Environmental Pollution Reduction in Cement Industry for Co₂ combustion of Waste Tyre and Coal as a Fuel

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Abstract

In recent years, there are several problems encountered in waste management system particularly waste tyre as well as coals. The energy generation on incineration provides large amount of polycyclic aromatic hydrocarbon (PAH) emissions which is the cause of major environmental threat. Therefore, the combustion of coal and tyre were carried out in cement industry in order to generate heat energy at 1300ºC and the only remaining residue (steel powder) to enhance the strength of the cement. At the outset, the particle size of coal and tyre was cut into 63-75 and 180-212 μm respectively. Combustion experiments were conducted using Nelson reactor under controlled conditions in presence of air and also in presence of nitrogen gas (INOX) atmosphere. The temperature range was varied from 300-1300⁰C and several fuel mass loading in the furnace, expressed in terms of bulk equivalence ratios in the range of 0.7-2.4. At fixed bulk equivalence ratios, as the furnace gas (Air) temperature increased the polycyclic aromatic hydrocarbon yields from both fuels decreased drastically, while the CO_2 yields increased. At the highest temperature around 1300⁰C, the effluent of combustion of both (coal and tyre) fuels was practically devoid of polycyclic aromatic hydrocarbon (PAH) (at a detection limit of 0.3 μg of a PAH component/g of fuel burnt). In order to understand the rate of thermal effect and morphology of co combustion material (coal and tyre), the preliminary results are very essential to explore. Therefore, the thermo gravimetric analysis (TGA) and environmental scanning electron microscopy (ESEM) were carried out and results of coal and tyre mixture at various temperature conditions will be highlighted.

Keywords: Environmental Emission, Cement Industry, Carbon dioxide, polycyclic aromatic hydrocarbon (PAH), Nelson reactor.

INTRODUCTION

Coal is the predominant fuel for power generation in the world. India alone produces 1.5 and consumes approximately 1.0 billion of coal yearly for power generation. Thus, a thorough study of the emissions of coal is warranted. Waste tyres, on the other hand, are generated by the billions every year, with India alone discarding an estimated quarter of a billion tyres, but they are not currently used for energy generation to any significant extent. Instead, they are either land filled or stored in tyre dumps, creating health problems and fire hazards. Because of their high heating value (29-37 MJ/kg, which is higher than most coals), however, waste tyres are being considered as an attractive potential fuel. With an average weight for tyres of 10 kg, a total of 2.5 million ton of tyre-derived fuel can be produced in India per year amounting to 0.5% of the coal consumption. In addition to this amount, more fuel can be deduced from existing tyre stockpiles, and the yearly electric energy production potential from tyres could reach 2% of that from coal.

While pulverized coal is widely used in most utility fired boilers, pulverized rubber from waste tyres is still a costly proposition, mainly because it is made desired smaller sizes using cryogenic processes that are currently used to produce it and the small scale of existing operations. According to certain sources, the current

price of pulverized tyres is currently 3-5 times higher than that of coal (Rs. 9000-15000 vs Rs.3000/ton). This price differential can be bridged, however, if cost effective large scale tyre grinding processes are invented and/ or if higher fees are implemented. First of all, the waste tyre will be grinded after dipping into liquid nitrogen (-196^0C). This will avoid the high cost of building dedicated tyre-to-energy combustion facilities. Therefore the combustion and emissions of both fuels in pulverized form will be examined.

In this study, combustion of waste tyre, coal and tyre-coal blends of 1%, 3% and 6% were investigated by means of Thermogravimetric Analysis (TGA) which was carried out at 100C min-1 in Thermogravimetric Analyzer and in the range from 50^0C to 900^0C i.e. Thermogravimetric Analysis (TG), Derived Thermogravimetric Analysis (DTG) and Differential Thermal Analysis (DTA). For blends of coal and waste tyre, no interactions between blend components are observed in TGs. However, for DTG, comparatively difference was seen that could be related to a certain degree of interaction between the components. The co-combustion of coal and waste tyre cannot be predicted from the weighted sum of the blend components. The incorporation of waste tyre can improve the combustion characteristics of coal, especially the ignition performance and the peak weight loss compared with the separate burning of waste tyre and coal. This indicates that the combustion of waste tyre and coal as fuel is feasible. With this in view, the study attempts to investigate the effect of percentage blending waste tyre with coal.

Six industries have been identified as energy intensive industries globally: Cement, Aluminum, Fertilizer, Iron and Steel, Glass and Paper [1]. Cement industry consumes about 4 GJ per tons energy of cement produced. Indian cement industry accounts for 10.3 % of total fuel consumption in the manufacturing sector [2]. Out of total, about 50% carbon dioxide is generated during calcinations and remaining during the combustion processes [3]. Cement industry had emitted 43 million tCO_2 in 1990 that has increased to 59 million tCO_2 in 1995. In 1995, energy use contributed 40% of total cement sector emissions while the remaining was due to calcinations process [4]. Worrell et al., [5] have carried out an in-depth analysis of the US cement industry. They found that the use of blended fuel is a key cost-effective strategy for energy efficiency improvement and CO_2 emission reductions. Xiang - Guo et al., [15] have performed experiment on combustion of waste tyre, high ash coal and tyre-coal blends with 10, 30 and 50% waste tyre were investigated by means of thermogravimetric analysis (TGA). They found that incorporation of waste tyre can improve the combustion characteristics of high ash coal, especially the ignition performance and the peak weight loss compared with the separate burning of waste tyre and coal. This indicates that the co-combustion of waste tyre and low qualities coal as fuel is feasible. Giere et al., [16] have studied a mixture of 95 wt. % coal plus 5 wt. % Tyre-Derived Fuel (TDF) in the form of shredded automotive tyres by combusting it in a stoker boiler under plant conditions. They found that emissions of CO decreased slightly, whereas those of NO_x, SO_2, and total particulate matter remained virtually unchanged. Katsioti et al., [17] have stated the prerequisites for using of TDF as a supplement fuel for the clinker production. The compressive strength of cement produced was measured. In this specific study 6% of the total fuel used was TDF. It was concluded that no apparent problems occurred from the use of TDF as a supplemental fuel in the clinker burning. Kemm et al., [9] describes a Health Impact Assessment (HIA) of a proposal to change the fuel used in a cement plant. It concludes that there in no change in emission of tyre burning. It was carried out to support a health authority, known as a Primary Care Trust (PCT), in preparing its response to consultation under the Integrated Pollution Prevention and Control (IPPC) process.

