

5<sup>th</sup> US Combustion Meeting  
Organized by the Western States Section of the Combustion Institute  
and Hosted by the University of California at San Diego  
March 25-28, 2007.

## The effects of aromatic species on soot particle size distribution and species concentration in a well stirred reactor/plug flow reactor

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A well-stirred-reactor (WSR) followed by a plug flow reactor (PFR) is being used to study PAH growth and soot inception. For a given fuel-air system, there is a unique fuel-to-air equivalence ratio corresponding to soot inception. This point has been determined for ethylene-air combustion in the WSR/PFR and detailed characterization of the soot particle size distribution and species concentration in the vicinity of this point with and without the addition of specific species (aromatics) thought to be important for soot formation processes were investigated. Two different dilution probes designed for the WSR and PFR sections were coupled to a nano-differential mobility analyzer (nano-DMA) to understand the influence of aromatic species on soot particle size distributions. Concurrently, a gas chromatograph coupled to a mass spectrometer (GC/MS) was used to analyze samples extracted from the WSR/PFR at a known residence time for a given equivalence ratio and additive concentration. These highly resolved measurements are being used to develop and validate a quantitative kinetic database for PAH growth and a soot inception model. Results obtained for benzene are discussed.

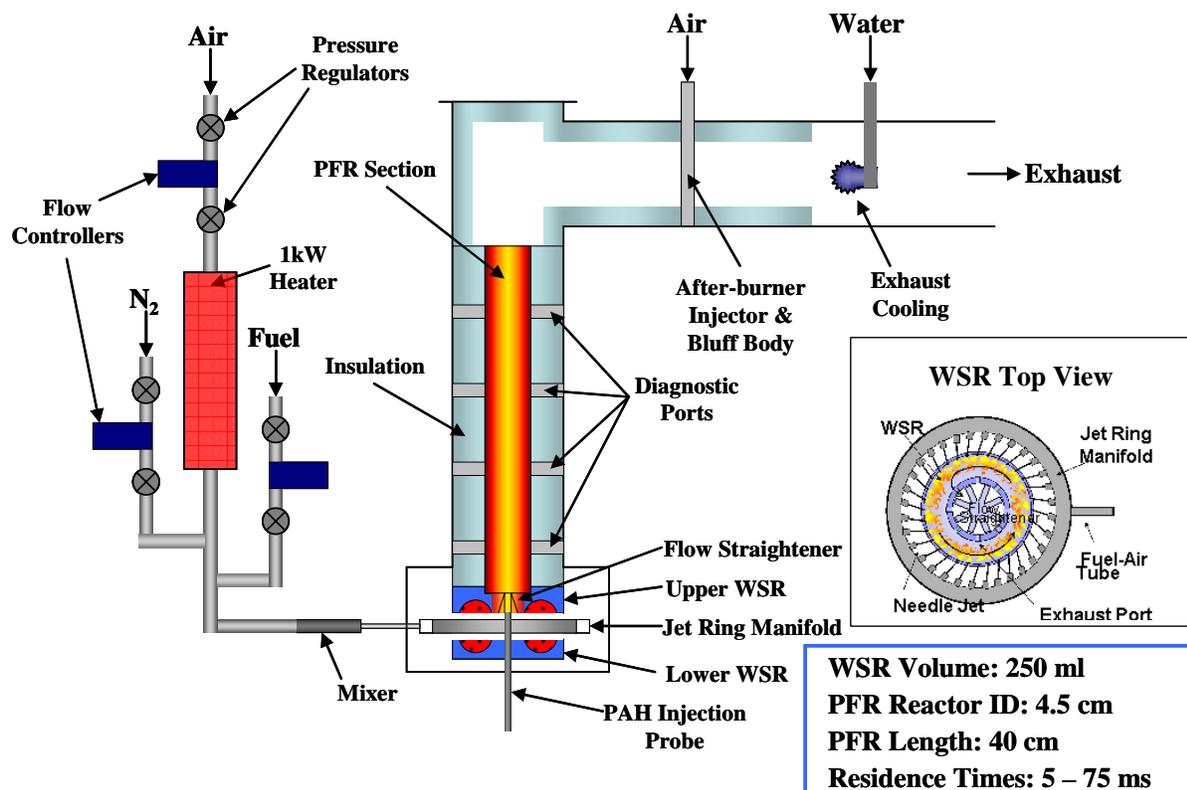
### 1. Introduction

Combustion generated particulates have become an increasingly important environmental issue. There are short term health effects as well as longer term issues related to global warming. As a result, there is much concern over PM<sub>2.5</sub> emissions (particulate matter with diameter of 2.5 microns or less). Clearly, there is the need for a minimization strategy regarding particulate emissions. Physical testing can be enormously expensive and the possibility of computer simulations to extend the range of applicability of direct testing is an attractive alternative. It is increasingly possible to consider the use of such codes with real fuels in real devices; provided such codes are validated using experimental observations.

To this end, a well-stirred-reactor (WSR) followed by a plug flow reactor (PFR) is being used to study PAH growth and soot inception. The focus of the work is to observe the response of the base ethylene PAH/Soot formation system to the addition of a number of aromatic compounds known to be important in soot formation mechanisms. An extensive series of measurements have been performed: determination of soot particle size distributions using differential mobility analysis, analyses of the volatile gases using gas chromatography coupled to mass spectroscopy (GC/MS), and transmission electron microscopy (TEM) of collected soot samples. Ultimately, state of the art particulate inception models will be applied to the experimental observations to provide input data for the modeling of soot formation in real systems with real fuels.

