

12-16 July 2015, Bellevue, Washington

Characterization of carbon particulates in the exit flow of a Plasma Pyrolysis Assembly (PPA) reactor

Robert D. Green¹, Marit E. Meyer², and Juan H. Agui³
NASA Glenn Research Center, Cleveland, OH, 44135, USA

Gordon M. Berger⁴
Universities Space Research Association, Cleveland, OH, 44135, USA

R. Vijayakumar⁵
Aerfil Corp., Liverpool, NY, USA

and

Morgan B. Abney⁶ and Zachary Greenwood⁷
NASA Marshall Space Flight Center, Huntsville, AL 35812, USA

The ISS presently recovers oxygen from crew respiration via a Carbon Dioxide Reduction Assembly (CRA) that utilizes the Sabatier chemical process to reduce captured carbon dioxide to methane (CH₄) and water. In order to recover more of the hydrogen from the methane and increase oxygen recovery, NASA Marshall Space Flight Center (MSFC) is investigating a technology, plasma pyrolysis, to convert the methane to acetylene. The Plasma Pyrolysis Assembly (or PPA), achieves 90% or greater conversion efficiency, but a small amount of solid carbon particulates are generated as a side product and must be filtered before the acetylene is removed and the hydrogen-rich gas stream is recycled back to the CRA. In this work, we present the experimental results of an initial characterization of the carbon particulates in the PPA exit gas stream. We also present several potential options to remove these carbon particulates via carbon traps and filters to minimize resupply mass and required downtime for regeneration.

Nomenclature

CRA	=	Carbon Dioxide Reduction Assembly
EDS	=	Electron Dispersive Spectroscopy
HACA	=	Hydrogen Abstraction-Actelyene Addition
MSFC	=	Marshall Space Flight Center
OGA	=	Oxygen Generation Assembly
PPA	=	Plasma Pyrolysis Assembly
SEM	=	Scanning Electron Microscopy
TRL	=	Technical Readiness Level

¹ Aerospace Engineer, Fluid Physics and Transport Processes Branch, 21000 Brookpark Rd, MS 77-5.

² Aerospace Engineer, Combustion Physics and Reacting Processes Branch, 21000 Brookpark Rd, MS 77-5.

³ Aerospace Engineer, Fluid Physics and Transport Processes Branch, 21000 Brookpark Rd, MS 77-5.

⁴ Research Associate, Combustion Physics and Reacting Processes Branch, 21000 Brookpark Rd, MS 110-3.

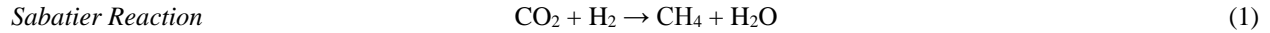
⁵ President, Aerfil Corp., Liverpool, N.Y.

⁶ Lead Aerospace Engineer, ES62 ECLSS Development Branch, MSFC, AL 35812.

⁷ Aerospace Engineer, ES62 ECLSS Development Branch, MSFC, AL 35812.

I. Introduction

IN order to achieve increased oxygen recovery in spacecraft air revitalization systems, NASA is developing oxygen regeneration systems with greater than 75% oxygen recovery. The state-of-the-art oxygen recovery system on ISS is the Carbon Dioxide Reduction Assembly (CDA) that incorporates a Sabatier reactor to reduce captured carbon dioxide from the ISS atmosphere with H₂ generated via the Oxygen Generation Assembly (OGA) The reaction, as seen in Equation 1 below, produces methane and water:



Presently, the methane is vented to space, but the NASA Marshall Space Flight Center (MSFC) is investigating a relatively new technology, based on a microwave-generated plasma used to partially pyrolyze methane to acetylene. This enables the life support architecture to recover more of the hydrogen and as a result, increase oxygen recovery. This technology, presently at the TRL 4, has achieved >90% conversion efficiency in extended testing [1] and is a prime candidate for an ISS flight demonstration to mature the technology. One challenge of the technology is that a small quantity of solid carbon particulates are generated as a by-product. These particulates must be filtered before the acetylene is removed and the hydrogen-rich gas stream is recycled back to the CRA to avoid fouling or deactivation of the Sabatier catalyst. Some work has been performed to develop a carbon trap [1] with the ability to capture some of the carbon particulate load, but conventional 10 and 40 micron filters downstream of the carbon trap have confirmed that some particulates remain in the gas stream.

