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# The Evaluation of Waste Tyre Pulverised Fuel for NO<sub>x</sub> Reduction by Reburning

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# Abstract

The combustion of coal for power generation will continue to play a major role in the future, however, this must be achieved using cleaner technologies than we use at present. Scrap tyre arisings in the UK are 400,000 tonnes per year amounting to 30 million tyres and in the EU as a whole, more than 2.5 million tonnes of tyres per year are scrapped. The recent EC Waste Landfill Directive (1999) sets a deadline for the banning of whole and shredded tyres from landfill sites by 2006. Consequently, there is an urgent need to find a mass disposal route for tyres. We describe, in this paper, a novel use for tyre rubber pulverized fuel in a NOx reburning process which may have an application in power station boilers. This method of disposal could represent a way of combining waste disposal, energy recovery and pollution control within one process. A preliminary study of micronised tyre combustion was undertaken to identify the suitable size ranges for application in NOx reduction by reburning. Tests were performed in a down-fired, pulverised fuel combustor (PFC) operating at about 80kW. Superior combustion characteristics i.e. burnout were achieved with particle sizes less than 250 µm. A South African coal was used as the primary fuel in the reburn tests and the tyre was fed pneumatically via a separate feed system. Parameters studied, were, reburn zone stoichiometry and reburn fuel fraction. Additionally, the carbon content of the ash was carefully monitored for any effect on burnout at the fuel-rich reburn stoichiometries. The NOx reductions achieved with tyres are compared with reburning with coal. NO<sub>x</sub> reductions up to 80% were achieved with tyres at half of the reburn fuel feed rate required to achieve the same reductions by coal. The results have been evaluated within the context of other studies available in the literature on NOx reburning by bituminous coal, brown coal, gas and biomass.

# Keywords

NO<sub>x</sub>, Reburn, Tyres, review

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# **1** Introduction

Coal combustion for electricity generation creates significant pollutant emission problems including oxides of nitrogen (NO<sub>x</sub>), principally from fuel-bound nitrogen. NO<sub>x</sub> emitted to the atmosphere forms gaseous nitric acid (HNO<sub>3</sub>) at night [1]. HNO<sub>3</sub> is then deposited via precipitation causing acidification to land, lakes and streams. Ground level O<sub>3</sub> is formed through a series of photolytic reactions between NO<sub>x</sub>, CO (carbon monoxide), and CH<sub>4</sub> (methane) and is a major component of smog in urban industrialised areas and can result in impacts to human health [2].

Technologies which may be implemented for NOx reduction from power stations include, air staging, selective catalytic reduction (SCR), selective non-catalytic reduction (SNCR) and reburning. This paper is concerned with reburning which can be defined as a three stage combustion process (Fig. 1) and consists of a primary zone, a reburn zone and a char burnout zone [3]:

- *Primary (burner) Zone:* The primary fuel (coal) is fired at a rate corresponding to 75 to 90 % of the total heat input. NO<sub>x</sub> created in this zone is slightly lower than normal operation due to the lower heat release and the reduced excess air level.
- *Reburn Zone:* Injection of the Reburn fuel occurs down-stream of the main burner through wall ports. Hydrocarbon radicals (CH<sub>i</sub>'s, CH<sub>2</sub>, HCCO etc.) are produced as a result of the fuel pyrolysis and partially combusted by the available oxygen which is strictly controlled to create a predominantly fuel-rich zone. The CH<sub>i</sub> radicals react with the NO<sub>x</sub> produced in the primary combustion zone reducing it to N<sub>2</sub> via the following outline reaction process:

$$CHi + NO = HCN + O$$
(1)

$$NO + NHi = N2 + H_2O$$
(2)

Hydrogen cyanide produced in reaction (1) is converted to  $N_2$  in the flame via reactions :

O + HCN = NCO + H
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$$NCO + H = NH + CO$$
 (4)

$$NH + H = N + H_2$$
(5)

$$N + NO = N_2 + O \tag{6}$$

Optimum  $NO_x$  reduction performance is typically achieved when the reburn zone is fuel rich (reducing conditions). A variation in the reburn fuel injection rate between 10% - 25% (total boiler heat input) is thought to produce optimum  $NO_x$  reduction [4].

• *Burnout (exit) Zone:* Oxygen (typically 20 percent of the total air flow) required to burn any remaining combustibles left over from the reburn zone is injected through overfire ports situated just downstream of the reburn zone. Optimisation of the air flow rate and injection point ensure the lowest possible levels of CO emitted and unburnt carbon in fly ash.