## 2. Experimental Description

The NIST Well Stirred Reactor / Plug Flow Reactor (WSR/PFR) was designed to examine chemical processes free from fluid mechanics and temperature gradient effects [1]. As seen from Figure 1, the reactor is comprised of four parts, namely the WSR, the PFR, the afterburner, and the cooling sections. The WSR, originally developed in 1955 [2], has been used extensively to study PAH and soot formation [3]. The NIST WSR reactor is based on the design currently implemented by Stouffer *et al.* [4]. A well stirred reactor (WSR) coupled with a plug flow reactor (PFR) has many advantages for soot inception studies compared to laminar flames.



**Figure 1:** Schematic of the NIST WSR/PFR experimental apparatus displaying the WSR/PFR assembly and detail of WSR jet ring.

The advantages of sampling particles from the PFR section are the large gas velocity, axial diffusion of species is negligible, the total residence time is spread over the entire length, so excellent spatial resolution is possible, disturbance due to sampling probes is minimal as a PFR does not have flame stability issues, and nearly isothermal conditions exist in the PFR [5]. A WSR/PFR provides combustion conditions that are closer to industrial scale combustors when compared to laminar flames. While many soot studies have been performed using WSR's, diagnostic capabilities have been limited to gas chromatography (GC) and soot collection and analysis using filter methods [2-7]. The NIST WSR/PFR is the most highly instrumented WSR/PFR facility in current use and permits investigation simultaneously of particle properties and gas phase constituents.

The original NIST WSR/PFR system was designed to detect aromatic compounds as they are formed upon passage of fuel through the well stirred reactor (WSR) section and a portion of the plug flow reactor (PFR) (depending on the sampling port). The capability has now been developed where specific compounds can be added directly to the WSR/PFR system itself. The liquid additive was controlled and vaporized using a peristaltic pump and a heated nebulizer. Liquid flow rates from the peristaltic pump can range from 0.3 to 2.5 ml/min. Argon gas was used to drive the nebulizer, which creates droplets ranging in size from 10  $\mu\text{m}$  to 30  $\mu\text{m}$ . The jet of nebulized additive was sprayed into a heated quartz mixing chamber. A stream of heated argon gas vaporizes the liquid droplets and carries the vaporized additive to the reactor. Flow of both argon gas streams are controlled by rotameters, and the total flow of argon is approximately 4 lpm (1 lpm through the nebulizer and 3 lpm as a carrier gas). The heated quartz mixing chamber, argon gas, and transfer lines were all heated to nominally 100  $^{\circ}\text{C}$  to 200  $^{\circ}\text{C}$  to completely vaporize the additive and prevent condensation. The specific additive compound used was benzene.