In this work, we present the experimental results of an initial characterization of the carbon particulates captured by these filters, along with additional short residence time filters to obtain a more accurate assessment of particle size range. Lastly, we will present several potential options to remove these carbon particulates, given the size range, with minimizing resupply mass and required downtime for regeneration as prime considerations. The paper is composed of two sections. In section II, we discuss the result of scanning electron microscopy (SEM) imaging from three separate sources: a 10 μm pore filter, a paper towel temporarily wrapped around the 10 μm pore filter, and a separate 40 μm pore filter mounted downstream of the 10 μm filter. In section III, we present the initial SEM imaging results for a series of 37 mm sampling cartridges, designed specifically for capturing low loads of particulates to gain better insight on particle size and characterization.

II. Characterization of carbon particulate samples from 40 micron and 10 μm pore filters

As part of the operation of the PPA, two different types of carbon traps were installed and evaluated [1]. In addition, two types of filters were installed downstream to capture remaining particulates that passed thru the carbon trap. Figure 1 contains photos of these two filters, along with a paper towel that was wrapped around the outer diameter of the 10 μm pore filter for a short duration. These filters were exposed the PPA exit stream for several hours at 2 and 4 crew member (CM) gas flow rates, 700 sccm and 1400 sccm respectively, which are the CH₄ corresponding to the CO₂ processing rate necessary for a 2 and 4 member crew.

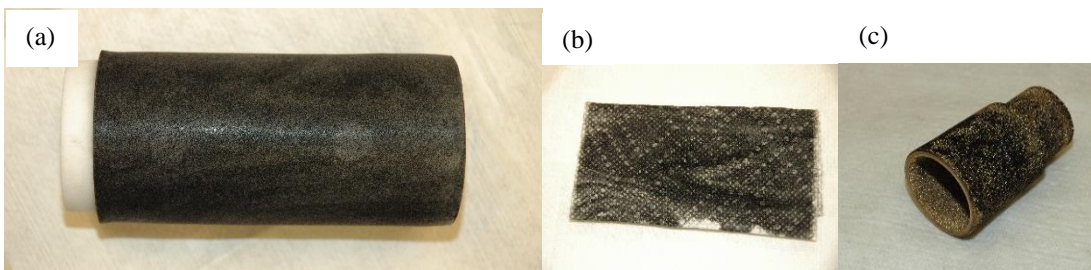


Figure 1. Photographs of the various filters sampled for particulates. (a) 10 μm pore filter (porous polyethylene) (b) paper towel (c) 40 μm pore filter (porous brass).

The 10 micron pore filter, shown in Figure 1 (a) was installed ~6 inches downstream of the PPA carbon trap to capture carbon particulates that passed through the carbon trap. Both the paper towel (wrapped around outer diameter surface of a 10 μm stainless steel filter in place of the polyethylene filter for a short period of time (<1hr)), and the 40 μm pore filter (mounted downstream of the 10 μm filter) were used to confirm that carbon particulates were getting

past the 10 μm pore filter. [Note that it is a good practice in filtration design to position first the largest pore size filter and cascade to the smallest pore size filter in series to optimally capture particulates in all size ranges. In our particular example, it was a matter of convenience to mount the paper towel and 40 μm pore filter in the manner described, with the primary reason to simply detect if particulates were getting past the 10 μm pore filter.]

Preparation of samples for SEM imaging. The sample was taken from the external surface of a 10 μm pore filter, from the 2 light “spots” visible in Figure 1 (a), by manually “dabbing” the filter surface with a 1 cm diameter carbon tape “dot” commonly utilized to mount loose material samples for SEM imaging. The sample was then sputtered with a 5-10 nm layer of platinum to enhance conductivity and reduce localized charging of the sample from the electron beam. Although the carbon particulates and carbon tape substrate are highly conductive, we surmise the low interfacial contact of sample to substrate did not provide sufficient conductivity for optimum SEM imaging. A Hitachi S-4700 scanning electron microscope was utilized for imaging and for electron diffraction spectroscopy (EDS). Low magnification manual scanning of the sample was performed to assess uniformity. Images were taken with emphasis on places where the sample stuck off the edge of the larger clumps of material. This was of primary interest in order to observe true particle adhesion and avoid any falsely-induced agglomeration due to manual pressing of the sample onto the carbon tape. Samples from the 40 μm filter and paper towel were prepared in a similar manner.

