Emissions from the Premixed Combustion of Gasified Polyethylene

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An investigation was conducted on pollutants emitted from steady-state, steady-flow gasification and combustion of polyethylene (PE) in a two-stage furnace. The polymer, in pulverized form, was first pyrolyzed at 1000 °C, and subsequently, its gaseous pyrolyzates were burned, upon mixing with air at high temperatures (900–1100 °C). The motivation for this indirect type of burning PE was to attain nominally premixed combustion of the pyrolyzate gases with air, thereby achieving lower pollutant emissions than those emanating from the direct burning of the solid PE polymer. This work assessed the effluents of the two-stage furnace and examined the effects of the combustion temperature, as well as the polymer feed rate and the associated fuel/air equivalence ratio ($0.3 < \varphi < 1.4$). It was found that, whereas the yield of pyrolysis gas decreased with an increasing polymer feed rate, its composition was nearly independent of the feed rate. CO_2 emissions peaked at an equivalence ratio near unity, while the CO emissions increased with an increasing equivalence ratio. The total light volatile hydrocarbon and semivolatile polycyclic aromatic hydrocarbon (PAH) emissions of combustion increased with an increasing equivalence ratio. The generated particulates were mostly submicrometer in size. Overall, PAH and soot emissions from this indirect burning of PE were an order of magnitude lower than corresponding emissions from the direct burning of the solid polymer, obtained previously in this laboratory using identical sampling and analytical techniques. Because pyrolysis of this polymer requires a nominal heat input that amounts to only a diminutive fraction of the heat released during its combustion, implementation of this technique is deemed advantageous.

1. Introduction

The total oil production in the world in 2005 was 81 million barrels per day. This constituted an 8.20% increase from 2000. In the same period of time, the oil production of Brazil increased by 35.5%. To the contrary, the oil production of the United States decreased by 11.7%.[1] As a result, the U.S. imported 11.6% more oil in 2005 than the 9.1 million barrels per day that it imported in 2000.[2] However, the dependence of a country on imported fuels can be lessened through use of its waste fuels. Plastics are a large component of waste streams and have a specific energy content (>40 MJ/kg) that is comparable to that of oil.

Growing amounts of waste plastics are produced every year, and their fraction in municipal solid waste (MSW) streams is also increasing progressively. It is estimated that 26 and 15 million tons of plastic wastes are generated yearly in the U.S.A. and Europe, respectively.[3,4] Of such amounts, polyethylene (PE) accounts for 60 wt %, followed by polystyrene (PS) at 20 wt %, polypropylene (PP) at 10 wt %, polyvinyl chloride (PVC) at 5 wt %,[4] with polyethylene terephthalate (PET) and other polymers making up the rest. Most of these postconsumer plastics are landfilled, ~72 wt %;[5] the rest are incinerated or recycled. Although, in recent years, there has been an increasing effort to recycle waste plastics, only 2 wt % is actually being reused to produce low-grade polymeric products, such as plastic sacks, pipes, fencing, and garden furniture.[6] Hence, even when plastics are partially collected in municipalities that maintain recycling programs, they are often not reused because of a variety of issues, mostly related to economics. Other recycled materials, such as metals and glass, remelt at high temperatures and can thereby be cleaned and sterilized during their recycling process. However, plastics, because of their thermal instability, cannot be heated to high temperatures to burn out or neutralize contaminants. For this reason, plastic food and beverage containers are not reused as such.[6] A promising technique for the reuse of some plastics is the generation of monomer precursors by pyrolysis, followed by repolymerization. Alternatively, for most plastics, upgrading to energy dense materials (i.e., fuels) is technologically feasible. Achieving good use of polymeric wastes, currently collected separately in some municipalities, is important. Favorable economics of reuse may encourage additional recycling of plastics.

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Some recycled polymers can be partially converted to their monomer precursors by pyrolytic thermal treatment. For example, PS can be heated to break down mostly into its original monomeric structural unit, styrene. Different from PS, pyrolysis of PE and PP produce only small quantities of their respective monomer precursors; instead, they yield light hydrocarbon gases. Conesa et al.[7] reported that thermal treatment of PE can convert up to 97.5 wt % of its mass to gaseous pyrolyzates at a temperature of 800 °C. The remaining 2.5% is a mixture of oils and tars. Similarly, Kaminsky[8] pyrolyzed PE wastes in a pilot plant and reported a gaseous hydrocarbon yield of 96% at 810 °C. Finally, Westerhout et al.[9] recorded conversions to gas in the range of 80–90%, with compositions depending upon the temperature. The gaseous stream of hydrocarbons may then be mixed with air and burned in furnaces operating with premixed flame burners, such as those found in natural-gas-fired boilers. Part of the heat released in the furnace may be used in a heat-exchanger/gasifier unit to gasify incoming fuel.

The present study concentrates primarily on PE, the most abundant waste plastic; a subsequent study will address polystyrene. This investigation was partly motivated by the work of Jinno et al.,[10,11] who measured the heat of pyrolysis of PE to be 254 kJ/kg and found this value to be nearly independent of the heating rate. When the heat of pyrolysis is compared to the heating value (energy content) of this polymer, which is 46 300 kJ/kg, it becomes evident that only a rather insignificant fraction of the heat released during combustion may be needed to be fed back to pyrolyze this fuel. This illustrates that a gaseous fuel stream may be produced from such wastes by implementing a very favorable heat integration. Only a small penalty in energy and thus in the operating cost of a power plant will be encountered in running the gasifier.

PE, either as high density (HDPE) or low density (LDPE), starts decomposing at 290 °C by scission of weak links and progressively by scission of tertiary carbon bonds or ordinary carbon bonds in the β position to tertiary carbons.[12] Extensive weight loss is not observed until 370 °C is reached. The main products of its decomposition are an oil/wax product dominated by alkenes, alkynes, and alkadienes, a gas consisting mainly of alkanes and alkenes, and negligible char.[4,12] The monomer precursor ethylene (ethane) is only one of many constituents of the volatile primary products. For instance, there is also the formation of aromatic species, such as benzene and toluene. As the temperature of pyrolysis increases, gaseous products are favored. Extensive work by Conesa and co-workers[7,13] examined the effects of the polyethylene type, the effects of polymer branching, the effects of batch versus continuous operation, as well as the influence of the heating rate on the decomposition yields. They found variations in both the yields and the composition of the pyrolyzates, with branched PE yielding 91.8% gas with a higher aromatic content and less branched PE yielding 97.5% gas with lower aromatic content, both at 800 °C. These results are in good agreement with those of Scott et al.[14] and Kaminsky.[8] Westerhout et al.[9] found that, at 800 °C, the product contains more methane than ethylene and low amounts of aromatics, but most importantly, they determined that the type of pyrolyzed PE, i.e., LDPE or HDPE, had no significant influence on the product spectrum produced. The effect of the residence time and the temperature of pyrolysis on the product distribution were studied by Mastral et al.[15] in two free-fall reactors, placed in series. Their experiments showed that, up to 700 °C, the main products obtained were waxes and oil fractions and that the gas yield increased as the temperature increased. The generation of aromatics started to be significant at 800 °C and showed an increasing trend with temperature and residence time. The main compounds in the gas fraction were hydrogen, methane, and acetylene at temperatures up to 1000 °C. Longer residence times led to a more intense cracking of the aliphatic fractions, and the methane and ethylene yields increased significantly.

