

# In-Cylinder Study of Soot and Polycyclic Aromatic Hydrocarbon Formation during the Combustion Cycle of a D.I. Diesel Engine Burning Tetradecane

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## ABSTRACT

The effect of the air/fuel ratio on the carbon and hydrocarbon distribution inside a direct injection diesel engine has been studied by means of fast sampling and chemical analysis of the combustion products collected during the combustion cycle in a given location of a single cylinder diesel engine burning tetradecane.

As expected it has been found that the formation of soot and light and heavy hydrocarbon formation was enhanced for the richer fuel-air mixture. The composition of light hydrocarbons was different for the two different air/fuel ratios investigated ( $\alpha=20$  and  $\alpha=35$ ).  $C_2H_2$  and  $C_2H_4$  are the main components of light hydrocarbons in richer conditions whereas their absence and the prevalence of  $CH_4$  and  $C_2H_6$  have been observed in leaner conditions. On the opposite the PAH formed at different air/fuel ratios showed the same qualitative composition and they are mainly constituted of two-seven ring unsubstituted PAH. The prevalence of light alkylated PAH observed in the exhaust has to be due to further reactions which occur late in the engine cycle and/or in the exhaust manifold.

Preliminary characterization of the mono-ring aromatics having long side chains and high molecular weight species has been made since they can give interesting information on the combustion process of a large hydrocarbon in a diesel engine.

## INTRODUCTION

The emission of soot and polycyclic aromatic hydrocarbon (PAH) from a diesel engine depends on the balance between the formation and burnout processes which occur during the combustion cycle. The reduction in these undesirable emissions by controlling the combustion parameters and the fuel composition, requires the knowledge of their effect on soot and PAH evolution directly inside the engine.

In a previous work [1] fast sampling and analysis of carbon and hydrocarbon species were carried out during the combustion cycle in a direct injection diesel engine when

burning an aromatic diesel oil. The formation of soot occurred during the diffusion controlled burning phase of the combustion cycle whereas the formation of PAH was not observed probably because of the prevalence of unburned fuel PAH hindered the detection of combustion-formed PAH.

In a subsequent work [2] we were able to follow the formation of soot and PAH in a diesel engine burning tetradecane as model fuel and the effect of the air/fuel ratio and fuel aromatic content on their evolution was studied. Besides the unsubstituted PAH, identified by chromatographic techniques, a large number of species with molecular weight higher and lower than the parent fuel molecule was detected and unsubstituted PAH resulted to be only a small fraction of the unburned carbon. In this work a great analytical effort has been devoted to the identification of the light and heavy carbon-containing species produced during the tetradecane diesel combustion at two different air/fuel ratios in order to study the effect of the air/fuel ratio on the pyrolytic and oxidative transformation of the fuel and the molecular mass growth process which eventually bring to soot formation.

## EXPERIMENTAL ARRANGEMENT

### *Engine and fuels*

A single-cylinder direct injection 0.75 l diesel engine was coupled directly to a dynamometer and automatically governed at 1200 rpm. A piezoquartz transducer detected pressure signal, an inductive transducer detected needle lift, and a shaft encoder with 0.1 crank angle maximum resolution were used to compute the ignition delay and the rate of heat release. The engine was governed at a constant speed varying the air/fuel mass feed ratio ( $\alpha$ ). Two operating conditions, low air/fuel ratio ( $\alpha=20$ , maximum cylinder pressure=80 bar) and high air/fuel ratio ( $\alpha=35$ , maximum cylinder pressure=60 bar) were studied. The fuel injection, as determined by the injector needle lift, started at 3 crank angle degrees before the top dead center (TDC)

in both conditions and stopped at 5 crank angle degrees after TDC at  $\alpha=20$  and 2.5 at  $\alpha=35$ . The ignition, as determined by the pressure rise in the cylinder, took place at TDC for both air/fuel ratios.

A chemically defined fuel, *n*-tetradecane, and a synthetic aromatic free lubricant oil were used. The low ignition delay of the fuel caused its ignition just after the injection, so that the combustion process during the engine cycle proceeded mainly in diffusion controlled burning conditions.

