

Emissions from Combustion of Pulverized Polystyrene at a High Equivalence Ratio

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Abstract

This is an investigation into the formation of products of incomplete combustion (PIC) of poly(styrene) (PS) particles burned in an externally-heated drop-tube furnace at a bulk equivalence ratio of approximately 2.5. Steady-flow dispersions (clouds) of PS particles were introduced into the furnace and burned therein. Iso-kinetic sampling was performed at four different heights along the centerline of the furnace to investigate the evolution of yields of fixed product gases, polycyclic aromatic hydrocarbons (PAH) and light hydrocarbons at different stages of combustion. The flow field and gas temperature distribution in the furnace were calculated with a 3-Dimensional model using the CFD software FLUENT. Work is in progress to assess the profiles of PAH species along the post-combustion zone, however, preliminary results found the yields of 15 selected PAH species (gaseous and condensed) at the lowest probe position to be consistent with data, sampled at the exit of the furnace. Of the measured light hydrocarbons, acetylene had the highest overall concentration, followed by methane, ethylene and benzene. PAH profiles were fairly constant in the sampling zone with yields between 100 μ g and 10mg per each gram of polystyrene burned.

Introduction

The widespread consumption of plastics raises a growing environmental concern since no effective method is known to discard them. Considering their large specific volume [1,2] and the scarcity of landfill space [2], landfilling may not be the best option to get rid of waste plastics. As their heating value is comparable to that of petroleum, incineration combined with energy production is a viable option for the destruction of plastics, if emissions of toxic combustion by-products are controlled to be within acceptable levels. Combustion of polystyrene (PS), which amounts to 22wt % of all the high-volume waste plastics [3], generates larger amounts of polycyclic aromatic hydrocarbons (PAH) and soot than other plastics. This is attributed to the aromatic structure of PS [4,5,6]. Among PAH species, benzo(a)pyrene, fluoranthene and cyclopenta(cd)pyrene are important combustion products which are considered mutagenic/carcinogenic [7]. Phenanthrene has also been identified as potentially hazardous. Inhalation of soot promotes pulmonary and cardiovascular diseases.

Combustion of PS involves two major steps: (a) melting and devolatilization to produce light hydrocarbon species, (b) oxygen diffusion into the pyrolysis product cloud. Upon ignition, a diffusion flame is established. Consequent to examining photographic evidence of the combustion of single particles and groups of particles in a

drop-tube furnace, the high PAH and soot emissions from PS were attributed to combustion in diffusion flames, which form around burning particles. Free-falling, burning particles form flame wake regions, from where most of the soot escapes, see Panagiotou et al. [4,5]. The flames of PS particles burning in groups were more elongated than in single particle combustion, and at high particle loadings (globally fuel rich conditions) all particles merged in a large group flame. In single particle combustion, flame temperatures were recorded to be around 1800°C when the gas temperature was 1000°C. The furnace gas temperature did not affect the flame temperature much [5].

The bulk equivalence ratio has been shown to have a substantial effect on the amount of PAH and soot produced. In fuel lean conditions little soot is produced and most of the PAH are in the gas phase. As the equivalence ratio increases the amounts of soot and condensed PAH increase at a higher rate than the gaseous PAH emissions [4]. At bulk equivalence ratio, $\phi_{bulk}=3.4$, the condensed and gaseous amounts of PAH are similar. As follows, the percentage of mass converted to PAH increases with ϕ_{bulk} , with the highest recorded value being 4 wt %, (during pyrolysis of a thick particle cloud in Nitrogen). [4]

Shemwell et al. [6] reported that 9-25 % of the polystyrene was converted into soot, depending on the temperature and equivalence ratio, and 16-34 % of the total soot was reported to be smaller in diameter than 2 micrometers ($PM_{2.5}$).

Durlak et al. [3] found that there was an exponential decrease in the total number of PAH species and total mass yields when the temperature was increased in their particular conditions, with virtually no PAH observed at 1200°C. At lower temperatures the percentage of PAH mass in the gas phase was substantially higher than in the particulate phase, but at higher temperatures the reverse was true. They also confirmed that there is a significant shift to larger particulates as the furnace temperature increases. They suggested that this increase in particulate size may be due to faster combustion at the higher temperatures, allowing more time for the nucleated particles to grow by coagulation and/or condensation into larger sizes in the furnace.