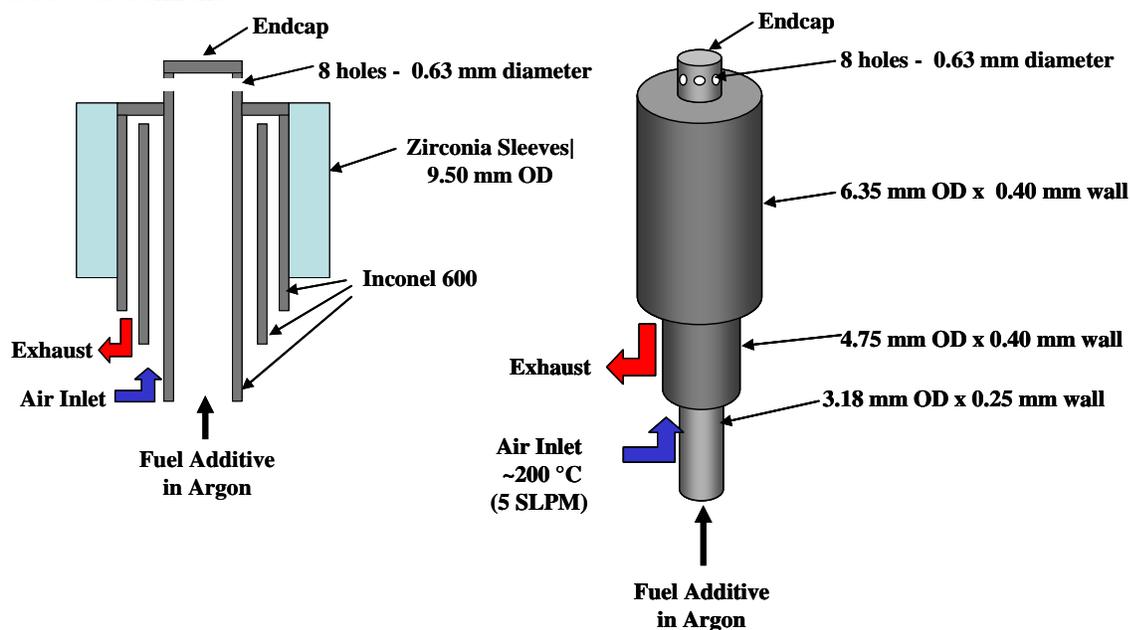
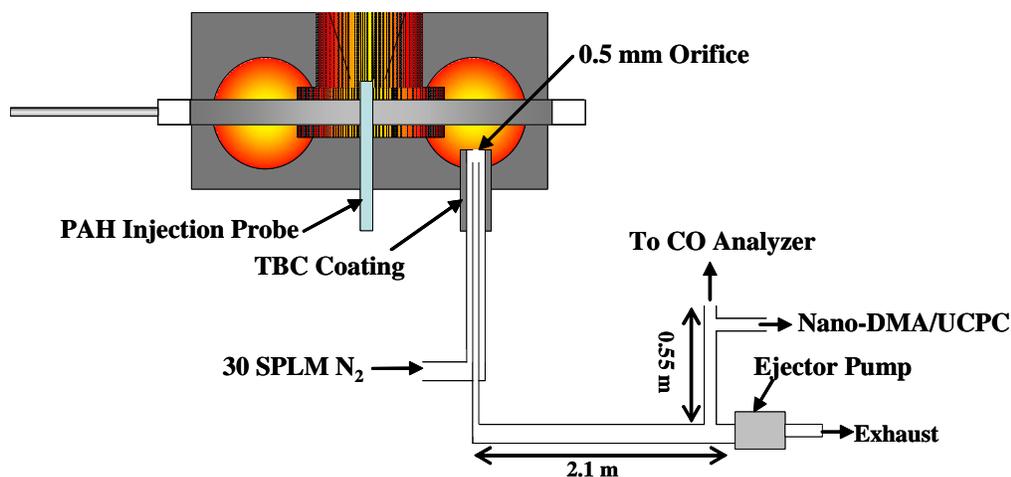


Figure 2: Schematic of Additive Injection Probe.

