APPLICATION NOTE

ACCELERATED AUTOMOTIVE EMISSION CONTROL CATALYST RESEARCH

PROBLEM

Engine manufacturers conduct emissions reduction research using test equipment that feeds a simulated automotive exhaust stream through candidate emissions abatement technologies. Once it has passed through the abatement system, the gas stream is analyzed to determine the efficiency with which the technology eliminates pollutants. Electronic mass flow controllers (MFCs) are used to produce the different gas mixtures that simulate the exhaust gas composition for a wide range of conditions. Precise knowledge of the independent operating parameters in an engine, the fuel formulation, and the chemical composition of the exhaust gas stream before and after the abatement technology enables the development of chemometric models that can be used to minimize engine emissions while maintaining acceptable performance. Robust chemometric modeling is only enabled if there are very low levels of variation in the controlled inputs. This demands precise, accurate and reproducible MFC calibration.

BACKGROUND

SOx (SO_2, SO_3) and NOx (NO, NO_2) form during the fuel combustion process in an engine [1]. Today, engine emissions of SOx are effectively controlled through the removal of the sulfur and sulfur containing compounds in gasoline and diesel fuels [2]. The reduction of NOx emissions is, however, more problematic. NOx is formed by the oxidation of nitrogen and the main source of nitrogen in combustion is the ambient air that supplies oxygen to the process. There is no cost-effective way to remove nitrogen from air in the combustion process within a conventional engine. For this reason, almost all research into engine emissions reduction focuses on the post-combustion elimination of NOx. EPA regulations on NOx emissions specify only nitrogen dioxide, NO_2, accepting it as a surrogate for all nitrogen oxides [3].

Since NOx has carcinogenic properties [4], it is a hazardous pollutant in its own right. Of even greater significance, however, is the fact it reacts with volatile organic compounds (VOCs) in the atmosphere to generate ozone, O_3, a pollutant of equal or greater hazard, as shown in Figure 1.

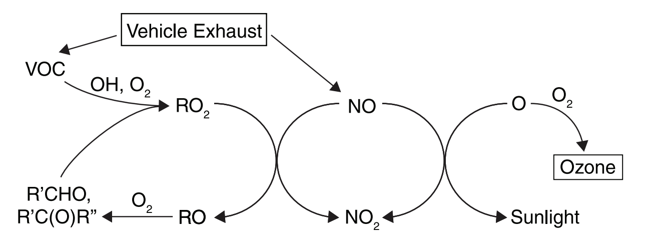

Figure 1 - Photochemical production of ozone [1].

The cyclic nature of NO_2/NO participation in ozone generation means that each NO_2 molecule can produce an ozone molecule multiple times. The EPA has identified ozone as a "criteria air pollutant" meaning that levels in outdoor air must be limited owing to the health hazard that they represent. EPA recognition of the link between even relatively low levels of NOx emissions and unacceptable ambient ozone levels is one of the driving forces for the increasingly strict regulation of NOx emissions from mobile or stationary energy sources, including automobiles, trucks, construction equipment, boats, power plants, boilers, kilns, turbines, etc. [3]. Starting in 2017, EPA Tier 3 will set new, lower standards for NOx emissions in all mobile and stationary engines.

