

POLYCYCLIC AROMATIC HYDROCARBONS FROM GASOLINE-ENGINE AND LIQUEFIED PETROLEUM GAS ENGINE EXHAUSTS

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ABSTRACT

Exhaust gases from an internal combustion engine, alternatively powered by gasoline or by liquefied petroleum gas, were analysed for polynuclear aromatic hydrocarbons. The engine operated a lift truck for the handling of warehouse goods. A combined condensation-filtration apparatus was constructed for sampling of the exhausts. The basic steps of the analytical procedure are summarized here. Several polycyclic aromatic hydrocarbons were identified and determined both in the gasoline engine and in the liquefied petroleum gas engine exhausts. In the liquefied petroleum gas engine exhausts, all detected polynuclear hydrocarbons were present in significantly lower concentrations.

INTRODUCTION

Accumulated evidence has indicated that polycyclic aromatic hydrocarbons (PAH) are present in automotive-engine exhausts. This source contributes significantly to urban atmospheric pollution in terms of known or potential carcinogenic factors such as some of the polynuclear compounds^{4, 5, 11, 13-15, 18, 19, 21, 23-25, 29, 33}. It has been established that the production of PAH by an internal combustion engine depends upon several variables such as type of fuel used, mileage of engine, number of revolutions per minute (rpm), change of speed, and load under which the engine is running^{7, 9, 11, 15, 20, 21}. Several investigations have shown that many of the recovered polynuclear compounds are common to both gasoline and diesel exhausts. However, notable quantitative differences were found^{3, 11, 12, 15, 16, 19, 26, 27}.

Nonetheless, no references pertaining to similar studies on internal combustion engines powered by liquefied petroleum gas have been found in the literature. This fuel is very little used in automobile engines; therefore, the question of its contributing appreciably to air pollution does not exist. However, in several industrial activities, liquefied petroleum gas is often used to power internal combustion engines which operate lift trucks in loading, unloading, moving and stowing goods. Due to the theoretical possibility of attaining conditions which are closer to the ideal air/fuel ratio and, thus, reducing exhaust emissions (especially as regards carbon monoxide and unburned hydrocarbons), the replacement of gasoline by liquefied petroleum gas would be a preventive measure for the workers involved in the operations mentioned above.

This report is concerned with the qualitative and quantitative determinations of PAH in the exhaust gases from a lift truck alternately powered by gasoline and liquefied petroleum gas. The results are compared and discussed. The first section of this paper consists of a description of the sampling apparatus and analytical procedure used.

EXPERIMENTAL

A lift truck with the following characteristics was employed: model Towmotor, 461 HF type, continental engine, 4 cylinders, 2200 cc displacement, peak 2400 rpm, 2000 kg mx load. At the time of these experiments, the lift truck had operated for 8450 working hours. The engine was alternately powered by gasoline (84 NO) and a propane-butane mixture.

The trials on the lift burning liquefied petroleum gas were accomplished under the following conditions:

- (a) on a simulated working schedule with load of 1000 kg,
- (b) while the engine was idling (500 rpm) at zero load.

The gasoline-powered engine was only subjected to condition (a).

1. Collection of samples

A combined condensation-filtration apparatus was constructed. The system is illustrated in *Figure 1* and a photograph of the apparatus is shown in *Figure 2*.

A glass probe (8 mm in diameter) with a dual series of holes along the sides, and fitted with a container for condensed water, was introduced about 30 cm into the exhaust pipe to withdraw the sampled gases. These were first passed through a condenser, at the bottom of which was attached a second container for condensed water, and then through a series of three traps cooled in 'dry ice' placed in a Dewar flask.