A detail of the injection probe is displayed in Figure 2 (see Figure 1 for location of injection probe in the context of the WSR/PFR). The injection probe in the present study was inconel and used three concentric tubes to minimize heat transfer to the fuel additive. The tubes of the injector probe were made from Inconel 600 tubing, the outer tube was made from 200 mm long 6.35 mm OD with 0.40 mm wall thickness, the middle tube was made from 300 mm long 4.75 mm OD with 0.40 mm wall thickness, and the inner most tube was made from 400 mm long 3.18 mm OD with 0.25 mm wall thickness. A small endcap was welded onto the center most tube and eight 0.063 mm holes were evenly spaced along the circumference of the tube. The probe used 8 evenly spaced holes around the circumference of the ceramic probe; the holes were 0.063 mm.

Previously reported soot particle size distribution measurements in the NIST WSR/PFR have been limited to those made in the PFR section [1]. In the present study, two different dilution probe designs were utilized in conjunction with the additive injection system to understand the influence of aromatic species on soot particle size distributions as well as delineate how soot is formed in the WSR and PFR sections. The first dilution probe, which was linear in design and located in the PFR section, was based upon the design of Zhao *et al.* [8]. This probe has been described in detail by Manzello *et al.* [1] and will not be discussed further here.



**Figure 3:** Schematic of the coannular nano-DMA dilution probe applied in the WSR section of the reactor.

The second dilution probe was designed specifically to enable soot particle size distribution measurements in the WSR toroidal chamber. The design required a coannular design of limited diameter. Figure 3 shows a schematic of the diluter. The dilution probe was made from a 250 mm long Inconel 601 tube (9.5 mm OD, 7.75 mm ID). An endcap was welded to one end of the tube and a single 0.50 mm orifice was placed in the center of the endcap. A second 350 mm long Inconel 601 tube (6.25 mm OD, 5.15 mm ID) was inserted into the center of the large tube. A gap of 2.5 mm was left between the end of the smaller central tube and the endcap. Nitrogen flow (30 SLPM) was used as a diluent and was directed through the gap between larger and smaller Inconel tubes prior to entrainment and quenching of the particles from the orifice. The exterior of the probe was coated with thermal barrier coating to reduce the heat transfer. Using this probe, temperature of the dilution exhaust ranged from 200 °C – 300 °C depending on the

sampling location in the cross-section of the torriod. Although these exhaust temperatures were higher than probe used by Manzello *et al.* [1], additional insulation was not possible due to the constraints in the port sizes of the torriod chamber.

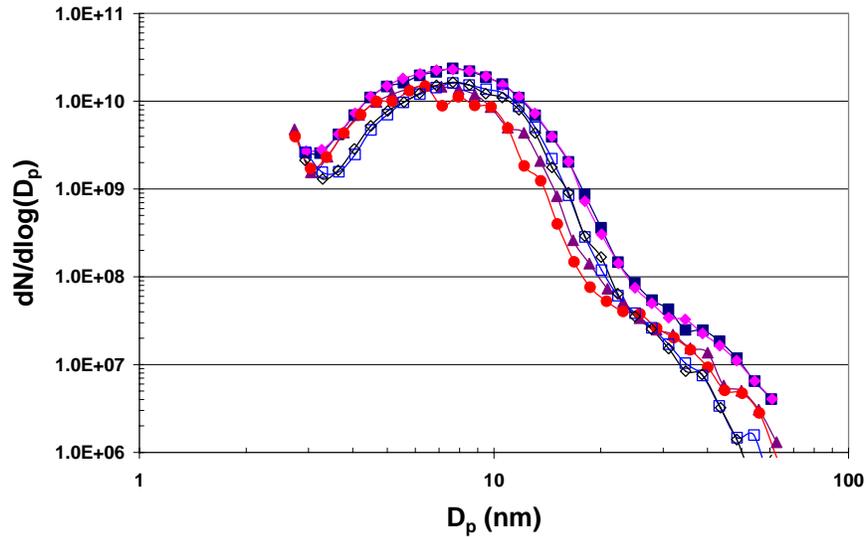
In either probe design, an ejector pump was used to adjust the pressure drop across the orifice to vary the dilution ratio from  $10^2$  to  $10^4$ . Copper tubing, 9.35 mm OD, 2.1 m long, was used to connect the diluter with the ejector pump. A portion of the diluted flow immediately prior to the ejector pump was directed to a nano-differential mobility analyzer (nano-DMA) for particle size and concentration measurements and a non-dispersive infrared (NDIR) analyzer for CO measurements (Horiba Model VIA-510). Copper tubing, 6.25 mm OD, 0.55 m long, was used to direct the particles to a nano-DMA. To determine the dilution ratio, a second CO measurement was made of the undiluted PFR stream at the top most port. The undiluted CO measurement was dried through a combination of wet and dry ice baths. The particle measurement system consisted of a nano-DMA (TSI Electrostatic Classifier Model 3080N) and an ultrafine condensation particle counter (TSI Ultrafine CPC Model 3025A). A detailed description of the nano-DMA measurement technique and associated theoretical foundation are reported elsewhere [1].

