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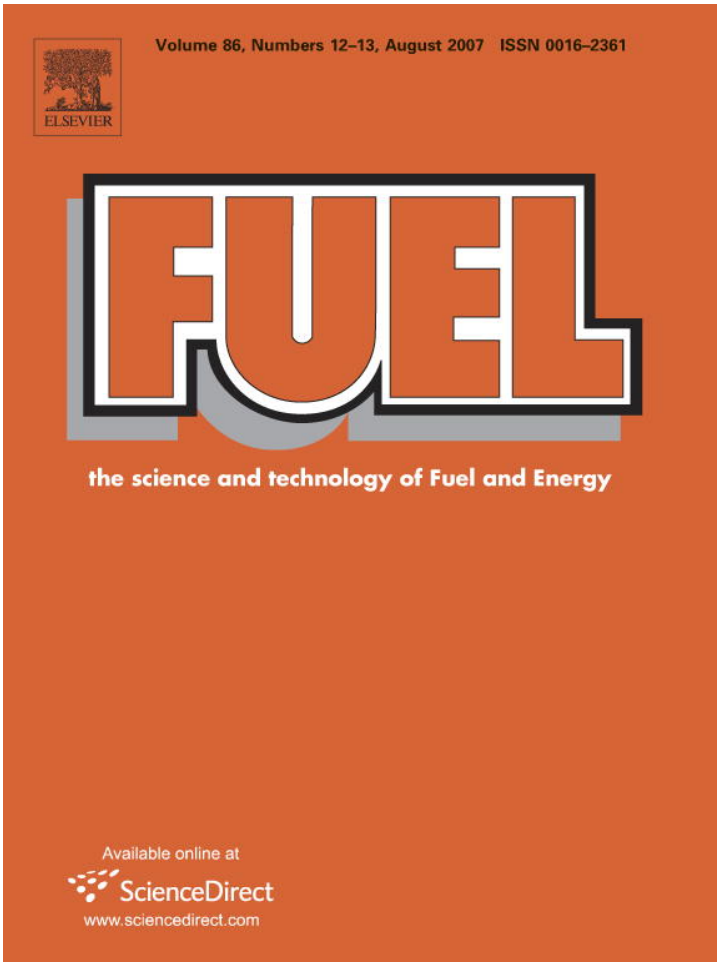

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Emissions from the combustion of polystyrene, styrene and ethylbenzene under diverse conditions

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Abstract

This experimental study contrasts the products of incomplete combustion (PIC) of polystyrene, a widespread solid waste, with those from the combustion of its predominant pyrolyzate, styrene. The study also included ethylbenzene, as it has been reported to convert to styrene extensively and extremely fast in combustion conditions. Emissions were compared from: (i) steady-state combustion of vaporized ethylbenzene in premixed flames, (ii) steady-state combustion of polystyrene powders in a drop-tube furnace, (iii) batch combustion of fixed beds of polystyrene in a muffle furnace, and (iv) batch combustion of pools of liquid styrene in a muffle furnace. PICs, sampled in post-combustion zones, included unburned hydrocarbons, with emphasis to polycyclic aromatic hydrocarbons (PAH), particulates, CO_2 and CO. Yields of major PIC were compared to underscore the differences in the underlying physics of premixed and non-premixed (diffusion) flames. Combustion of polystyrene and styrene in diffusion flames generated soot at any nominal global (bulk) equivalence ratio, no matter how fuel-rich or fuel-lean. On the other hand, combustion of ethylbenzene in premixed flames did not generate any soot up to its soot onset limit, which typically occurs well-within the fuel-rich domain. However, conditions that were not conducive to the formation of soot did not preclude the presence of other PIC, such as PAH.
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Keywords: Polystyrene; Combustion mode; Emissions; PAH; Soot

1. Introduction

Plastics are non-bio-degradable man-made organic materials found in municipal waste streams. They have high volume-to-mass ratios, are discarded at ever increasing rates and create grave landfill concerns. However, since the heating values of plastics are comparable to those of gasoline and higher than those of most types of coal, incineration in waste-to-energy-plants appears to be an attractive solution if emissions of toxic combustion by-products are curtailed.

During combustion of commercial plastics, large quantities of soot and its precursors, polycyclic aromatic hydrocarbons (PAH), are produced. Both soot and PAH are potentially health hazardous. The second most common commercial plastic is polystyrene (PS), accounting for 22 wt% of all the high-volume plastics [1]. Its combustion produces larger amounts of soot and PAH than most other plastics, presumably because of the presence of aromatic rings in its structure [2–4].

To explore effective ways of burning plastics, while minimizing emissions, previous work has studied various modes of combustion. The burning characteristics and emissions of polystyrene (PS) have been extensively investigated in this laboratory [2–12] and elsewhere [13–16], along with other plastics commonly disposed in the municipal waste stream. A brief review of previous research on PAH and soot emissions, in addition to other pollutants, such as CO, benzene and light hydrocarbon species, from the combustion/pyrolysis of polystyrene under batch or

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steady flow conditions in various types of furnaces can be found in Ref. [7].

Experiments involving injection of single particles and groups of polymer particles in a vertical (drop-tube) furnace allowed for observations of their burning characteristics [2–4]. Combustion of PS particles involved two major steps: (a) melting and devolatilization to produce pyrolyzates (hydrocarbon species), (b) oxygen diffusion into the pyrolysis product cloud. Upon ignition, envelop diffusion flames were established. Free-falling burning particles formed flame wake regions, from where most of the soot escaped.

Steady-flow injection and combustion of PS particles in the vertical (drop-tube) furnace was regulated to result in various global (bulk) equivalence ratios, ϕ_{global}. Yields of products of incomplete combustion (PIC), such as PAH, soot and CO increased with ϕ_{global} [3–6].

Batch combustion of fixed beds of various kinds of PS pellets and *Styrofoam* shreds was studied in a two-stage horizontal muffle furnace apparatus [7–11]. The effects of staged combustion, furnace temperatures, oxygen partial pressure, and sample mass were investigated, among other parameters. The first three parameters were found to be influential in minimizing the emissions of PIC. It was also determined that *once soot is formed in a flame, its destruction in a post-flame region is difficult, because of its slow oxidation kinetics therein under typical furnace gas temperatures and residence times.* Thus, a high-temperature ceramic filter was ultimately implemented to capture, retain for extended time, and eventually oxidize soot. Those studies were complemented with efforts in chemical kinetic modeling to elucidate the fate of PAH. Styrene was used as the fuel in the model calculations since PS undergoes complicated depolymerization processes prior to ignition and styrene is the primary pyrolysis product of PS.

