

**2F.1**

**The Optimal Operation Conditions in Iron Ore Sintering Process for Depression of PAH Emissions.** Ai-Yun Hsieh, Perng-Jy Tsai, YU-CHENG CHEN, National Cheng Kung University; Jin-Luh Mou, Chung Hwa University of Medical Technology.

The aim of this study is to optimize the operational parameters applying Experimental design to depress Polycyclic Aromatic Hydrocarbon (PAH) emissions in iron ore sintering process. The test facility of pilot scale sinter pot simulated the sintering condition of the real sinter plant was used. The feasible operation conditions including water content, bed height, suction pressure and types of hearth layer were selected as Taguchi Experimental Design factor. PAH samples were collected from the exhaust by using an isokinetic sampling system. Twenty-two PAH compounds of both gas and particle phases were analyzed by GC/MS. The mean total PAH and total BaP<sub>eq</sub> concentrations was able to depressed 23.3% and 58.1%, respectively, through optimization of the operational parameter. The most decisive decline about 40% was observed in particle-phase PAH. The optimization of the operational parameter, where set as the water content of 6.0%, bed height of 550 mm, suction pressure of 1400 mmH<sub>2</sub>O, and hearth layer of 10-15 mm sinter was obtained. The water content and packed bed height had significant contribution to reduce PAH emissions by using ANOVA analysis. Furthermore, the sinter productivity was not significant difference based on optimization of operational parameters for reducing PAH emissions to compare that with the initial design of the sintering process. The valuable information could be applied to real-scale sinter plant operations, to depress not only PAH emissions but also other organic compound emissions.

**2F.2**

**Towards 2010 NO<sub>x</sub> and PM Emission Levels: Overview of CARB's Investigations of Advanced Heavy-duty On-road Vehicle Retrofits and Other Technologies.** Jorn D. Herner, ALBERTO AYALA, William H. Robertson, Paul Rieger, Oliver Chang California Air Resources Board; Constantinos Sioutas, Michael Geller, University of Southern California; Jean Ospital, South Coast Air Quality Management District.

The California Air Resources Board (CARB) has promulgated new particulate matter (PM) and NO<sub>x</sub> emission standards for heavy-duty (HD) vehicles that are in alignment with standards being promulgated nationally by the U.S. EPA. As of 2007, the PM standard for new HD engines has been lowered by 90% from last year's 0.1 g/bhp-hr to the current 0.01 g/bhp-hr limit and, similarly, the NO<sub>x</sub> emission standard is being lowered gradually from 2007 to 2010 from 2 g/bhp-hr to 0.2 g/bhp-hr. The expected enabling diesel vehicle technology for meeting the new standards include particle filtration systems (PFS) and NO<sub>x</sub> reduction devices in the form of the diesel particle filters (DPF) and selective catalytic reduction (SCR), respectively. At the same, alternative fuels such as compressed natural gas (CNG) and hybridization are also meeting the challenge for achieving ultra low emissions. As technology evolves, so do the emission profiles and the need for research to keep pace.

CARB, in close collaboration with the University of Southern California, the University of California at Los Angeles, and the South Coast Air Quality Management District, has initiated a project to characterize the emissions and their relative toxicity from HD vehicles equipped with advanced engine and retrofit technology, some of which is of the type expected as original equipment in diesel engines for meeting the new 2007 and 2010 emission standards. The vehicle test matrix includes diesel-fueled vehicles equipped PFSs such as a CARB Level III DPF, a DPF and vanadium-based SCR catalyst, a DPF and zeolite-based SCR catalyst, a vehicle equipped with hybrid electric drive and a DPF, a baseline diesel vehicles without emissions control, a biodiesel-fueled vehicle, a gasoline-fueled vehicle, and finally a fully 2010 compliant CNG engine power plant in a transit bus application. The test fleet represents the type of HD vehicle technologies expected on California's roads in the near future.

Vehicle testing is taking place at CARB's Heavy-duty Diesel Emissions Test Laboratory in Los Angeles. Emission samples from these vehicles have been collected for subsequent PAH, water soluble ion, trace metal, organic and elemental carbon analysis. In addition samples of the solid and non solid PM fractions are collected for subsequent toxicity analysis. Real time instrumentation was used to collect particle number and size distributions, particle bound PAH, and particle surface area data at 1Hz. Gas phase emissions measurements include CO, CO<sub>2</sub>, total and speciated hydrocarbons, NO<sub>x</sub> and NO<sub>2</sub>.

**2F.3****Development of a standard methodology for characterizing sample line losses in measurements behind aircraft engines.**

ANUJ BHARGAVA - P&W David S. Liscinsky - UTRC; Bruce E. Anderson, Eddie Winstead - NASA Langley; Don Hagen, Prem Lobo, Phil Whitefield - UMR; Chowen Wey - NASA Glen; Rick Miake-Lye - ARI; Robert Howard - AEDC.

Recent US EPA Federal Clean Air Act has led airports that want to expand, to provide estimates of particulate matter (PM) emissions from airports for existing and future aircraft traffic. This has led to the need of measuring PM emissions from aircraft engines. Extractive sampling is utilized and long sample lines are often required as the environment in the proximity of the engine exhaust is very harsh and dangerous, and trailers housing the instruments and researchers are ~100 ft from the engine exit. Even though care is taken to minimize line losses, long sample lines lead to significant particle losses and hence it is critical to characterize and measure line losses.

In 2006, several tests were carried out at NASA Langley and Glenn in order to characterize line losses. Measurements of particle concentration, size and mass were performed. Several different sources of particle emissions like Lear Jet exhaust, flame torch, salt aerosols and polystyrene latex spheres were used in the study. The instrument suite used in the study consisted of couple of CPC, EEPS, DMS500, MAAP and SMPS. This effort involved researchers from NASA, University of Missouri-Rolla, Arnold Engineering Development Center, Aerodyne Research Inc., United Technologies Research Center, and Pratt and Whitney.

The results show penetration efficiency increasing from around 20% for 10 nm particles to around 70-80% for 40-50 nm particles. Penetration efficiencies then plateau till about 80-100 nm particles. Beyond 80-100 nm, data from the EEPS and DMS500 indicate a roll-off in particle penetration. Penetration efficiency was also found to decrease as the diameter of the sampling line was reduced. Line loss data with heated and unheated lines were also obtained. Overall results from the different instruments indicate robustness in terms of repeatability and consistency of the line loss measured with the different instruments for different sample lines.

**2F.4****On-wing Characterization of Emissions from Commercial Airliners.** Harshit Agrawal, Karel Jansen, J. Wayne Miller, DAVID R. COCKER III, University of California-Riverside, CE-CERT; Aniket A. Sawant - Currently at Johnson Matthey Inc.

