Supplementary Materials

Filterable $PM_{2.5}$, Metallic Elements, and Organic Carbon Emissions from the Exhausts of Diesel Vehicles

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S1. Diesel engines testing

Exhausts from diesel vehicles were settled from the tailpipe through a dilution tunnel full-flow, which is coordinating a constant volume sampling (CVS) system. Such exhausts were drained from the tunnel of dilution to a manifold of stainless steel, where it get segregated into three streams and directed, through 1/4 in stainless steel and Teflon lines, to canister, and sorbent-backed filter sampling systems employed for the collection of $PM_{2.5}$, correspondingly. Furthermore, all amount of fuel is passed under a constant flow rate of volume in l litre/hour throughout the testing period. Fuel utilization quantity was measured by a regulated measuring cylinder in litre/minute (L/min). With the purpose of removing the impediment of the oil residual in the emissions of combustion, each testing run is performed with 100% diesel for an half hour prior to the set-up of exact sampling (Yang *et al*., 2015; Lin *et al*., 2019).

The performance of diesel engines is significantly influenced by their injection system designs. In actual fact, the most prominent advances attained in diesel engines resulted directly from superior fuel injection system designs. Although the main purpose of the system is to deliver fuel to the cylinders of a diesel engine, it is how that fuel is delivered that makes the difference in engine performance, emissions, and noise characteristics (Lin *et al.*, 2019; Khair and Jääskeläinen, 2013; Bosch, 1971). Unlike its spark-ignited engine counterpart, the diesel fuel injection system delivers fuel under extremely high injection pressures.

In order for the engine to efficiently make use of this fuel must be injected at the proper time, that is, the injection timing must be controlled and the correct amount of fuel must be delivered to meet power requirement, that is, injection metering must be controlled. However, it is still not enough to deliver an accurately metered amount of fuel at the proper time to achieve good combustion. Additionally, other characteristics are important to ensure proper fuel injection system performance, including fuel atomization and complete evaporation of fuel, ensuring that the evaporated fuel has sufficient oxygen during the combustion process is similarly as significant to guarantee high combustion efficiency and optimum engine performance. The oxygen is provided by the intake air trapped in the cylinder and a sufficient amount must be entrained into the fuel jet to completely mixed with the available fuel during the injection process and ensure complete combustion (Stanfel, 2009). The fuel injection system of a diesel engine plays a crucial role in reducing exhaust emissions by determining the spray formation ignition and combustion (Lin *et al*., 2019; Pilusa *et al*., 2012; Corkwell *et al*., 2003).

S2. Sampling procedures for pollutant emissions

Under this study, the pollutant emissons for each test was examined and assessed through a CLD (chemiluminescent detection) (model 404, Rosemount, UK). Whereas carbon monoxide (CO) was similarly distinguished with a NDIR (nonedispersive infrared detector) (model 880A, Rosemount, UK). The PM for each sampling filter was measured and weighed using an electronic analytical balance, entirely automatic calibration technology (AT200, Mettler, Switzerland) to set up the net mass of the collected PM. The exhaust samples were composed from the ignition of the diesel vehicle engines according to the US EPA method to quantify pollutant emissions. All pollutant emissions were at that point, captured in the cartridge and converted to equivalent hydrazone derivatives. The active carbons filters were applied to decontaminate the ambient air concentration. Consequently, ambient clean air was used for the dilution of the original exhaust to drop down the initial exhaust temperature. The quartz filters were used to collect the PM during the experiments. There was no upper volume limit used throughout this experimental phase. The sampling period was arranged at 60 minutes per test route. The diesel engine flue gas collection in this study was in accordance with the US federal test procedure, and an exhaust dilution channel was installed in the exhaust tail pipe. The exhaust dilution channel primarily provides a fixed and standard dilution ratio for the measurement of conventional contaminants (CO, NO_x) and aerosols ($PM_{2.5}$). Besides the European NEDC, other driving cycles have been developed and are used in different parts of the world to determine fuel economies and pollutant emissions (EEA, 2016; GFEI, 2015). The emissions under this investigation were collected by means of a dilution sampling method, as specified in the U.S. EPA’s Federal Test Procedure (FTP). United States Environmental Protection Agency (US EPA) test cycles Federal Test Procedure (FTP)-75 is commonly used for emission certification and to determine the fuel economy of light-duty vehicles in the USA. Subsequently 2000, vehicles have also had to be tested on two Supplemental Federal Test Procedures (SFTP) designed to address shortcomings with the original FTP-75 in representing demanding, high-speed driving and the use of air conditioning (Emisia, 2015; GFEI, 2015). Furthermore, this study have employed a steady state cycles in our investigation as the FTP Transient Cycle. This steady state cycle was applied to all the 15 tested vehicles and 3 replicates emission tests was conducted for each vehicle under this study.

