Controlling NOx emission from boilers using waste polyethylene as reburning fuel

Ibukun Oluwoye a,b, Zhe Zeng a,c, Sara Mosallanejad a, Mohammednoor Altarawneh d, Jeff Gore e, Bogdan Z. Dlugogorski f,

a Murdoch University, Discipline of Chemistry and Physics, College of Science, Health, Engineering and Education, 90 South Street, Murdoch, WA 6150, Australia
b Curtin Corrosion Centre, Curtin University, GPO Box U1987, Perth, WA, 6845, Australia
c State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China
d United Arab Emirates University, Chemical and Petroleum Engineering Department, Sheikh Khalifa bin Zayed St, Al-Ain 15551, United Arab Emirates
e Dyno Nobel Asia Pacific Pty Ltd, Mt Thorley, NSW 2330, Australia
f Charles Darwin University, Energy and Resources Institute, Ellengowan Drive, Darwin, NT 0909, Australia

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A B S T R A C T

Literature lacks data on the performance of waste plastics in controlling NOx emissions in practical combustors operating typically in the temperature window of 1000–1200 °C, under a range of fuel-oxygen equivalence ratios, preventing recycling of plastics in this application. In this contribution, we demonstrate that waste plastics, in particular polyethylene, can serve as a reburning fuel for converting nitrogen oxides (NOx) into environmentally-benign combustion products, in practical large-scale combustors such as pulverised coal power plant, circulation fluidised bed combustion plant, entrained flow boilers, and incinerators. The experiments involved a high-temperature vertically-entrained reactor operating in the range of 600–1200 °C, in conjunction with online infrared spectroscopy, chemiluminescence and gas chromatography. Chemical kinetic modelling, supported by DFT calculations with DMol3 package revealed the underlying chemistry of the NOx mitigation reactions, especially the importance of C2H4 and C2H5 radicals. We modelled the process kinetically and performed a techno-economic assessment of the new technology, to prove its financial feasibility. The reaction of pyrolytic fragments with NOx yields excellent removal efficiency of nitrogen oxides of up to 82% and selectivity to N2 up to 85%, within the temperature range of 1000 °C–1200 °C, and fuel-oxygen equivalent ratios of Φ = 0.8–1.2. While we observed the formation of HCN, the overall nitrogen selectivity shifts towards the formation of N2. Both the conversion of NOx and the selectivity to N2 can be improved further by increasing the residence time. The economic assessment indicates that, the use of waste plastics is comparable to other mainstream solid fuels and becomes less expensive when considering renewable benefits.

1. Introduction

Persistent global accumulation of polymeric materials infers that millions of metric tonnes of waste plastic could litter the environment and oceans by 2030 [1]. Solid-waste management programs [1] encourage the recycling of plastic through (bio)chemical, and energy recovery approaches [2–5]. In addition to the viable energy resource of polymer solid waste (PSW), the hydrocarbon-rich fragments of some plastics should further serve in mitigating atmospheric pollution (nitrogen oxides, NOx) from stationary combustion plants. This kind of system could be termed as NOx control through plastic waste reburning.

From an environmental viewpoint, the emission of NOx (about 800 ppm in untreated combustion plants) [6] has adverse effects on the natural ecosystem. In addition to post-combustion treatments (e.g., selective catalytic reduction) [7] strategic modification of combustion processes, e.g., via flue gas recirculation [8] boiler modification [9,10] and reburning technology [11] often control NOx emission economically. Conventional reburning fuels such as natural gas and biomass have been reported to achieve the average NOx conversion efficiencies of about 65% in combustion systems [11–22] while coal resulted in approximately 80% conversion efficiencies [23–28] in commercial boilers. However, a sustainable reburning technology should rely on...
conduct high-temperature isothermal experiments in a drop-tube reactor, to account for the flash-particle heating conditions, the effects of oxygen presence, and mass transfer limitations on the reaction of NO\textsubscript{x} with PE pyrolysates under realistic reburning temperatures (i.e., 1000–1200 °C). We determine accurately the selectivity of formation of molecular nitrogen during the thermal reduction of NO\textsubscript{x} with waste polyethylene, both experimentally and theoretically. We explain in detail the underlying reaction chemistry and model the process. The paper also covers the techno-economic analysis of the new technology to compare the cost of employing waste PE as a reburning fuel with that of conventional fuels, to demonstrate its financial viability.

