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Determination of the initial exothermic reaction of shredded tyres with wire content

This paper presents the cause of exothermic reactions in shredded tyre with exposed wire content in shredded tyre piles. Data indicate that the oxidation of exposed steel wires is the exothermic reaction in shredded tyre embankments. This would lead to spontaneous combustion. Reaction of the steel with the sulphur or the carbon black appears not to be the source of the exothermic. Laboratory tests have been conducted to determine the heat transfer properties of the materials that compose tyres (i.e., tyre rubber and wires) by using a hot-plate apparatus. In addition, one-dimensional heat conduction experiments were conducted to compare the flow of heat through the materials while varying the physical and environmental conditions. The physical conditions were the size of tyre shred, water content, and wire contents. An exothermic reaction occurred when exposed wire was present but not when it was absent. A one-dimensional heat transfer equation was developed, and parametric studies were conducted to verify the laboratory model. Exothermic reaction was found to increase linearly with temperature, size and shape of the shredded tyres, density, amount of wire in shredded tyres, and water content.

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Introduction

Since 1988, more than 70 tyre shred fills, with a thickness of less than 1 m, and an additional ten fills with a thickness of 4 m, have been constructed. In 1995, three fills with a thickness over 8-m experienced catastrophic internal heating reactions. Roadways utilizing tyre fills spontaneously heated and started fires. These fires created fear among the engineering community, and resulted in a drop in the use of recycled tyres (Humphrey, 1996).

Tyres have a low combustion temperature and contain flammable materials that make stockpiled tyres a serious fire hazard (Freakley & Payne 1978). Spontaneous heating reactions can occur in scrap tyre fills leading to fires which are hard to extinguish and which release hydrocarbons and other toxic materials into the air, soil and groundwater systems (Frank & Blackham 1952). The low thermal conductivity of the shredded tyres and their lightweight are good for insulating purposes behind backfills and for construction of embankments, respectively. However, there is the problem of spontaneous combustion. As a result of this problem, our research was performed to find out the cause(s) of fires in shredded tyre embankments.

Much research about shredded tyres has been done on engineering properties, but not on spontaneous combustion (Ahmed and Lovell 1992, Tweedie *et al.* 1996, Oshaugnessy 1997). However, our research particularly dealt with the causes of internal heating in a shredded tyre embankment.

To accomplish this objective, a one-dimensional hot plate apparatus was utilized in the laboratory. A hot plate is the most precise method for determining the initial exothermic reaction at various temperature gradients, and was adopted

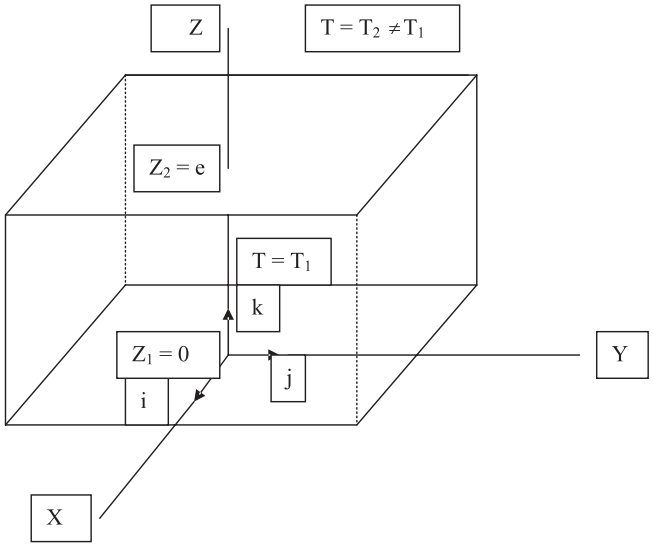

Fig. 1: One-dimensional heat flow.

by the American Society for Testing and Materials (ASTM, 1992; Ad Hoc Civil Engineering Committee, 1997).