#### Sampling and analytical procedure

In-cylinder sampling of combustion products during the engine cycle was carried out by means of a fast acting sampling valve mounted in the combustion chamber at about 20 mm from the nozzle outlet of a four-hole injector on the geometrical axis of one of the sprays. The sampling valve used was an electro-magnetic needle type valve (Tsukasa-Sokken Instruments), capable of opening and closing in 1 millisecond (about 7 engine crank angle degrees at a revolution speed of 1200 rpm) at specific times in the combustion cycle. The sampling procedure was repeated for at least 10,000 cycles in order to collect a sufficient amount of soot and condensed hydrocarbons. A lay-out of the sampling valve and the engine head is shown in Fig.1.

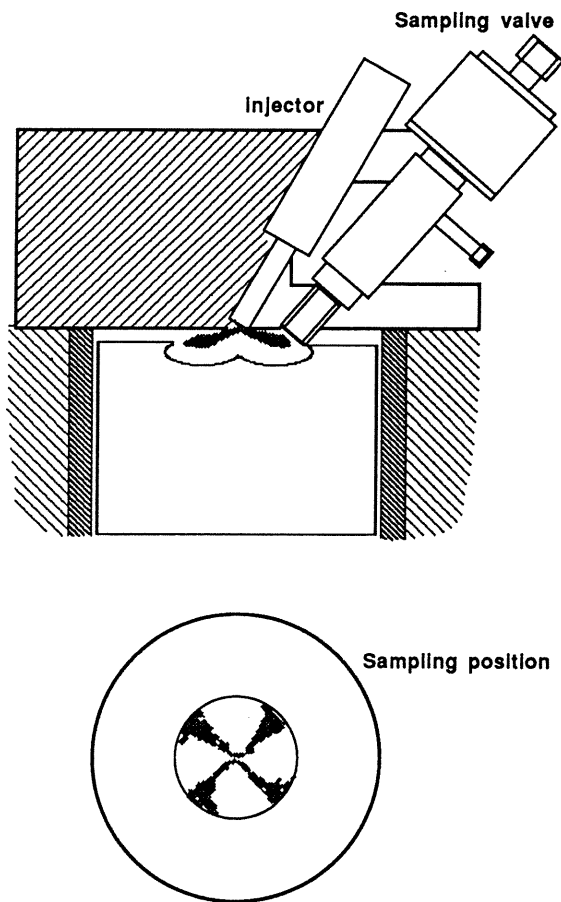


Fig.1 Lay-out of the engine head and the sampling valve.

The gas withdrawn from the sampling valve was condensed in an ice-trap and passed through a quartz fiber filter to remove the particulate. Gaseous products were collected in a glass sampling bulb and analyzed by gas chromatography (GC) with a thermal conductivity detector. The light hydrocarbons ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ ) were analyzed by gas chromatography with a flame ionization detector. A schematic of the sampling line is shown in Fig.2.

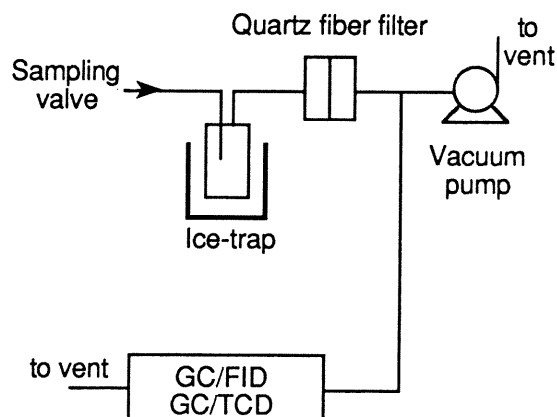


Fig.2 Schematic of the sampling line

Condensed hydrocarbons collected in the sampling line and on the filter were recovered by washing the line with acetone and dichloromethane and by extraction from the filter with dichloromethane. The carbonaceous material (extraction residue) was classified as soot. The weight of soot and condensed hydrocarbons was related to the sampled volume (70 l at STP) in order to calculate the concentration of the combustion products in the sampled control volume.