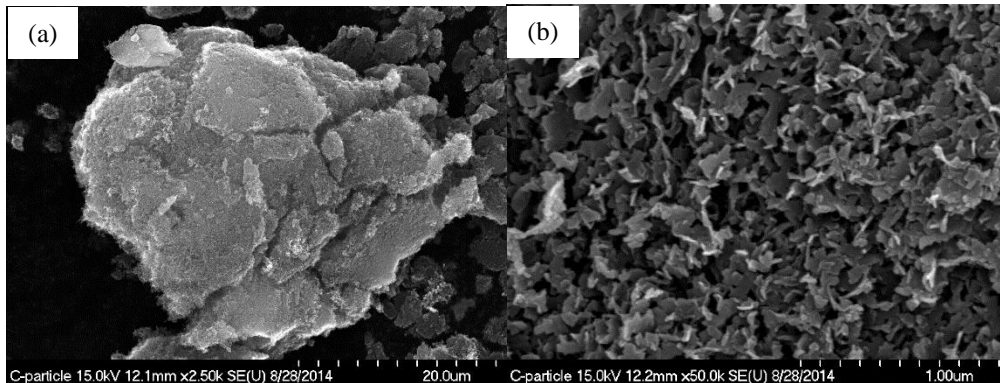


Figure 2. SEM images of loose carbon debris from 10 μm pore filter. (a) low magnification of a typical sample of filter cake. (b) high magnification image of “plate-like” formations.

10 μm pore filter sample. In Figure 2 are SEM images at low and high resolutions. The sample consisted of a wide range of fairly large particles dislodged from the filter “cake” or layer formed on the outer surface of the filter in the process of transferring a sample to the carbon tape substrate; Figure 2 (a) shows a low magnification of a ~ 30 μm size particle with a near uniform slightly filamentary structured surface. Figure 2 (b) displays a high magnification image of the particle surface; the thin “plate-like or sheet-like” structure of the particles is the main feature of the surface, indicating the likely formation of graphitic-type carbon.

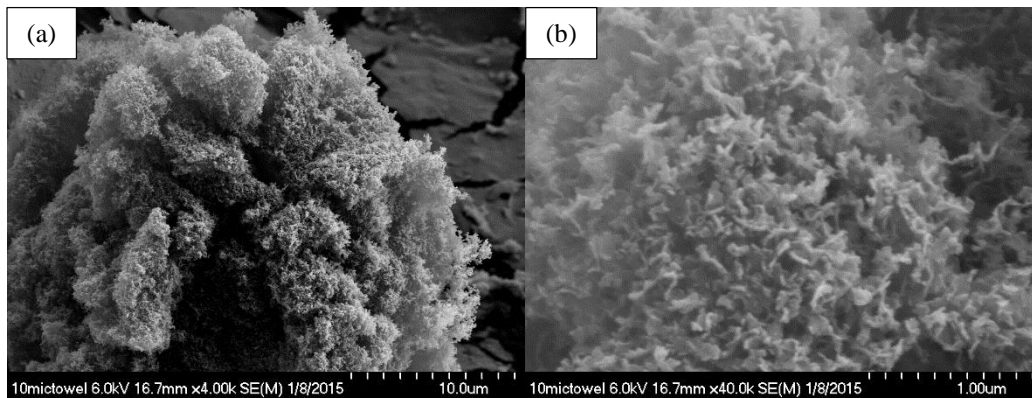


Figure 3. Low (a) and high (b) magnification image of particle from paper towel sample.

10 μm pore filter paper towel sample. Figure 3 shows a typical set of images, both a low and high magnification. The morphology of the sample does appear to contain more filamentary-type structures, as can be seen in Figure 3 (b); although the structures are smaller than those in Figure 2 (b), they are of a similar order of magnitude and are also sheet-like in form comparable to those sampled on the 10 μm pore filter.

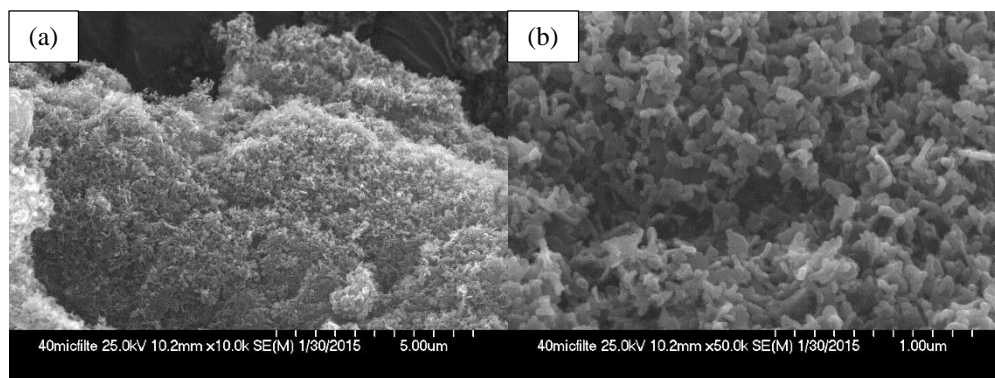


Figure 4. Low (a) and high (b) SEM images from 40 μm pore filter sample.

