

# **KISS: KINETICS AND STRUCTURE OF SUPERAGGLOMERATES PRODUCED BY SILANE AND ACETYLENE**

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## **INTRODUCTION**

The objective of this study is to understand the process of gas phase agglomeration leading to superagglomerates and a gel-like structure for microgravity (0-g) silane and acetylene flames. Ultimately one would apply this understanding to predicting flame conditions that could lead to the gas phase production of an aero-gel. The approach is to burn acetylene and silane and to analyze the evolution of the soot and silica agglomerates. Acetylene is chosen because it has one of the highest soot volume fractions and there is evidence of super agglomerates being formed in laminar acetylene flames<sup>1</sup>. Silane has the advantage that silica particles are the major combustion product resulting in a particle volume fraction a factor of ten greater than that for a carbonaceous smoke.

## **COMBUSTION FACILITY**

The condition of autoignition for silane gas coming in contact with air poses a safety challenge different from those faced by previous drop tower experiments. Another safety issue for silane is its production of fine silica particles, which contaminate gas lines and prevent check valves from operating. In collaboration with contacts from the semiconductor industry and the gas handling staff at NIST, a system has been designed to ensure the safe burning of silane. Key design features are the use of metallic pneumatic and metering valves, butt-weld plumbing to minimize contaminants and dead volume, both vacuum and nitrogen purge, and the use of a minimum amount of silane (about 1 g). This small amount of silane assures that even if all of it were released to the combustion chamber, the pressure would remain below the maximum allowable value of about 0.41 MPa gauge (60 psig). A filter collection system has been assembled to prevent personnel exposure to silica particles during testing in the laboratory. The facility has passed NIST safety inspection for use in a chemical fume hood and results for normal gravity (1-g) experiments involving silane and acetylene will be described below.

## **IMAGING MEASUREMENTS**

Acetylene was burned in the standard NASA cylindrical combustion chamber with a diameter of 25 cm and a height of 53 cm. The burner consisted of a 4.52 mm diameter stainless steel tube positioned along the centerline about 15 cm from the base of the chamber. A digital camera with backlighting through a diffuser was used to photograph both the flame and smoke plume as illustrated in the lower portion of the Fig. 1. The photographs show the flame and plume just past the onset of sooting at a fuel flow rate of 0.66 cm<sup>3</sup>/s and the intense sooting condition with superagglomerates appearing as specks for a fuel flow of 2.10 cm<sup>3</sup>/s.

The upper series of photographs was taken at a location about 9 cm from the burner exit with the digital camera and a Xenon flash lamp with a pulse duration of 1.3 μs and a pulse energy of 0.35 J to "freeze" the motion of the soot agglomerates. The shutter speed of the camera was synchronized with the flash lamp, and the lens was selected to provide a long working distance of 15 cm and a magnification of 1:4.4. At the lower flow rate the soot appears as a relatively

gray background while at the larger flow, individual  $50\ \mu\text{m}$  to  $100\ \mu\text{m}$  particles appear to be connected across much of the plume. Other noteworthy features are the increasing plume width with increasing fuel flow rate and the sharpness of the smoke boundary. A comparison between these observations and plume calculations will be given below.

