Comparative Study of Butadiene and B, T, X Tailpipe Emissions for Gasolines of Different Octane Levels

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Abstract

Real time differentiated hydrocarbon tailpipe emission monitoring on a lambda one controlled vehicle, driven in the NEFZ („Neuer Europäischer Fahrzyklus") driving cycle on the chassis dynamometer, showed dramatic variations of the concentrations of butadiene and benzene when operated with gasolines of different octane rating. Butadiene as well as benzene emissions were enhanced in 91 octane (RON) fuels compared to 95 and 98 octane fuels, although the aromatics content of RON 91 fuel is significant lower and the content of benzene is equal to the RON 95 fuel. The measured emissions of THC can not reflect these differences whereas cold start behaviors as well as highway driving emissions are derived from the test program.
Test results from a 1-cylinder research engine with specific fuel compositions and in cylinder monitoring of differentiated hydrocarbons are the basis of an interpretation of these vehicle test results.

Introduction

Overall hydrocarbon emissions from a today's vehicle under moderate highway speeds are in the range from 3 to 6 ppm as determined in standardized test procedures. Many arguments attribute these emissions solely to the cold start sequence, the time interval from the start of the cold engine to the light off of the catalyst. Only a very sensitive instrument detecting sub ppm levels of differentiated hydrocarbons can realize a deeper insight into the total emission characteristic. Under real driving conditions, the startup of the engine - significant in emission pattern - is a small fraction of time on everyday driving. Highway emissions are characterized by low level emissions of temperature stable hydrocarbons and low values of NOx.

This study compares different octane ratings, hence different contents of aromatics in the fuels with the low-level emissions during the last 200 seconds in the FTP 75 test cycles.

Butadiene, benzene, toluene and xylene were chosen from the emission spectrum because of their toxic and ozone forming potential and because they characterize Otto fuelled car emissions.

The origin of hydrocarbons in engine out (EO) emissions

Otto fuel is a mixture of aliphatic, aromatic and olefinic compounds in the range from C4 to C9.
Regarding the emissions, a zero order assumption could be described as follows:

"What we feed to the engine is likely to be found in the exhaust"

We shall see that this crude assumption can explain the observed data only to a fraction of less then 8 % under normal operating conditions of an engine. Figure 1 shows the relative hydrocarbon concentrations in two different types of engines (GDI and FI) reaching from methane to trimethylbenzene. For simplicity oxygenated as well as minor intensity species were omitted.
The two different engines, operating under the similar conditions (2000 RPM and 25 % load) use the identical fuel but they do have very different fingerprints.
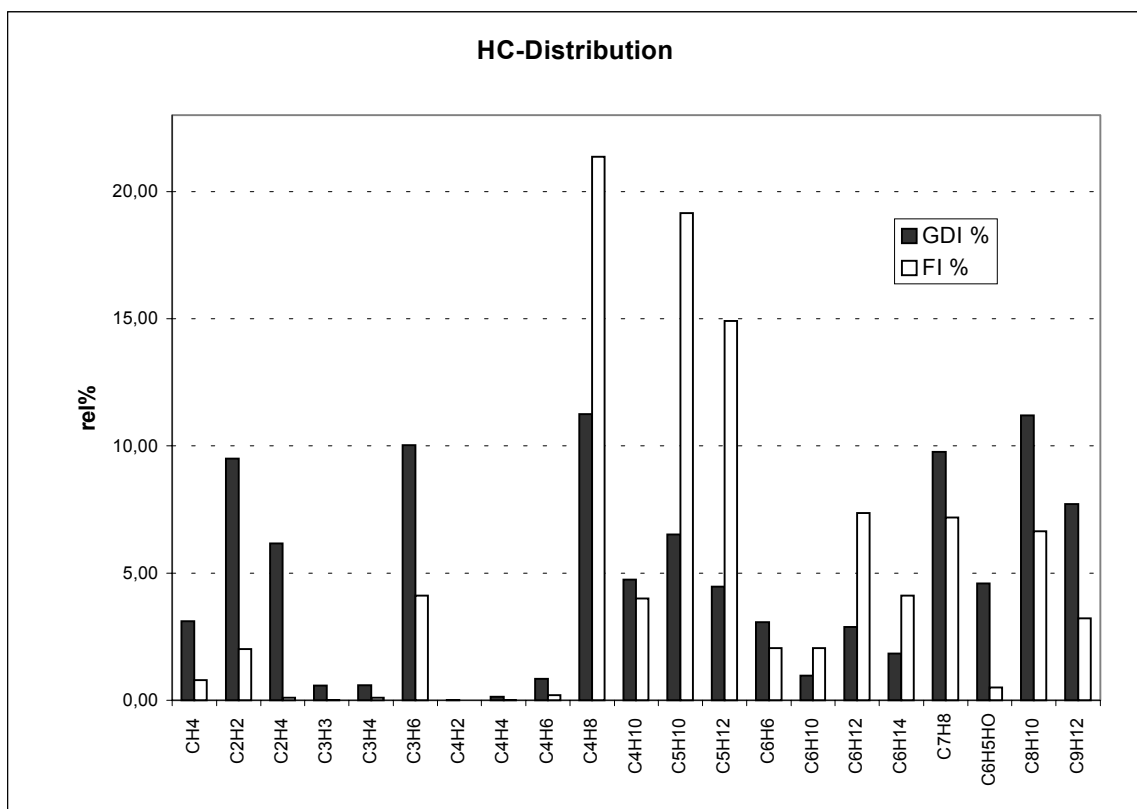

