

PAH and other emissions from burning of JP-8 and diesel fuels in diffusion flames

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Abstract

Jet fuel JP-8 is of technical interest to the military aviation industry. JP-8 is now the single battlefield fuel for all US Army and Air Force equipment, replacing gasoline altogether and gradually replacing diesel fuel. Hence, emissions from the combustion of this fuel are the subject for this investigation. The emissions from the combustion of JP-8 fuel are examined and are compared to those from diesel fuel No. 2, burned under identical conditions. Combustion occurred inside a laboratory furnace in sooty diffusion flames, under adverse conditions that typically emit large amounts of products of incomplete combustion (PIC). Under such conditions, even compounds that otherwise might appear only in trace amounts were present in sufficient quantities for detection. The study reports on emissions of CO, light volatile organic compounds, semi-volatile organic compounds with an emphasis on polycyclic aromatic hydrocarbons (PAH), particulate emissions, oxides of nitrogen (NO_x) and oxides of sulfur (SO₂). Some PAH compounds are suspected of posing a threat to human health, benzo[a]pyrene being listed as a bio-accumulative toxin by the EPA. An afterburner was also used to examine the effects of longer furnace residence time. Results have demonstrated that PAH emissions from the combustion of diesel fuel were higher than those of JP-8, under most conditions examined. Moreover, as the temperature of the primary furnace was increased, in the range of 600–1000 °C, most of the emissions from both fuels increased. Particulate emissions were reduced by the afterburner, which was operated at 1000 °C, only when the primary furnace was operated at the lowest temperature (600 °C), but that condition increased the CO emissions. Overall, transient combustion of these two fuels, burning in laminar and sooty diffusion flames, did not reveal major differences in the emissions of the following PIC: C1–C4 light aliphatic hydrocarbons, PAH, CO and particulate matter.

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1. Introduction

JP-8, a kerosene-based fuel consisting of aliphatic and aromatic hydrocarbons, is currently used by the US military in aircraft engines, ground vehicles as well as all kinds of diesel engine powered systems and furnaces.

Over the past half-century, several types of aviation fuels have been developed for military use. After World War II, the US Air Force used 'wide-cut' fuel (JP-4), which was

a mixture of hydrocarbons. Due to JP-4's considerably large evaporative losses at high altitudes, the Air Force converted from 'wide-cut' to kerosene-based fuels, JP-5 and JP-6 in the 1950s, and JP-7 in the 1960s. Currently, there are two main types of fuels that the military uses: JP-8 and JP-8+100. JP-8 is approximately 99.8% kerosene by weight [1–3] and additives. JP-8+100 is a version of JP-8 that includes supplementary additives to enhance its thermal stability.

According to the Department of Energy (DOE) the US military's consumption of jet fuel has more than doubled over the last 25 years. The US is the largest worldwide consumer of jet fuel. The annual worldwide use of JP-8 is more than 60 billion gallons per year, almost 5% of which

(2.5 billion gallons per year) is used by the US Air Force. This fuel also powers aircraft in use by the US Navy; the ships are powered by lower grade fuel. Finally, following the 'one fuel forward' concept, the US Army has adopted JP-8 for all ground and aircraft systems, thus simplifying fuel transport and distribution operations [3–5].

1.1. Health concerns

Initially, JP-8 was adopted with few environmental or health studies having been conducted, apparently because as a kerosene-based fuel it was not considered significantly different from kerosene. JP-8 is indeed based on JET A-1 fuel, which is currently the industry standard fuel for all commercial airline carriers worldwide. However, JP-8 contains three mandatory additives: (i) fuel systems icing inhibitor, (ii) corrosion inhibitor and (iii) static dissipator [2,3]. This is an important distinction. From the very beginning there were concerns with personnel that came in contact with the fuel about possible health effects. Fuel handlers have reportedly complained that fuel adhered to their skin, that they could taste it, and that they would sweat it out. Studies showed that fuel tank workers would have 100 times the amount of JP-8 detectable in their bodies as that found in the general civilian population [5]. Exposure to the raw fuel as well as to its combustion emissions may result in a number of potential short-term and long-term health effects [6]. Therefore, investigations on the constituents of JP-8 as well as on its combustion byproducts are of scientific and regulatory interest.

To aggravate the above concerns there has been considerable negative publicity surrounding JP-8, mainly associated with the naval air station at Fallon, Nevada. There were 15 documented cases of childhood leukemia in the town of Fallon, adjacent to the base [7]. This is an alarming statistic in a town so small that even one case every 5 years would be considered unusual. The base began using this fuel in 1993 for the needs of its 'Top Gun' flight school located at that facility. Four years later the first case of childhood leukemia was diagnosed. The International Agency for Research on Cancer has stated that there is not enough information to determine whether JP-8 promotes cancer. This case has been under investigation. Currently 34 million gallons of JP-8 a year are used at that location. Little has been concluded about human health effects caused by JP-8, and researchers are still studying its effects in terms of environmental pollution, fire technology, toxicology [6], etc. Because the formulation of JP-8 is relatively new, the hazards of the fuel are not fully known. The Operational Safety and Health Administration (OSHA) and the American Conference of Governmental and Industrial Hygienists (ACGIH) have not yet set promulgated exposure standards for this fuel. The Navy has a permissible exposure limit (PEL) of 350 mg/m³ for 8 h, and a short-term exposure limit (STEL) of 1800 mg/m³ for 15 min [8]. The high flash point of JP-8, see Table 1, along with its low volatility cause

Table 1
Chemical and physical properties of the two fuels

Chemical and physical properties	USAF JP-8	Diesel No. 2
Aromatics (vol%)	25	35
Average molecular formula	C ₁₁ H ₂₁	C ₁₂ H ₂₆
Average molecular weight	153	170
Higher heating value (kJ/kg)	46,500	44,500
Equilibrium adiabatic flame temperature (K), as calculated by the STANJAN code ^a	2300	2200
Stoichiometric fuel/air ratio ^b	12	14.7
Flash point (°C) min	38	52
Density range (kg/l, 15 °C)	0.75–0.84	0.82–0.86

For extensive information on the fuel's composition and properties see http://www.chevron.com/prodserv/fuels/bulletin/aviationfuel/4_at_fuel_comp.shtm.

^a W.C. Reynolds, STANJAN Multicomponent Equilibrium Program v. 3.60, 1986.

^b The chemically correct air to fuel ratio to achieve complete combustion.

difficult cold starts and engine coking. Cold starts result in human exposure to unburned aerosolized fuel, and the low volatility makes it easier for fuel to remain on surfaces such as skin and clothes.

