Dynamic Monitoring of Differentiated Hydrocarbons in Direct Engine Exhaust: A Versatile Tool in Engine Development

J. Villinger, W. Federer, A. Dornauer, A. Weissnicht, M. Hönig, T. Mayr

V&F Analysetechnik

ABSTRACT

In the compression and combustion strokes different individual hydrocarbons are generated through a complex reaction chemistry and can be monitored by a rapid V&F multicomponent gas analyzer system. They give detailed information on the physical properties of an engine.

Through all different reaction sequences of the combustion, surface quenching reactions leave a characteristic pattern of hydrocarbons in the exhaust gas. Toluene and xylene, for example, represent direct monitors for unburnt fuel, alkenes and alkines show thorough fuel decomposition, allowing a rapid combustion when the spark is ignited, whereas aldehydes indicate autoignition processes.

Ratios of hydrocarbon concentrations describe engine parameters like fuel / air mixing properties, EGR characteristics, autoignition processes, and engine oil combustion. So an optimized engine performance can be set by the hydrocarbon pattern measured in the direct exhaust gas.

INTRODUCTION

Ever since the mathematical expression $\eta \leq 1 - T_2/T_1$, correlating the mechanical efficiency of a thermo-dynamic engine with it's temperature or pressure differences, was formulated, engineers have been trying to increase the mechanical output of engines at given fuel input [1].

Material, friction, and fuel characteristics as technical boundaries, and today more and more environmental restrictions define the engineers' workfield. With the realization of modern motor management techniques a great step towards realization of high mechanic efficiency is possible.

In the development of high efficiency engines the boundary between a controlled fast combustion of fuel and the smooth formation of a high cylinder pressure on one side and the oxidizing action generated by autoignition processes, which is devastating for pistons and valves, on the other side becomes smaller.

The differentiated hydrocarbon composition in the exhaust gas tells us on which side we operate the engine.

Hydrocarbon compounds represent a minor fraction of all the gases in an engine exhaust.

So far, about 160 different species have been identified [2,3,4]. Their concentrations in the exhaust gas of a λ -1- driven engine can range from 0,001 to several hundred ppm. Up to now, hydrocarbons have been measured as a sum by using flame ionization detectors.

These instruments do not differentiate between methane and benzene molecules, for example, but over the last years more and more interest in speciation of hydrocarbons in the exhaust gas has been developed. This demand, mainly generated by environmental and health authorities, who want to distinguish between non toxic, toxic, and ozone forming hydrocarbon species, is currently fulfilled by the use of gas-chromatography and liquid chromatography in laboratory analysis.

The information derived from these techniques, however, represents only integrals over driving cycles. In order to minimize the formation of toxic hydrocarbons, engineers need to know under which operating conditions of the engine and converter they are generated.

The development of a rapid multi-component gasanalyzing system over the past years [5] brings a new dimension into differentiated hydrocarbon monitoring.

We can study concentrations of individual hydrocarbons from 0,01 to several hundred ppm in time intervals from 10 to 100 msec per measurement.
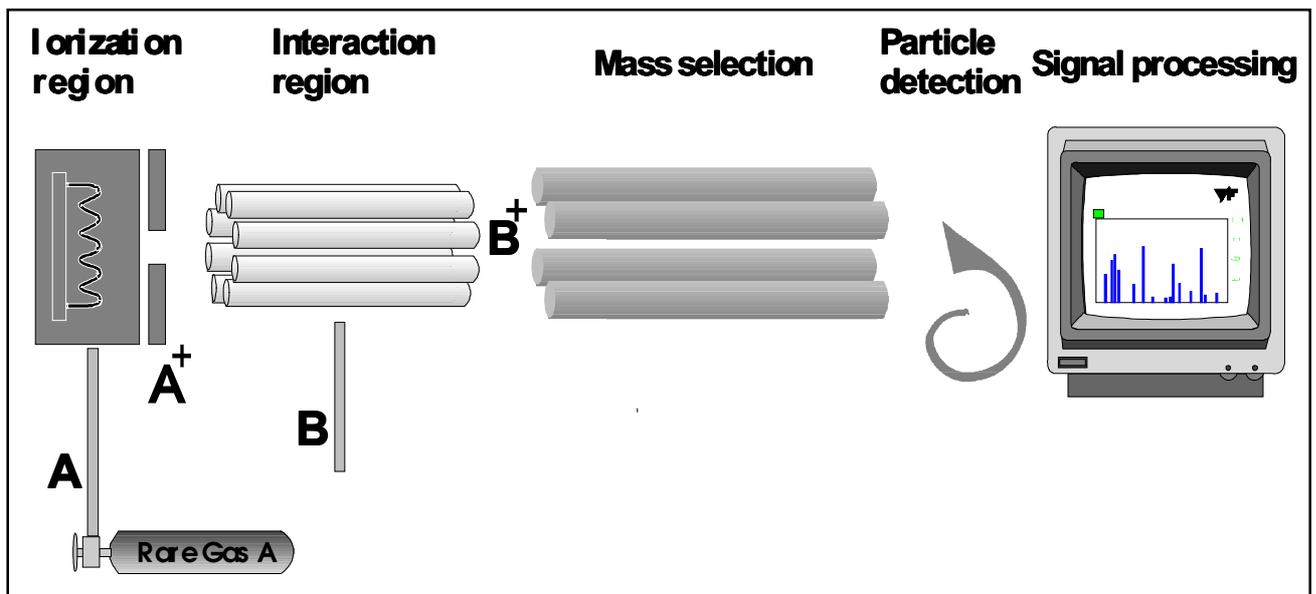
FIGURE 1 : Schematic Setup of the Analyzer