In these experiments, spontaneous heating occurred when the shredded tyre with wire reacted with oxygen from the air. The reaction is known as oxidation, and results in the evolution of heat. Chemical oxidation requires a continued supply of oxygen to proliferate, but it can advance slowly even under some low oxygen conditions.

During the experiments, which were run at various temperatures, the temperature increment was continuous until an initial exothermic reaction occurred and the time was noted for that initial exothermic reaction. This procedure was repeated through five increasing temperatures until the initial exothermic reaction occurred. All the points for the initial exothermic reaction were plotted and an equation was obtained by using a computer program, SIGMA PLOT (SPSS Inc., Chicago, IC), to utilize in the 'real world' (equation 9).

A specific time and temperature are needed to initiate an initial exothermic reaction in a shredded tyre embankment (Frank & Blackham 1952). Our investigation was focused on how an initial exothermic reaction varied in shredded tyre and wire embankments at various temperature and time. After running the tests on shredded tyres with varied wire content, the laboratory results were compared with Fourier's unsteady state equation (Carslaw & Jaeger 1959, Thomas 1992) as an approximation for comparison, and the exact solutions from which parameters are derived to verify the model to utilize in the field.

An unsteady state Fourier equation was calculated at various wattage values and the energy change for the standard-state combustion reaction was recorded, at the chosen reference temperature, to get an approximate value for comparison purposes.

Utilizing boundary conditions as shown below the following experiments were performed (as shown in Figs 1 and 2)

$$\begin{aligned}\phi &= -k \operatorname{grad} T. \text{ (Heat flux density} \\ &= -\text{ thermal conductivity } \times \Delta T \end{aligned} \quad (1)$$

with

$$\begin{aligned} z_1 &= 0, T(0) = T_1 \\ z_2 &= e, T(e) = T_2 \neq T_1 \\ (\delta T_1/\delta t) &= (\delta T_2/\delta t) = 0 \\ \delta T/(\delta z) &= \text{constant} \end{aligned}$$

The thermal field boundary condition in the scrap tyres is:

$$T(z) = \left(\frac{T_2 - T_1}{e} \times z\right) + T_1. \quad (2)$$

The proportionality constant is the thermal conductivity k of the medium at point under consideration, e and z are distances from hot plate as shown in Fig. 1. The hot plate method works in a given boundary condition to ensure a unidirectional heat flow, through a material sample of finite size.

When a constant power (W) per unit length is supplied to the heater, the temperature rise T degrees after time t at a distance of z from the heater source in an infinite extent was given by Carslaw and Jaeger (1959). Determination of temperature at any point of the shredded tyre pile at a given heat input is calculated.

The equation from Carslaw and Jaeger was plotted and later on computed with the experimental data. The plotted curve was computed with both the exact solution's curve and the experimental data (see Figs 7 and 8) at 91 and 108 W, respectively.

Materials and method

Figure 1 shows a one-dimensional heat flow, the boundary conditions and the thermal field in the scrap tyres. A hot plate apparatus was used in the study (Fig. 2). Requirements for a steady-state one-dimensional heat flow are described in the American Society for Testing and Materials (ASTM, 1992; Ad Hoc Civil Engineering Committee, 1997). In order to achieve steady-state conditions and a one-dimensional heat flow, a hot surface assembly inside an insulator was utilized. Type 'T' thermocouples measure the temperature of both the plate and specimen.

The heat conductivity of the specimen and the initial exothermic reaction were calculated from measured temperature differences of hot and cold plates and the temperature at the given point, thickness of the specimen, and measured electrical heat input to the hot plate. Shredded tyres without exposed wires and with wire contents were used in the experiment. Ethylene-diamine tetra acid (EDTA) was used to clean the corroded steel wire.