1.2. Exposure studies

Laboratory animal studies showed that even a single, hour-long exposure to an aerosol containing 50 mg/m³ of JP-8 resulted in increased lung permeability in mice and caused loss of cilia, the hair-like projections that waft dirt out of bronchial tubes. This allows dust, pollen and irritants to collect in the lungs, causing a chronic inflammatory state [9]. Exposure of mice to air containing 1000–2500 mg/m³ of JP-8 disrupted vision and proprioception, the sense of where one's body is in space [10]. Rats exposed to kerosene, a substantial component of JP-8 and known to cause hepatic, hematological, and immune toxicity, showed increases in liver weights, decreases in the relative weights of the spleen and thymus (a small organ located in the upper/front portion of the chest), and decreased activity of enzymes involved in the metabolism of environmental chemicals, including polycyclic aromatic hydrocarbons (PAHs). Thus it is evident that kerosene may be an important contributor to JP-8's induced immuno-toxicity potential [11]. From animal studies, it is concluded that brief exposure to JP-8, in an aerosol form or a raw phase, can cause severe immuno-suppression. It can also result in modulation of dermal, ocular, and renal systems involved in the metabolism, detoxification, and/or elimination of constituent chemicals of JP-8, as well as other xenobiotics [12]. Excessive inhalation may result in irritation to the nose, throat, lungs and respiratory tract. Acute effects may include headache, dizziness, loss of balance and coordination, unconsciousness, coma and even death [13].

1.3. Fuel fumes and combustion byproducts

Contact with JP-8 liquid, aerosols or vapors may occur during fuel transport, fueling of engines, cold starts, spills, operation of vehicles, operation of stoves, heaters, etc. Alternatively, bystanders may also come in contact with the products of combustion of this fuel. The exhaust effluents of devices burning this fuel contain a variety of species, including unburned fuel components, pyrolyzed fuel, and products of incomplete combustion (PIC). A great number of species are pyro-synthesized in combustion systems, and are eventually emitted to the atmosphere as volatile organic compounds (VOC) and semi-volatile organic compounds (SVOC). Some of these compounds are not only known carcinogens, but are known persistent bio-accumulative toxins (BIT). Benzene is an important example of toxic VOCs, whereas a large number of PAHs, such as benzo[a]pyrene, are examples of toxic SVOCs. Table 2 lists PAH targeted in this study and indicates their toxicity.

1.4. Combustion studies

A limited number of studies can be found in the literature on the emissions from the combustion of JP-8. This fuel is composed of hundreds of compounds (often given as 228 [1]), mainly naphthenes, paraffins, aromatics (mostly toluene, but also some benzene), additives, and solvents. The components of JP-8 may change from purchase-to-purchase even from the same supplier, hence there is no single chemical specification [8,12]. Therefore, researchers have focused on combustion of either JP-8 surrogates or its main components in a variety of combustors, in order to predict its combustion behavior and emission characteristics, see Refs. [14–31]. Notably, Kouremenos et al. [32] conducted a comprehensive experimental investigation on the performance and exhaust emissions of a swirl chamber diesel engine burning JP-8 aviation fuel. They contrasted these emissions against baseline engine operation using diesel fuel. Nitrogen oxides, unburned light hydrocarbons and carbon monoxide emissions were monitored under a variety of engine operating conditions. That study showed that the exhaust emission levels were not much different for operation with the two fuels. Kobayashi and Kikukawa [33] found higher concentrations of formaldehyde, a severe eye and respiratory irritant, in the exhaust of jet engines after the fuel was changed from JP-4 to JP-8. Zhu and Cheng [27] investigated human exposure to aerosols from un-vented heaters in tents, so that the contribution of this exposure to the 'Gulf War Syndrome' could be estimated. Three types of portable kerosene heaters and three fuels (JP-8, JA-1 and 1-K Kerosene) were examined. Particulate emissions were sampled, characterized for particle size distributions and chemically analyzed. Elemental and organic carbons were detected, as well as large amounts of sulfur. Amounts of fine particles that can be deposited in the lungs were calculated. Treynor et al. [28] assessed semi-volatile and non-volatile

Table 2
List of targeted PAH and their toxicity in combustion effluents

SVOC compound name		SVOC compound name	
Naphthalene	T, M, R	Benzo[a]fluorine	T, M
Benzothiophene	U	11H-Benzo[b]fluorine	T, M
2-Methylnaphthalene	T, M, E	1-Methylpyrene	T, M, N
1-Methylnaphthalene	M	Benzo[ghi]fluoranthene	U
Biphenylene	U	Benzo[c]phenanthrene	T, M, C
Biphenyl	T, M, E	Cyclopenta[cd]pyrene	T, M, E
Acenaphthene	M	Benz[a]anthracene	T, M, C
Acenaphthylene	M	Triphenylene	T, M
Dibenzofuran	M	Chrysene	T, M, E
Fluorene	T, M	Benzo[b]fluoranthene	T, M, C
2-Methylfluorene	M	Benzo[k]fluoranthene	T, M, E
1-Methylfluorene	M	Benzo[a]fluoranthene	T, M, N
Dibenzothiophene	U	Benzo[e]pyrene	T, M, R, E
Phenanthrene	T, M, E	Benzo[a]pyrene	T, M, R, C
Anthracene	T, M, E	Perylene	T, M
3-Methylphenanthrene	M	Dibenz[a,j]anthracene	T, M, E
2-Methylphenanthrene	T, M	Indeno[7,1,2,3-cdef]chrysene	U
2-Methylanthracene	M	Indeno[1,2,3-cd]pyrene	T, M, C
4H-Cyclopenta[def]phenanthrene	U	Benzo[ghi]perylene	T, M
4-Methylphenanthrene	M	Anthanthrene	T, M, C
1-Methylphenanthrene	T, M	Dibenz[a,h]anthracene	T, M, C
Fluoranthene	T, M, E, U	Benzo[b]chrysene	T, M, N
Acephenanthrylene	U	Picene	U
Pyrene	T, M, E		

T, tumorigen; M, mutagen; R, reproductive effector; E, equivocal tumorigenic; N, neoplastic; C, carcinogenic; U, unknown; as defined by RTECS criteria. RTECS stands for Registry of Toxic Effects of Chemical Substances, see <http://www.cdc.gov/niosh/rtecs.html>. Benzo[a]pyrene is identified as a persistent bio-accumulative toxic (BIT) compound.

organic pollutant emission rates from un-vented kerosene space heaters. They reported that kerosene heaters emit PAHs, nitrated PAHs, alkylbenzenes, phthalates, hydro-naphthalenes, aliphatic hydrocarbons, alcohols and ketones. Six PAH species were reported, including naphthalene, phenanthrene, fluoranthene, anthracene, chrysene and indeno[cd]pyrene. Four nitrated PAHs were detected, 1-nitronaphthalene, 9-nitroanthracene, 3-nitrofluoranthene, 1-nitropyrene. Skopek et al. [34] have showed that kerosene soot is indirectly mutagenic; Kaden et al. [35] have reported that the mutagenic activity of kerosene soot was due to un-nitrated PAH compounds. Tokiwa et al. [36] showed kerosene soot to be directly mutagenic and attributed most of the direct mutagenic activity to di-nitropyrenes.

Rosenkranz and Mermelstein [37] observed that 3-nitrofluoranthene and 1-nitropyrene are mutagenic, but 1-nitronaphthalene and 9-nitroanthracene show low mutagenicity.