INSTRUMENTATION

The technology of the V&F multichannel gasanalyzer system is described elsewhere [6], so here we concentrate only on the main features.

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 1**).

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 [7]. 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.

The method of ionization by different energy levels allows a multiple use of the mass scale and allows to see molecules from different perspectives.

TABLE 1: performance data for the AIRSENSE 500 model

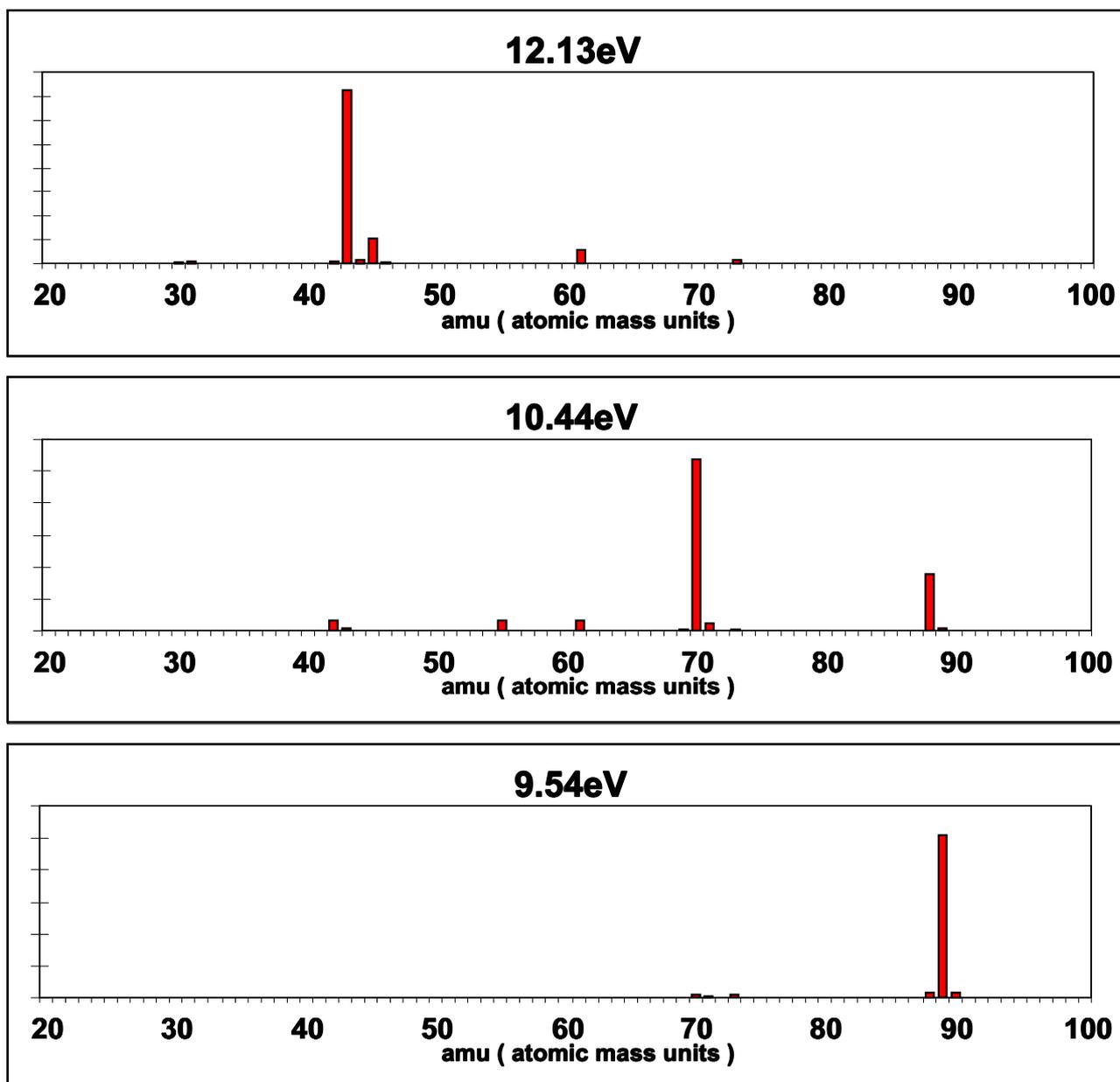|	
Gas response time:	T 90 $\cong$ 30 msec
Gas transfer temperature:	60° - 210° C
Measurement cycle / Detection level : (ref.: benzene)	1 msec 0,5 ppm 10 msec 0,05 ppm 5 sec 0,05 ppb
Dynamic range:	$1:10^4$
Operation:	Selection of up to 40 channels per set from application orientated control library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