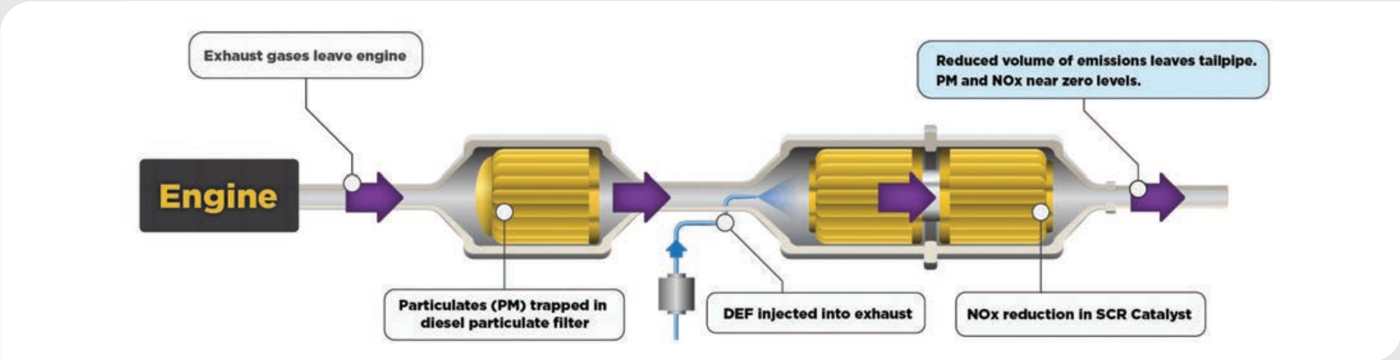

Figure 2 - Typical diesel emission control system.

For light duty vehicles and trucks, non-methane organic gases (NMOGs) and NOx emissions must be reduced by more than 80%, from today's fleet average of 160 mg/mile down to 30 mg/mile by 2025. For medium duty trucks, the reduction is 75%, from 200 mg/mile down to 50 mg/mile by 2025. Heavy duty vehicles will be required to reduce these emissions by 40-50%, depending on weight. Stationary engine emissions will be required to reduce NOx emissions by ca. 90%.

The proliferation of these stringent (and global) air quality regulations, fuel economy standards, and fuel formulation regulations requires ongoing research and verification of advanced engine emission control technologies. As a consequence, large global manufacturers of automotive and stationary internal combustion (ICE) and diesel (GCI) engines maintain extensive networks of research laboratory facilities that are dedicated to the development of fuel and engine technologies with reduced emissions of hazardous pollutants such as NOx. Because EPA Tier 3 requirements (2017) consider the vehicle and its fuel an integrated system, engine manufacturers must develop advanced chemometric models that incorporate the effects of the fuel type, engine operational parameters and exhaust gas treatment systems on performance and emissions. Catalytic converter technology has been the primary emission control solution employed by combustion engine manufacturers over the past four decades. Catalytic converters accelerate the reaction of harmful combustion exhaust gases such as NOx with other chemical compounds in the exhaust stream, converting them to less toxic emissions that comply with legislative specifications. Figure 2 shows the components in a diesel engine exhaust system that reduce particulate emissions and NOx emissions.

Leading catalyst suppliers (BASF, Johnson Mathey, Umicore and Haldor Topsoe) are multi-national corporations with multiple verification and validation test beds distributed across several laboratories in different geographic locations. Owing to the importance of catalyst performance, related testing is carried out at various points in the automotive supply chain including OEMs, Tier 1 and Tier 2 engine, powertrain, and emissions control test labs along with university and government labs.

Manufacturers' catalyst development programs typically evaluate a given catalyst's emission reduction performance by subjecting it to a series of different gas mixtures that simulate engine exhaust gas profiles over a wide range of engine exhaust temperatures, mass flow rates, fuel formulations and engine control algorithms. The response of the catalyst under different conditions can be used for the development of chemometric models that predict the performance of different configurations of fuel/engine/catalyst components. Advanced chemometric models enable the concurrent development of catalysts for emission control in next generation combustion engine designs and new fuel formulations that meet emerging and future legislation. The verification test beds that are used for catalyst development (often referred to as SCAT – Synthetic Catalyst Test – Rigs) require precise, reproducible and repeatable mass flow controllers (MFCs) to automatically control the different gas flows that are mixed together to simulate or synthesize combustion engine (gas and diesel) exhaust gas flows. Since these test beds are highly automated, the MFCs used in them must be able to interface with supervisory control and data acquisition systems (SCADA) or programmable automation controllers (PAC). Robust chemometric modeling is only enabled if low variation exists with regard to the controlled inputs (multi-variant) and especially with regard to MFC calibration. Any significant variation in MFC calibration will adversely impact the effectiveness of the customer's chemometric models which, in turn, can cause problems for their products' time to market and in compliance with air quality standards. Given the highly distributed nature of lab testing (by multiple suppliers at several different lab sites), this makes the reproducibility of the MFC calibration one of the most critical parameters in the effort for continuous improvements in catalyst performance and the development of chemometric models to predict emissions control performance.