The above studies on JP-8 fuel and its constituents indicate that there are concerns with environmental and health issues regarding the handling of such fuel and the exposure to its fumes as well as its combustion byproducts. Of course, these concerns also apply to other fuels, however, the unique military application of JP-8 may have precluded the rigorous overall testing applied to most commercially fired fuels. Thus, a comparative study of the emissions of JP-8 with the rather conventional fuel diesel oil No. 2 was performed in this work. After all, the former has replaced the latter fuel in many military applications, thus a comparison was warranted. Both fuels were supplied by the US Army and were burned in the laboratory in batches, as fixed pools of liquid. Combustion occurred in sooty diffusion flames, under adverse locally fuel-rich conditions sometimes encountered in practical applications. The combustion emissions of both fuels were characterized comprehensively for volatile C1–C4 aliphatic and volatile aromatic hydrocarbons, semi-volatile PAH compounds, CO, CO₂, SO₂, NO_x and particulate emissions.

2. Experimental techniques and procedure

2.1. Fuel specifications

The fuels used in this study were JP-8 jet fuel and diesel fuel No. 2. A partial list of properties is shown in Table 1.

2.2. Experimental apparatus

A two-stage setup was used to investigate combustion characteristics of the two liquid fuels (Fig. 1). A pool of the liquid fuel (0.5 g), contained in a porcelain boat, was inserted at mid-length of a 1-kW horizontal, split-cell

electrically heated muffle furnace, 4 cm i.d. and 87 cm long, fitted with a quartz tube. Upon ignition, batch combustion of the fuel took place in this primary furnace in a transient diffusion flame. Combustion continued in a second muffle furnace (afterburner), 2 cm i.d. 38 cm long, connected in series with the primary furnace. Additional preheated air was added to the effluent while it traveled through a mixing venturi, with 8 mm i.d. After it passed the venturi, the effluent/air mixture was divided into two equal parts. One half was sampled at the exit of primary furnace while the second half was passed to the secondary furnace to enable further reactions take place therein. Therefrom, the second half was sampled at the exit of secondary furnace. Prior to each sampling stage, the effluent was quenched with dilution nitrogen. The flow rate of air, additional air at the venturi, and dilution nitrogen at the furnace exits were 4, 2, and 2 l/min, respectively. Therefore, the flow rate of mixture at each furnace exit was 4 l/min. The temperature of the primary furnace was set at 600, 700, 800, 900 and 1000 °C, whereas the temperature of the secondary furnace was kept constant at 1000 °C. The gas temperature, as measured by a suction pyrometer, was roughly 25 °C lower than the temperature of furnace walls through the furnaces. The temperature between the furnaces ranged between 250 and 300 °C, depending on the temperature of the primary furnace. The gas residence time between the sample and the venturi in the primary furnace was in the range of 80–130 ms, depending on the furnace temperature, whereas the gas residence time in the secondary furnace was 0.7 s. According to calculations done by Wang et al. [38–40], four additional air jets, radially placed at the venturi, penetrate the effluent to its centerline, hence good mixing of streams is expected.

2.3. Combustion emissions monitoring

PAH emissions as well as NO_x, CO, CO₂, and particulates from the combustion of JP-8 and diesel oil No. 2 were

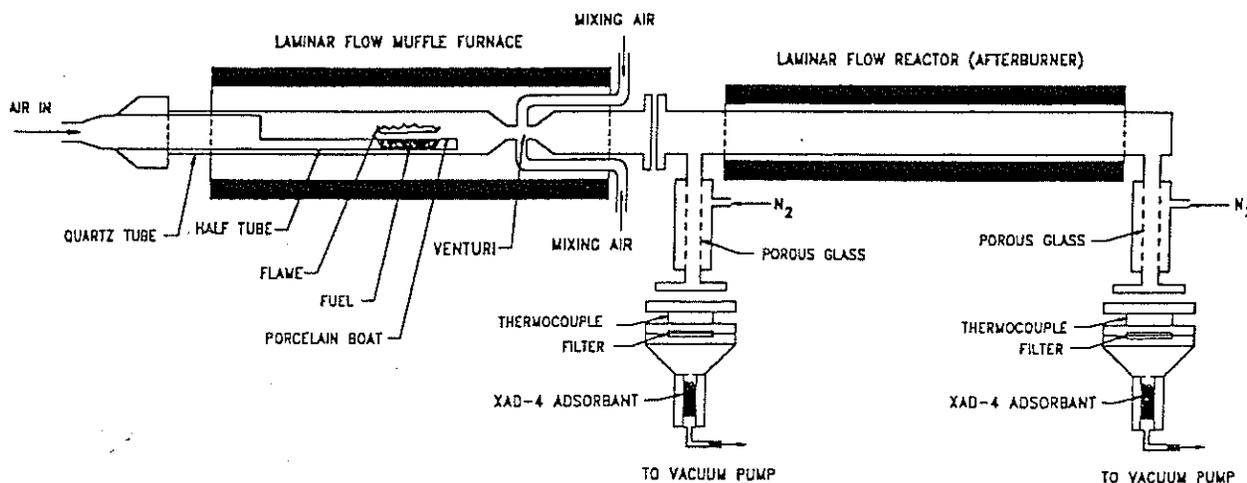


Fig. 1. Schematic of the experimental two-stage laminar-flow reactor, where pools of fuel were inserted and burned in diffusion flames.

simultaneously monitored at the exits of the two furnaces (Fig. 1). PAH and particulates were collected using Graseby sampling heads with a filter stage and a glass cartridge containing Supelco XAD-4 adsorbent as the effluent passed through. Nitrogen dilution took place in the annulus of two concentric tubes. After that, the particulate emissions were trapped on a 90 mm diameter, 1 mm thick Fisherbrand glass fiber filter with a nominal pore size of 0.45 μm . Subsequently, gas-phase PAHs were adsorbed on the bed of XAD-4 resin. Upon removing moisture with a mildly heated Permapure dryer, a Beckman 951A chemiluminescent NO/NO_x analyzer was used to monitor NO_x; a Rosemount Analytical 590 UV was used to monitor SO₂; Horiba infrared analyzers were used to monitor CO/CO₂; and a Beckman 350 paramagnetic analyzer was used to monitor O₂. Finally, a Data Translation DT-322 board in a microcomputer was used to record the obtained data. The integrated acquisition system used DT-VPI within an HP-VEE visual programming environment. The signals from the gas analyzers were recorded for the duration of the experiment and subsequently they were converted to partial pressures and, upon numerical integration, to mass yields.

2.4. Extraction and concentration of PAH emissions

Following the combustion experiments, the filters and resins were removed and placed in separate glass bottles with Teflon-lined caps, and stored at 4 °C. Prior to extraction with methylene chloride, a 50 μl internal standard containing 100 μg each of naphthalene-d₈, acenaphthene-d₁₀, anthracene-d₁₀, chrysene-d₁₂, and perylene-d₁₂ was directly applied to the filters and resins in each bottle. To ensure the purity of the XAD-4 resin and cellulose filters, blanks of XAD-4 resin and filter were also extracted and analyzed. In addition, combustion blanks were analyzed during which the furnace was operated in the presence of the XAD-4 and filter but in the absence of fuel. Target compounds that appeared in any of the blanks were appropriately qualified.