40 μm pore filter sample. Figure 4 shows a pair of low and high magnification SEM images for comparison with the previous two samples. The morphology of this sample is again, filamentary in nature (Figure 4 (a)), with individual structures up to 500 nm in length. The high magnification images, Figure 4 (b), reveal short-chain aggregates with rounded edges; this type of structure is similar to that observed in soot formation in combustion processes [2], although they are planar-like structures overall. Again, these structures appear to have some morphology differences from the other two samples, they are on the same order of magnitude in size so it is likely that particle growth has either slowed or stopped in these portions of the exit gas stream.

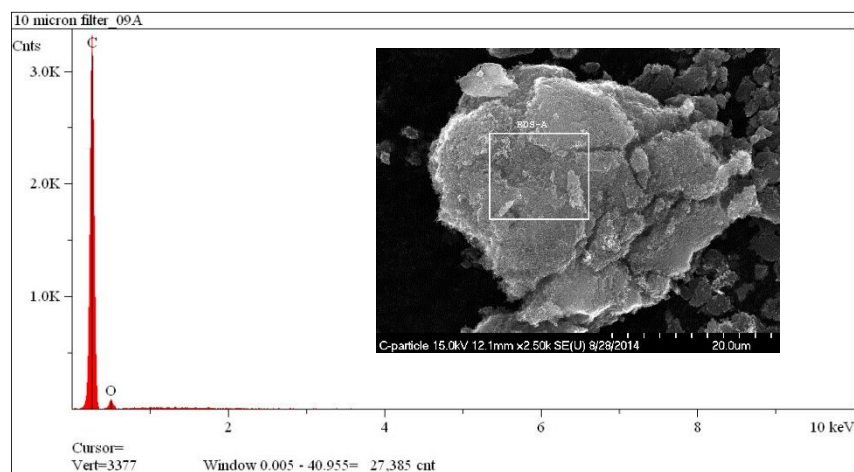


Figure 5. Example of EDS measurement showing primarily carbon. EDS scan indicating primarily carbon. Inset SEM image shows the area scanned with EDS on an individual filter cake particle to obtain the Figure 5 results.

In addition, we performed Electron Dispersive Spectroscopy (EDS) on all 3 filter samples. A typical result is shown in Figure 5, showing a dominant peak for carbon (C). The inset image shows the area, scanned by EDS, on an $\sim 30 \mu\text{m}$ size particle from the 10 μm pore filter producing this result. Carbon is the most abundant element measured on all samples; occasionally, traces of Na, Ca, and P were detected but appear to be very isolated, likely due to minor contamination of the samples in handling.

III. Characterization of carbon particulates collected on 37mm sampling filters

In the filter tests discussed in the previous section, the sampling was not optimal, as fairly long residence times allowed a filter “cake” to build up on the filter media which probably obscured the true range of sizes of the particles, and transfer of samples from the filter media surface to a carbon tape substrate, caused further alteration of the sample

morphology. In this section, we describe additional sample results using standard 37 mm sampling filter media with matching filter cartridges (also referred to as cassettes) that are specially designed to capture small particulate samples for SEM, gravimetric, and other particulate characterization techniques, and come in a range of cartridge types for installation into systems with either flowing air or other gas streams [3]. Figure 6 shows an image of one of these filter cassettes installed in the PPA exit gas stream. For our work, the filter media chosen was a polycarbonate substrate containing 100-200 nm size pores and coated with a thin layer of Pd.

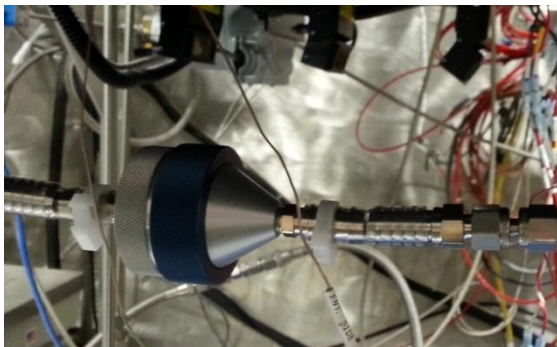


Figure 6. Photo of sampling cartridge (or cassette) installed in PPA exit line. Gas flow is from right to left.