Two ceramic wool fibre layers, with thermal conductivity 0.0008 W (m °C-cm)$^{-1}$, inner 7.62 cm thick and outer 5.08 cm

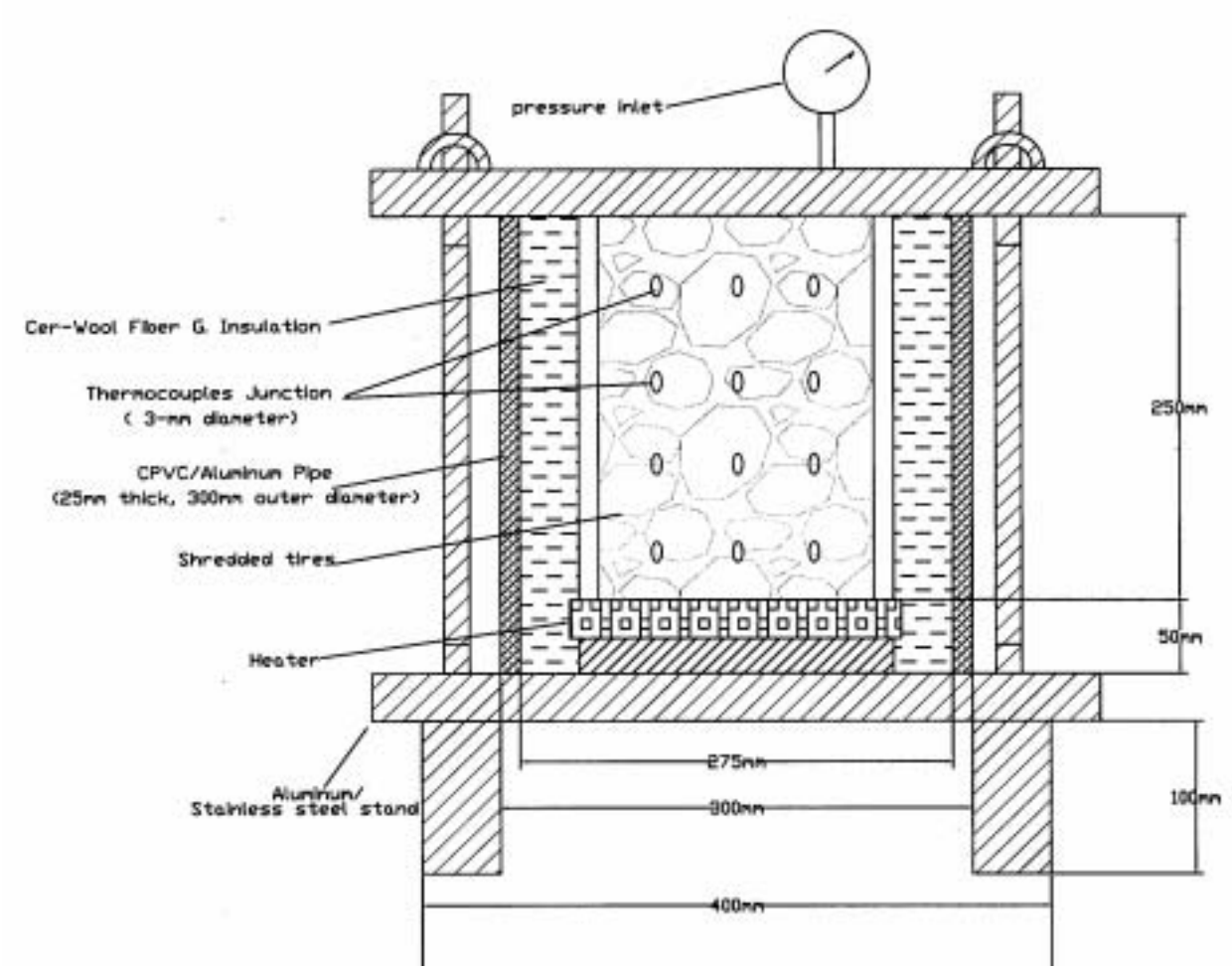

Fig. 2: Cross-section of hot plate apparatus.

