

Recycling Waste Polyurethane as a Carbon Resource in Ironmaking*

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Abstract

Globally, major avenues available for dealing with waste Poly-Urethane (PU) are disposal at landfill sites and incineration. However, PU contains high levels of carbon and hydrogen that can be recovered for use as reductant in metal extraction processes. In this work the use of post-consumer PU as reductant for the production of metallic iron from iron oxide was investigated in a horizontal tube furnace through the composite pellet approach. Composite pellets were formed from mixtures of iron oxide and post-consumer PU. The iron oxide-PU composites were heated from room temperature to 1200 °C and then between 1200-1600 °C in a continuous stream of pure argon and the off gas was analysed continuously using an infrared (IR) gas analyser. Elemental analyses of samples of the reduced metal were performed chemically for its oxygen content using a LECO oxygen/nitrogen analyser. The extent of reduction was then determined at two temperatures 1200 °C and 1550 °C. Gas emission studies revealed the emission of large volumes of the reductant gas CO along with CO₂. It is further demonstrated that post-consumer PU is effective at reducing iron oxide to produce metallic iron with complete reduction achieved in less than 4 min at 1550 °C.

Keywords: Polyurethane, Composite Pellets, Infrared gas Analyser, LECO Carbon/Sulphur Analyser

1 Introduction

Globally, major avenues available for dealing with Poly-Urethane (PU) are disposal at landfill sites and incineration. However, PU contains high levels of carbon and hydrogen that can be recovered for use as reductant in metal extraction processes. In Ghana, recycling figures for waste PU are not available, although it is believed that significant amounts of PU are produced annually. Conventional methods for recycling PU have concentrated largely on disposal at landfill sites. Decreasing landfill space along with increasing landfill costs call for novel ways for its recycling.

Large amounts of waste PU are generated annually from various households, as part of medical waste from various hospitals and constitute a significant portion of automotive shredder waste.

PU (Fig. 1) contains appreciable levels of carbon and hydrogen and its thermal decomposition at high temperatures generates large amounts of the gaseous reducing species CO and CH₄ along with solid C which are known reductants of metal oxides. It has no sulphur content, making it an ideal sulphur-free carbonaceous reductant for ironmaking. The use of waste polymeric materials as chemical feedstock in iron and steelmaking is currently gaining the attention of researchers [Matsuda *et al.*, (2006), Matsuda *et al.*, (2008), Murakami *et al.*, (2009), Murakami and Kasai, (2011), Ueki *et al.*, (2008), Dankwah *et al.*, (2011), Nishioka *et al.*, (2007), Dankwah *et al.*, (2012), Dankwah *et al.*, (2013), Dankwah and Koshy,

(2014), Dankwah and Baawuah, (2015) and Dankwah *et al.*, (2015).].



Fig. 1 Soft Polyurethane Foam

The interest in getting carbon from various sources has been extended to household items like bowls made from bakelite, melamine and compact discs (CDs) [Kongkarat *et al.*, 2011; Mansuri *et al.*, 2013; Nath *et al.*, 2012; Rajarao *et al.*, 2014a; Rajarao *et al.*, 2014b].

However, not much is known about the use of PU as reductant in iron and steelmaking technologies. In the present work, the potential for producing metallic iron from hematite using waste PU as a reducing agent is investigated under inert atmosphere in a custom made horizontal tube furnace.

2 Resources and Methods Used

2.1 Materials

Commercial grade PU (pulverised to 125 µm using a ring mill) was employed in this study as carbonaceous material. The chemical composition

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(wt %) and the ash analyses as determined at the Analytical Centre, UNSW, Australia are given in Tables 1. Pulverised reagent grade iron oxide (assaying 96.89% Fe₂O₃) was obtained from Ajax FineChem Pty Ltd, Taren Point, NSW, Australia; its composition (determined by XRF analysis) is given in Table 2.

Table 1 Elemental Analysis of Polyurethane

Component	C	H	O	N	S
Composition wt %	65.6	4.9	20.5	9.0	-

Table 2 Elemental Analysis of Fe₂O₃

Component	Composition (wt %)
Fe ₂ O ₃	96.89
SiO ₂	0.445
CaO	0.0225
MnO	0.020
ZnO	0.0115
TiO ₂	0.134
SO ₃	0.257
LOI	2.22
TOTAL	100

Pulverised carbonaceous materials were prepared from PU using a Cutting Mill Pulverisette 15 (Fig. 2), equipped with a cutting rotor, sieve inserts and grinding chamber. Pulverised carbonaceous materials used for the reduction studies were in the size range -470 + 450 μm.