The condensed hydrocarbon species were dissolved in *n*-hexane and fractionated by semipreparative high pressure liquid chromatography (HPLC) on a silica-bonded alkyl nitrile column using *n*-hexane as eluent (4 cm<sup>3</sup>/min) and a 254 nm UV and a differential refractometer as detectors. This technique permits the separation of the aliphatic compounds, the first eluted fraction, from the polycyclic aromatic hydrocarbons and the mono-ring aromatic compounds which elute between aliphatic and PAH fractions. The PAH fraction contains alkyl substituted and unsubstituted PAH ranging from two-ring (naphthalene) to seven-ring (coronene) PAH. Polycyclic aromatic compounds with more than seven rings and organic compounds containing oxygen and nitrogen are strongly retained on the top of the column so that their elution was accomplished by backflushing the column with *n*-hexane immediately after the elution of PAH. The comparison between thermogravimetric

profiles of each hydrocarbon class showed that the hydrocarbon species retained on the top of the column were less volatile than the PAH fraction so that these compounds will be referred to as high molecular weight species (HMW).

Quantitative analysis of the most abundant unsubstituted polycyclic aromatic hydrocarbons was performed by HPLC on a octadecylsilyl reverse phase column using a Vista 5500 liquid chromatograph, equipped with a 254 nm UV detector and a LS-4 Perkin-Elmer spectrofluorimeter. Gas chromatography-mass spectrometry (GC/MS) of single components of each hydrocarbon class was on a Hewlett-Packard 5890 gas-chromatograph equipped with a Hewlett-Packard 5970B mass spectrometer. The analysis of the HMW species by means of GC/MS resulted to be almost ineffective so that infrared spectroscopy and thermogravimetric measurements were performed on these samples.

Infrared absorption spectra were by a Perkin-Elmer 1600 Fourier transform infrared spectrometer. Thermogravimetric analysis was carried out in inert flow ( $N_2$ , 20  $cm^3/min$ ) at a heating rate of 40°C/min using a Perkin Elmer TGS-2 system.

## RESULTS AND DISCUSSION

Diesel engines generally operate with lean air/fuel ratios,  $\alpha$ , greater than 18, but even in these overall lean conditions a small change of the air/fuel ratio causes a dramatic change of soot and hydrocarbon emission [3-5] so that it must necessarily affect soot and hydrocarbon evolution during the combustion cycle. The aim of the present work is to study the effect of the air/fuel ratio on the distribution of carbon and hydrocarbon species formed inside the combustion chamber during the engine cycle for a relatively fuel-rich ( $\alpha=20$ ) and fuel-lean condition ( $\alpha=35$ ) paying particular attention to the compositional histories of the light hydrocarbons and aromatic species.

The conversion of the fuel injected in a diesel combustion chamber proceeds during the combustion cycle through either pyrolytic and oxidative routes which bring to the formation of water gases ( $CO, CO_2, H_2$  and  $H_2O$ ), soot, and light and heavy hydrocarbons.  $CO$  and  $CO_2$  are typical products of oxidation reactions whereas soot and heavy hydrocarbons are characteristic pyrolysis products. Both pyrolysis and partial oxidation of the fuel can be sources of the light hydrocarbons and their composition is indicative of the different origin.

An overall view of the combustion process in two different fuel-air mixture conditions is given in Figs.3,4 where the concentration profiles of  $CO, CO_2, O_2$ , and light hydrocarbons are shown. The change of the air/fuel ratio in a diesel engine is accomplished changing the fuel load so that the higher amount of fuel injected per cycle at  $\alpha=20$  respect to  $\alpha=35$  causes the higher formation of  $CO$  and  $CO_2$  observed at  $\alpha=20$ . As

$O_2$  concentration decreases  $CO$  and  $CO_2$  increase for both a values, but it is evident that  $CO$  concentration at  $\alpha=35$  increase later.