thick was utilized all around the container as an insulator (Fig. 2). A wattmeter was used to measure the power supplied to the hot plate. The power supply was varied and the time period and the temperature for the initial exothermic reaction that occurred was noted. After running four or more tests, a curve was constructed to obtain an equation to be utilized for the 'real world' in the field. The data obtained from the experiments were also compared with Fourier's unsteady state equation and the exact solution equation. From the estimated equation, which was fitted with the experimental data, the parameters: thermal diffusivity, *a*; and heat coefficient, *H*; were determined. An ammeter and a voltmeter were used to measure the current and the voltage, respectively. The container (Fig. 2) was an aluminium pipe 30.48 cm high and 30.48 cm in diameter. Atmospheric air was supplied by an air pump. An air controller limited the amount of air supply to 4 psi air (gauge). Leakage was minimal. When exposed to the air, the shredded tyres with certain minimum wire content oxidized at some critical temperature with the evolution of heat.

A reaction of sulphur in the rubber with the iron was considered. As there is much more sulphur than oxygen in the total sample we believe that the primary oxidant is oxygen because there was no exothermic reaction at low air pressure. This will be discussed later.

The electrolytic reaction for corrosion of iron is:

$$\text{Anodic:} \quad Fe \rightarrow Fe^{2+} + 2e^{-}. \tag{3}$$

The excess electrons are consumed at cathodic sites as follows:

$$\text{Catodic:} \quad \frac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-} \tag{4}$$

At neutral pH and under aerobic conditions, Fe^{2+} spontaneously oxidizes as follows:

$$Fe^{2+} + \frac{1}{4}O_2 + H^{+} \rightarrow Fe^{3+} + \frac{1}{2}H_2O \tag{5}$$

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_3 \tag{6}$$

The net of the above reaction is

$$4Fe + 3O_3 + 6H_2O \rightarrow 4Fe(OH)_3 \tag{7}$$

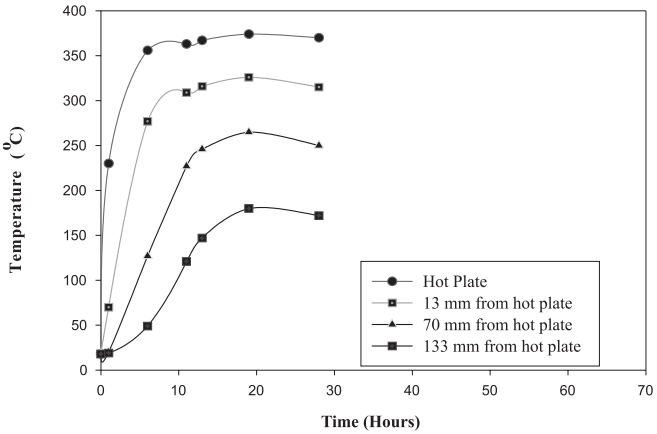

Fig. 3: Temperature versus time curve with no wire, 120 W and 4 psi. (no exothermic reaction occurred).

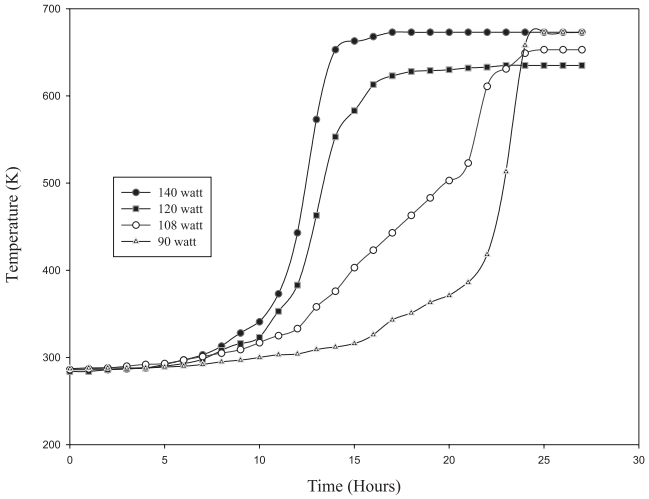

Fig. 4: Temperature versus time curve for shredded tyres (3% wire) at 91, 108, 120 and 140 W at a height 133 mm from hot plate.