The effects of the heating rate have not been entirely clarified. Conesa et al.[7] reported that high heating rates favor the production of waxes, which, when cracked, lead to the formation of benzene as opposed to ethylene and propylene. Darivakis et al.[16] reported that high heating rates reduce the yields of condensable material above 625 °C. Bagri and Williams[17] found that catalysts (Y zeolites) further promote the gas yield. Finally, Darivakis et al.[16] developed a global reaction model for correlating the condensable and volatile yields from PE particles pyrolyzed at 400–800 °C, whereas Faravelli et al.[5] modeled the gas product distribution.

Several investigations examined the direct combustion of solid pellets or particles of PE, where the solid polymer was inserted in a furnace where it was pyrolyzed and burned in air, in nonpremixed (diffusion) envelope flames. The emissions of products of incomplete combustion (PIC), such as CO, light hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), and particulates were monitored.[18–22] Therein, efforts to minimize pollutant emissions were made using techniques such as combustion staging, regulation of furnace temperatures and feeding rates, installation of an afterburner, and employment of high-temperature barrier filters.[23–25] Conditions were identified where most of these pollutants could be curtailed.

To further minimize the emissions of pollutants, this research aims at preventing their formation and/or promoting their oxidation by conducting indirect combustion, instead of direct combustion, where the ubiquitous diffusion flames experience widely varying local equivalence ratios, φ. To the contrary, in

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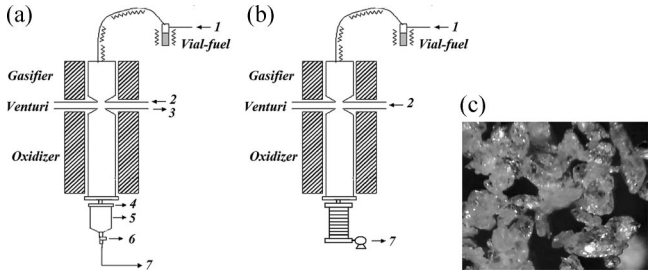

Figure 1. (a) Schematic of the two-stage drop tube furnace (gasifier plus oxidizer furnaces) fitted with the sampling stage. (b) Gasifier and oxidizer furnaces fitted with the multistage impactor: (1) entrance of N_2, (2) entrance of the N_2/O_2 mixture, (3) light hydrocarbon collection point, (4) condensed PAH and particulate matter material (filter paper), (5) volatile PAH (XAD resin), (6) light hydrocarbon collection point, and (7) online analyzers O_2, CO_2, and CO. (c) Detail of the polyethylene particles used in the tests.

indirect combustion, gaseous pyrolyzates of the polymer are burned in a nominally premixed flame. Therefore, it was hypothesized that premixed combustion, at suitably selected φ values, should afford better control of pollutant formation/destruction reactions and should result in drastically lower emissions of PIC. Consequently, to enable premixed combustion, polyethylene was first pyrolyzed, followed by effective mixing of the gaseous pyrolyzates with air, resulting in a nominally uniform φ. The fuel/air mixture was then ignited and burned. Emissions were monitored and contrasted with those from direct combustion of the same polymer, obtained previously in this laboratory using identical sampling and analytical techniques.

2. Experimental Apparatus and Procedure

To evaluate the emissions from the sequential pyrolysis and combustion of polyethylene particles, tests were conducted in a two-stage, electrically heated, drop-tube furnace (manufactured by ATS) at atmospheric pressure (see Figure 1a). Table 1 summarizes the test conditions. Quartz tubes were fitted to both furnace sections, 3 cm i.d., 0.25 cm thick. The pyrolyzer/gasifier furnace section was 30 cm long, whereas the oxidizer furnace section was 60 cm long. Pulverized PE (Aldrich, sieved to 38–125 μm particles, detail in Figure 1c) was introduced to the gasifier/pyrolyzer through a long hypodermic tube, 1.114 mm in diameter (MicroGroup), from a bed of particles placed in a vibrated glass vial coupled to a syringe pump (Harvard Apparatus). Particles from the bed were entrained in a 2 lpm stream of N_2. The tube was vibrated to its natural frequency by two vibrators (Vibro-Graver by Alltech) to warrant a steady flow of polymer particles to the gasifier/pyrolyzer furnace. This furnace was operated at 1000 °C, which was found to be necessary to gasify the polymer. The injection rate of the particles was controlled to obtain the targeted equivalence ratios, defined as $\varphi = [(m_{fuel}/m_{air})_{actual}/(m_{fuel}/m_{air})_{stoichiometric}]$.

Upon pyrolysis of the fuel in the first furnace, the effluent went through a venturi, 8 mm in diameter, where it was mixed with four radially placed jets ejecting 3.6 lpm total of oxygen–nitrogen gases, preheated at 300 °C. The resulting mole fraction of oxygen in the gas exiting the venturi was kept at 21%. The venturi was designed so that the radial jets were expected to reach its centerline to ensure effective mixing.[26] Afterward, the mixture was forwarded to the secondary (oxidizer) furnace, where combustion occurred. The oxidizer furnace was operated at 900, 1000, and 1100 °C to evaluate the effects of the combustion temperature.

Sampling for the composition of the volatile components took place at the exits of both furnaces (see Figure 1a), by withdrawing gases with microsyringes and analyzing their contents with gas chromatography with a flame ionization detector (GC–FID). Sampling for the composition of the semivolatile components of combustion took place with a sampling stage (Graseby) at the exit of the oxidizer furnace. Therein, a paper filter (Whatman) captured condensed-phase PAH as well as particulate matter, and a quantity of 30 mL of XAD-4 resin captured gas-phase PAH. Because this sizable sampling stage would not fit between the furnaces, to sample condensed-phase species in pyrolysis effluents, one of the furnaces was temporarily removed.

Upon sampling, the filters and resins were removed and placed in glass bottles with Teflon-lined caps and stored at 4 °C. Prior to extraction with methylene chloride, a 100 μL internal standard containing equal amounts each of naphthelene-d_8, acenaphthelene-d_{10}, anthracene-d_{10}, chrysene-d_{12}, and perylene-d_{12} was applied to each of the glass bottles containing the samples. Blanks of resin and filters were also extracted and analyzed. Chemical analysis of extracts was conducted at the U.S. Army Natick Laboratories by means of GC–MS using a Hewlett-Packard (HP) Model 5890 gas chromatograph equipped with a HP Model 5971 mass selective detector. The extraction technique along with the analysis of individual PAH species by GC–MS has been explained in detail in previous work.[18,25,26] The isomers were quantified according to their known retention times, using GC–MS standards, such as the NIST SRM 1597, a PAH standard solution. Gaseous samples were extracted from the effluent with microsyringes, and analysis was conducted with gas chromatography (Agilent 6890 Series GC system). Light hydrocarbons were analyzed with a HP-5/Al_2O_3 30 m × 0.32 mm capillary column with a film thickness of 0.25 μm, connected to a FID. Targeted products were quantified using a calibration gas mix.

