# Combustion of High Calorific Value Waste Material: Organic Atmospheric Pollution

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Waste tire combustion in an atmospheric fluidized-bed (AFB) reactor (7 cm i.d., 76 cm height) has been performed in a laboratory plant with the aim of studying the polycyclic aromatic hydrocarbon (PAH) emissions as a function of combustion temperature. The main aim has been to compare these organic emissions with the ones obtained when coal is burned at the same combustion conditions. PAH emissions have been analyzed in solids collected in two cyclons at the exit of the reactor and in a trap system formed by a condenser, a filter (20  $\mu$ m), and an adsorbent. After PAH extraction with dimethylformamide (DMF) by sonication, fluorescence spectroscopy in the synchronous mode (FS) has been used as an analytical technique to quantify the PAHs emitted. It could be concluded that higher PAH emissions are generated when this waste material is burnt at the same conditions used for coal atmospheric fluidized-bed combustion (AFBC).

#### Introduction

In the last part of this century, the increase in the automotive and trucking industry has generated a huge amount of waste tires (1). Due to the economic and environmental problems that these wastes create, the non-biodegradability and the adverse environmental effects (2) have led to looking for new ways of elimination. On the other hand, the high calorific value (28–37 MJ/kg) (3) of tires as well as the low mineral matter are their most important advantages, which makes tires a potential nonfossil fuel.

Tires are formed primarily by a copolymer mixture (4, 5): about two-thirds natural rubber and synthetic rubber, composed mainly of styrene-butadiene (SBR) and polybutadiene (PB) and approximately one-third carbon black (CB). CB (6) is one of the constituents used to strengthen rubber to avoid abrasion. It is an aggregate of esferic coal particles (7) characterized by a high ratio of surface/weight. Moreover, there are other additional components such as aromatic hydrocarbons, trace metals (8), and stearic acid that appear in different proportions for several kinds of tires for variation in some of their properties.

The main ways of eliminating waste tires (9, 10) have been related to landfilling (11), incineration (2), and combustion in power generation (12). One of the most used ways has been pyrolysis (13, 14) with the aim of obtaining oils that can be used as fuels or solvents in coal liquefaction (14, 15).

Comparing the nature of tires and coal, used worldwide as the main fuel in power generation, it can be deduced that, although both of them are very different materials, their

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#### TABLE 1. Efficiencies (%) at the Different Combustion Temperatures Used in an AFBC Pilot Plant (860 L/h, 20% Excess 0<sub>2</sub>)

temperature (°C)	650	750	850	950
efficiencies (%)	90	94	95	92

elemental analysis shows that their contents in C, N, H, O, and S are very similar with similar aromatic structures in some aspects (*16*). Anyway, tires show a remarkable difference in the moisture (*17*) content and ashes, which are lower than in coal.

In general, in fluidized-bed combustion, it will be necessary to use higher combustion temperatures than for coal due to the lower reactivity of CB (18). This has been observed in coal-tire blend combustion (19). However, it is also necessary to study the different behavior of tires with regard to organic emissions. During combustion and pyrolysis processes of fossil fuels, polycyclic aromatic hydrocarbons are released (20). Although, studies about PAH emissions in coal combustion are receiving interest, very little is known about PAH emissions in tire combustion. First, due to the different nature of the fuels, different combustion conditions could be required. In this paper, PAH emissions from the fluidized combustion of waste tires have been studied in a pilot plant working at the same conditions used in coal combustion (21) varying the combustion temperature and keeping constant the air total flow and the percentage of excess oxygen.

### **Experimental Section**

A fluidized-bed combustion laboratory plant described in previous work (*22*) was used to perform the combustion of waste tires, a nonspecific sample supplied by AMSA enterprise after shredding and separating the metal components (0.6-mm particle size).

The elemental analysis is as follows: % C = 86.35 (ar); % H = 7.29 (ar); % S = 1.60 (ar); % N = 0.18 (ar). The proximate analysis is as follows: % moisture = 0.94 (ar); % ashes = 3.28 (ar); % volatiles = 56.09 (ar); % Zn = 1.49. Calorific value (kcal/kg) = 9220.