Analysis of statistical data

Goodness of fit for the linear values were evaluated using the coefficient of determination (r^2), defined below.

$$r^2 = 1 - \frac{\sum (T_f - T)^2}{\sum (T - T_m)^2} \quad (8)$$

where T_f is the fitted temperature (K), T is the observed temperature (K), T_m is the mean observed temperature (K).

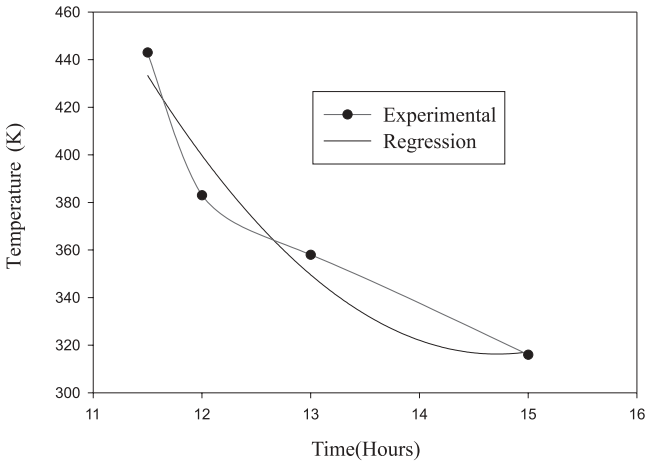

Fig. 5: Temperature versus time curve, experimental calculated onset of exothermic (obtained from Fig. 4) for shredded tyres (3% wire) at 91, 108, 120 and 140 W at a height of 133 mm from hot plate

Results

Experimental

Laboratory test results showed the time and temperature for the initial exothermic reaction of the shredded tyres with wire content under various conditions. The process took several hours as shown in the figures and discussed in the discussion section later. The data showed that the rate of the oxidation reaction increased with the temperature.

Figure 3, which was run with no wire, showed no spontaneous combustion. It also showed that the thermocouple at 13.33 cm above the hot plate was the most sensitive and our results are reported at this distance.

Four tests for each material were run in the hot plate apparatus and thermocouple measurements were taken at four power levels as shown in Fig. 4. Each experiment began by taking readings at hourly intervals until a subsequent rate increase in temperature showed that an exothermic reaction was occurring. The exothermic heat of a chemical reaction can quickly heat the surrounding volume to a very high temperature. As temperature increases, the rate of chemical reactions was shown to increase as well. Thus, once an exothermic reaction begins, it can quickly 'run away' by accelerating its rate because of the heat produced. In this particular experiment, the input energy rate is measured directly by a wattmeter. At 91 W, an initial exothermic reaction started after a period of 15 h and at a temperature of 43 °C (316 K), with 108 W after 13 h at a temperature of 85 °C (358 K), with 140 W after a period of 11.5 h and at a temperature of 110 °C (383 K), and with 140 W after 11 h and at a temperature of 170 °C (443 K), respectively (Fig. 5). The end of the reaction period at t_e = 24 h was found from the thermocouple reading and was calculated empirically. The criteria being that $t_e + \Delta t_{ex}$ became constant for $t > t_e$.

Figure 5, is a representation of the starting initial exothermic reaction obtained from Fig. 4 compared with a regression curve from which an equation and its parameters were obtained from a SIGMA PLOT computer program, equations (9) and (10).