The relatively dry gas was then filtered through a series of three filters: a fibre glass filter (Gelman, type A-DOP 99-95 per cent efficient, 4.5 in. in diameter), followed by two cellulose triacetate filters (Gelman, GA-6, 0.45 microns pore size, 2 in. in diameter). A vacuum pump sampled at a constant rate of 1 CFM. A vacuum gauge was included to correct the indicated flow for error due to pressure drop across the filters. A running time meter indicated cumulative operating time. Teflon connecting tubes were used. The sections of the system were connected by means of glass standard joints. The apparatus guarantees the quantitative recovery of organic materials of high molecular weight and the accurate measurement of the actual gas volume sampled.

2. Extraction of the PAH from condensed water and filters.

After sampling, the entire condensation section was washed with a definite amount of methanol which had been collected, together with condensed water, in the container placed at the bottom of the condenser. The water-methanol mixture was adjusted to obtain the 4:1 ratio between methanol and water, according to Hoffmann and Wynder¹⁰. This solution was shaken three times with cyclohexane to enrich the PAH in the cyclohexane phase after separation from the hydrophilic compounds. The filters were extracted in a Soxhlet apparatus with cyclohexane for 20-30 hours.

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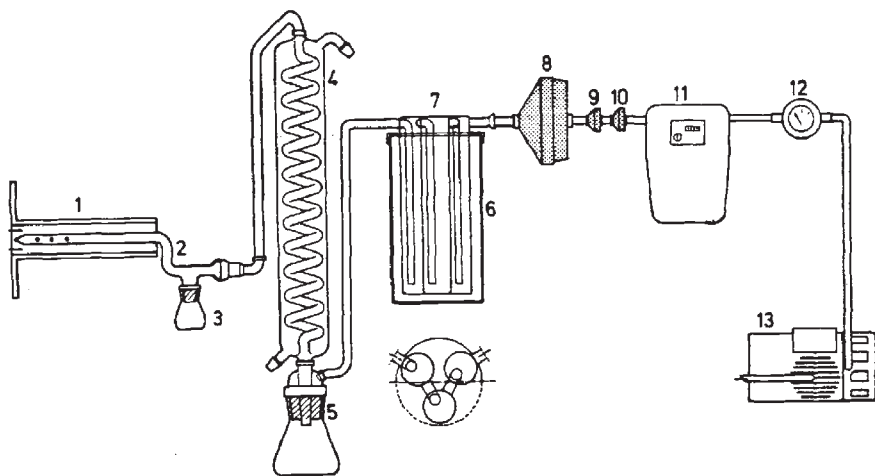


Figure 1. Schematic drawing of the engine exhaust sampling apparatus for determination of polycyclic hydrocarbons. (1) Exhaust pipe (2) Probe (3) Condensed water flask (I) (4) Condenser (5) Condensed water flask (II) (6) Dewar flask (7) Traps in dry ice (8) Glass fibre filter (9, 10) Cellulose triacetate filters (11) Dry gas meter (12) Vacuum gauge (13) Vacuum pump.



Figure 2. Engine exhaust sampling apparatus for determination of polycyclic hydrocarbons.

3. Analysis of samples for PAH.

The analytical procedure has previously been described³⁰⁻³². A preliminary adsorption of PAH into a series of superimposed alumina columns, avoids evaporation to dryness and the resulting losses due to the appreciable volatility of polynuclear compounds. This also enables the extracts to be purified from many extraneous materials which give rise to an intense background in the ultraviolet absorption spectra and allows a first separation to be achieved of PAH into two large fractions. The basic steps of the method are summarized below and shown schematically in *Figure 3*.

(a) *Adsorption of PAH*. The combined cyclohexane extracts were concentrated to 150 ml in a rotary evaporator, at a reduced pressure and at a temperature of 40°. The residual solution was percolated through a series of three superimposed columns which contained respectively:

- (i) aluminium oxide (neutral, Woelm) with 6 per cent of water (Column A);
- (ii) aluminium oxide with 3 per cent of water (Column B);
- (iii) highly activated aluminium oxide (Column C).

Columns with an outer grinding at the top and an inner grinding at the bottom were used.

