

Infrared analysis of E85 engines

■ The increasing use of new automotive fuel mixtures such as E85 and biodiesel is dramatically changing the chemical monitoring landscape in the development and manufacture of catalysts used to reduce vehicle emissions. Catalyst manufacturers have found that achieving regulatory compliance with these new and chemically complex fuels requires a level of knowledge of the combustion chemistry that goes well beyond the conventional need for CO, CO₂, NO, NO₂ and THC_s analyses.

The ongoing development of emission reduction catalysts for new fuels requires accurate, real-time chemical analyses of all of the hydrocarbons that are present in the exhaust, both before and after it passes through the catalyst. Consider fuels such as E85, in which the hydrocarbons in

the exhaust are split between oxygenated and non-oxygenated species. The impact that oxygenated versus non-oxygenated hydrocarbons have on catalyst behavior can vary greatly. It is therefore important in catalyst development to determine the ratios of these species in the engine exhaust gases and to fully understand the effect that exposure to these very different chemical species can have on the emission reduction characteristics of a catalyst. Traditional flame ionization detector (FID) hydrocarbon analyzers fail to differentiate between oxygenated and non-oxygenated species and therefore fail to provide enough of the information needed for engineering purposes. Plus, many traditional approaches have failed to detect certain EPA-designated hazardous air pollutants

(HAPs), such as formaldehyde, which may be present in the exhaust of oxygenated fuels.

One method that is rapidly gaining acceptance in meeting these new analytical requirements is infrared spectroscopy, specifically FT-IR (Fourier transform infrared spectrometry). This analytical tool performs pre- and post-catalyst monitoring that measures all of the traditional compliance gases as well as NH₃ and N₂O (at sub-ppm levels) and provides speciation and concentration data for the different oxygenated and non-oxygenated hydrocarbons present in the exhaust. It does this in a single instrument without the need for moisture removal. As only one instrument is used and it does not require continuous zeroing and calibration procedures, the use of FT-IR in this application greatly reduces the time that catalyst manufacturers need to screen test samples.

The following discussion describes the information obtainable by using the MKS MultiGas 2030HS FT-IR analyzer in characterizing the exhaust from an E85 fueled engine. Figures 1a and 1b show raw infrared spectra for the exhaust gases from an engine during start-up. The spectra were collected in real time and at 15-second intervals. Each Figure shows the sample IR spectrum along with IR spectra of the primary chemical constituents of the exhaust. Inspection of the Figures shows that the sample spectrum is the sum of spectra of the primary chemical constituents. Figure 1a shows that the exhaust gas at start-up is composed primarily of methane, ethanol and acetaldehyde. Figure 1b shows that after 15 seconds run time the composition of the exhaust changes, becoming a mixture of methane, ethanol, and formaldehyde. Figure 2 shows longer-term profiles for the primary constituents' concentrations over time. Figure 2a shows the independent species profiles (methane, ethane, acetaldehyde, ethanol, and formaldehyde) over a 90-second span. Figure 2b shows the overlapped scans of all species over the 90-second timeframe. The Y-axes in Figure 2 are parts per million on a wet basis. This data clearly demonstrates the ability of FT-IR analyses to identify and quantitate both the oxygenated (acetaldehyde, ethanol, formaldehyde) and non-oxygenated (ethane, methane) hydrocarbon constituents in the