There are a number of reburning studies in the literature which examine the possibility of utilising waste materials and biomass. Kicherer et al. [5] examined  $NO_x$  reduction using different reburning fuels in the solid, liquid, and gaseous phase. Light fuel oil (100% volatiles), natural gas (100% volatiles) and straw (75 % volatiles) produced higher  $NO_x$ reductions to that of coal (volatiles, typically 32 %). For light fuel oil, natural gas and straw, good burnout efficiencies were observed even at extremely fuel rich conditions in the reburn zone. Temperature is also important since slow release of volatiles may impart a delay on the initiation of the reactions between CHi radicals and NO. Alzueta et al [6] established that when  $CH_4$  and  $C_2H_6$  individually or mixed (ratio 9:1) were used as a reburn fuel  $NO_x$ reductions of 25% - 85%, were achieved for initial concentrations of NO<sub>x</sub> from 650 ppm – 1100 ppm. The reduction of NO by  $CH_i$  radicals proceeds via a complex reburn mechanism involving the intermediate HCN [7-9]. Maly et al [10] carried out reburn tests with natural gas ( $CH_4$ ), biomass, orimulsion, coal, coal pond fines (CPF), and carbonised refuse derived fuel (CRDF) using  $CH_4$  as a primary fuel. The parameters investigated, as in this present study, were reburn zone stoichiometry and initial NO<sub>x</sub> concentrations. The resulting NO<sub>x</sub> reductions observed for natural gas (CH<sub>4</sub>), biomass, orimulsion, coal, CPF, and CRDF were 25% - 85%. In a reburn study performed by Nimmo et al [11] using calcium magnesium acetate (CMA) as a reburn fuel NO<sub>x</sub> reductions of 80% were achieved in addition to acid gas capture by the calcium component of the additive.

In this paper we suggest that waste tyre rubber may be a potential alternative, novel reburn fuel due to the high volatile hydrocarbon content of > 60% daf. Evidence for waste tyres being an ideal source of  $CH_i$  radicals is clear from thermal treatment studies of waste tyres [12-16] and show that they are a rich source of gas phase hydrocarbons (methane (CH<sub>4</sub>) ethane (C<sub>2</sub>H<sub>6</sub>), propane (C<sub>3</sub>H<sub>8</sub>) butane (C<sub>4</sub>H<sub>10</sub>); butene (C<sub>4</sub>H<sub>8</sub>)) readily producing CH<sub>i</sub> radicals that are required in the reburning zone to generate NO<sub>x</sub> destruction, further favouring tyres as an excellent reburn fuel. Waste shredded tyres also have low nitrogen content (<0.5% ar), low chlorine content (~0.01%), and a high calorific value (35-39 MJ/kg) [17].

# 2. Experimental

Tests were performed in down-fired, refractory-lined, pulverised fuel combustor (PFC), operating at 80kW<sub>th</sub> using waste shredded tyres of different particle size ranges supplied by SRC LTD (Cheshire, UK) and pulverised South African coal ( $<100\mu$ m) supplied by E.On (Nottingham, UK). The rubber is recovered from the waste tyre by scrubbing followed by shredding under ambient conditions for further size reduction. The burner was housed at the top of the PFC, in circular flanged stainless steel sections. The burner could be operated in a reduced NOx mode by staging the combustion air. The main body of the PFC is structured in 8 steel box sections each of 500 mm in vertical length, with a square cross section of length 350 mm; it was also fitted with ports for sampling or injection. The inner part of the box sections is lined with low density refractory, approximately 75 mm in thickness. The overall height of the PFC is 4.5m.

The primary combustion zone air to fuel stoichiometry (SR<sub>1</sub>) was set at 1.05 for all reburn experiments undertaken. The reburn zone stoichiometry (SR<sub>2</sub>) et by controlling the feed rate of waste shredded tyres, coal and the primary zone oxygen levels and the residence time was 0.8s. Reburn fuel fractions (*Rff*) up to 25% were studied. Propane, when used as the primary fuel, was doped with ammonia gas to simulate fuel-NO<sub>x</sub> formation in order to create a range of desired initial NO<sub>x</sub> concentrations for tyre-on-gas reburn (TGR), coal-on-gas reburn (CGR). A South African coal was used as the primary fuel for tyre-on-coal reburn (TCR), and coal-on-coal reburn (CCR). Reburn waste shredded tyres and coal were metered via screw feeders (Rospen) and delivered pneumatically using nitrogen as a carrier gas. Temperature profiles at different heights within the PFC were recorded by types R and K thermocouples. Flue gas sampling was performed by extracting and quenching the gas through water-cooled or short silica probes and subsequently through traps, filters and a chiller unit. Analysis was performed online for NO<sub>x</sub> (Chemiluminescence), CO<sub>2</sub>, CO, SO<sub>2</sub> (non-dispersive infrared), and O<sub>2</sub> (paramagnetic). SO<sub>2</sub> concentrations were obtained by sampling via heated sample line and magnesium perchlorate drying system through a separate sampling probe. All gas analyser measurements and temperature data were recorded on a data logger. NOx concentrations were obtained from averaged data over a period of steady state operation at the desired condition. The results are reported with a confidence of  $\pm$  5ppm for NOx measurement which gives an uncertainty in reductions of  $\pm 2\%$  if the initial NOx level is 500ppm.