The compounds having four or more condensed aromatic rings were retained by alumina placed in column B. Those having a lower number of condensed rings remained adsorbed on the activated alumina of column C. Most of the coloured matter, oxygenated products and other substances with greater chromatographic adsorbability were firmly held on alumina containing 6 per cent of water (Column A).

(b) *Alumina deactivation*. Alumina in the columns was then deactivated to allow the desorption of the PAH. For this purpose, a stream of nitrogen, saturated with water, was passed through columns B and C for one hour in a downward direction. To retain the naphthalene eventually drawn off from alumina by the gaseous stream, a gas dispersion tube was attached at the bottom of column C and the fritted glass disc was immersed in the cyclohexane.

(c) *Chromatographic separation of PAH*. Following deactivation, column C (lighter compounds) was made to overlap a new column containing alumina with 4 per cent of water and the desorption of the PAH was carried out with cyclohexane. The PAH passed quantitatively in the lower column where the chromatographic development occurred. Column B (heavier compounds) was made to overlap another new column containing alumina with 5 per cent of water. The rest of the procedure was the same as that mentioned above.

(d) *Spectrophotometric analysis*. An automatic recording spectrophotometer was used for qualitative and quantitative analysis. The absorption spectra of the eluates were recorded and quantitative estimations were carried out by the base-line technique, according to the method of Cooper⁶. Cyclohexane was used for all determinations.

RESULTS

The analytical results are summarized in *Tables 1* and *2*, and illustrated in *Figure 4*. The recovered amounts of PAH were expressed as $\mu\text{g}/100 \text{ m}^3$ of exhausts.

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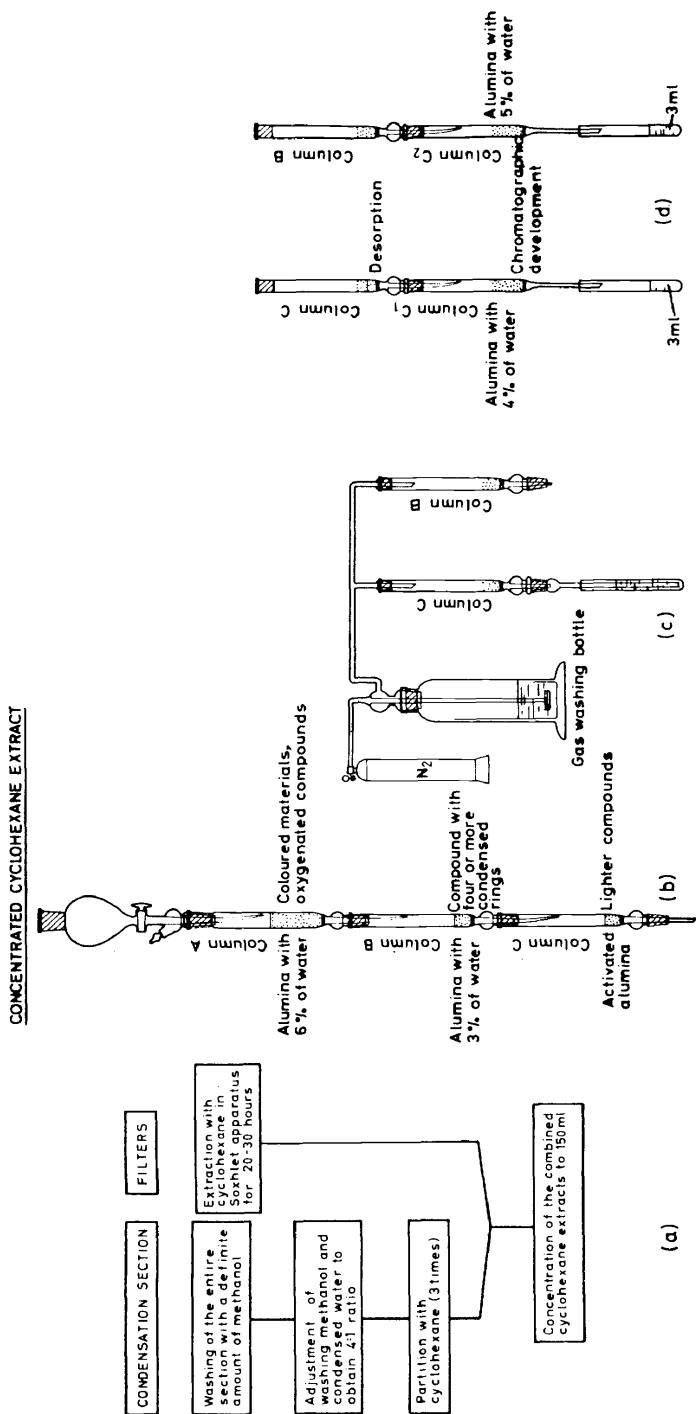