Gas chromatography (GC) coupled with mass spectroscopy (MS) was performed on combustion samples extracted from the plug flow reactor at known residence times for a given flame equivalence ratio and additive concentration. Cryogenic cooling of the gas chromatographic system was used in order to have the capability of carrying out a complete analysis of all the gas phase species with a single column. This simplification of the analytical system leads to a corresponding improvement in the relative uncertainty of the measurements that can be made. Further details of the GC/MS experimental methodology are described by Stroud *et al.* [9] in another paper in these proceedings.

### 3. Results and Discussion

The soot size distribution results are plotted in Figure 4 for two different residence times and the two different probe configurations for  $\Phi = 2.0$ . For the present experiments, ethylene was used as the fuel with the air flow rate was kept constant at 175 SLPM and the ethylene fuel flow rate was varied near the soot inception point. All of the soot particle size distributions reported were obtained at a nominal dilution ratio of 1000. The CO measurement technique enabled dilution measurements with an expanded uncertainty of  $\pm 9\%$ . Multiple size distributions were measured for each residence time and probe configuration. Two representative scans are shown in each figure to illustrate the stability and repeatability of the measurements. Two different resident times were examined with the linear probe in the PFR section of the reactor using the bottom most port (closest to the WSR section, Port #1) and Port #3 (305 mm, 12" above the bottom most port). Under the flow conditions, the residence time difference between the two ports was on the order of 28 ms. The peak in the size distribution at the bottom port was nearly identical to that of the longer residence time port. The peak in the size distribution for both residence times occurred at a particle size of 7 nm. One notable difference was the net decrease in the number of particles associated with the longer residence times. Radial temperature measurements in the PFR section showed an approximate temperature decrease of 100 °C near the wall surface, indicating that thermophoretic losses may be the cause of the net decrease in

particle concentrations. The expanded uncertainty in particle diameter and concentration was  $\pm 5\%$  and  $\pm 22\%$ , respectively.