Batch combustion of fixed pools of liquid styrene monomer was also experimentally studied in the two-stage horizontal furnace apparatus [12]. While useful conclusions were obtained from that study, observations were often hampered by the unsteady, unpredictable and, at times, explosive combustion behavior of styrene. The unstable character of styrene combustion may be attributed to simultaneous polymerization of styrene and pyrolysis of styrene/PS. Emissions of organic pollutants and soot were higher in styrene combustion than in polystyrene combustion. This is because in the case of styrene, pyrolysis was more intense as the additional depolymerization steps of PS were absent. This could have resulted in locally more fuel-rich conditions.

In the diffusion flames, which were present in the above cases, a broad range of local equivalence ratios existed at any given instant and it is only possible to correlate emissions with global fuel and air mixing ratios, which is some average of local equivalence ratios. To examine the effects of the local equivalence ratio and to observe the evolution of chemical species in the combustion region, premixed combustion is necessary. Although the physics of diffusion and premixed flames differ, the underlying chemical processes that form carbonaceous species have been reported to be essentially similar: "... the properties of the carbon formed in flames are remarkably little affected by the type of flame, the nature of the fuel being burnt and the other conditions under which they are produced" [19]. Because of the unstable combustion characteristics of styrene, ethylbenzene was selected as a surrogate, since it has been reported to convert to styrene extensively and extremely fast [17]. For this purpose, ethylbenzene vapor was premixed with oxygen and then it was ignited and burned in stable, one-dimensional, atmospheric pressure flames [18,22]. As fuel and air were premixed, the equivalence ratio, ϕ_{actual}, of the fresh gas mixture could be well-defined. Fuel-rich flames were implemented to create combustion conditions that generate sufficient amounts of PIC for reliable analysis. A non-sooting ($\phi_{\text{actual}} = 1.68$) flame was contrasted with a strongly-sooting ($\phi_{\text{actual}} = 2.5$) flame to assess emissions of other PIC at the absence and presence of soot.

Given the previously reported evidence of the similarities in the pyrolysis chemistry of ethylbenzene, styrene and polystyrene, the present work contrasts the combustion byproducts of these fuels. The fuels were burned in a variety of disparate apparatuses and operating conditions, such as flat flames, vertical and horizontal furnaces, in either pre-mixed or diffusion flames, at either steady-state or transient conditions. Previous data generated in our laboratory over the years, see publications, [2–12,18,20,22], was combined with some newly-collected data and is presented herein. The impetus of this work is not really to determine emissions, this was mostly already done in previous work, but rather to contrast emissions from disparate combustion conditions/apparatuses, while keeping the sampling and analytical techniques identical. The purpose is to investigate how different fuel properties and widely-different combustion conditions affect the absolute values as well as the relative values of emitted pollutants, such as unburned hydrocarbons (including PAH species), soot, CO and NO_x. The goal is to identify conditions for the combustion of these fuels that are environmentally-benign and, accordingly, to point the way for future research and applications.

2. Experimental apparatus

2.1. Vertical (drop-tube) furnace

Tests that involved continuous injection of polystyrene (PS) powders were conducted in an electrically heated, drop-tube furnace (manufactured by ATS) (4.8 kW max), shown in Fig. 1, see Refs. [2–6,20,21]. To introduce PS particles into the furnace, a bed of PS in powder form was placed in a vibrated glass vial (test-tube), which was advanced by a constant velocity syringe pump (*Harvard Apparatus*). PS particles were entrained in a regulated stream of air, and entered the furnace through a water-

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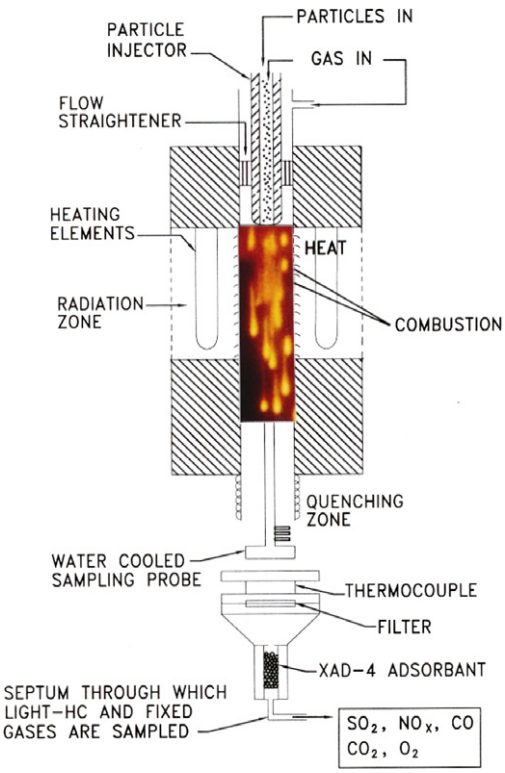

Fig. 1. Vertical (drop-tube) furnace with a sampling stage [2–6,20]. Streams of polystyrene particles were injected and burned under steady-state, steady-flow conditions. The water-cooled sampling probe was only used in the case of investigation of time resolved evolution of species [20].

cooled stainless steel injector. The injection rate of the particles was varied at a constant airflow, to achieve different particle loadings in the furnace and, thus, different global equivalence ratios (ϕ_{global}[1]). The fluidization system, which was used to direct PS particles into the furnace, consisted of a long hypodermic tubing (1.14 mm or 0.045″ inner diameter) from (*MicroGroup*) and two vibrators (*Vibro-Graver* from *Alltech*). The tubing was vibrated to its natural frequency to ensure an unimpeded flow of particles to the furnace injector. The PS particles burned under steady-state, steady-flow laminar conditions forming particle clouds in the combustion zone of the furnace, which was defined by an alumina tube, 3.0 cm in diameter and 25 cm long. As the particles entered the furnace cavity, they gasified/burned in 20–100 ms [2,3]. The gas temperature was set to be 1000–1100 °C for the tests reported herein. The sampling stage was placed directly at the exit of the furnace for the tests where the entire amount of the furnace effluent was sampled. In the case of the investigation of the temporal evolution of the species [20], data was collected with a 4.2 mm inner diameter, water-cooled, insulated stainless-steel probe which was inserted into the furnace from the bottom-end through a Cajon™ fitting (Fig. 1). Sampling proceeded at several vertical distances from the tip of the particle injector, along the centerline of the furnace. The bottom-end of the probe, which was outside the furnace, was connected to a sampling stage through which the exhaust gases were directed to on-line analyzers by a vacuum pump.

