

A Review on Polycyclic Aromatic Hydrocarbon (PAH) Emissions from Energy Generation

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Polycyclic aromatic hydrocarbons (PAH) emitted from fluidized bed combustion have been reviewed. Firstly, the PAH origin is undertaken. Secondly, the state of the art on their sampling and analytical procedures are commented. Finally, the influence of the fuel, fossil and nonfossil fuels, the combustor type and the combustion variables are analyzed concerning PAH formation and emission in solid/gaseous phase.

Introduction

Most of studies concerning emissions in combustion for energy generation have been aimed to abate inorganic emissions, CO_x , NO_x and SO_x , mainly due to the strict legislation at which these compounds have been submitted and because they are emitted in higher amounts than the organic emissions. The necessary technical modifications to reduce inorganic emissions have affected organic emissions, so nowadays, growing attention is being paid to volatile organic compounds, particularly to polycyclic aromatic compounds (PAC) and especially, due to their carcinogenic character (1–5), to polycyclic aromatic hydrocarbons (PAH).

Although there is not a definitive legislation concerning PAH abatement, the Environmental Protection Agency (EPA) has fixed 16 PAH as priority pollutants, the latest being effective from 1997 (6). These compounds are as follows: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno(1,2,3-c,d)pyrene, benzo(g,h,i)perylene and dibenzo(a,h)anthracene (7). It is expected that air quality would be improved soon (8) if the emission of these PAH was controlled.

PAH Sampling, Extraction and Measurement Techniques

One of the main problems joined to polycyclic aromatic compounds analysis from combustion is due to the difficulty of the sampling procedure. A review about sampling and analysis of PAC from combustion systems was produced by P. T. Williams (9) in which were found prominence glass-fiber filters with a resin trap to collect PAC. It is worth pointing out that at that time, fluidized bed combustion (FBC), the last technology in power generation, was under development.

The last congress held in Venice about Air quality in Europe Challenges for the 2000s, pointed out that results differed by a 40%, depending on the sampling system and the analytical technique (10). There are a number of problems associated with the analysis of trace organic compounds and therefore of PAH, mainly due to their reactivity, decomposi-

tion, temperature sensitivity and volatility (11). Until 1970, the classic system used was composed of a high volume capturer containing glass fiber filters which allowed collecting enough particles in order to analyze PAH. Afterward, due to physical and chemical problems, adsorbing systems were introduced to trap PAH present on gas phase. PAH sampling methods have been varied utilizing different types of filters (12, 13) and adsorbents (14–16).

Once solved the sampling system, the next problem to be undertaken is the extraction of the trapped polycyclic aromatic compounds. Extraction methods have used traditional methods such as ultrasonic (17–23), Soxhlet (18–20, 22–24) and other more modern ones such as supercritical fluid extraction (25–29). The effect of sonication and Soxhlet extraction on PAH recovery was studied by Stephens et al. (20) who obtained higher recoveries in Soxhlet extraction for coal stack ash. However, when Soxhlet and ultrasonic extractions were compared for urban atmospheric particulates (23), ultrasonic extraction with acetonitrile was more useful for recovering of PAH. The same techniques, ultrasonic and Soxhlet extractions, were compared for sediments and air particulate material (22) finding that ultrasonic extraction was the better technique. This technique has also been used by other authors for combustion samples (16, 30), and results showed that ultrasonic extraction produced better reproducibility than manual shaking. Desorption of PAH in long term field contaminated sediment has also been studied and compared with laboratory experiments finding that it is not possible to compare results because only a very slowly desorbing fraction was detectable after a long contact time (31).

Analytical methods have been changing progressively. UV/visible absorption spectrometry was utilized as a general technique for analysis of organic particle material in ambient samples. At the same time, the technique of fluorescence spectrometry was developed for PAH samples analysis. Its main advantage over absorption methods of UV/visible was its high sensitivity by a factor of 10^2 – 10^3 (32); its main disadvantage was the interference by trace fluorescent compounds. Both optical methods were not adequate to analyze complex matrices containing a lot of isomeric PAH.

