Ultrasmall-angle X-ray Scattering of Diesel Soot: Size Range Analysis

A. Braun,[1] F.E. Huggins,[1] J. Ilavsky,[2] P. Jemian,[3] K.E. Kelly,[4] A. Sarofim,[4] G.P. Huffman[1]
[1]Department of Chemical and Materials Science, University of Kentucky, Lexington, KY, U.S.A.
[2]Department of Chemical Engineering, Purdue University, West Lafayette, IN, U.S.A.
[3]Frederick Seitz Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, IL, U.S.A.
[4]Department of Chemical and Fuels Engineering, University of Utah, Salt Lake City, UT, U.S.A.

Introduction

Soot from combustion processes has been the subject of uncounted studies for decades and is a continuing topic of investigation. The reasons for studying soot and its formation are manifold. First, combustion engineers want to optimize combustion processes to suppress soot formation, which may be harmful to materials in engines and furnaces. Second, environmental scientists are concerned with soot because of its adverse health effects [1, 2] and its possible impacts on global climate [3-5]. Third, the study of the mechanisms of soot formation as a special modification of carbon is of significant fundamental interest.

We investigated soot from a test facility for small diesel engines by using ultrasmall-angle x-ray scattering (USAXS). Three soot samples produced by using a reference diesel fuel and the reference fuel plus two oxygenate additives were investigated. The presence of objects at three typical size ranges (i.e., aggregates, primary particles, and subunits) was observed. By studying soot powders and pellets from pressed powder, a separation of scattering contributions from aggregates and primary particles was possible. The scattering curves (SCs) of soot from oxygenated diesel from samples obtained under idle and load conditions showed significant differences. Soot from regular diesel fuel did not show such differences. To the best of our knowledge, this is the first such USAXS study on diesel soot.

Methods and Materials

Soot was produced at the diesel engine test facility at the University of Utah from three diesel fuels in a two-stroke diesel test engine operated under idle and load conditions. The three diesel fuels included a reference fuel, the reference fuel plus 5-wt % diethyl carbonate (DEC) (Mix A), and the reference fuel plus 1.5-wt % DEC and 4.3-wt % ethanol (Mix B). DEC and ethanol served as oxygenates. The reference fuel was a 50:50 mixture of the Chevron/Phillips diesel fuels T-22 and U-15. The soot was collected on quartz filters, then separated from the filters for further analysis. In addition, the National Institute of Standards and Technology (NIST) 1650 reference diesel soot sample was studied. For the USAXS experiments, the soot was evenly distributed on scotch tape at a thickness of approximately 200 _m. In addition, soot pellets about 1-mm thick and 6 mm in diameter were pressed at a pressure of 3.47 GPa. USAXS was carried out using synchrotron radiation at UNI-CAT beamline 33-ID at the APS. At this beamline, a Bonse-Hart setup allows one to record USAXS SCs by using a photodiode detector with an angular resolution of 0.0001 $Å^{-1}$ at a q-range of 0.0001 to 1.0 $Å^{-1}$. The SCs were desmeared and background-corrected with the beamline-specific software. The data acquisition time for an SC with 150 equidistant data points over the q-range was typically 15 minutes per sample. All USAXS data were fully corrected for all instrumental effects. The x-ray energy was 10,000 eV.

Results and Discussion

SCs of all soot powders are displayed in Fig. 1. All curves show bending ranges for very large scattering vectors at around 0.3 $Å^{-1}$. Subtraction of Porod background intensity in this range then revealed the presence of scatterer with a 1.3- to 2.0-nm diameter. The next population of scatterer was found at slightly smaller q vectors, around q = 0.03 $Å^{-1}$, and yielded particle sizes of 10 to 20 nm. These are typically spherically shaped primary particles, as usually observed with transmission electron microscopy (TEM). The former, smaller particles are so-called spherical subunits, also observed with electron microscopy [8].

The pronounced curvature of SC in the q-range of 0.01 $Å^{-1}$ comes from the scattering of the fractal aggregates, built up from primary particles. Their analysis appears easier when the SC is plotted in Kratky representation, as shown on the left in Fig. 2.