Wang et al. [8,9] studied the effects of combustion temperatures in two-stage batch combustion of fixed beds of polystyrene. The primary furnace temperature, where polystyrene gasifies and burns in a diffusion flame, was found to be very important for the formation and subsequent emissions of organic species and soot. At low temperatures, large amounts of styrene oligomers were identified at the exit of the primary surface [8], but they did not survive the treatment in the secondary furnace. As the temperature of the primary furnace was raised, the yield of PAH and particulates increased.

The secondary furnace decreased the total amount of PAH, but the amount of some of the larger PAH increased under certain conditions (e.g. cyclopenta[cd]pyrene), such as an increase in either the oxygen mole fraction or temperature [8,9,10]. The emissions of soot were also reduced in the secondary furnace but not drastically, which indicates that soot is resistant to oxidation at furnace post-flame gas temperatures and residence times typical of municipal waste incinerators. Particulate yields decreased with increasing oxygen mole fraction in the afterburner, and at around 50% they vanished. CO yields were also reduced by the afterburner, while CO₂ yields increased. However, as the oxygen mole fraction increased, the CO yields increased, reached an inflection point and then decreased. [10]

This study is aimed at examining the consecutive steps in the chemical processes that occur during and after the combustion of thick clouds of polystyrene particles in a drop-tube furnace. The sequence of chemical and physical processes that cause the previously reported results is probed by sampling the products of incomplete combustion at various stages inside the furnace.

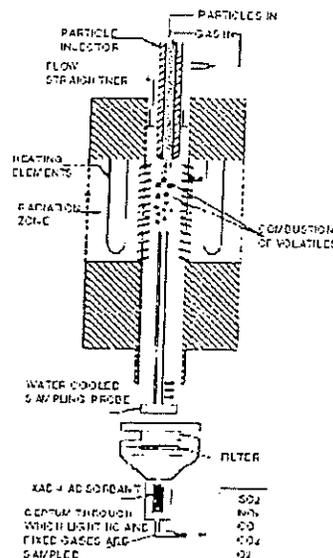


Figure 1. Schematic of the drop-tube furnace with the probe assembly and sampling stage.

Experimental Apparatus and Procedure:

Polystyrene was obtained from *Aldrich Chemical* in the form of large pellets. The pellets were broken into small pieces in a coffee grinder and then they were sieved to various size ranges. Particles in the 180-212 μm size range were used for this particular project. The tests were conducted in an electrically heated, drop-tube furnace (manufactured by *ATS*) (4.8 kW max), Fig. 1. To introduce polystyrene particles into the furnace, a bed of particles 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-cooled stainless steel injector. The injection rate of the particles was around 0.7 g/min, according to targeted bulk equivalence ratio ($\phi_{bulk}=2.5$) and arranged airflow (3 lpm) through the combustion zone.

The fluidization system, which is used to direct PS particles into the furnace, consists of a long hypodermic tubing (1.14 mm or 0.045" inner diameter) from (*MicroGroup*) and two vibrators (*Vibro-Graver* by *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 laminar-flow conditions in the combustion zone of the furnace, which is defined by an alumina tube, 3.0 cm in diameter and 25 cm long. The gas flow rate and temperature were set to 3 lpm and 1100°C, respectively; the resulting gas residence time was ~1s. Furnace wall temperatures (T_w) were continuously monitored by type-S thermocouples embedded in the

wall. Gas temperatures (T_g) inside the furnace, at the absence of injection, were previously measured at various axial and radial positions by an aspirated shielded thermocouple (suction pyrometer), see Steciak et al. 1995 [11]. The gas temperature profile along the centerline of the furnace was found to be fairly isothermal in the radiation zone (see Atal et al., 1995, Figure 2 and Steciak et al. 1995a) [11,12]; ($T_w - T_g \sim 50^\circ\text{C}$).