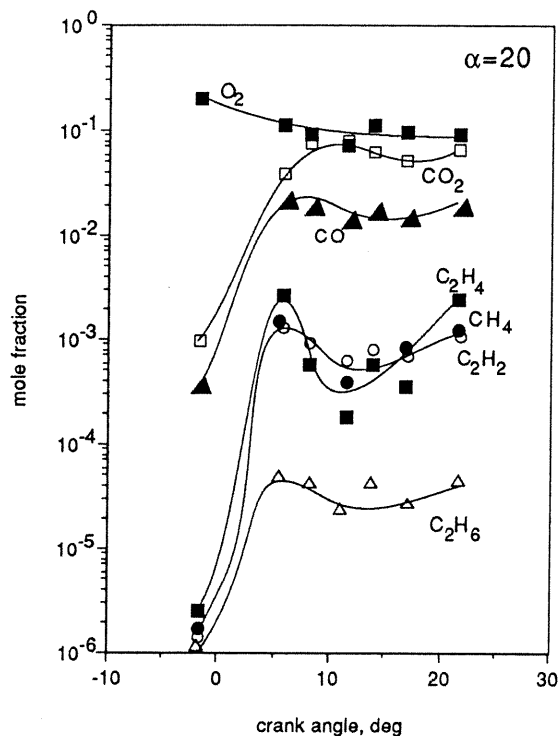


Fig.3 Concentration profiles of  $CO, CO_2, O_2$  and light hydrocarbons at  $\alpha=20$ .

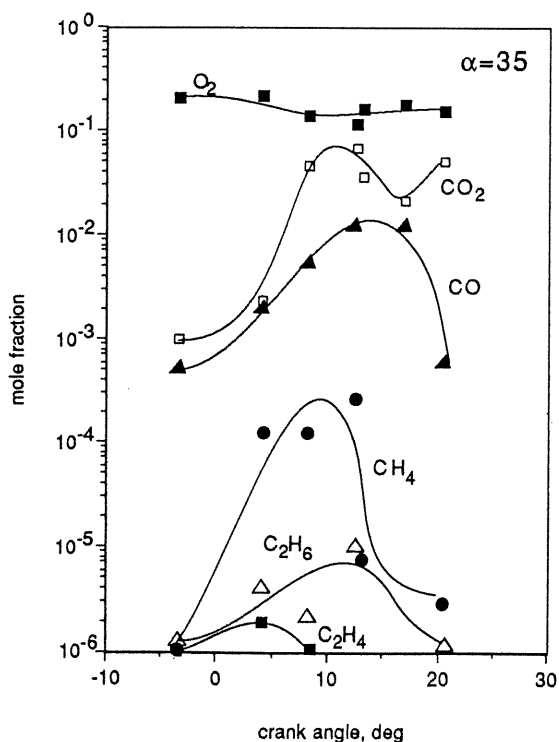


Fig.4 Concentration profiles of  $CO, CO_2, O_2$  and light hydrocarbons at  $\alpha=35$ .

Also the formation of light hydrocarbons at  $\alpha=35$  occurs later and at a lesser degree respect to  $\alpha=20$  and they show a very different composition. At  $\alpha=20$  they are mainly constituted of  $C_2H_4$  and  $C_2H_2$  which are either intermediates of the fuel oxidation and products of the thermal decomposition of the fuel [6]. Both reactions are favoured by the high temperature conditions so that the presence of  $C_2H_2$  and  $C_2H_4$  gives evidence of the high temperature environment connected to the richer fuel-air mixture. Moreover, the low availability of  $O_2$  at  $\alpha=20$  does not allow the complete oxidation of  $C_2H_2$  and  $C_2H_4$  formed. Accordingly the lower formation of light hydrocarbons and the absence of  $C_2H_2$  and  $C_2H_4$  at  $\alpha=35$  (Fig.4) are due to the the relatively low temperature and fuel lean environment which reduces the thermal decomposition of the fuel; the high  $O_2$  availability enhances the oxidation of these species when formed by oxidative attack.

Further insights on the effect of the air/fuel ratio on the pyrolytic routes through which the fuel is converted are given by the examination of the concentration profiles of soot and aromatic compounds which are representative species of pyrolytic reactions, but before to discuss their concentration profiles the qualitative composition of the aromatic compounds is described.

As shown in the experimental section the aromatic species are separated in mono-ring aromatics and two-, seven-ring PAH whereas the so-called high molecular weight species comprise oxygen and nitrogen substituted compounds and eventually polycyclic aromatic compounds with more than seven rings. Few oxygen-containing aromatic species such as benzaldehyde, naphthaldehyde, and fluorenone were revealed by GC/MS in the HMW, but the presence of heavier oxygen-containing species, not eluted by GC, cannot be excluded since evident infrared peaks characteristic of oxygen functionalities (C=O, OH) were found.