Techniques such as gas chromatography (33–35), liquid chromatography: LC-MS (36), LC-FD (34, 37), LC-ED (38), HPLC-FD (39, 40), HRMS (41) and other techniques such as supercritical fluid chromatography (42–44), spectrometry of nuclear magnetic resonance RMN (45), capillary electrophoresis with fluorescence detection (46), Fourier transform infrared (47), and laser-mass (48) have been utilized to identify PAH mixtures more specifically.

PAH Emissions from Anthropogenic Sources

PAH emissions from human activity processes and anthropogenic sources can be divided into stationary combustion

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sources and mobile combustion sources (49). In this way, the PAH studies are very varied and depend on the process and on their variables such as reactor type, fuel, etc. The most important sources of atmospheric PAH are the combustion processes or pyrolysis of materials containing carbon and hydrogen (50). A particular case has been the coking process (51, 52), in which the coal heating in an oxygen absence atmosphere takes place being secondary reactions, like aromatization/cyclation reactions promoted (53). PAH emissions are produced mainly as a consequence of poor sealing, particularly of the oven doors and during the charging, pushing and cooling processes. As a result, workers are typically exposed to high atmospheric PAH concentrations. The high mortality indices by skin and lung cancer are the most notable examples of the carcinogenic potential of PAH, so improved techniques have been adopted to abate emissions to a safe level including a careful control in the coke making. P. J. Kirton et al. (14) demonstrated that graphitized carbon retained all PAH compounds and that a three-stage sampler allowed determination of a wide range of the constituents of coke oven emissions. The PAH content of contaminated soils from former manufactured gas plants or coke production plants was determined by Haeseler et al. (54) showing that there is an association of PAH with heavy organic matter in this type of contaminated soils. Biodegradation has been used to transform PAH supporting the application of bioremediation of soils at hazardous waste contaminated sites (55).

Aluminum production is also a source of PAH emissions, and PAH ambient air concentrations were determined in four residential areas close to aluminum industries (56). The results indicated that PAH concentrations were high compared to levels in other polluted areas with industry and dense traffic. These concentrations were also variable with time and as a consequence of the meteorological conditions.

Data relating PAH with coal combustion have only been accumulated since 1967 (57), the first review being in 1980 (50) and the most recent in 1993 (58). A review about atmospheric polycyclic aromatic hydrocarbons, sources, fate and behavior, has been performed by Baek et al. (59) studying mainly PAH formed by anthropogenic processes, especially the combustion of organic fuels.

Distribution of PAH Emissions into Solid/Gas Phases

Organic compounds, independent of the process which originated them, can be released in gas phase or can be associated with particles by nucleation and condensation, forming associations of big size which constitute particulate matter.

The results published are mainly related to VOC (60) and PAH supported on the particulate matter. Masclet et al. in 1987 (61) produced the first report on the PAH distribution between gas and solid phase. Generally, the particulate matter at high combustion temperatures initially forms in the gas phase, but, when the temperature decreases, part of the same can be adsorbed and/or deposited on fly ash particles. The smaller particles, with a greater surface area with respect to their mass, adsorb more organic compounds, which can associate between them or with other compounds, forming undesirable bigger associations known as soot.

Mastral et al. (62, 63) studied the PAH distribution between solid and gas phase and the PAH associated to particulate matter from coal combustion in an atmospheric fluidized bed pilot plant at different conditions finding that the contribution of gas phase is very important in the total PAH emitted. In conventional combustion processes on particulate matter, emission from stacks is controlled through a combination of cyclones systems, fabric filters, and electrostatic precipitators, the efficiency of these two last systems being of 99% or better (64).