Figure 3. Schematic diagram of the analytical procedure.

Table 1. Comparison of polycyclic aromatic hydrocarbons from gasoline engine and liquefied petroleum gas engine exhausts. ($\mu\text{g}/100 \text{ mc}$ of exhausts)

Hydrocarbons	Gasoline	Liquef. gas	Variations%
naphthalene	140454.5	101449.2	- 27.7
acenaphthene	4000.0	—	—
fluorene	4090.9	3840.6	- 6.1
phenanthrene	8500.0	3571.4	- 57.9
anthracene	1454.5	1242.2	- 14.6
pyrene	9081.8	6314.6	- 30.5
4-methylpyrene	500.0	217.4	- 56.5
fluoranthene	7436.3	5072.5	- 31.8
benzo (mno) fluoranthene†	2500.0	1138.7	- 54.5
1:2-benzanthracene	1963.6	993.7	- 49.4
chrysene	1272.7	683.2	- 46.3
perylene	545.4	283.1	- 56.3
3:4-benzpyrene	2000.0	1097.3	- 45.1
1:2-benzpyrene	3363.6	1086.9	- 67.6
3:4-benzfluoranthene	772.7	393.4	- 40.1
11:12-benzfluoranthene	1354.5	569.4	- 57.9
anthanthrene	454.5	434.8	- 4.3
1:12-benzperylene	3900.0	1956.5	- 49.8
coronene	1854.5	786.7	- 57.6