After sampling tests were completed, the sampling cartridges were shipped to R.J. Lee Group (Monroeville, PA) where they were disassembled in a clean room, and SEM imaging performed with a Hitachi S-5500. A total of 6 sampling tests were completed with exposure durations ranging from 1 sec to 360 sec.

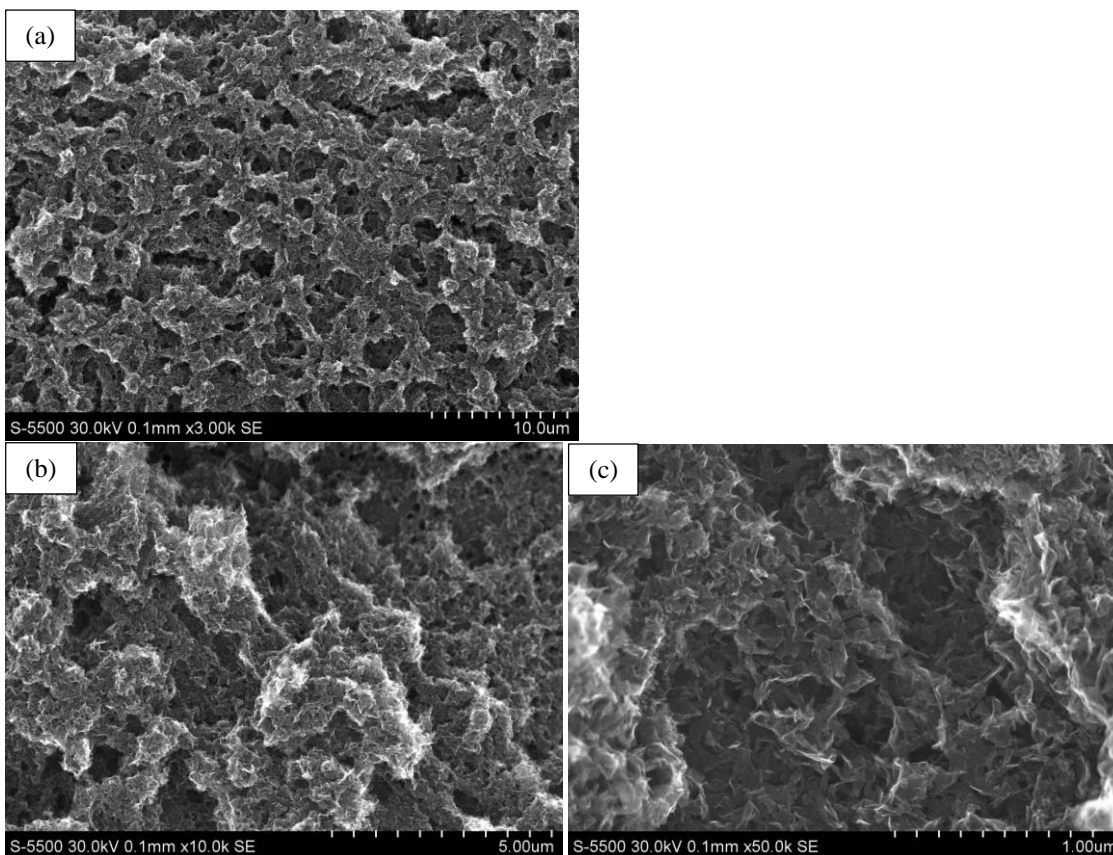


Figure 7. Sampling filter cartridge #1. (a) Low, (b) medium, and (c) high magnification SEM images of sampling cartridge filter exposed to exit flow stream for 360 secs.

Sampling filter cartridge #1 was exposed to the PPA exit stream for 360 sec. As shown in Figure 7, an extensive filter cake has already formed, despite what we anticipated would be a low residence time for capturing a monolayer of particulates. The microstructure of this filter cake, which obscures the polycarbonate filter substrate, looks similar to the microstructure observed for the 10 μm pore filter sample, although the web-like texture, noticeable in the lowest magnification image in Figure 7 (a), was not observed in any of the previous section filter samples. These more macro features were likely altered due to handling of the samples as reported in section III. An error in our flow rate calculation along with uncertainty in the carbon generation rate caused our over-estimate of the residence time for this first sample measured, but we present the results here as they provide some qualitative information on initial filter cake formation.