Growth in air traffic and proximity of airports to residential areas has increased the concerns over the impact of aircraft emissions on the air quality. Stringent regulations for on-road emissions have led to increased scrutiny of other non-road sources of air combustion emissions. The current and projected growth in air travel is expected to lead to increased contributions to the local inventory of gaseous and particle emissions from the operations associated with airports, like ground support equipment (GSEs) and aircraft engines.

Little information exists on emission indices of speciated PM, carbonyls, PAH, metals and speciated hydrocarbon as a function of engine load for commercial aircraft needed for evaluation of air quality impacts on communities surrounding airports. Accordingly, an on-wing investigation for commercial aircraft emissions in U.S. were carried out in August, 2005, at Ground Run up Enclosure (GRE) at Oakland International Airport. This study included comprehensive measurements of PM mass, metals, elemental and organic carbon, carbonyls and PAHs from two Boeing 737-700s equipped with the newer CFM-56-7 engines and two Boeing 737-300s equipped with the older CFM-56-3 engines. Additional, realtime PM measurements conducted with the Dekati Mass Monitor compared favorably with filter based measurements. The nominal power settings used for CFM-56 engine were, idle, 30%, 40%, 65% and 85%. Emission indices (EIs) for PM, metals, elemental and organic carbon, carbonyls and PAH's in aircraft engine exhaust will be reported. Aircraft EIs were found to be much lower than those from heavy-duty diesel engines operating on similar fuel types and the chemical emissions profile compared well with other diesel emission sources. The EIs and chemical profile comparison of aircraft emissions to other sources will be discussed in detail.

## 2F.5

**Particle Size Distribution Measurements of Ultrafine Particle Emissions from a Gasoline Vehicle.** BRIAN P.

FRANK, New York State Department of Environmental Conservation; Fangqun Yu, Hua Du, University at Albany, State University of New York; Aaron Pulaski, Jillian Grygas, New York State Department of Environmental Conservation.

Emissions from a gasoline vehicle were measured at steady state speeds of 30, 45, 60 and 70 mph, with particle size distributions determined using an Engine Exhaust Particulate Spectrometer (EEPS). Samples were taken after ambient dilution, with a Semtech-D Portable Emissions Monitoring System (PEMS) used to calculate instantaneous dilution ratios based on carbon dioxide which ranged from 10:1 to 450:1. For both the 30-45 mph speeds and the 60-75 mph speeds, some bi-modality was observed in the particle size distributions with modes at ca. 11 and 35 nm. For the 30-45 mph speeds, the 35 nm mode was dominant and dilution-corrected number concentrations were as high as  $10^5$  particles/cubic centimeter. For the 60-75 mph speeds, the 11 nm mode was dominant and dilution-corrected number concentrations exceeded  $10^7$  particles/cubic centimeter. In addition, mass concentrations were observed of up to 9 micrograms/cubic meter for the 30-45 mph steady states and up to 1165 micrograms /cubic meter for the 60-75 mph steady states. These high number and mass concentrations suggest that gasoline emissions can be a significant contribution to mobile source emissions in the fine and ultrafine range and warrant further investigation.

## 2F.6

**In-use Diesel Vehicle Emission as a function of Vehicle Operation and Exhaust Standard in Bangkok, Thailand.**

EKBORDIN WINIKUL, Tami C. Bond, R. Subramanian, Univeristy of Illinois at Urbana-Champaign; Kim Oanh N. T., Worrarat Tiansathit, Asian Institute of Technology; K. G. Duleep, EEA, Inc.

Diesel vehicles are the main particulate matter contributors in several countries. According to Thailand Pollution Control Department (PCD), diesel vehicles emit more than 80% of total particulate matter emission from mobile sources in Bangkok. Consequently, PCD is regulating several exhaust emission standards for new vehicles. However, the real contributors in Bangkok are not new vehicles, but in-use vehicles that are currently running on the street.

To obtain emissions of in-use vehicles on the road, about 70 in-use diesel vehicles with different exhaust emission standards were recruited to the Automotive Emission Laboratory (AEL) to simulate driving pattern on Chassis Dynamometer. The driving cycles used in the test comprised of driving pattern of vehicles on the road in Bangkok (Bangkok driving cycle) and other European countries (European Transient Cycle). The primary study was funded by the World Bank to produce model inputs of particulate matter and gaseous emissions. We made additional measurements to determine the climate-relevant properties of these vehicles. Pall Tissuquartz quartz, Millipore PTFE, and Pall Tissuglass filters were used for OC/EC, mass, and light-absorption measurement. The results of these measurements, along with real-time data, were then analyzed in terms of mode of vehicle operation and engine exhaust standard.

The primary results show the average PM emission rates reduce with the newer vehicles. However, we also see considerable vehicle-to-vehicle variation within each emission-standard subgroup, which suggests that other factors such as vehicle maintenance and usage pattern likely play a bigger role in the emissions from a particular vehicle rather than the vehicle age.

This paper shows emission of in-use vehicles based on real-world driving pattern, and also correlates different driving speed with emission from different vehicle exhaust standard. We conclude with some recommendations about extrapolating the data from these measurements to other fleets within Asia.

## 2F.7

**Biodiesel Effects on Radiocarbon ( $^{14}\text{C}$ ) PM Emissions from a Diesel Engine.** Maren Bennett, JOHN VOLCKENS, Rudy Stanglmaier, Colorado State University; Ann P. McNichol, Woods Hole Oceanographic Institution; Charles W. Lewis (deceased), U.S. EPA.

Cosmic irradiation of the upper atmosphere provides a continual source of the  $^{14}\text{C}$  radiocarbon isotope. This isotope is in equilibrium with living and recently living materials at the earth's surface that absorb  $^{14}\text{C}$ , in the form of  $^{14}\text{CO}_2$ , through photosynthesis. Due to radioactive decay (5730 yr half-life) fossil carbon (i.e., oil) is virtually devoid of  $^{14}\text{C}$ .

The lack of  $^{14}\text{C}$  in fossil fuels allows EPA to employ a two-source model classifying carbonaceous aerosol as derived from either fossil or modern sources. The main assumption of this model is that fossil carbon stems only from anthropogenic activities (e.g., oil and gas combustion), while modern carbon stems only from biogenic sources (i.e., forest fires). The relative amount of  $^{14}\text{C}$  in a sample of atmospheric particulate matter (PM), defined as percent modern carbon (pMC), allows EPA to infer the fraction of PM derived from anthropogenic pollution sources. With increased use of biofuels that contain  $^{14}\text{C}$ , the main assumption of the two-source model may become invalid. The goal of this study was to determine the  $^{14}\text{C}$  content of PM emitted from an off-highway diesel engine running on commercial grade biodiesel.