A Dionex ASE 200 accelerated solvent extractor was used to extract the SVOCs from the XAD-4 resins and cellulose filter papers. The XAD-4 resins and the filter papers were transferred to extraction cells, 33 and 11 ml, respectively. The extraction cells were allowed to initially equilibrate at 40 °C in the ASE 200 system for 1 min. Then, they were filled with methylene chloride and allowed to thermally equilibrate at 40 °C and 34 bar for 15 min. Following the 15 min. soak time, the cells were each flushed with 80% of the cell volume with fresh methylene chloride and finally purged for 90 s with nitrogen. The methylene chloride extracts were collected in separate bottles for concentration. Two extraction cycles were used per cell, which lasted around 25 min. About 45 ml of methylene chloride was used for the XAD-4 resins while 20 ml for the filter papers. No more than 30 ml of XAD-4 resin could be placed within a 33-ml extraction cell due to

the expansion of this resin in methylene chloride. The samples were then analyzed by using gas chromatography-mass spectrometry (GC-MS).

The GC-MS system consisted of a Hewlett-Packard (HP) Model 6890 GC equipped with a HP Model 5973 mass selective detector. The GC-MS conditions and data reduction were described previously [38]. The instrument was tuned in accordance with EPA semi-volatile criteria prior to the GC-MS analysis of each set of samples. The instrument passed initial and continuing calibration criteria. Each of the target compounds as well as the tentatively identified compounds were quantified using appropriate deuterated internal standards.

2.5. Measurement of light hydrocarbons

The gaseous effluent samples were extracted with syringes and analyzed with gas chromatography using a Hewlett Packard instrument (HP6890), equipped with a flame ionization detector (FID). The capillary column was a HP-5 type, crosslinked 5% phenyl methylpolysiloxane, with a length of 30 m, an inside diameter of 0.32 mm and a film thickness of 0.25 μm . By matching the retention times of samples with the retention times of known compounds several aliphatic and light aromatic compounds could be identified. Gas chromatographic conditions were as follows, initial oven temperature was held at 28 °C for 3 min; followed by a temperature programming at a rate of 25 °C/min to 120 °C, held for 7 min; followed by an additional heat up at a rate of 50 °C/min to 225 °C, held again for 13 min. The back inlet temperature was 280 °C and the detector temperature was 300 °C. The instrument was calibrated once a week for the identification of retention times; three Scotty IV analyzed gas mixtures were used, containing known amounts of C1–C4 aliphatic hydrocarbons and light aromatic compounds.

3. Results and discussion

Low primary furnace temperature (500 °C) oxidative pyrolysis of the two fuels in air produced the profiles shown in Fig. 3, as obtained by GC-MS analysis of XAD resin and filter extracts at the exit of the primary furnace. The fuel did not ignite under these conditions. The diesel fuel is a basic hydrocarbon fraction ranging from C9 to C24 of primarily straight chain aliphatics. For the diesel fuel the maximum in the hydrocarbon fraction is observed at C16, see Fig. 3a. This distribution may be slightly skewed from the original sample as lower molecular weight hydrocarbons are more easily vaporized and oxidized. Small amounts of methyl substituted aliphatic hydrocarbons are observed in between the primary straight chain aliphatics. The JP-8 appears to be much more complex, see Fig. 3b. Whereas the straight chain aliphatics are easily observed, there are a greater number of substituted aliphatics present plus a large

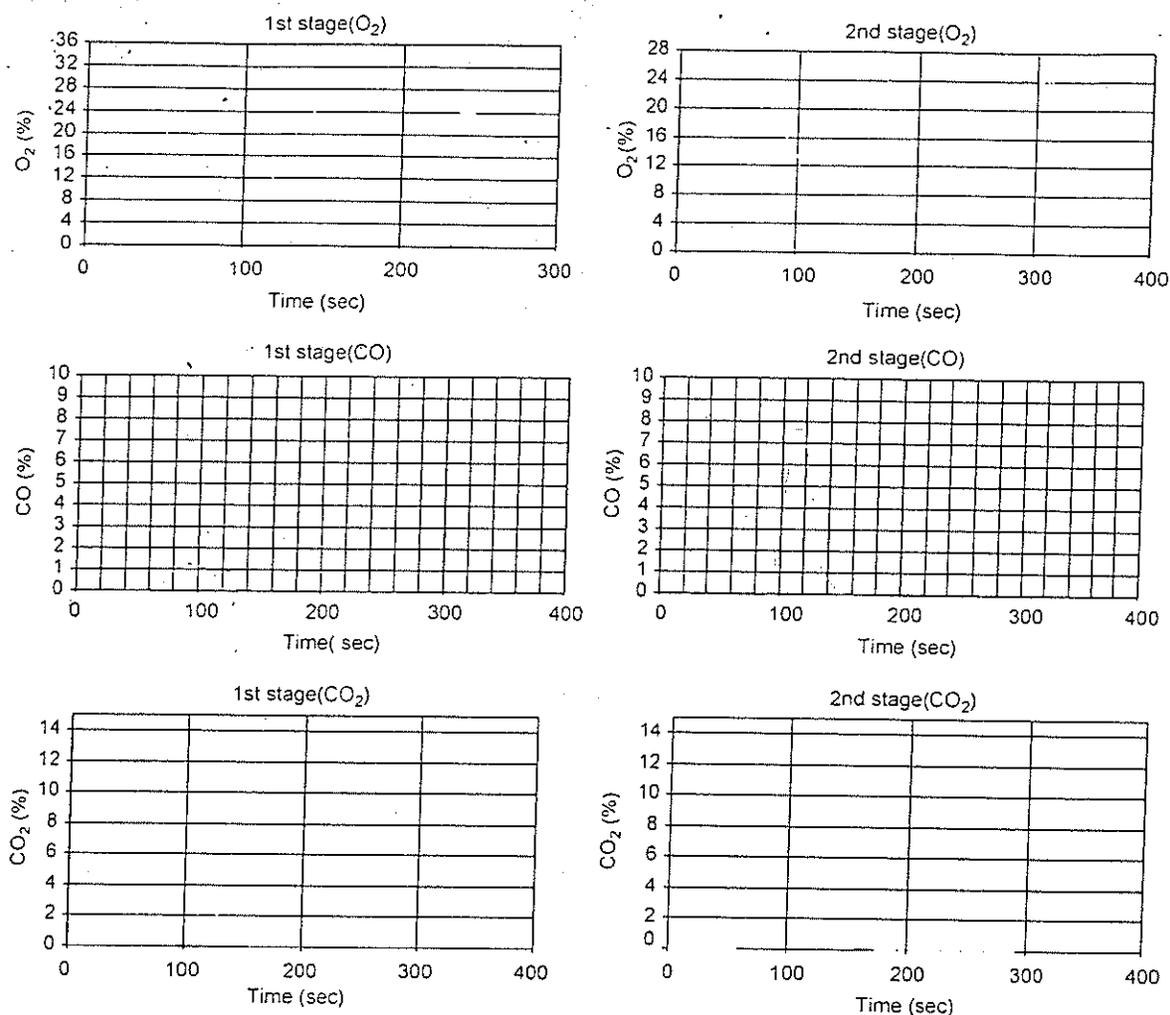


Fig. 2. Sample profiles of CO, O₂, and CO₂ from the combustion of diesel fuel No. 2. Sampling was performed at the exits of the primary furnace (first stage, left column) and of the secondary furnace or afterburner (second stage, right column). The primary furnace temperature was 600 °C, whereas that of the afterburner was 1000 °C.

number of aromatics, which are not shown in these spectra. The aliphatic range observed was C10 through C18 with a maximum in the distribution of about C13 (tridecane). As with the diesel fuel, the lower molecular weight fractions are more easily vaporized and may not be observed in the spectra displayed in Fig. 3b.