Distribution of atmospheric PAH between particulate and gas phases is determined by several factors (65–68): PAH vapor pressures (function of the temperature), the amount of fines (surface area for PAH adsorption), ambient temperature, PAH concentration and the affinity of each PAH by the particles of organic matrix.

The adsorption of PAH in different matrices is dependent on the vapor pressure. Most of the vapor pressure values for PAH were determined by Sonnefeld et al. (69). Lao and Thomas studied the influence of the vapor pressure jointly with the temperature on the initial PAH amounts present on the surface of sample (70). The ambient temperature had a marked effect on the coefficient of PAH gas-particle distribution, and, although all PAH are solid at ambient temperature, they found varied volatility and boiling points higher than the ones corresponding to *n*-alkenes with the same number of carbons at ambient temperature (25 °C). Naphthalene was 100% found in gas phase, while benzo[*a*]pyrene (BaP) and other compounds with 5 and 6 rings are adsorbed on particulate matter. Naphthalene was also found at high levels in the ashes from pulverized coal power generation therefore associated to the particulate matter (71). PAH of intermediate boiling point were distributed between two phases. The influence of meteorological parameters also plays an important role on PAH concentrations in the atmosphere. Authors such as Lee et al. (72) studied the influence of the meteorology and air masses on daily atmospheric PCB and PAH concentrations at U.K. They concluded that several factors, daily air concentrations, temperature, passage over marine and land masses source areas and the deposition events determined PAH concentrations.

PAH Formation and Emission Mechanisms

In any fuel combustion, PAH formation and emission mechanisms can be classified in two processes (63, 73): pyrolysis (62) and pyrosynthesis (74–77). On heating, the organic compounds are partially cracked to smaller and unstable fragments (pyrolysis). These fragments, mainly highly reactive free radicals with a very short average lifetime, lead to more stable PAH formation through recombination reactions (pyrosynthesis). So, BaP and other PAH are formed through pyrolysis processes of methane, acetylene, butadiene and other compounds. Authors such as Badger (3) suggested a pyrosynthesis process for BaP production. PAH formation in combustion has also been explained like a waterfall mechanism in which PAH compounds are formed through small radicals to which radicals add (71, 78) forming compounds of higher molecular weight, soot and fullerenes (79). Taking into account this mechanism, it has been explained that, although the individual PAH amount found in atmospheric fluidized bed combustion (AFBC) as a function of the combustion temperature follows a random distribution, the total of PAH keeps a determined trend (16). The PAH rearrangement and interconversion processes during combustion have also been shown by Visser et al. (80).

PAH formation in pyrolysis oils has been attributed to Diels–Alder reactions of alkenes to form cyclic alkenes (81). The dehydrogenation of these cyclic alkenes produces single rings aromatic compounds of an only ring, which react further, leading to the PAH formation (82). However, the complex hydrocarbons do not have to necessarily break into small fragments before performing recombination processes. Compounds with several rings can suffer partial cracking followed by dehydrogenation of the primary radicals. So, references have been found in the review that suggest that lipid acids with a long linear chain play an important role in the PAH formation mechanism because they allow the alkylation of aromatic units in fossil fuels (83). On the other hand, the intermolecular and intramolecular hydrogen

transfer as well as the phenyl radicals play an important role as intermediary compounds in high-temperature reactions, that lead to polycyclic compounds formation (84).

In combustion processes, tars are also produced as a consequence of condensation of released emissions, and the typical reactions of PAH formation in tars have been explained through dehydrogenating polymerization processes together with an aromatization process (aromatization growth) (85). Intermolecular reassociations (85), fragmentation reactions (due to hydrogen transfer and posterior division of simple C–C bonds formed initially) and alkylation reactions have also been observed (86). Fetzer et al. (87) identified large PAH in a coal tar pitch and suggested that many different reaction pathways occur in the production of coal tar pitches. Nishioka et al. (88) identified and quantified PAH isomers in coal tars and combustion products.