Fig. 1   Relative HC-distribution of GDI vs. FI

The emission pattern of the GDI engine is more evenly distributed through the molecular mass scale then the ordinary fuel injected emission pattern. Higher methane, acetylene, ethene and propylene levels in the GDI combustion stand against higher C4,

C5 and C6 alkene emissions from the FI combustion. Relative intensities of benzene is higher in the FI engine whereas the GDI engine emits more toluene and xylene. Detailed experimental studies (SAE941961, 941897,942007) relate the different hydrocarbon distributions determined in the exhaust spectrum to engine parameters like inlet flow mixing, gas temperatures, cylinder pressure, spark timing, air fuel ratios and detailed fuel compositions.

The typical HC distribution of Otto fuels is in the range of 65 % paraffins, 31 % aromatics and 4 % olefines. Above shown mass spectra shows the distribution of individual compounds far off their expected intensity when fuel is gasified.
Hexane or heptane concentrations, the major fraction in the fuel, are far lower than hexene or heptene which have minor contents in the fuel whereas methane, acetylene, propyne, propylene or butadiene are not contained in fuel at all.
Obviously, the hydrocarbons we monitor in the raw exhaust are not pure leftovers from an uncompleted combustion process kept in the residual gases of piston ring crevices, but represent different steps of combustion process.
Fuel molecules undergo a number of reactions as decomposition, recombination, and addition in the cylinder before they oxidize to CO, CO_2 and H_2O.

The hydrocarbon zoo as found in the exhaust spectrum may be structured in three main groups (SAE 941966):

a) Feed through species: hydrocarbons as part of the fuel passing the combustion
        without modification.
b) Offset species: hydrocarbons not only found in fuel but being generated by the
        combustion.
c) Non fuel species: hydrocarbons not present in the fuel and entirely generated by the
        combustion process.

The type of species falling into categories a, b or c is related to their thermal stability and reactivity as well as their thermodynamic pathways during the combustion.
W.J. Piltz et.al (SAE 881605) study the decomposition of a stoichiometric butane air mixture in a CFR engine under spark off condition as a function of the compression ratio. The CFR engine is powered by an electric motor and the only energy input to the fuel molecules is the gas temperature, generated by the compression of the intake charge. When the compression ratio in this engine is raised above 6.5:1, the gas temperatures in the compression stroke reach values that are high enough to start unimolecular decomposition reactions (Lindemann 1922).
In collisions between butane molecules, N_2 and O_2, the molecules transitional energy is transferred into internal energies of vibrations of the C-H Atoms and an exited butane molecule is formed according to B+M→B*+M.
During the next collision, the molecule may transfer its energy back to the colliding partner and relaxes to a lower energy state - B*+M→B+M - or will take up another fraction of energy which leads to the dissociation of the molecule into fragments and the formation of lower molecular weight compounds and radicals.