For both  $\alpha$  values the formation of mono-ring aromatic compounds which comprise alkylated benzenes with from 8 to 14 C-atoms in one or more side chains has been observed, but not quantified. The presence of monosubstituted alkyl benzenes of the form  $C_6H_5CH(R_1)R_2$  is particularly evident and, among these, the more abundant species are of the form  $C_6H_5CH(CH_3)R_2$ . During the combustion cycle it has been observed the enrichment in a compounds of formula  $C_6H_5CH(CH_3)C_{11}H_{23}$  which could derive from the reaction between aromatic and tridecyl radicals coming from tetradecane decomposition and/or oxidation. The study of the origin of the mono-ring aromatic compounds could be significant for the knowledge of the combustion mechanism for a large hydrocarbon such as tetradecane and further work is necessary.

The concern about the environmental impact of PAH emitted from a diesel engine and their possible role in soot formation give particular relevance to the analysis of their evolution during the combustion cycle.

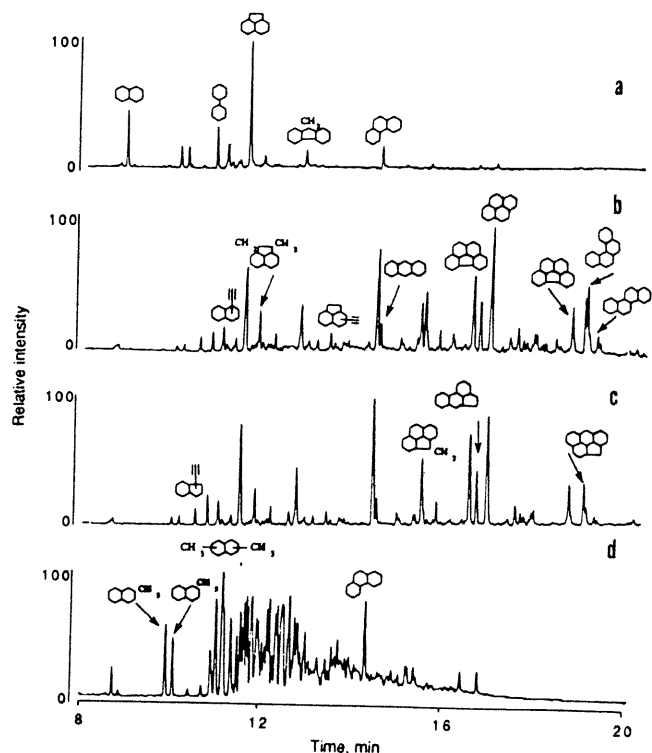


Fig.5 Chromatographic profiles of the total PAH collected at different crank angle degrees: 4.2 deg (a), 8 deg (b), 13.7 deg (c) and in the exhaust (d) for  $\alpha=20$ .

The PAH fractions at  $\alpha=20$  and  $\alpha=35$ , analyzed by GC/MS, are composed of the same substituted and unsubstituted species. The chromatographic profiles of the PAH collected at different crank angle degrees, reported in Fig.5 for  $\alpha=20$ , show the prominent presence of unsubstituted PAH, e.g. naphthalene, acenaphthylene, phenanthrene, fluoranthene and pyrene, but many other substituted and unsubstituted PAH contribute to the total PAH as shown by the presence of a lot of small, often unresolved, chromatographic peaks. It is noteworthy the presence of acetylenic and ethylenic PAH such as ethynyl naphthalene, ethynyl acenaphthylene, etc. which can derive from the addition of  $C_2H_2$  to aromatic radicals and are considered intermediates in the process leading to the aromatic ring closure. The composition of the PAH collected in a diesel engine is very similar to that found in atmospheric and low pressure flames [7], but further reactions occurring late in the engine cycle and in the exhaust have to be responsible of the emission of light alkyl substituted PAH, e.g. methyl and dimethyl naphthalenes, (last chromatogram of Fig.5) which cannot derive from the lubricant oil since an aromatic free lube oil has been used.