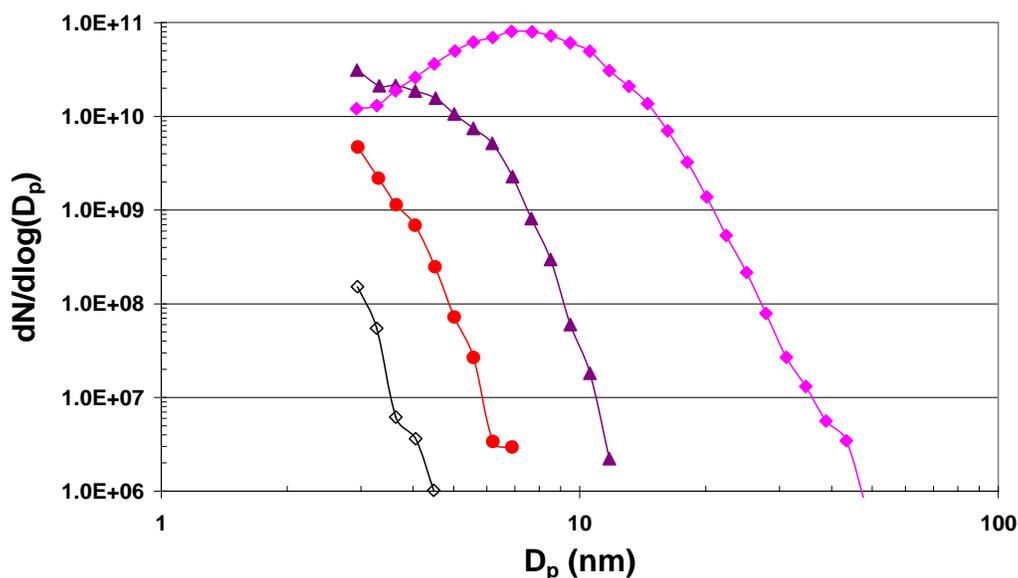
**Figure 4:** Soot size distribution profiles in the PFR section of the WSR/PFR at two different residence times and two different probe designs for ethylene/air ( $\Phi = 2.0$ , 175 SLPM air): (■) Linear probe, Port #1, Scan #1; (◆) Linear probe, Port #1, Scan #2; (▲) Coannular probe, Port #1, Scan #1; (●) Coannular probe, Port #1, Scan #2; (□) Linear probe, Port #3, Scan #1; (◇) Linear probe, Port #3, Scan #2.

A comparison of the two probes was performed at the bottom most port in the PFR; port 1. The number concentration obtained with the coannular diluter begins to diverge from the linear diluter at particle sizes above 6 nm. It is important to note that the orifice in the coannular probe was perpendicular to the flow field of the PFR. This limitation in the highly turbulent environment of the WSR should not impose a significant problem. The integrated results for the total number concentration and the mass concentration are presented in Table 1 for the data of Figure 4. These results demonstrate that soot size distributions obtained using our WSR/PFR at  $\Phi = 2.0$  were not sensitive to residence time in the PFR section and the coannular nano-DMA dilution probe is an acceptable design for sampling in the WSR section of the WSR/PFR.

Probe	Port	Particle Diameter at peak number concentration, Nm	Number Concentration, #/cm <sup>3</sup>	Mass Concentration, $\mu\text{g}/\text{cm}^3$
Linear	1	7.6	$2.20 \times 10^{10}$	$15.3 \times 10^{-3}$
Coannular	1	6.4	$1.29 \times 10^{10}$	$6.2 \times 10^{-3}$
Linear	3	7.6	$1.37 \times 10^{10}$	$9.4 \times 10^{-3}$

**Table I** Integrated results for the total number concentration and the mass concentration based on a soot density of  $1800 \text{ kg}/\text{m}^3$  for the data of Figure 4.

In the WSR and PFR section, the soot size distributions did not show the pronounced inception peaks observed by Maricq *et al.* [10] and Zhao *et al.* [8] in pre-mixed ethylene-air flames generated by a 6 cm diameter, water cooled, McKenna burners. To determine if the lack of an inception peak was the result of the mixing characteristics of the WSR and to begin to investigate the importance of aromatic and PAH species thought to be important in the soot inception process, the fuel additive probe was installed in the transition region between the WSR and PFR. For the aromatic seeding, the flow reactor was operated under non-sooting conditions; specifically,  $\Phi = 1.8$ . Nitrogen (30 SLPM) was added as a diluent to enable long-term operation of the reactor within safe operating temperatures. Benzene was selected as the additive as it is the smallest aromatic in the liquid phase, and has a relatively low boiling point.