FIGURE 2 : Molecule Spectra of $C_4H_8O_2$ for different ionization energies

Figure 2 shows mass spectra of a fragile molecule ionized with three different ion beams. This method of " secondary ion gas phase mass spectrometry " allows a very fast, sensitive, and interference free monitoring of anorganic compounds and - currently up to 45 - relevant hydrocarbon species in exhaust gas matrices.

ENGINE EFFICIENCY, FUEL, AND SPARK ADVANCE

To achieve the necessary cylinder pressure at top dead centre of the piston we generally set a spark advance. This means the spark is fired some time before the piston reaches TDC. The common explanation therefore is the necessary time the fuel / air charge needs to burn and to build up pressure in the cylinder thereby. When we compare the spark setting of two engines we realize that fuel can burn at very different speeds. For example, a Ford Model T engine at 800 rpm, full load, operates at 25 degree spark advance, whereas a Rotax engine at 12900 rpm, full load, operates at 0 degree spark advance.The speed or overall rate of any chemical reaction between neutral molecules is governed by two factors:

a.) The molecules have to meet each other in a

collision

b.) The collision must be intense enough to push the electron clouds of the molecules so close through their Coulomb fields that they can start to communicate energetically, form new products, and release heat hereby. The collision rate is governed by the pressure in the cylinder, the collision energy by the thermal energy or heat within the system.

Otto fuel is a mixture of C_5 to C_{10} hydrocarbons [8,9]. They are present as mostly saturated alkanes and as aromatic hydrocarbons like toluene. Depending on their saturation and molecular structure the C-C and C-H bonds have different strength or bond energy[10].

When the thermal energy in the gas, kT, which is e.g. generated by the compression stroke, overcomes the bond energy within the molecule it will decompose into smaller species C_1 to C_4 and so the number of available molecules for the combustion process is multiplied.

So, the more molecules, the higher the pressure, the higher the temperature, the faster the fuel/air charge will burn.

FUEL IN THE COMPRESSION STROKE

When we feed a CFR engine with a mixture of heptane and toluene, run it in spark off condition, and vary the compression ratio we observe the following effects:

Figure 3 shows the concentration of a number of hydrocarbons together with NO as a function of the compression ratio. At compression ratios above 6:1 [11,12] we observe the thermal decomposition of heptane into smaller molecules like ethene C_2H_4 or propene C_3H_6 and butadiene C_4H_6. Along with the decrease in the heptane concentration we also find a decrease in toluene. This, however, is not due to thermal decomposition but to CH_3 radical addition onto toluene which forms xylene. Toluene has a strong tendency to accept CH_3 radicals and thereby stabilizes the gas mixture against autoignition.

