

Book of Abstracts

27th June 2014

University of Cambridge, Department of Engineering, Trumpington Street, Cambridge, CB2 1PZ, UK

www.cambridgeparticlemeeting.org



08:30			REGISTRATION	
			Session I (Chair: Adam Boies)	
09:00			Welcome	
09:10	David Kittelson	University of Minnesota	Prospects of meeting EU number emission standards with a diesel engine without a DPF	
09:30	Chongming Wang	University of Birmingham	Characteristics of PM Composition and Soot Oxidation in a DISI engine	
09:50	Elina Koivisto	University College London	Investigating the trade-off between particulate emissions and thermal engine efficiency of a diesel engine	
10:10	Hartmut Sauter	Topas GmbH	Enhanced Measurement Technology to Characterize Aerosol of Crankcase Ventilation	
10:30			BREAK	
	Session II (Chair: Chris Nickolaus)			
11:00	Heather Hamje	CONCAWE	Effect of Oxygenates on Gasoline Direct Injection particulate emissions as measured in two European passenger cars	
11:20	Felix Leach	University of Oxford	Predicting Particulate Matter Emissions from Gasoline Direct Injection Spark Ignition Engines – the PN index	
11:40	Aaron Eveleigh	University College London	Using the Carbon-13 Isotope as a Tracer in the Formation of Soot	
12:00	Edward Yapp	University of Cambridge	Soot formation in a laminar ethylene diffusion flame	
12:20	Huayong Zhao	Loughborough University	Effect of adding hydrogen on the particulate emissions in ethylene combustion systems	
12:40			LUNCH	
			Session III (Chair: Jonathan Symonds)	
13:40	Bo Tian	University of Cambridge	High Spatial Resolution Laser Cavity Extinction Measurements of Soot Volume Fraction In Low Soot Producing Flames	
14:00	Mark Crooks	TSI Inc	Employing a Novel Classifier for Fast Particle Size Distribution Measurements with SMPS	
14:20	Christian Hoecker	University of Cambridge	Catalytic Nanoparticle Growth and Nanotube Morphology in a Continuous Gas Phase Process for Carbon Nanotube Synthesis	
14:40	Davide Mariotti	University of Ulster	Plasma-particle interactions at atmospheric pressure: from inorganic nanoparticles synthesis to bacteria charging.	
15:00			BREAK	
			Session IV (Chair: Marc Stettler)	
15:30	Imad Khalek	Southwest Research Institute	Particle Generator for Engine Exhaust Simulation	
15:50	Greg Smallwood	National Research Council Canada	Current and Future Methods for Calibration of Black Carbon Real-Time Mass Instruments	
16:10	Josep Grau-Bove	University College London	Simulation of aerosol deposition: from the laboratory to the building scale	
16:30	James Allan	University of Manchester	Measurements of wintertime combustion particles in central London during ClearfLo	
16:50			END	

Contents

09:10-09:30 - D. Kittelson. Prospects of meeting EU number emission standards with a diesel engine without a DPF
09:30-09:50 – H. Xu. Characteristics of PM Composition and Soot Oxidation in a DISI Engine4
09:50-10:10 – E. Koivisto. Investigating the trade-off between particulate emissions and thermal engine efficiency of a diesel engine5
10:10-10:30 – H. Sauter. Enhanced Measurement Technology to Characterize the Aerosol of the Crankcase Ventilation6
11:00-11:20 – H. Hamje. Effect of Oxygenates on Gasoline Direct Injection particulate emissions as measured in two European passenger cars7
11:20-11:40 – F. Leach. Predicting Particulate Matter Emissions from Gasoline Direct Injection Spark Ignition Engines – the PN index8
11:40-12:00 – A. Eveleigh. Using the Carbon-13 Isotope as a Tracer in the Formation of Soot9
12:00-12:20 – E. Yapp. Soot formation in a laminar ethylene diffusion flame10
12:20-12:40 – H. Zhao. Effect of adding hydrogen on the particulate emissions in ethylene combustion systems11
13:40-14:00 – B. Tian. High Spatial Resolution Laser Cavity Extinction Measurements of Soot Volume Fraction in Low Soot Producing Flames12
14:00-14:20 – M. Crooks. Employing a Novel Classifier for Fast Particle Size Distribution Measurements with SMPS13
14:20-14:40 – C. Hoecker. Catalytic Nanoparticle Growth and Nanotube Morphology in a Continuous Gas Phase Process for Carbon Nanotube Synthesis14
14:40-15:00 – D. Mariotti Plasma-particle interactions at atmospheric pressure: from inorganic nanoparticles synthesis to bacteria charging16
15:30-15:50 – I. Khalek Particle Generator for Engine Exhaust Simulation18
15:50-16:10 – G. Smallwood Current and Future Methods for Calibration of Black Carbon Real-Time Mass Instruments19
16:10-16:30 – J. Grau-Bové. Simulation of aerosol deposition: from the laboratory to the building scale21
16:30-16:50 – J. Allan. Measurements of wintertime combustion particles in central London during ClearfLo22

09:10-09:30 - D. Kittelson.