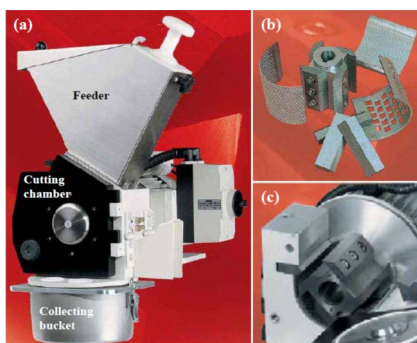


Fig. 2 (a) Cutting Mill Pulverisette 15, (b) Cutting Rotor and Sieve Inserts and (c) Grinding Chamber

2.2 Reduction Studies

Spherical pellets were formed from pulverised iron oxide and polyurethane (~ 30 wt %) with about 2 wt % flour as binder and appropriate amount of water without flux addition (Fig. 3). After curing and drying for 96 hours the composite pellets were then ready for firing in a resistance heated horizontal tube furnace (Fig. 4).

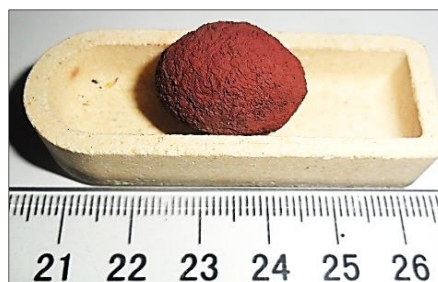


Fig. 3 Spherical Pellet of Fe₂O₃-PU Composite



Fig. 4 Horizontal Tube Furnace used for Reduction Studies

The furnace was purged continuously with argon gas (99.995% purity) to ensure an inert atmosphere. The furnace was preheated to the desired temperature and the sample was inserted; gas measurement commenced immediately after insertion and continued for 1800 s. No appreciable change in gas composition was observed beyond 1800 s. Reacted carbonaceous material/iron oxide samples were quenched by rapidly withdrawing the tray from the hot zone into the cold zone of the furnace. Particles of reduced iron metal, which were clearly visible to the naked eye, were removed by a magnetic screw driver and its oxygen content was determined by LECO Nitrogen/Oxygen analyser (model TC-436 DR 602-500-600, LECO Corporation, Michigan, USA) for its O content.

3 Results and Discussion

3.1 Reduction Studies

3.1.1 Gas Generation Behaviour during Heating of Fe₂O₃-PU at 1200 °C and 1500 °C

The gas generation behaviour in the preheated furnace at 1200 °C is illustrated in Fig 5. The major component of the offgas is CO with a maximum concentration of about 7.13 vol %; some CO₂ is also observed.

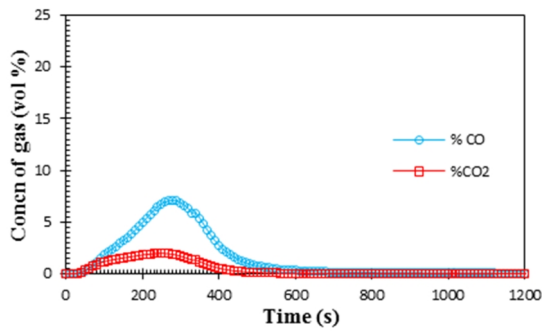
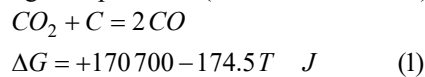


Fig. 5 Gas Generation Behaviour during Heating of Fe₂O₃-PU Composite at 1200 °C

Temperature appears to have a very significant effect on gas generation, especially CO as illustrated in Fig. 6. The maximum concentration of CO increased from about 7.13 vol % at 1200 °C to about 23.0 vol % at 1550 °C, implying that reduction (oxygen removal) is influenced by temperature. The effect of temperature on CO₂ is rather the reverse of what was observed for CO, judging from the area under the graphs of CO₂ in Figs (5 and 6). This is explained by the consumption of CO₂ by solid carbon through the highly endothermic Boudouard reaction (Equation 1), which is favoured at high temperatures (Knacke *et al.*, 1991)