EXPERIMENTAL STUDY

Fine powder of tyres was prepared by shredding and grinding of waste tyres. Coal powder was prepared by crushing the coal pellets. The material whose thermal decomposition was studied consists of waste tyre, coal and tyre-coal blends of 1%, 3% and 6%. The percentage of waste tyre refers to weight of coal. Waste tyre and coal was mixed properly. The combustion characteristics of coal, waste tyre and tyre-coal blends were determined in Perkin Elmer TGA 7 Thermogravimetric Analyzer. Sensitivity variation was ± 0.1 μg. The specimen size was approximately 1 to 100 mg. The temperature variation of furnace was from room temperature 25^0C to 1000^0C. The heating rate of sample was varied from 0.1 to 200^0C. The furnace temperature was increased from 50^0C to 900^0C at 10^0C min-1 under Nitrogen atmosphere. Then sample was cooled to room temperature under Nitrogen atmosphere. The weight of sample was monitored continuously as function of temperature. The TG, DTG and DTA were performed.

RESULT AND DISCUSSION

      The analysis results were obtained in the form of plot of temperature vs. weight loss with Heat Flow Endo Down. Figure 1 shows Thermogravimetric Analysis (TG) of Coal, Tyre, and Tyre blended with coal. Figure (1a) shows the typical TG profile of coal with weight loss (~9%) and result of thermal decomposition and loss of volatiles as well as char gasification (hydrocarbon of low molecular weight up to C6). Figure (1b) shows the TG profile of waste tyre. It was found that tyre shows typical TG profile of waste tyre with maximum weight loss (~70%). Figure (1c) shows the TG profile of 1% tyre blended with coal. It shows typical TG profile with maximum weight loss (~8.5 %). Figure (1d) shows the TG profile of 3% tyre blended with coal. It was found that typical TG profile with maximum weight loss (~9%). Figure (1e) shows the TG profile of 6% tyre blended with coal. TG analysis curve showed weight loss was (~11%).