Particle sizing was performed using a Malvern Mastersizer and thermogravimetric analysis was performed using a Shimadzu TGA-50H with a heating rate of  $25^{\circ}$ C/min under N<sub>2</sub> to110°C (hold 10mins) then  $25^{\circ}$ C/min to  $925^{\circ}$ C (hold 15 mins). Then switch to air for ashing (20mins).

The aims of the study reported here are threefold, namely;

- Assess the effect of particle size on tyre pulverised fuel (Tyres 1, 2 and 3) combustion with regard to emissions and completeness of combustion (burnout) and suitability as a fuel for NOx reburning.
- 2. Investigate the NOx reductions which may be achieved using Tyre 3 as a reburn fuel.

 Compare the performance of tyre and coal from this study with the results from other literature studies. An assessment of tyre vs biomass, coal and gaseous fuel is a particular feature of the review study.

Waste tyres and pulverised coal were combusted under reburn conditions at reburn fuel fractions between 0.3 % - 13.9 % in order to determine and assess their NO<sub>x</sub> reduction efficiencies and potential as reburn fuel. The resulting data may be used in understanding the characteristics of waste tyres, particularly the optimum reburn zone stoichiometry (SR<sub>2</sub>), required for maximum NO<sub>x</sub> reduction.

# 3.0 Results and Discussion

# Pilot scale combustion tests and the effect of particle size.

A preliminary assessment of the combustion behaviour of the three tyre samples was performed by combusting the material under different furnace oxygen levels in the down-fired furnace. In these experiments the fuels were fed directly through the burner with no secondary fuel added. Particle size distributions are shown in Fig. 2. Maximum particle diameters of 1200 $\mu$ m, 500 $\mu$ m and 250 $\mu$ m were measured for tyre samples 1, 2 and 3 respectively with d(0.5) of 600 $\mu$ m, 150 $\mu$ m and 100 $\mu$ m. The South African (SA) coal included in this study had a similar top size to tyre 3 but a significantly lower smaller fraction as evidenced by a d(0.5) of 40  $\mu$ m. The different tyre particle size ranges gave different levels of burnout (Fig. 3) and generally improved with increasing oxygen, however, Tyre 1 performed badly throughout the range due to the large size, up to 1200  $\mu$ m. Tyre 2 performed better showing improved burnout throughout the range of stoichiometries, but still below that expected from a viable pulverized fuel. Tyre 3 (<250  $\mu$ m), however, performed as well as the SA coal tested here with burnouts greater than 99.5 % at oxygen levels greater than 3%. This represents less than 1% carbon in ash. At oxygen levels in the region of 1%, typical of the

primary zone stoichiometry used during reburning, the carbon in ash rose to 3.8% and 5.6% for Tyre 3 and the S.A. coal, respectively, with corresponding burnout levels of 99.4% and 98.7%. We can, therefore conclude that Tyre 3, although having a comparatively large size has shown the potential to burn out to the level of a typical coal of much smaller size and indeed shows slightly greater reactivity at lower oxygen levels. Tyres 1 and 2 were rejected as potential fuels for reburning in this study.

Further characterization of the tyre and coal fuels by TGA (Fig. 4) shows that the three tyre samples show similar DTG patterns at the slow heating rates employed in the TGA although the particle size differences are significant (Table 1). The raw data was smoothed with a 10 point moving average method. Three release peaks are observed for Tyre 3 with the onset taking place at 190°C with peaks at around 270°C, 370°C and a shoulder at 425°C. In contrast the SA coal onset is at the higher temperature of 350°C with a peak at 460°C. Significantly there is a large proportion of the volatiles still being released at temperatures greater than 500°C which is the temperature at which Tyre 3 has already completely devolatilised. Release rates are an order of magnitude higher for the tyre (1.6E-02) over the coal (3.33E-03) due to the heavier nature of the hydrocarbons.