Upon exiting the sampling stage of the oxidizer furnace, the combustion effluent gas was channeled to CO and CO_2 nondispersive IR analyzers (Horiba) and O_2 paramagnetic analyzers (Beckman model 250). The analyzer signals were recorded with a data-acquisition card (Data Translation model DT-322), as mole fractions. The consistency of the element mass balance (carbon) between the inlet and outlet of the gasifier/pyrolyzer and the oxidizer furnaces was checked. Test durations were 2–4 min and processed 1–3.4 g of polymer. On the basis of the overall inputs of fuel and air, calculated equivalence ratios in the oxidizer furnace were in the range of 0.3–1.4.

To measure the size distribution of the combustion-generated particulates, the aforementioned sampling stage was replaced with a multistage Andersen impactor (1 ACFM nonviable ambient particle-sizing samplers), as illustrated in Figure 1b. This is an instrument that simulates the human respiratory system. It is composed of a series of perforated disks (stages). In each of the stages, the size of the holes and their distribution results in the following particle size cuts: 9, 5.8, 4.7, 3.3, 2.1, 1.1, 0.7, and 0.4 μm. The apparatus also has a bottom filter, which retains smaller particles (<0.4 μm).

3. Results

3.1. Gas Temperature Measurements. Temperature profiles of the gas in the gasifier and oxidizer furnaces were obtained along their vertical centerline using a 48 in. type-K Omega thermocouple. Results are displayed in Figure 2, from which it may be inferred that a polymer particle, upon exiting the injector, would travel 5 cm in the quartz tube before entering the gasifier furnace and then 3.5 cm inside the furnace before reaching its heating zone. The length of the heating zone of the furnace is 11 cm; therefore, the particle should gasify before exiting the heat zone, thereby traveling 19.5 cm. However, after the hot zone, there are an additional 3.5 cm before the end of the gasifier furnace, which could serve as an "extra length" to gasify the particles.

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Table 1. Types of Tests, Species Analyzed, Temperatures, and Number of Tests[a]

tests	temperature	number of tests
pyrolysis (analysis of LH and PAH)	1000 °C	2
pyrolysis followed by combustion (analysis of LH after pyrolysis, LH after combustion, PAH, O_2, CO, and CO_2)	F1, 1000 °C; F2, 900 °C	7
	F1, 1000 °C; F2, 1000 °C	11
	F1, 1000 °C; F2, 1100 °C	9
pyrolysis followed by combustion (total soot, classification of soot per size of particles, O_2, CO, and CO_2)	F1, 1000 °C; F2, 1000 °C	2
	F1, 1000 °C; F2, 1100 °C	2

[a] F1, pyrolyzer furnace; F2, oxidizer furnace.

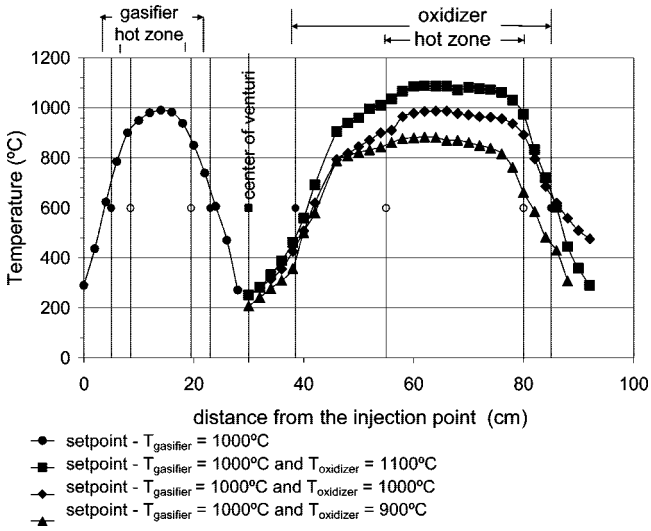

Figure 2. Measured centerline temperature profiles in the gasifier and oxidizer furnaces (temperature in °C).

Upon polymer pyrolysis, the gas reaches the venturi, where its temperature drops to 200 °C. Thereafter, when the gas enters the second furnace, it reaches again a maximum temperature inside the heating zone, which is the nominal temperature of the oxidizer furnace. Both the temperature distribution and the velocity flow field in the two-stage furnace were assessed by numerical modeling using the Fluent 6.0 software package.

3.2. Particle Gasification Calculation/Simulation. Calculations were performed to determine whether gasification of the injected PE particles (38–125 μm) was to be expected within the heated zone of the first-stage furnace. In the calculation method, three parameters were computed: the time to gasify one particle, the length the particle travels before it gasifies, and the velocity of the particle during its flight. For this calculation, outlined in refs 27 and 28, increments of 10 °C in the particle temperature were used starting from room temperature and ending at the pyrolysis temperature of polyethylene, assumed to be 500 °C.[11] After the particle reached such a temperature, it was assumed that the diameter of the particle decreased at a constant temperature. Thus, iterative steps were taken, subtracting 5 μm of the diameter of the particle until complete gasification was achieved. In each iteration, the temperature of the wall of the furnace was approximated using the measured temperature profile, shown in Figure 2. Results from these calculations were compared to the numerical computations executed with the finite-difference code Fluent 6.0.

In the numerical computation, the furnace was designed on Gambit as a 3D cylinder. The code was used to predict the time and distance to gasify a single droplet, released with an initial velocity in the injector corresponding to that of the entering N_2 gas flow. Inputs to this numerical calculation were the temperatures of the gasifier furnace wall, initial particle and gas temperatures, as well as the fluid and material properties (of the gas, polymer, and furnace wall). The program calculated convective heat and mass transfer, as well as the trajectory of the particle based on a force balance.

The residence time of the N_2 gas flowing through the gasifier furnace was found to be 1.6 and 1.56 s in numerical computation and calculation, respectively. The particle heat-up and gasification times along the furnace centerline and the distance traveled by a 125 μm polymer particle in the gasifier furnace, as calculated from both methods, are shown in Figure 3. In the calculation, the time to gasify the PE particle was found to be 160 ms, and in numerical computation, the result was very similar, 154 ms. The distance that the solid particle traveled was found to be 6.15 and 9.76 cm, in calculation and numerical computation, respectively. Both of these values are still much smaller than the aforementioned 19.5 cm length of the pyrolyzer furnace. Even, if an error factor of 2 is applied to the distance encountered in the numerical computation, the 125 μm polymer particle should still gasify within the hot zone of the gasifier furnace. The calculated particle gasification times herein are shorter than those experimentally determined by Derivakis et al.[16] (63–90 μm particles of PE in 700–800 ms) because of the higher heating rates associated with the apparatus herein.