The importance of the mechanism - B*+M→C+D+M - in combustion engines is the increase of the number of reactive species resulting in a fast combustion process. Radicals have much lower reaction barriers for exothermic pathways compared to saturated hydrocarbons reflected in their short lifetimes. Radicals may undergo recombination steps to form more stable species but may also take an oxidation step and release energy thereby.
The balance between radical recombination and oxidation steps determines the stability of the fuel air charge against increase of number of individual hydrocarbon molecules and complete autoignition or uncontrolled combustion.

Figure 2 shows the formation of butene (C_4H_8), propylene (C_3H_6) and ethylene (C_2H_4) out of a butane $C4H_{10}$ air mixture fed to a single cylinder engine operating under spark off conditions and driven by an electric motor. The x-axis in this graph represents the compression ratio in the engine. Leaving out losses of energy by radiation and cylinder wall collisions of the molecules, the compression ratio determines solely the thermal energy brought to the gas in the compression stroke. This increase in temperature and pressure causes the butane molecule to decompose to radicals, which thereafter recombine to different hydrocarbon molecules again. In the decomposition process hydrogen atoms are formed and due to their much higher diffusion constant or speed in the gas-mixture, they find other hydrogen atoms and recombine to molecular hydrogen. From the formation of hydrogen follows that the new recombined hydrocarbon molecules are unsaturated molecules having double and triple carbon bonds.
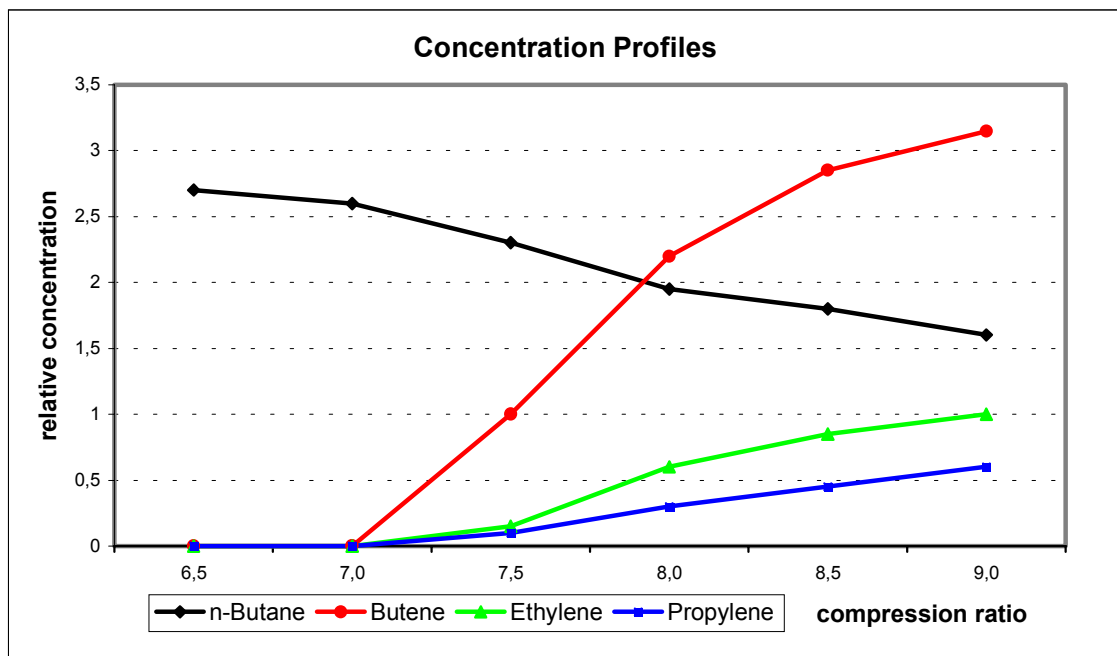

Fig. 2   Decomposition products of butane

However not only lower molecular weight compounds are formed as a result of radical recombination, a number of aromatic compounds ranging from C4 to C10 rings are generated in a high temperature pre ignition of air fuel mixtures in the cylinder.
The most important representative of all aromatic compounds is benzene.