A qualitative study on PAH in cyclones and bottom ashes from a Turkish lignite fluidized bed combustion has been performed by Citiroglu et al. (89) using GC/FID. They showed the presence of many PAH compounds, some of them carcinogens, in the cyclone and bottom ashes. The majority of PAH formation has been linked to the formation of soot particles (90, 91). PAH emissions in soot from combustion of polystyrene, polypropylene and wood have been studied by Elomaa et al. (92) in a tubular oven showing clear differences between the materials. The source of the soot was polystyrene. In all studies performed, it has been deduced that PAH are directly involved in the soot particle (93). Pfefferle et al. suggested that the dimerization of PAH species could be a possible way for soot formation (94) and that soot particles can serve as support for pollutants such as polycyclic aromatic compounds (95, 96) and trace elements (97). Smedley et al. (93) supported the theory that PAH were directly involved in soot particle inception, while C_2H_2 was directly involved when PAH were depleted. It has also been shown that the probe temperature affects the initial deposit formation mechanism of soot influencing to PAH quantities found (98). PAH were also detected in diesel soot by HPLC, where emissions in mutagenic and carcinogenic PAH were low but the emissions of comparatively harmless compounds were high (99).

Influence of the Combustor Type

One of the pollution sources to which the population is exposed is the consequence of the use of automobile motors: diesel and gasoline (100) as a combustion process. One of the most common and ancient combustion practices to produce energy still used is the coal domestic firing for heating (fire residential stoves) (101), but, despite the high oxygen availability and due to the poor mixing efficiencies of air and fuel and to the low combustion temperatures, the organic compounds formation is promoted. Emissions factors for PAH in domestic combustors have been studied by Davies et al. (102) finding emissions of 3 orders of magnitude greater for domestic combustion than those obtained for industrial combustors. Bayram (103) studied PAH emissions in domestic combustors, industrial stokers and fluidized bed combustion (FBC) burning Turkish coals and lignites. They concluded that PAH emissions from domestic heating were higher than in the other two controlled systems. Other authors (104) studied PAH emissions from domestic combustion of wood chips, other wood type wastes and newspapers in small woodstoves. The results showed that emissions from wood were more mutagenic than those from waste and newspapers combustion. It is also remarkable that their corresponding nitrogenated (105), sulfurated (2) and oxygenated derived compounds are more carcinogenic than the parent PAH. Some polycyclic polar compounds have been studied by Knobloch et al. (101) in lignite emissions in domestic heating.

Fluidized Bed Combustion

Though the traditional methods of coal combustion was fixed bed, (106) pulverized coal combustion (107–109) was not introduced successfully to reach this aim until 1920. This kind of combustion is characterized by the utilization of high combustion temperatures (between 1000 and 1400 °C), small fuel feed size, long residence times and large units. Its main advantage was the utilization of coals of wider rank than those used in stokers (110), and the amount of generated power was 2 orders of magnitude higher than that obtained in stokers. Spuznar (111) compared PAH emissions from three coal-fired power stations (pulverized coal/oil, burning low-sulfur coals with electrostatic precipitators, and with electrostatic precipitators and a fuel gas desulfurization (FGD) unit) detecting the lowest emissions for the largest unit.

During the 1950s, a new technology of coal combustion started to be developed, the fluidized bed combustion, although its use for generation of energy did not start till the 1960s. Coal is burned in a suspension with air. The main difference is found in the reactor design that induces a movement that facilitates ash elimination. Fluidized bed combustors can be divided into two groups: the atmospheric (AFBC) (112) and the pressurized (PFBC) (113). Both beds can be classified as bubbling or circulating as a function of the velocity at which they work. The main advantages (114) from the utilization of fluidized bed combustion are directly related to inorganic emissions abatement in such way that in fluidized beds these inorganic emissions (NO_x , CO_x , SO_x) are under control (115–119).