This theoretical analysis suggests that, in principle, it should be feasible to gasify the 38–125 μm PE particles in this specific furnace. However, experiments showed that it was actually difficult to avoid some clumping of the polymer particles because of electrostatic forces, especially at higher equivalence ratios, where high feeding rates were implemented. This adversity may alter the effective particle size and impair gasification.

3.3. Oxygen, Carbon Monoxide, and Carbon Dioxide Emission Yields. Pyrolysis/gasification and subsequent combustion of PE particles at steady-state, steady-flow conditions generated major products, such as those shown in Figure 4. Results shown in Figures 5 and 6 correspond to average values in each test, with the pyrolyzer/gasifier furnace operating at 1000 °C and the oxidizer furnace at operating 900, 1000, or 1100 °C.

Oxygen as well as CO and CO_2 mole fractions are shown in Figure 5 and are compared to theoretical values at different φ values. Corresponding CO and CO_2 yields are presented in Figure 6, along with data from other studies, which are discussed in an ensuing section. The O_2 mole fraction decreased from 15 to 1% as the equivalence ratio increased from 0.3 to 1.4, because increasing amounts of fuel were injected and consumed in the furnace. CO_2 mole fractions reached a maximum of 11% at an equivalence ratio around 1.0 and thereafter decreased. The CO mole fractions were observed to increase with the equivalence ratio. A steep increase was experienced in near-stoichiometric and fuel-rich conditions. There was almost no change in CO_2 and CO mole fractions at different furnace temperatures.

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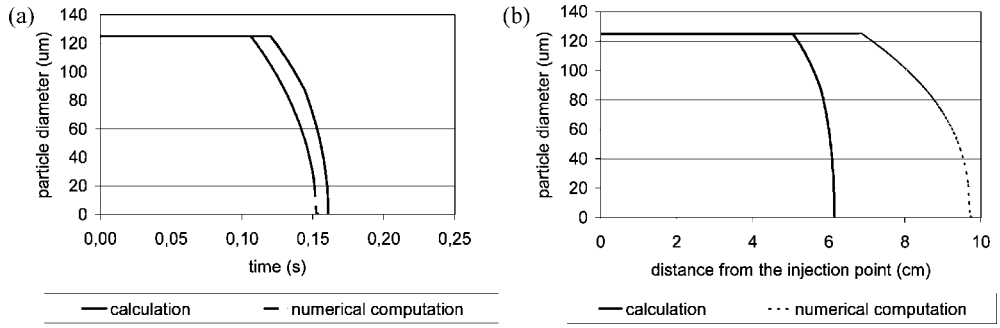

Figure 3. Change in the diameter of an initially 125 μm PE particle versus (a) time to gasify in seconds and (b) traveled distance to gasify in centimeters.

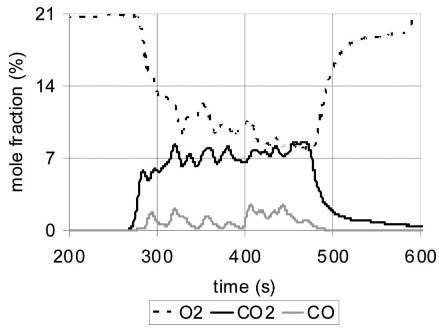

Figure 4. Typical mole fraction–time profiles of fixed gases: CO, CO_2, and O_2. $T_{gasifier} = 1000$ °C; $T_{oxidizer} = 1100$ °C; $\varphi = 0.5$.

According to theoretical calculations, the CO formation at equivalence ratios lower than unity should be minimal. However, the results in the range of $\varphi = 0.5$–1.0 indicate that the particle fluidization and the subsequent mixing of products of pyrolysis with the N_2/O_2 gas in these experiments were perhaps not as effective as expected, given the tendency of PE powders to flash-pyrolyze forming locally fuel-rich regions,[18] and/or local temperatures were conducive to dissociation of CO_2.

The ratios of CO/CO_2 yields are also presented in Figure 6. Note that, the lower equivalence ratios resulted in the lowest CO/CO_2 ratios, showing that only small amounts of CO were generated (especially at the temperature of 900 °C). At higher equivalence ratios, the CO/CO_2 ratios approach unity, because much higher amounts of CO were produced at all temperatures studied.

3.4. Light Aliphatic Hydrocarbon Emission Yields. *3.4.1. Yields from PE Pyrolysis.* A total of 20 light hydrocarbon species were identified and quantified at the exit of the pyrolyzer (kept at 1000 °C). The relative amounts of the most prominent components, representing 90% of the total detected light hydrocarbons (LHs), are shown in Figure 7a. The total and individual LH yields are shown in Figure 8. Yields of these gaseous species decreased somewhat with an increasing particle injection feed rate, in the range of 0.15–0.82 g/min. This range corresponds to nominal equivalence ratios of 0.3–1.4 in the subsequent oxidizer furnace.

3.4.2. Yields from PE Pyrolysis followed by Combustion. Increasing equivalence ratios increased the total unburned light hydrocarbon yields from combustion of PE at the studied temperatures (900–1100 °C), as shown in the superimposed curves in Figure 8. Most individual compound yields followed the same trend. Methane and acetylene emissions exhibited similar behavior to each other; i.e., their yields after combustion increased from 0.01 to 10–30 mg/g PE injected with increasing equivalence ratios. The increase in the yields of these compounds was more accentuated at equivalence ratios up to 1. Thereafter, their yields tapered off. One may observe that the combustion effluent yields of these compounds matched or exceeded the input pyrolysis yields for $\varphi > 0.9$. This was taken as evidence of the formation of methane and acetylene in the oxidizer furnace. This was also the case for the oxygenated compounds benzaldehyde and phenol.

Upon combustion of the pyrolysis effluent in the oxidizer furnace, the yields of ethylene, propylene, 1,3-butadiene, benzene, and styrene remained well below the levels of the corresponding pyrolysis yields, in the broad range of φ studied. This suggests that these compounds are pyrolysis products that are consumed during oxidation, even though some formation during this stage cannot be entirely precluded.

Ethylacetylene, benzene, benzaldehyde, and phenol exhibited mixed results, i.e., their yields were mostly independent of φ. Surprisingly, the toluene yields decreased with φ. The yields of ethylene, propylene, benzene, and toluene from the effluent of combustion at 1100 °C were lower than those at the other temperatures, for the same equivalence ratio. This possibly shows that higher temperatures are more effective in minimizing these compounds because oxidation kinetics are faster, which is in general agreement with the literature.[22,23] They may also be consumed by PAH/soot formation reactions (see Figure 9).

3.5. PAH Emission Yields. In this work, 53 detected PAH species were detected and the 14 most prominent ones are shown in Figure 9. These selected compounds amount to 80% of all of the PAH detected. The condensed-phase (filter paper) and gas-phase (XAD-4 resin) PAHs were combined and analyzed together; thus, every PAH species presented herein is the sum of both phases.