2.2. Horizontal (muffle) furnaces

Two-stage batch combustion of fixed beds of polystyrene pellets, Styrofoam shreds [7–11] and liquid styrene pools [12] was carried out in two horizontal furnaces, placed in series. The first stage was a horizontal split-cell muffle furnace (1 kW), fitted with a quartz tube, 4 cm i.d. and 87 cm long. A porcelain boat, loaded with either the solid or the liquid samples, was inserted from the tube's entrance and it was positioned at half-length distance in the pre-heated quartz tube. This primary furnace was connected to a secondary furnace (afterburner), also fitted with a quartz tube, 2 cm i.d. and 38 cm long (see Fig. 2). The effluent of the primary furnace passed through a venturi (8 mm i.d.), where it was mixed with four radially-positioned perpendicular jets of preheated air discharging at the periphery of the venturi. Half of this charge was then sampled at the exit of the primary furnace while the other half was channeled to the secondary furnace. The results referred to in this manuscript correspond to the samples collected at the exit of the primary furnace (i.e., before the afterburner), at an operating temperature of 1000 °C. The entire array of results at the exits of both furnaces has been reported in [7–12]. Unlike the case of polystyrene, the transient diffusion flames over styrene pools were unstable.

2.3. Premixed flat flames on a burner

Premixed, laminar, atmospheric-pressure flat-flames of ethylbenzene were stabilized on a 50.8 mm diameter sintered bronze burner, Fig. 3 [18,22]. Ethylbenzene was chosen over styrene as its flames were stable. The burner temperature was controlled with air flowing through copper tubing embedded in the sintered bronze. Flames were isolated from the ambient air by concentric nitrogen flow, and were stabilized by a water-cooled copper coil, positioned 30 mm from the burner surface. Liquid ethylbenzene (*Aldrich*), placed in 50 ml glass syringes (*Hamilton*) and driven by a dual infusion/withdrawal syringe pump (*World Precision Instruments Inc.*) was introduced into a stainless-steel vaporizer (2 l), which was equipped with a nitrogen-flow-assisted atomizer. Vaporized ethylbenzene was introduced to the bottom of the burner through heated tubing. The vaporizer and the tubing were heated to 150–180 °C, i.e., higher than the boiling point of ethylbenzene (137 °C). The vaporized fuel was mixed with preheated oxygen/nitrogen mixture (50 vol%O_2–50 vol%N_2) prior to the burner and one-dimensional, atmospheric pressure flat flames were stabilized over the burner. Results from two fuel-rich flat flames are reported herein: (a) A heavily

[1] $\phi_{global} = [m_{fuel}/m_{air}]_{actual}/[m_{fuel}/m_{air}]_{stoichiometric}$.

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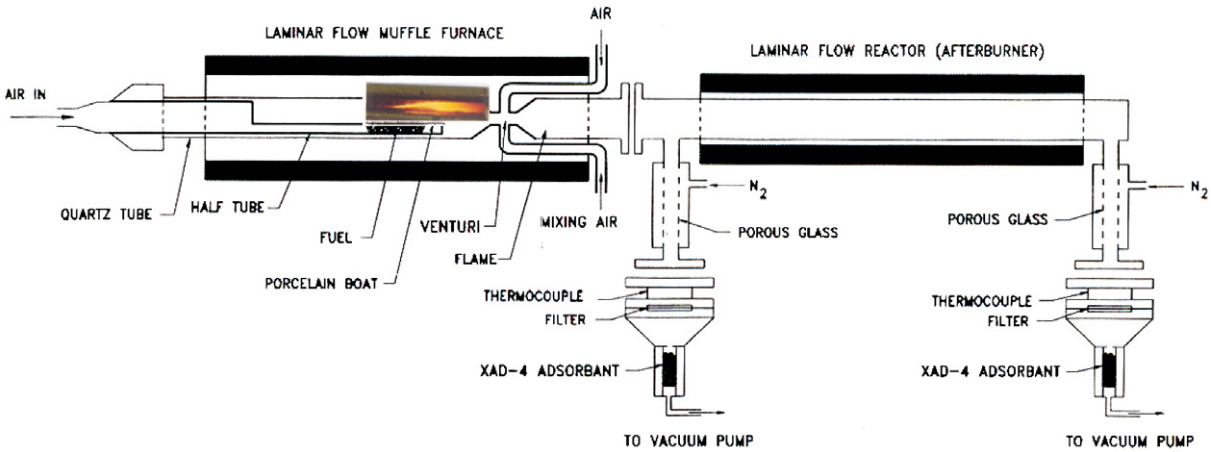

Fig. 2. The two-stage, horizontal, laminar flow muffle furnace with sampling stages [7–12]. Fixed beds of polystyrene pellets or pools of liquid styrene were burned in batches in the first stage. The second stage is an afterburner.

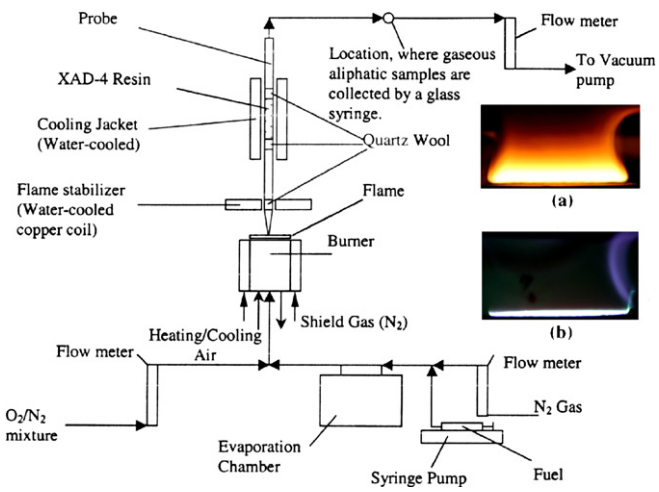

Fig. 3. Flat flame burner, ethylbenzene vaporizer and sampling gear. Ethylbenzene–oxygen–nitrogen premixed flames occurred at (a) $\phi = 2.5$ (heavily sooting) [18] and at (b) $\phi = 1.68$ (non-sooting) [22].

sooting flame at an equivalence ratio ϕ_{actual}[2] $= 2.50$, diluted with 48 wt% N_2, at an initial cold gas velocity of 6.40 cm s^{-1} (at 1 atm, 25 °C), see Fig. 3a [18]. (b) A non-sooting flame, at the verge of the soot onset point, at an equivalence ratio $\phi_{\text{actual}} = 1.68$, diluted with 59 wt% N_2, at an initial cold gas velocity of 7.45 cm s^{-1} (at 1 atm, 25 °C), see Fig. 3b [22].

2.4. Sampling and analysis of exhaust products

Product gases over the burner were withdrawn at different heights in the flame by a water-cooled quartz probe as outlined by McKinnon [23]. A 1-cm i.d. quartz probe was used, with a tip diameter of 4.4 mm. The probe was cut into two sections at a distance of 75 mm from the tip. The bottom portion, containing the tip, was sealed into the cooling jacket with two o-rings to prevent leaks and to keep the piece in a straight position. Quartz wool (from *Ohio Valley Specialty Chemical*) was inserted in this portion and was positioned 10 mm above the tip, to capture condensed species. The advantage of this arrangement was that the quartz wool could be easily inserted to and removed from the probe without significant losses by deposition to the walls of the probe. The remaining 310 mm part of the probe was inserted into the cooling jacket from above through another o-ring, which prevented leaks therefrom. In this part of the probe, pre-cleaned XAD-4 resin adsorbed volatile PAH not captured by the quartz wool. Isokinetic and isoaxial sampling was conducted in the flame, based on an experimentally-determined temperature profile.