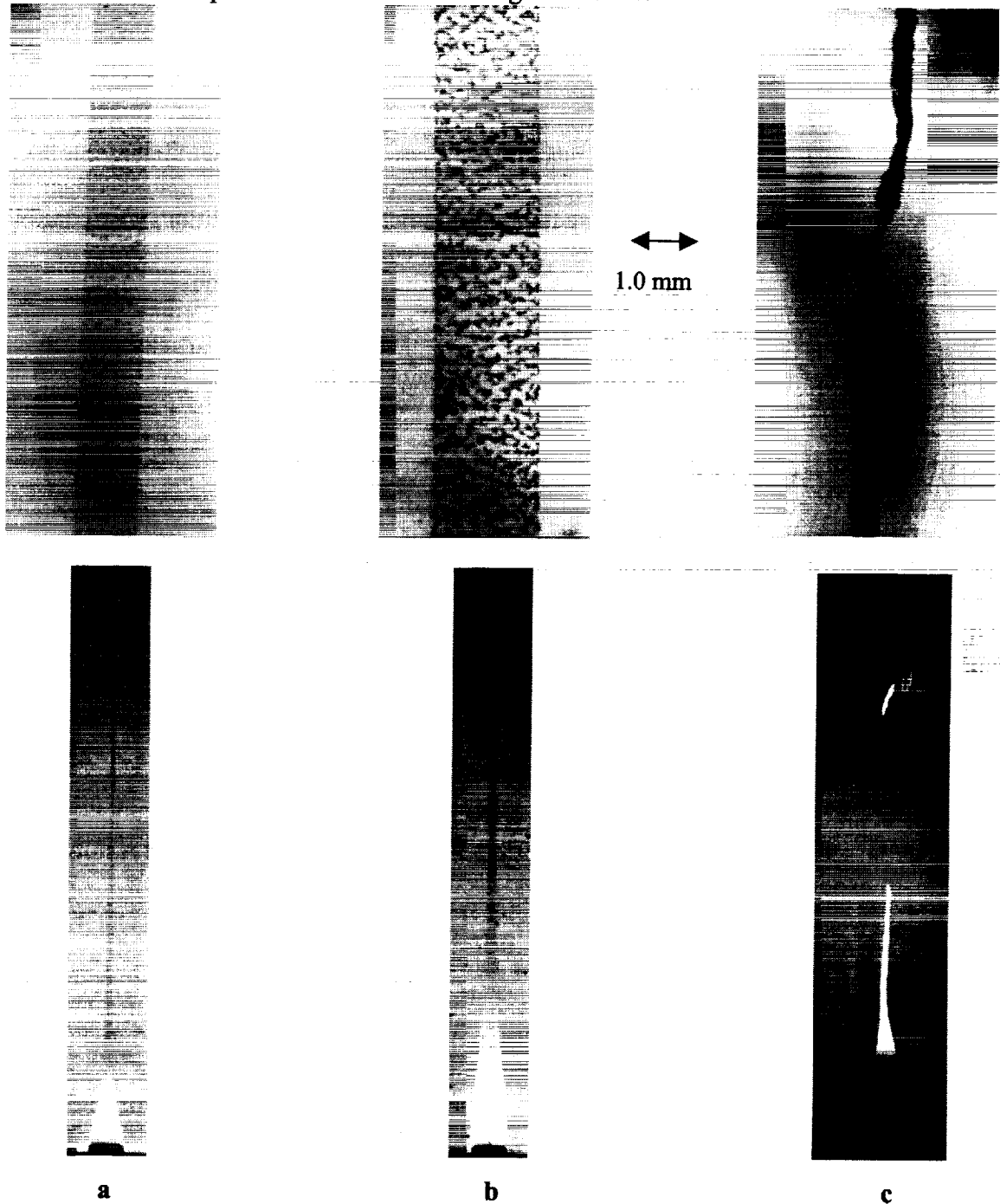


Fig. 1 Photographs of low flow (a) and high flow (b) acetylene flames, and a low flow silane flame (c). Flash photos of the plume are taken 9 cm above the burner .

For the silane experiment, the flow was controlled/monitored with a metering valve and analog pressure gauge. One difficulty with silane is that an  $\text{SiO}_2$  "crust" coats the burner tube and forms a conical deposit at the burner exit as indicated by the restriction of the flame in Figure 1. Even over a period of 10 s there is a noticeable decrease in the visible flame height. We were surprised to observe filaments leaving the flame zone rather than superagglomerates such as for acetylene. The photograph of the silane flame in Fig. 1 shows one fiber that has broken off and another forming in the flame. A  $\mu\text{s}$  flash photograph of a filament 9 cm above the flame is shown in Fig. 1. Thermophoretic sampling from the plume indicates a high concentration of particles smaller than  $10\ \mu\text{m}$  in addition to the fibrous particles.

Fibrous particles were examined with a stereomicroscope and a field emission scanning electron microscope. The digital image (Fig. 2) obtained with a video camera attached to the stereomicroscope indicates a complex filament structure. The scanning microscope images are for fragments from the original fiber, since most of the fiber attached with double stick carbon pads was lost when the chromium deposition chamber was evacuated. The SEM micrograph shows evidence of partially fused spherule structures with diameters as small as about  $150\ \text{nm}$ . It is possible that the original structures started as agglomerates that coalesced as a result of the flame temperature exceeding the melting point of  $\text{SiO}_2$ .

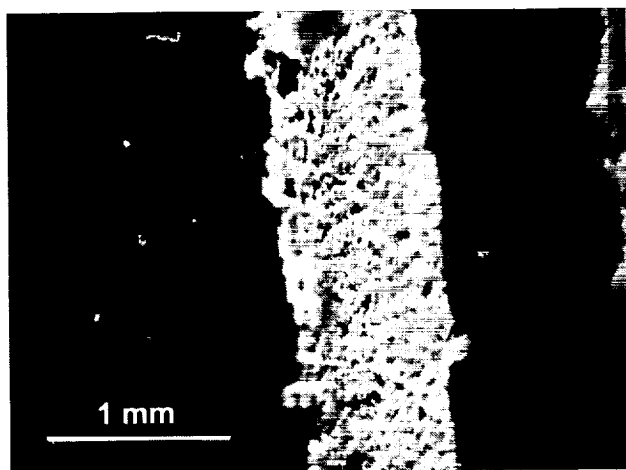


Fig. 2a. Optical micrograph of silica fiber.

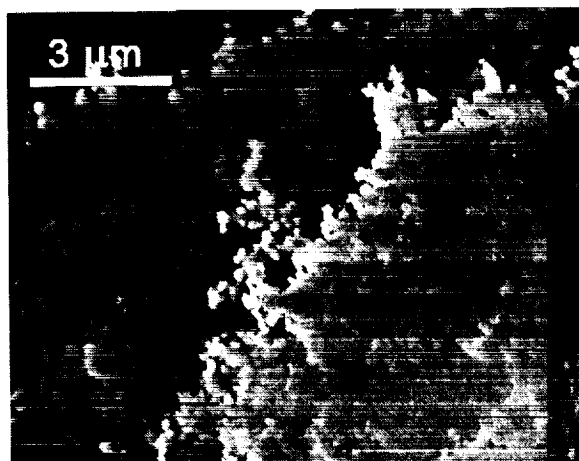


Fig. 2b. SEM of fiber residue coated with a few nm of Cr.