We also observe the formation of benzene which is not present as a primary fuel component; it is formed as a recombination product of alkines like acetylene and diacetylene and stabilizes the mixture against autoignition too.

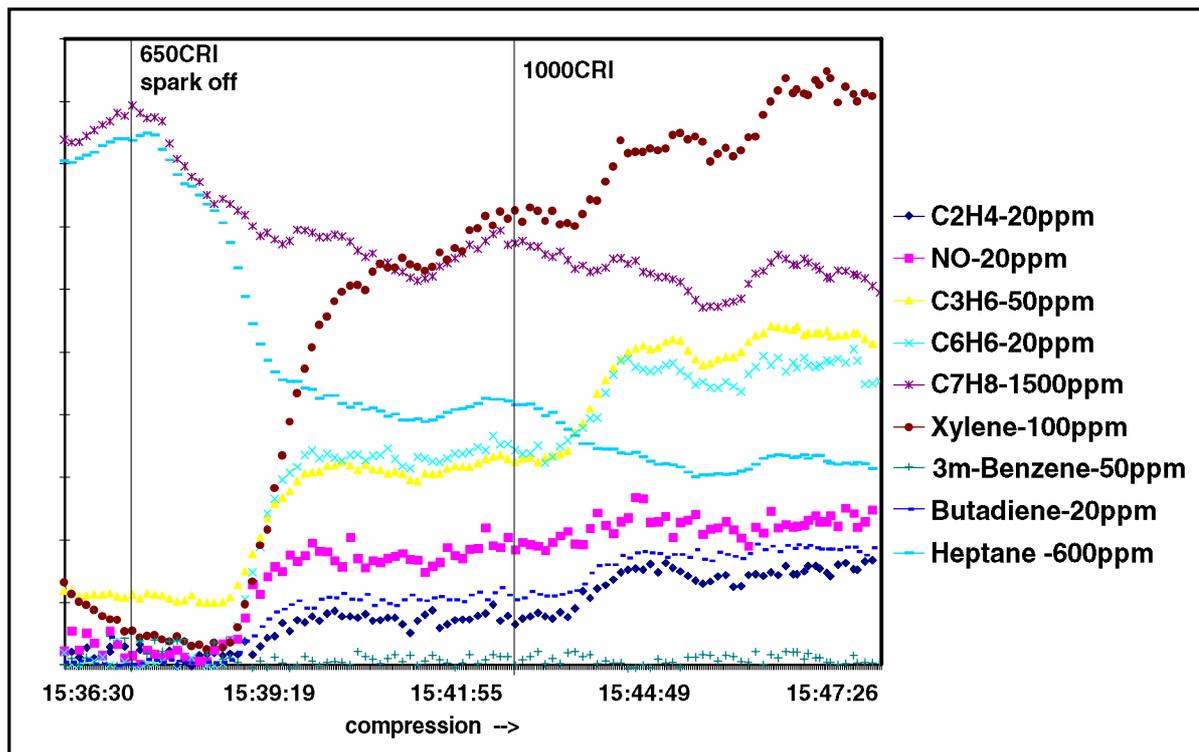In **figure 3** we observe the appearance of a NO signal as soon as heptane starts to decompose.

**FIGURE 3: Selected HC compounds in del. exhaust from CFR engine
Heptane Toluene mix, spark of as function of compression**

4

This " prompt NO " [13] is a clear indication for energy released by exothermic oxidizing reactions of radicals into aldehydes.The overall gas temperature in the cylinder is too low for any thermal NO formation, however. O and OH radicals generated in the autoignition steps form NO in three body collisions. We believe autoignition processes to be the main cause for the NO formation in engines.

Figure 4 describes the transition of the gas mixture from the quasistatic equilibrium of thermal decomposition of heptane into radicals, their partial stabilization through recombination into more stable molecules like acetylene, benzene, or xylene, and the partial oxidation of radicals into aldehydes to the full autoignition process at very high compression ratios.

The high time resolution of the instrument allows to study the individual hydrocarbons as they ignite. Due to their thermal stability the concentrations of ethene and benzene still increase when heptane, butadiene, and propene ignite (Zone B) until at last (Zone C) all hydrocarbons ignite and the NO concentration goes extremly high (Vol %).