(Fig 1a) Coal

(Fig 1b) Tyre

(Fig 1c) 1% Tyre blended with coal

(Fig 1d) 3% Tyre blended with coal
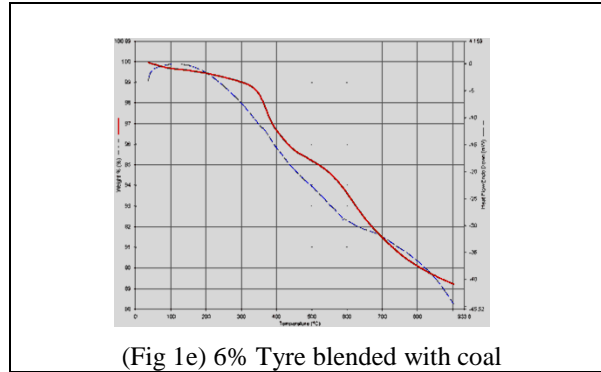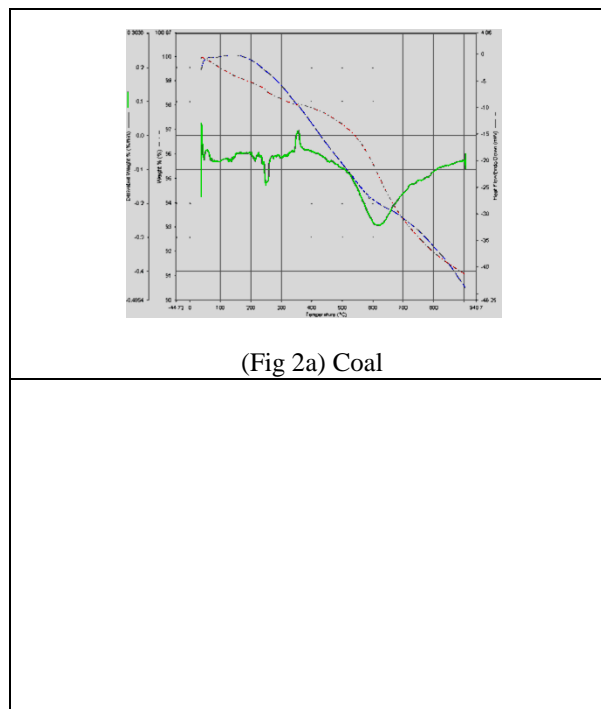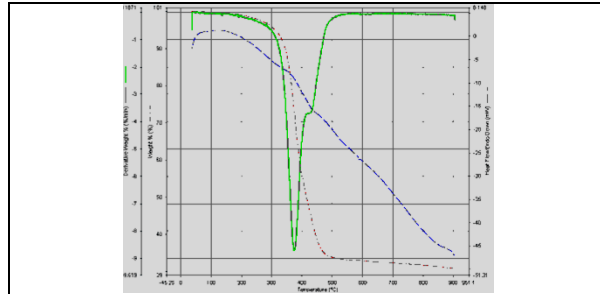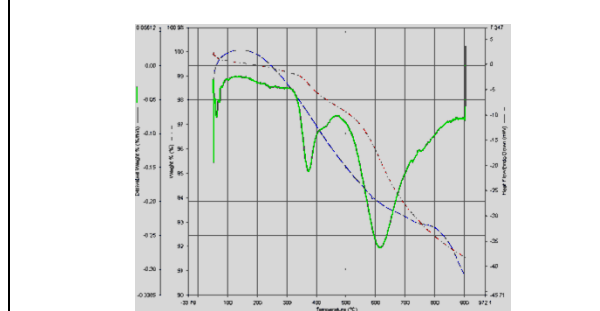
(Fig 1e) 6% Tyre blended with coal
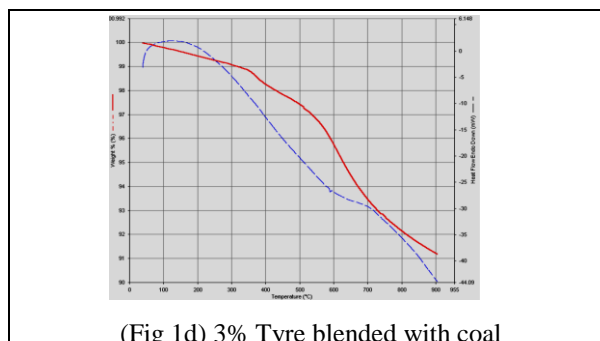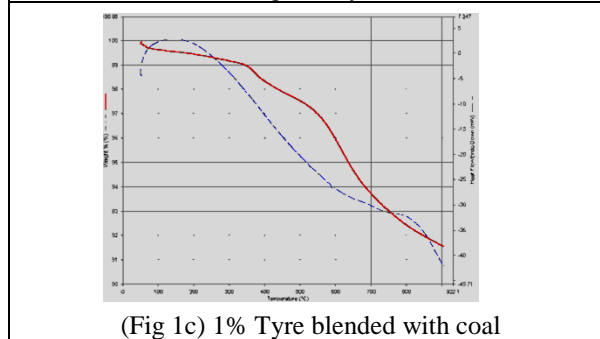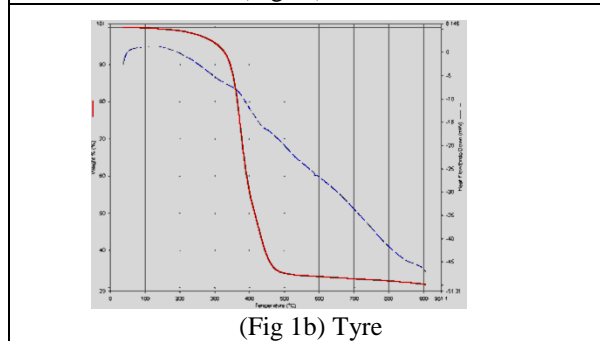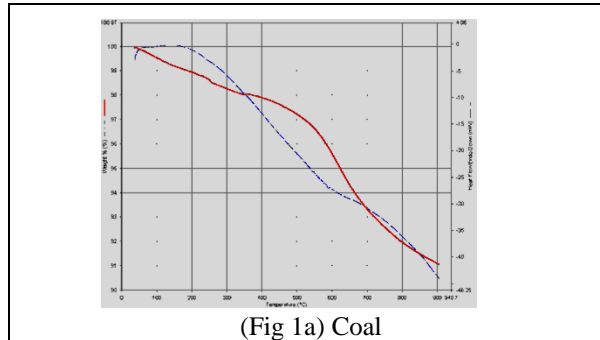
Figure 1 Thermogravimetric Analysis (TG) of Coal, Tyre and Tyre blended with coal

Figure 2 shows Derived Thermogravimetric Analysis (DTG) of Coal, Tyre, and Tyre blended with coal. Figure (2a) shows the DTG analysis of coal. Two distinct peaks were obtained at 250^0C and 630^0C respectively which may be attributed due to volatile product elimination. Figure (2b) shows the DTG analysis of tyre of two stages. The first peak is at 377.87^0C due to the thermal decomposition of the mixture of oils, moisture, plasticizers and other additives. The second peak at 417.87^0C may be attributed due to the thermal decomposition of natural rubber, polybutadiene and polybutadiene – styrene, the main constituents of tyres. Figure (2c) shows the DTG analysis of 1% tyre blended with coal. The weight loss observed at two temperatures 380^0C and 620^0C respectively. Waste tyre at 380^0C showed weight loss (~ 4.8%), where as the pure tyre showed (~ 70%) weight loss and the remaining (~ 30%) was steel. The second peak at 620^0C is due to combustion of coal and (~ 8.5%) weight loss occurred. The weight loss of coal was (~ 7 %) in comparison with the result obtained in the blend (~ 8.5%). The disappearance of the peak at 250^0C occurred in case of 1% blend sample. Figure (2d) shows the DTG analysis of 3% tyre blended with coal. There are two broad peaks appeared at 380^0C and 620^0C respectively. However, the nature of the peaks is broader in comparison with 1% blending. The weight loss was (~ 3.3 %) at 380^0C and (~ 4.5%) at 620^0C respectively. The disappearance of the peak at 250^0C also observed in case of 3% blended sample. Figure (2e) shows the DTG analysis of 6% tyre blended with coal. There are two broad peaks. The peak appeared at 380^0C showed (~ 11.2%) weight loss and the second peak at 620^0C showed (~ 7%) weight loss.
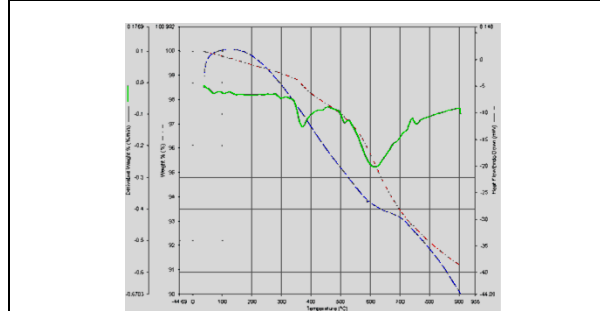

(Fig 2a) Coal

(Fig 2b) Tyre

(Fig 2c) 1% Tyre blended with coal

(Fig 2d) 3% Tyre blended with coal

(Fig 2e) 6% Tyre blended with coal

Figure 2 Derived Thermogravimetric Analysis (DTG) of Coal, Tyre and Tyre blended with coal.