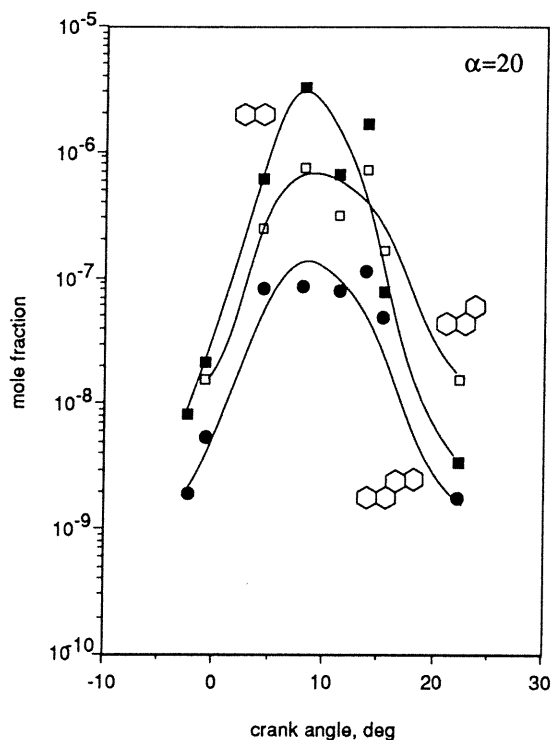


Fig. 6 Concentration profiles of naphthalene, phenanthrene and chrysene at  $\alpha=20$ .

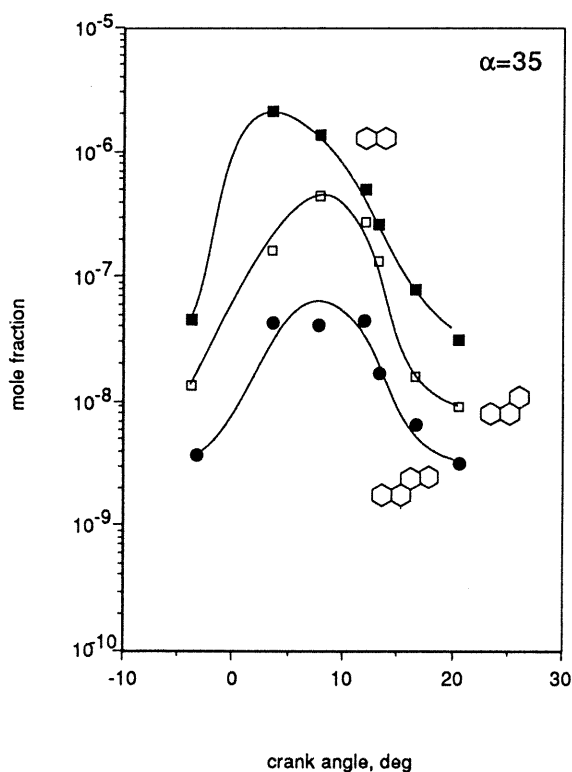


Fig. 7 Concentration profiles of naphthalene, phenanthrene and chrysene at  $\alpha=35$ .

It has been found that the formation of the most abundant unsubstituted PAH is higher in fuel-rich conditions. This is clearly shown in Figs. 6,7 where the concentration profiles of some typical PAH (naphthalene, phenanthrene, and chrysene) are reported for  $\alpha=20$  and  $\alpha=35$ . The maximum formation of these unsubstituted PAH slightly precedes the maximum of soot concentration for both  $\alpha$  values as shown in Figs. 8,9 where the concentration profiles of soot, high molecular weight species, and total PAH are reported for  $\alpha=20$  and  $\alpha=35$ .

Soot is the most abundant pyrolytic product whereas PAH concentration is about one or two orders of magnitude lower than soot concentration. As expected, soot and PAH formation is enhanced in fuel-rich more than in fuel-lean conditions. On the contrary the concentration of high molecular weight compounds, which always overcomes PAH concentration, is higher for the leaner fuel-air mixture and approaches more closely the soot concentration (Figs.8,9). It can be hypothesized that the large formation of HMW species is due to a larger contribution of partially oxidized compounds whose formation in leaner conditions is more favoured but further investigation on their chemical characteristics is necessary to give more details on their origin.

#### FINAL REMARKS

The change of the air/fuel ratio in a direct injection diesel engine even in overall fuel-lean conditions affects significantly the formation of soot and light and heavy hydrocarbons during the combustion cycle. As expected the formation of soot and light and heavy hydrocarbons is strongly enhanced when a richer fuel-air mixture is burned.