Tests were conducted with an off-highway diesel engine running at 80% load fueled by various blends of soy-based biodiesel. PM<sub>10</sub> emissions were collected on quartz filters and analyzed for their  $^{14}\text{C}$  content using accelerator mass spectrometry (AMS). Results show that pMC increases linearly with the percentage of biodiesel present in the fuel, indicating that PM from biodiesel engines will have an effect on contemporary C<sub>14</sub> apportionment. Emissions of other regulated compounds (CO, NO<sub>x</sub>, THC) from the combustion of diesel and biodiesel blends are also presented.

## 2F.8

**Emissions from Auxiliary Engines of Ships Associated with Port Activities.** Abhilash Nigam, William A. Welch, David R. Cocker III, J. Wayne Miller, University of California Riverside, CE-CERT.

The status of marine ports as a gateway for international commerce and a local, regional and national economic resource has resulted in increased air emissions from predominantly diesel-fueled equipment used to transport the cargo destined for all parts of the nation. Projected emissions in the south-coast air basin for 2020 estimate 190 tons/day NO<sub>x</sub> and 13 tons/day PM from port-related sources. Out of these about 150 tons/day NO<sub>x</sub> and 11 tons/day PM is estimated to be contributed exclusively by ships burning heavy fuel oil (HFO).

The present study deals with the investigation of these regulated (PM, NO<sub>x</sub>, CO) and non-regulated (carbonyls, PAHs, metals, elemental and organic carbon, and sulfur) emissions from three auxiliary ship engines.

Measurements were made as per ISO 8178- D2 cycle at the following load points: 25% 50% and 75% of rated power. Testing was performed using on engines burning two common fuel types: Heavy Fuel Oil (HFO) and Marine Distillate Oil (MDO), which have about 4% and 1.5% sulfur, respectively.

Results show significant PM and NO<sub>x</sub> emissions reductions for MDO over HFO. Ion chromatography analysis shows higher sulfate content in the PM for HFO as compared to MDO. The XRF analysis of HFO fuel derived PM showed high vanadium and nickel content in addition to high sulfur and calcium also present in MDO fuel. The PM had high OC fraction and a low EC fraction for both HFO and MDO fuel. Amongst the carbonyl emissions, acetone, formaldehyde and acrolein formed the major fraction for both the fuels tested. The emission data is used to estimate the reduction in source contribution of ships to overall emissions inventory by switching from HFO to MDO will be presented.

**2F.9**

**Aerosol Size-Distribution Measurements Resulting from On-Road Light-Duty and Heavy-Duty Vehicle Particulate Emissions.** MELISSA LUNDEN, Thomas Kirchstetter, Lawrence Berkeley National Laboratory; George Ban-Weiss, John McLaughlin, Robert Harley, University of California, Berkeley.

Gaseous and particle-phase pollutants were measured during summer 2006 at the Caldecott tunnel in the San Francisco Bay area. Measurements were made in two separate tunnel bores with high traffic volumes: the first bore was reserved for light-duty (LD) vehicles, and the second bore carried a mix of LD passenger vehicles and heavy-duty (HD) diesel trucks. Aerosol size distributions were measured with a TSI scanning mobility particle spectrometer. Size distributions were determined at both 2 minute and 20 second intervals. In addition, high-time resolution (1 Hz) of total particle concentrations, black carbon (BC), CO, CO<sub>2</sub>, and NO<sub>x</sub> concentrations were measured. This presentation will compare size distributions measured for light duty and heavy-duty vehicles emissions from the 2-minute measurements. The 20-second, high-time resolution measurements are compared with gas phase measurements and video of the traffic to investigate emission from individual vehicles. This presentation will present the averaged size distributions compared with individual distributions from vehicles. There will be specific focus on the size-resolved emissions from different types from heavy-duty vehicles, comparing emission from high BC emitters and newer, cleaner heavy-duty vehicles. These data will be compared to emission factors from individual HD truck exhaust plumes, and the distribution of these emission factors will be compared to the fleet average.

**2F.10**

**A Compact System for the Generation and Sampling of Diesel Particulate Matter.** ALI FARNOUD, Alfredo Juan Armendariz, Southern Methodist University.

Many epidemiological and toxicological studies show that diesel particulate matter (DPM) can have adverse health effects to workers like miners and garage workers who are exposed to diesel exhaust. DPM is also one of the largest contributors to ambient PM pollution in urban areas around the world. The objective of this study was to design and build a compact laboratory system for the generation, sampling, and analysis of diesel particulate matter. DPM was produced by a 10 HP diesel-powered electric generator and directed from the muffler exit through 1-inch ID galvanized steel and silicone piping. Diesel exhaust number concentration was measured with a portable condensation particle counter (CPC), and mass concentration was measured by sampling with teflon fibrous filters. The DPM size distribution was measured with a 6-stage cascade impactor. Prior to number and mass sampling, the DPM was diluted using compressed air that was dehumidified and filtered through a 4-stage purification system. The dilution and sampling system was designed to optimize the mixing of dilution air and exhaust, minimize nucleation of vapors, and to allow for either number, mass, or size distribution analysis with few adjustments. The total cost of the entire system, including diesel generator, piping, flow meters, CPC, balances, and impactor was \$24,500, and the footprint of the system in the laboratory was approximately 7 m<sup>2</sup> (78 square feet).

**2F.11****Enhanced Oxidation of Iron-containing Carbon Particles.**

YONG HO KIM, Kwang Seung Lee, Jae Wook Jung, Song Kil Kim, In Dae Choi, Donggeun Lee

The Regulation for vehicle emission which gets more and more strict initiates a variety of researches on the natural regeneration of diesel particulate filter (DPF). Reducing oxidation temperature of carbon-based particulate matter (PM) accumulated on the DPF up to exhaust gas temperature has been regarded as one of the biggest challenges in this research society. In this paper, we have tested metallic fuel additives such as ferrocene as oxidation catalyst. As a model system, a hydrogen-air diffusion flame was employed to burn the diesel droplets containing the ferrocene. As contents of the ferrocene increase, the oxidation gets faster together with reduction of the corresponding activation energy. A variety of tools such as SIMS, TGA, FTIR, HR-TEM, EDS, and SAD are employed to explain the catalytic behavior of ferrocene and characterize the metal-containing PMs as well.

**2F.12****Evolution of Particle Size Distribution Function of Nascent Soot in Premixed Ethylene Flames.**

AAMIR ABID, Nicholas Heinz, Erik D. Tolmachoff, Denis J. Phares, Charles S. Campbell, Hai Wang

The transition from apparent unimodal size distribution to bimodal distribution is studied for soot produced in premixed ethylene-oxygen-argon flat flames at equivalence ratio  $\phi = 2.07$  over a range of maximum flame temperatures. The objective of the study is to provide insights into the relation between the evolution of particle size distribution function (PSDF) and particle morphology. Experiments are carried out using an in-situ probe sampling methodology in tandem with a scanning mobility particle sizer (SMPS). The evolution of PSDFs was followed as a function of distance from the burner surface. Particle morphology and properties was examined by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The transition of the unimodal PSDF in a high temperature flame ( $T_f < 1730$  K) to a bimodal PSDF of low temperature flame ( $T_f \sim 1500$  K) shows a continuous shift of the trough between the nucleation and coagulation modes to larger particle sizes. The location of the trough was previously understood to be fixed. TEM and AFM evidence suggest that particles are liquid-like and undergo spreading on a solid substrate.