Figure 3 shows Differential Thermal Analysis (DTA) of Coal, Tyre and tyre blended with coal. Figure (3a) shows the DTA analysis of coal. The area under the DTA peak may be related to the heat produced in combustion process that is the high calorific value (HCV). This was the consequence of a greater process of volatile matter in the coal at 250^0C and 630^0C. Figure (3b) shows the DTA analysis of the waste tyre. The result

derived from DTA analysis also showed two peaks at 377.87^{0}C and 417.87^{0}C respectively. Figure (3c) shows the DTA analysis of 1% tyre blended with coal. The result derived from DTA analysis also showed two peaks at 380^{0}C and 620^{0}C respectively. Figure (3d) shows the DTA analysis of 3% tyre blended with coal. The result derived from DTA analysis also showed two peaks at 380^{0}C and 620^{0}C respectively. Figure (3e) shows the DTA analysis of 6% tyre blended with coal. The result derived from DTA analysis also showed two peaks at 380^{0}C and 620^{0}C respectively. The low boiling point organic compounds present in the coal can mix with waste tyre and decomposes at 380^{0}C which is a broader range from 300^{0}C to 400^{0}C.
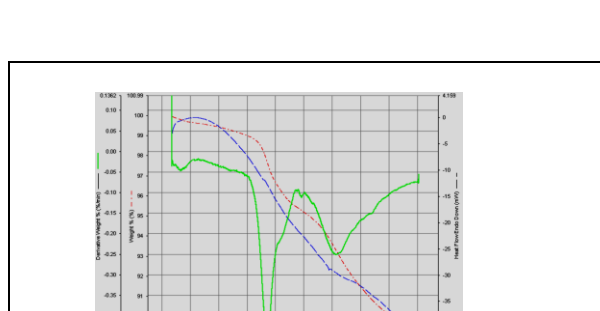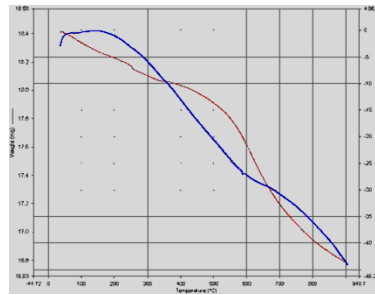
(Fig 3a) Coal

(Fig 3b) Tyre
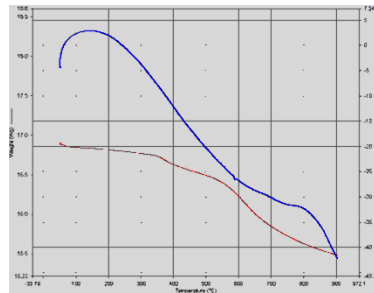
(Fig 3c) 1% Tyre blended with coal

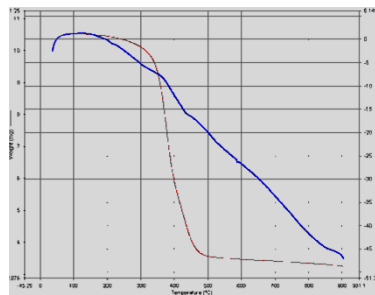(Fig 3d) 3% Tyre blended with coal

(Fig 3e) 6% Tyre blended with coal

Figure 3 Differential Thermal Analysis (DTA) of Coal, Tyre and Tyre blended with coal.

For blends of waste tyre and coal, no interactions between blend components are observed in TGs. However, DTGs indicated that a comparatively important difference can been s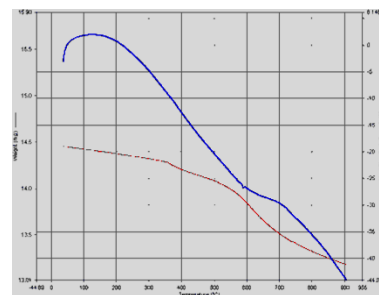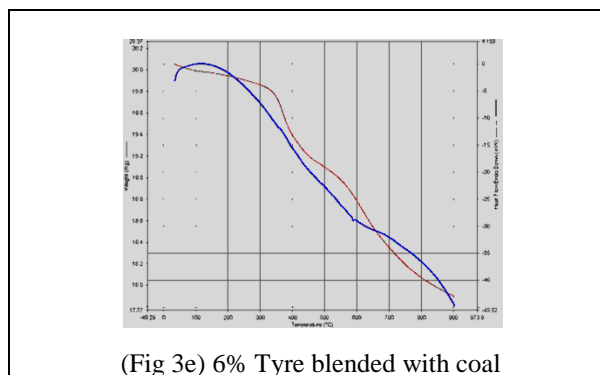een that may be related to a certain degree of interaction between the components. The co-combustion of waste tyre and coal cannot be predicted from the weighted sum of the blend components. The incorporation of waste tyre can improve the combustion efficiency of coal, especially the ignition and the peak weight loss compared with the separate burning of waste tyre and coal, which indicate that the combustion of waste tyre and coal as alternative fuel is feasible in industry.

Combustion Behavior - The combustion characteristics of pulverized coal have been extensively studied, but little has been reported on the combustion of waste tyres. A comparison on the combustion characteristics of single particles (80-200μm) of both fuels was recently conducted in this laboratory, under high heating rates ($10^5\ {}^0C/s$). In this study, separate volatile and char combustion phases were detected for the coal particles examined. Tyre particles experienced an intense primary volatile combustion phase, followed by a phase of secondary evolution and burning of volatiles, of lesser intensity, and simultaneous char combustion. During the initial volatile phase combustion, the peak flame temperatures were comparable for both materials and were in the range of 2200-2400 K at a gas temperature of $1150^0C(1423K)$. The secondary volatile/char combustion phase observed for the tyre particles was cooler i.e.1423K. The coal chars burned even cooler, with surface temperatures of 1850-2000K. Combustion was found to be diffusionally controlled. Char burnout time were much shorter for tyre particles than for coal particles of the same size, which can be attributed to the secondary devolatilization and the lower density of the former.