In this work, suction pyrometry is used to determine the temperature profile in the post-combustion zone along the centerline of the furnace when PS particles are injected and burned. Temperatures are being measured at various distances from the tip of the injector and the temperature profile is obtained along the centerline. This information is then used to verify the computational results obtained from the software FLUENT.

The products of PS combustion were sampled at several points along the centerline of the drop tube furnace. For that task, a 4.2 mm inner diameter, water cooled stainless steel probe was inserted into the furnace from the bottom end through a Cajon™ fitting (Fig.1). The outside surface of the probe was insulated with alumina paper and alumina cement (Zircar Ceramics Inc.) to protect it from high temperatures of the furnace. The end of the probe, which is outside the furnace, was connected to a sampling stage through which the exhaust gases were directed to digital analyzers by a vacuum pump. The sampling through the probe was done isokinetically, i.e. the sampling flow rate was arranged through a precision flow meter to be at the same speed as the gases flowing through the furnace during combustion. The sampling stage encompassed a glass fiber filter for capturing the soot and, thus, the condensed-phase PAH and a bed of XAD-4 resin for adsorbing the gaseous-phase PAH.

After every test the glass fiber filter 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 50 μg each of naphthalene-d8, acenaphthene-d10, anthracene-d10, chrysene-d12 and perylene-d12 was applied to each of the glass bottles containing the samples. To ensure the purity of the XAD-4 resin and glass fiber filter, blanks of resin and filter were also extracted and analyzed. Target compounds that appear in any of the blanks were appropriately qualified based on their concentration. The extraction technique along with analysis by gas chromatography coupled to mass spectrometry was explained in detail in the previous work [8,9]. The GC-MS system consisted of a *Hewlett-Packard* (HP) Model 6890 GC equipped with a HP Model 5973 mass selective detector. The instrument was tuned in accordance with EPA semi-volatile criteria prior to the GC-MS analysis of each set of samples. The instrument passed initial and continuing calibration criteria. Each of the target compounds as well as the tentatively identified

compounds were quantified using the appropriate deuterated internal standard.

In addition, light gaseous hydrocarbons and fixed gases were analyzed using a GC-FID/TCD apparatus (*Agilent* 6890 Series GC system). Samples were collected by gas tight glass syringes at a location after the XAD-4 resin (Figure 1), at the same sampling rate as in the probe. After the tests, the sample in the syringe was injected into the GC apparatus and target products were quantified, using calibration gas mixtures. For the analysis of the light hydrocarbons, an HP-5/ Al_2O_3 capillary column with a length of 30 m, inner diameter of 0.32 mm and film thickness of 0.25 μm was connected to a flame ionization detector (FID). For fixed gases, a 100/120 Carbosieve S-II, 10' x 1/8" stainless steel column was connected to a thermal conductivity detector (TCD).

Thereafter, the effluent was channeled to continuous flow analyzers to measure emissions of NO_x (*Beckman* chemiluminescent NO/NO_x), CO and CO_2 (*Horiba* infrared), and O_2 (*Beckman* paramagnetic). The output of all analyzers was recorded in a microcomputer using a DT 322 Board from *Data Translation, Inc.* The amount of gas that was sampled through the narrow probe (4.2-mm inner diameter) was too small for the analyzers to detect any signal, so it was mixed with additional nitrogen before entering into the analyzers. The signals from the analyzers were recorded for the duration of each experiment, and were later converted from voltage to partial pressures, with the correction for dilution with the nitrogen, before entering the analyzers. Numerical integration of the signals was performed to obtain average values for concentrations of each of the species over the 2-3-minute duration of each experiment. The output of the CO , CO_2 and O_2 analyzers were then compared with the results obtained from the GC to assess the agreement.

Results and Discussions:

Data was collected with a probe at several vertical distances from the tip of the injector, along the centerline of the furnace. Sampling started at a distance of 8.8 cm from the tip of the injector and continued at 15.3 cm, 18.6 cm and 21.8 cm. Noting that the heating zone is 25 cm long and that the tip of the injector was placed at 4.5 cm in the heating zone, the last point is about 1 cm below the heating zone, where the gases start to cool down.