Regarding the vertical and horizontal furnaces, the sampling stages at their exits encompassed a paper filter for capturing the particulates and the condensed phase PAH, and a bed of XAD-4 resin for adsorbing the gaseous-phase PAH. After removing moisture by a mildly-heated *Permapure* dryer, CO/CO_2 were monitored using *Horiba* infrared analyzers, O_2, using a *Beckman 350* paramagnetic analyzer and NO_x, using a *Beckman 950A* chemiluminescent analyzer. The output was recorded using a *Data Translation* DT-322 board in a microcomputer. The integrated acquisition system used DT VPI within a *Hewlett-Packard* HP VEE visual programming environment. The signals from the gas analyzers were recorded for the duration of each experiment; subsequently they were converted to partial pressures and, upon numerical integration, to mass yields.

Upon termination of each experiment, the XAD-4 adsorbent and the paper filter or the quartz wool were removed and placed in pre-cleaned vials. Methylene chloride, used to rinse the interior of the quartz probe was also collected to account for all PAH in premixed flames. The samples were spiked with deuterated naphthalene-d_8, acenaphthene-d_{10}, anthracene-d_{10}, chrysene-d_{12} and perylene-d_{12}. After extraction with methylene chloride in a *Dionex* ASE 200 Accelerated Solvent Extractor, analysis was conducted by gas chromatography coupled to mass

[2] $\phi_{\text{actual}} = [m_{\text{fuel}}/m_{O_2}]_{\text{actual}}/[m_{\text{fuel}}/m_{O_2}]_{\text{stoichiometric}}$.

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spectrometry (GC–MS) using a *Hewlett-Packard* (HP) Model 6890 GC with an HP Model 5973 mass selective detector. Details of analysis and calibration have been reported previously [7–12]. The extraction recovery for internal standards for most of the cases was above 80%.

For some tests, samples of light gaseous hydrocarbons and fixed gases were collected by gas-tight 1 mL glass syringes downstream of the XAD-4 resin, and were injected in an HP 6890 Series GC with flame ionization and thermal conductivity detectors (GC-FID/TCD). O_2, N_2, CO, CO_2, C_1–C_4 and small aromatic hydrocarbons were quantified with two parallel columns (100/120 Carbosieve S-II and HP-5/Al_2O_3 capillary column). The instrument was calibrated regularly with CO–CO_2 mixtures and with *Scotty IV* analyzed gas mixtures containing C_1 to C_4-hydrocarbons and single ring aromatics.

Paper filters and quartz wool were weighed before and after every test to quantify the amount of collected particulate matter gravimetrically.

3. Results and discussion

3.1. Cumulative PAH and particulate emissions

Emissions from burning polystyrene, styrene and ethylbenzene in the aforementioned experimental setups were compared at different nominal equivalence ratios ϕ (which for the specific experiments were either ϕ_{actual} or ϕ_{global}). The cumulative emissions of all detected PAH, as well as the emissions of particulates are shown in Fig. 4, whereas the emissions of major individual PAH species are shown in Fig. 5. Please note that the analysis was made with GC/MS, and the isomers were quantified according to their known retention times. Identification of isomer species was accomplished by using GC/MS standards, such as the NIST SRM 1597a PAH standard solution.

Results from injection and combustion of PS powders at steady-state, steady-flow conditions in the drop-tube furnace show that both individual and cumulative PAH emissions increased drastically as the equivalence ratio was augmented from fuel-lean conditions ($\phi_{global} \leqslant 1$) to stoichiometric conditions ($\phi_{global} = 1$). Thereafter milder, but yet substantial increases were observed in the fuel-rich region up to the maximum $\phi_{global} = 3.4$ examined herein, see Fig. 4. The trend of PAH with ϕ_{global} may be characterized as "convex". Particulate emissions also increased with the equivalence ratio, however the trend of the yields of particulates vs. ϕ_{global} is rather different and may be characterized as "concave". Particulate emissions were found to be fairly high at all equivalence ratios, even fuel-lean; in fuel-rich conditions they increased substantially. The above trends illustrate two observed regimes of non-premixed combustion:

I. Under *globally fuel-lean and near-stoichiometric conditions*, PAH are mostly generated in locally fuel-rich conditions in envelope flames surrounding individual particles or particle groups. PAH precursors readily form soot in the furnace, operated at gas temperatures of 1000–1100 °C (1273–1373 K), as maximum measured envelope flame temperatures in single particle combustion or in dilute particle cloud combustion are in the range of 1800–2000 K [4]. Such temperatures are in the range where maximum sooting tendencies have been reported to occur in diffusion flames, i.e., 1900–2300 K [25]. Unconverted PAH, or PAH condensed on soot, readily oxidize at the presence of plentiful bulk oxygen at the aforementioned furnace gas tempera-

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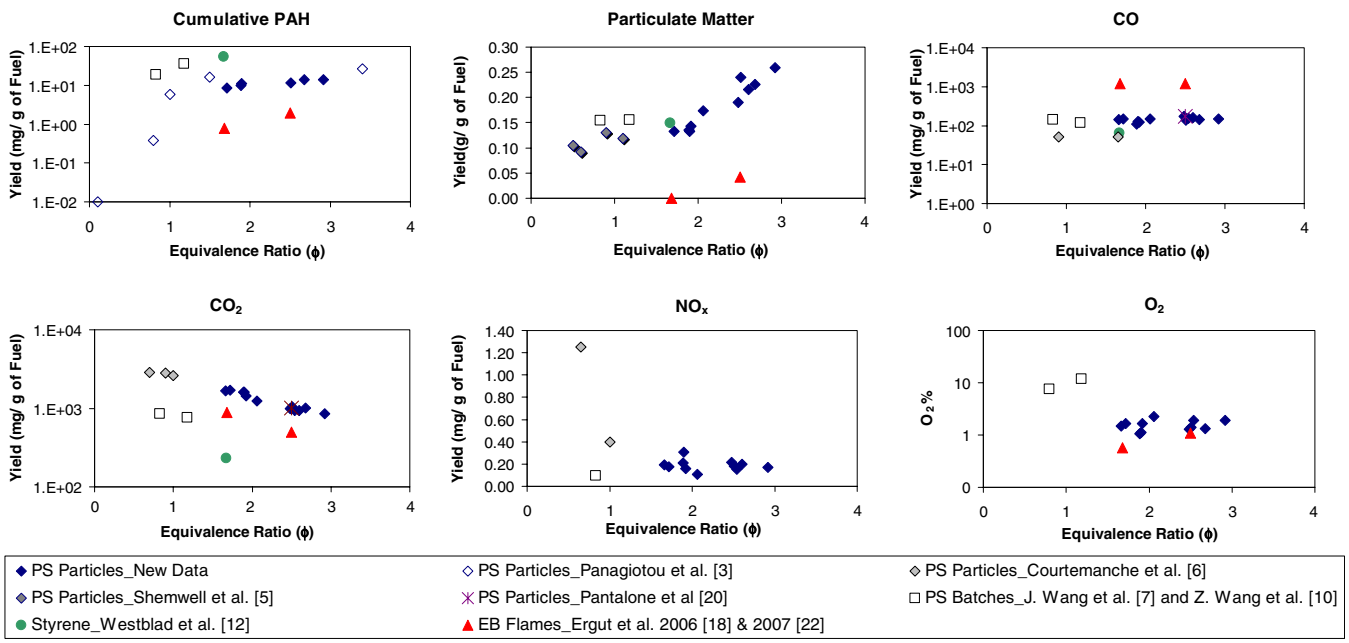