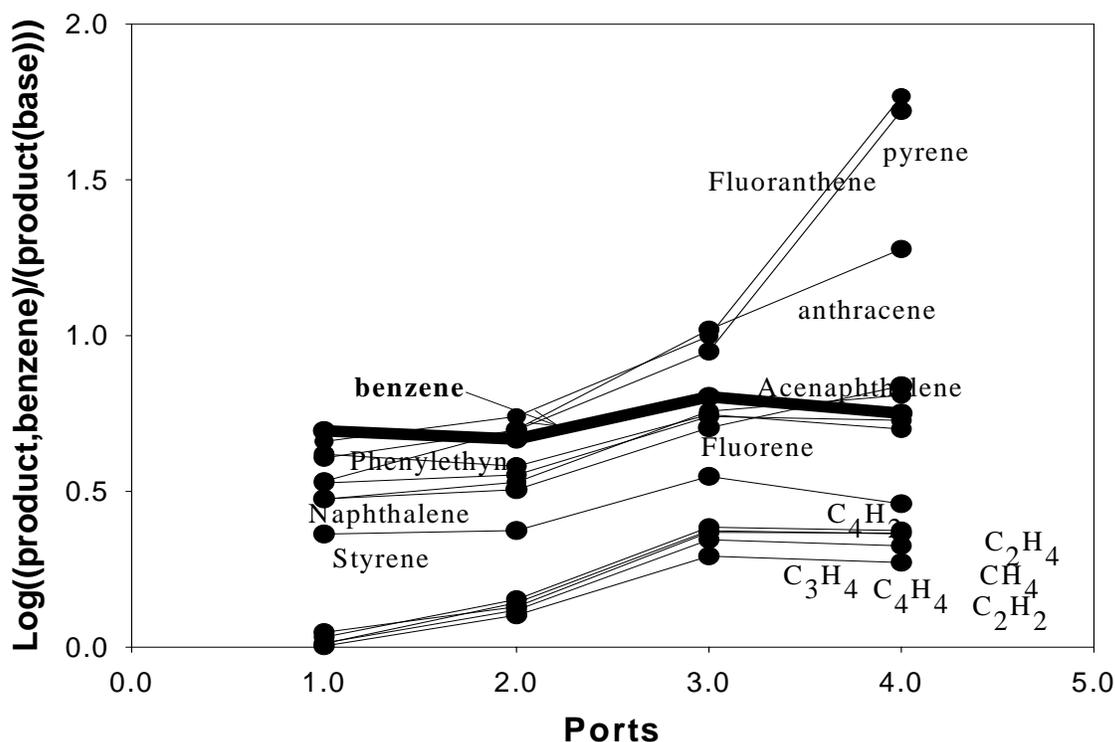


**Figure 5:** Soot particle size distributions using the linear probe in the PFR section of the WSR/PFR at two different residence times for ethylene/air/nitrogen with benzene injection ( $\Phi = 1.8$ , 175 SLPM air, 30 SLPM nitrogen): (●) 0.66 ml/min Benzene injection, Port #3; (▲) 0.97 ml/min Benzene injection, Port #3; (◆) 1.6 ml/min Benzene injection, Port #3; (◇) 1.6 ml/min Benzene injection, Port #1.

Figure 5 displays the soot size distribution measurements for the benzene injection at two different residence times in the PFR section. At benzene flow rates less than 0.3 ml/min, no particle inception was observed at the longest residence times investigated. Appreciable formation of incipient particles was observed once benzene flow was increased to above 0.66 ml/min. As the flow rate was increased further, the peak in the size distribution shifted away from the smallest particle size. At this highest flow rate, the nano-DMA dilution probe was translated to the bottom most port. The soot size distribution changed significantly; the peak in the distribution shifted to the smallest particle sizes and significantly fewer particles were detected. The addition of benzene would result in a shift in the global equivalence ratio of the mixture. At 0.66 ml/min, approximately 725 ppm of benzene was being injected into the reactor, which resulted in an increase of the global equivalence ratio to approximately 1.82. At 0.97 ml/min and 1.6 ml/min, the global equivalence ratio increased to 1.84 and 1.86 respectively.

However, if the ethylene flow rate was increased into the WSR to these equivalence ratios, no particle formation was observed. These results clearly demonstrate that soot inception process can be initiated through the seeding of aromatic species into the WSR/PFR and that the soot inception process is more sensitive to benzene addition than ethylene. It is clear that this methodology represents a powerful tool for unraveling the details of PAH/Soot formation mechanisms.