3.5.1. Yields from PE Pyrolysis. Total PAH yields from pyrolysis of the PE particles are shown in Figure 9. Therein, the PAH yields from the gasifier furnace were related to the equivalence ratio of 0.95 and 1.2 in the oxidizer furnace through the feed rate (0.6 and 0.7g/min). The major PAH products of pyrolysis found were phenanthrene, naphthalene, acenapthylene, anthracene, cyclopenta[*cd*]pyrene, indene, benz[*a*]anthracene, fluorene, fluoranthene, and pyrene. The relative amounts of the components are shown in Figure 7b. Such compounds were also reported in the literature, as major PAH products from the pyrolysis of PE at high temperatures.[18,22]

3.5.2. Yields from PE Pyrolysis followed by Combustion. Upon combustion, the total PAH yields were reduced from their pyrolysis levels; this was also the case for most individual compounds. Total PAH amounted to as much as a few mg/g of polymer injected under fuel-rich conditions. Yields increased with increasing equivalence ratios and also with the temperature in most cases (see Figure 9). An exception was anthracene, which varied little with φ. As in the pyrolysis effluent, naphthalene was the most pronounced compound in the combustion effluent, followed by acenapthylene and phenanthrene.

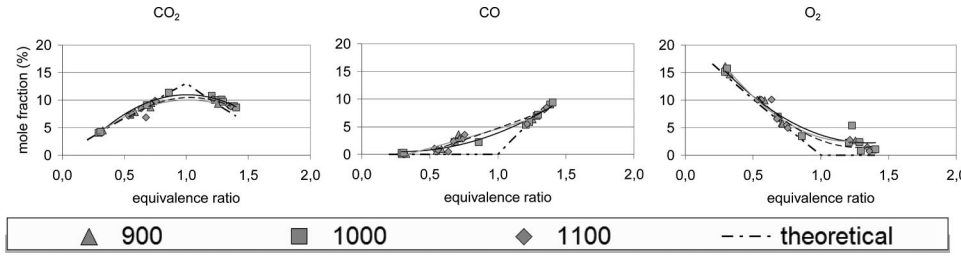

Figure 5. Mole fractions (%) of CO_2, CO, and O_2, as monitored by online analyzers at the exit of the oxidizer furnace, along with superimposed calculated profiles, versus the equivalence ratio.

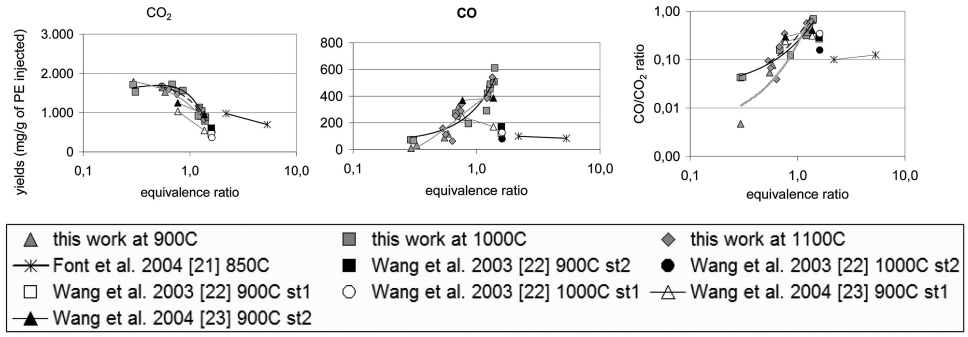

Figure 6. CO_2 and CO yields (mg/g) in the oxidizer furnace effluent versus the equivalence ratio. CO_2/CO ratio versus the equivalence ratio, from data obtained elsewhere.

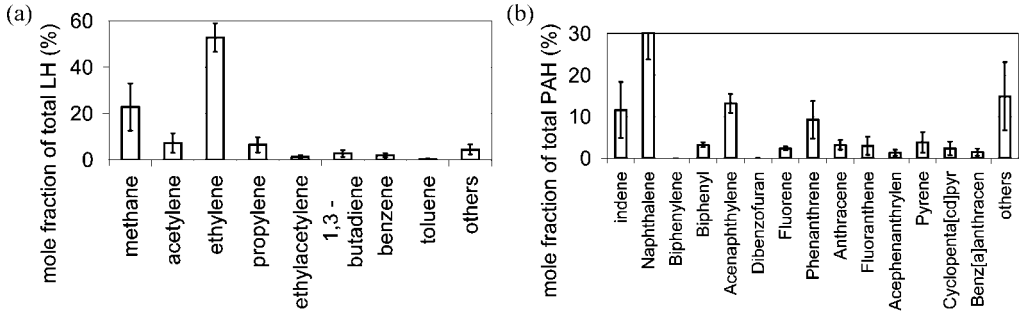

Figure 7. Mole fractions (%) of (a) prominent LHs and (b) prominent individual PAH compounds in the pyrolysis gas.

Whereas most PAH compounds were largely consumed in the combustion process, some aromatic species, such as biphenylene and dibenzofuran, which accounted for a small fraction of the pyrolysis gas, exhibited higher yields in the combustion effluent at the lowest temperature (900 °C). Moreover, the yields of these compounds increased with an increasing equivalence ratio at 900 and 1000 °C, but they decreased with increasing equivalence ratios at 1100 °C. This behavior is likely to indicate that the temperature of 900 °C at high equivalence ratios is not sufficient to promote the oxidation of these specific pyrolyzates. In addition, the PAH/soot formation at higher temperatures may have consumed these compounds.

3.6. Particulate Matter Yields. Average size distributions of particulates produced in the tests using the multistage impactor are shown in Figure 10. The largest amount of soot was found to be smaller than 0.4 μm. Under the nominally fuel-rich conditions, where particulate sampling was conducted, combustion at 1100 °C generated more particulate matter than at 1000 °C and the particle size distribution was also broader. The cumulative soot yields were found to be less than 5 mg/g of polymer injected (see Figure 11a); thus, less than 0.5% of the polymer mass was emitted as soot. The percentage of particulate matter smaller than 2 μm (PM_2) over the total produced (PM_2/PM_{total}) at the conditions of the premixed combustion herein was found to be nearly 100% and was not affected by the temperature of the furnace, as shown in Figure 11b.

4. Discussion

4.1. Emission Yields from Pyrolysis. Conesa et al.[7] studied the steady-flow pyrolysis of PE particles. They found the maximum gas product to account for 97.6 wt % of the polymer, at 800 °C, and its composition to be light hydrocarbons and small aromatics; at lower or higher temperatures, the gas product was lower. The total volatile hydrocarbons (LHs) recovered in the present work at the furnace temperature of 1000 °C amounted to around 70 wt % of the overall pyrolysis gas yield. Moreover, it has been previously shown that increasing polymer feed rates decreases the total gas yields[7] and slightly increases the total PAH yields.[18] The present work also found that increasing the feed rate in the range of 0.15–0.82 g/min (corresponding to equivalence ratios from 0.3 to 1.4) decreased the total gas product, as indicated by the total LH plot of Figure 8.