Fig. 4. Emissions of cumulative PAH, particulates, CO, CO_2, NO_x, and un-reacted oxygen from combustion of injected PS particles, batches of PS pellets in beds and pools of liquid styrene, and premixed gaseous ethylbenzene in flat flames as a function of nominal equivalence ratio.

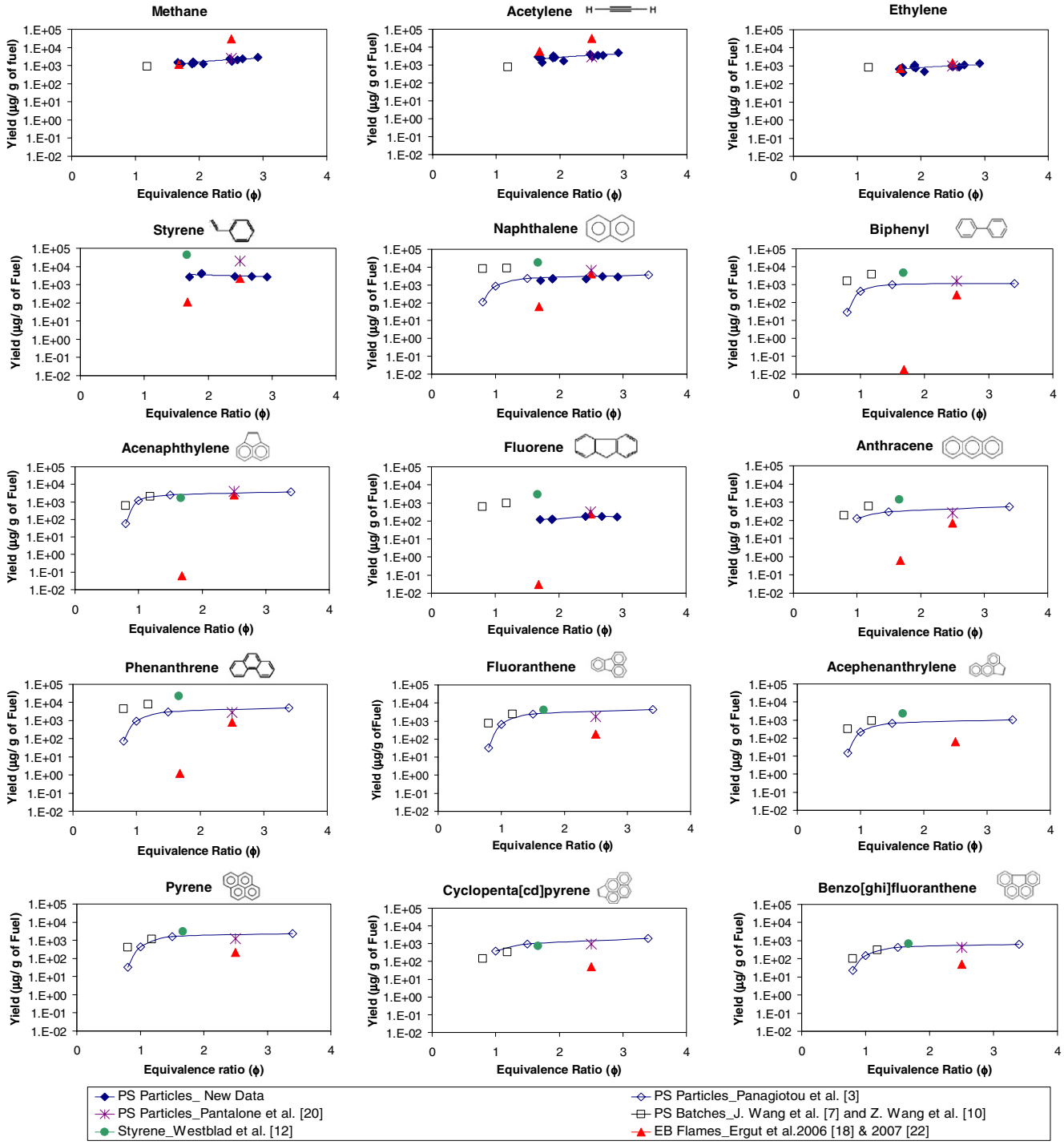

Fig. 5. Emissions of unburned light hydrocarbons and PAH species from combustion of injected PS particle streams, batches of PS pellets in beds and pools of liquid styrene, and premixed gaseous ethylbenzene in flat flames, as a function of nominal equivalence ratio.

tures [3,9]. Most of the remaining PAH, detected at the exit of the furnace, were found to be in the gas phase [3]. Generated soot survives the oxidative conditions in the furnace, as it is very resistant to oxidation at these gas temperatures, given the brief residence time therein (in the order of one second). The resistance of soot to oxidation in the furnace, after extinction of envelope flames, is illustrated in the photographic sequence of burning PS particles depicted in Fig. 6, taken in the same furnace [24]. Soot agglomerates, i.e., soot particles stuck to each other forming chain like structures, are seen to linger in the furnace. Thus, it is sensible to prevent soot formation in the first place; conditions that accomplish this were investigated in Refs. [7–11].