### MODEL CALCULATIONS

It is important to compute the profiles for particle volume fraction, temperature, species, and velocity to establish the environment for the computer simulations of the agglomeration process. The calculation method by Sivathanu and Gore<sup>2</sup>, which is based on a boundary layer jet flow, a chemical kinetics model by Lueng *et al.*<sup>3</sup>, and radiation loss and gain was used for computing these quantities for acetylene. The trend of an increasing width of the soot volume fraction profile with flow rate follows the same trend as measured experimentally. The 0-g condition leads to a broadening of the concentration profile almost a hundred fold; however, the predicted peak soot volume fraction is almost the same for both cases. The much broader profile and the shifting of the peak concentration to a downstream location at 0-g conditions will require a broader field of view and lower magnification for the flame imaging and the microsecond flash photography compared to the 1-g imaging.

For silane, a global reaction model based on state relationships is used. Essentially, the model assumes that any time oxygen and silane comes into contact, silicon dioxide particulate is formed. The availability of silane and oxygen at any location is obtained from the local gas phase mixture fraction. The silicon dioxide formed is then convected with a low diffusion coefficient (1000 times lower than gas). The predicted width of the  $\text{SiO}_2$  particulate profile is about half the width of the acetylene profile because the oxygen requirement for silane combustion is less than for acetylene combustion (2  $\text{O}_2$  molecules compared to 3  $\text{O}_2$  molecules for acetylene) and because every silicon atom forms  $\text{SiO}_2$  compared to about 10 % of the carbon atoms becoming soot. The other difference is that the peak  $\text{SiO}_2$  particulate volume fraction is about 100 fold larger than for soot for 1-g and decreases to about 30 fold larger for 0-g conditions.

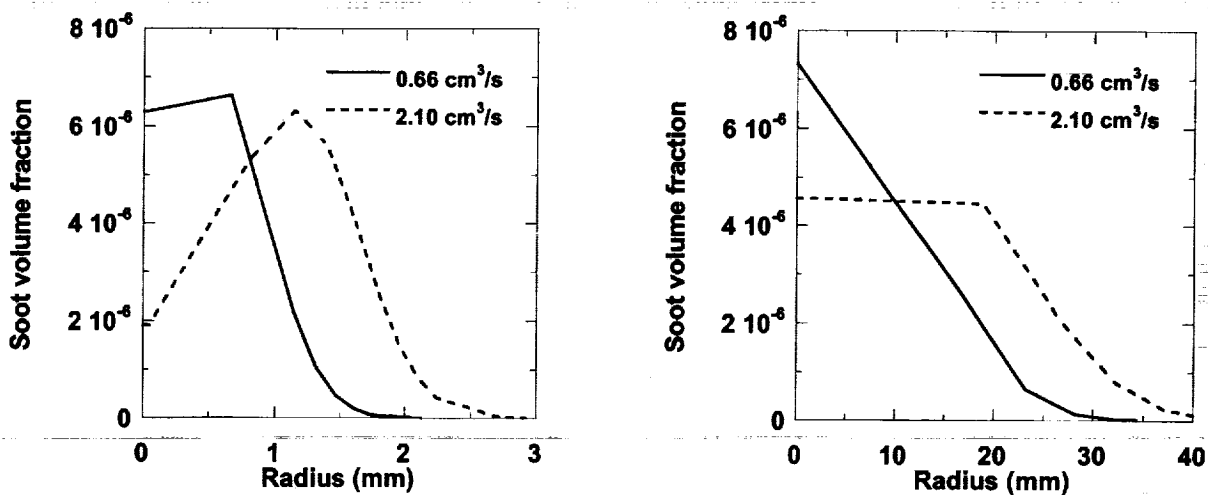


Fig. 3 The predicted soot volume fraction profile 90 mm downstream from the burner for 1-g (left plot) and for 0-g (right plot).

## DISCUSSION

The apparently interconnected structure of soot observed in this study at high fuel flow rate is similar to that reported in the study of Sorensen *et al.*<sup>1</sup> We expected that the much larger particulate volume fraction for the silane flame would lead to a totally interconnected gel-like structure and were surprised to observe a fibrous material. It is likely that the combination of the higher flame temperature for silane combustion together with the lower melting point of  $\text{SiO}_2$  particulate has resulted in the formation of the filaments. Our original plan to vary the flame temperature by varying the oxygen concentration will likely be important in controlling the morphology – gel-like or fiber – of the silica particles.

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## REFERENCES

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- <sup>2</sup> Sivathanu, Y.R. and Gore, J.P. *Combust. Flame*, 97: 161 (1994).
- <sup>3</sup> Leung, K.M., Lindstedt, and Jones, W.P., *Combust. Flame*, 87:289 (1991)