Origin of benzene in tailpipe emissions

Various speculations try to explain the appearance of a gasphase of benzene in engine out emissions ranging in concentrations from 0,2 ppm in modern diesels to generally 30 to 50 ppm in lambda one operated engines. With the exception of pure hydrogen and natural gas fuelled engines, the order of magnitude of the benzene level seems rather independent of the fuel formulation. One explanation of benzene formation comes from demethylation of higher substituted rings like toluene, xylenes and ethylbenzene being present in the primary fuel.
This picture may be attractive but fails in any quantitative work to describe benzene levels in engine out. This easy picture guides environmentalists and politicians throughout the world to demand lower aromatic levels for Otto fuels. In cylinder reactions are gasphase reactions and hence mainly two body reactions. Whenever a demethylation step of toluene may occur the free electron of the benzene core may find a number of free radicals. The probability to find a free hydrogen atom is by orders of magnitudes smaller, plus the recombined benzene molecule is highly exited and needs a third collision partner for stabilization. For the explanation of benzene found in tailpipe emissions where a catalyst is included in the overall system there is one theoretical pathway for the demethylation of high substituted aromatic compounds into benzene:
When the oxygen level in the engine out gas drops below 500 ppm which is very unlikely, a direct demethylation and direct formation of benzene out of e.g. toluene or xylene is observed. As reactions on catalysts do not have gasphase behavior, they offer radicals and atomic hydrogen to the phenyl core and hence the formation of benzene is a fast process.

Figure 3 shows concentration profiles of heptane, benzene and NO as a function of compression when a stoichiometric heptane air mixture is fed to the above described engine. Many more compounds are formed as a result of the heptane fragmentation but are not shown in this picture. From a certain compression we detect benzene formed as a recombination product from radicals generated by the heptane decomposition. The graph also indicated the formation of the so-called prompt NO thus indicating exothermic oxidation reactions of radicals with air.
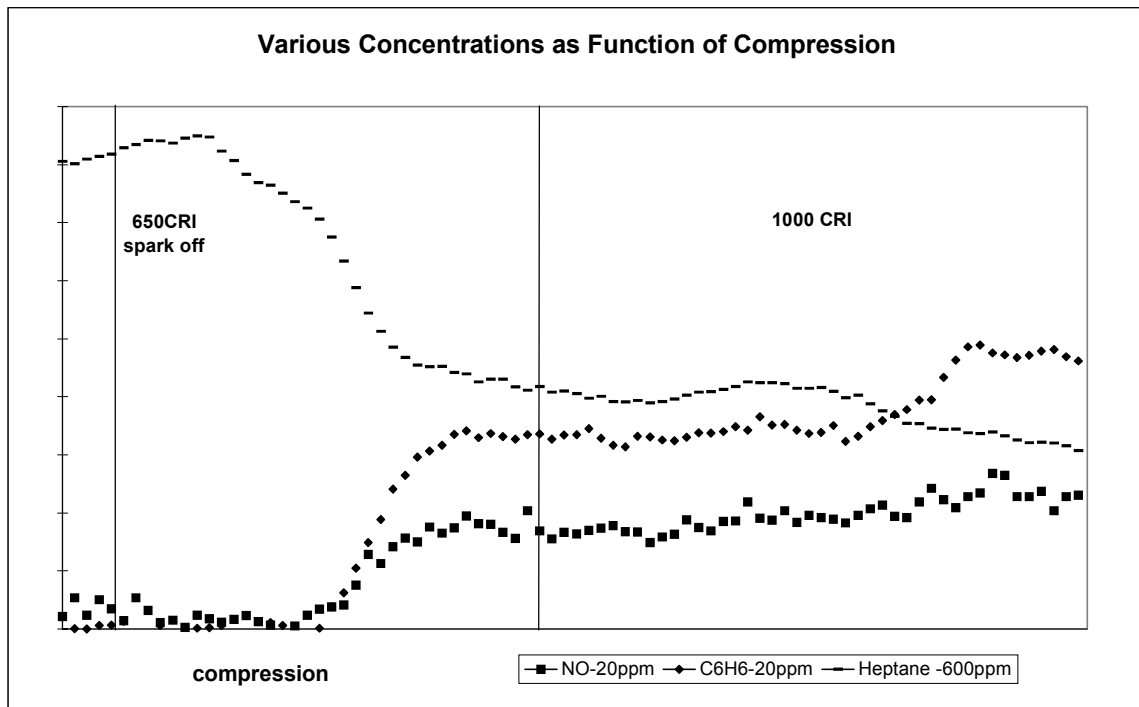
Various Concentrations as Function of Compression