Sand was utilized as the fluidizing agent. Due to problems in the feeder because of the friction between particles, a blend 1:1 of tire—sand was used to feed the tire into the reactor.

The combustion experiments were carried out keeping constant the air total flow (860 L/h) and the percentage of excess oxygen (20%) and varying the combustion temperature (650, 750, 850, and 950  $^{\circ}$ C).

The combustion experiences were performed during 2 h once the plant worked at the regime conditions. Every experiment was carried out at least in duplicate.

The five samples from first cyclone, second cyclone, condenser, nylon filter, and XAD-2 resin obtained in each experiment were extracted with an ultrasonic bath for 15 min with DMF, filtered and concentrated in rotary vacuum. Afterward, they were analyzed by fluorescence spectroscopy at the conditions for each specific PAH (*22*) previously determined with model compounds.

The combustion efficiencies at each temperature were calculated, and the results are shown in Table 1.

#### **Results and Discussion**

All combustion processes are influenced by three factors that must be considered when PAHs emissions are studied: (a)



FIGURE 1. Total PAHs emitted ( $\mu$ g/kg) during tire combustion from the reactor (AFBC, 860 L/h, 20% excess oxygen) as a function of the combustion temperature.

bad combustion or incomplete combustion in which fragments, mainly aromatic, from the fuel structure are emitted as unburned material, (b) the pyrolytic process, a consequence of the thermal changes that consist of the rupture of the fuel structure into radicals, and (c) oxidation reactions with the elimination of radicals as oxides.

**Influence of Incomplete Combustion.** Concerning incomplete combustion, the combustion efficiencies reached give an idea about the influence of this factor. From Table 1 it can be deduced that, in general, the higher the combustion temperature, the higher the efficiency. The efficiency values reached are high, but not so high as to discard the influence of the entrainment of unburned material that could increase the organic emissions. Therefore, to study PAHs emitted by waste tires as a function of the combustion temperature, not only will the pyrolytic and oxidation processes be taken into account but also the influence of unburned emissions. In comparison, when a sub-bituminous coal is burnt at the same conditions (*21*), the efficiency values are very close to 100%.

**Influence of the Pyrolytic Process.** The influence of the previous volatilization step to the combustion process on PAH emission as a function of the combustion temperature has been analyzed. As consequence of the thermal breaking or devolatilization, rubber structures release organic radicals. These radicals have a very brief average life due to reduction both by reaction between themselves (condensation) or by reaction with oxygen (combustion). These two possibilities will compete depending on the oxygen availability, which at the same time will depend on the proximity to the flame. The higher radical concentration leads to a higher rate of their association.

When radicals interact in order to stabilize, and as a consequence of their association, aromatic structures are promoted or preferentially formed. These reactions are the origin of PAHs formation during the combustion process. These reactions will be more prominent close to the burning particle.

**Oxidation Reaction.** When conforming radicals or molecules resulting from the pyrolytic process are entrained by the flow, their ability to react with oxygen will increase and their gradual oxidation will be carried out. The further the fuel particle is from the flame, the easier radical elimination is by oxidation. The final reaction being their conversion into  $CO_2$  and  $H_2O$ . That means elimination of PAHs formed in a previous step and a good combustion.

The consequences of the influence of the three analyzed steps, the total PAH amounts emitted, are shown in Figure 1. The distribution of the total PAHs emitted in tire combustion as a function of the temperature shows the existence of three different trends. The first trend is between 650 and 750 °C, in which a decrease of the total PAHs emitted is produced with an increase of the temperature. A second trend is from 750 to 850 °C, in which a huge increase in the PAHs amount is emitted. Finally, a third trend is from 850 to 950 °C in which PAH emissions are maintained practically constant. In general, the increase of the temperature seems to favor the PAHs formation.