Figure 6 compares the calculated heat content for the 120 W experiment with the standard heat of CO_2 from oxidation of carbon. Note the lack of relationship, thus the spontaneous exothermic reaction appears to be due to another reaction. In this study, the reaction is due to the

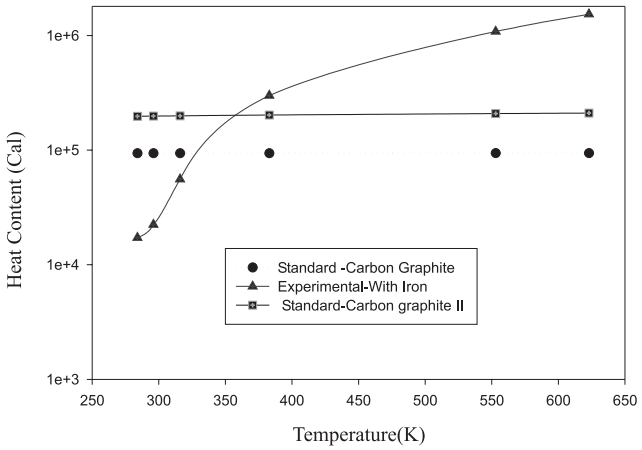

Fig. 6: Comparison between standard heat of formation and experimental values at 120 W.

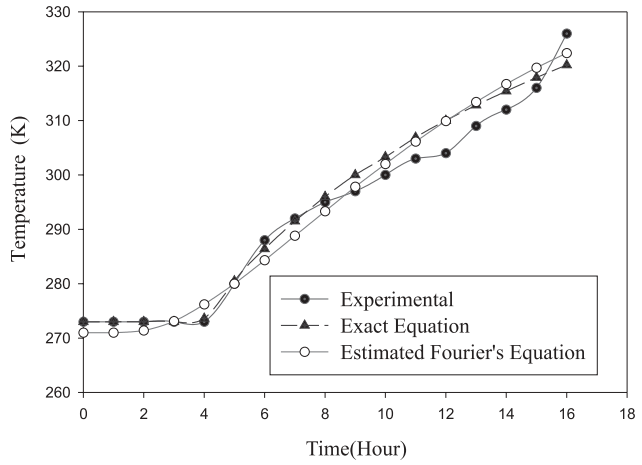

Fig. 7: Comparisons between the experimental value (3% wire), estimated Fourier equation and exact equation at 91 W.

exposed wire in a shredded tyre as shown by comparing Figs 3 and 4. The temperature versus time curve was plotted as a power versus time curve by calibrating the power supply to the thermocouple reading at corresponding power and temperature. By integration of the power versus time curve, the heat content versus temperature was calculated and is shown in Table 1. Furthermore, the standard heat of formation of CO_2 was calculated at varying temperatures (equation (11)) and plotted in Fig. 6.

Figures 7 and 8 compare the experimental values, Fourier's equation, and an exact solution plotted at 91 W (Fig. 7) and 108 W (Fig. 8), respectively. Statistical analyses were performed for both curves. Goodness of fits for the linear value was evaluated using the coefficient of determination (r^2). The correlation coefficients, r^2 values for 91 and 108 W were 0.966 and 0.91, respectively. (Note: as wattage increased the correlation declined). The curve was plotted until it fitted both the unsteady Fourier equation and the exact solutions. The heat transfer coefficient and the diffusivity of a shredded tyre were also found empirically from the fitted curve of the equation.