2. Experimental and kinetic modelling

2.1. Sample and characterisation

Dyno Nobel Asia Pacific donated extruded black cylindrical pellets of polyethylene to the present research. As discussed earlier [40], the recycled plastic comprised mostly polyethylene, with elemental composition of carbon (C, 86.17%), hydrogen (H, 14.23%), chlorine (Cl, <0.1%) and inorganics (±0.7%), as elucidated by Fourier transform infrared spectroscopy (FTIR) assisted by attenuated total reflectance (ATR), carbon-hydrogen-nitrogen-sulfur (CHNS, ±0.3%) elemental analysis, ion (anion) chromatography, and inductively coupled plasma optical emission spectroscopy (ICP-OES) for determination of trace metals, respectively.

2.2. Experimental methods

Fig. 1 presents the experimental design for NO\textsubscript{x} conversion, comprising a vertically-entrained reactor and gas monitoring systems. A calibrated electronic powder doser (Lambda Laboratory Instruments) feeds the recycled plastic (cryogenically pulverised, 150–355 μm) at a constant low feeding rate of 7 mg/min, through a water-cooled probe, into a quartz reactor housed in an electrically heated three-zone furnace. The reactive gas mixtures of helium, nitric oxide (NO), and oxygen carried the particles downstream, reacting in the uniform-temperature region of the furnace. We maintained a total gas flow rate of 400 mL/min at STP (NIST) by adjusting the internal rod, which was 9.5 mm in outside diameter (denoted as 9.5 mm O.D. in Fig. 1), to ensure that the volume of the isothermal reaction-zone allows a total gas residence time of 1 s. The expansion of gases has been accounted for through Charles' temperature-volume relationship. Our previous isoviscous model [40] demonstrated that, the isothermal decomposition (pyrolysis) of PE in NO\textsubscript{x} atmosphere requires 0.45 s for a complete conversion into pyrolysate fragments at 600 °C. Therefore, the total reaction time of 1 s is sufficient for all the isothermal (i.e., 600–1200 °C) experiments in this study. The concentration of NO entering the reactor amounted to either 5 or 500 ppm. We tested the effect of oxygen concentration at pre-defined fuel-oxygen equivalence ratios Φ. Solving Equation (1) for Q\textsubscript{o2} yields the required inlet volumetric flow rate of oxygen Q\textsubscript{o2} to maintain a moderately fuel-rich (Φ = 1.2) or fuel-lean (Φ = 0.8) condition.

\[
\Phi = \frac{m_{\text{fuel}}/m_{\text{O}_2}}{(m_{\text{fuel}}/m_{\text{O}_2})_o} = \frac{m_{\text{O}_{2,n}}}{m_{\text{O}_2}} = \frac{m_{\text{O}_{2,n}}}{\rho_{\text{O}_2}Q_{\text{O}_2}}
\]

\[
Q_{\text{O}_2} = \frac{m_{\text{fuel}}(2.667C + 8H)}{\rho_{\text{O}_2}} \tag{2}
\]

The parameter ρ\textsubscript{O}_2 represents the density of molecular oxygen, keeping in mind that the stoichiometric mass flow rate of oxygen m\textsubscript{O}_2,\textsubscript{n} depends on the mass feeding rate of the fuel (i.e., 7 mg/min) as expressed in Eq. (2), where C and H represent the fractional composition of carbon and hydrogen in the waste PE sample, i.e., 0.8617 and 0.1423, respectively, while their coefficients denote the ratio of oxygen needed for stoichiometric combustion of elements, respectively.

Analyses of gaseous products involved three parallel stages. Firstly,
FTIR spectroscopy (Perkin Elmer) facilitated online monitoring of the combined product species exiting the tubular reactor. This setup incorporated a small volume (100 mL) 2.4 m path-length gas sampling cell (Pike) placed inside the FTIR compartment. The spectrometer averaged 64 accumulated scans per spectrum at 1 cm$^{-1}$ resolution. The chemiluminescence NO$_x$ analyser (Thermo Scientific model 42i-HL) monitored the concentration of NO, and the $\mu$GC (Agilent 490 micro-gas chromatograph, 20 m MolSieve-5A column, heated injection) quantified the production of nitrogen. Being a continuous-flow reactor, the reported concentrations of the gaseous products represent the average values of replicated 10 min runs, achieving reproducibility within 5% for all experimental conditions. These uncertainties originate from the accuracy of mass flow controllers, the furnace temperature, and the background noise of the analytical instruments. The nitrogen balance is reported in Section 2.3.