Prospects of meeting EU number emission standards with a diesel engine without a DPF

David Kittelson

Mechanical Engineering, University of Minnesota kitte001@umn.edu

Diesel particulate filter (DPF) technology has proven performance and reliability. However, the addition of a DPF adds significant cost and packaging constraints. Consequently some manufacturers have designed engines to meet Tier 4 emission standards without a DPF by reducing particulate matter in-cylinder. Such engines utilize high fuel injection pressure, moderate exhaust gas recirculation and modified injection timing to mitigate soot formation, combined with SCR for NOx control. This study examines an engine designed to meet US EPA Interim Tier 4 off-highway standards without a DPF. The engine was operated at four steady state modes and aerosol measurements were made using a twostage, ejector dilution system and a scanning mobility particle sizer (SMPS) equipped with a catalytic stripper (CS) to differentiate semi-volatile and solid components of the PM. Gaseous emissions were measured using an FTIR analyzer and particulate matter mass emissions were estimated using SMPS data and an assumed particle density function. Though the tested engine is predicted to largely meet current US particle mass standards it has significantly higher particle number emissions compared to the Euro 6 solid particle number emissions standard. Our work suggests that engine out solid particle mass would have to be reduced to extremely low levels, much lower than current standards, in order to meet the number standard without DPF aftertreatment.

09:30-09:50 – C. Wang. Characteristics of PM Composition and Soot Oxidation in a DISI Engine

Hongming Xu, <u>Chongming Wang</u>
University of Birmingham
h.m.xu@bham.ac.uk

Particulate matter (PM) composition and soot oxidation were investigated in a singlecylinder direct injection spark ignition (DISI) research engine using the thermogravimetric analysis (TGA) technique. The engine was operated under the condition of 1500 rpm, rich fuel/air ratio (λ =0.9) and late fuel injection, representing one of the worst scenarios of PM emissions from DISI engines. A TGA method featuring devolatilization and soot oxidization functions was developed and optimized. PM produced from the combustion of gasoline, ethanol, 25% volumetric blend of ethanol in gasoline (E25), and a new biofuel candidate, 2,5-dimethylfuran (DMF) was collected and analysed by such method. A kinetic model was applied to quantitatively describe the reactivity of the soot oxidation process. The results show that volatile components were the main contributor to the PM mass whilst soot fraction was only up to 35% for PM produced from gasoline, E25 and DMF combustion at 8.5 bar IMEP, and 6.3% for PM from ethanol combustion. Soot activity were highly dependent on fuel and sensitive to engine load. Soot from ethanol combustion was the most easily oxidized, indicated by the lowest temperature and activation energies (83 kJ/mol) required for oxidization reaction. The oxidation of soot from gasoline combustion was the most difficult and required the highest temperature and activation energy. For gasoline generated soot, oxidization behaviour varied more with engine load compared with soot from DMF combustion.

09:50-10:10 – E. Koivisto. Investigating the trade-off between particulate emissions and thermal engine efficiency of a diesel engine

Elina Koivisto, Nicos Ladommatos and Ramanarayanan Balachandran University College London elina.koivisto.11@ucl.ac.uk

Development of renewable transportation fuels has become increasingly important over the last few decades due to concerns about energy independence and the environment. One of the main research areas is renewable fuels compatible with existing compression engines. An ideal fuel would produce low levels of emissions and have high engine thermal efficiency. The wide variety of naturally occurring oils and fats provides a large raw material base for biofuel production, but the optimal chemical and physical properties of a compression engine fuel, however, are not fully understood.

Fundamental engine studies have been conducted to gain more insight into the effect of fuel properties on both the exhaust emissions and the thermal efficiency and of a diesel engine. Additionally, the effect of injection timing and injection pressure on particulate emissions was investigated. In this presentation the key results of these experiments are shown. Experiments were performed in a single cylinder direct injection diesel engine with a novel efficiency measurement system and particle emissions were measured with Cambustion DMS500 analyser.

As was expected, a decrease in the weight of particulate emissions was observed when efficiency increased. However, there was a slight trade-off between the amount of particulates sized 5-1000nm and the engine efficiency. Furthermore, the formation of particulate emissions was shown to be affected by both injection conditions and the physical fuel properties. A rigorous multivariable regression analysis was done to investigate the effect of physical fuel properties on the formation of particulate emissions.