The composition of LHs in the PE pyrolysis gas collected herein at 1000 °C bears distinct similarities with that reported by Conesa et al.[7] from pyrolysis experiments at 700–900 °C (see Figure 12) and, also, fits the aforementioned temperature trend. Furthermore, the total PAH yields collected from pyrolysis

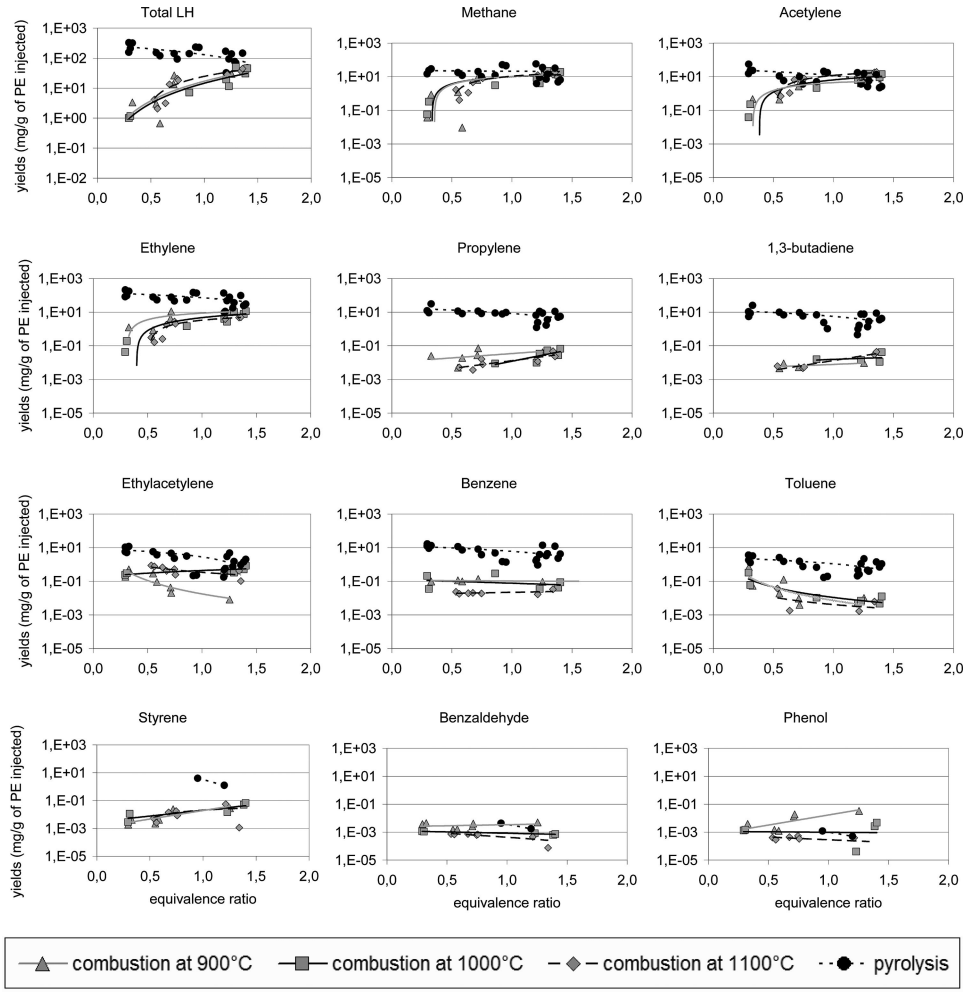

Figure 8. Total LH yields and prominent individual LH yields (mg/g) upon pyrolysis at 1000 °C and combustion at 900, 1000, and 1100 °C, as functions of the equivalence ratio.

of PE herein are of the same order of magnitude as those of others,[18,22] who also employed steady-flow pyrolysis of pulverized PE at 850 and 1100 °C, respectively.

During pyrolysis of PE at high temperatures, direct depolymerization through the β-scission of hydrocarbon chains leads to the production of a gas formed essentially of ethylene, propylene, and other LHs. However, if the residence time is long and the temperature sufficiently high for these compounds to react, the formation of products of secondary reactions, such as methane, hydrogen, acetylene, and PAH, takes place.[15] As in this study, Mastral et al.[15] also detected a considerably large amount of methane, as a final product of pyrolysis, and attributed it to its stability. Moreover, the high amounts of benzene, naphthalene, and phenanthrene in the pyrolysis gas herein confirm the importance of secondary reactions.

4.2. Emission Yields from Pyrolysis followed by Combustion. The CO_2 yields produced by the indirect combustion of PE were comparable to those reported by Wang et al.[22] from direct batch combustion of PE, in conjunction to an afterburner and hot flue-gas filtration. However, CO yields from the indirect combustion of PE were higher than those from the direct combustion of this polymer (see Figure 6). The higher CO yields from indirect combustion, which is nominally premixed, are most likely indicative of the rather uniform mixing of fuel and oxidizer therein, facilitating the partial oxidation of intermediate species to CO.

The total LH yields from indirect combustion of PE, shown in Figure 13, were higher than the yields from direct batch combustion;[22] they were comparable, however, to the yields of direct continuous combustion[21] and direct batch combustion in conjunction with high-temperature filtration.[23] However, the yields of some individual light hydrocarbons, such as acetylene, are at least an order of magnitude higher under the fuel-rich conditions of this work as compared to the effluents of direct combustion. Remarkably, these higher yields of acetylene did not generate higher yields of PAH and soot. Acetylene has been reported to play an important rule in the formation of the first ring of the PAH, as well as in their growth process through the H-abstraction–C_2H_2-addition mechanism.[29–32] Longwell[32] mentioned that acetylene often survives into the post-flame zone, because of its relative low rate of reaction with OH, suffering much less fractional loss in the concentration.

The total PAH yields from indirect combustion of PE were at least 10 times smaller than the yields from the direct combustion experiments in different apparatuses, at all examined temperatures (see Figure 14). The most prominent PAH component, naphthalene, also had lower yields compared to those from direct combustion, but the difference was not as accentuated.