In this figure the reaction products of the autoignition process, CO_2, CO, H_2O, and H_2, methane CH_4, formaldehyde $CHCHO$, acetaldehyde CH_3CHO, propionaldehyde CH_3CH_2CHO, benzaldehyde C_6H_5CHO, formic acid $HCOOH$, acidic acid CH_3COOH, and hydrogen cyanide HCN, are not shown.

"FROZEN PRODUCTS" AND THE REAL ENGINE

The physical boundaries of the combustion chamber and the piston's surface trap reaction products of the combustion because of the low surface temperatures. This means all molecules entering the cool zone near the cylinder wall by diffusion are frozen. As the gas flow near the walls goes to zero we collect reaction molecules during the whole combustion process of < 18 msec in a layer of gas which is moved to the exhaust system by the piston; thus we can monitor the history of the combustion [14].
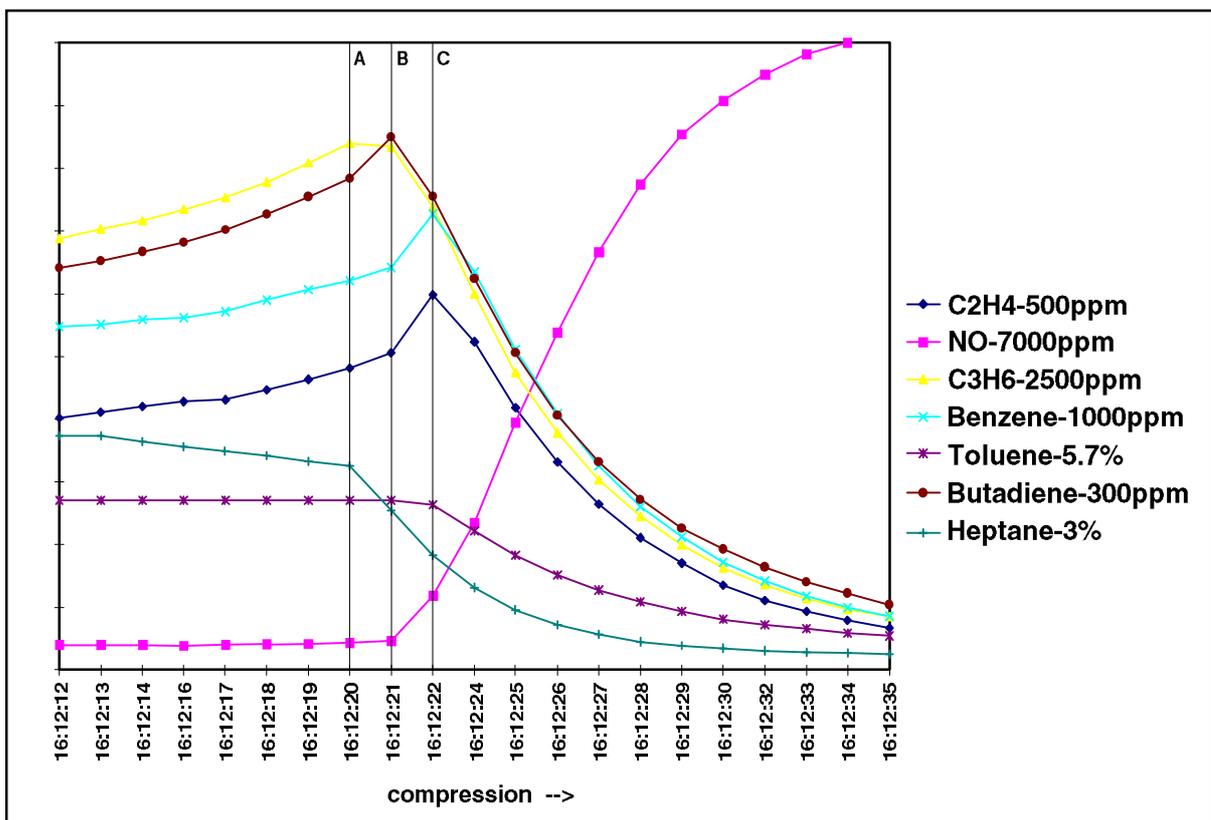

FIGURE 4 : Heptane / Toluene mix direct exhaust compression ratio from 9:1 to knock spark off

Figure 5 shows the differential mass spectra from raw exhaust at different spark advance angles. The engine was operating at 1500 rpm / min at a load of 50 %.