II. Under *globally fuel-rich conditions* more fuel is injected and larger amounts of PAH and particulate matter are formed. PAH oxidation is impeded by the lack of bulk

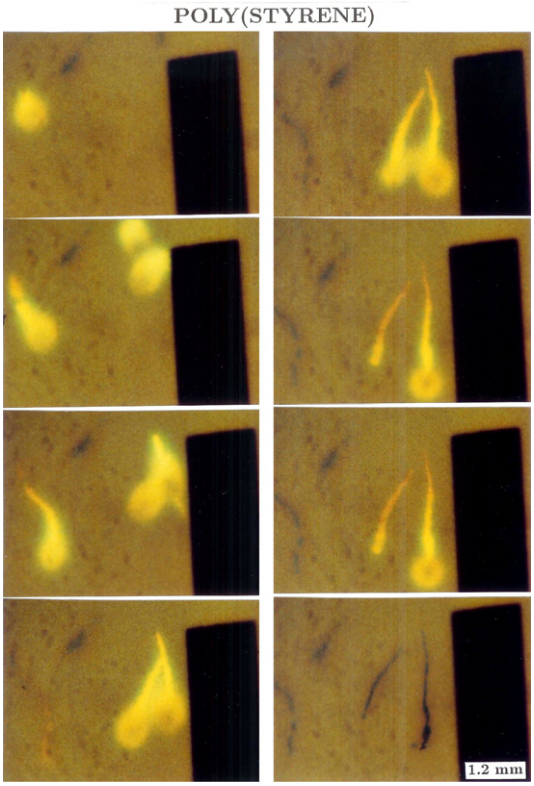

Fig. 6. Combustion of a few spherical and monodisperse polystyrene (60 μm) particles injected in the vertical (drop-tube) furnace captured by high speed shadow photography [24]. A 1.2 mm diameter rod is shown inserted in the furnace to provide a sense of magnitude. Soot filaments were observed to linger in the furnace for a long time upon extinction of the flames at $T_{gas} = 1400$ K.

oxygen and by the moderate flame temperatures. Measured average flame temperatures in dense particle cloud (group) combustion (fuel-rich) were down to 1500–1550 K [4]. Such temperatures are still higher than the 1400 K value above which soot has been reported to form in diffusion flames [25]. In dense particle clouds, where the ratio of the inter-particle distance (l) to the particle diameter (a), $l/a \ll 75$ [3], presumably there are big pools of soot precursors and free radicals which are promoting the formation of soot and hence the consumption of PAH. This results in a relatively flat total PAH yield profile and a steep increase in soot yield profile. In PS combustion this phenomenon became pronounced at global equivalence ratios, $\phi_{global} > 1.5$ (Fig. 4).

The cumulative PAH and particulate emissions from batch combustion of fixed beds of *Styrofoam* shreds or polystyrene pellets (for example, total PAH yields of 19 mg/g of PS burned at $T_g = 1000$ °C (1273 K), $\phi_{global} = 0.83$) were somewhat higher compared to the yields from the steady state combustion of particles injected into the drop-tube furnace. In the latter case, better fuel dispersion, faster heat up and pyrolysis of the smaller fuel entities as well as enhanced mixing of the emanating pyrolyzates with air, etc., improved the combustion efficiency and curtailed the amounts of PIC. This phenomenon is also evident from the lower oxygen concentrations at the exit of the drop-tube furnace, i.e., 2% vs. 10% at the exit of the muffle furnace (see Fig. 4).

Combustion of pools of liquid styrene monomer was unsteady, unpredictable and often explosive, therefore yields of cumulative PAH (totaling 55 mg/g of styrene burned at $T_g = 1000$ °C (1273 K) and $\phi_{global} = 1.67$) were substantially higher than the aforementioned PAH yields from polystyrene powder combustion, see Fig. 4. Particulate yields were also higher, but the difference from steady-state combustion of PS particles was not as pronounced as their difference in the total PAH. During sudden/explosive combustion of styrene vapors, presumably considerable amounts PAH were generated and were exposed to flame temperatures for only short periods of time. Since the flames were unstable, most of these PAH might not have stayed at sufficiently high temperatures to form soot. As a result, a lot of PAH remained un-reacted, whereas particulate matter generation in styrene flames was lower than expected.

The premixed fuel-rich non-sooting ethylbenzene flame ($\phi_{actual} = 1.68$) as well as the sooting ethylbenzene flame ($\phi_{actual} = 2.5$), produced considerably lower PAH yields (totaling 1 and 2 mg/g of ethylbenzene burned, respectively). Corresponding particulate yields from ethylbenzene were 0 mg/g and 42 mg/g of ethylbenzene burned. These values are obviously drastically lower than corresponding emissions produced from the diffusion flames of polystyrene or styrene. The maximum temperature of the non-sooting fuel-rich ethylbenzene flame ($\phi_{actual} = 1.68$) was 1870 K and the temperature at the endpoint of its luminous region (i.e., 7 mm above the burner, at which point results are reported herein), was 1790 K [22]. The corresponding temperatures of the sooting ethylbenzene flame ($\phi_{actual} = 2.5$) were much lower, at 1660 K and 1400 K, respectively [18].

It has been documented elsewhere [25,26] that the role of temperature is opposite in premixed and non-premixed (diffusion) flames. Increased temperatures suppress soot formation in premixed flames; to the contrary, they promote soot formation in diffusion flames. In premixed flames there is competition between the rate of pyrolysis to form soot precursors and the rate of oxidative attack. The oxidation rate increases faster with temperature than the pyrolysis rate. Hence, the hotter ethylbenzene flame ($\phi_{actual} = 1.68$) resulted in much smaller soot yields than the cooler ($\phi_{actual} = 2.5$) flame. In diffusion flames, where there is no oxidative attack on the precursors (at the fuel side), the higher the temperature the greater the pyrolysis rate. This enhances soot precursor formation and, thus, the generation of incipient soot [25]. Hence, the locally hotter dilute particle clouds of burning PS powders ($\phi_{global} < 1$) generated soot yields comparable to those in denser but cooler clouds ($\phi_{global} \sim 2$). As clouds got even denser ($\phi_{global} > 2$), soot yields rose in such oxygen-starved conditions, even if temperatures dropped further.

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3.2. Individual PAH and light hydrocarbon emissions

The yields of most of the individual PAH species experienced similar profiles to that of cumulative PAH, with varying equivalence ratio. Batch combustion of liquid styrene pools, polystyrene pellets and *Styrofoam* shreds generated the highest yields, followed by steady-state combustion of PS powders. Discrepancies became less pronounced for larger PAH, such as four- and five-ring compounds, leading to soot, in the emissions of which discrepancies were also mild (Fig. 4). Premixed flames of ethylbenzene generated the lowest yields of all, especially for the higher molecular weight PAH. Naphthalene and phenanthrene were the most prominent PAH species in all combustion products, closely followed by fluoranthene and acenapthylene. In the diffusion flames encountered in PS combustion as well as in combustion of liquid styrene pools the magnitudes of phenanthrene yields were comparable or marginally higher than the naphthalene yields. However, in the case of the premixed ethylbenzene flames, the yield of naphthalene was one order of magnitude higher than the yield of phenanthrene. Naphthalene, acenapthylene and fluorene as well as styrene were found in relatively high yields in sooting ethylbenzene flames; in the highly sooting flame ($\phi_{\text{actual}} = 2.5$) they were comparable to yields from PS and styrene flames.