The behavior and the properties of a fluidized bed depend on the superficial velocity of the fluidization gas. Up to the minimum fluidization velocity, the bed is fixed (120). When the fluidization velocity increases, the particles move freely and the bed behaves as a boiling fluid with bubbles (121, 122). If the fluidization velocity is increased it becomes a turbulent bed, with a higher bed expansion and more violent movement forms. For circulating beds, also known as fast beds (123, 124), the superficial gas velocity is higher to promote solid entrainment, in such a way that the solids are re-circulated through cyclones and the conventional bed is eliminated completely.

Influence of the Combustion Parameters in Fluidized Bed Combustion

Bibliography on fluidized bed combustion (125–138) (FBC) is very extensive mainly because many studies have aimed at reducing inorganic emissions. In these studies, the physical properties of the fluidized beds that allow controlling specific factors concerning the energetic combustion costs, generated residues, emissions, etc. have been studied. On the contrary, studies on PAH emissions in FBC are scarce. The influence of coal size and the solid–gas distribution was studied by Bayram (103)m and it was concluded that higher PAH emissions were produced with smaller size coal when gas-phase emissions were higher. The release of PAH emissions has been compared for coals, a low rank coal and a high rank coal, at different combustion temperatures (64), the temperature having a less remarkable effect on the high rank coal. The influence of the combustion parameters, the temperature, the percentage of air and the total airflow rate have also been reported (16, 62, 73, 139–141) for the same system, an AFBC reactor. Regarding the temperature, the highest PAH emissions were produced in the range between 750 and 850 °C. For the percentage of excess air (140), it was concluded that a great decrease in PAH emissions was observed when the percentage of excess air was increased from 5 to 10%. Similar results were observed by Karunaratne (142) deducing that the percentage of excess air is the most influential parameter on PAH formation. PAH emissions

decreased up to a level about 80% excess air after which emissions rose again probably due to the quenching of combustion reactions by the high level of air. The airflow total also had a main contribution to the total of PAH emitted (141). So, the lowest PAH emissions were emitted at flows of the double of the minimum fluidization velocity, good fluidization conditions. At high flows, a deformation in the bed increased remarkably PAH emissions.

The effect of combustion parameters, including combustion temperature, particle size, moisture content and secondary air, on PAH emissions from coconut shell combustion in a FBR was also performed by Karunaratne (142). The effect of combustion parameters (temperature, amount of excess air, post combustion zone temperature) from biomass combustion on PAH formation was also studied by Karunaratne et al. (143) but in a drop tube furnace. It was concluded that one of the most influential parameters on PAH formation was the excess air and that the temperature influenced only beyond 850 °C. Tobias et al. (144) studied PAH emissions in circulating beds CFBC at atmospheric pressure as a function of the combustion temperature and the percentage of excess air (20–30%). They found that low combustion temperature and high percentages of air favored high PAH emissions.

A thermodynamic and kinetic study on the formation of PAH from coal combustion in high-temperature pulverized flame combustion and lower temperature fluidized bed combustion has been carried out by Chagger et al. (145). They found that the thermodynamic predictions underestimate the amount of PAH compounds and that in pulverized flame combustion, at high temperatures above 1100 K, coal molecules decomposed to form light olefins, mainly ethyne, which reacts to form PAH during cooling and quenching. In the case of fluidized beds, the temperature could not be high enough for the devolatilization products to be totally converted to ethyne, although the initial products released to undergo further reactions. Compounds of two rings as naphthalene and its derivatives are the major species according to their modeling study. The major presence of naphthalene has been reported in ash from pulverized coal power station (71).

PAH emission in fluidized bed reactors at pressure has been studied by Szpunar (111). Emissions were lower in pressurized systems than in atmospheric systems, and both systems produced lower emissions than in conventional systems. Emissions from FBC units were higher than those from pulverized coal combustion.

