Crossdisciplinary Applications of Microscopy Techniques, e.g. Physic-Life Science Interfaces

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Preparation of Soot-in-oil samples from diesel engines for HRTEM analysis

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The combustion process in an internal combustion engine produces an amount of particulate matter, most of which is carbon soot. Although much of this is expelled with the exhaust gases, a small proportion is transferred to the lubricating oil. Over time, the amount of carbon soot will accumulate to levels that affect the performance of the lubricating oil, worsening fuel economy, increasing CO_2 emissions, and increasing engine wear [1,2,3].

Soot is widely accepted to be constituted by irregular, branched agglomerates formed by several spherical primary particles. It is important to characterise the structure of these agglomerates as they are found in the lubricating oil. In particular, it is important to know the concentration of soot particles of size thicker than the lubricating film thickness, and to understand their formation.

TEM and HRTEM are commonly used to investigate the characteristics of individual and agglomerated particles from diesel exhaust, to understand the structure and distribution of the carbon sheets in the primary particles and the nanostructure morphology. While the aggregate structures reported in the literature vary in size from tens to hundreds of nanometres, the primary particles are reported as being generally below 50nm, in some reports as small as a few nanometres across. However, high resolution imaging of soot-in-oil is more challenging, as mineral oil is a contaminant for the electron microscope and leads to instability under the electron beam. Cryogenic vitrification and imaging have been used in the past [4], but issues related to viscosity of the typical used engine oil lead to localised thick layers. Alternatively, solvent extraction and ultracentrifugation have been used to prepare specimens for conventional TEM.

In this work we have compared solvent extraction and centrifugation techniques on soot-in-oil samples drawn from the sump of a diesel engine. Solvent extraction, diluting the oil in heptane, followed by dispersion onto the grid and a 30 second 25%O_2/75%Ar plasma clean is suitable for limited TEM imaging, but not for high resolution analysis due to significant carbon contamination. The Centrifugation process, where the soot samples are first cleaned with heptane and then followed by five stages of centrifugation, has been found to produce samples with minimal remnant oil and hydrocarbon contamination, suitable for high resolution TEM analysis, but is found to produce a differing particle size distribution to samples produced using the solvent extraction process.

1. Christine Esangbedo, André L. Boehman, Joseph M. Perez Characteristics of diesel engine soot that lead to excessive oil thickening Tribology International (November 2011)
2. D A Green, R Lewis Proceedings of the Institution of Mechanical Engineers Part D Journal of Automobile Engineering (2008) Volume: 222, Issue: 9, Pages: 1669-1689
3. M. Gautama, K. Chitoora, M. Durbhaa, J. C. Summers, Tribology International 32 (1999) 687–699
4. M. Kawamura, T. Ishiguro, K. Fujita and H. Moromoto, Wear, 123 (1988) 269-280