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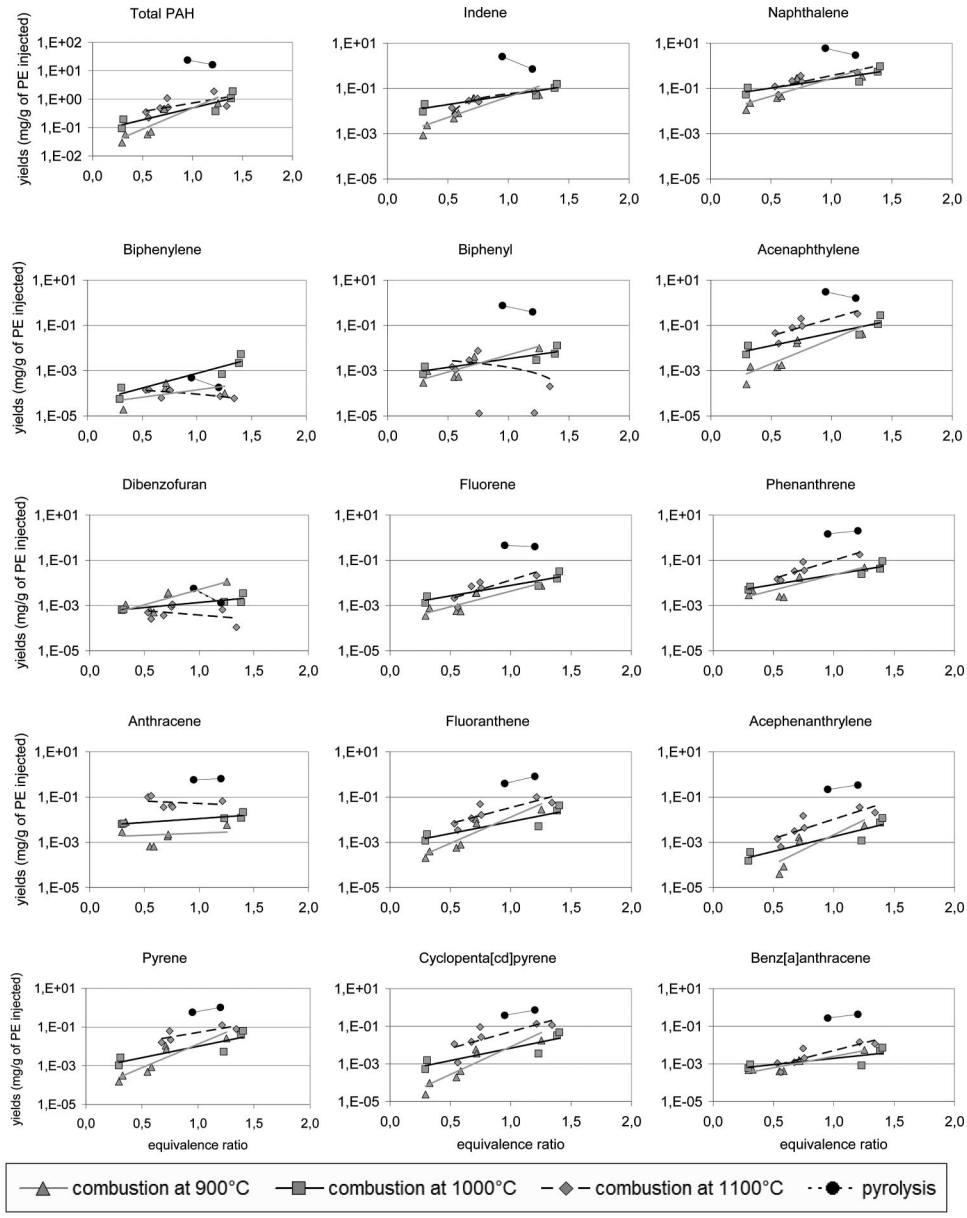

Figure 9. Total PAH yields and yields of individual PAH components (mg/g), upon pyrolysis at 1000 °C and combustion at 900, 1000, and 1100 °C, as functions of the equivalence ratio.

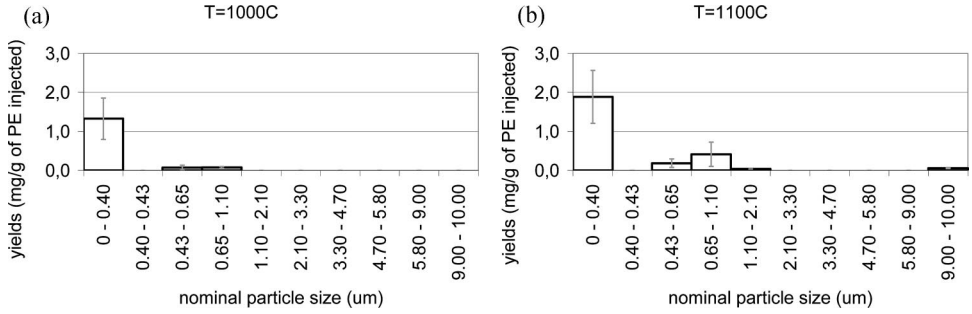

Figure 10. Particulate size distributions (μm) upon pyrolysis at 1000 °C and combustion at (a) 1000 and (b) 1100 °C (yields in mg/g of polymer).

Shemwell and Levendis[24] studied the characterization of particulate emissions (soot) from the direct combustion of pulverized PE in a drop-tube furnace at steady-state, steady-flow conditions (non-premixed flame). They found that the total amount of emitted soot increased with the equivalence ratio φ. They also found that the fraction of PM_2 soot accounted for most (71–97%) of the total soot yield. This is in line with the present work, where nearly the entire mass of soot was found to be PM_2. However, as shown in Figure 11a, the total amount of soot found herein is an order of magnitude lower than that emitted from direct combustion of this polymer. This was somewhat expected on the basis of the relative magnitudes of the aforementioned PAH emissions, because PAHs are precursors of soot.[29–32] The overall smaller size of particles from

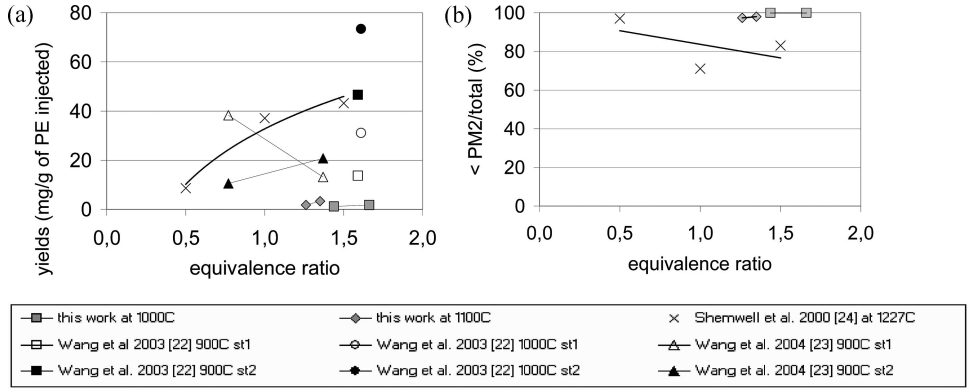

Figure 11. (a) Total soot yields (mg/g) from PE combustion at different temperatures and equivalence ratios from either indirect (this work) or direct (previous work) combustion. (b) PM_2/PM_{total} (%) upon combustion at different temperatures and equivalence ratios.