† Also 2:13-benzfluoranthene

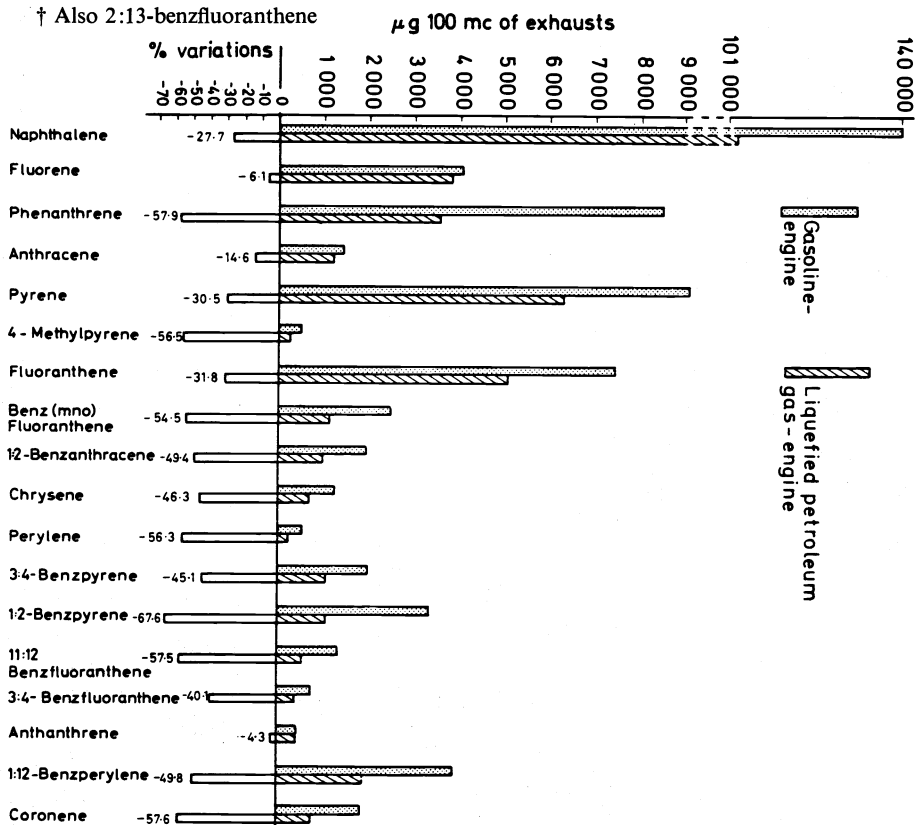


Figure 4. Comparison of aromatic polycyclic hydrocarbons from gasoline engine and liquefied petroleum gas engine exhausts

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(i) In the gasoline engine exhausts, nineteen PAH were identified and determined: naphthalene, acenaphthene, fluorene, phenanthrene, anthracene, pyrene, 4-methylpyrene, fluoranthene, benzo(mno)fluoranthene, 1:2-benzanthracene, chrysene, perylene, 3:4-benzpyrene, 1:2-benzpyrene, 11:12-benzfluoranthene, 3:4-benzfluoranthene, anthanthrene, 1:12-benzperylene and coronene (*Table 1*). Among the detected compounds, some possess strong carcinogenic activity to animals under several experimental conditions, some show smaller activity and others are considered, although not unequivocally, inactive. Several other peaks of unidentified compounds were observed in the absorption spectra of the eluates.

(ii) In the liquefied petroleum gas engine exhausts, eighteen PAH were identified and determined: naphthalene, fluorene, phenanthrene, anthracene, pyrene, 4-methylpyrene, fluoranthene, benzo (mno) fluoranthene, 1:2-benzanthracene, chrysene, perylene, 3:4-benzpyrene, 1:2-benzpyrene, 11:12-benzfluoranthene, 3:4-benzfluoranthene, anthanthrene, 1:12-benzperylene and coronene (*Table 1*). The absorption spectra of the collected fractions were almost identical with those observed for gasoline-engine exhausts. Acenaphthene seemed to be present but it could not be estimated quantitatively. In the trials in which the lift truck operated with a load on the simulated working schedule, the PAH concentrations in the exhausts proved to be notably inferior to those found in the gasoline engine operating under the same conditions. Percentage reductions (*Table 1*) varied, for individual hydrocarbons, from a minimum of 4.3 (anthanthrene) to a maximum of 67.6 (1:2-benzpyrene).

(iii) In the trials in which the engine powered by liquefied petroleum gas was idling at 500 rpm and at zero load, the concentrations of the individual compounds proved to be markedly inferior to those found for the same fuel in the trials based on the simulated working schedule. Naphthalene is an exception, whereas acenaphthene and 11:12-benzfluoranthene were not present (see *Table 2*).

Table 2. Polycyclic aromatic hydrocarbons from liquefied petroleum gas engine exhausts ($\mu\text{g}/100\text{ mc}$ of exhausts).

<i>Hydrocarbons</i>	<i>Work cycles</i>	<i>Idle</i>	<i>Variations %</i>
naphthalene	101449.2	114075.0	+ 12.4
fluorene	3840.6	934.0	- 75.7
phenanthrene	3571.4	1313.0	- 63.2
anthracene	1242.2	178.6	- 85.6
pyrene	6314.6	1029.4	- 83.7
4-methylpyrene	217.4	31.5	- 85.5
fluoranthene	5072.5	735.3	- 85.1
benzo (mno) fluoranthene	1138.7	241.6	- 78.8
1:2-benzanthracene	993.7	168.1	- 83.0
chrysene	683.2	126.0	- 81.5
perylene	238.1	63.0	- 73.5
3:4-benzpyrene	1097.3	388.6	- 64.6
1:2-benzpyrene	1086.9	231.1	- 78.7
3:4-benzfluoranthene	393.4	94.5	- 75.6
11:12-benzfluoranthene	569.4		
anthanthrene	434.8	283.6	- 34.7
1:12-benzperylene	1956.5	693.3	- 64.5
coronene	786.7	273.1	- 65.3