Influence of the Fuel in PAH Emissions

One of the main fuels used in this century is coal, but other new fuels, nonfossil fuels, are being taken into account. In the particular case of coal and wood (91), other classical fuel, the combustion is normally incomplete due to the low burning temperatures and the scarce air. Truesdale and Cleland (146) compared PAH emissions from coal and wood with those from alternative fuels in conventional stokers obtaining that wood and peat, generally, emitted higher amounts of carcinogenic PAH by energy unit than the bituminous coal. The effect of fuel type (coconut shell, coal, coconut husk, coconut shell charcoal) was also studied by Karunaratne (143) in a drop tube furnace obtaining that PAH emissions showed the following order: Coconut shell < Coconut husk < Coconut shell charcoal < Coal. García et al. (147) studied hydrocarbon emissions on several coal-fired power stations concluding that the fuel type had less effect on emissions than the furnace type or the load size.

Several studies have been performed based in PAH emissions from coal power stations (147). These emissions have also been studied in experimental furnaces under coal combustion conditions more controlled (73), concluding that the effect of coal type is much less influencing than the reactor

type in PAH emissions. The nature of PAH emitted during the cooling of combustion products was reported by H. K. Chagger (148) in a propane flame and a coal particle flame. They considered that exhaust gas products derived from hydrocarbon species and radicals present in the original flame undergo quenching during the cooling process leading to PAH and VOC formation. PAH were also measured in seven power stations burning coals of different origin (Polish, French, South African, Australian) and different oils (gas turbine, diesel oil) (61). They concluded that the emissions depended on the combustion conditions, the nature of the fuel and the type of furnace. The emissions were lower in diesel-powered stations than in oil fired stations although diesel ones emitted higher amounts of heavy compounds than the oil fired stations. A study performed by Herod et al. (149) allowed identification of the organic matter released during the heating of coal and peat, observing that all coals contained light volatile materials, the amount of emission decreasing when the rank coal increased.

The Use of New Fuels in Combustion

The markets for coal have altered meanly since 1950, due to the growth in oil production/consumption and the disposability of natural gas from 1960. In addition, the restrictive legislation concerning inorganic emissions has meant that in power stations petrol and particularly natural gas have been introduced as additional fuels to coal in order to abate emissions. PAH emissions have been studied in gasoline and diesel vehicles (12). Lighter PAH emissions have been detected in diesel trucks, while gasoline vehicles emitted higher molecular weight PAH. The diesel combustion of an alkylated PAH was performed by Tancell et al. (150), and their results suggested that under the conditions used no significant dealkylation occurs.

The use of new fuels such as biomass (94, 151–153), synthetic waste materials (154, 155) and urban waste (37, 156–157), in general, as a way of eliminating residues that these materials produce, are acquiring considerable importance in combustion processes. PAH incidence in soils close to pine biomass combustion have been studied at different conditions (158) using gas chromatography–mass spectrometry showing that the main types of PAH isolated have naphthalene and phenanthrene structure. The effect of biomass combustion (paper-mill residue, hard pine-wood, particle board) on soot particles and polynuclear aromatic compounds (PAC) has also been studied (95) showing that the temperature–time history and C/O ratio are important parameters which affect PAC formation and destruction in biomass combustion. Authors such as P. Oesch (159) studied and characterized polyaromatic compounds in tar formed in pressurized fluidized-bed gasification of biomass by gel permeation chromatography (gpc) and pyrolysis-gas chromatography-atomic emission detector (Py-g.c.-aed), controlling tar compound condensation at 150 °C and establishing a quite rapid and easy analytical method for heavy tar compounds. PAH emissions of five different polymers combustion in a vertical furnace and in a horizontal furnace were studied concluding that destruction of organic compounds was enhanced with increasing post-flame residence time and temperature (155).