Yields of light hydrocarbons, such as acetylene, methane and ethylene were often higher in the case of the premixed ethylbenzene flames. Moreover, it is worth noting that the mole fraction of acetylene was especially high in the sooting ethylbenzene flame. According to Glassman [25], in premixed flames original fuel structures break down to acetylene and soot is formed in the high-temperature post-flame zone. Such a mechanism may comprise elementary reactions involving a sequence of H-atom abstraction and acetylene addition reactions (HACA mechanism) and formation of intermediates, such as vinyl, butadienyl, vinylacetylene and phenylacetylene radicals. In recent years, in addition to the HACA mechanism, the importance of resonantly stabilized radicals in soot formation has also been established. These, relatively un-reactive radicals, such as propargyl (C_3H_3–) formed by the combination of vinyl and methyl radicals with subsequent hydrogen abstraction, may be building blocks of aromatic rings, particularly in the combustion of aliphatic fuels [26,27]. Cyclopentadienyl self-combination has been reported to be the dominant route in the multi-ring aromatic formation process in aromatic fuel flames [28]. Acetylene has also been reported to be an important intermediate in soot formation in diffusion flames through addition to *n*-butadienyl radical (C_4H_5) [25]. Multiple decomposition and formation pathways exist for each aromatic hydrocarbon; their relative importance depends on the flame conditions and the fuel structure. A detailed review of hydrocarbon formation and destruction pathways in large hydrocarbon flames was recently conducted by McEnally et al. [29].

Perhaps a more direct comparison of PIC can be made by contrasting time-resolved sampling data sets form burning PS and EB under steady-state conditions, at the same nominal equivalence ratio of 2.5 (ϕ_{global} and ϕ_{actual}, for the two fuels, respectively). Results are shown in Fig. 7 as a function of the residence time in the post-combustion zone. Again, it should be kept in mind that the mode of combustion was different, as PS powders burned in the drop-tube furnace in particle cloud diffusion flames, whereas ethylbenzene vapors burned in premixed flames. However, combustion was conducted under atmospheric pressure in both cases and measured temperatures, both in the combustion and in the post-combustion zones were not too different. In the case of PS, the maximum measured particle cloud flame temperature was in the neighborhood of 1550 K [4], whereas that in the post-combustion zone it was 1420 K [20]. In the case of premixed combustion of ethylbenzene, the corresponding flame and post-flame temperatures were 1660 K and 1400 K, respectively [18]. Whereas, the absolute values of PAH in PS particle combustion are higher than those detected in ethylbenzene flames, there are often consistent similarities in trends. Styrene, naphthalene, biphenyl, fluorene, phenanthrene, and anthracene, seem to be consumed in the post-combustion zones. Fluoranthene, benzo[*b*]fluoranthene and cyclopenta[*cd*]pyrene seem to plateau in the post-flame region, whereas yet some others, like benzo[*a*]pyrene appear to be on an increasing trend. Chemical pathway analysis was performed extensively in previous work [7–12,18,20,22]. The conditions of each study vary so widely that proposing a common pathway is not possible yet.

3.3. Emissions of CO, CO_2, NO_x and unreacted O_2

CO yields from the two premixed ethylbenzene flames were distinctly higher than those from diffusion-type combustion of PS or styrene, see Fig. 4. In the latter cases a steep increase was experienced in fuel-lean near-stoichiometric conditions [6]. Thereafter, CO yields increased less sharply, ranging from 50 to nearly 200 mg per gram of fuel burned as ϕ_{global} increased from 1 to 3. The much higher CO yields in premixed flames are presumably indicative of uniform mixing of fuel and oxidizer at the fuel-rich conditions therein, facilitating partial oxidation of pyrosynthesized intermediate species to CO.

CO_2 yields experienced a decreasing trend as a function of increasing global equivalence ratio in the fuel-rich domain, see Fig. 4. The results were contrasted to those obtained by Courtemanche and Levendis [6], and the almost linearly decreasing trend was confirmed for the tests conducted in the same drop-tube furnace. The CO_2 yields obtained from burning batches of polystyrene pellets, *Styrofoam* shreds and liquid styrene pools in the horizontal furnace were almost one order of magnitude smaller than the yields obtained from combustion of polystyrene particle clouds in the vertical furnace. This is attributed to poorer pyrolyzate dispersion and mixing with air in the

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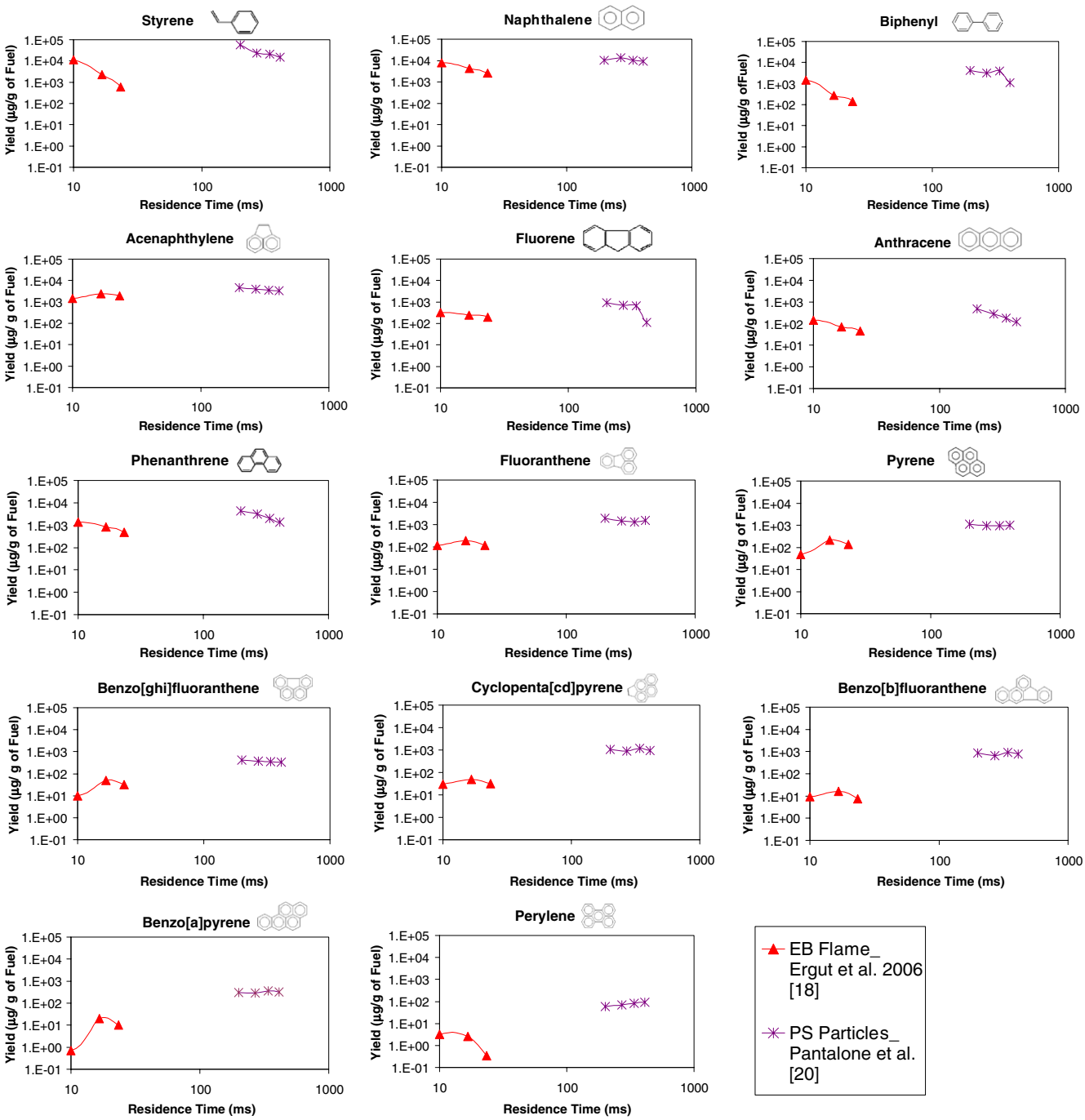