3.1. Oxygen profiles and evolution of CO and CO₂ during combustion

The primary furnace temperature was varied between 600 and 1000 °C, whereas the secondary furnace temperature was kept at 1000 °C at all times. In all experiments, 0.5 g of liquid fuel were poured in a porcelain boat. Upon placing the boat in the primary furnace, the fuel heated up and devolatilized. After ignition, a gaseous diffusion flame formed and remained anchored over the sample. In principle there was enough oxygen in both furnaces to allow the fuel to burn completely as the observed minimum

global oxygen level never fell below 3%, see Figs. 2 and 4. For both fuels, minimum oxygen concentrations were much lower at the exit of the second furnace than at the exit of the first furnace, see Fig. 4. This is simply because further combustion reactions took place in the afterburner and, thus, additional oxygen was consumed. As the primary furnace temperature was increased the minimum oxygen concentration increased. This suggests that better combustion occurred in the system at low primary furnace temperatures, when the fuel devolatilization fluxes were low and the furnace was not overwhelmed by high concentration of pyrolyzates.

These trends are supported by those observed in the CO₂ profiles, shown in Fig. 4. CO₂ yields were higher at low primary furnace temperatures, in the vicinity of 500 µg/g, whereas at high temperatures they were in the vicinity of 150 µg/g. Moreover, CO₂ yields were higher at the exit of the afterburner, which is indicative of supplemental combustion therein, aided by the additional

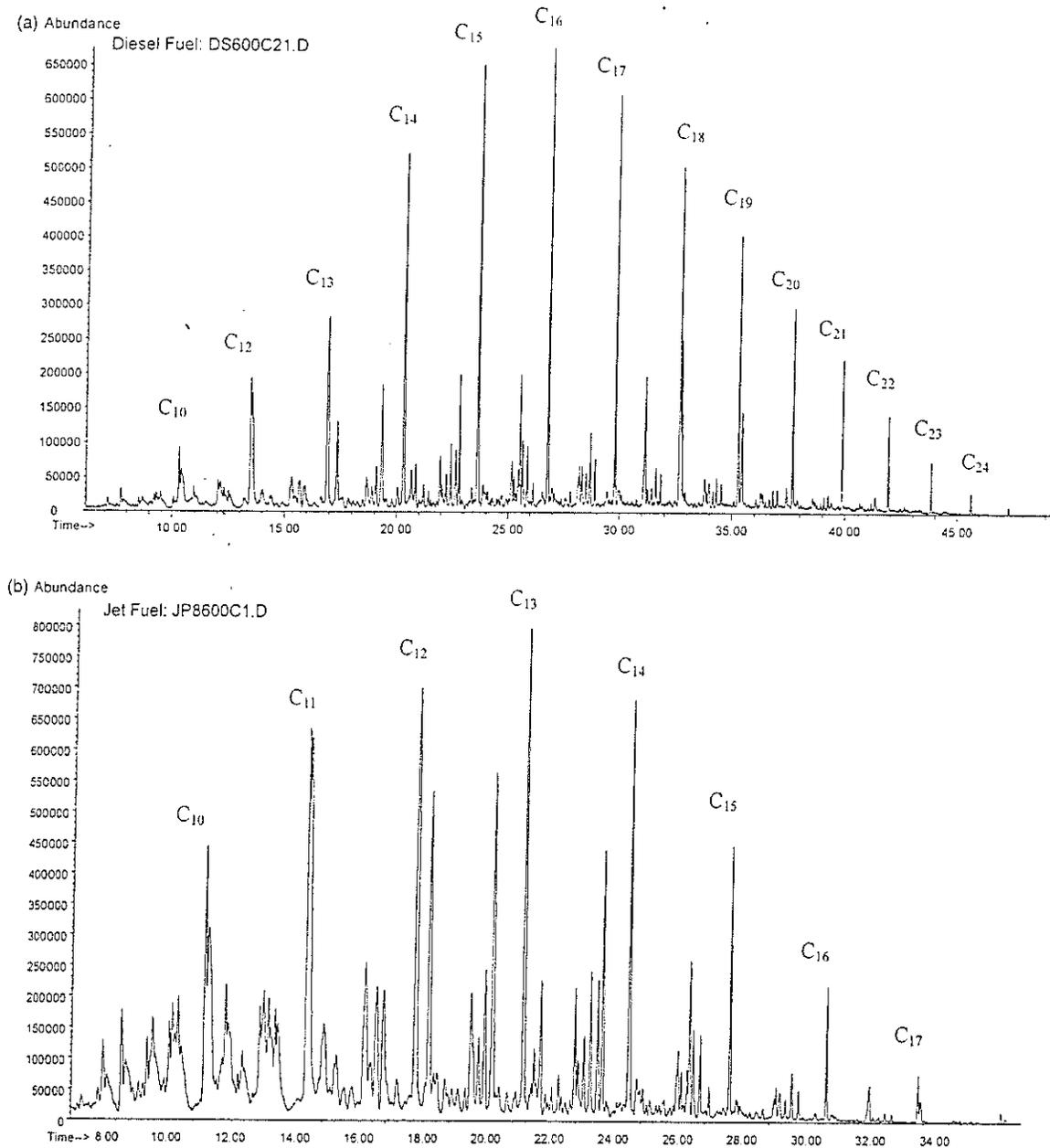


Fig. 3. Oxidative pyrolysis (no flame) GC spectra of diesel fuel No. 2 and JP-8, reflecting the fuel composition. Sampling was performed at the exit of the primary furnace, operated at 500 °C.

air introduced to the venturi. The CO₂ yields from JP-8 were lower than those from diesel oil No. 2, and the associated oxygen consumption was also lower. The reason may be attributed to the difference in chemical composition, molecular weight and volatility of the two fuels, see Table 1. The calculated average global equivalence ratios (ϕ) were between 1 and 1.5 in the experiments, hence, overall fuel-rich conditions prevailed. The calculation of global ϕ was based on the mass flow-rate of air and on the mass of fuel, in conjunction to the observed combustion duration period inferred from the CO/CO₂ profiles, such as those shown in Fig. 2. Although the same

amount of either fuel (0.5 g) was used in each experiment, the calculated global ϕ for diesel No. 2 was lower than that of JP-8 at all times; it was rather closer to 1. This indicated that the JP-8 fuel-air mixtures were somewhat richer in fuel vapors than those of diesel No. 2.