Differential scanning calorimetry, performed on a Netzsch STA 449 F3 Jupiter instrument, served to assess the energy recovery and efficiency of employing waste polyethylene as a reburning fuel. We conducted the thermo-analytical experiments in a lidded platinum–rhodium crucible (Pt:Rh = 80:20, height = 4 mm, outside diameter = 6.8 mm, diameter of lid perforation = 0.05 mm) with approximately 20 mg of the recycled PE (and coal) samples, heated from 25 °C to 800 °C at the rate of 20 °C/min in synthetic air. The continuous flow rate of the purge gas (i.e., synthetic air) amounted to 60 mL/min, as measured under the standard temperature and pressure (STP). The heat calibration routine involved the use of a reference standard for the heat capacity (i.e., a single crystal sapphire disc) and baseline corrections, resulting in accurate estimation of the calorific budgets of the process.

2.3. Theoretical calculation and kinetic modelling

DMol$^3$ package enabled the structural optimisation of a representative polyethylene model [43,44] and served to calculate the energy and vibrational frequencies. The density functional theory (DFT) method involved the generalised gradient approximation of Perdew–Burke–Ernzerhof (GGA-PBE) [45,46] functional, a double
numerical plus polarization (DNP) basis set, and all-electron relativistic effects. The total energy achieved a tolerance of $1 \times 10^{-6}$ Ha and the calculated energies were adjusted via a dispersion correction term based on the Tkatchenko and Scheffler approach (i.e., a van der Waals DFT-D functional) [47]. Moreover, the kinetic modelling comprised a comprehensive nitrogen chemistry, with reaction subset for reburning of Glarborg et al. [48] and some modifications as explained in the next section.

3. Research results and discussion

3.1. Energy implication of waste PE as reburning fuel

Fig. 2 illustrates the advantage, in terms of energy conversion and efficiency, of waste PE as reburning fuel in a typical coal-fired plant. The figure confirms that, thermal decomposition of waste PE in air leaves no residue, unlike coal. The heat of reaction (from DSC plot) of PE is much lower than its HHV due to the production of lower molecular weight hydrocarbons that burn in the gas phase. Moreover, the relatively higher energy density of PE alters the linear temperature curve. Waste PE sample displays a higher specific heat capacity and therefore requires more sensible heat as compared to the coal sample. One can estimate the total energy input into the system directly from the calorific HHV, recalling that reburning fuel comprises 20% of the total fuel input. Accordingly, PE reburning should improve the thermal input to a utility boiler by approximately 18% (25 MJ/kg × 0.8 + 47 MJ/kg × 0.2 = 29.5 MJ/kg, higher than the calorific value of primary coal fuel), translating into the overall efficiency of the system.

3.2. Reaction chemistry and efficiency of NOx conversion

We calculated the isothermal NOx conversion based on the molar flows according to Eq. (3), relying on the NOx concentrations entering and exiting the reactor, i.e., $[NOx]_{in}$ and $[NOx]_{out}$, respectively. The total inlet gas volumetric flow rates amounted to $Q_{in} = 400$ mL/min at STP. However, the outlet gas flowrate represents the sum of $Q_{out}$ and $Q_{volatile}$, the latter denoting the estimated dilution term due to the generation of volatile products (from pyrolysing PE) in the reactor as shown in Eq. (6).

$$X = \frac{F_{NOx} - F_{NOx}}{F_{NOx}} \times 100\%$$

\[ \text{Table 1} \]

Updated reactions in Glarborg’s reburning mechanism. Units of $E_i$ and $A$ correspond to kJ/mol and cm$^3$/mol-s, respectively.

$$F_{NOx} = \frac{[NOx]_{in} \cdot Q_{in}}{\rho} \quad (4)$$

$$F_{NOx} = \frac{[NOx]_{out} \cdot Q_{out}}{[NOx]_{out} \cdot (Q_{in} + Q_{volatile})} \quad (5)$$

$$Q_{volatile} = \frac{m_{volatile}}{M_{ethylene}} \cdot \frac{RT}{P} \quad (6)$$

where, $\rho$ denotes the average density of volatile species, taken merely as the density of ethylene. According to Eq. (6), the volumetric rate of the volatile product of PE (i.e., from the “low” 7 mg/min solid feed rate) equals approximately 5 mL/min at STP, i.e., about 1.3% of the $Q_{in}$.