Typical experimental results on gas phase measurements in the PFR section of the WSR/PFR are displayed in Figure 6. This data is normalized relative to the baseline data of  $\Phi = 1.8$  with no additive. It is clear that as the residence time increases, higher molecular weight molecules are being formed. Particularly interesting is the increasing rate of growth with molecular size. The soot that is collected is yellow in color and appears to be far different than the soot from samples obtained at the exit of the PFR under sooting conditions. One finds that the smaller compounds that are present in the largest amount are least sensitive to benzene addition; this is to be expected. The formation of the larger ring compounds appeared to have some of the characteristics of a branched chain process. However there does not appear to be any evidence that there any single pathway is especially favored.



**Figure 6:** Comparison of changes at four ports in PFR section of some compounds found when 725 ppm benzene is added to system with base ethylene-air combustion. Temperature is 1300 K. Pressure is 1 bar.

#### 4. Conclusions

Two different dilution probes designed for the WSR and PFR sections were coupled to a nano-differential mobility analyzer (nano-DMA) to understand the influence of aromatic species on soot particle size distributions. Concurrently, a gas chromatograph coupled to a mass spectrometer (GC/MS) was used to analyze samples extracted from the WSR/PFR at a known residence time for a given equivalence ratio and additive concentration. These results clearly demonstrate that soot inception process can be initiated through the seeding of aromatic species into the WSR/PFR and that the soot inception process is more sensitive to benzene addition than ethylene. As the residence time increases, higher molecular weight molecules are being formed. It is clear that this methodology represents a powerful tool for unraveling the details of PAH/Soot formation mechanisms. These highly resolved measurements are being used to develop and validate a quantitative kinetic database for PAH growth and a soot inception model.

#### Acknowledgments

The project was funded by grant to W. Tsang and S.L. Manzello through the Strategic Environmental Research and Development Program (SERDP) under the DoD; Mr. Charles Pellerin is the program manager. DBL acknowledges support from an NRC Post-Doctoral Fellowship. The assistance of Mr. Marco G. Fernandez, Engineering Technician at BFRL-NIST, was crucial in performing these experiments.

#### References

- [1] S.L. Manzello, D.B. Lenhart, A. Yozgatligil, M.T. Donovan, G.W. Mulholland, M.R. Zachariah, and W. Tsang, *Proc. Combust. Inst.*, 31 (2007) 675-683.
- [2] J.P. Longwell and M.A. Weiss, *Ind. Eng. Chem.*, 47 (1955) 1634-42.
- [3] F.W. Lam, J.P. Longwell, and J.B. Howard, *Proc. Combust. Inst.*, 22 (1988) 323-332.
- [4] S.D. Stouffer, R.C. Striebich, C.W. Frayne, and J. Zelina, "Combustion Particulates Mitigation Investigation Using a Well-Stirred Reactor," 38th Joint Propulsion Conference & Exhibit, 7-10 July 2002 Indianapolis, Indiana, AIAA 2002-37.
- [5] F.J. Wright, *Proc. Combust. Inst.*, 12 (1969) 867-875.
- [6] W. Blazowski, *Combust. Sci. Tech.*, 21 (1980) 87-93.
- [7] J.E. Nenniger, A. Kridiotis, J. Chomiak, J.P. Longwell, and A.F. Sarofim, *Proc. Combust. Inst.* 20 (1984) 473-479.
- [8] B. Zhao, Z. Yang, J. Wang, J., M.V. Johnston, and H. Wang, *Aerosol Sci. Tech.*, 37 (2003) 611-620.
- [9] C.B. Stroud, W. Tsang, and S.L. Manzello. "Detailed Modeling and Analysis of Aromatic Additive Effects in Ethylene-Air Flames," 5<sup>th</sup> Joint Meeting of the US Sections of the Combustion Institute, 26-30 March 2007, San Diego, CA.
- [10] M.M. Maricq, *Combust. Flame*, 37 (2004) 340-350.