When the polystyrene particles are injected into the high temperature zone, it takes 20-100 ms [4,5] for them to devolatilize, ignite and burn completely in present conditions, which corresponds to 2-2.5 cm from the tip of the injector. Hence, sampling was conducted in the post-flame zone for all of the tests. This is currently under examination.

Yields of fixed product gases, light hydrocarbons and PAH are plotted as a function of the sampling location in the furnace in Fig. 2. The CO yields increased from approximately 110 to 200 mg for each gram of

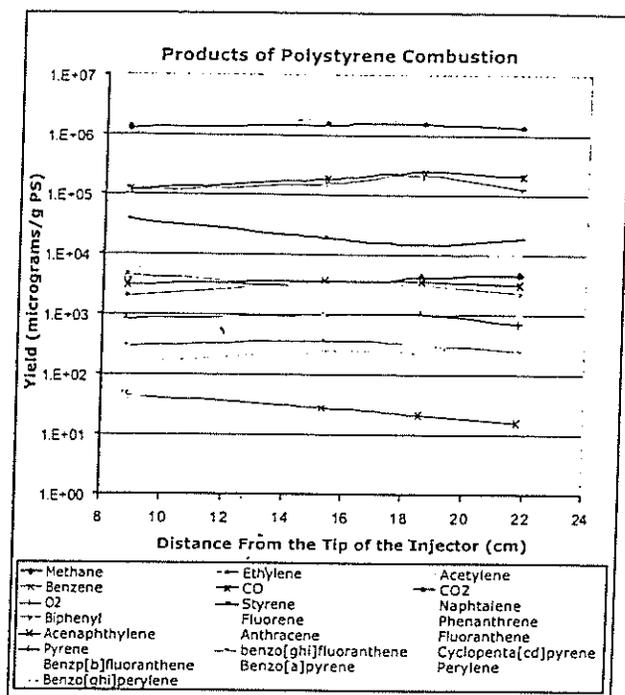


Figure 2. Yields of some major PAH species.

polystyrene injected as the probe moved away from the injector. These yields are slightly higher than those recorded in previous tests, which found a little less than 200 mg per each gram of polystyrene burned at the exit of the furnace [14].

The data for CO₂ showed yields between 1,230 and 1,480 mg for each gram of polystyrene injected, and was fairly consistent for all sampling points, with a slight decrease noticeable towards the end of the furnace. Previous tests for CO₂ at the exit of the furnace showed yields around 1,000 mg per gram of polystyrene burned. This lower yield confirms the drop between the last sampling point in this work and the sampling location in the previous work [14], i.e., the exit of the furnace, 55 cm below the tip of the injector.

Oxygen yield had the same trend as CO and CO₂ had. It increased from 100 to 200 mg for each gram of polystyrene burned between first and third sampling locations, i.e. between 8.8 and 18.6 cm from the tip of the injector. Then it decreased back to 120mg at the end of the heating zone. The averages recorded at the exit of the furnace were slightly below 100mg, suggesting that the drop continued in the cool-down zone.

Light hydrocarbons sampled at the exit of the furnace [14] were in agreement with the values obtained by probe sampling. Acetylene, methane and ethylene, respectively, were the most abundant light hydrocarbons. The yields ranged from 3,000 to 9,800 µg for each gram of polystyrene combusted. Acetylene was the most prevalent light hydrocarbon, and ethylene and methane followed it.

The magnitudes of the yields were comparable to some of the higher molecular weight aromatic species discussed below. Benzene yields were about three orders of magnitude lower, i.e. 15-45 µg for each gram of polystyrene burned. The yields of styrene, the most prevalent pyrolyzate of polystyrene, were an order of magnitude higher than those of the PAH species (Fig. 2). It is consumed downstream in the furnace, hence, experiencing a descending trend.

Work to quantify PAH is in progress. Results reported herein are only from one set of data. Experiments are being triplicated, but the analytical process is laborious and time consuming.