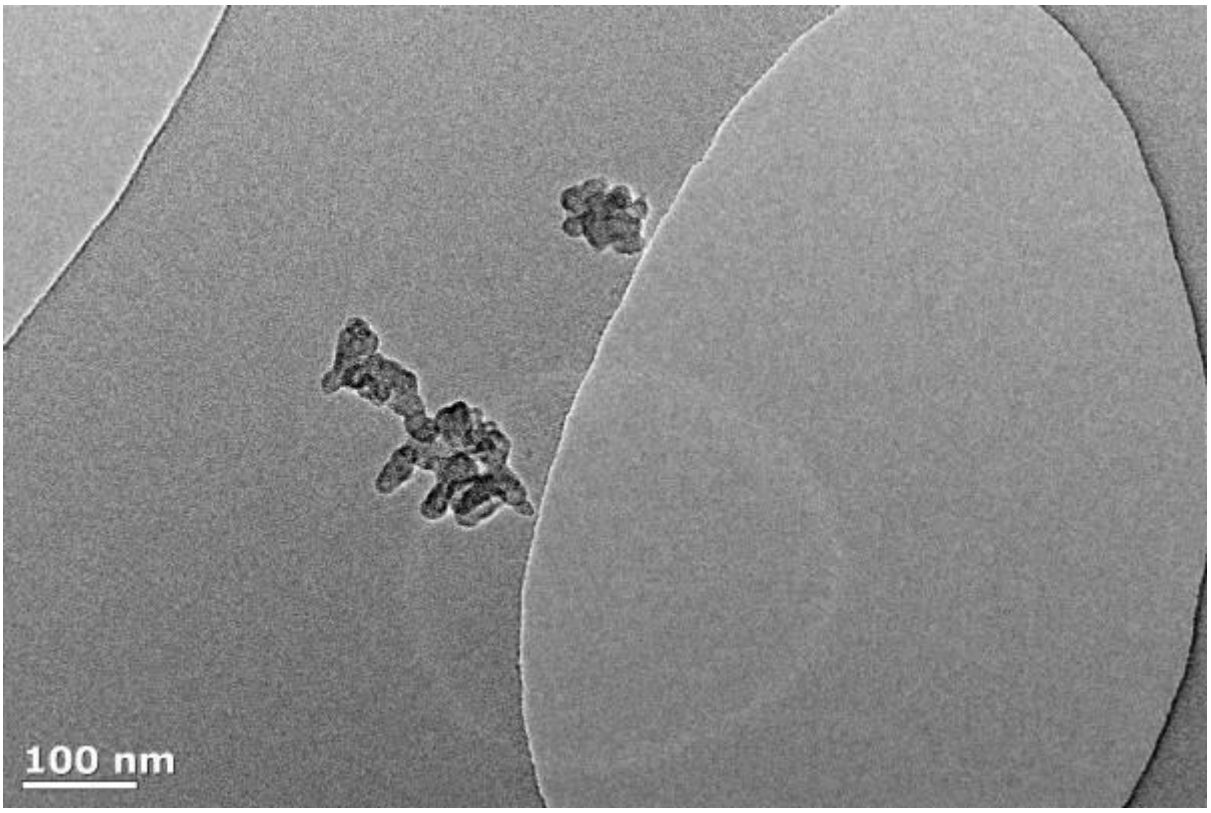

Figure 1. Bright field TEM image of soot-in-oil agglomerates extracted from a diesel engine operating on second generation biodiesel fuel and its blends, after the centrifugation process.

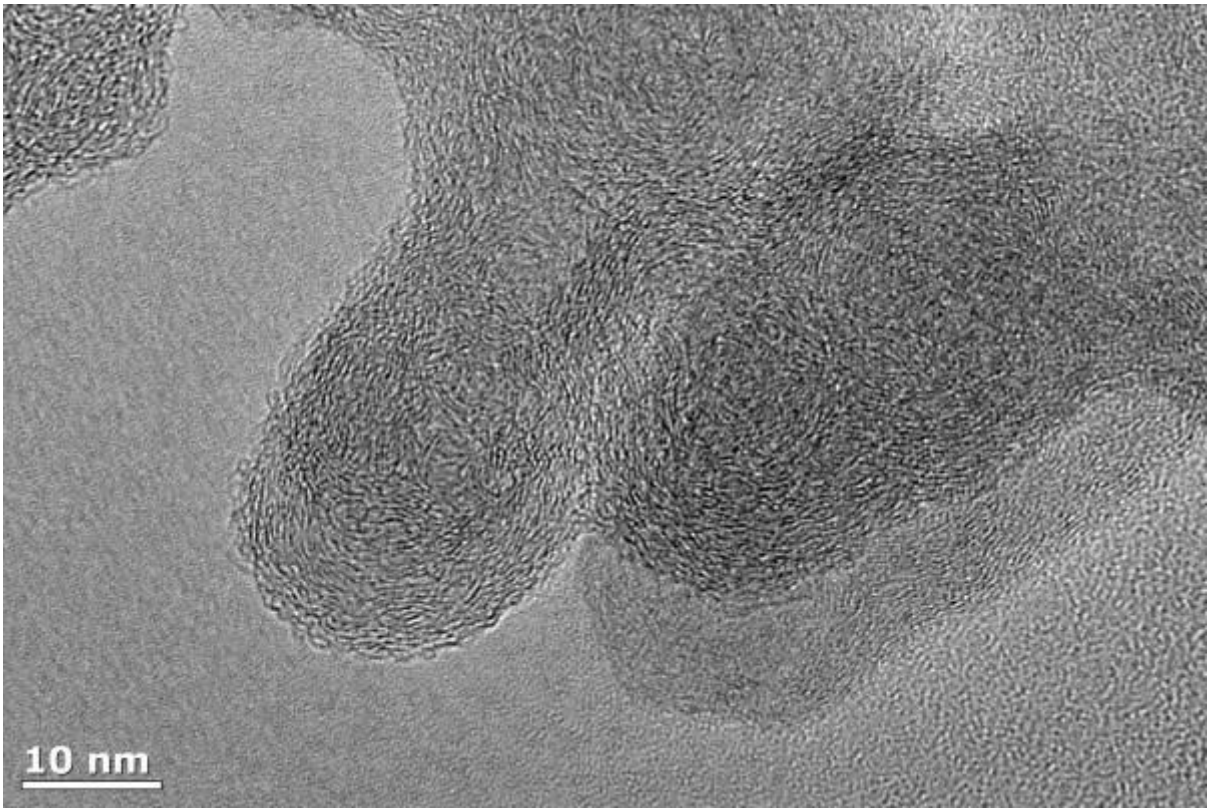

Figure 2. High Resolution TEM image showing primary particles within an agglomerate, extracted from soot-in-oil from a diesel engine operating on second generation biodiesel fuel and its blends, after the centrifugation process. Minimal remnant oil and hydrocarbon contamination after this cleaning process allows HRTEM images to be acquired.