Combustion Emissions - The most important emissions from the combustion of coal and tyres are the inorganic gases sulphur dioxide(SO_2) and nitrogen oxide (NOx), submicron metal aerosols (fumes), and toxic organic emissions, such as polynuclear aromatic hydrocarbons (PAHs), soot, and carbon monoxide(CO). Of recent concern are also the emissions of carbon dioxide (CO_2).

Polynuclear Aromatic Hydrocarbon Emissions - Work on the toxic organic emissions, volatile organic compounds (VOC), and semivolatile organic compounds (SVOC), a subset of which are the polynuclear aromatic hydrocarbons (PAHs), of coal and especially tyres is limited. While at present, CO_2, CO, and total volatile hydrocarbons can be monitored online by a variety of analyzers, techniques are not available to continuously monitor and quantify individual organic products of incomplete combustion, primarily the PAHs. Investigations are further complicated due to the large number of organic compounds that are formed as a result of incomplete combustion of fuels such as coal, oil, tyres, etc. and the labor-intensive process for their detection. The importance of identification and quantitation of many PAHs arises from the known carcinogenic nature of some of these compounds. For some fuels, such as coal, emitted PAHs may be formed from the combustion reaction. Also, the formation of PAHs is highly dependent on the conditions existing in the vicinity of burning fuel.

The present study was undertaken to assess and compare PAH emissions and CO2 emissions from pulverized coal and waste wire-in-tyre crumb burning under well-controlled conditions. The compositions of fuels were tabulated in Table no 1.

Table 1.Composition of Fuels

Property	Ground tyre (SBR)	Coal
Particle size (µm)	180-212	63-75
Fixed carbon (%)	21.7	51.9
Volatiles (%)	52.3	34.4
Ash (%)	26.0	13.7
Carbon (%)	60.9	71.9
Hydrogen (%)	5.3	4.7
Sulfur (%)	2.46	1.36
Nitrogen (%)	0.28	1.36
Oxygen (%)	7.1	7.0
Heating value(MJ / kg)	29	29.2

The goal was to understand the influence of combustion parameters on toxic emissions. Combustion of clouds of particles (aerosols) of pulverized coal and tyres under steady-state/steady-flow conditions took place in Nelson reactor, in air, at a gas temperature of 1150^0C. Emissions were monitored at various fuel mass flow rates that resulted in overall bulk equivalence ratios that differed widely. Experiments were also conducted under pyrolytic conditions (in an inert gas atmosphere i.e.argon) to simulate a worse-case scenario in a pulverized-fuel furnace, i.e. severe oxygen deficiency. Finally, the above results on the emissions from steady flow combustion of particle clouds were contrasted with those from batch combustion fixed beds of particles in a horizontal muffle furnace. CO_2 and PAH emissions are reported from all runs.

Extraction and Concentration of PAH Emissions - Polynuclear aromatic hydrocarbons (PAHs) were monitored at the exit of the furnace by trapping the particulate (condensed) and gas-phase compounds separately. The sampling stage was placed directly below the furnace to minimize losses. Particles (soot, ash, unburned carbon) were trapped in a bed of Supelco XAD-4 resin. XAD-4 and the filters were precleaned before use. Precleaning was performed by running in Soxhlet apparatus for 12-h periods(twice) using methylene chloride as the solvent, with changing the solvent between the two periods. All glassware was precleaned with a similar procedure before use. The water bath was maintained at approximately 60^0C during the extraction procedure. The resin and the filters were then air-dried before use.

After the experiments were completed, the used resin and the filters were stored in Teflon-lined jars at 0^0C and were extracted separately by Soxhlet extraction for a 24-h period with methylene chloride, at 60^0C. Before extraction, 100µg of naphthalene-d8 was added to the resin as well as to the filter as an internal standard. After extraction, the samples (200 and 300 mL for filter and resin, respectively) were concentrated to a final volume of 10 mL using a Buchi rotavapor, at a rate of 300 mL/h and a bath temperature of 25^0C and, again, stored in Teflon-lined vials at 0^0C before being analyzed by gas chromatography/mass spectrometry (GC/MS) techniques. The product was analyzed by using GC/MS techniques.

Particle Combustion- Combustion of individual particles of coal and tyre rubber was monitored pyrometricaly. Experiments were also conducted for the particle sizes of the present study and typical results are shown in tables 4 and 5. Temperatures were derived based on the gray radiation assumption, i.e., the emissivity was assumed to be independent of the wavelength of observation. The initial hump in each profile corresponds to evolving volatiles burning in envelope flames. The first two cases depict coal particles in the size ranges of 63-75µm and 180-212µm, figure 4 a, b, respectively. The third case depicts a burning tyre particle in the size range of 180-212µm. Maximum flame temperatures reached 2250 K, and char temperatures were 2000 K or below. Overall particle combustion durations were less than one-fourth of a second. It is worth noticing, by contrasting figure 2 b, c, that from similar size coal and tyre particles the combustion of the latter was much

briefer (by a factor of 3), which can be partially attributed to their lower density (0.47 and 1.18 g/cm for tyre and coal, respectively) and to their higher volatile fraction.

Examples of combustion of steady-flow clouds of coal and tyre particles (180-212μm) are shown in Tables 4 and 5. Combustion took place in air at a bulk equivalence ratio Φ around 1.0. Notice the large bright flames during the volatile combustion phase, followed by the dimmer char combustion phase.