**2F.13**

**Effects of Fuels on the Characteristics of Exhaust Particles from 4-Stroke Motorcycle Engine.** Wen-Yinn Lin, Hsiang-Hsi Hsu, Yung-Yi Zhang, You-Ru Xie, National Taipei University of Technology; CHIH-CHIEH CHEN, National Taiwan University.

In Taiwan, motor vehicles are a major source of air pollution. There are about twenty-million motor vehicles in Taiwan. Particles emitted from motorcycles and formed by gas reaction or condensation deteriorate ambient air quality. Not many researches had been conducted to study motorcycle emissions. Researches on exhaust gas from motorcycle were most focused on effect of engine speed. In this study, the particle measurement system consisted of a 4-stroke Motorcycle Engine (125 c.c.), Dynamometer, ELP, MOUDI and Nano-MOUDI. Different fuels, 92 unleaded gasoline and 95 unleaded gasoline, were used to study their effects on the particulate emission. An IC and an EA were used to analyze characterization of particles.

The results suggested that particle number concentration decreased as engine rotational speeds increased. However, it increased as torque increased. Using 92 unleaded gasoline as the tested fuel, the results suggested that number concentration was  $5.6 \times 10^{10} \text{ #/cm}^3$  when rotational speed at idle and number concentration was  $1.1 \times 10^{10} \text{ #/cm}^3$  when rotational speed at high speed (5775 rpm). Moreover, number concentration was  $3.5 \times 10^9 \text{ #/cm}^3$  when torque was 2.0 Nm, number concentration was  $3.2 \times 10^{10} \text{ #/cm}^3$  when torque was 4.0 Nm. Using 95 unleaded gasoline as the tested fuel, the results suggested that number concentration was  $2.1 \times 10^9 \text{ #/cm}^3$  when rotational speed at idle and number concentration was  $2.4 \times 10^8 \text{ #/cm}^3$  when rotational speed at high speed (5775 rpm). Moreover, number concentration was  $4.1 \times 10^8 \text{ #/cm}^3$  when torque was 2.0 Nm, number concentration was  $9.3 \times 10^9 \text{ #/cm}^3$  when torque was 4.0 Nm. By using 92 unleaded gasoline and 95 unleaded gasoline as the tested fuel, carbon content and organic carbon content decreased as rotational speeds increased, while element carbon content increased as rotational speeds increased. Organic carbon content increased as torque increased, while element carbon content decreased as torque increased.

**2F.14**

**Influence of Driving Conditions on Particle Size Distribution, Chemical Composition, and Mass Emission Rates from In-Use Heavy Heavy Duty Diesel Trucks.** AJAY KUMAR CHAUDHARY, George Scora, Wayne Miller, David R. Cocker III, Matthew Barth, University of California, Riverside.

Real-time particulate matter measurements using a Dekati Mass Monitor (DMM) and a fast scanning mobility particle sizer (f-SMPS), and a DustTrak were obtained from several heavy heavy-duty diesel trucks (HHDDT) operating on Southern California roadways. The key objectives of this work were to 1) fully characterize the response characteristics of these realtime instruments and compare their responses to integrated filter substrates (federal compliance method), during various on-road vehicle operations, 2) identify changes in size-resolved chemical composition of emissions during on-road transit due to changes in traffic density, and 3) provide critical modal PM emissions data for development of a particulate module for a vehicle emissions model, under development at CE-CERT. Total engine out emissions were captured using the CE-CERT mobile emissions laboratory (MEL), a CVS full flow dilution tunnel system that captures total emissions from the HHDDT that tows the laboratory. The MEL was attached to the tractor pulling our mobile emissions laboratory (MEL). The MEL was used for total capture of emissions from several HHDDTs driven on Southern California highways and arterial roads. The HHDDTs were driven over a wide range of operating conditions, such as freeway and city driving, to obtain a representative activity and emission data set for the California air basin.

We will present a comparison of real-time PM devices to integrated measurements as they relate to the changing chemical composition (such as elemental vs. organic carbon) of the vehicular exhaust. We will then discuss the application of this data into a vehicle emissions model designed to predict second-by-second emissions from HHDDTs. Such microscopic emission models are useful in evaluating operational improvements from traffic control measures and can also be used to support large-scale emission estimation models involved in evaluating transportation policy.

## 2F.15

**Air Pollution with Particulate Matter and Heavy Metals of Kosovo Thermal Power Plant.** AGRON VELIU, Afrim Sylja, Kadri Berisha

Kosovo is a mountainous farm region which at past was in the process of industrialization because of its reach coal and mineral resources. The problem of air pollution in the surroundings of Power Plants appeared as early as 1954 when Thermal Power Plant of Kosovo has started work in Obiliq.

The city of Obiliq, approximately 5 km north of Prishtina-capital of Kosovo, is the site of one the largest air pollution. Coal - related industries have been a major element of the economy of Kosovo, but created extensive health risk due to environmental pollution with PM and a variety of other substances.

Electricity in Kosovo is produced by two lignite-fired TPP (Thermal Power Plant) \Kosovo A\ - (five units) and \Kosovo B\ - (two units), with total installed generation capacity of 1,513 MW. Most of the units of the two thermal plants are in poor operating conditions so that the present available capacity of the system is only 841 MW.

The combustion process leads to the generation of emissions to air, water and soil, of which emissions to the atmosphere are considered to be one of the main environment concerns. The most important emissions to air from the combustion of fossil fuels are SO<sub>2</sub>, NO<sub>x</sub>, particulate matter (PM), heavy metals and greenhouse gases such as CO<sub>2</sub>. The problem with dust emissions is serious and apparently cannot be solved without major redesign of the boilers. Ash from the both power plants is currently transported by open belt conveyors and is deposited at dumpsites. No environmental protection measures in the dumpsites are taken to prevent ash spreading by wind. Deposition of ash in dumpsites must stop as soon as possible and instead use ash for backfilling of mined parts of the lignite mines. Closed belt conveyors should be used to prevent spreading of fine dust particles during transportation of ash.

## 2F.16

**Comprehensive Characterization of Ultrafine Particulate Emission from 2007 Diesel Engines with Aftertreatment: PM Size Distribution, Loading and Individual Particle Size and Composition.** ALLA ZELENYUK, Pacific Northwest National Laboratory; Luis A. Cuadra-Rodriguez, University of Colorado at Boulder; Dan Imre, Imre Consulting; Shirish Shimpi, Alok Warey, Cummins Inc.