650CRI
spark off

1000 CRI

compression

NO-20ppm   C6H6-20ppm   Heptane -600ppm

Fig. 3   Concentration profiles of heptane, benzene and NO as a function of compression

Emission comparison of of selected hydrocarbons for different octane fuels in the NEFZ test cycle

For many considerations the above demonstrated processes and results are of more academic then real value argued by the fact that in the real world there is always a catalyst to remove unwanted hydrocarbon species from the EO gases. Again only a standardized test allows true comparison of the measured data.
To fulfill these requirements we operated a standard vehicle (1998 VW Passat 1.8 turbo) on a standardized dyno and CVS sampling system on the standardized NEFZ test cycles. The car was fuelled with three standardized fuel samples (91, 95, 98 octane) and had to perform three complete test runs in each fuel.
As analyzing equipment a Testa FID detector for the total hydrocarbon signal was used. All other components were determined dynamically with a repetition rate of 400 msec by an AIRSENSE 500 based on the CIMS technology. This monitoring technology is briefly described in the following section.

The CIMS Technology – Instrumentation

The technology and the main features can be described as follows.

The detection principle of the instrument is the analysis of the molecular weight of the substances. Sample gas is introduced to a high vacuum chamber and transformed into ions that are subsequently mass selected by electromagnetic fields and counted in a particle detector (figure 4).
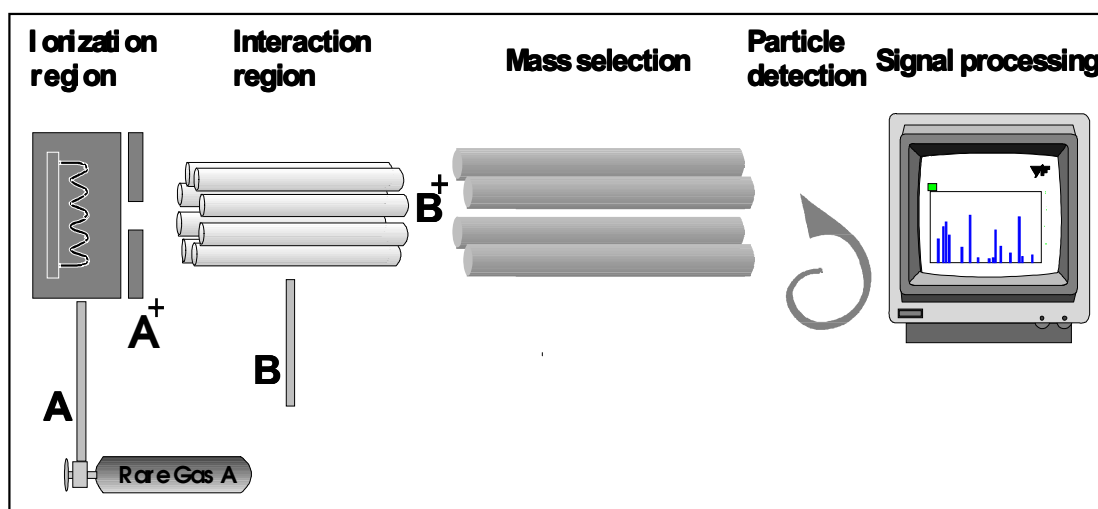
Fig. 4   Schematic setup of the "V&F-CIMS"