Fig. 3 depicts the NOx conversion efficiency under various conditions. The recycled PE sample resulted in an excellent NOx removal efficiency of ca. 82%, especially under practical conditions of fuel-rich reburning of $\Phi = 1.2$ and within the temperature window of 1000 – 1200 °C.

The reaction chemistry of NOx reduction centres on the global interaction of hydrocarbon fragments with NO (R1) [48,49].

$$\sum CH_2 + NO \rightarrow HCN + ... \rightarrow N_2 + ... \quad (R1)$$

The low-carbon fragments arise from the pyrolytic and oxidative conversions of PE (43,44,50,51) as formulated in (R2) in Table 1, using a long-chain triacontane ($C_{30}H_{62}$), based on molar ratio of products of PE decomposition. Our DFT calculations illustrate (in Fig. 4) how the presence of radical sites and random distribution of oxygen atom (from primary oxidation of PE) disrupt the C–C bonding configurations, and influence the enthalpic requirements for the homolysis of the C–C bond and unzipping of the polymer in the successive $\beta$-scission reactions. Therefore, the kinetic model incorporated the realistic Arrhenius parameters in R2, comparing well to the experimental activation energy for isothermal decomposition of PE [33].

Table 1 lists the reactions adjusted or added into the Glarborg mechanism [48]. In (R1), we assumed the thermochemical parameters of PE to be identical to that of C$\text{6}H_{12}$ in Burcat’s data base, but employed the kinetic parameters based on the DFT calculation. The updated (R3) and (R4) addressed the issue of theoretical accumulation of NO below 1500 °C. The well-studied channel between CH$_2$ and NO converts NO into HCN. However, the competing reaction between CH$_2$
and supplementary O_2 consumes CH_2 easily, resulting in earlier accumulation of NO and disappearance of HCN. To account for this, we added reaction channels for NO to react with C_2H_5 and C_3H_7 radicals, respectively in (R5) and (R7). This is logical as these radicals represent important intermediates in the decomposition of PE.

As it will be discussed later, HCN appears to be the major nitrogen-derived by-product (intermediate) of the thermal reaction. The absence of fuel-N in PE shuts the other NH_3 pathways. The inclusion of excess oxygen switches the pool of chain-carrying radicals, sustaining other competitive pathways such as oxidation of hydrocarbons (into CO/CO_2) and HCN (HCN + OH, O, O_2 → NO + ...). This is evident from the lower NO_x conversion (Fig. 3) obtained at Φ = 0.8. Fig. 5 demonstrates the normalised sensitivity coefficients for the consumption of HCN, reinforcing the competing effect of residual oxygen and the importance of the primary fragmentation of PE. Besides, N_2 reactions do not contribute to the formation of HCN (hence, thermal NO_x) at these temperatures. The production of NCO facilitates the formation of N_2 via (R10 – R11). Moreover, the kinetic model demonstrates that the use of nitrogen as the carrier gas (instead of helium) will not influence the NO_x reduction performance of PE within the studied temperature range (i.e., between 600 °C and 1200 °C).

\[
\begin{align*}
NCO + H & \rightarrow NH + CO \\
\text{(R10)} \\
NH + H & \rightarrow N + H_2 \\
\text{(R11)}
\end{align*}
\]

This finding does not appear in the literature but is important because it shows that large-scale reburning systems can rely on waste plastics inasmuch as they are properly sorted to eliminate polymers containing hazardous additives and blends [52–55]. Polyethylene, as well as other hydrogen-carbon based polymers represent an excellent choice of fuel for this application. In comparison to other conventional fuels, the NO_x reduction efficiency of recycled PE exceeds those of natural gas and biomass fuels (e.g., wood, straw, rice husk, bio-oil, sewage sludge, and carbonised municipal solid waste) that has been reported to achieve average NO_x conversion of about 65% in combustion systems [11–22]. PE should perform with similar conversion efficiency to coal (±80%) [23–28] in commercial boilers. However, employing waste PE for NO_x remediation provides additional socio-economic benefits, such as carbon credits, recycling credits, ecological impact (of plastic litters) relief, sustainable management of waste resources, and reduction in national waste management budget.