For the remaining sample cartridges, the residence times were successively reduced to capture a disperse monolayer of particles to better estimate size and aspect ratio of the particulates. Figure 8 shows the results from Sampling Filter Cartridge #5, which saw an exposure time of ~ 1 sec in the PPA exit gas stream.

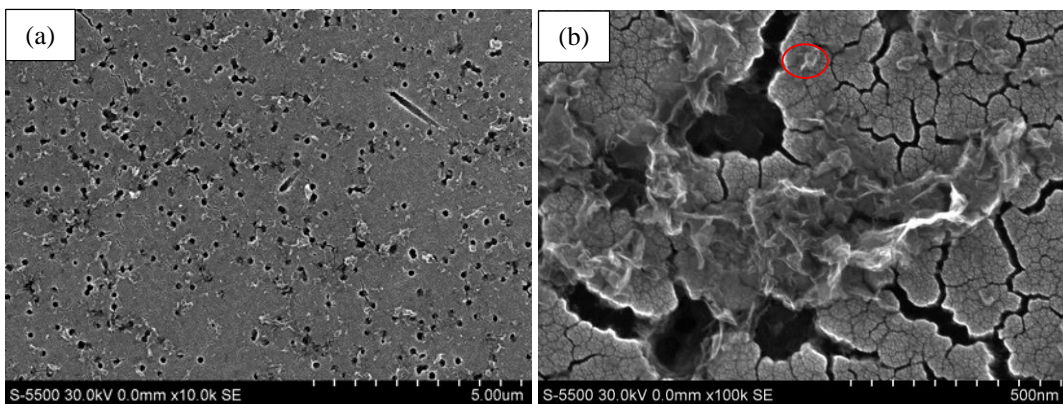


Figure 8. Sampling filter cartridge #5. (a) Low resolution SEM. (b) High resolution image showing several separate particulates. Particulate < 100 nm circled in red.

In Figure 8 (a) the Pd-coated polycarbonate filter substrate with fairly regular spaced micropores can be seen (this was obscured in the heavily loaded Filter Cartridge #1), along with finely dispersed carbon particulates. Figure 8 (b) is a high resolution image showing several individual particulates. They are sheet-like in geometry and very-irregular shaped, almost like “crumpled sheets of paper”. From preliminary inspection, it appears the majority of the particulates are in the 100-200 nm range in size (shortest dimension) and larger, although a few particulates are observed that are smaller than the reference dimension micropores (for example, see particulate circled in red in Figure 8 (b)).

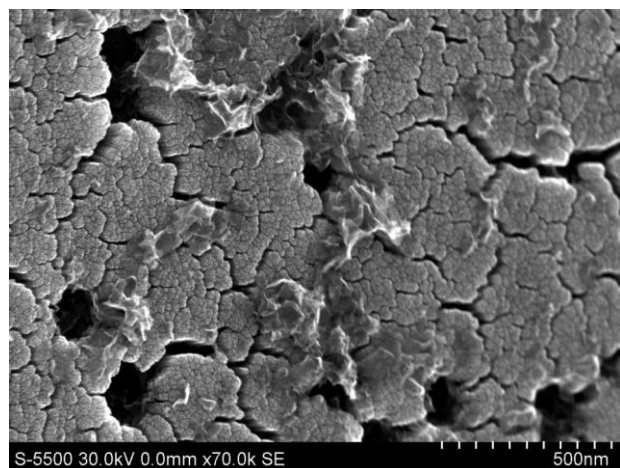


Figure 9. Filter cartridge #5 secondary electron image (25° tilt).

Finally, a few secondary electron beam images were taken; an example is shown in Figure 9. These give a perspective in three dimensions and indicate the height of the particles are of the same order as the other dimensions and the particulates are not likely undergoing growth after deposition on the filter surface, or at least not preferential growth perpendicular to the substrate.

These preliminary conclusions are limited, as the irregular shape of the particulates did not allow image-processing software to be utilized to analyze size and aspect ratios of a statistically significant number of particles.