Figure 5 a shows alkenes, alkines, recombined radicals from the thermally decomposed higher alkanes in the fuel together with benzene, toluene, and xylene. This spectrum describes a charge in the cylinder which is rich in hydrocarbons and leads to a rapid but soft overall combustion. The dissapearence of C_3H_4, and C_4H_2 is a sensitive monitor for autoignition processes. As soon as autoignition occurs the intensity of these alkines drops to zero immediately.

When we advance the spark further and drive the engine into knocking conditions under constant operating conditions we find **figure 5 b** as differential spectrum. Here the concentration of aldehydes increases strongly as they are formed through the reactions of the radicals with O, OH, and O_2H radicals [15] (NO is not shown in this spectrum as the ionisation of the sample gas with 12,2 eV does not ionize NO; it also generates M-1 ions for C_3H_6, Toluene, Xylene and M-15 for C_4H_6).
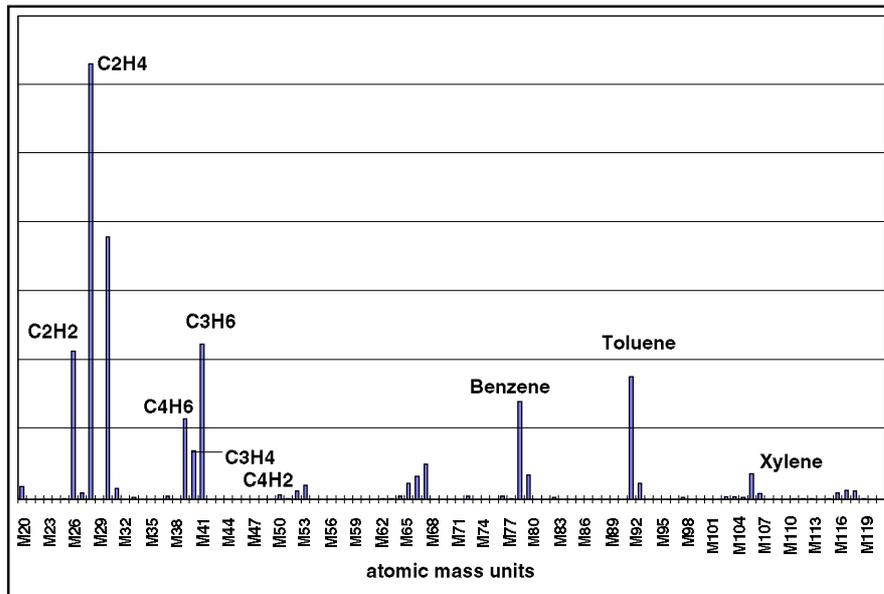

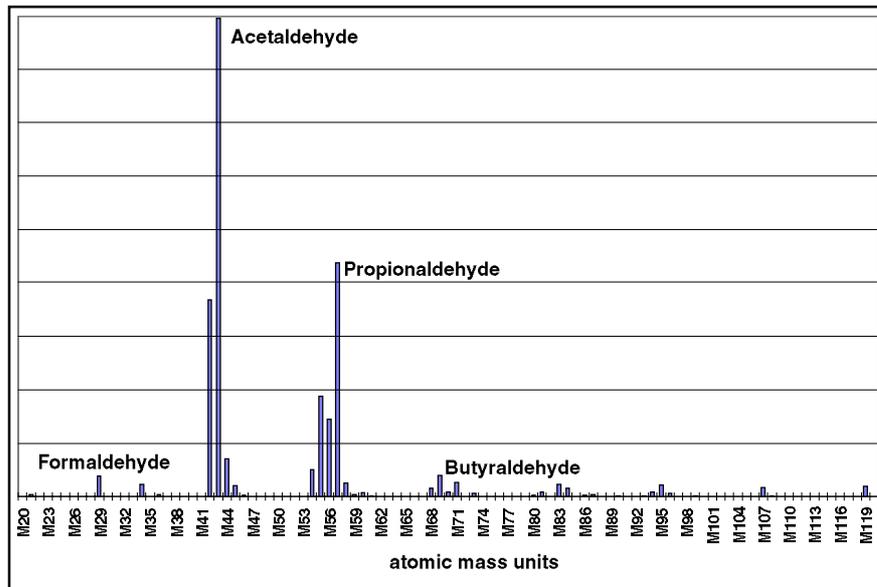**FIGURE 5 a : 9 deg spark advance with knock as background**