The temperature variation is the determining factor taking into account that the total air flow is kept constant (860 L/h) along with the percentage of excess oxygen (20%). With variable temperatures, the exit velocity of the flue gas will vary; therefore, the contact time between the radicals released will vary as a function of the combustion temperature. At low combustion temperatures, the exit velocity of the gas is lower and the residence time in the reactor is higher. This indicates that, for the reactions in the reactor, both oxidation and condensation reactions will be favored because the residence time is higher. Anyway, at these conditions, elimination by the radical oxidation appears to be the predominant factor since the fluidization and the effective oxygen are under control. When the combustion temperature is increased, the exit velocity of the gases in the interior of the reactor is higher and the oxidation time is lower. As a consequence, PAH emissions increase. Moreover, it is necessary to take into account the influence of the tire combustion efficiency since incomplete combustion is important in these emissions. CB seems to be the responsible component due to its high ratio of surface/weight and inertness. It is also important to consider the physical aspects of the bed.

The composition of the tire, formed mainly by a mixture of styrene, polybutadiene, and carbon black (approximately one-third) will also influence the amount of total PAHs emitted. Tire pyrolysis leads to ethene, propene, and 1,3butadiene formations that react to form cyclic alkenes. Because all combustion process experiments involve a pyrolytic process, which implies secondary reactions of the pyrolysis, the formation of aromatic and polycyclic compounds has been attributed to Diels-Alder ciclyzation reactions with alkenes (23, 24). These are produced especially at high temperatures with long residence times. The lowest combustion efficiency values favor these kinds of processes, but also the inertness of CB must be considered. This favors soot formation and greater associations of aromatics with coronene (Co) in elemental structures such as nanotubes, semifullerenes, etc. In this way, Sahouli et al. (6) have stated that, during tire pyrolysis, the long elastomer chains break down and are adsorbed on the CB surface. As a result, carbon deposits and small aromatic compounds are formed, depending on the pyrolysis conditions. The deposits increase with increasing temperatures. We have also observed this phenomenon (20, 25). According to Figure 1, combustion temperatures between 700 and 750 °C for tires are more desirable due to lower PAH formation and emissions.

The PAHs distribution in different parts of the trap system (Table 2) shows that most of the PAHs emitted are trapped on the particulate matter of the cyclons and on the nylon filter. That is to say, most of the PAHs emitted are supported on the particulate matter. The high PAH emissions supported on particulate matter of the cyclons are more pronounced at high combustion temperatures.

When the individual PAHs emissions are studied as a function of the combustion temperature (Table 3), it is observed that the highest contribution to the total PAHs is due to fluorene (Fu), pyrene (Py), chrysene (Cry), anthracene (An), acenaphthene (Ac), benz[a]anthracene (BaA), and Co.

It is more interesting to examine the PAHs variation as a function of the combustion temperature of the compounds with higher carcinogenic properties—benzo[*a*]pyrene (BaP),

TABLE 2. PAHs Distribution ( $\mu$ g/kg) between Five Traps in Tire Combustion (AFBC, 860 L/h, 20% Excess O<sub>2</sub>) as a Function of Combustion Temperature

	temperature (°C)					
	650	750	850	950		
cyclone 1	681	19	18107	19745		
cyclone 2	1316	314	7925	5581		
nylon	2172	33	5617	6655		
condenser	267	20	279	401		
XAD-2	41	4	270	244		
total (μg/kg)	4477	390	32198	32626		

TABLE 3. Totals of Individual PAHs ( $\mu$ g/kg) Collected in Five Traps from Tire Combustion (AFBC, 860 L/h, 20% Excess 0<sub>2</sub>) as a Function of Combustion Temperature

	temperature (°C)			
	650	750	850	950
fluorene	792	90	5531	9893
benzo[a]pyrene	nd <sup>a</sup>	1	611	375
pyrene	309	18	8136	8704
chrysene	697	16	3067	2656
antraceno	9	7	2093	1976
acenaphthene	145	238	8060	2605
benz[a]anthracene	351	7	3926	3951
dibenz[a,h]anthracene	338	4	65	42
coronene	1836	9	590	2317
perylene	nd	nd	119	107
benzo[k]fluoranthene	nd	nd	nd	nd
total (µg/kg)	4477	3990	32198	32626
<sup>a</sup> nd, not detected				