### 3.3. Product N-selectivity

We employed online FTIR and μGC to identify (and quantitate) the reaction intermediates and by-products. The μGC monitors molecular nitrogen, while FTIR examines all the IR active species. Fig. 6 exemplifies the FTIR traces recorded in a 2.4 m gas cell, illustrating hydrogen cyanide (HCN) as the major N-containing intermediate. Spectroscopy techniques [56] have proven highly effective in the detection and quantitation of the aforementioned gaseous nitroous compound. QASoft database (Infrared Analysis, Inc., Anaheim, CA) enabled semi-quantitation of the aforementioned nitrogenous species. The accuracy of the measurements depends upon the tolerance of the absorption coefficients of the reference spectra. This is estimated to be within ±5%, from traces included in the QASoft library. Furthermore, Fig. 7 plots the product concentration of N_2 and HCN, as well as their respective selectivity calculated based on Eqs. (13) and (14). The somewhat acceptable inconsistencies between the model and the experimental results are due to the complexity of PE decomposition reactions. Previous works have shown that the reburning large hydrocarbons behaves fairly differently as compared to the respective models. We have achieved an acceptable nitrogen balance varying from 91 to 95%, depending on the reaction conditions.

\[
S_{N_2} = \frac{2\times100}{\left[N_{2}\right]_{\text{out}} - \left[N_{2}\right]_{\text{in}}}
\]

**Fig. 5.** Sensitivity analysis for HCN in the proposed reburning mechanism of PE at 926 °C (1200 K) with initial NO concentration of 700 ppm and fuel-rich (Φ = 1.2) condition.

**Fig. 6.** Typical FTIR spectrum of the product gases, e.g., at τ = 1 s, temperature = 900 °C, inlet NO concentration = 700 ppm and Φ = 1.2, as recorded by the spectrometer equipped with by 2.4 m gas cell. The abundance of most species appears above the quantitation limit (absorbance > 0.8); however, the selected Q-branch of HCN (at 712 cm⁻¹) has absorbance values below 0.8.
The N-selectivity results indicate that most of the converted NO\textsubscript{x} ends up as non-toxic molecular nitrogen (selectivity of N\textsubscript{2} up to 85%). This can be further improved by optimising the reaction time. Likewise, in a typical reburning process, the addition of air in the final stage (i.e., Fig. 7), formation of product species during reburning of NO\textsubscript{x} with waste PE at inlet NO concentration of 500 ppm, Φ = 0.8 (a) and Φ = 1.2 (b). The symbols and dashed lines denote experimental and modelled results, respectively. The converted NO\textsubscript{x} in Fig. 3 selectively forms N\textsubscript{2} and HCN both at Φ = 0.8 (c) and Φ = 1.2 (d), based on the experimental data. The t corresponds to 1 s, while the inlet feed of waste PE equals 7 mg/min. The overall nitrogen balance can be estimated as $(100 - X_{\text{NO}}) + (S_{\text{N}_2} + S_{\text{HCN}}) X_{\text{NO}}/100 = ([\text{NO}]_{\text{out}} + 2 \cdot [\text{N}_2]_{\text{out}} + [\text{HCN}]_{\text{out}})/[\text{NO}]_{\text{in}} = 93\%$.

**Fig. 8.** Scenario block diagram for the relative static cost analysis of fuel reburning of NO\textsubscript{x}. HHV represents the thermal high heating value. ‘**’ denotes the instances where the periodic characteristic comes in. The final functional unit is the relative cost per NO\textsubscript{x} reduction within a unit period of time. ‘**’ denotes the instances where the seasonal characteristic comes in.

$$S_{\text{HCN}} = \frac{[\text{HCN}]_{\text{out}}}{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}} \times 100\%$$ (14)

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Table 2
Relative economic analysis of reburning of NOx

| Coal       | Natural gas | Biomass | Waste PE | Note             |
|------------|-------------|---------|----------|------------------|
| Specific fuel cost ($/GJ) | 3.97 (0)       | 6.43    | 9.38     | 4.30             | Average price of waste PE [70] |
|            | (2.46)       | (5.41)  | (0.23)   |                  | (200 $/t, includes sorting and processing into usable pellets) |
|            |              |         |          |                  | divided by the calorific value [30,64] (HHV, 46.5 GJ/t). |