Major PAH, except perylene, were emitted between 100 µg to 10 mg for each gram of polystyrene burned. The most abundant PAH species were identified to be naphthalene, acenaphthalene, biphenyl, phenanthrene and fluoranthene all of which had yields higher than 1000 µg per each gram of Polystyrene burned. Biphenyl and acenaphthalene increased up to 15.3 cm away from the tip of the injector and after this point they started to decrease in yields, suggesting that destruction reactions of these species become more dominant after this point than the formation reactions. Naphthalene yields are in an increasing trend till the end of the heating zone. Phenanthrene yields decrease monotonically in the post combustion zone.

The yields of all of the detected higher molecular weight PAH were between 100µg and 1 mg for each gram of polystyrene burned, except perylene which had yields between 40 and 70µg.

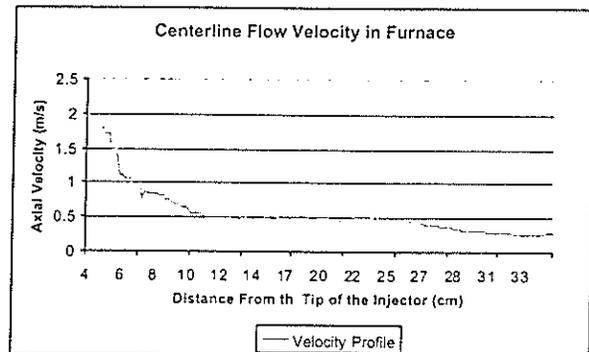
For most of the PAH, the trend was fairly constant in the sampling zone. The yields increased slightly between 8 cm and 18 cm from the tip of the injector, from that point on there was a slight decrease. (Fig. 2)

The assessment of soot yields was somewhat problematic for the following reasons. A fraction of the generated soot was deposited on the inner and the outer surfaces of the water-cooled probe, and could not be quantified. Therefore, the amount of the soot particles that were sampled through the probe was not deemed representative of the entire yield. Especially at locations closer to the tip of the injector, the dispersion of particles is under investigation as it apparently led to a somewhat non-homogeneous distribution. The polystyrene particles entered the furnace entrained in air at 2 lpm, and the auxiliary airflow entered at 1 lpm. Thus, the particle-laden flow through the injector exits as a jet. As stated above, it takes approximately 2-2.5 cm for the particles to devolatilize, ignite and burn completely, therefore, upon combustion soot particulates formed therein have approximately 6 cm to disperse before reaching the tip of the probe, when it is at the uppermost sampling position (8.8 cm). There are some indications, based on hand calculations for axi-symmetric, incompressible ideal-gas flow into quiescent ambient air at constant pressure, that

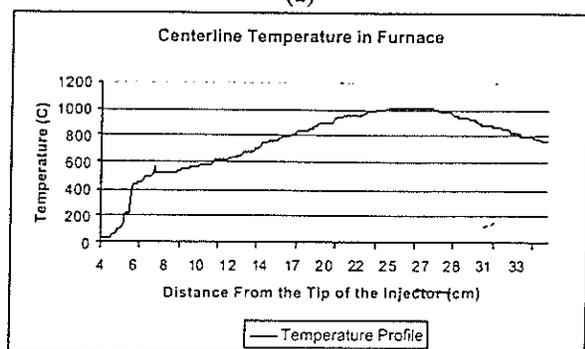
because of the initial momentum of the jet, it does not spread out completely until the latter half of the heating zone. More work in FLUENT is needed to fully establish the velocity profiles based on the sudden expansion and increase in gas temperature. Compared with the soot production of the previous tests at the exit of the furnace, the total soot yield dropped by a factor of three. This could be an indication that relatively more soot was lost in the exhaust collection.

Numerical Simulation of Temperature and Velocity Profiles in the Furnace:

The finite-difference simulation code, FLUENT 5.0, was used to model the air flow in the furnace. This numerical method solves the Navier-Stokes equations simultaneously, using principles of fluid dynamics and heat transfer in order to predict temperature, velocity and concentration profiles. The experiment was modeled with a 3-dimensional cylindrical representation of the furnace and injector, and an implicit, steady state, laminar flow solution was found. The furnace wall temperature and inner injector surface temperature were held constant, while the outer insulated injector surfaces were assumed only to be affected by radiation, with an emissivity factor of 0.9. A cool-down zone was added below the hot zone to simulate conditions as the flow leaves the furnace.