From the intensity maximum in the Kratky plot, the size of the fractal aggregates was determined to be several 100 nm, depending on the soot sample. Although rich in structure, SAXS analysis of soot is not always straightforward, particularly since several structural features, such as power law and Guinier ranges, may be convoluted. Pressing soot powder in pellet form showed that the aggregate scattering could be suppressed. Dissolving soot in acetone had a similar effect (i.e., larger agglomerates are destroyed and allow

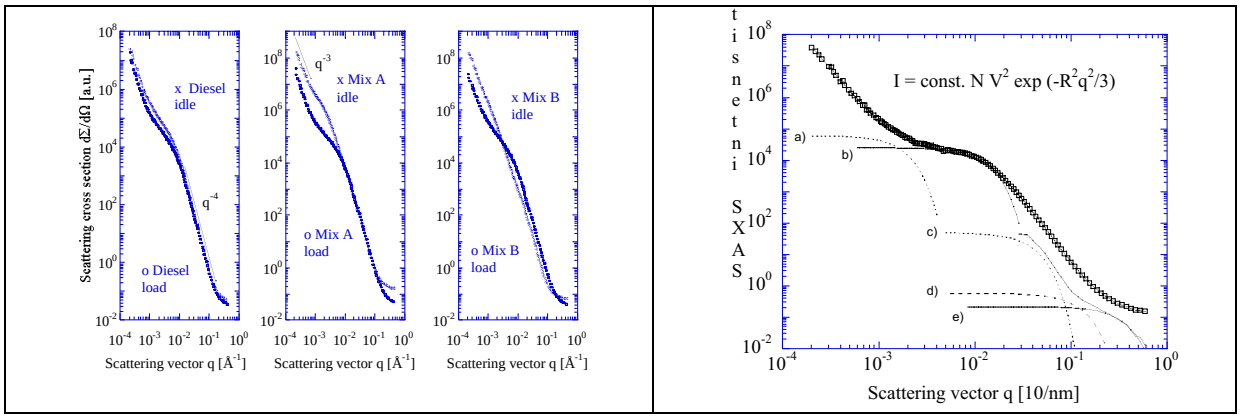

FIG. 1. Image on the left shows SCs of diesel soot of reference fuel, Mix A fuel, and Mix B fuel under idle and load conditions. Image on the right shows Guinier analysis of SC. Fits c), d), and e) were made after Porod background subtraction.

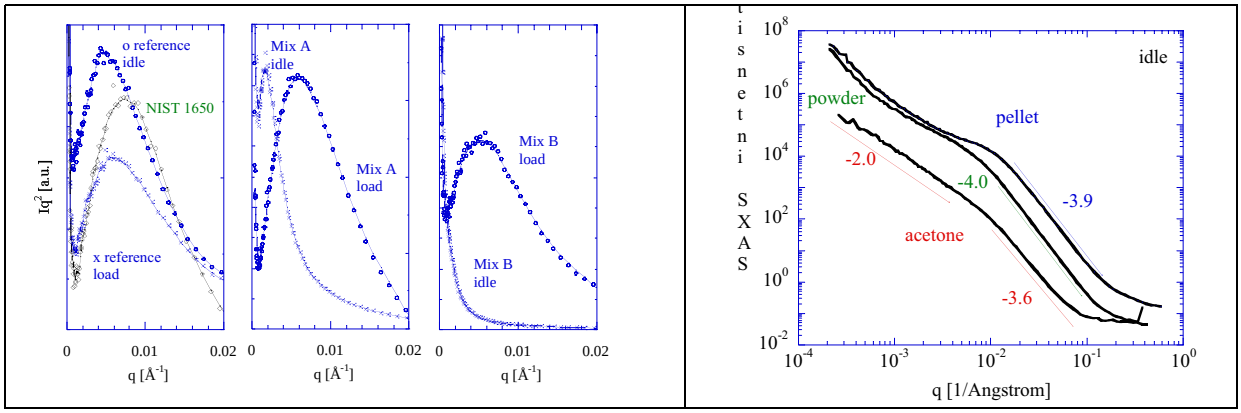

FIG. 2. Image on the left shows Kratky plot of soot SC, including a NIST soot standard sample. Image on the right shows SC of idle soot in pellets, powder, and acetone dispersed form.

for better analysis of the aggregates). Besides SAXS, other x-ray techniques are also applied to help analyze the structure of soot [9, 10].

Like electron microscopy, USAXS can basically detect the nano- and mesostructure of soot. USAXS has the advantage that samples can be analyzed faster and in an ambient environment, and it allows for a more robust statistical analysis of the data. Issues that arise from overlapping of scattering structures can be addressed by pressing soot into pellets or dissolving it in solvents.

Acknowledgments

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