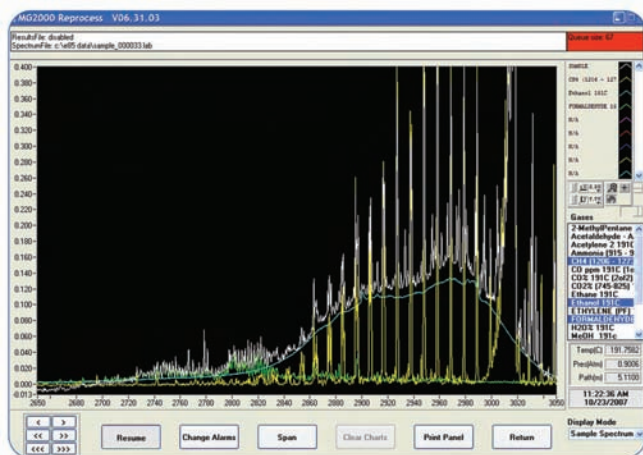
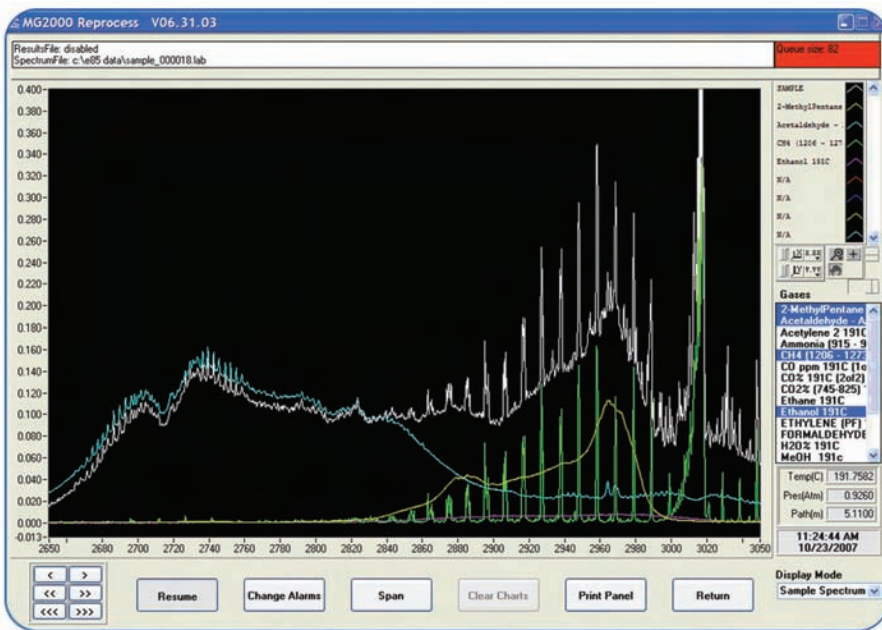


Figure 1a: Raw FT-IR scans of the E85 engine exhaust at start-up (above)
Figure 1b: After 15 seconds run time (left)

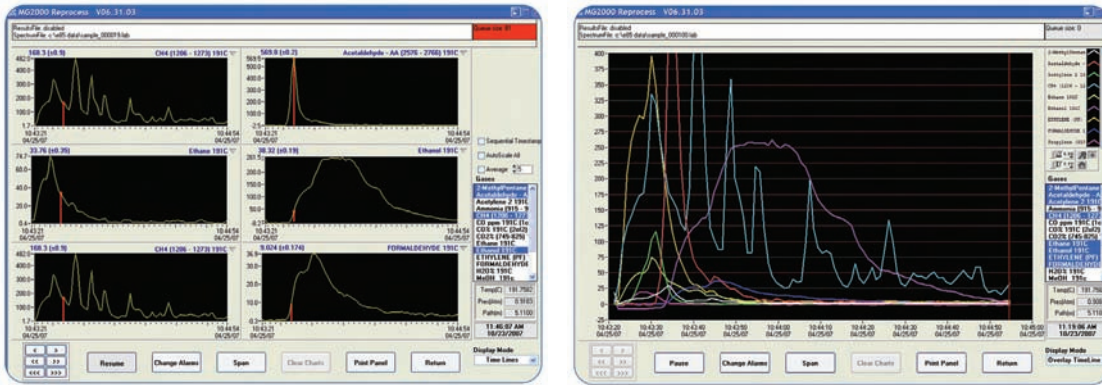


Figure 2a (far left): Individual traces for the concentrations of different hydrocarbons in the E85 engine exhaust over a 1.5 minute start-up, as determined by FT-IR
 Figure 2b (left): Graph showing FT-IR concentration data overlay

engine exhaust. The determination of such data in raw exhaust and in the catalyst-treated exhaust facilitates a more sophisticated understanding of the origins and remediation of these species, and thus facilitates the process of catalyst formulation and optimization. Furthermore, as fuel compositions vary, FT-IR analysis can provide qualitative and quantitative data

for other hydrocarbon constituents that may be present. Such information is critical for the optimal engineering of emission reduction catalysts.