One of the most important sources of BC is vehicular emissions, of which diesel represents a significant fraction. The new EPA regulations significantly limit the amount of particulate mass that can be emitted by diesel engines. New engines are equipped with aftertreatments that reduce PM emissions to the point, where filter measurements are subject to significant artifacts and characterization by other techniques presents new challenges.

We will present the results of the multidisciplinary study conducted at the Cummins Technical Center in which a suite of instruments was deployed to yield comprehensive, temporally resolved information on the diesel exhaust particle loadings and properties in real-time: Particle size distributions were measured by Engine Exhaust Particle Sizer and Scanning Mobility Particle Sizer. Total particle diameter concentration was obtained using Electrical Aerosol Detector. Laser Induced Incandescence and photoacoustic techniques were used to monitor the PM soot content. Single particle mass spectrometer (SPLAT) provided the aerodynamic diameter and chemical composition of individual diesel exhaust particles. Measurements were conducted on a number of heavy duty diesel engines operated under variety of operating conditions, including FTP transient cycles, ramped-modal cycles and steady states runs. We have also characterized PM emissions during diesel particulate filter regeneration cycles. We will present a comparison of PM characteristics observed during identical cycles, but with and without the use of aftertreatment. A total of approximately 100,000 individual particles were sized and their composition characterized by SPLAT. The aerodynamic size distributions of the characterized particles were between 50 and 300 nm, depending on engine operating conditions and particle compositions. We will show that while the drastically reduced diesel PM emissions often render the PM filter measurements inadequate due to organic vapor artifacts SPLAT provided in real-time the size and composition of individual diesel exhaust particles as function of engine operating conditions.

**2F.17**

**BioDiesel Combustion.** DABRINA D DUTCHER, Joakim Pagels, University of Minnesota, Minneapolis; Deborah S. Gross, Carleton College; Anil Singh Bika, Luke Franklin, Mark Stolzenburg, David Kittelson, Peter H. McMurry, University of Minnesota, Minneapolis.

The world is currently moving toward increased use of biomass-derived alternative fuels. This move is motivated primarily by concern over carbon dioxide emissions and dependence on foreign sources of petroleum products. Biodiesel from several sources has been promoted as an alternative to traditional diesel fuels. Several states and regions have mandated the use of biodiesel mixtures. This increased use of biodiesel has potential implications for air pollution and the emissions from biodiesel combustion have been studied much less than those from traditional petroleum-based diesel. In this work, we focus on the combustion products from soy-based biodiesel/diesel mixtures burned in a dynamometer-mounted, 1999 1.9 liter displacement Volkswagen TDi engine. The engine was run at constant speed and load (2000 RPM and 15% load) for all tests. A dilution system that can replicate typical atmospheric dilution conditions was used to condition the aerosol before sampling. Instrumentation included two Aerosol Time of Flight Mass Spectrometers covering different size ranges for analysis of single particle composition, an Aethalometer for black carbon, a Scanning Mobility Particle Sizer for particle size distributions, a Photoelectric Aerosol Sensor for particle bound polycyclic aromatic hydrocarbon species and a Tapered Element Oscillating Microbalance for mass concentrations. The biodiesel/diesel experiments were run with fuels containing 0, 2, 20, 50, and 99.9% biodiesel, with the remainder of the fuel consisting of commercial low-sulfur diesel fuel. Particles of various compositions were detected for each of these fuel blends, with certain particles being attributed to uncombusted lubricating oil and others attributed to unburned or partially burned fuel. Trends in composition and size distribution across the various fuel mixtures will be presented. Preliminary results show that the addition of biodiesel does not reduce the particulate mass concentration and that the typical tracers used for diesel emissions are not applicable to biodiesel emissions.

**4D.1**

**Modeling of Soot Formation in Diesel Engine with a Sectional Aerosol Model.** CHOWDHURY MONIRUZZAMAN, Fangqun Yu, State University of New York at Albany.

Study of soot particle formation in the combustion engine becomes one of the important research fields because of the harmful effects of soot on human health and on climate. Controlling soot emission is one of the important goals in engine design to improve air quality. A clear understanding of the key processes and parameters controlling soot formation and size distribution evolution is important and remains to be achieved. A simple eight steps chemical kinetic model for soot formation was included into a sectional aerosol dynamics model to simulate the size distribution evolution of soot inside a diesel engine. Typical fuel injection and pressure profiles that give the temperature profile in a diesel engine were used as input to study the soot formation and evolution. In the simple soot formation scheme, a 2-carbon-atom soot nucleus is formed from an intermediate radical specie which is formed from the fuel molecules. Then soot grows by surface reaction, oxidation and coagulation. NO<sub>x</sub> formation equation was also included into the kinetic model to balance soot-NO<sub>x</sub> formation because high temperature gives less soot but more NO<sub>x</sub> and vice versa. Effects of different nucleation rates, oxidation rates, surface reaction rates, fuel injection rates and temperature profiles on soot size distribution were studied. The effect of number of carbon atoms in a fuel molecule was also studied. The model results were compared with a simple model and other studies as well as some observations. Our simulations show that in the earlier stage of particle formation, soot number concentration was dominated by nucleation and then it was limited by coagulation. Temperature is the most important parameter in the soot growth process. Detailed evolution of soot size distributions under different key parameters of engine will be presented.

**4D.2****Nucleation Mode Particle Emissions from In-use Heavy Duty Vehicles Equipped with DPF and SCR Retrofits.**

JORN D. HERNER, Alberto Ayala, William H. Robertson, Oliver Chang, California Air Resources Board; Constantinos Sioutas, Subhasis Biswas, University of Southern California.

The emissions standard for particulate matter from new heavy duty engines was reduced from 0.1 g/bhp-hr to 0.01 g/bhp-hr in 2007. Similarly, the NO<sub>x</sub> emissions standard for these same types of vehicles will be reduced from last year's 2 g/bhp-hr to an eventual 0.2 bhp-hr limit in a stepwise fashion between 2007 and 2010. While diesel engine manufacturers have been able to meet previous emissions standards with engine design modifications and combustion process improvements, the new very low emission limits called for in California and the rest of the US will lead to nearly universal introduction of advanced after-treatment devices such as particle traps of various configurations and NO<sub>x</sub> scrubbers. Some of those systems are currently being investigated in retrofit demonstrations.

Many studies have shown these devices to be very effective at reducing the mass emissions of the targeted pollutants emitted by diesel engines as measured in units of mass emitted per power output. There is, however, some concern regarding how these aftertreatment devices may affect the emission of ultrafine (D<sub>p</sub><100nm) particles and the formation of nanoparticles (D<sub>p</sub><50nm). Some researchers have suggested that emissions of these very small particles may, under certain conditions, increase even as PM mass is decreased with the use of these aftertreatment devices.