Useful data on the post-flame residence times in the furnace are also observed from the length of the particle combustion zone in the furnace can be directly seen. Thus subtracting the ignition and combustion lengths from the total length of the furnace, the length of the post-combustion zone can be measured. Based on the known flow rates, the post-combustion residence times are thus inferred. The particle combustion occurs in the middle height of the furnace: thus, only a fraction of the given nominal residence time is actually available for post-combustion reactions in this particular case (tyre particles 180-212μm). Other cases vary according to the particle type and size, temperature, Φ and adverse conditions (high Φ, low gas temperature, and large particle size) may stretch the combustion zone to the bottom of the furnace. Thus, for all cases reported herein, the actual post-flame residence time of the combustion products was always less than the aforementioned nominal times of 0.75-1.0 s.

NO$_x$, SO$_2$ and CO Emissions- Emissions from the combustion of steady-state/steady-flow clouds of particles (aerosols) in the reactor are listed in Table no.6, under fuel-lean, stoichiometric, and fuel-rich conditions.

Table 6. NO$_x$, SO$_2$ and CO Emissions from Combustion of Steady-State-Flow Groups of Particles in Drop-Tube Furnace at Tg=1150^{0}C

Fuel	Φ	NOx (ppm,mg of NO/ g of fuel, wt % fuel N)	SO$_2$ (ppm,mg of SO^2/ g of fuel, wt % fuel S)	CO (ppm,mg of CO/g of fuel, wt % fuel C)
Coal	0.7	809, 13.0, 35	688, 20.1, 74	0.02, 3, 0.1
	1.0	806, 8.4, 23	754, 16.8, 62	0.05, 5.3, 0.3
	1.5	543, 5.4, 15	875, 18.0, 66	0.68, 62.5, 2.4
tyre	0.6	205, 3.7, 42	916, 34.6, 70	0.01, 1.8, 0.1
	1.0	302, 3.6, 43	1340, 35.0, 71	0.07, 8.9, 0.6
	1.8	177, 1.3, 15	1940, 31.4, 64	0.85, 59.9, 4.2

The reported equivalence ratio corresponds to an overall bulk condition of the particle clouds. While knowledge of such a bulk is of little consequence for characterizing local conditions inside and outside diffusion envelope particle flames during the combustion of volatiles, it becomes meaningful for the char combustion phase as well as useful in assessing the availability of oxygen in the post-combustion zone. The entries in Table 6 represent the emissions in partial pressures in the effluent gas as well as in milligram per gram of fuel burned, i.e., after the combustion efficiency was accounted for. Thus.

$$m_{fuelburned} = \eta_f [(m_{fuel\ supplied} - m_{ash}) \eta_{combustion} + m_{ash}] - (1)$$

Where η$_f$ is the fluidization efficiency, which accounts for particle losses in the delivery tubing (set equal to 95%), η$_{combustion}$ was measured from ashing of the solid residue collected at the bottom of the furnace.

NO$_x$(NO+NO$_2$) emissions of tyre were much lower than those of coal (by a factor of 3), reflecting their lower nitrogen content. The nitrogen content of the tyre crumb burned herein is equal to a typical average nitrogen content of tyres, i.e., 0.29%. As the equivalence ratio increased, the partial pressure of NO$_x$ initially increased because of higher fuel loading and then decreased as stoichiometry was approached or exceeded because of limited oxygen availability. When these results were expressed in (mg of NO)/(g of fuel burned), the emissions dropped drastically with Φ throughout the range examined (for these calculations all NO$_x$ was expressed as NO since this is the predominant component. This trend indeed shows that at the conditions of the primary fuel-rich region of low-NO$_x$ burners the formation of NO$_x$ is suppressed. The last entry of this column lists the percentage of the parent nitrogen that was converted to NO$_x$. This calculation was made with the assumption that roughly 80% and 70% of the detected NO$_x$ originated from the fuel nitrogen content of the coal and tyre, respectively. Based on these assumptions and the values shown in Table 4, an elemental closure on fuel nitrogen was performed. Thus, for coal at Φ values of 0.8 and 1, 35% and 23% respectively, of the fuel nitrogen was converted to NO$_x$, which is comparable to what other investigators reported. At a Φ of 1.5, this value dropped to 15%. Most of the remaining fuel nitrogen is expected to have converted to N$_2$(4), even if some

of the intermediate species (HCN, NH$_3$) may still be present. For tyres, the calculations show that a higher fraction of the fuel nitrogen is converted to NO$_x$ than in the case of coal. This may be partly attributed to the fact that most of the combustible mass of tyre particles is volatile and burns in diffusion flames at high temperature and with adequate supplies of oxygen, hence, forming NO. To the contrary, most of the mass of coal is fixed carbon and burns heterogeneously in the diffusion-controlled regime III, i.e., at very low surface oxygen concentration and minimal penetration in the pores. Thus, the reducing atmosphere inside the chars favors the formation of N$_2$ instead of NO(4).

Combustion of this particular batch of tyre crumb generated higher SO$_2$ emissions than the bituminous coal examined. This is not surprising since the SO$_2$ emissions are proportional to the sulfur content of fuels, and this tyre sample contained 1.8 times more sulfur than coal (see Table 4). This is unusual however since the average sulfur content of tyres is 1.57% (38). Indeed, another sample obtained from the same supplier contained 1.7% sulfur (22, 49). The partial pressure of SO$_2$ in the effluent increased with the equivalence ratio because of the higher fuel loading in the combustion chamber. However, the specific SO$_2$ emissions in (mg of SO$_2$)/(g of fuel burned) showed little variation with the equivalence ratio, indicating only a mild dependence on the oxygen concentration. An elemental balance on the sulfur shows that most of the sulfur converted to SO$_2$. A total of 5-6% of the initial sulfur content of tyre crumb was found in the ash. Other species, such as Hydrogen sulphide (H$_2$S), elemental Sulpher, Sulpher dioxide, etc. may account for the difference.

CO emissions from tyre and coal were rather low (0.01-0.02 mol%), in the fuel-lean region (Φ=0.6-0.7) (see Table 7). The corresponding combustion efficiencies as deduced from ashing experiments (48) were 98% and 99% for tyre and coal, respectively. This signifies that a small percentage of the carbon content in the fuel was converted to CO (see Table 7) because of oxygen deficiency.