The composition of the light hydrocarbons changes drastically at changing air/fuel ratios. For the richer fuel-air mixture a lot of light hydrocarbons are formed and  $C_2H_2$  and  $C_2H_4$  are the main components whereas their absence and the prevalence of  $CH_4$  and  $C_2H_6$  has been observed in leaner conditions. On the contrary the PAH formed in leaner and richer conditions show the same qualitative compositions and are mainly constituted of unsubstituted PAH. Further reactions which occur late in the engine cycle and in the exhaust have to be responsible of the strong enrichment in light alkylated PAH which has been noted in the PAH collected at the exhaust manifold.

As found in atmospheric pressure premixed and diffusion flames the PAH formation, as well as soot formation, is higher in richer conditions and the maximum of PAH formation occurs slightly before soot formation for both air/fuel ratios.

The formation of alkylated mono-ring aromatics having long side-chains and high molecular weight species having oxygen functionalities has been observed and further analytical work on their chemical composition

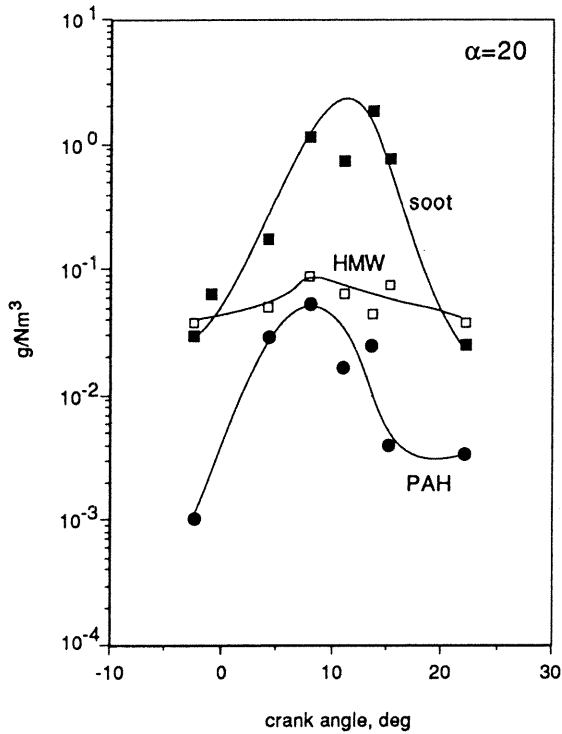


Fig.8 Concentration profiles of soot, polycyclic aromatic hydrocarbons and high molecular weight species at  $\alpha=20$ .

can give interesting information on their origin and on the mechanism of combustion process of a large hydrocarbon such as tetradecane.

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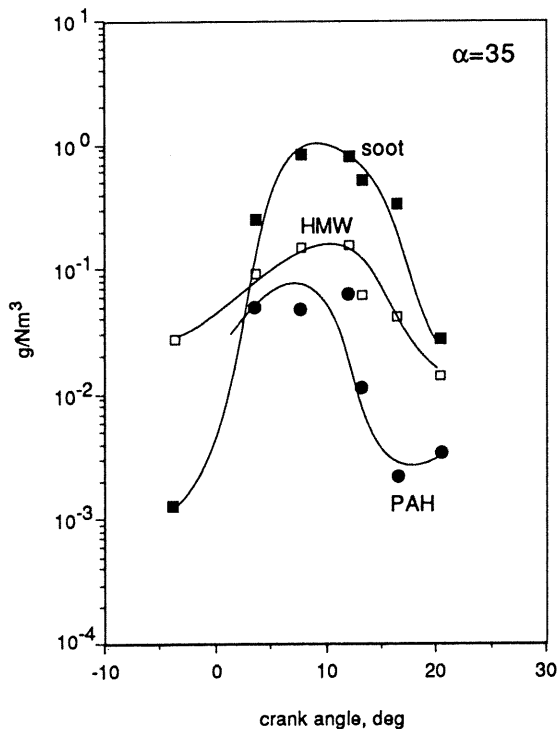


Fig.9 Concentration profiles of soot, polycyclic aromatic hydrocarbons and high molecular weight species at  $\alpha=35$ .