 65.27                         | 20.14                                    | 110                                    |
| Run 3 Thermal blank   | 635                                           | 65.27                         | 6.04                                     | 99                                     |
| Run 3 Experimental test run 3 | 1,090,000                           | 67.15                         | 67.15                                    | 284.95                                |
| Run 3 Steam clean     | 382,000                                       | 51.94                         | 19.84                                    | 314                                    |
| Posttest Steam clean  | 24,400                                        | 53.66                         | 1.31                                     | 0.03                                   |
| Posttest Thermal blank| 477                                           | 66.07                         | 0.03                                     | 0.03                                   |
| Overall mass          |                                               | 284.95                        |                                           | 314                                    |
| Collection efficiency (%) |                                             | 90.7                          |                                           |                                         |

\(a\)Volume is based on weighing impinger sample bottle assuming density of H\(_2\)O is 1 g L\(^{-1}\).

\(b\)Not quantifiable; compound detected between limit of quantitation (25 ng L\(^{-1}\)) and limit of detection (5 ng L\(^{-1}\)).

\(c\)Not detected; limit of detection is 5 ng L\(^{-1}\).

**Conclusion**

Material characterization of EPA’s 2017 MSW composition information indicates that lignocellulose accounts for roughly half of the annual feed to municipal waste-to-energy facilities. The ‘surrogate’ of lignocellulose is confirmed by comparison of CO performance between the full-scale plant in Spokane (Figure 4) and the bench-scale model when operated at temperature, gas residence time, and oxygen values representative of typical waste-to-energy facilities.

**Materials and Methods**

The full-scale plant in Spokane was operated at conditions representative of full-scale waste-to-energy facilities. Direct evaluation of chemical similarity: Chemical similarity is not assessed in this work. This work focuses on the comparison of CO performance between MSW and a surrogate for lignocellulose.

**Discussion**

Overall, the bench-scale reactor system has been successfully used to evaluate the performance of the reactor system under conditions similar to those found in full-scale plants. The bench-scale reactor system allows for testing of various waste-to-energy technologies in a controlled environment. The results obtained from the bench-scale reactor system are representative of full-scale waste-to-energy plants.

**Conclusion**

The bench-scale reactor system has been used to evaluate the performance of waste-to-energy technologies. The results obtained from the bench-scale reactor system are representative of full-scale waste-to-energy plants. The bench-scale reactor system allows for testing of various waste-to-energy technologies in a controlled environment. The results obtained from the bench-scale reactor system are representative of full-scale waste-to-energy plants.
While the bench-scale reactor system described herein was designed to model municipal waste-to-energy combustion, the system can also be used to simulate other types of waste combustion across a wide range of solid organic materials. For example, by gasifying a polymer via the pyroprobe and injecting liquid solvent representative of hazardous waste, this system can be adapted to study hazardous waste incineration. Should such simulation require higher gas flow rates at combustion temperature, it would be important to match impinger sizing with gas flow and to compensate for radiation effects during gas temperature profiling. Use of additional exhaust gas monitoring instrumentation such as Fourier-transform infrared (FTIR) spectroscopy would extend the range of components sensed in real time.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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