S3. Sampling procedures and particle component analysis for EC/OC

Teflon filters were store for the duration of 24 h in a steady temperature humidity chamber prior and subsequently the test. Prior and after collection, filters were enfolded in baked aluminum foil. Before weighing, the filters were kept under a steady temperature and humidity condition of 25 °C and 50% for 24 h. Each and every filter was enfolded in an aluminum foil, before placed in an airtight bag, and taken to the laboratory for weighting by microbalance (Tsai *et al.,* 2010).

The concentrations of particle-bound total and elemental carbons (TC and EC, respectively) were determined using an elemental analyzer (Carlo Erba EA 1110). Notably, different measurement methods normally lead to a variation of determined carbon content. Recently, Chow *et al.* (2001) compared the carbon content measured using the IMPROVE and NIOSH methods. According to that study, the two methods differed mainly in the allocation of carbon evolving at 850 ◦C set by the NIOSH in a helium atmosphere to OC rather than to EC. This study attempted to determine the carbon content of particles by using a method (compatible OR comparable) with IMPROVE-TOR. For carbon species analysis, a weighted sample in a tin capsule was placed in an autosampler drum for deaeration. The sample was then introduced with helium into a 1000 ◦C vertical quartz tube to oxidize the He-carried flow and yielded a gas mixture flowing into a chromatographic column followed by a thermoconductivity detector (TCD). Next, a quarter of each sample filter was heated in a 340 ◦C oven for 100 min to expel the OC content, followed by feeding the sample into the element analyzer to obtain the EC content. Another quarter of each filter was fed directly into the elemental analyzer without 340 ◦C-heating pretreatment to quantify the TC concentration. The OC concentration was obtained from the difference between the TC and EC values. Finally, carbon content was determined using an organic analytical standard (OAS, Elemental Microanalysis Limited, B2038) containing purified urea was used as a routine working standard.

References:

Bosch. (1971). "Fuel Injection Equipment for Diesel Engines - Fuel Injection Pumps PE and PF", Robert Bosch GmbH, 1st ed., 1971.

Corkwell, K.C., Jackson, M.M., and Daly, D.T. (2003). Review of exhaust emissions of compression ignition engines operating on diesel fuel blends. *SAE Technical Paper*, 18.

Chow, J.C., Watson, J.G., Crow, D., Lowenthal, D.H., and Merriifield, T. (2001). Comparison of IMPROVE and NIOSH carbon measurements. *Aerosol Sci. Technol.* 34, 23-34.

Emisia. 2015. 'Copert 4'. Available from: http://emisia.com/copert (Accessed on 27th August 2019).

European Environment Agency (EEA). (2016). Explaining road transport emissions: A non-technical guide. Luxembourg: Publications Office of the European Union, 2016.

GFEI. (2015). International test cycles for emissions and fuel economy. Available from: http://www.unep.org/transport/gfei/autotool/approaches/information/test_cycles.asp (Accessed 21st September 2019).

Khair, M.K., and Jääskeläinen, H. (2013). Fuel Injection System Components. https://www.dieselnet.com/tech/diesel_fi_comp.php (Accessed 05 May 2019).

Lin, C-Y, Li, Y.C, Amesho, K.T.T., Chou, F-C, and Cheng, P.C. (2019). Characterization and quantification of $PM_{2.5}$ emissions and PAHs concentration in $PM_{2.5}$ from the exhausts of diesel vehicles with various accumulated mileages. *Sci. Total Environ.*, 660, 188-198.

Pilusa, T.J., Mollagee, M.M., and Muzenda, E. (2012). Reduction of Vehicle Exhaust Emissions from Diesel Engines Using the Whale Concept Filter. *Aerosol Air Qual. Res*., 12: 994-1006.

Stanfel, C.M. (2009). "Fuel filtration: protecting the diesel engine", Filtration + Separation, May/June 2009, 22-25.

Tsai, J.H., Chen, S.J., Huang, K.L., Lin, Y.C., Lee, W.J., Lin, C.C., and Lin, W.Y. (2010). PM, carbon, and PAH emissions from a diesel generator fuelled with soy-biodiesel blends. *J. Hazard. Mater.,* 179, 237-243

Yang, P.M., Lin, Y.C., Lin, K.C., Jhang, S.R., Chen, S.C., Wang, C.C., and Lin, Y.C. (2015). Comparison of carbonyl compound emissions from a diesel engine generator fueled with blends of *n*-butanol, biodiesel and diesel. *Energy*. 90, 266-273