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Formation of PAH and soot during acetylene pyrolysis at different gas residence times and reaction temperatures

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ABSTRACT

The formation of polycyclic aromatic hydrocarbons (PAH)[1] and soot from the pyrolysis of acetylene was studied, taking into account the influence of the operating conditions, such as gas residence time and temperature. The influence of gas residence time was considered between 1.28 and 3.88 s for the experiments carried out under different temperatures from 1073 to 1223 K. The total PAH was calculated as the addition of PAH concentration found in different locations, namely adsorbed on soot and on the reactor walls, and at the outlet gas stream. The relationship between the PAH concentrations and their carcinogenic equivalence sum (*KE*)[2] was also evaluated. The results obtained showed that temperature and residence time have a high influence on pyrolysis products, especially on the PAH concentration adsorbed on soot, which exhibited the highest *KE* in all cases studied.

1. Introduction

Vehicle emissions consist of a complex mixture of a large number of compounds in the form of gases, solids and liquid aerosols. In the case of gasoline engines, exhaust gases leaving the internal combustion chamber of a spark ignition engine may contain up to 6000 ppmv of hydrocarbon components, equivalent to 1–1.5% of the fuel consumed. About 40% of this amount corresponds to unburned gasoline fuel components. The other 60% consists of partially reacted components that were not present in the original fuel. The final hydrocarbon compound emission depends on the original fuel components [1]. These emission levels have in fact changed in more modern vehicles mainly because of the use of catalytic converters.

The components in diesel fuel have higher average molecular weights than those in a gasoline blend, resulting in higher boiling and condensing temperatures [1]. A higher amount of heavy hydrocarbons and particulate matter (PM) are formed, becoming a serious problem in diesel engines. PM is formed in locally fuel rich areas where the molar ratio of carbon and oxygen (C/O) is high. These areas, inside the combustion chamber, may produce an environment close to pyrolysis conditions due to the fact that some fuel particles may not find enough oxygen to react. Consequently, the PM coming from the cylinder inside the combustion chamber is the result of a number of different environments caused by gas concentrations, mixing effects and different operating conditions (pressure, temperature profiles and gas residence times).

Soot is PM formed during combustion under conditions that allow polymerization/condensation reactions of compounds such as PAH formed from fuel [2]. PAH are compounds formed by carbon rings connected by means of consecutive reactions which involve acetylene (C_2H_2) as the major species, leading to multiple ring formation [3–5]. It is well-known, that PAH are dangerous pollutants, especially with regard to their potential harmful implications for human health [6–8]. PAH and soot are closely related, since PAH play an important role in soot formation and they can also appear adsorbed on the soot surface. The combination of PAH and soot generates toxic effects. Thus, the well-known carcinogenic and mutagenic effects of soot particles can be increased because they are directly associated with the presence of the PAH adsorbed on the soot surface [9].

Several operating conditions, including residence time and reaction temperature, potentially affect the amount of soot particles and PAH inside the engine [10]. The influence of these operating conditions on PAH formation is a subject of some controversy.

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[1] Polycyclic aromatic hydrocarbons.

[2] Carcinogenic equivalence sum.

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Recent studies have shown that in pyrolysis conditions using acetylene as a direct PAH-soot precursor, a major amount of PAH is formed under temperature conditions from 1073 to 1223 K [11], while a high amount of soot results at higher temperatures [12].

Regardless of these studies, the influence of gas residence time on PAH-soot formation has scarcely been studied and consequently it is not well understood. Residence time may be a very important subject, since it potentially determines to a large extent the conversion of small hydrocarbons to PAH and the soot growth. In this context, the aim of this work is the study of the influence of gas residence time and temperature on PAH and soot formation in acetylene pyrolysis using well-controlled laboratory operating conditions. Thus, the present results may be valuable for assessing the complex combustion conditions occurring inside a real internal combustion engine.

The aromatic compounds selected are the 16 classified by the US Environmental Protection Agency (EPA) as priority pollutants due to their high carcinogenic potential [13]. These are NAPH, ACNY, ACN, FLUO, PHEN, ANTH, FANTH, PYR, B(a)A, CHR, B(b)F, B(k)F, B(a)P, I(123-cd)P, DB(ah)A, and B(ghi)P. The corresponding abbreviation for each EPA-PAH is shown in Table 1 together with its molecular mass. The PAH amount formed depends on the operating conditions, and their distribution on different surfaces (soot and reactor walls) and at the outlet gas stream depends on their molecular weights but also on the environment temperature, pressure, PAH concentration and soot characteristics [14]. The analytical method for PAH quantification in the different phases is based on Soxhlet extraction, extract concentration by rota-evaporator and gas chromatography coupled to mass spectrometry analysis (GC-MS).