Gas-Phase PAH Emissions-The predominant PAHs (EPA List) that were detected in both the gas-phase effluent (on XAD-4) and in the solid phase (on filters) during combustion/pyrolysis experiments with pulverized coal and tyre, are listed in Tables 5 and 6. Results from combustion experiments steady-flow clouds of particles in the vertical furnace (VF), at values ranging from 0.1 to 5, in air are included. Results from batch experiments, involving combustion of fixed beds of particles in air, in the horizontal furnace (HF) are also included. In this section, specific PAH emissions are expressed per mass of fuel introduced in the furnace and not per mass fuel actually burned, as was done earlier for the cases shown in Table 4. The main reason for this difference is that ashing experiments could not be performed herein to obtain the combustion efficiency, since the residue was used for Soxhlet extraction.

A review of the gas-phase PAH yields (i.e., the emissions trapped in the XAD-4 resin) from the experiments involving steady-state combustion of clouds of particles (aerosols) in the vertical drop-tube furnace reveals the following;

Pyrolysis- Under pyrolytic conditions in N$_2$ at Tg=1150°C and a gas residence time of 0.75s, both fuels emitted the highest total amounts of PAHs as well as the highest amount of most individual PAHs (see Tables 5 & 6). Individual PAH emissions from pulverized tyres exceeded those of coal typically by a factor of 1.6-3.6, with benzo(*ghi*)flouranthene emitted 11 times more (see Table 8). The total amount of PAHs emitted per gram of coal fed was 7.58 mg, while that emitted per gram of tyre crumb was 22.26 mg. Thus, cumulative PAH emissions from the pylorysis of pulverized tyres exceeded those of pulverized coal by a factor of 3. The larger four-ring structures of pyrene and the five-ring structures, such asperylene, are likely to be flash-vaporized from the surface of coal/tyre and survive the pyrolysis process.

Combustion- When at the same temperature and gas residence time as above, oxygen was introduced in the furnace to achieve an overall Φ in the vicinity of 5, i.e., extremely fuel-rich conditions, the concentration of most PAHs was reduced. For coal, a few of the PAHs, such as flouranthene, pyrene, and cyclopental pyrene, showed an increase in concentration (by a factor of 2) when oxygen was introduced, but most PAHs decreased, and the total amounts were 7.58 mg/(g of coal) in N$_2$ and 6.39 mg/(g of coal) in ther presence of O$_2$ at Φ=4.6(see Table 5).

Table no.5 Relative Gas-Phase Emissions (Tire/ Coal) of selected PAHs

PAH	Pyrolysis N_2 ,VF	aerosol Comb .air, VF		fixed bed comb,air,HF, air,HF
phenanthrene	3.6	2.3	3.2	27
pyrene	1.6	0.9	1.3	13.6
fluoranthene	1.7	0.9	1.5	9.4
acephenanthrylene	2.3	0.8	1.5	9.4
Benzo[*ghi*]fluoranthene	10.8	0.8	2	>45
Cyclopenta[*cd*]pyrene	1.8	0.6	2.1	>117
Benzol[*a*]pyrene	3	2	-	>27

For tyre, the concentration of nearly all PAH componenets was reduced in the presence of oxygen, and the total amounts were 22.26 mg/(g of tyre) in N_2 and 7.17 mg/ (g of tyre) at Φ=5.0 (see Table 6). When more oxygen was introduced and Φ was reduced in the neighbourhood of 2, the concentrations of PAHs were further reduced by as much as an order of magnitude. For example, at Φ=2.3, the total PAH emissions were 1.82 mg/g for tyre and 0.72 mg/g for coal. When additional oxygen was introduced, the PAH emissions diminished. For coal, PAHs emissions were hardly detected at equivalence ratios below Φ1.8 (with the exception of naphthalene). For tyre crumb, PAHs could not be detected at Φ< 0.6. Morever, only small amounts of a limited number of PAHs (naphthalene, acenapthylene, phenanthrene, flouranthene, and pyrene) were present in the effluent of tyre crumb in the vicinity of the stoichiometric point. These trends are shown in Tables 5 and 6) The fact that PAHs were not present in the effluent of burning fuel-lean and stoichiometric aerosols of coal is in agreement with results reported by Longwell concerning nonquenched, premixed flames of hydrocarbon fuels at Φ <=1.

It is interesting to note that while PAH emissions from combustion of tyre crumb commenced at a lower than coal, at severely fuel-rich conditions PAH emissions from both fuels were comparable. This was not the case, however, for batch combustion of fixed beds of particles in the horizontal furnace (HF). Even if the sample size therein was small, 0.75 g of powder, PAH emissions from coal and tyre were drastically different. The total as well as the individual PAH amounts from tyres were substantially lower than those emitted under pyrolytic conditions and were somewhat lower than those emitted from steady flow combustion of aerosols at Φ=5. Batch combustion of coal produced rather low PAH concentrations, comparable to the combustion of its aerosol at Φ≈2.4. While the emissions from the steady-flow combustion in the vertical furnace and the batch combustion in the horizontal furnace are not exactly comparable, because the mixing conditions in the latter are ill-defined, an overall trend becomes obvious. PAH emissions from the fixed bed combustion of tyres were 1-2 orders of magnitude more severe than those of coal under identical conditions. Generally, the types of PAHs produced from the batch combustion of fixed beds as well as pyrolysis and combustion of clouds of particles varied only in their amounts, but rarely varied in identity.