FIGURE 5 b : Knock spectrum with 9 deg as background

6

To demonstrate the sensitivity of aldehyde - monitoring in respect to autoignition we focus on propionaldehyde and vary the spark angle step by step while all the other engine parameters are kept constant (**Figure 6a**). **Figure 6b** shows the same aldehyde together with acetylene and butadiene in the exhaust of a high performance engine operating at 12900 rpm and full load as we vary the spark advance.

Butadiene does not vary significantly, whereas the concentrations of acetylene and acetaldehyde change dramatically when we vary the spark time.
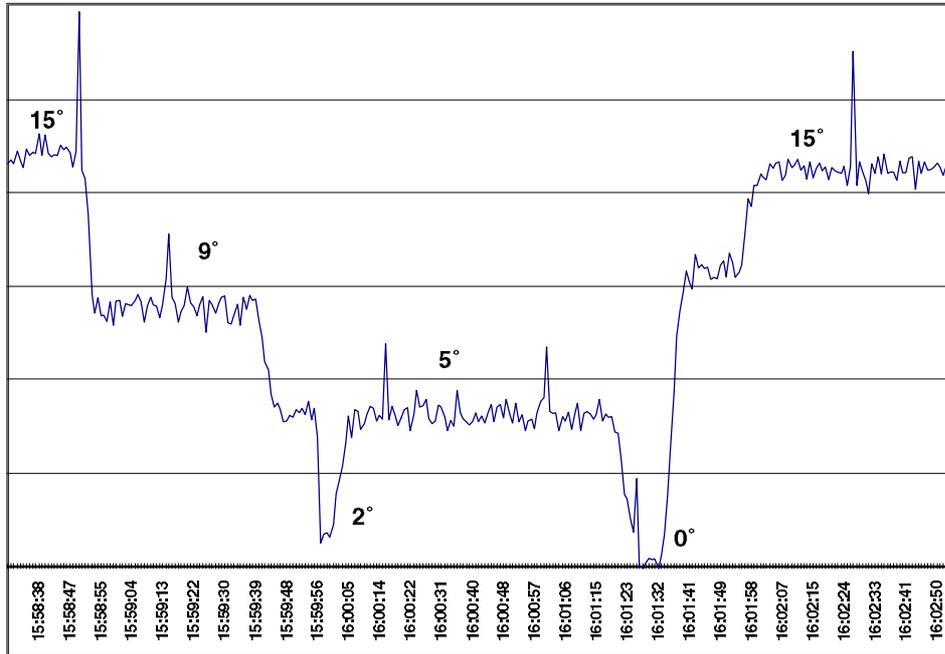

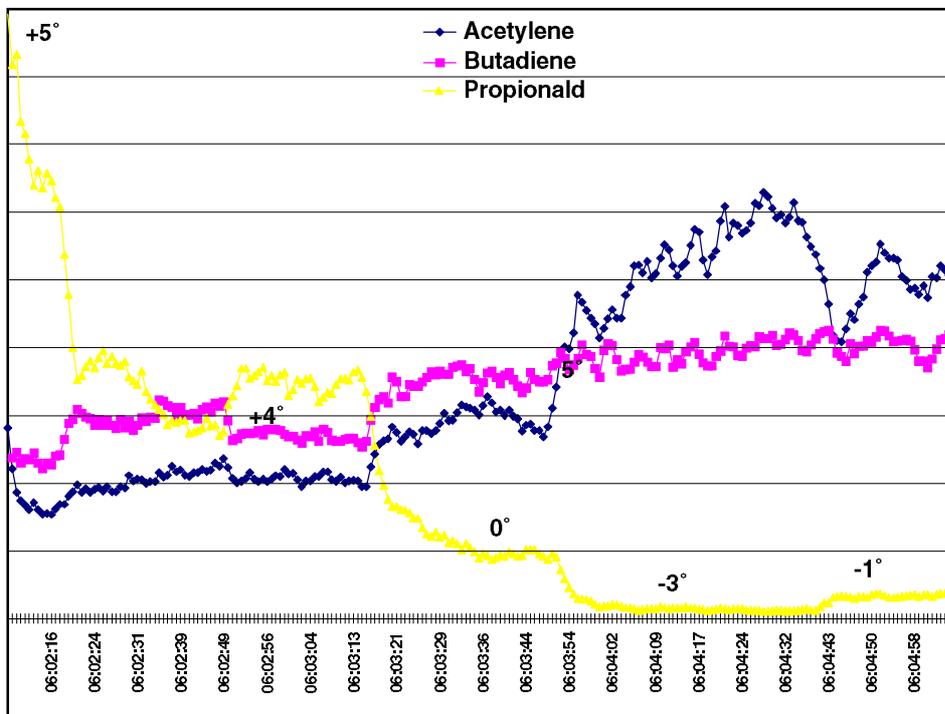**FIGURE 6a : Aldehyde formation at different spark advance**