# NO Reburning using Tyre and Coal

Tyre 3 was chosen for the reburning tests since it performed well in the initial combustion tests showing excellent burnout characteristics (Fig 3). NO reduction with tyre as the reburn fuel was compared with the performance of a South African coal for furnace conditions where either propane or coal was used as the primary fuel. In the case of the propane tests the NO concentration was varied by the addition of ammonia to the primary air feed to the burner. The effect of increasing the reburn fuel fraction on NO emissions is shown in Fig. 5. The concentrations are expressed in mg/Nm<sup>3</sup> with the upper and lower dashed horizontal lines indicating the 2008 and 2016 NO<sub>x</sub> (as NO<sub>2</sub>) emission targets, respectively, as set by the Large Combustion Plant Directive (LCPD, 2001/80/EC).

Reductions in NO emission obtained with tyre 3 in the furnace employed here are shown on figure 5A with decreasing emissions with increasing reburn fuel fraction (*Rff*).

Maximum reductions with tyre 3 are achieved at an *Rff* level of 6% to 7% and are consistently below the 500mg/m<sup>3</sup> limit for initial NO levels up to 1500mg/m<sup>3</sup>. However, for the lower initial NO levels, around 600mg/m<sup>3</sup> or less, then the NO emissions better the more stringent emission target of 200mg/m<sup>3</sup> at a reburn fuel fraction between 3% and 8%. In contrast, coal reburning (Fig. 5B) can only attain the same emission limits at much higher reburn fuel fractions. Levels of coal reburn fuel input in between 8% and 20% of the total thermal input are required to achieve NO emissions less than the 200mg/m<sup>3</sup> limit for the same range of initial NOx levels. In particular, it is apparent that coal on coal reburning is unlikely to achieve the lower limit with the current reburn configuration on this furnace.

This is partly due to the relatively high initial NO levels and partly due to the fact that char-N in the reburn coal is oxidised in the burnout zone to NO<sub>x</sub>. However, tyre on coal reburning attains  $300 \text{mg/m}^3$  from the same high initial levels at an *Rff* of 10%. In reality a power station with low NOx burners and over-fire air will have already attained the upper NO emission limit before the requirements for attaining the lower limit must be satisfied, therefore the results from tests with initial NO levels of  $500 \text{mg/m}^3$ , or less, will be more representative of the required performance of tyre or coal reburning.

NO reductions have been calculated and are shown in Fig 6 and includes both the tyre reburning data and the coal reburning data. The solid lines of the tyre reburning results show reductions at much lower reburn fuel fractions. Reductions in NO emission by tyre reburning can be achieved at one half the required feed rate for equivalent reductions using coal (Fig 6). NO reductions are greater when the initial levels are higher due to the dependence of the rate of CHi radical reaction with NO on the species concentrations. We have demonstrated here

the superior performance of pulverised tyre over pulverised coal reburning despite the large difference in particle size (table 1).

In the following discussion TGR, CGR, TCR and GCR refer to the rig configurations which were used to obtain experimental data in this study. Having selected tyre 3 as a suitable candidate for the reburning tests, the principal objective was to characterise  $NO_x$  reduction capabilities under N-doped (propane), and coal firing conditions and compare with previously reported results for other reburn fuels. The South African coal was also included in the experimental study as a baseline study for coal. The test variables that were shown to have an impact on  $NO_x$  reduction were the type of reburn fuel used, initial  $NO_x$  concentrations and the reburn zone stoichiometry (SR<sub>2</sub>). Volatile matter content and its rate of release are the principal fuel characteristics that have an influence on  $NO_x$  reduction. A higher  $NO_x$  reduction performance was observed with waste tyres which had a greater volatile matter (typically >60% ar) content than that of South African coal (26% ar).

#### Effect of stoichiometry on NOx reburning using tyres

The reburning results for TGR and TCR show comparable  $NO_x$  reduction efficiencies under NH<sub>3</sub>-doped propane and coal as primary fuels (Figs. 7 a, b respectively). TGR gives a  $NO_x$  reduction of 79% at an SR<sub>2</sub> of 0.92. The same can be seen for TCR which has a similar  $NO_x$  reduction of 77% at SR<sub>2</sub>=0.92.

The TGR shows a decrease in NO<sub>x</sub> reduction at SR<sub>2</sub> = 0.78 (77%) in comparison to a lower SR<sub>2</sub> of 0.92 (79%). This decrease in NO<sub>x</sub> reduction is highlighted when it is then compared to the highest NO<sub>x</sub> reduction for TCR at an SR<sub>2</sub> = 0.84 (81%). This may indicate that the maximum NO<sub>x</sub> reduction efficiency has been exceeded and that beyond an SR<sub>2</sub> of ~ 0.88 for TCR and TGR hydrocarbon volatiles are in excess of NO<sub>x</sub> within the PFC.