In this work we will present our findings with respect to the particle number and particle size distribution in the emissions from several heavy duty vehicles of relevance to the California on-road fleet. The study was conducted at the California Air Resources Boards' Heavy Duty Diesel Emissions Test Laboratory in Los Angeles. In our laboratory, vehicles are exercised on a chassis dynamometer and emission samples are collected in concert with the protocols promulgated in the Code of Federal Regulations for emission certification. Results from vehicles equipped with diesel particulate traps and selective catalytic reduction (SCR) technology as well as a fully 2010 compliant CNG bus, a biodiesel and a medium heavy duty gasoline truck will be presented. These are some of the vehicles that make up the test vehicle fleet in our investigation.

Initial indications are that the formation of the nucleation mode is dependent on the amount of catalytic loading in the aftertreatment device and exhaust temperature with some cases resulting in sustained high concentrations of nanoparticles. Some chemical speciation and the volatility of these particles will also be presented.

**4D.3****Investigation of Diesel Nanoparticle Nucleation Mechanisms.**

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Most of the nanoparticle number emissions from diesel engines are found in the nucleation mode (D<sub>p</sub> < ~ 30 nm). These particles are mainly formed by nucleation as diesel engine exhaust gas cools and dilutes in the atmosphere. They have raised concerns because of their suspected human health effects. There are two main theories describing diesel nanoparticles nucleation: homogeneous nucleation, most likely binary of sulfuric acid and water; and ion-induced nucleation. In this study we assess the likelihood of the ionic mechanism. Previous studies have shown that diesel nucleation mode particles carry little or no electrical charge (Jung and Kittelson 2005). This could be due to the fact that they were never charged or that they were neutralized quickly during dilution and sampling. In the first part of this work we estimate the extent of neutralization of charged nuclei during dilution process and find it too slow compared to the residence time in our system to account for the absence of charge observed in previous work. In the second part of this work we compare nuclei mode formation with and without chemi-ions during dilution and sampling by using an ion trap at the upstream of dilution. Removing upstream ions had no significant influence on the nucleation mode suggesting that ionic nucleation did not play an important role. We also calculate ion concentration histories, accounting for recombination and attachment during expansion stroke in after combustion. This calculation indicates that ion concentration in the exhaust is too low to account for nucleation mode formation.

**4D.4**

**Physical, Chemical, and Toxicological Characteristics of Combustion Generated Iron-Soot Aerosols.** AUDREY T. TURLEY, North Carolina State University; Jost O.L. Wendt, University of Utah; Seung-Hyun Cho, C. Andrew Miller, M. Ian Gilmour, William P. Linak, U.S. Environmental Protection Agency.

A number of commercial diesel fuel additives contain metal catalysts designed to reduce emissions of carbon monoxide, hydrocarbons, and soot as well as improve engine performance. However, as these metals are not consumed during combustion, they can be emitted into the environment and result in human exposures. This research examines how one such iron-based organo-metallic fuel-borne catalyst, ferrocene, intended to improve fuel efficiency and reduce emissions, modifies the physical and chemical properties of soot, and the potential health consequences associated with iron addition. Previous experiments examining ultrafine particle emissions from both residual fuel oil and pulverized coal combustion have indicated relationships between particle size, composition, and toxicity. Further, these results were consistent with mechanisms whereby transition metals interact with soot to produce reactive oxygen species and oxidative stress.

As a first step toward examining the behavior of such metal catalysts in diesel engines, ongoing experiments are examining soot generated from atmospheric pressure ethylene/air laminar diffusion flames. Without ferrocene addition, pure soot particles are collected, characterized, and compared to particles collected from the exhausts of diesel engines. Addition of controlled quantities of ferrocene produces particles containing both iron and soot with iron contents up to 20%. The physical and chemical characteristics of the samples are characterized using a scanning mobility particle sizer, X-ray fluorescence spectroscopy, carbon aerosol analysis, and electron microscopy. Results indicate that iron addition causes a substantial reduction in the soot aerosol mass emissions, and a notable modification of the particle size distribution. Corresponding toxicological experiments involving intratracheal instillation of particles in mice are examining indicators of pulmonary inflammation and induced allergic asthma-like responses to samples composed of soot only, soot-iron additive composites, and physical mixtures of soot and commercially purchased gamma-Fe<sub>2</sub>O<sub>3</sub> nano-particles. (This abstract does not reflect EPA policy.)

**4D.5**

**Effects of sampling conditions on size-segregated PM mass and its chemical composition emitted from a diesel backup generator.** KWANGSAM NA, CE-CERT; Abhilash Nigam, Ajay Chaudhary, William Welch, Kent Johnson, Wayne J. Miller, David R. Cocker III, University of California-Riverside, CE-CERT.

Information on exhaust speciation profiles of particulate matter (PM) from modern ship engines is insufficient/lacking. This study seeks to obtain particle size distribution and size segregated chemical characterization for representative commercial ship engines using low and high sulfur (S) fuel. Accordingly, preliminary tests were conducted with a diesel source-back up generator (CAT/3406C/00) as a ship-engine substitute. The effect on particle size distribution and chemical characterization on a size segregated basis using a rotational Micro-Orifice Uniform Deposit Impactor (MOUDI) was investigated using these parameters: temperature of the dilution air (ambient temperature and 48 degrees C); dilution ratio (5:1 and 10:1); and effect of fuel S content (0.0015% and 2%). The cumulative size based weights obtained from the MOUDI were compared with Teflon filter based PM mass for different sets of conditions. The effect of dilution and fuel S was also studied using the Scanning Mobility Particle Sizer (SMPS) and Dekati Mass Monitor (DMM) in addition to Teflon-filter based and MOUDI based measurements. The number and/or mass concentrations obtained from MOUDI, DMM, SMPS, and Teflon filter sampling will be assessed.

Tests indicate that the MOUDI sampling gives higher PM mass than the filter-based sampling. This difference is clearer in high S and low dilution conditions. The results show that high S fuel generates more particles than low S fuel on mass basis. The effect of dilution ratio varies with fuel in MOUDI sampling--higher dilution ratio for high S fuel witnessed higher particle mass. Conversely, for filter-based sampling, PM mass collected was higher for low dilution ratio. The effect of dilution ratio, temperature, and S content on particle size distribution and chemical characterization on a size segregated basis will be discussed. Additionally, chemical compositions of after filter will be assessed in terms of the three parameters.

**4D.6**

**Characteristics of Diesel Exhaust Particles and their Health Effects in Mice.** SEUNG-HYUN CHO, William P. Linak, C. Andrew Miller, National Risk Management Research Laboratory, U.S. EPA; Jost O.L. Wendt, University of Utah; M. Ian Gilmour, Q. Todd Krantz, National Health & Environmental Effects Research Laboratory, U.S. EPA; Tina Stevens, University of North Carolina; Kymberly Gowdy, North Carolina State University.