10:10-10:30 – H. Sauter. Enhanced Measurement Technology to Characterize the Aerosol of the Crankcase Ventilation

Hartmut Sauter¹, Jan Müller¹, Stephan List¹ and Colin Jenkins²

¹Topas GmbH ²Adaptive Instruments mail@hartmut-sauter.com

Nowadays both SI and Diesel engines have closed crankcase ventilation systems. Oily blow-by gases out of the crankcase affect the life time of parts of the engine and of the intake as well as the engine emission of a motor vehicle. The determination of the performance of oil mist separator systems is complex, as they depend on the operational point of the engine operation map. Well-established gravimetric methods for the characterization of oil mist emissions provide comparatively poor information in spite of high costs. With the use of the enhanced measurement technology presented, it is possible to collect complete engine operation maps in one day using a combination of an intelligent gravimetric procedure and optical measurement devices. Changes in particle sizes of droplets can also be determined. Therefore, many applications like improvements of closed crankcase ventilation systems, optimization of piston geometry or the examination of the droplet generation in turbochargers are possible.

11:00-11:20 – H. Hamje. Effect of Oxygenates on Gasoline Direct Injection particulate emissions as measured in two European passenger cars

<u>Heather Hamje</u>, Rod Williams, Liesbeth Jansen, Richard Clark, Corrado Fittavolini, and Dolores Cardenas Almena

CONCAWE

heather.hamje@concawe.org

Particle emission limits have been part of diesel legislation for many years. Gasoline particulates are a more recent addition and have been in the legislation since Euro 5 for Gasoline direct injection (GDI) engines only. Gasoline direct injection (GDI) vehicles are known to emit higher numbers of particulates than traditional port fuel injected vehicles due to the reduced time for fuel atomization and the higher possibility of fuel impingement. New Euro 6 legislation comes into force in 2014 which will require that for the first time gasoline direct injection vehicles will also be required to meet particulate number (PN) standards (less than 6 x10¹² per km) as well as the existing particulate matter (PM) standards. From 2017, new Euro 6 more stringent limits already in place for diesel will also apply to GDI engine cars and particle numbers in exhaust will need to be less than 6 x10¹¹ per km. In addition, renewable fuel mandates may require an increased use of oxygenates in gasoline in the future. In order to facilitate this recently the maximum ethanol content in the EN228 standard was increased from E5 to E10. To date there is little data which combines the study of gasoline particulates with oxygenate content of the fuel.

This study has two main objectives 1) to assess how close the chosen vehicles are to achieving the new particulates requirements and 2) to look at the effect of a matrix of fuels with varying levels of oxygenate on particulate matter and particulate number. A matrix which included splash blended and matched ethanol and ETBE containing fuels at different levels were tested in two GDI engines meeting Euro 4 and Euro 5 regulations respectively. Particulate data was correlated with the fuel properties and conclusions made on the effect of these properties.

11:20-11:40 – F. Leach. Predicting Particulate Matter Emissions from Gasoline Direct Injection Spark Ignition Engines – the PN index

Felix Leach¹, Richard Stone¹ and David Richardson²

¹University of Oxford ²Jaguar Cars <u>felix.leach@eng.ox.ac.uk</u>

The use of Direct Injection Spark Ignition (DISI) engines for passenger cars has increased; providing greater specific performance and lower CO2 emissions. DISI engines, however, produce more particulate matter (PM) emissions than Port Fuel Injected (PFI) engines. Forthcoming European exhaust emissions legislation is addressing concerns over health effects of PM emissions by regulating particle number emissions from GDI engines for the first time. Accordingly, research into PM emission formation has increased.

A model developed by Aikawa et al (2010) for PFI engines correlated PM number emissions with the vapour pressure and the double bond equivalent (DBE) of the components of the fuel. This study reports using a similar particulate emissions index to predict PM emissions but for DISI engines.

A single-cylinder optical access Spray Guided DISI engine was used to validate a particulate number (PN) index using industry standard measurements – through the use of a matrix model fuels to independently evaluate the constituent parameters of the PN index and commercially available fuels.

Modelling of fuels has also been undertaken, to ensure that model fuels are representative of commercially available gasolines.

The PN index has also been tested using commercial fuels on a single cylinder engine and a Jaguar V8 engine; the results again show that the PN index is also an excellent predictor of PN emissions for market fuels from both of these engines.

PN emissions have been evaluated from two fuels representing the EU5 reference fuel specification, developed using the PN index to give a difference in PM emissions. Testing these fuels on both a single cylinder engine and a Jaguar V8 engine has shown up to a 40% variation in observed PN emissions. This has important implications for forthcoming European emissions legislation.

The PN index has also been investigated in a Jaguar V6 engine with five different fuels with a spread of calculated PN indices over a simulated NEDC. Here the PN emissions have been measured using two PN, and one PM instrument and the results compared. The results show that the trends of the PN index are followed, but not as closely as predicted. Detailed analysis shows that this discrepancy is due to other effects, for example cold start, dominating the PN emissions in certain phases.