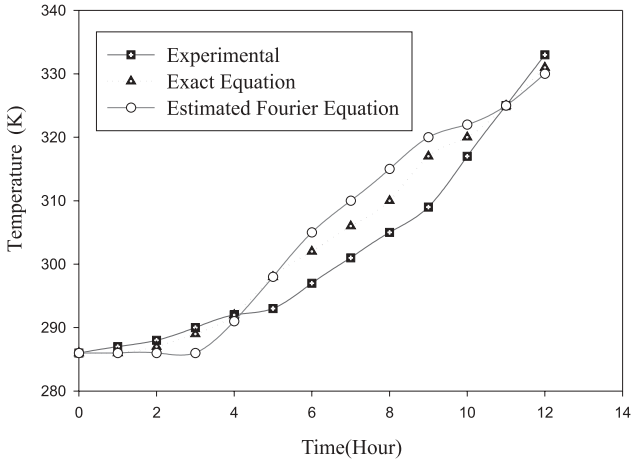

Fig. 8: Comparisons between the experimental value (3% wire), estimated Fourier equation and exact equation at 108 W.

Table 1: Experimental heat of formation with iron content.

Time (h)	Power (W)	Temperature (°C) (K)	Energy (W-h)	Energy Q (Calorie)
1	2	11 (284)	2	–1721
6.5	4	23 (296)	26	–22371
9	7.2	43 (316)	64.8	– 55755
12	29	110 (383)	348	–299426
14	90	280 (553)	1260	–1084130
17	105	350 (623)	1785	–1535851

The result showed that in insufficient air supply, there was no initial exothermic reaction. The air supply was then increased incrementally from 1 up to 4 psi. No reaction occurred until 4 psi.

We believe that the initial exotherm was due to oxidation rather than the formation of FeS. As stated above, at low air pressure there was no exotherm. It is most likely that the sulphur is immobilized and in a low energy state in the vulcanization process and considerable endothermic energy would be needed to free the bonded sulphur.

Discussion

The initial exothermic reaction only was noticed when the air supply was at least 4 psi. To prevent the fire hazard in a shredded tyre pile, the embankment should be well sealed to avoid the penetration of air and water. The results showed (Figs 3 and 4) that the cause of the problem for the initial exothermic reaction was the exposed wire in the shred. Before utilizing the shredded tyre for embankment construction, exposed wire should be removed, otherwise the use of fresh shredded tyre material for embankment construction should be avoided. In the case of larger shred size, the possibility for initial exothermic reaction was minimized. These

tests were done on 50, 100 and 150 mm shred sizes. The laboratory test results were compared with the exact solutions and a standard heat of formation. In the case of standard heat of formation, the comparison was made to get the approximation value, as a standard heat of formation is only temperature dependent.

At various temperature gradients, the reaction period and temperature value for the initial exothermic reaction of the shredded tyres was noted and compared to a Fourier equation for an approximation comparison and standard heat of formation. Increased temperature accelerates the rate of oxygen absorption and results in further temperature increase. The process continued and the temperature of the tyre shred gradually rose until ignition occurred spontaneously. The process usually took several hours. As the rate of the oxidation reaction was greater at high temperatures, spontaneous ignition would occur more readily during the hot summer season or in a warm area in a backfill during cold weather (Meyer, 1989).

Figure 5 is a representation of all four tests, showing the starting initial exothermic temperature obtained from Fig. 4, so that it can be incorporated into large atmospheric and combustion models. In this case, parameters were determined by utilizing a computer program, SIGMA PLOT, for a non-linear equation and with those parameters, temperature was determined as a function of time. The parameters and units are given in Table 2.

In this case the curvature is greater at high temperature and it can be used in the following equation (which is exponential), of three parameters.

$$T_f = T_0 + a_1 e^{-b_1 t} \tag{9}$$

where T_f is the final temperature (K), T_0 is the minimum initial temperature to initiate exothermic reaction (K), t is the time (hours), a_1 and b_1 are parameters derived from non-linear regression analysis.

Table 2: Parameters.