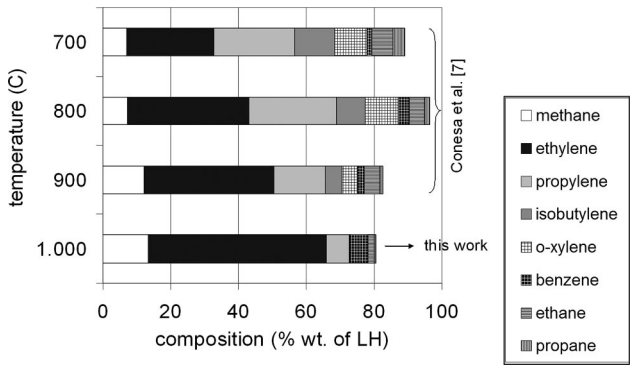

Figure 12. Comparison of the composition of pyrolysis gas (light hydrocarbons) in this work and that of Font et al.[21] at different temperatures.

indirect combustion, as shown in Figure 11b, may be attributed to better mixing of gases, creating fewer regions with fuel-rich conditions, which promote soot growth by condensation and agglomeration.

5. Experimental Uncertainties

Errors may arise from the variabilities in the experimental technique, such as fluctuations in the fluidization of the fuel through the system (as shown in Figure 4), sampling LH and PAH, and transfering of the XAD resin and filter paper to containers for chemical analysis. Calculated carbon balances showed an average recovery of 60% for these tests, where PE pyrolysis was followed by combustion. The standard deviation (σ) of the composition of the gas of pyrolysis, shown in Figure 7, illustrates the repeatability of the tests. For the pyrolysis tests, it was assumed that the unaccounted carbon had the same chemical characteristics as that which was collected, because the gas composition detected herein was in good agreement with that reported by Conesa et al.[7] As mentioned before, the total volatile hydrocarbons (LHs), i.e., the gas, recovered herein amounted to around 70 wt % of the collected pyrolyzate yield. Hence, it was assumed that LH also amounted to 70 wt % of the total yield (collected plus uncollected). The rest was PAHs and particulates (condensed phase). Carbon balances were not calculated for the tests where the impactor stage was used, because PAHs and LHs were not monitored.

6. Conclusions

This work examines the emissions from indirect combustion of PE. Concurrent work, reported elsewhere,[33] has examined the emissions from indirect combustion of polystyrene (PS). Pyrolysis/gasification of the polymer was implemented to generate a predominately gaseous fuel. Upon mixing of the pyrolyzate gases with air, the mixture was burned homogeneously to minimize the products of incomplete combustion. Pyrolysis/gasification was conducted in a furnace operated at 1000 °C. The temperature in the mixing venturi was maintained above 200 °C. Three oxidizer furnace gas temperatures (900, 1000, and 1100 °C) and several fuel/air equivalence ratios ($0.3 < \varphi < 1.4$) were implemented. The O_2 consumption as well as the emissions of CO, CO_2, LHs, PAHs, and particulate matter were monitored.

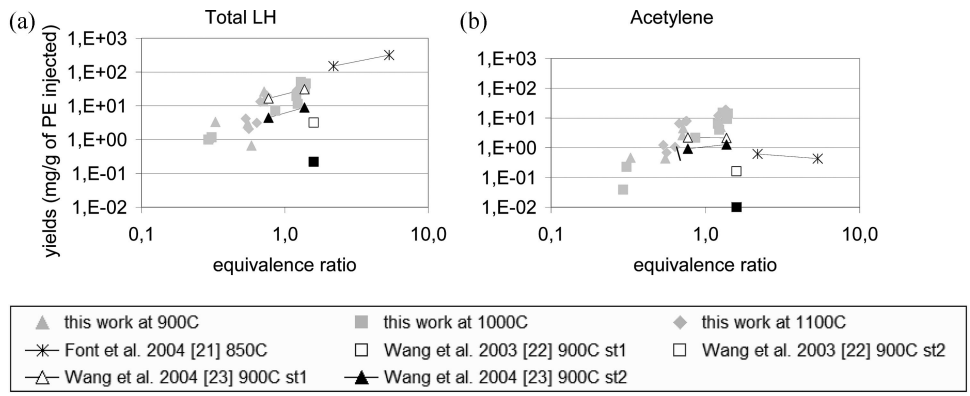

Figure 13. (a) Total LH yields and (b) acetylene yields (mg/g) in the oxidizer furnace effluent, compared to direct combustion yields reported elsewhere.

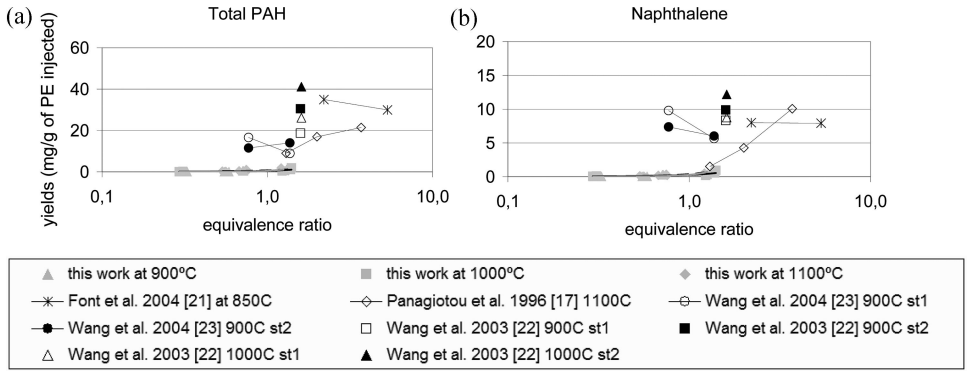

Figure 14. (a) Total PAH yields and (b) phenanthrene yields (mg/g) in the oxidizer furnace effluent, compared to direct combustion yields reported elsewhere.

The CO_2 yields were nearly steady until the equivalence ratio reached unity, thereafter they decreased. There was almost no change in CO_2 yields at different temperatures. CO emissions increased drastically with the equivalence ratio. Whereas the total LH yields from the pyrolysis of PE decreased as the fuel injection rate (related to φ) increased, the total LH yields from the ensuing combustion of the PE pyrolyzates increased as φ increased. The same trend was observed in the total PAH emissions. Combustion at the highest furnace temperature tested resulted in a higher consumption of ethylene, propylene, benzene, and toluene, and consequently, it promoted PAH formation.

A comparison of the indirect homogeneous combustion of PE pyrolyzates, implemented herein, to the direct non-premixed combustion of PE showed that the former combustion mode was very effective in minimizing PAH and particulate (mostly soot) emissions. The total amounts of PAHs and particulates found herein were both 10 times lower than those in the case of the direct combustion of the polymer.

In the combustion effluent, ethylene and naphthalene were the most pronounced LH and PAH compounds, respectively. The major PAH compounds formed in pyrolysis were drastically minimized after combustion; however, some minor compounds, such as biphenylene and dibenzofuran, appeared to be generated during combustion, especially at the lower temperature tested. The majority of the generated particulates was submicrometer in size ($<0.4\ \mu$m). Overall, on the basis of the aforementioned results, it can be concluded that gasifying PE prior to combustion and then homogeneously burning the pyrolyzates with air minimizes the hazardous PAH and soot emissions.

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