Fig. 7. Temporal evolution of aromatic hydrocarbons in the post-combustion zones of the premixed ethylbenzene flame, and of the injected PS particle streams in the drop-tube furnace both at a nominal equivalence ratio, ϕ, of 2.5. Residence times in the ethylbenzene flame are calculated from the burner surface, whereas in the PS case they are calculated from the tip of the particle injector in the furnace.

former cases as discussed before. Yields of CO_2 in the post-flame zone of premixed ethylbenzene flames were lower than those found in the effluent of the PS particle combustion in the drop tube furnace, but were higher than that of styrene liquid pool combustion in the muffle furnace, at comparable nominal equivalence ratios. Apparently, the prevailing temperatures, short residence-times and low oxygen concentrations in the fuel-rich premixed flames were not favorable for conversion of CO to CO_2. The higher CO_2 emissions from the steady-state combustion of PS particles in the drop tube furnace may be attributed to existence of domains of fuel-lean and stoichiometric conditions in the diffusion flames therein.

Finally, available data for NO_x ($NO + NO_2$) yields are also shown in Fig. 4 both from steady-state and transient combustion of polystyrene. The highest yield in PS particle combustion in the drop tube furnace, 1.2 mg per gram of PS burned, was obtained at a fuel-lean global equivalence

ratio. Therein combustion occurred in dilute clouds and, as mentioned before, maximum measured temperatures of envelope flames reached above the 2000 K mark where the kinetics of "thermal-NO" formation become very favorable. Thereafter, NO_x yields dropped drastically with ϕ_{global}, reaching a plateau at around 0.2 mg for each gram of PS burned in fuel-rich conditions, as maximum flame temperatures subsided to 1550 K. Batch combustion of PS pellets generated lesser yields of NO_x, i.e., 0.1 mg for each gram of PS burned at $\phi_{global} = 0.83$. Such comparatively low values are attributed to the strongly fuel-rich local equivalence ratios that exist in the larger diffusion flames over the bed of fuel in the horizontal furnace, see Fig. 2. To the contrary, dispersed particle combustion provides for a more expansive contact area between fuel pyrolyzates and air, see Fig. 1. Hence, there are many stoichiometric regions (pockets), and the associated higher temperatures favor NO_x generation.

4. Conclusions

This study combined various data sets, either from previous work in this laboratory or newly acquired, on the combustion of polystyrene, on the combustion of this polymer's precursor styrene and on the combustion of ethylbenzene. The latter has been reported to, at least partially, convert to styrene. Combustion conditions among different data sets varied widely (combustion of solids, liquids and gases, steady-state vs. transient, premixed vs. non-premixed, etc.) and comparisons were made over a broad range of equivalence ratios (either ϕ_{global} or ϕ_{actual}). Products of combustion were monitored, including CO, CO_2, light unburned hydrocarbons, polycyclic aromatic hydrocarbons (PAH), particulates and NO_x. Some of the conclusions were predictable or familiar whereas others were unexpected. The reader is invited to examine the presented data and make additional observations.

One of the most basic conclusions of this investigation is that particulate emissions from *diffusion flames* of hydrocarbon fuels extend over a broad spectrum of ϕ_{global}, including the fuel-lean domain, as even therein fuel-rich ϕ_{local} regions (pockets) exist. Even a *single* particle/droplet of a fuel burning alone in the furnace may generate soot, which then may survive in the furnace effluent, as illustrated photographically in this work (Fig. 6). Soot is expected to form, unless the maximum diffusion flame temperatures are lowered below a certain threshold value, reported elsewhere to be 1400 K [25]. This can be accomplished, for instance, by lowering the overall furnace operating temperature, as illustrated in [7]. Moreover, pyrolysis of a fuel under moderate furnace temperature conditions is slowed down to such a degree that the precursors enter the flame and are consumed before they can form particulates. Otherwise, once soot (the carbonaceous core of particulates) forms it is difficult to destroy in post-flame regions of furnaces. To the contrary, in *premixed flames* combustion of fuels can be accomplished smoke-free at equivalence ratios, ϕ_{actual}, that are fuel-lean, stoichiometric or even well into the fuel-rich region, till the soot onset limit is reached (in the neighborhood of 1.7 for ethylbenzene) [22], and not too different for many other fuels [30–32]. This greatly facilitates control in the particulate emissions of premixed flames. However, generating premixed combustion for liquid and, especially, solid fuels is not always practical. As common polymers such as polystyrene, polyethylene and polypropylene are solids, to enable premixed combustion, the solids would have to be first gasified in a pyrolyzer furnace at the near-absence of oxygen. The gaseous pyrolyzates would then become the fuel. The effluent of the pyrolyzer would then be mixed with air in a venturi mixer, and the air/fuel mixture would finally be burned in a separate oxidizer furnace. Accordingly, research currently in progress in this laboratory is focused on such indirect combustion of waste polymers [33]. However, efficiency, reliability and cost are principal issues that need to be addressed in practical systems.

The PAH and light hydrocarbon emissions exhibited trends rather different than those of particulate matter. In diffusion flames, considerable soot emissions may be experienced at the exit of a combustor even in the near-absence of PAH emissions (e.g., in very fuel-lean conditions). To the contrary, in premixed flames one may experience very significant PAH emissions even in the complete absence of soot emissions (slightly leaner than the soot onset limit). Nevertheless, despite the differing phases of the fuels (solid, liquid, gas), and the disparate combustion conditions, there were similarities in the relative concentrations of PAH as well as in their temporal evolution in the post-combustion domains, indeed suggesting commonalities in the chemical mechanisms [25].

A final conclusion pertains to the relatively-higher CO yields in fuel-rich premixed flames as compared to those from fuel-rich diffusion flames. The contrary is true for CO_2 emissions.

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