The emissions of NO<sub>x</sub> from tyre-on-coal reburn (TCR) in comparison to coal-on-coal reburn (CCR) are similar; however the SR<sub>2</sub> at which these NO<sub>x</sub> emissions for TCG and CCR take place vary significantly as shown in Figure 7. The TCR gave NO<sub>x</sub> emissions of 317 ppm (SR<sub>2</sub> = 0.98), 277 ppm (SR<sub>2</sub> = 0.97), and 173 ppm (SR<sub>2</sub> = 0.92) at an initial NO<sub>x</sub> concentration of 740 ppm. This equates to respective NO<sub>x</sub> reductions of 58%, 63% and 77%. CCR exhibits NO<sub>x</sub> emissions of 452 ppm (SR<sub>2</sub> = 0.98), 301 ppm (SR<sub>2</sub> = 0.86), 217 ppm (SR<sub>2</sub> = 0.81) and 184 ppm (SR<sub>2</sub> = 0.77) the respective NO<sub>x</sub> reductions being 42%, 62%, 72% and 77%. Waste tyres appear to be a superior reburning fuel to the SA coal used in this study as they produce much lower emissions of NO<sub>x</sub> at higher stoichiometric ratios i.e. a more fuel lean environment. Fuel characteristics such as a high volatile content and rapid devolatilisation are the key attributes of waste tyre particles that provide such a high NO<sub>x</sub> reduction performance of 77% at an SR<sub>2</sub> of 0.92 (slightly fuel rich) [5]. The significance of the difference in SR<sub>2</sub> between TCR and CCR is made apparent from the highest NO<sub>x</sub> reduction of 77% can be achieved with TCR at an SR<sub>2</sub> of 0.92 which is a lot less fuel rich to that of CCR (SR<sub>2</sub> = 0.77).

Results for tyre on coal reburning suggest that an SR<sub>2</sub> of about 0.9 may be the optimum point for NO<sub>x</sub> reduction efficiency. The NOx reduction efficiency of CCR showed little variation between an SR<sub>2</sub> of 0.81 (72%) and 0.77 (77%) indicating that an SR<sub>2</sub> of 0.81 may be the optimum NO<sub>x</sub> reduction point. Exceeding an SR<sub>2</sub> 0.92 (TCR) and 0.81 (CCR) may only lead to a poorer burnout as the majority of the reburn fuel does not have sufficient residence time in the reburn zone to undergo adequate devolatilisation and reaction. As mentioned previously a higher proportion of partially devolatilised fuel is entering the burnout zone which can lead to a higher carbon in ash content (Fig 3). The same may be said for nitrogen, which which may be partitioned between the volatile products of devolatilisation and the solid char which persists into the burnout zone where it burns with the consequence that  $NO_x$  may be slightly increased compared with the emission at slightly lower reburn fuel fractions.

As shown in the TGR and CGR experiments high initial  $NO_x$  levels exhibit the highest  $NO_x$  reduction efficiency. This trend is also observed in TCR and CCR experiments. Lower operational reburning stoichiometries for waste tyres compared to coal carry significant economic implications.

# Pulverised tyre as an alternative fuel for NOx reburning

Pulverised tyre as a reburn fuel has been compared, from the available literature, with gaseous fuels and "alternative" reburn fuel candidates such as biomass, low grade coal fuels and orimulsion. Before any comparison between the results of tyre reburning could be made with NO<sub>x</sub> reductions of previous reburn studies the literature data was carefully analysed and presented in a standard form involving the correction to 6 % O<sub>2</sub>, and converted from mg/m<sup>3</sup> to ppm as was the case for the research by Spliethoff *et al* [19]. The reburn study carried out by Maly et al [10] was reported as a function of the reburn fuel fraction ( $R_{\rm ff}$  %). Extreme care was taken when applying the conversion procedures for the literature data so that the comparison of NOx reduction results could be made with the greatest confidence. The NO<sub>x</sub> reduction efficiencies of previous reburn studies were grouped into high (Fig 8)and low (Fig 9) initial NO<sub>x</sub> concentrations since it is recognised [18] that initial NOx concentration is a factor in determining the efficiency of the reduction process.