Another possible reaction that could contribute to the observed surge in the concentration of CO at 1550 °C is the water gas reaction illustrated in Equation 2 (Knacke *et al.*, 1991):

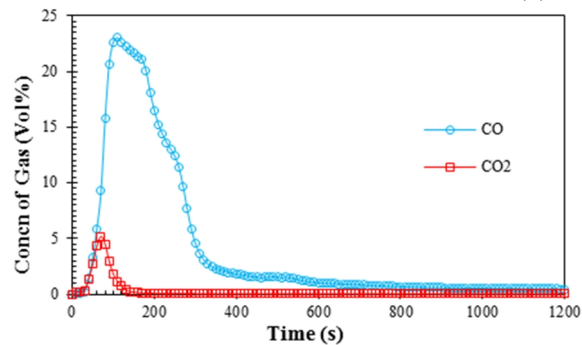
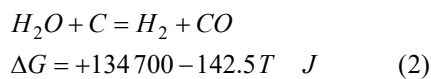


Fig. 6 Gas Generation Behaviour during Heating of Fe₂O₃-PU Composite at 1550 °C

The accumulated amount of gases evolved (*n*CO and *n*CO₂) are shown in Figs 7 and 8 at 1200 °C and 1550 °C, respectively. This again shows that an increase in temperature leads to an increase in the amount of CO and a decrease in the amount of CO₂ produced.

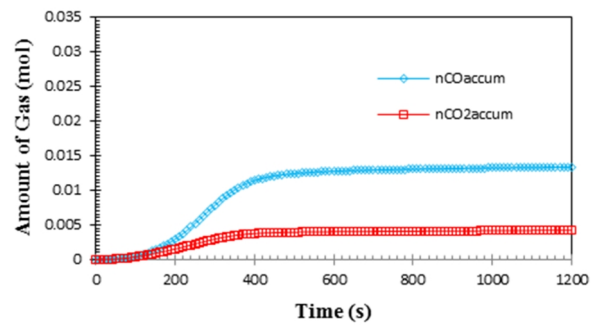


Fig. 7 Accumulated Amount of Gas Generated at 1200 °C

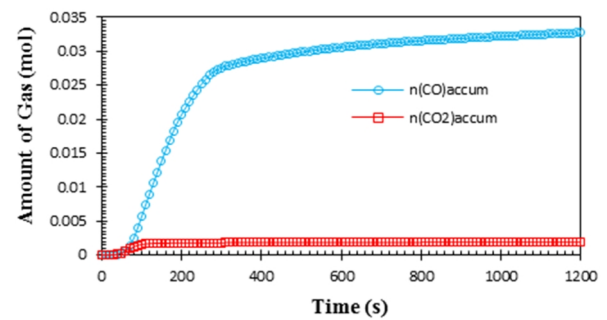
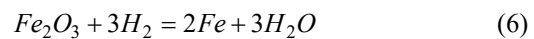
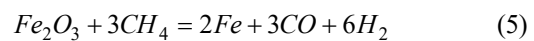
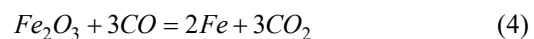


Fig. 8 Accumulated Amount of Gas Generated at 1550 °C

Possible reactions for the reduction of Fe₂O₃ to Fe are:



The plots of $\ln(P_{CO}/P_{CO_2})$ versus time are shown in in Fig 9 and Fig 10 at 1200 °C and 1550 °C respectively. The plots are asymptotic at both temperatures, with the plot at 1200 °C approaching 1.3 whilst that at 1550 °C approaches 3.0. This implies that the Boudouard reaction has a significant influence over the reduction process at both temperatures.