IV. Discussion

The combustion community has done extensive fundamental work on the kinetics and mechanisms of solid carbon formation, primarily in soot. The hydrogen abstraction-actelyene addition (or HACA) is generally accepted as the reaction route leading to the formation of polycyclic aromatic hydrocarbons (initially) and soot in combustion flames [4, 5]. From the combustion perspective, the general consensus is that soot formation occurs by a nuclei condensation mechanism and results in spherical particulates in the 30-50 nm diameter size range and formation of chain-like aggregates [2]. Char particulates, on the other hand, tend to form larger (1-5 μm) porous structures that can be spherical or irregular shaped [2]. Caution must be exercised in comparing the PPA carbon formation to soot formation in combustion processes, as combustion occurs primarily under oxidizing conditions, whereas the PPA atmosphere in the exit stream, consisting of ~89% H_2 , 2% methane, 9% actelyene, is under reducing conditions, much like coking processes. We should also note that the sheet-like morphology observed in the particulates collected resemble graphene, a carbon allotrope of recent interest due to its unique electronic and structural properties [6]. In particular, flakes of 'few layer graphene' were reportedly grown by introducing methane in a hydrogen microwave plasma as a method for mass production for use in future nanoelectronic devices [7], a process analogous to the PPA device we discuss here. They were able to synthesize micrometer-wide flakes consisting of several atomic layers of stacked graphene sheets, which curl and crack, and have a similar appearance to the PPA carbon particle morphology. This crumpled sheet morphology we observed may be of technological interest due to the higher specific area, desirable as some workers report difficulties in producing graphene sheets that do not restack upon themselves [8]. We did not confirm these particulates indeed consist of graphene, but would like to note to those interested, that plasma pyrolysis may be a possible new method of producing crumpled carbon sheets.

In addition, this work [8] also reveals that the graphene material formed is primarily generated on the plasma-locating "stub" in these reactors. This may provide rationale that for the PPA, the carbon particles may be generated at the stub, as opposed to the plasma gas phase of the reactor. Given our interest in reducing carbon formation for the PPA application, it may be useful to investigate the geometry of the aluminum plasma-locating stub to potentially reduce carbon particle formation, and potentially reducing the filtration requirements for the PPA recycled gas stream.

Temperature readings were not taken in the PPA exit gas stream where the filter were installed, but the exit stainless steel tubing was cool to the touch a few cm downstream of the PPA exit during steady-state operation, and, performing a preliminary heat transfer analysis utilizing the Nusselt (Nu) number correlation for cylindrical tubes [9], indicates the gas stream temperature drops to nearly ambient temperatures less than 10 cm downstream of the PPA reactor. A final observation is that a fine carbon dust is observed when disconnecting fittings in the exit gas stream line. The dust is loose and does not clog the tube nor stick to the inner tube surface. Since iron is a good catalyst for coking, the carbon would be expected to coat the inner steel tube walls if these chemical processes were occurring in this section of the apparatus. [It should be noted that in early PPA testing, there was some clogging of the exit tubes but this was before we realized carbon formation was occurring.] These observations, along with the SEM results, indicate that the particulates are not likely continuing to grow in size in the PPA gas exit stream.

Although the morphology of the particulates on the 10 micron pore filter differed slightly from the sample collected on the 40 micron pore filter downstream, there is no evidence that the particulates are continuing to grow in size, but rather that the particulates are significantly smaller than 0.3 micron size, and thus in the diffusive regime, and a significant portions of them are captured in fairly large pore diameter filters.

Images of the sampling Filter #1 indicate the particle are caking as opposed continued growth after desposition on the filter substrate. Although the formation of a filter cake on Sampling Filter #1 is undesirable from a particulate sizing perspective, it does provide some insight to the carbon particulate formation process. The structure of the

partially formed filter cake is rather non-uniform and random, indicating that the growth of these layers are not due to growth due to carbon formation kinetics, but rather prior formed particulates accumulating on the filter substrate due to the filtration process.

We feel this initial assessment indicates the size of the particulates are in the 100-200 nm range. There is a concern that given the pore size of the substrate (100-200 nm), smaller particulates may be escaping the filter. In general, these etched-type filters like this design should be able to capture particulates up to 2 orders of magnitude smaller than the pore-size, in particular due to the diffusive regime, i.e. significantly smaller than 0.3 micron diameter.