Gas, coal and biomass reburn studies [5-7, 11, 19 -22] show a similar trend to that of TCR and TGR in that  $NO_x$  emissions decrease with a lowering reburn stoichiometric ratio. Therefore, as the reburn zone becomes more fuel rich an increased  $NO_x$  reduction is measured up to a critical point. It is, however, noted that the  $NO_x$  reductions of TCR and TGR show a significantly narrower range of stoichiometry in which this occurs in

comparison to some previous gas, biomass and coal reburn studies. A reburn stoichiometry of 0.92 was taken as a reference point since it corresponds to a reburn fuel fraction of around 13% which is a moderate NOx reburning condition. At this condition, TCR and TGR show a better NO<sub>x</sub> reduction to that of gas reburning studies (Fig. 8a) at high initial NO<sub>x</sub> concentrations carried by Spliethoff *et al* [19]; Kicherer *et al* [5] and Bilbao *et al* [23] reported as being 53%, 58% and 24%, respectively, at an SR<sub>2</sub> = 0.92. In order for these previous gas reburning studies to reach a performance (77% reduction) matching that for tyre reburning at SR<sub>2</sub> = 0.92, a more fuel rich environment of 0.82, 0.8, and 0.5, respectively, is required. It is also found that gas reburn at a low initial NO<sub>x</sub> concentration [5] is significantly less efficient at reducing NO<sub>x</sub> than waste tyre (Fig. 9a). A NO<sub>x</sub> reduction of ~53% is reached at an SR<sub>2</sub> of 0.92 for TGR, which is lower by 21%.

Kicherer *et al* [5] looked at a series of reburn fuels including coal, the NO<sub>x</sub> reduction performance of this coal has been compared to that of TCR and TGR (Fig. 8b). The NO<sub>x</sub> reduction efficiencies for coal start at a slightly more fuel rich SR<sub>2</sub> of 0.9 which has a NO<sub>x</sub> reduction efficiency of 43%, even when TCR and TGR are compared at this slightly higher SR<sub>2</sub> the NOx reduction efficiency for coal is still ~ 32% lower. Even when the reburn zone is at an extremely fuel rich ratio of 0.5 the coal is still only able to manage ~64% NO<sub>x</sub> reduction. This high SR<sub>2</sub> would be unacceptable for industrial purposes resulting in high carbon in ash levels.

The performance of alternative reburn fuels (coal pond fines and orimulsion) compared with tyre on gas reburning (TGR) at lower initial NO<sub>x</sub> concentrations are shown in Fig. 9b. Harding et al (Coal); Maly et al (orimulsion, bituminous coal) and Folsom et al (brown coal) found NO<sub>x</sub> reduction efficiencies of 56%, 52%, 34%, and 54% at an SR<sub>2</sub> of 0.92 respectively. These NO<sub>x</sub> reduction efficiencies approximate to a difference of 17%, 21%, 39%, and 19%

respectively lower than TGR. As discussed previously with gas reburn studies a more fuel rich region has to be achieved to reach  $NO_x$  reductions greater than 60%.

 $NO_x$  reduction by straw [5] shows a similar trend to that of the TCR and TGR results presented here where  $NO_x$  reduction begins in a fuel lean region ( $SR_2 = 1.04$ ), however at the reference  $SR_2$  of 0.92 the NOx reduction efficiency for straw is shown to be 55% compared to 77% and 79% for TCR and TGR, respectively (Fig. 8c). It is only at moderately fuel-rich conditions ( $SR_2 = 0.74$ ) that a significant NOx reduction of 75% is achieved.

The NOx reduction efficiencies of Maly et al and Harding et al, like Kicherer et al, require more fuel rich conditions (SR<sub>2</sub> = 0.83 and 0.84) to reach NO<sub>x</sub> reductions of 70% and 60%, respectively. Under these conditions, NOx reduction with TGR is ~73% which is similar to the results of Maly et al. It is clear that the quality of the biomass fuel, with particular reference to the hydrocarbon content, is responsible for its lower NO<sub>x</sub> reductions compared with waste tyres.

Biomass is composed mainly of a cellulose material therefore a high yield of oxygenated volatiles (carbon-to-oxygen bond) result from the thermal degradation of wood. This large fraction of CO and CO<sub>2</sub> produced diminishes the fraction of CH*i* radicals essentially responsible for NO<sub>x</sub> reduction in a reburn environment [20]. The results suggest (Figs. 8c and Fig 9c) that waste tyres could be a more efficient reburn fuel compared to biomass due to the higher portion of hydrocarbon volatiles (Carbon-to-hydrogen bond) to that of oxygenated volatiles which predominates for biomass decomposition.