(a)



(b)

Figure 3 (a) Axial velocity and (b) temperature profiles along the centerline of the furnace calculated using FLUENT.

Since the tip of the injector is in the heating zone, temperature and velocity change did not occur along the first 4.5 cm of the heating zone. The axial velocity decreased from 2 m/s inside the injector down to 47 cm/s in the region where gas temperature approached the furnace wall temperature outside the injector (Fig 3a). The average velocity of the gas flow in the furnace based on a flow rate of 3 lpm, the furnace cross-sectional area and a gas temperature of 1100°C, is calculated to be 33 cm/s. The difference may be attributed to the parabolic profile of laminar flow, as the fluent results are maximum centerline velocities. The temperature was predicted to increase up to 425°C from the initial injection temperature of 25°C in the first 1.5 cm from the tip of the injector and then increased asymptotically to near the wall temperature of 1000°C at a distance of 21 cm from the injector tip. Thereafter it decreased in the cool-down zone. See Fig. 6b. The temperatures measured with suction pyrometry were higher than the values predicted by FLUENT and they were almost isothermal throughout the heating zone. FLUENT predicted an increase from 550°C at 8.8 cm from the tip of the injector to 1000°C at the end of heating zone, whereas the measured temperatures increased from 1092°C to 1116°C in the same zone. It has been reported by Cumper [15] that increasing the injection flow rate leads to greater differences between the centerline gas temperature and the wall temperature, most acutely in the region directly below the injector. For example, at a flow rate of 0.1 lpm and a wall temperature of 1230°C, he found that a numerical simulation predicted the centerline gas temperature to be approximately 50°C below the wall temperature at 5 cm from the injector tip. However, at a flow rate of 0.5 lpm the departure from the wall temperature rose to approximately 200°C at the same distance. In general, as the injection flow rate increases to 1 lpm and higher, both numerical and experimental methods produce greater differences of gas centerline and wall temperatures, with the numerical simulation temperature profile tending to diverge more rapidly in the area right below the injector.

Conclusions

When 180-212 μm polystyrene particles are injected into an electrically heated drop-tube furnace at 1100°C, they devolatilize, ignite and burn completely in 20-100 ms [4,5], which corresponds to 2-2.5 cm from the tip of the injector. Hence, sampling was nominally conducted in the post-flame zone for all of the tests in this study. This is being verified. Since PAH are primarily produced in the flame, as it is observed elsewhere in premixed flames [16], the yields recorded herein were fairly constant for each sampling point. Although the combustion herein takes place in diffusion flames, the reactions that take place in the post-combustion zone cause only small changes in the yields. Styrene, the monomer precursor of

polystyrene, resulted in the highest yield, still in the post combustion zone and was consumed till the end of the heating zone of the furnace.

The yields of CO, CO₂ and O₂ had similar trends, all of which increased monotonically until 18.6 cm away from the injector tip, and then dropped. These results were also confirmed with data obtained at the exit of the furnace, 55 cm below the injector. [14]

The flow field and the temperature profiles in the furnace were modeled with the CFD software FLUENT, in order to compare to the temperature measurements conducted with suction pyrometry along the centerline of the furnace. The results of the numerical computation under-predicted the measurements, presumably because the temperature predictions of FLUENT are highly dependent on the injection flow rate which influences the momentum of the flow as it enters the furnace and mixes with the main combustion air.

In future work, the numerical computation will be enhanced to more accurately predict the dynamics of the flow in the region directly below the injector, and will include injection and combustion of polystyrene particles in the flow field. Sampling tests will be repeated to obtain reliable trends. Gas temperature measurements and numerical simulations will be finalized at the presence of burning polystyrene particles in the furnace. Sampling for particulates will be improved. Finally, it is planned to perform computations using a detailed kinetic model, allowing for the prediction of formation and depletion of major PAH and soot particles of different sizes. The computed PAH yield profiles will be compared to experimental data.

Acknowledgements

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