FIGURE 6 b : ROTAX 12900 rpm full load spark advance variation

7

CONCLUSION

Information on the relative concentration of individual hydrocarbon compounds in the raw exhaust of the engine can clearly be correlated to engine design and operation parameters.

Dynamic analysis of differentiated hydrocarbons is a tool for the engineer to develop engines, not only towards low emissions, but also to high mechanic efficiency.

Appearance of aldehydes and disappearance of alkines in the exhaust gas indicate autoignition processes before pressure transducers or optical detection systems indicate autoignition and allow the development of engines towards higher mechanic efficiency.

REFERENCES

1. Kovarik, B., Charles F. Kettering and the Development of Tetraethyl Lead in the Context of Alternative Fuel Technologies, SAE Paper 941942 (1994).

2. Chrysler Corp., Ford Motor Comp., GM Corp. Navistar Int. Transportation Corp., Specifications for advanced emissions test instrumentation, Environmental Research Consortium.

3. Shuichi, K., Masami, Y., Yoshimi K., Satoshi Y., Speciated Hydrocarbon Emissions of SI Engine During Cold Start and Warm-up, SAE Paper 932706.

4. Kröll, M., Decker, G., Hartung, A., Postulka, A.,Georgi, B., Influence of Fuel Composition on NMOG-Emissions and Ozone Forming Potential, SAE Paper 932676.

5. V&F Analysetechnik, Gas Analyzer, US Patent US-PS 4.975.576.

6. Villinger, J., Federer, W., Resch, R., Dornauer, A., Lubich, M., Sejkora, W., SIMS 500-Rapid Low Energy Secondary Ion Mass Spectrometer for In-Line Analysis of Gaseous Compounds- Technology and Applications in Automotive Emission Testing, SAE Paper 932017.

7. Henglein, A., Lacmann, K., Jacobs, G., Ion-Molecule-Reactions, Physical Chemistry 69279 (1965).

8. Leppard, W., Benson, J., Gorse, R., Knepper, J., Rapp, L., Burns, V., Hochhauser, A., Koehl, W., Reuter, R., How Heavy Hydrocarbons in the Fuel Affect Exhaust Mass Emissions: Correlation of Fuel, Engine-Out, and Tailpipe Speciation - The Auto/Oil Air Quality Improvement Research Program, SAE Paper 932725.

9. Cheng, W., Hamrin, D., Heywood, J., Hochgreb S., Min K., Norris, M., An Overview of Hydrocarbon Emissions Mechanisms in Spark- Ignition Engines, SAE Paper 932708.

10. Barry, R., Rice, S., Ross, J., Physiacal Chemistry, John Wiley (1980).

11. McFarland, M., Albritton, D., Fehsenfeld, F., Ferguson, E., Schmeltekopf, A., Journal of Chemical Physics 59, p 6620 (1973).

12. Smith, D., Adams, N., Kinetics of Ion Molecule Reactions, P. Ausloos (1979).

13. Fenimore, C., General Electrics (1971).

14. Leppard W., Benson J., Gorse R., Knepper J., Rapp L., Burns V., Hochhauser A., Koehl W., Reuter R., How Heavy Hydrocarbons in the Fuel Affect Exhaust Mass Emissions: Correlation of Fuel, Engine-Out, and Tailpipe Speciation - The Auto/Oil Air Quality Improvement Research Program, SAE Paper 932725.