11:40-12:00 – A. Eveleigh. Using the Carbon-13 Isotope as a Tracer in the Formation of Soot

Aaron Eveleigh¹, Nicos Ladommatos¹, Rama Balachandran¹ and Alina Marca²

¹University College London ²University of East Anglia <u>aaron.eveleigh.10@ucl.ac.uk</u>

Increasingly stringent legislation that limits emissions from vehicles, and growing concern surrounding anthropogenic pollutants on human health, are motivating efforts to ensure that future fuels are cleaner burning than the current generation. To inform the processing and design of fuel molecules, it is useful to know how specific chemical groups influence the conversion of carbon to particulate matter (PM). In order to better understand how carbon at specific localities within oxygenate or hydrocarbon molecules convert to particulate matter, and other emissions, an isotope tracking method has been used. A number of molecules have been assessed using isotope tracking; ethanol, propanol, propan-2-ol, ethyl acetate, pentanol, cyclopentanol, and toluene have been evaluated in terms of individual carbon atom conversions to PM in a flow reactor under pyrolysis conditions. Significant differences in the conversion rates of carbon atoms within molecules have been identified.

Isotope tracking methods have not been widely used in combustion studies, partly due to the cost associated with purchasing or synthesising large quantities of specifically labelled hydrocarbons. This presentation outlines a method that requires low quantities of 13C labelled molecules, at levels typically below 0.2% v/v. This diagnostic tool can provide some useful insights into the kinetic effects on fuels during pyrolysis and may also be used in combustion studies.

12:00-12:20 – E. Yapp. Soot formation in a laminar ethylene diffusion flame

Edward K Y Yapp¹, Jethro Akroyd¹, Sebastian Mosbach¹, Anthony Knobel¹, Alastair J Smith¹, Dongping Chen¹, Erin M Webster², J Houston Miller² and Markus Kraft¹*

¹University of Cambridge

A detailed population balance model is used to investigate soot formation in a laminar ethylene co-flow diffusion flame. The model incorporates the aggregate structure of particles and includes detailed compositional knowledge of the individual primary particles that constitute an aggregate. It thereby extends the range of comparisons that can be made with experimental measurements. A parametric sensitivity study on the computed soot volume fraction was performed and was found to be most sensitive to the growth factor, the reduced rate at which PAHs within particles grow. It had a more pronounced effect on soot formed in the wings than on the centreline. A small growth factor in the range of 3 to 10 % resulted in qualitative agreement in the soot volume fraction. Soot formation on the centreline and in the wings of the flame was also studied using transmission electron microscope-like projections of aggregates. Two different growth mechanisms were identified where soot particles formed on the centreline were made up of a larger number but smaller primaries than in the wings, consistent with experimental observations. Computed C_xH_y (x = 6 to 42 and y = 6 to 16) structures within particles were compared to the most thermodynamically stable aromatics (stabilomers) and a good correspondence was found. While some of the comparisons between numerical simulations and experimental data were satisfactory, the results of this study shows that further work is required to improve the soot chemistry model, particularly the oxidation rates on different surface site types.

²The George Washington University

^{*}mk306@cam.ac.uk

12:20-12:40 – H. Zhao. Effect of adding hydrogen on the particulate emissions in ethylene combustion systems

Huayong Zhao¹, Richard Stone^{2,3} and Ben Williams³

¹Loughborough University ²University of Oxford ³Imperial College London H.Zhao2@lboro.ac.uk

The effect of adding hydrogen on the particulate emissions in ethylene combustion systems has been investigated experimentally in both a laminar diffusion flame burner and an optical engine. In burner tests, 5 different fractions of helium and hydrogen have been added into the pure ethylene laminar diffusion flames to compare the dilution effect and direct chemical reaction effect. The spatially distributed soot temperature, diameters and volume fractions have been measured by using the Cone-Beam Tomographic Three Colour Spectroscopy (CBT-TCS). Statistical results across the whole flame can then be abstracted to show that adding hydrogen usually leads to a higher flame temperature and smaller soot volume fraction. In addition, the flame heights when adding hydrogen can be predicted by the correlation develop by Roper if the ethylene diffusion coefficient is used. The optical engine tests by using Cambustion DMS500 indicated that adding 5% of hydrogen by stoichiometry can speed up the combustion and reduce the particulate emissions in both rich and stoichiometric conditions.

13:40-14:00 – B. Tian. High Spatial Resolution Laser Cavity Extinction Measurements of Soot Volume Fraction in Low Soot Producing Flames

<u>Bo Tian</u>, Saravanan Balusamy and Simone Hochgreb Department of Engineering, University of Cambridge bt312@cam.ac.uk

Accurate measurement techniques for in situ determination of soot are useful in understanding the process of soot particle production. One such technique is line-of-sight extinction measurement, which is a fast, low-cost, and quantitative method to investigate the soot volume fraction in flames. However, the extinction-based technique suffers from relatively high measurement uncertainty due to the low signal-to-noise ratio (SNR) in low soot flames, as the attenuation of the laser beam intensity is often insufficient. Multipass techniques can improve the sensitivity, but may suffer from low spatial resolution. To overcome this problem, we have developed a high-spatial resolution laser-cavity extinction technique to measure the soot volume fraction from low-soot producing flames.