V. Future Work

With an initial assessment of the range of sizes of the carbon particulates measured in the PPA exit stream, the next step is a determination of an appropriate filtration solution. An initial selection of filter options is being assessed and include a scroll filter design that is being developed at NASA GRC that mechanically allows new filter media to be exposed to the flow as the filter media becomes saturated [10]; a HEPA-grade filtration media will likely be selected for this scroll filter to accommodate the particulate size range measured and reported here. This scroll filter would allow, via manual or automated operation, new filter media to be exposed to the PPA exit stream without interrupting PPA operation for filter change-out. Another potential option is an improved carbon trap utilizing an ceramic-based (aluminum titanate) matrix material [11] developed for automotive diesel particulate filter applications. Although it does not provide HEPA-grade filtration, this ceramic matrix filter material is regenerable, it may be mounted as a pre-filter in series with a HEPA-grade filter downstream, potentially lowering the carbon particulate load, and thereby reducing the filter media resupply mass of the HEPA secondary filter.

VI. Conclusion

This work was focused on capturing the carbon particulates from the exit gas stream of a methane Plasma Pyrolysis Assembly and performing an initial characterization such that an optimum filtration technology can be selected and demonstrated for long-term operation and low resupply mass. Two separate sets of filtration samples were evaluated via scanning electron microscopy (SEM). The first set of samples were taken from a 10 μm pore filter, a paper towel applied to this primary filter, and a 40 μm pore filter that had operated. All three sources provided similar morphologies of the carbon particle cake captured. A second set of samples were collected utilizing 37 mm diameter sample filter cartridges and the SEM results from these samples provided a first look at individual carbon particulates captured in a monolayer on the filter substrate. This initial assessment has determined the carbon particulates generated by the PPA are in the 100-200 nm range, have widely varying aspect ratio, and are sheet-like in geometry, resembling graphene, an allotrope of carbon that is known to form in plasma reactors.

Acknowledgments

This work was funded by the Advance Exploration System's Life Support Systems (LSS) Project and is gratefully acknowledged. We would also like to thank the R.J. Lee Group (Monroeville, PA) for providing the SEM images in Section III and preliminary evaluation of the results.

References

1. Wheeler, R. R., Hadley, N. M., Wambolt, S. R., and Abney, M. B., "Third Generation Advanced PPA Development," *44th International Conference on Environmental Systems*, 13-17 July 2014, Tuscon, AZ.
2. Chen, Y., Shah, N., Braun, A., Huggins, F. E., and Huffman, G. P., "Electron Microscopy Investigation of Carbonaceous Particulate Matter Generated by Combustion of Fossil Fuels," *Energy & Fuels*, Vol. 19, No. 4, 2005, pp. 1644-1651.
3. See for example: <http://www.zefon.com/store/37mm-cassette-w-mce-filters.html>. Similar sampling filter products are available for other applications including microbiological collection, water supply analysis, in addition to aerosol measurements in gas streams.
4. Kislov, V. V., Sadovnikow, A. I., Mebel, A. M., "Formation Mechanism of Polycyclic Aromatic Hydrocarbons beyond the Second Aromatic Ring," *Journal of Physical Chemistry A*, Vol. 117, No. 4, pp. 4794-4816.
5. Richter, H., Howard, J. B., "Formation of Polycyclic Aromatic Hydrocarbons and Their Growth to Soot – a Review of Chemical Reaction Pathways," *Progress in Energy and Combustion Science*, Vol. 26, 2000, pp. 565-608.
6. <http://www.graphene.manchester.ac.uk/explore/the-story-of-graphene/>, The University of Manchester. 09/10/2014. Last accessed 04/02/2015.
7. Malesevic, A., Vitchev, R., Schouteden, K., Volodin, A., Zhang, L., Tendeloo, G. V., Vanhulsel, A., and Haesendonck, C. V., "Synthesis of few-layer graphene via microwave plasma-enhanced chemical vapour deposition," *Nanotechnology*, Vol. 19, No. 30, 2008, 305604.

8. Luo J., Jang H.D., Sun T., Xiao L., He Z., Katsoulidis A.P., Kanatzidis M.G., Gibson J.M., Huang J., "Compression and aggregation-resistant particles of crumpled soft sheets", *ACS Nano*, Vol. 5, No. 11, 2011, pp.8943-8949.
9. Bird, R. B., Stuart, W. E., and Lightfoot, E. N., *Transport Phenomena*, first edition, Wiley, New York,1960, pp. 399.
10. Agui, J. H. and Vijayakumar, R., "Development of an Indexing Media Filtration System for Long Duration Space Missions", AIAA 2013-3486, *43rd International Conference on Environmental Systems*, 14-18 July 2013.
11. Borger, T., Jamison, J., Warkins, J., Golomb, N., Warren, C., and Heibel, A., "Next Generation Aluminum Titanate Filter for Light Duty Diesel Applications," *SAE International*, 2011.