Naphthalene is a highly volatile compound and it is therefore difficult to ascertain losses during sampling and subsequent treatments. In addition, according to Moore and Monkman²², the presence of the parent substances is sufficient "to shift the diagnostic ultraviolet absorption peaks a few millimicrons, or enough to make positive identification doubtful". The same can be said of acenaphthene. With regard to 11:12-benzfluoranthene, however, it is possible that this hydrocarbon was present in amounts below the detection limits of the analytical method.

The marked reduction in PAH emissions found in the idling engine seems to disagree with the results of other authors who maintain that high production of all PAH occurs when the engine is idling at a lower number of revolutions per minute and decreases as the speed of the engine increases. One must remember, however, that these statements are based on trials in which the engine was running at a constant speed. In fact, evidence was presented that the production of PAH is greatly influenced by change of speed: the largest production of all PAH occurred during acceleration and deceleration. These two conditions prevail while the lift truck is running on the simulated working schedule. Thus, the high quantities of PAH emitted in the exhausts are understandable.

(iv) The results of this study show that, from a qualitative point of view, the formation of PAH is independent of the fuel used. Thus the same compounds are found in the gasoline-engine and in the liquefied petroleum gas-engine exhausts. On the basis of several studies, a free radical mechanism appears to be the most logical way of explaining the presence of PAH in combustion products from all types of fuels. Kinney and Crowley¹⁷, Egloff⁸ Tebbens and co-workers²⁸, Badger and co-workers^{1, 2} and other authors have suggested that the PAH are formed at high temperatures from aliphatic and simpler aromatic hydrocarbons by free radical reactions. These radicals recombine in various ways to give less hydrogenated and more condensed products.

An attempt by Tebbens and his co-workers²⁸ to determine the relationship of combustion to the formation of condensed-nuclei aromatic compounds has demonstrated the presence of multinuclear aromatics among combustion products. It has also been suggested that PAH in the exhaust products of internal combustion engines are produced by a mechanism involving acetylene as the starting material, this hydrocarbon resulting from pyrolytic breakdown of the aliphatic hydrocarbon fuels. At high temperatures, acetylene condenses through a free radical mechanism to form higher molecular weight aliphatic and aromatic hydrocarbons.

CONCLUSIONS

An engine exhaust sampling apparatus for PAH determination was constructed. The apparatus guarantees the quantitative recovery of organic materials of high molecular weight and the accurate measurement of the actual gas volume sampled. Exhaust gases were analyzed for PAH by an analytical procedure, previously described, which is a combination of chromatography (on alumina) and absorption spectrophotometry. A preliminary adsorption of PAH onto a series of superimposed alumina columns makes possible:

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- (a) the avoidance of evaporation to dryness or small volume and of the resulting losses due to the volatility of polynuclear compounds;
- (b) the purification of the extracts from many extraneous materials which give rise to intense background in the ultraviolet absorption spectra;
- (c) a first separation of PAH into two large fractions.

In the gasoline engine exhausts, nineteen PAH were identified and determined. Several other peaks for unidentified compounds were observed. In the liquefied petroleum gas engine exhausts, eighteen PAH were identified and determined. The absorption spectra of the collected fractions were almost identical with those observed for gasoline engine exhausts. The PAH concentrations all proved to be notably inferior. The results support the evidence that the formation of PAH, from a qualitative point of view, is independent of the fuel used. A free radical mechanism appears to be the most logical way of explaining the presence of PAH in combustion products from all types of fuels.

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