Additionally, the carcinogenic equivalence sum (*KE*) has been determined in the different experiments and an attempt has been made to evaluate the influence of different operating conditions on the harmful effect for health of exhaust gases.

2. Experimental equipment and procedures

2.1. Overview of the experimental set-up and procedures to obtain samples

The experimental installation used in the present work consists of a gas feeding system, a reaction system, a soot and PAH collection system and a gas analysis system. A detailed description of the experimental set-up has been given elsewhere [15,16], and therefore only a short description is given here. The gases are fed through mass flow controllers while reaction takes place in a quartz tube reactor situated inside an electric furnace. The reactor outlet used in this research can be adjusted at different positions in order to vary the gas residence time by means of changing the reaction zone volume, determined as the zone where a temperature profile of ±25 K is achieved. The longitudinal temperature profile inside the reactor was determined by means of an S type fine-wire thermocouple.

The soot formed in the reaction is swept out to the reactor outlet by the gas flow and collected on quartz fibre filters (with a 30 mm external diameter, 100 mm length, and pore diameter lower than 1 μm). The PAH collection in gas phase, at the outlet gas stream, was done by means of XAD-2 resin, supplied by Supelco, and packaged in a thin-tube of 300 mm length and an external diameter of 10 mm, placed immediately after the above mentioned soot collecting filter. Experiments were run for 1.5 h, using an acetylene-nitrogen mixture and keeping the acetylene concentration constant at 30,000 ppmv.

Previous studies [11] have revealed that the critical temperature in PAH formation from acetylene pyrolysis is in the range from 1073 to 1223 K. Therefore, the present work focuses on this temperature interval, analysing the influence of residence time between 1.28 and 3.88 s. The total gas flow was 1000 mL/min (STP) except for a gas residence time of 2.28 s, in which different total gas flow rates were used (Table 2) at the different temperatures tested.

The gas residence times used in this paper correspond to two different positions of the reactor outlet (reaction zone lengths of 6 and 16 cm, respectively). In this way, the gas residence time was calculated as a function of the reaction volume, total gas flow rate and the reaction temperature in each experiment.

2.2. Analytical method for PAH quantification

With the main objective of collecting PAH during the experiments, the experimental procedure used took into account the fact that the 16 PAH-priorities span a broad spectrum of vapour pressures, and that they may be distributed both within the gases and condensed on solid surfaces such as the soot or the reactor walls. Thus, it was necessary to develop a method which permitted the collection of PAH from all phases.

The sampling of PAH formed during acetylene pyrolysis was thus carried out in different ways. The heaviest PAH, which appear either adsorbed on soot or the reactor walls, were collected by means of both the soot collection system and washing the reactor with 100 mL of dichloromethane, respectively. The lightest PAH, which due to their vapour pressures do not appear condensed and

Table 1
Abbreviation and molecular mass of every EPA-PAH studied.

PAH abbreviation used	PAH analysed	Molecular mass (g/mol)
NAPH	Naphthalene	128
ACNY	Acenaphthylene	152
ACN	Acenaphthene	154
FLUO	Fluorene	166
PHEN	Phenanthrene	178
ANTH	Anthracene	178
FANTH	Fluoranthene	202
PYR	Pyrene	202
B(a)A	Benzo(a)anthracene	228
CHR	Chrysene	228
B(b)F	Benzo(b)fluoranthene	252
B(k)F	Benzo(K)fluoranthene	252
B(a)P	Benzo(a)Pyrene	252
I(123-cd)P	Indene(1,2,3-cd)pyrene	276
DB(ah)A	Dibenzo(a,h)anthracene	278
B(ghi)P	Benzo(g,h,i)perylene	276

Table 2
Experimental conditions of PAH-soot formation in the pyrolysis of 30,000 ppmv of acetylene.

Set	L_r[a] (cm)	T[b] (K)	t_r[c] (s)	Q_N[d] (STP) (mL/min)
1	6	1073	1.46	1000
2	6	1123	1.39	1000
3	6	1173	1.33	1000
4	6	1223	1.28	1000
5	6	1073	2.28	640
6	6	1123	2.28	610
7	6	1173	2.28	585
8	6	1223	2.28	560
9	16	1073	3.88	1000
10	16	1123	3.71	1000
11	16	1173	3.55	1000
12	16	1223	3.41	1000

[a] Reaction length.
[b] Reaction temperature.
[c] Gas residence time.
[d] Gas total flow rate.