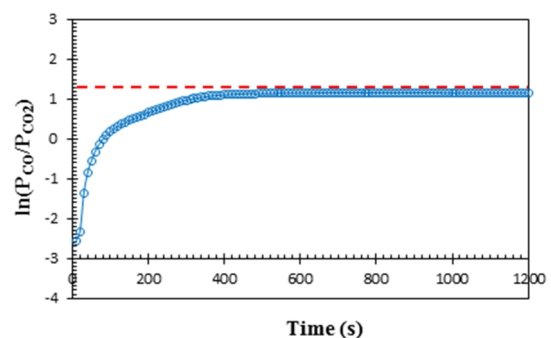


Fig. 9 Variation of $\ln(P_{CO}/P_{CO_2})$ with Time at 1200 °C

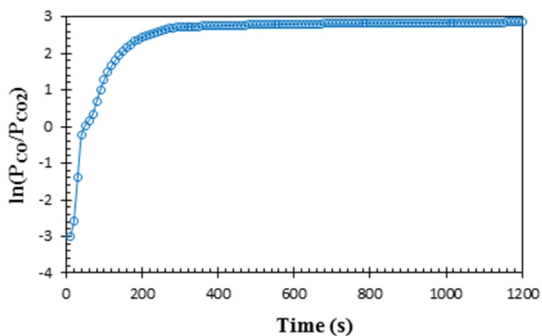


Fig. 10 Variation of $\ln(P_{CO}/P_{CO_2})$ with Time at 1550 °C

3.1.2 Nature of Metal Produced

Samples of reduced metal were obtained at all temperatures. However, separation of the metal from the slag depended on the temperature of the furnace. At 1200 °C, metal-slag separation was not attained, as illustrated in Fig. 11.

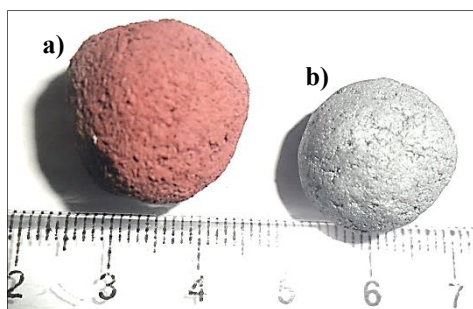


Fig. 11 Fe_2O_3 -PU Composite Pellet a) Before and b) After Reduction at 1200 °C

However, when the temperature was increased to 1550 °C a clear separation of reduced metal from the slag layer was observed, as shown in Fig. 12. A LECO O/N analyser revealed a reduction in oxygen content from 28.6 wt % to 0.0532 wt, corresponding to about 99.80 % reduction.



Fig. 12 Droplets of Metallic Iron obtained after Reduction of Fe_2O_3 -PU Composite at 1550 °C

3.3 Extent of Reduction

The extent of reduction was calculated from the oxygen content of the reduced metal produced from the reaction of the iron oxide with PU. The results are

shown in Figs 13 and 14 for reduction at 1200 °C and 1550 °C, respectively. At 1200°C, PU is able to reduce Fe_2O_3 , attaining an extent of reduction of about 64%, after 20 min. As the reduction temperature increased from 1200 °C to 1550 °C, reduction essentially reached completion in less than 4 min.

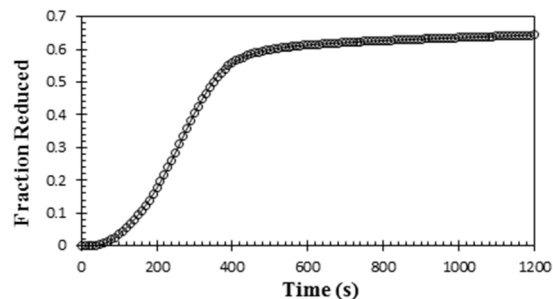


Fig. 13 Variation of Fraction Reduced with Time at 1200 °C

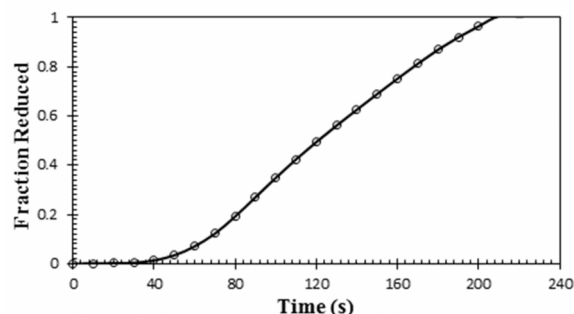


Fig. 14 Variation of Fraction Reduced with Time at 1550 °C

4 Conclusions

The reduction of iron oxide (Fe_2O_3) has been investigated using carbonaceous material prepared from waste PU as reductant. Major findings of the investigation are:

- (i) Waste polyurethane foam (PU) is a potential source of carbonaceous materials for iron oxide reduction;
- (ii) CO emissions showed an increase with an increase in temperature;
- (iii) At 1200 °C extent of reduction could only reach about 64 %. However, complete reduction of iron oxide was observed in less than 4 min of reaction when the temperature was increased to 1550 °C.

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