Diesel exhaust particles (DEP) have become a health concern because of their small size and complex chemistry and have been linked to increased risk of respiratory diseases. As part of a broad research program, a series of inhalation exposure studies were conducted over the course of two years to investigate the pulmonary toxicity of DEP in mice in association with development of respiratory allergy or influenza infection. A four-cylinder diesel engine with a compressor was used to generate the DEP. Mice were housed in inhalation chambers and exposed to the DEP. During the exposure, gas and particulate concentrations as well as particle size distributions were monitored in real-time, and DEP was collected on filters from the chambers and in a baghouse at the engine exhaust for chemical analyses. Filter samples were analyzed for organic and elemental carbon (OC/EC) and bulk samples were analyzed for extractable organic matter (EOM) and inorganic elements. Geometric mean diameter of the airborne DEP ranged 82-102 nm, OC/EC mass ratio ranged 0.2-0.8, and EOM comprised 10-40% of the DEP mass. These results suggest that the DEP from this engine has organic characteristics between the NIST SRM2975 and Japanese DEP reference samples most commonly studied. Alkanes and organic acids were most abundant in the organic extracts comprising ~85% of the analyzed organics and polycyclic aromatic hydrocarbons comprised ~10%. S, Cl, Zn, Ca, Fe were the most abundant inorganic non-carbon elements in the DEP typically comprising less than 5% of mass. Toxicological endpoints showed that DEP exposure produced inflammation, caused allergic adjuvant effect and increased viral susceptibility. Microarray analyses indicated gene expressions were altered after exposure to DEP. (This abstract does not reflect EPA policy.)

**5D.1**

**Spark Ignition Exhaust Particle Composition from Ethanol-Gasoline Blends: A Single Particle Perspective.** DABRINA D DUTCHER, University of Minnesota; Deborah S. Gross, Carleton College; Marcus Drayton, Mark Stolzenburg, David Kittelson, Peter H. McMurry, University of Minnesota.

Ethanol is being promoted as an alternative biomass-based fuel for use in spark ignition vehicles. Due to its agricultural origin and its function as a fuel oxygenate, many states and regions mandate its use. Blends consisting of 10% ethanol and 90% gasoline are commonly burned as a spark ignition fuel in ordinary vehicles while 85% ethanol and 15% gasoline can be burned in specially equipped vehicles. While it is well established that the addition of ethanol to a fuel reduces the particulate mass concentration in the exhaust, little attention has been paid to changes in the composition of the particles. In this work, a dynamometer-mounted 1994 GM Quad-4 spark ignition engine run at 1500 RPM and 100% load was used with five different fuel blends, containing 0, 10, 20, 40 and 85 percent ethanol. A dilution system that can replicate typical atmospheric dilution conditions was used to condition the aerosol before sampling. Instrumentation included two Aerosol Time-of-Flight Mass Spectrometers covering different size ranges for analysis of single particle composition, an Aethalometer for black carbon, a Scanning Mobility Particle Sizer for particle size distributions, a Photoelectric Aerosol Sensor for particle-bound polycyclic aromatic hydrocarbon (PAH) species and gravimetric filter measurements for mass concentrations. It was found that adding ethanol to the fuel decreases the particulate mass concentration, changes the PAH molecular weight distribution, decreases the concentration of black carbon, and changes the particle size distribution. PAHs produced from higher ethanol fuels are more highly associated with  $\text{NO}_2^-$  ( $m/z=46$ ) in the single-particle mass spectra, indicating the presence of nitro-PAHs. Compounds associated with the gasoline (e.g. sulfur) are diminished relative to those associated with the lubricating oil (e.g. calcium, zinc, phosphate) in the single particle spectra as ethanol is added.

**5D.2**

**Regulated Emissions from Yard-tractors: In-use and Futuristic Technologies.** ABHILASH NIGAM, Ajay K. Chaudhary, J. Wayne Miller, Kent C. Johnson, and David R. Cocker III, University of California Riverside, CE-CERT.

World-wide marine ports are major hubs of economic activity and facilitate cargo movement to support country's economies. This global movement of goods occurs through a chain of logistic support at ports and countryside and indirectly this movement also contributes to certain adverse environmental impacts. The California Air Resources Board (ARB) estimated that ports were responsible for 21% of the total diesel PM emissions in the California South Coast Air Basin in 2002. The Hahn report emphasized that cargo handling equipment (CHE) contributes about 26% of the NO<sub>x</sub> and 36% of the PM emissions at the port. With over 60% of CHE units represented by yard-tractors, ARB estimated that yard-tractors accounted for significant percentage of NO<sub>x</sub> and PM emissions from CHE units. Yard tractors are units powered with diesel engines and designed for the movement of containers within the port-terminals. There is lack of any peer-reviewed literature on emissions from yardtractors. The UCR/CE-CERT Heavy-Duty Mobile Emissions Laboratory (MEL) was used to quantitate regulated emissions (PM, NO<sub>x</sub>, CO, THC) from these sources. The engines were chosen to represent baseline off-road engines and to evaluate the effectiveness of futuristic technologies. The ARB 8<sup>th</sup> Mode Cycle for certifying off-road vehicles and diesel-powered off-road industrial equipment was used for our testing. The testing included a baseline ultra-low sulfur diesel (ULSD) fuel and a water-emulsified fuel.

A comparison between the emissions with the ULSD and emulsified fuels showed that the emulsified fuel have lower NO<sub>x</sub> and PM emissions. Emissions of CO and THC increased when CARB fuel was replaced with emulsified fuel. Comparison of emissions for a similar on-road engine showed lower emissions of NO<sub>x</sub> and PM when compared to the off-road engine technology even though both engines were 2004 Cummins 5.9L versions.

**5D.3**

**Elemental Composition of Motor Vehcile Fuel, Oil, and Particulate Matter Emissions.** MICHAEL A. ROBERT, Chris A. Jakober, Peter G. Green, Michelle A. Gras, Michael J. Kleeman, University of California, Davis

The present study examines the elemental composition of gasoline, diesel fuel, and/or motor oil sampled from in-use light-duty gasoline vehicles (LDGVs) and heavy-duty diesel vehicles (HDDVs). These results are compared to PM elemental composition measured in six size fractions between 0.056-1.8 micro-meter particle diameter from chassis dynamometer experiments that employed the same motor vehicles, data which in turn is compared to the size-resolved elemental composition of PM collected near a busy freeway.

The most abundant elements observed in gasoline from LDGVs were S, Si, Ni, Fe, and Cu, while the most abundant elements found in diesel fuel from HDDVs were S, Zn, Ca, P, Si, and Sr. Trends between LGDV and HDDV motor oil data sets are consistent with Ca most abundant followed by Zn, P, S and K. The source of elements in gasoline is likely residual contamination from the refining process or contamination from within the vehicles sampled whereas the primary source of elements in diesel fuel and motor oils is likely from additive packages.