	Symbol	Unit
Area	A	m^2
Distance from hot plate	z	m
Diffusivity	a	$m^2\ h^{-1}$
Thermal conductivity	k	W $(m\text{-}K)^{-1}$
Power	W	W
Heat capacity	C_p	KJ $(kg\text{-}K)^{-1}$
Density	r	Kg m^{-3}

The equation for the regressed curve, for the crumb rubber and wire content (experimental, Fig. 5) is:

$$T_f = 312 + 530652 e^{-0.731t} \tag{10}$$

This equation gives T_f for the temperature of shredded tyres with wire content as a function of time. It will permit the calculation of the temperature at any time by inserting the time. The accuracy this equation is determined by the precision with which the specific heats and the heat of reaction have been determined. This equation will be valid where the specific heat is determined.

Carbon (graphite)

The purpose of calculating a standard heat of formation of ($\Delta H_0 CO_2$) was to determine the experimental heat content as shown in Fig. 6. This was done to explore the oxidation of carbon black as the possible cause of the exotherm. In this case, the value to be compared was the data for carbon graphite. ΔH is a function of temperature. At 298 K, $\Delta H_0 =$ –94050 cal, the following equation provides the ΔH calculation at temperature T:

$$\Delta H = \Delta H + (-0.71T) + 0.07 \times 10^{-3} T^2 - 0.40 \times 10^5 T^{-1} + (-93710) \tag{11}$$

From the above equation, at various temperatures the corresponding heat content was calculated (Chase 1985). From calculated values a curve was plotted (Fig. 6) from which the experimental value and the standard heat of formation was computed. Since ΔHCO_2 is constant and the experimental curve is not, the oxidation of carbon black is not the cause of the exotherm. The calculated experimental heat content at various temperatures is given in Table 1.

When the value of ΔH is known for a specified reaction at some temperature, the value at any other temperature may be calculated if H is known for each of the individual reactants and products, the value of heat capacity, C_p, or of the heat content, H for which the calculation is to be made (Eckert 1959).

From the comparison, at heat inputs of 91, 108, 120 and 140 W, the respective heat coefficients were 3.0, 3.5, 4.0 and 5.0 W m^{-2}-K; the diffusivities were 2.2 E–4, 3.7 E–4, 5.0 E–4 and 8.4 E–4 $m^2\ h^{-1}$; and the thermal conductivities were 0.19, 0.28, 0.34 and 0.52 W m^{-1}-K.

Conclusions

Low temperature oxidations of the shredded tyres with wire content are directly related to their adsorption capacities for atmospheric oxygen. Oxidation is accompanied by the liberation of energy in the form of heat. The temperature increase

is greater with lower rate of heat transfer to the surroundings. As shown in these experiments, higher temperature accelerates the chemical reactions with oxygen, which in turn provides a greater heat build up. Thus, physical adsorption is followed by subsequent chemical oxidation and spontaneous ignition if the heat is not dissipated to the surroundings rapidly enough to prevent achieving the auto ignition temperature in the material

In these tests, finely divided materials were more susceptible to spontaneous ignition, probably because of the presence of a greater amount of exposed steel. This indicates that the cause of the heat generation in shredded tyre embankments is the oxidation of the belting steel. The reaction of sulphur with the steel does not seem to be a factor since there was no exotherm when the air pressure was low. The oxidation of carbon black was also ruled out.

For the exothermic reaction to occur a minimum temperature, time and air content are required. All minimum temperatures and time required for the initial exothermic reaction to start are derived from Fig. 4 and given in Fig. 5. The correlation coefficients (r^2 values) for 91 and 108 W were 0.966 and 0.91, respectively.

To prevent exothermic reaction in a shredded tyre embankment, the shredded tyres might well be pre-oxidized by exposure to the atmosphere. Immediate use of shredded tyres after they are shredded is not deemed advisable. Further experiments are needed to determine the degree of pre-exposure.

The rate of oxidation, at normal temperatures, was usually so slow that the released heat was transferred to surrounding areas as rapidly as it was formed, with no increase in temperature of the material.

The experiment has indicated that heating in the container resulted in initial exothermic reaction within a period of 15 h at a power supply of 91 W, 13 h (108 W), 11.5 h (120 W) and 11 h (140 W).

Acknowledgements

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