FIGURE 2. Total distribution of BaP and D(a,h)A emitted during tire combustion (AFBC, 860 L/h, 20% excess O<sub>2</sub>) as a function of the combustion temperature.

dibenz[*a*,*h*]anthracene (D(a,h)A), and the most stable, Co. BaA is also represented due to the abundance of this compound in tire combustion and its carcinogenic properties, although it has a lower incidence than BaP and D(a,h)A. These variations are shown in Figures 2 and 3. As shown in Figure 2, it is deduced that BaP has the highest emission at 650 °C. D(a,h)A shows a maximum at a temperature of 850 °C.

Both compounds have high carcinogenic properties and are emitted at the extreme combustion temperatures. At 750  $^{\circ}$ C, their emissions are minimum, which seems to be the most favorable combustion temperature to diminish these emissions.

Figure 3 illustrates results similar to those with D(a,h)A in that BaA, in general, shows the same distribution as a



FIGURE 3. Total distribution of Co and BaA emitted during tire combustion in the plant (AFBC, 860 L/h,  $20\% excess O_2$ ) as a function of the combustion temperature.



FIGURE 4. Distribution of the total PAHs ( $\mu$ g/kg) emitted between solid and gas phases during tire combustion (AFBC, 860 L/h, 20% excess O<sub>2</sub>) as a function of the combustion temperature.

function of the temperature although it is emitted in higher amounts. As happened with the other two compounds, the lowest emissions of BaA and Co are produced at 750  $^{\circ}$ C.

Concerning environmental pollution control, it is important to study how PAHs are distributed between solid and gas phases. The PAHs supported on particulate matter of the first and second cyclone are considered as a solid phase. The PAHs trapped in the system composed of the condenser, the nylon filter, and the XAD-2 resin are considered as gas phase. The representation of the PAH distribution as a function of both phases (Figure 4) shows that both phases have the same profile in PAHs emissions at different combustion temperatures. Between 650 and 750 °C, emissions are practically constant. Upon increasing the temperature to 850 °C, there is a remarkable increase in solid phase emissions. At this temperature, PAH emissions seem to be associated or supported on the particulate matter of cyclones as a consequence of the high flow and the entrainment of particles partially burned corresponding to CB. At the lowest combustion temperature, gas phase contributes the majority to the total PAHs emitted. An important difference between coal and tire combustion emissions is that, with coal, emissions in the gas phase are more prominent. In tire combustion, the solid phase emissions show a higher contribution, especially at 850 °C, a temperature that power stations commonly use. This seems to be due to the nature of the tire and the CB that serves as a support to PAHs formation.

At 850 °C, most of the PAHs emitted are deposited on the particulate matter of the cyclones. In this way, the contami-



FIGURE 5. Distribution of total PAHs ( $\mu$ g/kg) by ring size during tire combustion (AFBC, 860 L/h, 20% excess O<sub>2</sub>) as a function of the combustion temperature.

nation focus can be controlled more easily than if it were emitted as gas phase.

It is also worthy to comment that from the five traps used as the sampling system, biphenyl (Bf) has been detected. This has not been quantified because it is not present in the U.S. EPA list of priority PAH pollutants.

The PAHs distribution by ring size as a function of the combustion temperature is shown in Figure 5. PAHs with three and four rings are the main compounds emitted at all combustion temperatures, especially at the highest temperatures in which the increase of three- and four-ringed polyaromatics is drastic. So, at high temperatures the radicals formed are released and entrained quickly in such way that the recombination and interaction between radicals is less favored, leading to the formation of the most volatile compounds.

In summary, PAH emissions obtained during tire combustion in a fluidized-bed combustion system have been analyzed, and the results are reported and discussed. The nature of the tires seems to promote PAHs formation as compared to coal combustion at the same combustion conditions, showing the importance of the pyrolytic process in PAHs formation and emission. Concerning PAH emissions, 750 °C seems to be the optimum temperature to burn tires in a fluidized-bed reactor.

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