As different molecules may carry the identical molecular weight, like e.g. N_2 and CO or formaldehyde and NO or CO_2 and N_2O, the instrument uses different ionization levels (i.e. different primary ion beams) to distinguish between mass identical molecules. Every molecule has an individual energy that is necessary to remove an electron and thus convert the molecule into an ion. An additional separation effect is gained through the formation of defined fragment ions. The interaction of the ion beam with the gas sample results in well-defined product ions. A krypton ion beam with 13,9 eV energy, for instance, separates the mass identical molecules N_2 (14.2 eV) and CO (13,7 eV). The mass identity of methanol CH_3OH and oxygen O_2 on mass 32 is solved by ionization with xenon (12,2 eV) that generates an O_2- ion on mass 32 and a CH_3O^+- ion on mass 31. Larger hydrocarbons, for example, need ionization energies in the range of 10 eV created by a mercury ion beam. Table 1 shows the general technical data of the "V&F-CI-MS"

Tab. 1 General technical data of the "V&F-CI-MS"

Gas response time:	T 90 $\cong$ 30 msec
Gas transfer temperature:	60° - 210 °C
Measurement cycle / Detection level (ref.: benzene)	1 msec 0,5 ppm 10 msec 0,05 ppm 5 sec 0,5 ppb
Dynamic range:	1:10^4
Operation	Selection of up to 40 channels per set from application orientated control library scripts

Results

Table 2 is divided in three main sections and lists the average concentrations over three test runs for the individual compounds. The first 120 seconds of the test describe the gross of the emissions in the cold start due to the cool inactive catalyst. The next block gives the averages over the whole test cycle as defined in the emission protocols. The last block contains data of the last 240 seconds of the test describing moderate highway conditions with a hot active catalyst and represents the largest amount of today's gaseous emission volume.

Tab. 2 Emissions of selected compounds in the NEFZ test cycle

first 120 sec	butadiene	benzene	toluene	xylene	HC tot	NO
ROZ 91	0,605	1,521	3,317	3,674	76,057	40,47
ROZ 95	0,587	1,537	4,409	4,632	72,315	32,779
ROZ 98	0,372	0,988	3,468	3,719	66,821	34,295

averages	butadiene	benzene	toluene	xylene	HC tot	NO
ROZ 91	0,06	0,247	0,414	0,452	10,493	6,628
ROZ 95	0,063	0,192	0,494	0,542	8,971	5,573
ROZ 98	0,043	0,127	0,407	0,426	8,317	7,375

last 240 sec	butadiene	benzene	toluene	xylene	HC tot	NO
ROZ 91	0,003	0,063	0,024	0,014	2,617	4,829
ROZ 95	0,002	0,012	0,013	0,02	1,208	1,071
ROZ 98	0,004	0,005	0,046	0,03	1,172	2,032

The first 120 sec data do not show strong variations in between different classes of fuel. It might surprise that toluene and xylene emission levels reflect a constant fraction of aromatic content in the three different fuels which of course is not true. The reason for these data is the characteristic adsorption on cool catalysts, where aromatic compounds are removed from the gas and are adsorbed on the catalytic structure until a saturation is reached. In the warm up process of the catalyst a considerable part of these masses is

desorbed to the gasphase again. Thereby creating the average emissions, we monitor in this startup phase.

The overall averages over the test start to indicate higher benzene, total hydrocarbon and NO levels for the 91 octane fuel compared to the 95 and 98 octane fuels.