The CO yields from the combustion of the two fuels were rather comparable, at corresponding experimental conditions, see Fig. 4. The operating temperature of the primary furnace had little influence on the CO yields at its exit; measured values were in the vicinity of 50 $\mu\text{g/g}$. Additional CO was generated in the afterburner, as evidenced from the higher yields recorded at its exit,

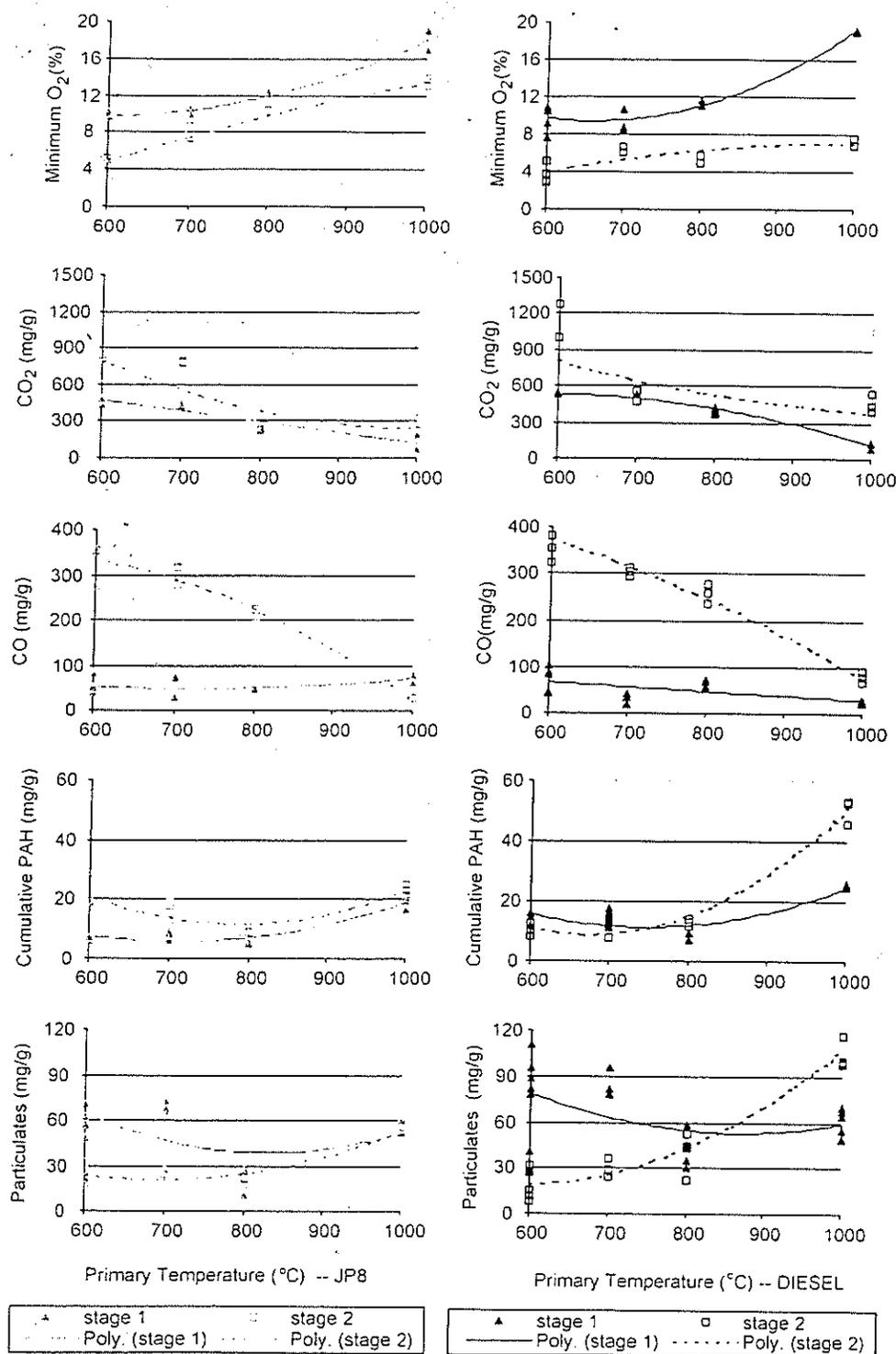


Fig. 4. Minimum O₂ mole fractions (%), and yields of CO₂, CO, cumulative PAH and particulate matter emissions, (all in mg/g fuel), at the exits of the primary furnace (stage 1) and of the secondary furnace (stage 2), as a function of the primary furnace temperature. Left column: JP8; right column: diesel oil No. 2.

which decreased rather monotonically with increasing operating temperature of the primary furnace. CO yields from the afterburner ranged from 350 $\mu\text{g/g}$ to under 100 $\mu\text{g/g}$, as the temperature of the primary furnace increased from 600 to 1000 °C.

3.2. Yields of PAHs from combustion of JP-8 and diesel No. 2

More than 120 semi-volatile PAH compounds were detected by GC-MS. XAD-4 resins and filters were used to

collect gas- and condensed-phase PAH, respectively. In this work combined quantities are presented. Whereas cumulative PAH yields are shown in Fig. 4, the 40 most prominent of the detected species are shown in Fig. 5. In general, 2

and 3-ring PAH were found in the gas-phase and heavier ones in the condensed-phase, as their boiling/sublimation points differ. Cumulative PAH emissions from combustion of JP-8 remained nearly steady at low primary furnace