Zn was the most ubiquitous element detected in tailpipe emissions, with PM<sub>1.8</sub> emission factors ranging from 36-6826 ng/km. Al, K, Ni, and Cu were also present in both LDGV and HDDV PM; however the LDGV data set contained unique elements of lower molecular weight than the HDDV data set. Ca and Fe tailpipe emissions from LDGVs were well correlated with gasoline concentrations, as were Mg, Cr, Mn, and Pb with motor oil concentrations. For HDDVs, Ca, Cu, Zn, Se, Sr, Cd, and Pb tailpipe emissions were well correlated with diesel fuel concentrations; no strong correlations with motor oil concentrations were observed. Freeway emissions of particulate Ca and Zn had size distributions that were bimodal and of similar shape to HDDV dyanometer emissions between 0.1-0.18 micro-meter and LDGV dynamometer emissions between 0.56-1.0 micro-meter.

**5D.4**

**Physical Properties of Particulate Matter (PM) from Newer Heavy Duty Diesel Vehicles Operating with Advanced Emission Control Technologies.** SHAOHUA HU, Subhasis Biswas, Constantinos Sioutas, University of Southern California; Jorn D. Herner, William H. Robertson, Alberto Ayala, California Air Resources Board.

Particulate matter (PM) emitted from vehicular sources consists of both non-volatile and semi-volatile fractions. Emission control technologies used in compliance with US07 Emissions Standards remove effectively the non-volatile fraction, but are less effective at controlling the volatile fraction. Removal of the non-volatile PM can favor the formation of nano particles ( $dp < 0.05$  micro-meter) by enhancing nucleation of condensing vapors. Epidemiological studies have associated ultrafine particles with adverse health effects. However, there are limited references about physicochemical and toxicological properties specific to the semi-volatile and non-volatile fractions respectively emitted from heavy duty diesel (HDD) vehicles equipped with advanced emission control technologies.

This paper will present the physical properties of emissions from a HDD vehicle operated with two different emission control technologies under different driving cycles.

Measurements are taken from a HDD vehicle equipped with selective catalytic (vanadium or zeolite based catalyst) reduction systems, combined with a diesel particulate filter (DPF) under three driving cycles: cruise, Urban Dynamometer Driving Schedule (UDDS) and Idle. Sampling is conducted at the California Air Resources Board's (CARB) Heavy-Duty Diesel Emissions Test Laboratory (HDETL). The sampling train includes heavy duty (HD) dynamometer chassis, constant volume sampling (CVS) dilution tunnel and aerosol samplers. Each cycle is repeated until enough PM mass is loaded onto the collection substrates for chemical and toxicological analysis.

Size-resolved samples are collected by a MOUDI- NanoMOUDI loaded with aluminum foil substrates. Volatilities of PM are investigated using two thermal denuders to remove portion of the volatile fraction of PM. Several real time instruments are employed to fully characterize the total number concentration, size distribution; particulate bound PAHs and active surface area of emissions at a high time resolution.

Preliminary results indicate significant reduction of NO<sub>x</sub> and PM mass emission rate. Considerable amounts of nucleation mode particles are observed under high load during cruise cycle as well as UDDS acceleration mode yielding PM number based emission factors comparable to HDDV without emission control technology.

**5D.5**

**Effect of Dilution Temperature on the Measured Particle Size Distributions from a Coal-Firing Power Plant.** ERKKI LAMMINEN, Henna Isherwood, Dekati Ltd.

Investigations of particle size distributions from combustion sources are typically preceded by conditioning of the sample with a purpose to eliminate condensation and nucleation of vapor species. While this method has been proven to be reliable and repeatable it does not necessarily represent ambient (i.e. real-life) dilution conditions accurately. In this study, we focused on the effect of dilution temperature on the measured particle size distributions from a coal-firing power plant.

The conditioning of the sample was carried out by using combined perforated tube and ejector dilution, namely the FPS-4000 (Fine Particle Sampler, Dekati Ltd.), which allows the control of dilution temperature over a range from 0 to 350 degrees Celsius. The effect on the particle size distribution was determined with the ELPI<sup>TM</sup> (Electrical Low Pressure Impactor, Dekati Ltd.). The measurement instrument was selected due to its wide particle size measurement range (from 7 nanometers to 10 micrometers) and capability to measure in real-time. The emission source was a 665 MW coal-firing power plant in southern Finland, where the measurements were carried out in February of 2007. The sample was taken at the stack after flue gas treatment devices. The measurements consisted of repeated dilution temperature ramps with stable temperature measurements with both heated and cooled dilution. The studied quantities were particle size distribution and particle number and mass concentration.

A repeatable decrease of the particle number distribution count median diameter from 700 nm to 200 nm was observed when the dilution temperature was lowered. In addition, a nucleation mode below 30 nanometers was formed with sufficiently low dilution temperature. The particle number concentration increased tenfold with the decrease of dilution temperature, while the effect on mass concentration was much more subtle. In addition to these results, experiences from performing particle measurements at sub-zero temperatures will be presented.

**5D.6**

**A Model for Sooting Limits in Diffusion Flames.** SCOTT SKEEN, Richard Axelbaum, Washington University in St. Louis; Ben Kumfer, University of California at Davis.

Oxygen enriched combustion has been shown to reduce soot formation in diffusion flames by altering the flame structure, i.e. the relationship between the local temperature and the local gas composition. The extent of oxygen enrichment and fuel dilution is quantified by the stoichiometric mixture fraction. Previous studies have shown a linear relationship between the limit flame temperature and stoichiometric mixture fraction for flames at their sooting limit [1, 2]. The sooting limit is obtained by varying the amount of inert gas until soot appears above a predefined height. In this work sooting limits based on particle luminosity are measured as a function of  $Z_{st}$ . For each limit flame, the flame temperature is measured and defined as the limit temperature. The limit flame temperature increases linearly with  $Z_{st}$ , for both normal and inverse flames. The effects of residence time are also investigated, and the soot inception temperature is found to be dependent on fuel stream velocity for both the normal and inverse configuration. Earlier experimental results and modeling indicated that a critical carbon to oxygen (C/O) ratio exists in the fuel rich region of the flame where soot inception is no longer favorable due to the presence of oxygen containing species [2]. We extend this model to include the effects of finite rate chemistry and thus residence time on the sooting limit. This involves considering two boundaries for the soot inception zone, one dictated by the C/O ratio and the other by the finite rate chemistry of fuel pyrolysis and soot inception. By combining these two boundaries, a simple model is developed that describes how a sooting limit is attained. By utilizing measured limit temperature data with the model we show the limit inception temperature for soot formation to be 1640 K and the critical carbon to oxygen ratio to be 0.53.