# 4. Conclusions

The results presented in this paper have addressed the following principal objectives with regard to the novel application of waste, pulverised tyre fuel as a NOx reburning fuel;

Combustion studies of a selection of different sized tyre fuels identified a candidate for application as a reburn fuel with a particle size d(90) of 250  $\mu$ m. Carbon burnout levels were

found to be acceptable at >99.5% (carbon in ash about 1%) for this tyre fuel (tyre 3) and was comparable or better than typical power station coal for overall flue gas  $O_2$  levels in the range 1%-6% (dry basis). This is despite the difference in particle size between tyre 3 and the coal tested.

The resulting data for waste shredded tyre and coal reburn with either coal or propane as primary fuels showed similar NO<sub>x</sub> reductions between 19% - 81% but, it is noted that this occurred at significantly different reburn zone stoichiometries. TCR and TGR showed a significantly better performance of NO<sub>x</sub> reduction at a higher SR<sub>2</sub> (0.92) to that of CCR and CGR. TCR and TGR show NO<sub>x</sub> reductions at similar SR<sub>2</sub> (0.92) this is the same for CGR and CCR. However, good burnout under reburning conditions was not achieved, with levels in the region of 96% with carbon in ash levels of about 15% with the South African coal as primary fuel.

The optimum  $SR_2$  for TCR and TGR showed small variation and was found to be ~ 0.92. results in the literature for a range of reactors and fuels show that The tyre reburning experiments ultimately show that much lower feed rates are required in obtaining desirable  $NO_x$  reductions that match and surpass coal reburning tests and literature reburn studies at high and low initial  $NO_x$  concentrations using gas, coal and biomass as reburn fuels.

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		Ultimate analysis, wt % AR					Proximate, wt % AR					
	C.V.										Size µm	
	(gross)								Fixed			·
Sample	MJ/kg	С	Η	Ν	S	Cl	Moist	Vols	Carbon	ash	(max)	D(0.5)
tyre 1	37	79.6	7.1	0.5	2.3	-	0.1	63.4	28.1	8.4	1200	600
tyre 2	39	84.6	7.48	0.25	1.49	0.1	1	64.1	29.4	5.5	500	150
tyre 3	35	77.6	6.4	0.44	1.4	0.02	1.4	51	36.4	11.2	250	100
SA coal	27	68.4	3.8	1.53	0.63	0.01	3.1	23.5	57.6	15.8	250	40

**TABLE 1**: Proximate, ultimate and size analyses of South African Coal and the 3 tyre fuels under test.



Fig. 1 Schematic diagram of PC combustor showing 3 stage reburning arrangement and typical temperature profiles for reburn fuel fractions (*Rff* thermal) of - 4% ■, 8% ●, 13% ▲ and 20% ▼.



Fig. 2 Particle size analysis for tyre samples and South African coal.



Fig. 3 Combustion efficiency of tyre and South African coal under different air to fuel ratios. Tyre 1 $\blacksquare$ , Tyre 2  $\blacktriangle$ , Tyre 3  $\bullet$ , SA coal  $\diamond$ , tyre on coal reburn  $\blacktriangleleft$  (*Rff*=5.1% and 19.1%), coal on coal reburn  $\blacktriangleright$  (*Rff*=3.5% and 18%).



Fig. 4 Thermo-gravimetric analysis of tyre and coal. dw/dt (mg/s) and temperature are plotted vs time showing peaks of maximum rate of release of hydrocarbon volatile material.



Fig. 5 NO emissions measured for a range of reburn fuel fractions (*Rff*) for different initial NO levels. A - tyre reburning; NO<sub>i</sub>, 217 mg/Nm3 **\blacksquare**, 390 mg/Nm3 **\bigstar**, 629 mg/Nm3 **\lor**, 1372 mg/Nm3 **\diamondsuit**, 1520(SA coal) mg/Nm3 **\bigstar**. B - coal reburning; NOi , 217 mg/Nm3  $\Box$ , 390 mg/Nm3  $\triangle$ , 629 mg/Nm3  $\bigtriangledown$ , 629 mg/Nm3  $\bigtriangledown$ , 1372 mg/Nm3  $\diamondsuit$ , 1372 mg/Nm3  $\diamondsuit$ , 1605(SA coal) mg/Nm3 **\bigstar**.



Fig 6. NO reductions measured for a range of reburn fuel fractions (*Rff*) for different initial NO levels. Tyre reburning; NO<sub>i</sub>, 217 mg/Nm<sup>3</sup>  $\blacksquare$ , 390 mg/Nm<sup>3</sup>  $\bigstar$ , 629 mg/Nm<sup>3</sup>  $\blacktriangledown$ , 1372 mg/Nm<sup>3</sup>  $\diamondsuit$ , 1520(SA coal) mg/Nm<sup>3</sup>  $\bigstar$ . Coal reburning; NO<sub>i</sub>, 217 mg/Nm<sup>3</sup>  $\Box$ , 390 mg/Nm<sup>3</sup>  $\triangle$ , 629 mg/Nm<sup>3</sup>  $\bigtriangledown$ , 1372 mg/Nm<sup>3</sup>  $\diamondsuit$ , 1372 mg/Nm<sup>3</sup>  $\diamondsuit$ , 1605(SA coal) mg/Nm<sup>3</sup>  $\bigstar$ .