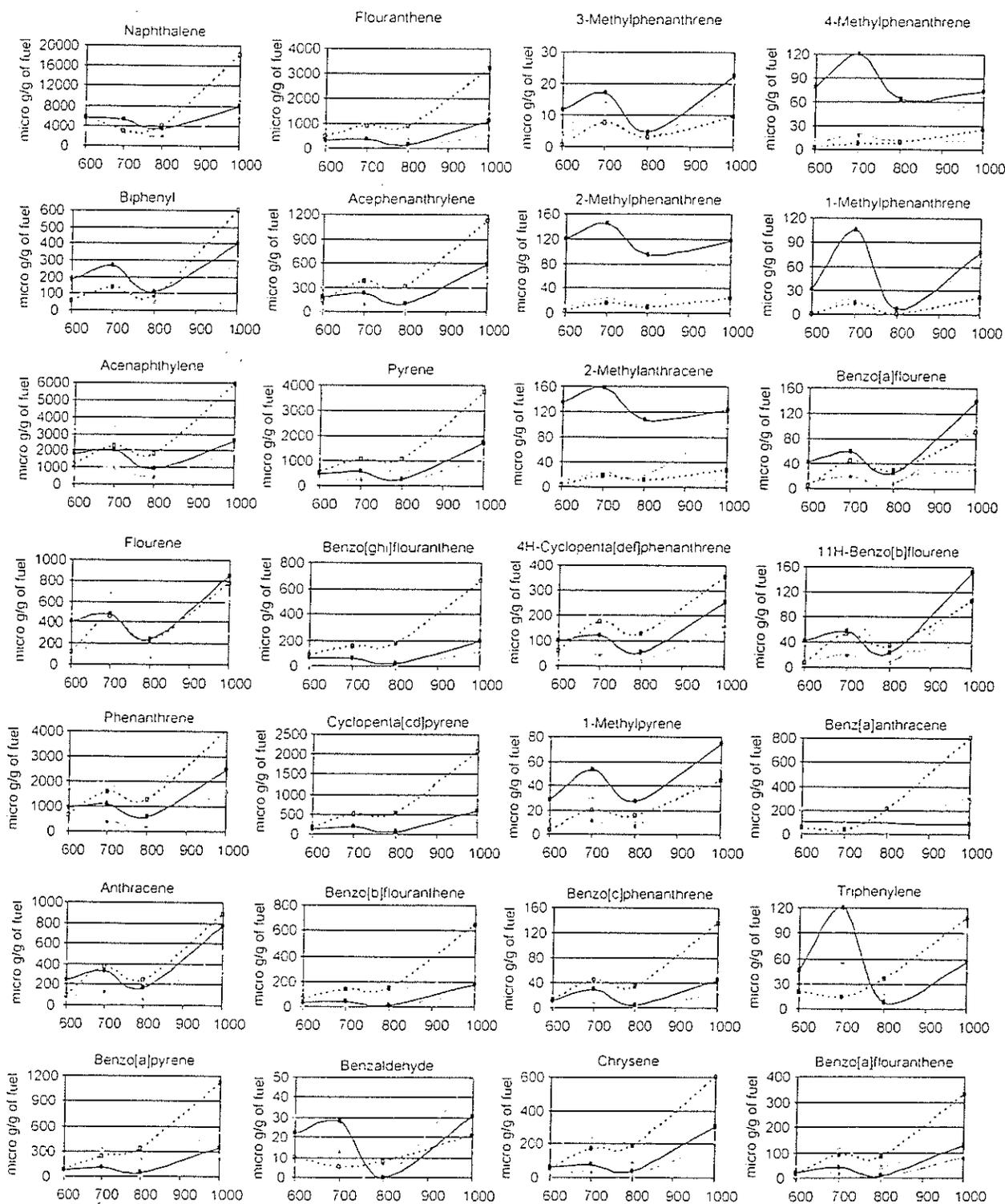


Fig. 5. Individual PAH species ($\mu\text{g/g}$ fuel) at the exits of the primary furnace (stage 1) and of the secondary furnace (stage 2), as a function of the primary furnace temperature ($^{\circ}\text{C}$).

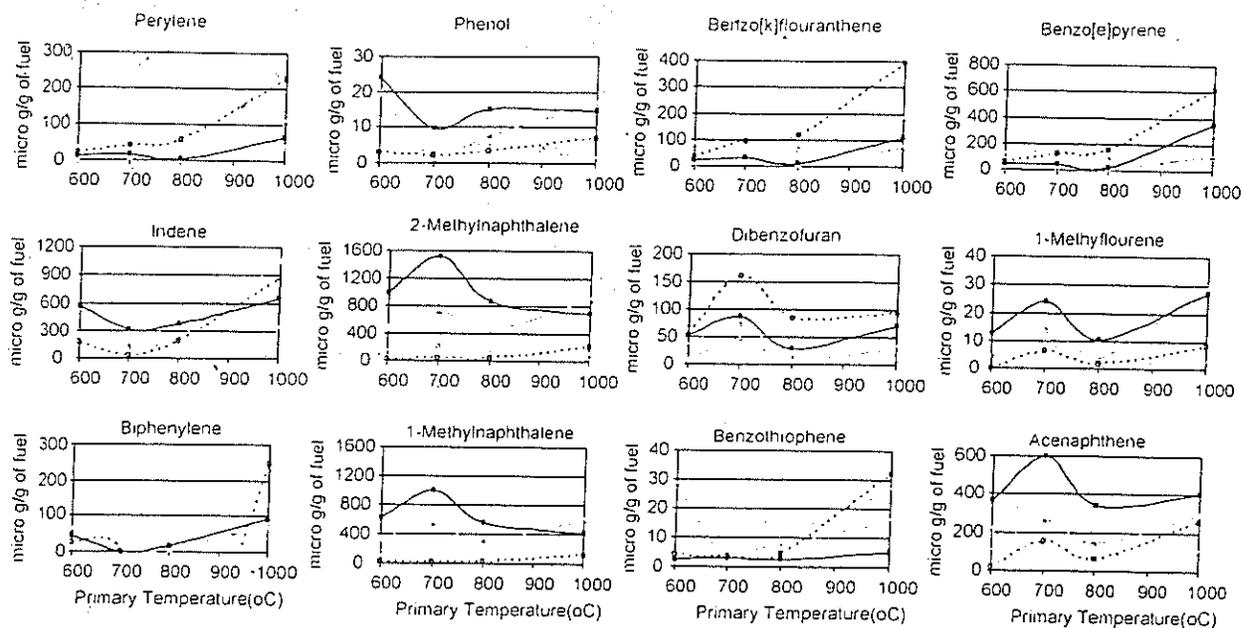


Fig. 5. (continued).

temperatures. Beyond 800 °C, they increased by factors of 2–3, see Fig. 4. The afterburner treatment increased the cumulative PAH emissions at all primary furnace temperatures by factors of 1.2–3. The biggest increase was noticed in conjunction with the low primary furnace operating temperatures. The cumulative PAH emissions from diesel oil No.2 were higher than those from JP-8, under most conditions. Trends were overall similar, except that in the case of this fuel the afterburner treatment did not have a significant effect at low primary furnace temperatures. However, it had a marked effect at 1000 °C, where it increased cumulative PAH emissions by a factor of 2 over those from the primary furnace.

Regarding the individual PAH species depicted in Fig. 5, trends are not universally consistent. Nevertheless, the following observations hold for most species: (a) individual PAH yields were higher from the combustion of diesel fuel No. 2 than from JP-8. Particularly, yields of substituted hydrocarbons containing methyl radicals appeared to be much higher in the case of diesel fuel. (b) There was no clear trend in yields with the primary furnace temperature. For the majority of PAH species yields were highest at the uppermost operating temperature tested, 1000 °C. (c) There was no clear trend in the effect of the afterburner treatment on the final emission yields. Some species increased, some decreased but not consistently in the same direction for both fuels. (d) At all temperatures, naphthalene emissions at both furnace exits were much higher than the other 39 detected PAH species, followed by acenaphthylene, phenanthrene, fluoranthene and pyrene. (e) Benzo[a]pyrene emissions from both fuels were very pronounced. (f) Although the afterburner did not reduce all PAH emissions when burning JP-8 fuel, some species were reduced by

afterburner treatment, such as fluorene and anthracene. Indeed, at 1000 °C the afterburner treatment reduced fluorene and anthracene emissions by a factor of ~2. (g) In the case of diesel fuel No. 2, at the lowest primary furnace temperature, the yields of some of the major PAH components (acenaphthalene, phenanthrene, acephenanthrylene, biphenyl, fluorene, anthracene) were reduced by afterburner treatment. The afterburner was beneficial especially for the species biphenyl ($C_{12}H_{10}$), fluorene ($C_{13}H_{10}$) and anthracene ($C_{14}H_{10}$), which were reduced by factors of ~4, 4, and 3, respectively. (h) Some additional compounds, such as methyl-naphthalenes and decahydro-2,6-dimethyl naphthalene were detected but not quantified. (i) No nitrated PAH compounds were detected under the present experimental conditions. (k) Benzothiophen was identified in the emissions of both fuels, indicative of the existence of sulfur in their composition. Sulfur is also found in surfactants, such as benzene sulfonic acid and sodium benzene sulfonate, which may be deliberately or accidentally introduced to the fuel.