From the above discussion, it can be concluded that the toxic organic emissions of both fuels are strong functions of the equivalence ratio; in fuel-lean mixtures, PAHs can be effectively destroyed in the combustion and post-flame zones. In fuel-rich mixtures, the emission of PAHs rapidly increases with Φ and eventually plateaus, asymptotically approaching the emissions under pyrolytic conditions. The onset of significant PAH concentrations with increasing occurs at substantially higher for coal (Φ =1.5-1.8) than for tyre crumb (Φ=0.6-0.8). The sample size and mixing with air also appeared to be extremely important for tyre, but much less so for coal. Tyres appeared to burn much "cleaner" when pulverized and injected in a furnace than when combusted in fixed beds (containing either multilayers of small particles or larger chunks) (see Table 6). The mode of burning of coal (fixed beds vs particle clouds) did not appear to influence PAH emissions of coal as much as those of tyre (see Table 5). Hence, dry-injection and combustion of tyres in pulverized form, if possible, is recommended. This is in complete agreement with the combustion observations outlined earlier and discussed in ref 4. Combustion of large pieces of tyres or fixed beds of tyre particles generated copious quantities of acrid smoke. To the contrary, no smoke was detected to escape the envelope flame around individual tyre particles (up to a size of 220 μm examined herein) or to remain in the furnace upon extinction of the volatile flame (4) in contrast to the case of burning polystyrene particles. This different combustion behavior of tyres and coal (i.e., bulk combustion vs aerosol) may be explained on the basis of the large volatile content of tyres. For the specific fuels examined herein, tyre contained almost twice as much volatile mass per unit weight than coal. Thus, the resulting higher volatile fluxes from tyre samples readily created diffusion-limited and locally pyrolytic conditions that favored the generation of condensed species, such as PAHs and soot.

Furthermore, TGA experiments reported in the literature revealed that evolution of volatiles from tyre commences at lower temperatures (200^0C) than from coal (300^0C). Hence, tyre pyrolysis may happen more readily, enhancing the formation of PAHs.

A few additional comments concerning the emissions of gas-phase PAHs from coal and tyre are as follows; benzo(*a*)pyrene, cyclopental(*cd*) pyrene, and fllouranthene, among others, are known to exhibit high mutagenic activities. Within the same sample, the following were found: (a) The concentrations of naphthalene and acenaphthylene were comparable, with the latter assuming lesser values, in agreement with results reported by Longwell for premixed flames.(b) The concentrations of phenanthrene, fluorathene, and pyrene were comparable to each other and were less than that of naphthalene. The striking analogy of concentrations of the isomers of pyrene and fluoranthene ($C_{16}H_{10}$) has also been reported by Longwell for toluene and acytelene flat flames as well as diesel engines and gasoline engines; however, absolute concentrations varied widely among the different fuels. (c) The concentration of cylopental pyrene was lower, by up to a factor of 2, than that of pyrene, except in the case of batch combustion of coal. (d) The concentration of benzo(*a*)pyrene was lower than cyclopental(*cd*)pyrene by an additional factor of 5. Given the completely different nature of the fuels herein as well as those discussed by Longwell, such similarities are notable and may indicate PAH growth by a similar mechanism.

Relationship of Φ to Gas-Phase PAH Emissions- In the steady-flow aerosol combustion in the VF, the equivalence ratio Φ was varied at a constant gas temperature of 1150^0C. At Φ of 1.0, small amounts of PAHs were detected from the combustion of pulverized tyre and even less from that of coal. As Φ was reduced, increasingly smaller amounts of PAHs were detected until a Φ value of 0.6, after which point no PAHs were detected from either fuel. Thus, PAH production exhibited an asymptotic behavior as approached zero. At Φ values greater than 1.0, the amount of PAHs detected increased exponentially with Φ. However, since at the most extreme fuel-rich conditions explored herein (Φ =5), the amounts of PAHs detected approached those emitted under pyrolytic conditions in N_2 (Φ of effectively ∞), it was assumed that an asymptotic maximum was reached thereafter. This suggests that when Φ→ ∞, at a given gas temperature, modest variations in Φ will cause insignificant changes in the amount of PAHs produced. The onset of the exponential relationship between Φ and the level of PAHs detected appears to be a function of the nature of the fuel being burned. Thus, the following sigmoidal relationship was established between Φ and the levels of specific as well as total PAH emissions at a given gas temperature;

$$[PAH] = c \times \left(\frac{1}{1+ e^{\left(\frac{a}{\Phi}\right)-b\Phi}} \right) \text{ -- (2)}$$

Where a represents a constant that influences the slope of the exponential relationship; b influences the range over which small changes in Φ represent little or no change in the amount of PAH produced; and c represents the largest amount of PAH observed. This equation suggests that as Φ→ 0 or when Φ→ ∞ modest variations in Φ will have little or no effect on the amount of PAHs produced, while throughout the remainder of the range of Φ values the level of PAHs produced will vary exponentially with Φ.

The total amounts of gas-phase PAHs as well as those for pyrene, phenenthrene, cyclopental pyrene, and benzo(a)pyrene were depicted in Tables 5 and 6. At low values of Φ , very small amounts (if any) of PAHs are observed for either fuel. At Φ higher than stoichiometry an exponential behavior is observed and the PAH emissions increase rapidly with small increases in Φ . While PAH emissions for values of Φ larger than 5 were not examined, it is presumed that an asymptotic relationship between PAH emissions and Φ will result. Again, this was suggested because the detected amounts of PAHs at Φ=5 were in the vicinity of those detected under pyrolytic conditions in N_2 (at an equivalent Φ of ∞).

Condensed-Phase PAH Emissions- The above discussion pertains to the gas-phase PAH emissions that were adsorbed on XAD-4. Condensed-phase PAHs are listed in Tables 6 and 7.These are PAHs extracted from material collected on the filters, i.e., soot, unburned carbon, and ash. Solid-phase PAHs wre only detected at fuel-rich conditions for both fuels, where combustion efficiencies are expected to be less than 80%. Hence, not all the amounts detected were generated during combustion/pyrolysis, but some may have been extracts of indigenous PAHs in the unburned fuel. It should be noted that more solid-phase PAHs were detected under severely fuel-rich conditions than under purely pyrolytic conditions in N_2.

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