Fig. 7. A. Emissions of NO<sub>x</sub> (ppm) at an SR<sub>2</sub> of 1.04 – 0.84 for tyre-on-coal reburn (TCR) ■, 0.98 – 0.77 for coal-on-coal reburn (CCR) ●, 1.01 – 0.78 for tyre-on-gas reburn (TGR) ◆ and 1.01 – 0.80 for coal-on-gas reburn (CGR) ▼. B. Percentage NO<sub>x</sub> reductions at an SR<sub>2</sub> 1.04 – 0.84 for tyre-on-coal reburn (TCR) ■, 0.98 – 0.77 for coal-on-coal reburn (CCR) ●, 1.01 – 0.78 for tyre-on-gas reburn (TGR) ◆ and 1.01 – 0.80 for coal-on-gas reburn (CGR) ▼. Initial NO<sub>x</sub> concentrations were 740 ppm (1520 mgNm<sup>-3</sup>), 782 ppm (1606 mgNm<sup>-3</sup>), 668 ppm (1372 mgNm<sup>-3</sup>), and 668 ppm (1372 mgNm<sup>-3</sup>), respectively. All emission data have been corrected to 6 % O<sub>2</sub>.



Fig. 8 A - represents NO<sub>x</sub> reductions (%) of gas reburning studies performed by Spliethoff et al (1996)  $\blacktriangle$ , Bilbao et al (1997)  $\blacktriangleleft$  and Kicherer et al (1994)  $\blacktriangle$  in comparison to TCR  $\blacksquare$  and TGR  $\diamondsuit$ . B - represents NO<sub>x</sub> reductions (%) of coal reburning studies of Kicherer et al (1994)  $\blacktriangle$  in comparison to TCR  $\blacksquare$  and TGR  $\diamondsuit$ . C - represents NO<sub>x</sub> reductions (%) of a straw reburning study by Kicherer et al (1994)  $\blacktriangle$  in comparison to TCR  $\blacksquare$  and TGR  $\diamondsuit$ . C - represents NO<sub>x</sub> reductions (%) of a straw reburning study by Kicherer et al (1994)  $\bigstar$  in comparison to TCR  $\blacksquare$  and TGR  $\diamondsuit$ . High initial NO<sub>x</sub> concentrations being 740 ppm (1520 mgNm<sup>-3</sup>), (TCR), 782 ppm (1606 mgNm<sup>-3</sup>) (TGR), 1135 ppm (2736 mgNm<sup>-3</sup>) (Spliethoff)  $\blacktriangledown$ , 600 ppm (1231 mgNm<sup>-3</sup>)(Kicherer)  $\bigstar$ , and 788 ppm (1616 mgNm<sup>-3</sup>)(Bilbao)  $\blacktriangleleft$ . All emission data have been corrected to 6 % O<sub>2</sub>.



Fig. 9 A. represents NO<sub>x</sub> reductions (%) of gas reburning studies performed by Folsom et al (1997)  $\bullet$  in comparison to TGR  $\blacklozenge$ . B. represents NO<sub>x</sub> reductions (%) of coal reburning studies of Maly et al (1999) ( $\nabla$  coal pond fines), (orimulsion  $\bullet$ ), (bit coal  $\blacktriangleleft$ ), Harding (coal) et al (2000)  $\blacktriangle$  and Folsom (brown coal) et al (1997)  $\star$  in comparison to TGR  $\blacklozenge$ . C. represents NO<sub>x</sub> reductions (%) of wood reburning studies of Maly et al (1999)  $\bigstar$  and Harding et al (2000)  $\blacktriangleright$  and Casaca  $\nabla$  (2005) in comparison to TGR  $\blacklozenge$ . Low initial NO<sub>x</sub> concentrations of 427 ppm (877 mgNm<sup>-3</sup>) (TGR), 560 ppm (1149 mgNm<sup>-3</sup>) Maly et al, 412 ppm (846 mgNm<sup>-3</sup>) Harding et al, 442 ppm (906 mgNm<sup>-3</sup>) (Folsom et al) and Casaca 350ppm (1718 mgNm<sup>-3</sup>). All emission data have been corrected to 6 % O<sub>2</sub>.