The expansion in transport has also generated a large amount of waste tires (160) producing a growing concern related to the economic and environmental problem associated with these nonbiodegradable residues. It has been shown that, as with other materials such as polystyrene and propylene (92, 154), waste tires (161) are also important sources of PAH emissions in combustion processes. The high calorific value (28–37 MJ/kg) (151) of tires, higher than most of sub-bituminous coals, combined with its low mineral matter content, enhances the opportunity to use tire as a

potential fuel.

Due to tire composition, (162, 163) mainly formed by natural rubber and synthetic rubber, majority styrene-butadiene (SBR) and polybutadiene (PB) and carbon black (CB), and due to the low reactivity of CB, more severe combustion conditions than those used in coal combustion will be necessary. This fact has been observed in coal-tire combustion in fluidized beds (164–166).

Studies of PAH analysis in tire combustion under controlled conditions in furnaces of laboratory scale or in power plants are scarce. A comparison of the combustion behavior of pulverized waste tires and coal in a thermogravimetric analyzer and in an electrically heat drop-tube furnace has been performed by A. Atal et al. (167) observing that char burnout times were shorter for tire particles than coal. A comparative study on PAH emissions in FBC, using fossil (coal) and nonfossil fuel (waste tire) and a blend of coal-tire (1:1) has been carried out by Mastral et al. (63, 168, 169) concluding that, at the same conditions varying combustion temperature, the highest PAH emissions were produced with tire as fuel.

Previous studies to waste tire combustion have been centered in tire pyrolysis under inert atmosphere (81) and in sulfur-PAH in two types of reactors: static batch slow pyrolysis reactor and a fluidized bed reactor (170). The study of PAH in oils from hydropyrolysis of different materials (coal, tyre and coal-tyre blend) has been studied by Callén et al. (171, 172) in two different reactors: tubing bomb and autoclave reactor, at different conditions obtaining the highest PAH concentrations in the coal hydropyrolysis oils and promoting the tubing bomb reactor retrogressive reactions. Levendis (161) studied PAH emission from waste tire and coal separately, in combustion and pyrolysis conditions but in horizontal and vertical furnaces observing that PAH emissions were higher during pyrolysis and always higher in tire than in coal combustion. Also Conesa (173) studied the evolution of volatile and semivolatile compounds from tire pyrolysis in three different types of equipment. Combustion of pulverized bituminous coal and ground waste automobile tires in an isothermal drop-tube furnace in air and in the absence of oxygen, pyrolysis, were studied by Atal et al. (174) suggesting that pyrosynthesis is the major mechanism contributing to PAH emissions from the combustion of these fuels. Combustion experiments based on the correlation of CO and PAH emissions from the combustion of pulverized coal and waste tires fuel have been performed (175) in a drop-tube furnace at temperatures in the range of 1000–1300 °C. It was found that the CO and especially the PAH yields from tire-derived fuel were much higher than those from coal although the relative amounts of individual PAH components were similar in the combustion effluent of the two fuels. Anyway, although PAH studies have been performed in combustion, most of the studies concerning waste tires are not related to fluidized bed combustion.

A complete study on the influence of different variables (fuel particle, combustion temperature, percentage of excess oxygen, air flow, residence time, etc.) on combustion emissions relating to NO_x, VOC, CO_x, particulate matter, PAH has not been yet performed. It would be very convenient to have knowledge, specifically about the CO/PAH relationship, due to the competition between oxidation and pyrosynthesis reactions, and about NO_x/PAH relationship in order to know how NO_x affects the PAH conversion into the corresponding diols which have the highest carcinogenic power.

In this paper, the importance of the PAH atmosphere impact from coal combustion at the current conditions is shown. Despite the scarce data published relating PAH emissions and FBC, it has reflected the necessity of establishing a determined regulation regarding the sampling system and the analytical procedure in order to compare

results on PAH emissions and to proceed to control them, specially those compounds of five rings such as benzo[a]pyrene and dibenzo(a,h)anthracene due to their high carcinogenic power (176).

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