FT-IR spectrometers in emission test cells can mimic the response of traditional FID analyzers, allowing the comparison of FT-IR data with FID data. Figure 3 shows such a comparison. The FT-IR data on

hydrocarbon speciation was collected concurrently with FID data and recalculated to a C-1 ppmv basis to mimic the response of a traditional FID calibrated with methane. Figure 3a shows an overlay of FT-IR data for eight independent hydrocarbons. Concentration data for formaldehyde was removed from the FT-IR data set as this is not detected by FID. The concentrations of the FID active species that were detected by FT-IR were totaled, time-aligned and graphically compared with the THC emissions as determined by FID (Figure 3b). The THC versus time plot for FT-IR versus FID only differed greatly during the first few seconds of engine start-up. At this time the FID analysis indicated almost twice the THC level of the FT-IR analysis. Some very short transients were also observed following start-up. The differences in the two analyses may be due to factors such as analyzer flow differences, different sampling points, chemical interferences from unaccounted for compounds, very fast transients that were not measured and/or over-ranging of the FID (the concentration at start-up appeared to exceed 5000ppmv). Although further investigation is needed, the difference in flow rates would appear to be the most logical explanation for the diverse results, as experiments in which the THC values varied more slowly did not show the discrepancy.

The data shows that there are many compelling reasons for using FT-IR in engine test cells. The ability of FT-IR to mimic FIDs coupled with the ability to differentiate HAPs versus non-HAPs, oxygenates versus non-oxygenates, and light versus heavy hydrocarbons makes FT-IR a powerful tool for the facilitation of catalyst development for emission reduction systems. ■

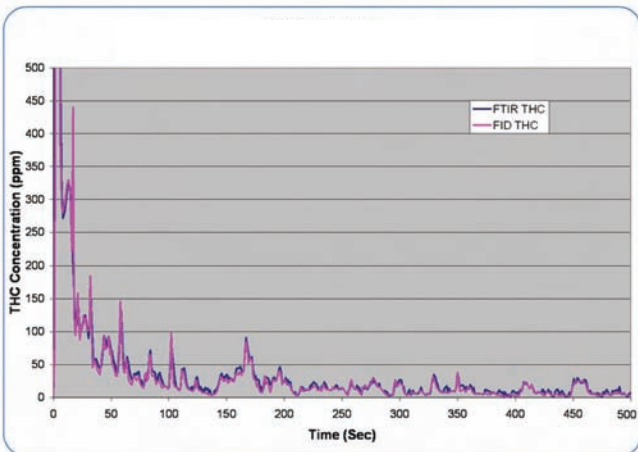
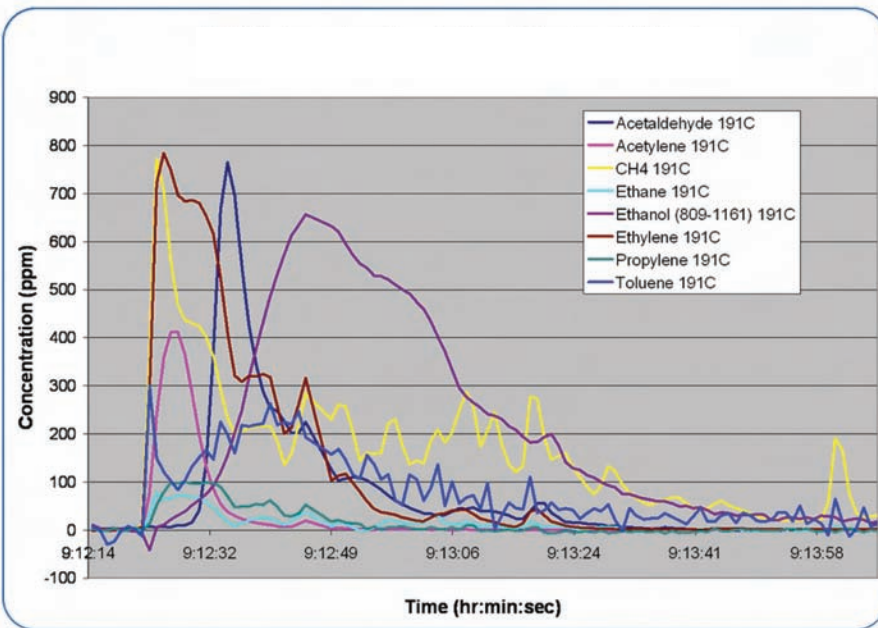


Figure 3a (above) An overlay of FT-IR concentration data on C-1 Basis for the primary species present in E85 engine exhaust during the first 1.5 minutes of runtime;
 Figure 3b (left) Comparison of FT-IR THC values and FID data

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