3.3. Light hydrocarbon emissions

Small amounts of light hydrocarbons were detected in this study, most in quantities under 0.015 mg/g fuel, see Fig. 6. The quantified species were methane, ethane, ethylene, propylene, acetylene and benzene. Methane was the most abundant species, followed by ethylene. Higher amounts of benzene were detected at the effluent of diesel fuel No. 2. Carbon balances did not exceed 85%, suggesting that there must be additional light hydrocarbon species, such as C5 and bigger, which were not measured in this work. For instance, Dagaut et al. [20] reported that the main

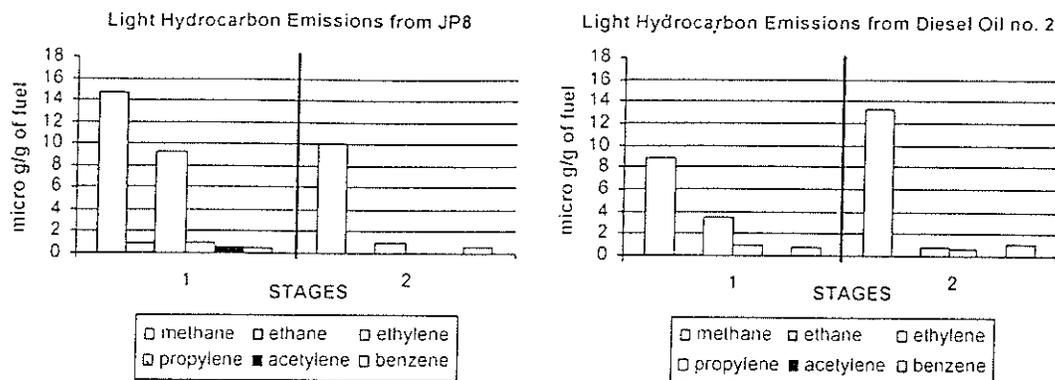


Fig. 6. Cumulative light hydrocarbons ($\mu\text{g/g}$ of fuel) from burning of (a) JP-8 and (b) diesel oil No. 2 at the exits of primary furnace (stage 1) and of secondary furnace (stage 2); the primary furnace temperature was $800\text{ }^\circ\text{C}$; the secondary furnace temperature was $1000\text{ }^\circ\text{C}$.

intermediate molecular products of kerosene oxidation were CO, lower alkenes (ethylene, propene, 1-butene) methane and lower unsaturated hydrocarbons. Among other products, they detected $\text{C}_6\text{--C}_9$ alkenes and aromatics (benzene, toluene, and xylenes).

3.4. Emissions of NO_x and SO_2

Yields of NO_x were only recorded at the exit of the primary furnace, and they were found to be at very low levels (1–6 ppm or 0.01–0.06 mg/g). SO_2 emissions were not detected, most likely because the sulfur content of the fuels was either converted to other compounds or remained in the soot. Yost et al. [15] showed that the CO emission level of JP-8 was lower than that of diesel fuel (as partly true in this study), and that the CO was influenced by the sulfur content of the fuel. CO emissions initially increased with increasing amounts of sulfur in the fuel and then decreased. As the sulfur content was increased, the NO_x emissions initially decreased rapidly and then reached a plateau. The effect of sulfur on particulate matter was found therein [15] to be considerably important, as sulfur enhanced the amount of particulate matter.

3.5. Yields of particulates

Flame temperature affects soot formation in diffusion flames. Montalvo and Ulman [25] showed that particulate emissions from JP-8 were lower than those from diesel No. 2. In agreement with those results, particulate emissions from burning of JP-8 herein were indeed lower than those from the diesel oil; 50–60 vs. 60–90 mg/g, respectively, as shown in Fig. 4. The afterburner treatment was very effective in reducing soot emissions at the lowest temperature from both fuel types (Fig. 4). A great deal of particulates emitted at these low temperatures was oils and tars, as evidenced by the particulates appearing light brown in color. Under these conditions, particulates most likely gasified in the afterburner. However, as the temperature of the primary furnace was increased,

particulates were mostly soot. At those conditions the afterburner did not reduce soot from burning of JP-8, and it managed to increase soot yields from burning of diesel oil No. 2.

3.6. Experimental uncertainty

At all operating conditions two experiments were performed in this work. If the results were not in agreement then extra experiments were performed. All experimental data points are included in Fig. 4. Uncertainties were probably due to small variabilities in manual sample insertion, ignition location and timing, manual sampling and handling of the resin and filters, small losses at all stages, etc.

4. Conclusions

JP-8 fuel is being adapted by the US military as a substitute to diesel fuel No. 2 for all applications. While this makes logistical sense, any possible adverse effects by exposure to the fuel, its vapors or its combustion byproducts should be examined carefully. This work conducted a comparative combustion study between JP-8 and diesel fuel No. 2, involving controlled laboratory experiments. The apparatus, procedure, and operating conditions were identical. The combustion conditions were chosen to be laminar diffusion flames. Such ill-mixed flames are known to produce large amounts of products of incomplete combustion (PIC). Indeed, they were chosen herein for this very reason, i.e. to provide sufficient yields of PIC for quantitative comparative analysis. The following PIC were sampled and quantified in this analysis: CO, total particulates, light (C1–C4) aliphatic hydrocarbons, volatile aromatic hydrocarbons, and semi-volatile PAHs. Quantitative analysis of individual hydrocarbon species was performed.

JP-8 and diesel fuel are seasonally conditioned fuels in which the maxima in the hydrocarbon distribution are adjusted for optimal combustion in different climatological

conditions. A comparison of the chromatograms generated from the combustion of JP-8 and diesel fuel in a horizontal laminar furnace shows only small differences in their combustion byproducts, under the same operating conditions in the furnace. This suggests that the formation of polycyclic aromatic hydrocarbons (PAH) in the horizontal furnace results from the combination of numerous products of incomplete combustion (PIC) to form complicated fused ring structures. This can only occur when the residence time is sufficient for pertinent chemical reactions to proceed and when air is not present at sufficient levels to produce CO and CO₂. This study was focused on analyzing the semi-volatile byproducts of the combustion, however, a large number of volatile hydrocarbons were also observed. In order to identify and quantify all volatile combustion effluents alternate methods for trapping the combustion effluents must be combined with new extraction and analysis procedures. This will be addressed in future work. Radicals produced in the combustion process are expected to react with the unburned fuel, in particular perhaps with single ring aromatics, to produce new compounds that are not observed in the fuel and are typically associated with combustion byproducts. This phenomenon was observed in several of the combustion effluents. Therefore, it is essential that an analytical study be designed to identify and quantify all volatile organics C1–C10 in the combustion effluents of this furnace facility as well as of practical military burners.

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