Technical factors (average NOx reduction efficiency, %)

| 80  | 65  | 65  | 80  | Relevant references are cited in the text. |
|-----|-----|-----|-----|-------------------------------------------|
| (0) | (−15)| (−15)| (0) |

Functional cost ($/NOx reduction y)

| 47,000,000 | 93,000,000 | 140,000,000 | 51,000,000 |
|------------|------------|-------------|------------|
| (0)        | (3,000,000)| (95,000,000)| (6,000,000)|

600 MW, power plant requires about $7 \times 10^6$ GJ/y, of which reburning process contributes 20%. The values are calculated as $(47 \times 10^6 \text{ GJ/y}) \times (0.2) \times (\text{specific cost, }$/GJ)/NOx reduction efficiency, $\%100$.

Italicised values (in brackets) correspond to the relative cost with respect to the base case of coal, i.e., Costfuel - Costcoal. Prices in US$. The burnout zone completes the combustion process by oxidising all unreacted fuels and reduced N-species.

4. Relative techno-economic analysis

This section combines the energy recovery and NOx reduction efficiency of waste PE to evaluate the techno-economic aspects of using waste PE in reburning technology. The economics of using waste PE for NOx reduction in real-world combustors can be expressed relative to that of conventional solid fuels. As shown in Fig. 8, the thermal heating value and NOx reduction efficiency signify the most critical technical inputs. These parameters transform the specific cost into meaningful values for comparison. Following the assumption that the investment and other operating expenses remain the same, Table 2 lists the key technical, environmental and cost indicators for the relative techno-economic assessment of solid-fuel reburning of NOx. As stated earlier, large-scale reburning systems can rely on waste plastics if they are adequately sorted to eliminate polymers containing hazardous additives such as halogenated blends. Municipal solid waste (MSW) comprises other low-energy substances; however, there are standardised means of retrieving and sorting out different components of MSW for energy recovery and thermo-chemical conversion [38,57]. Therefore, the cost of PE (in Table 2) includes sorting and processing into usable pellets. The energy prices of other fuels are based on the averaged five-year value in the industrial sector [58]. The alternative export prices for coal (FOB, piers, Newcastle/Port Kembla) and natural gas (Henry distribution hub, Louisiana) amount to approximately 3.30 and 3.17 $/GJ, respectively [59,60]. We employed the industrial prices in Table 2 as they are more relevant to thermal plants.

In this case study, an average power plant [61,62] with an electric output of 600 MW, utilises about 1.9 million tonnes of coal annually. This corresponds to about 1500 MHw (i.e., $47 \times 10^6$ GJ/y) thermal input to the boiler at 40% plant efficiency. Table 2 lists the cost of obtaining 20% (i.e., the amount needed for reburning) of the thermal energy input from the selected fuels, after adjusting for their respective NOx conversion efficiencies. Our cost evaluation sheds light on the relative financial feasibility of waste PE as a reburning fuel, identifying it as a competitive (and sustainable) alternative to other fuels. To our knowledge, this is the first observation of this consequence. The PE reburning compares favourably to other popular technologies, such as the selective catalytic reduction (SCR) [63]. The use of waste plastics as reburning fuel can also attract financial incentives from local authorities (e.g., green certificates), lowering the overall functional cost. In an environmental life cycle assessment (LCA), Eriksson and Finnveden [64] reported that efficient incineration of plastics could also yield a net negative contribution to greenhouse gases (mainly CO2) as compared to landfill disposal.

5. Conclusions

This study has developed a new cost-effective technology that deploys waste polyethylene for NOx control. Pyrolysates of PE can reduce NOx by about 82% under realistic reburning temperatures of 1000–1200 °C, in the presence of oxygen, with the selectivity to N2 as high as 85%. Based on this finding and the modelling of the process, the techno-economic analysis has demonstrated that, the injection of waste PE into the reburning zone of boilers can significantly reduce the emission of NOx at a cost comparable to that of coal and natural gas. The use of waste PE as a reburning fuel avoids landfilling costs, attracts recycling credits and evades storage hazards. Owing to the product selectivity towards N2 gas, waste PE can also serve in reburning-like technology to reduce fugitive NOx emissions during blasting of ammonium nitrate explosives by adding it as a supplementary fuel into the explosive formulation. Overall, reburning of waste PE offers an alternative, sustainable solution to worldwide recycling of common plastic waste.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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