SOLUTION

The MKS G-Series Mass Flow Controller Platform (Figure 3) provides the reproducibility and low calibration variability that is required by emission reduction catalyst manufacturers, engine OEMs, universities, and government agencies. This is directly due to the G-Series fully traceable automated calibration process with 6 sigma process capability. The G-Series mass flow devices are general purpose MFCs and mass flow meters. They offer Full Scale ranges from 5 sccm through to 250 slm with both multi-range and multi-gas capability. They have

Figure 3 - MKS Instruments G-Series Thermal Mass Flow Controllers.

an embedded user interface that facilitates changing the device range and monitoring the device health and measurement performance. They are available with a single-sided power supply of 15 to 25 VDC and analog I/O options of either 0 to 5 VDC or 4 to 20 mA. Digital I/O options include either RS485, Profibus®, EtherCAT®, or DeviceNet™. Other control and communication features include Modbus, an Ethernet user interface and available LabVIEW drivers. The MKS patented thermal sensor design provides exceptional zero stability and percent of set point accuracy. These MFCs exhibit less than 750 millisecond settling times and less than 0.1 or 1% of Full Scale (depending on Full Scale range) standard closed conductance leak rate.

As noted previously, precision, accuracy, repeatability and reproducibility are the most critical requirements for MFCs used in catalyst research. NIST-traceable calibration ensures that the MKS G-Series can meet these requirements. An Uncertainty Analysis was performed on approximately 6000 sequentially manufactured MKS G-Series MFCs and a summary of the results of this analysis is presented in Table 1.

The uncertainty metric used in the table is an ISO 17025 parameter associated with the result of a measurement

Set Point	10% Full Scale	25% Full Scale	50% Full Scale	75% Full Scale	100% Full Scale
Uncertainty (% Reading)	0.173	0.157	0.154	0.153	0.153

Table 1 - Uncertainty data for G-Series MFCs.

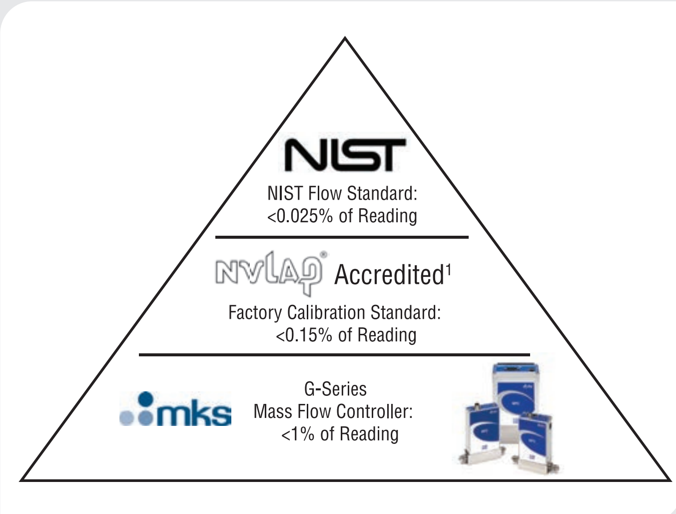

Figure 4 - The MKS flow measurement uncertainty pyramid.