A laser beam cavity is realised by placing two concave mirrors on either side of flame under investigation. This configuration makes the beam convergent inside the cavity thus allow the 2σ of the beam (whose intensity closely obey a Gaussian profile along radial distance) across through a flame to be within $200~\mu m$. Thus, the spatial resolution of the system is as high as $200~\mu m$. The beam is reflected in the cavity back and forth for infinite times in order to increase the absorption by soot particles. We have applied the technique to a series of laminar-diffusion flames. A standard Santoro burner is utilised to produce flames. Three different hydrocarbon fuels, methane, propane and ethylene are tested. The measurements show good agreement with available results using laser-induced Incandescence (LII) and single-point extinction in the range from 20~ppb to 15~ppm. Sensitivity analysis shows that the signal-to-noise ratio of this technique is significantly higher than a single-pass system, and the measurement threshold can be as low as in the range of ppb. Numerical analysis is also conducted to estimate the error yielded by the tomography algorithm. It shows that three points Abel Transform, which is used in this work, will contribute to 10% of error in the measurements.

14:00-14:20 – M. Crooks. Employing a Novel Classifier for Fast Particle Size Distribution Measurements with SMPS

Michael Beeston*¹, Mark Crooks¹, T. Tritscher², J. Farnsworth³, E. Filimundi⁴, S. Elzey³, H.-G. Horn², and O.F. Bischof²

¹TSI Ltd, Stirling Road, High Wycombe, UK.

²TSI GmbH, 52068 Aachen, Germany

³TSI Incorporated, 55126 Shoreview, MN, USA

⁴TSI France, 13382 Marseille Cedex 13, France

*Michael.beeston@tsi.com

The Scanning Mobility Particle Sizer (SMPS) technique is widely used and has become the method of choice for the characterization of aerosols in the size range from about 1 nm to 1 μ m. Therefore the development of the capability to provide particle number and size distributions from non-stable aerosol sources, an area of key importance to many areas of aerosol science, marks a key step in the development within this field.

During an SMPS measurement, particles are charged and subsequently selected in a Differential Mobility Analyzer (DMA), finally the size-selected particles are individually counted by a Condensation Particle Counter (CPC). The technique's reliability stems from the fact that it is based on basic physical principles. A common limitation of all SMPS spectrometers, including component systems such as those based on Electrostatic Classifiers (TSI Model 3080), is their relatively long response time, with typical scans about 1 min or longer, depending on particle distribution and concentration. In order to provide greater insight into non-stable aerosols using the same proven technology the next generation classifier (TSI Model 3082) has been developed. The faster response time of the HV control (<50 ms) enables the recording of sampling data with up to 50 Hz for higher time resolution scanning. Utilizing this improvement we demonstrate that SMPS systems based on the novel classifier now permit very short scan times down to 5 s. This therefore enables it's applicability to the characterization of non-stable aerosols from biomass combustion and vehicle emission applications for instance. Critically the system retains the functions and flexibility of the previous TSI classifier generation. The system also features essential improvements and additional characteristics such as dual polarity high voltage (HV) control, increased sheath flow of up to 30 L/min for improved size resolution, and integrated auto detection of removable accessories (soft x-ray neutralizer and lowerpressure drop pre-impactor, DMA and CPC). The calibration of the new classifier fully complies with ISO standard 15900, which provides the methodology for adequate quality control of differential mobility analyzers. We will demonstrate validation data with PSL reference particles and lab aerosols that demonstrate the good agreement of both the old and new classifiers at traditional scanning times as well as the advantages of the new classifier at short scan times. Data from case studies will provide practical examples of the extended possibilities with the novel SMPS in particle research and monitoring applications.

14:20-14:40 – C. Hoecker.

Catalytic Nanoparticle Growth and Nanotube Morphology in a Continuous Gas Phase Process for Carbon Nanotube Synthesis

Christian Hoecker¹, Fiona Smail², Martin Pick² and Adam Boies¹

¹Department of Engineering, University of Cambridge

ch634@cam.ac.uk

The decomposition of ferrocene and the nucleation of iron catalyst nanoparticles for carbon nanotube (CNT) synthesis in a continuous gas phase process are studied. The thermal decomposition of ferrocene and nucleation of iron catalyst nanoparticles take place in a horizontal tube furnace within a temperature range of 300–1300°C and in a hydrogen atmosphere at atmospheric pressure (Li, 2004). The iron nanoparticles act as a catalyst to form CNTs from decomposed methane or other carbon sources. The resulting CNTs agglomerate to form an annulus concentric within the reactor, which propagates down the reactor. To date few studies have examined the phenomena associated with the ferrocene breakdown, catalyst nucleation and growth within the reactor. These phenomena are critical to the quality and throughput of the CNT production, as the CNT diameter and chirality are coupled to catalyst diameter.