For the last 240 seconds averages, the strong difference in benzene and NO appearance between 91 octane and the higher octane fuels becomes apparent. More than 12 times as much benzene and more than two times as much total hydrocarbons and NO is present in the 91-octane fuel.

To enable a better overview, the described data are presented as columns in figure 5 (butadiene, benzene, toluene and xylene) and 6 (HC$_{tot}$, and NO).
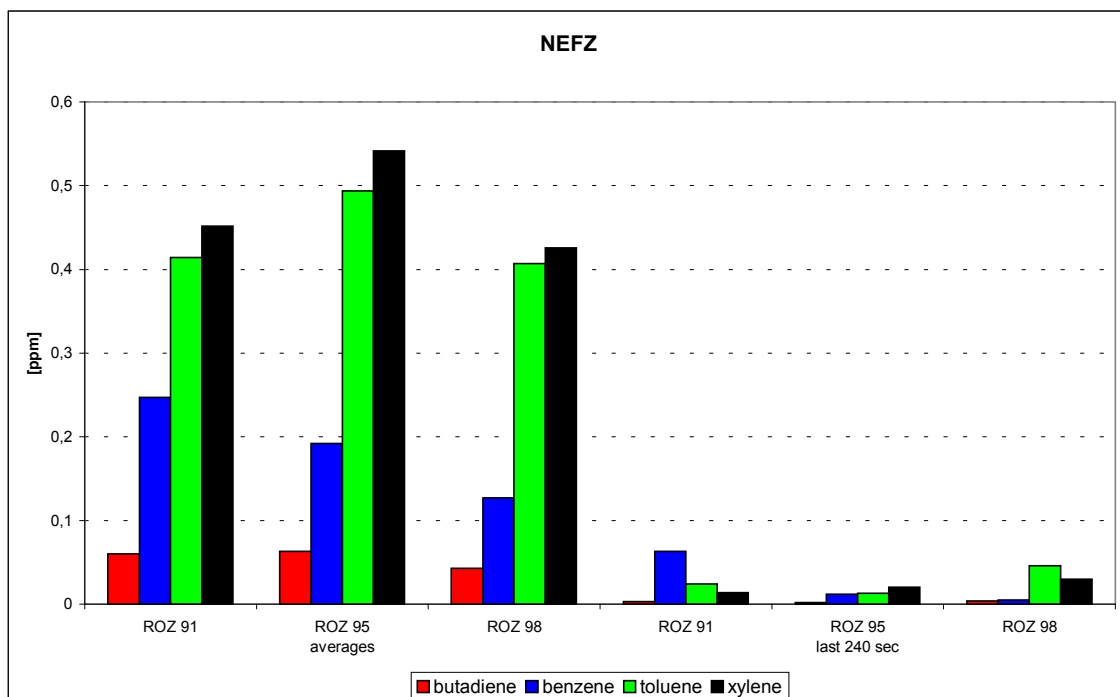