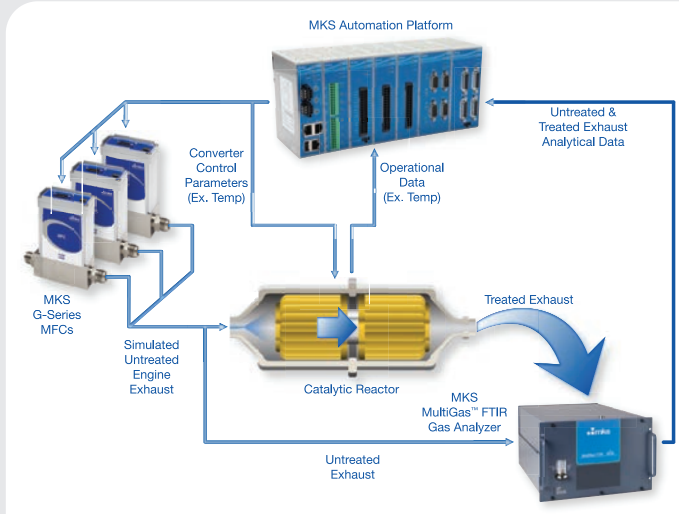

Figure 5 - Automotive emission catalyst research platform showing MKS technology.

that characterizes the dispersion of values that could reasonably be attributed to the measurand. This data affirms that the precision and reproducibility of the G-Series MFCs can fully enable automotive catalyst research, chemometric modeling and verification testing using Synthetic Catalyst Test Systems (SCAT Rigs) for operations with test labs distributed across multiple sites and different organizations.

The reliability and reproducibility of MKS Instruments G-Series MFCs is assured by the fact that their calibrations are directly traceable to NIST. All calibrations, both in-factory and worldwide, employ the same calibration equipment and procedures, ensuring the same NIST calibration traceability in all G-Series MFCs throughout an organization's laboratories, regardless of location. Figure 4 shows a flow measure uncertainty pyramid that defines the relationship between MKS calibration uncertainty and NIST flow standard uncertainty.

In addition to the G-Series of MFCs, a number of other MKS products have relevance for use in automotive exhaust catalyst research test beds. Figure 5 shows some of these product applications. The MKS Automation Platform can provide overall control and analysis of the research equipment. It can be configured to connect, monitor, control, and analyze the catalyst test bed and its process results. The Automation Platform fully leverages the concept of Learned Automation, employing MKS' advanced analytics solutions. It supports MKS SenseLink™ QM that employs Multivariate Analytics (MVA) for real-time analysis of test results. Combining the use of Design of Experiments (DoE) and MVA, the MKS Automation Platform can unlock knowledge hidden within the datasets for process optimization of the catalyst under study. It easily integrates with all other MKS devices and instruments including pressure gauges, mass flow controllers, valves, gas analysis solutions, etc.

As well, MKS provides chemical analytical tools that can be used to determine the results of catalyst process tests. The MKS MultiGas™ FTIR Gas Analyzer, Model 2030 is an operator-friendly FTIR-based analyzer capable of ppb to ppm sensitivity in determining the concentrations of multiple gas species in process monitoring applications. It has permanently stored calibration spectra, simplifying installation and calibration needs.

CONCLUSION

The precision, accuracy, and reproducibility of MKS G-Series MFCs enable both the researchers in industrial and university catalyst development laboratories and the testers in regulatory laboratories to focus their efforts on development, test and verification rather than on time consuming and often inaccurate MFC field calibration. Without direct NIST traceability such as exists with G-Series MFCs, field adjustment of MFC calibration (which may include adjustments to the MFC set point to account for calibration offsets) often results in a loss of traceability. This can adversely impact the overall accuracy and effectiveness of the customer's data which, in turn will negatively impact the ability of their chemometric models to predict the catalyst performance.

MKS also offers a comprehensive solution for the control of automotive emission catalyst research test beds and for the chemical compositional analyses that are critical for understanding the success of research activities.

References

[1] T. J. Wallington, E. W. Kaiser and J. T. Farrell, "Automotive fuels and internal combustion engines: a chemical perspective," Chemical Society Reviews, vol. 35, pp. 335-347, 2006.

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[4] "ToxFAQs for Nitrogen Oxides," Agency for Toxic Substances and Disease Registry, Atlanta, GA, 2002.