Studies along the axis of the furnace tube are carried out by means of a sample probe system and a scanning mobility particle size spectrometer, which can detect particles down to 2.5 nm. Products of reactions inside the tube are analyzed with help of Fourier transform infrared spectroscopy.

The decomposition of ferrocene as well as the nucleation and agglomeration of iron catalyst nanoparticles are modelled numerically by solving the general aerosol dynamic equation with inclusion of ferrocene decomposition, iron particle nucleation, aerosol coagulation and diffusion. The effect of different conditions (temperature, flow rate, background gas-atmosphere and tube diameter (ID 14 – 40 mm) on the decomposition, nucleation and agglomeration processes is studied in order to increase iron catalyst density for purposes of increasing CNT production.

Experimental measurements indicate that particles form within a narrow axial location (see Figure 2) that is influenced by the ferrocene time and temperature history. Our results indicate that ferrocene decomposition is also influenced by background gas properties, whereby higher particle mass and number concentrations are present in non-hydrogen atmospheres. Axial measurements downstream indicate that particles disappear very abrupt; a phenomenon which cannot be predicted by the modelled results including thermophoretic and diffusional forces.

References

Li Y., Kinloch, I., Windle, A., (2004). Science 304, 276–278.

D. Conroy, A. Moisala et al. (2010). Chemical Engineering Science 65 (2010) 2965–2977

² Q Flo Ltd

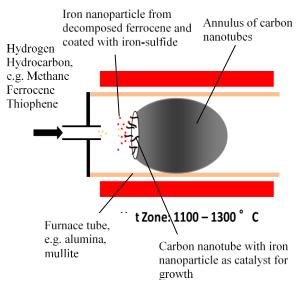


Figure 1: Ferrocene and thiophene are mixed with hydrogen and then injected into a tube furnace, in which an aerogel of nanotubes forms which is then wound out of the hot zone continuously as a fiber or film.

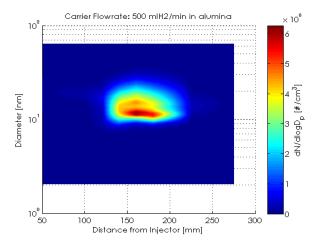


Figure 1: Particle size distributions along the furnace axis measured for ferrocene added to the system and at a H_2 bulk flow rate of 500 ml/min.

14:40-15:00 – D. Mariotti Plasma-particle interactions at atmospheric pressure: from inorganic nanoparticles synthesis to bacteria charging

<u>Davide Mariotti</u>¹, P.D. Maguire¹, C. Mahony¹, S. Askari¹, D. Rutherford², D.A. McDowell², D. Diver³, H. Potts³ and E. Bennet³

Non-thermal equilibrium atmospheric pressure plasmas (APPs) have attracted considerable interest due the expanded capabilities in low temperature synthesis, manufacturing and processing of materials for a wide range of applications [1]. Although major challenges remain, significant progress has been made recently with the commercialisation of an increasing number of APP-based applications. APPs offer unique plasma regimes and scientific opportunities for a range of interactions with other systems, including liquids, aerosols and living organisms. Here interesting phenomena arise due to the high electron plasma frequency and electron mobility that enables rapid particle charging, controlled particle heating via current fluxes and non-equilibrium chemical reactions.

In this contribution we will first present recent advances in both the synthesis and surface engineering of a range of nanoparticles (NPs), including metal (e.g. Au and Ag) and quantum confined group-IV NPs (i.e. Si, SiC and SiSn [2-5]). Analytical models will highlight key mechanisms of nanoparticle heating [6] and APP fabrication processes for third generation NP-based photovoltaic devices will be discussed.

APP induced charging of particles is important in a range of research disciplines from nanoparticle dispersion, aerosol dynamics and the interaction with living systems. The total particle charge depends primarily on APP electron temperature and particle diameter. There are indications that particles may remain in a highly charged state if they leave the plasma region sufficiently fast. Our main interest is to transport bacteria-laden water droplets through the APP in order to deposit high charge densities onto the bacterial surface upon droplet evaporation and study the effect of charge on isolated airborne microbial cells. Numerical models indicate that the initial droplet charge, determined by diameter at the APP exit, may reach and then track the Rayleigh limit as the diameter reduces due to evaporation. We are currently investigating the measurement of diameter and charge on individual droplets as the droplets evaporate for comparison with model predictions. Initial results on subsequent charge transfer to E coli will also be presented.

A final important aspect that brings together plasma-particle interactions for both inorganic and living organisms is represented by plasma-activated water chemistry, which is thought to depend on kinetic effects due to bombardment by gas phase electrons and subsequent solvation. However accurate measurement of transient chemical species has proved difficult and the proposed mechanisms are controversial. We will compare rapid transit

¹Nanotechnology & Integrated Bio-Engineering Centre, University of Ulster ²Microbiology, University of Ulster ³Physics & Astronomy, University of Glasgow <u>d.mariotti@ulster.ac.uk</u>

droplet chemistry with our existing body of work on plasma-bulk liquid reactions to evaluate the diagnostic potential of this approach and also the impact of transient water chemistry on bacteria.