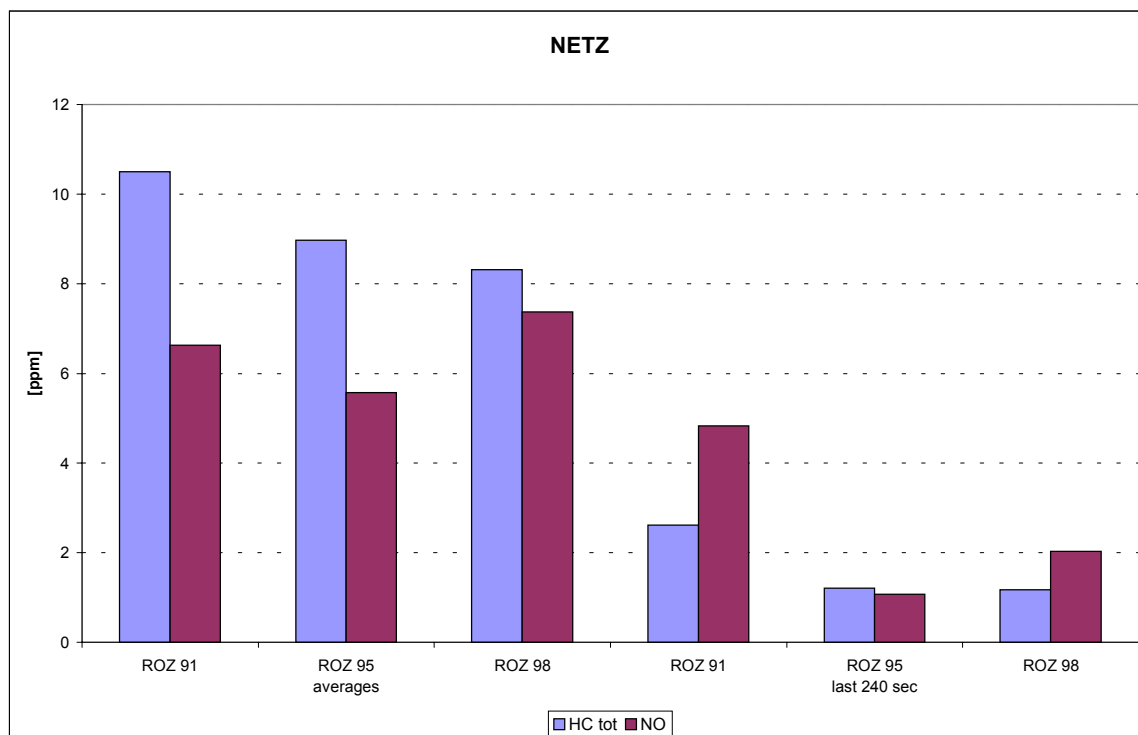Fig. 5   Butadiene, benzene, toluene and xylene in the NEFZ-test

Fig. 6   HC$_{tot}$ and NO in the NEFZ-test

Discussion

Octane rating of a fuel is its measure of stability against autoignition under the high temperature, pressure conditions in the compression stroke before regular ignition by the spark. Autoignition is caused by the number of radicals with low activation energies against exothermic oxidation reactions in the air fuel charge. Higher octane fuels contain more radical scavengers (radical stabilizers) mostly as toluene and xylene content in today's fuels. As low octane fuel generates more radicals it also generates more benzene in the gas. Benzene has a significantly higher thermal stability in the flame and at catalyst temperatures than all other substituted aromatics like toluene and xylene.

For this the reason we find significantly more benzene in the low octane tailpipe gas then in high octane fuels whereas toluene levels in tailpipe gases are independent of the octane number.

Higher total hydrocarbon signals are found in 91 octane fuel runs. The reason for this lies in a much higher formation of methane due to methyl radical recombination steps. Methane has the lowest tendency to stick on catalyst surfaces in comparison to all other hydrocarbons because of its low polarizability.

The residual NO level in tailpipe gases is higher in all runs with 91 octane fuels. The reason for this finding is twofold. A) More radicals undergo more individual oxidation steps forming more prompt NO thereby. B) NO conversion on catalysts is enhanced at higher toluene and xylene levels of the EO gases. This finding was demonstrated at Shell labs and can be explained by the high sticking probability of toluene and xylene on catalytic surfaces, offering more active hydrogen for the NO reduction process.

Conclusion

Compared to all possible hydrocarbon tailpipe emissions butadiene, benzene, toluene and xylene are classified as most harmful to the environment and therefor should be kept to minimum levels. This work demonstrates the variation in especially benzene emissions monitored under standardized test procedures, when the octane rating of the fuel is varied from 91 to 98 octane. With the use of a time resolved and ppb sensitive multi component monitoring technique, the overall test cycle may be split in different subsections like cold start or highway driving conditions. Under 40 to 70 percent load of the engine, as the highway driving demands, variations in benzene emissions of up to factor 12 were measured for different fuels. The finding was explained on the basis of fuel decomposition into fragments and radicals and the competing reactions of condensation into benzene which is higher on lower octane fuels against radical scavenging by the higher octane fuels.