Acknowledgements

Royal Society International Exchange Scheme (IE120884), the Leverhulme International Network (IN-2012-136) and EPSRC (EP/K022237/1, EP/K006088/1 and EP/K006142/1).

References

- [1] Mariotti D et al. J. Phys. D Appl. Phys. 43 (2010) 323001
- [2] Mariotti D et al. Adv. Funct. Mater. 22 (2012) 954
- [3] Švrček V et al. Appl. Phys. Lett. 97 (2010) 161502
- [4] Švrček V et al. Chem. Phys. Lett. 478 (2009) 224
- [5] Levchenko I et al. Carbon 47 (2009) 2379
- [6] Askari S et al. Appl. Phys. Lett. In press

15:30-15:50 – I. Khalek Particle Generator for Engine Exhaust Simulation

Imad A. Khalek¹, Robert Giannelli² and Matt Spears²

¹Southwest Research Institute ²US Environmental Protection Agency <u>ikhalek@swri.org</u>

A particle generator (PG) was developed to simulate engine exhaust aerosol composition. The PG uses a propane flame coupled with a catalytic stripper to generate "soot". It also uses multi-component hydrocarbons to produce particle phase hydrocarbons, and sulfate generation via catalysis and water to produce sulfuric acid. A novel approach was used to quantify particle phase hydrocarbons using CO₂ and sulfuric acid using SO₂ traces. The PG can produce a range of solid particle size distributions representative of engine exhaust, along with flexible levels of hydrocarbons, sulfate, water vapor, and ammonia.

The PG was applied to several research and development applications including the role of soot in hydrocarbon transport in sample lines, dry sulfate versus sulfuric acid nucleation and growth, hydrocarbon nucleation and growth, photoacoustic soot versus elemental carbon measurement, and solid and total particle instrument calibration, and other fundamental research processes.

This presentation will describe the PG in more details and give a few examples of its application to engine emissions R&D and aerosol research. The development of the PG was funded by the United States Environmental Protection Agency.

15:50-16:10 – G. Smallwood Current and Future Methods for Calibration of Black Carbon Real-Time Mass Instruments

<u>Greg Smallwood</u>¹, Kevin Thomson¹, Fengshan Liu¹, Dan Clavel¹, Matthew Dickau², Tyler Johnson² and Jason Olfert²

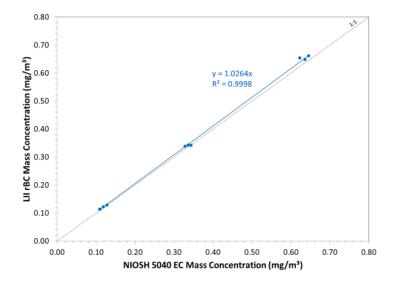
¹National Research Council Canada ² University of Alberta Greg.Smallwood@nrc-cnrc.gc.ca

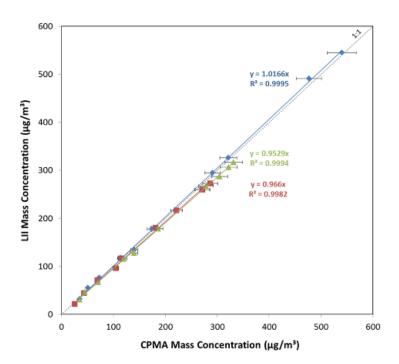
Black Carbon (BC) is a known health hazard and a critical climate forcer. Recent studies implicate BC as the second-most important climate-forcing agent after carbon dioxide. As such, reliable measurement of BC emissions from sources and in the environment is required. Real-time mass concentration measurement instruments, including those based on photo-acoustic principles or laser-induced incandescence principles, have been demonstrated many times to have excellent linearity and correlation with BC concentration. These instruments often demonstrate biases when engaged in comparisons, likely due to differences between the initial calibration and the instrument response to BC. There is a potential benefit in terms of improved measurement accuracy when instruments are calibrated against an absolute reference for black carbon.

Two approaches for the calibration of real-time BC mass concentration instruments are presented. In both cases, the source is a stable black carbon aerosol source, an inverted flame burner producing a soot aerosol with over 95% elemental carbon (EC). The output of this BC source is sampled, passed through a one micron cyclone to remove particles shed from the walls, and split into multiple streams.

In the first calibration method one stream is directed to the real-time measurement instruments while another stream is sampled with quartz filter collection. The quartz filter is then analyzed using a thermal/optical method to assess the EC and organic carbon (OC) masses. The results from the real-time mass instrument measurements are compared to the mass of elemental carbon (EC) determined from the thermal/optical analysis of the filter. This is performed over a range of concentrations.

The second calibration method involves the use of a centrifugal particle mass analyzer (CPMA) in conjunction with an aerosol electrometer to measure the mass concentration of a charged aerosol in real time. The CPMA selects the aerosol by mass-to-charge ratio and the electrometer measures the charge concentration. During calibration, the sample BC aerosol is charged using a unipolar charger and a target mass-to-charge ratio is selected by the CPMA before the sample is split and measured by the real-time mass instrument and the aerosol electrometer. The electrometer measurement and CPMA setting allows a direct measure of the charged particle mass concentration which can be compared to the real-time instrument reading. Uncertainties associated with the two methods are discussed.





16:10-16:30 – J. Grau-Bové. Simulation of aerosol deposition: from the laboratory to the building scale

Josep Grau-Bové¹, Luca Mazzei² and Matija Strlic¹

¹The Bartlett School of Graduate Studies, University College London ²Department of Chemical Engineering, University College London josep.grau-bove.11@ucl.ac.uk

We implemented a eulerian drift-flux model for fine particulate matter dispersion and deposition in a commercial CFD code (Ansys Fluent) and we have validated it experimentally in a test tunnel that uses untreated environmental air as input. We have used the same model in real buildings (Apsley House and the Wellington Arch at Hyde Park, or the Wellcome Collection building in Euston Road, London), where we have simulated the ingress and deposition of aerosols. In all the cases, the model shows a very good agreement with different kinds of experimental data: deposition measurements and suspended particle concentration, collected over periods of seconds, hours or even months.

We carried out the initial validation in the tunnel using simultaneous monitoring of inlet and outlet concentrations in the size range d = $0.02-1~\mu m$, which provided information on the deposition rates as well as the aerosol turbulent dispersion. This approach allowed us to validate dynamic simulations of deposition. We also validated the model against direct measurements of size-resolved particle deposition rates in the diameter range d = $0.5-5~\mu m$, measured by counting particles deposited on glass slides. In the larger case studies, we used particle counts in fixed locations as well as particle counting over extended periods of time as a means of validation.

The laboratory experimental set-up replicates the conditions which are commonly encountered in real buildings. Air in the tunnel is turbulent, with turbulent diffusivity predominating over Brownian diffusivity. The inner geometry of the tunnel resembles a sequence of rooms, with an internal arrangement of barriers that leads to tangential flows and gradients of turbulence. We experimented with different sources of particles: resuspended dust, combustion aerosols from a candle, and environmental air. These sources reflect the diversity of diameters and particle properties as well as the natural variation of concentrations typical of buildings located in an urban environment. These conditions allow us to extend the applicability of our approach to real case studies.

We studied the boundary conditions and the range of applicability of the constituent equations, and we obtained a set of non-dimensional parameters that defines the applicability of the model and allows comparisons with scenarios of very different scales. The Apsley House case study illustrates the ability of the model to predict non-trivial variations of deposition rates between rooms. The simulation of several operating regimes (considering heating, ventilation and leakage) demonstrates its great potential as a predictive tool.

16:30-16:50 – J. Allan.

Measurements of wintertime combustion particles in central London during ClearfLo

<u>James Allan</u>^{1,2}, Dominique Young¹, Dantong Liu¹, Paul Williams^{1,2}, Michael Flynn¹, Hugh Coe¹, David Green³, Roy Harrison⁴, Jianxin Yin⁴, Peter Zotter⁵ and Andre Prevot⁵

james.allan@manchester.ac.uk

Aerosols are a major contributor to air quality problems in urban areas. As part of the Natural Environment Research Council (NERC)-funded Clean Air For London (ClearfLo) campaign, measurements of ambient particulates were made using a variety of instrumentation at the North Kensington monitoring station during periods in the winter and summer of 2012. These included online measurements of composition using Aerosol Mass Spectrometers (AMS) and a Single Particle Soot Photometer (SP2), in order to study organic and elemental carbon with a high time resolution. Samples collected on filters were also analysed offline in the laboratory.

Using a variety of on- and offline techniques, attempts were made to apportion the particulate burden according to the various sources. Of particular interest was the investigation of the various contributions to the black carbon (BC) containing particles, as these are thought to have a large impact on human health. The various instruments were able to differentiate particles according to their organic chemical profiles, the amount of BC and other material per particle and the wavelength dependence of optical absorbance (as measured using an Aethalometer). Advanced multivariate techniques such as positive matrix factorisation and chemical mass balance were also used.

The BC-containing particulates were generally divided into those from diesel exhausts and those from solid fuel burning (for space heating) but depending on the technique, it was possible to further divide these according to fuel type (e.g. wood vs. coal) and burn conditions (e.g. flaming vs. smouldering). This work shows that with a combination of techniques, a more complete picture is obtainable and a more accurate apportionment can be gained.

¹University of Manchester

²National Centre for Atmospheric Science

³King's College London

⁴University of Birmingham

⁵Paul Scherrer Institute