RECYCLING USED PURE WATER SACHETS AND THEIR BLENDS WITH WASTE COCONUT SHELLS AS CARBON RESOURCES IN IRON MAKING

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ABSTRACT
Recycling postconsumer plastics is currently a huge environmental headache globally. In Ghana, several thousands of tonnes of used pure water sachets are daily discarded indiscriminately. In this work the production of metallic iron from iron oxide using blends of used pure water sachets (PWS) and coconut shells (cocos nucifera) as reducing agent have been performed through experiments conducted in a horizontal tube furnace. Composite pellets were formed from mixtures of iron oxide and carbonaceous materials consisting of chars of coconut shells (CNS), PWS and three blends of CNS-PWS. The iron oxide-carbonaceous material composites were heated very rapidly in a laboratory scale horizontal tube furnace at 1500°C in a continuous stream of pure argon and the off gas was analysed continuously using an infrared (IR) gas analyser and a gas chromatographic (GC) analyser equipped with a thermal conductivity detector (TCD). Elemental analyses of samples of the reduced metal were performed chemically for its carbon and oxygen contents using a LECO carbon/sulphur and LECO oxygen/nitrogen analysers, respectively. The extent of reduction after ten minutes and the level of carburisation were determined for each carbonaceous reductant. The results indicate that metallic iron can be produced effectively from iron oxides using CNS, PWS and blends of these carbonaceous materials as reductants. It was revealed that the extent of reduction improved significantly when CNS was blended with PWS. The results also revealed that blending of the carbonaceous materials has a beneficial effect on the environment through decreasing carbon dioxide emissions.

Keywords: Recycling, Sachets, Waste, Coconut shells, Iron making

INTRODUCTION
Recycling postconsumer plastics is currently a huge environmental headache globally. Whereas in Ghana several thousands of tonnes of used pure water sachets are daily discarded indiscriminately, only 23% of HDPE was recycled in Australia in 2011-2012 (PACIA 2012). The rest was either landfilled or dumped illegally. Pure water sachets are composed principally of the thermoplastic polymer high density polyethylene (HDPE), a category of waste stream that occupies large landfill space and is not biodegradable. However, HDPE contains high levels of carbon and hydrogen and its thermal decomposition at high temperatures generates large amounts of the gaseous reducing species H₂ and CH₄ (Dankwah, 2012), which are known reductants of metal oxides. CNS is a cheap and abundantly available solid waste material that is cultivated in several parts of Ghana, especially along the coastal belts. As a biomass material, it is a renewable fuel and generally considered as a ‘carbon neutral fuel’.

The use of waste polymeric materials as chemical feedstock in iron and steelmaking is

Currently gaining the attention of researchers. Furthermore, as a means of recycling waste plastics, low temperature pyrolysis along with combustion and thermal degradation (of coal, plastics, biomass and their blends) has been widely investigated by various researchers (Vamvuka et al., 2003a; Vamvuka et al., 2003b; Cai et al., 2008; Kastanaki et al. (2002); Sharypov et al., 2002; Chattopadhyay et al., 2008; Vivero et al., 2005; Zhou et al., 2006; Singh et al., 2010). However, not much is known about the use of blends of CNS/PWS as reductants or carburisers in iron and steelmaking technologies. Accordingly, in the present work, the potential for producing metallic iron from hematite using blends of CNS and PWS as reducing and carburising agents is the principal aim and is investigated under inert atmosphere in a custom made horizontal tube furnace.

RESEARCH METHODOLOGY

Raw Materials

CNS (collected from Koforidua, Ghana) and its blends in three different proportions (Fig. 1) with granulated PWS (collected from Koforidua, Ghana) were employed in this study as carbonaceous materials. The chemical composition (wt %) of the samples and the ash analyses are given in Tables 1-3. 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 4.

![Diagram: Blend compositions of the different carbonaceous materials utilised in this study](image)

Samples of CNS were ground and sieved to particle size in the range of -470 +450 µm while samples of PWS were crushed to smaller sizes after an embrittlement process. Pulverised PWS were sieved to a particle size -470 +450µm, similar to that of CNS. Blends of CNS/PWS were prepared in three different proportions.

<table>
<thead>
<tr>
<th>Component</th>
<th>C</th>
<th>H</th>
<th>S</th>
<th>N</th>
<th>O*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWS (wt %)</td>
<td>85.5</td>
<td>14.2</td>
<td>0.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CNS Raw (wt %)</td>
<td>52.4</td>
<td>5.72</td>
<td>0.03</td>
<td>0.11</td>
<td>41.77</td>
</tr>
<tr>
<td>CNS Char (wt %)</td>
<td>78.1</td>
<td>3.49</td>
<td>0.01</td>
<td>0.15</td>
<td>17.55</td>
</tr>
</tbody>
</table>

Table 1: Elemental analysis of PWS and CNS
TABLE 2: PROXIMATE ANALYSES OF PWS AND CNS

<table>
<thead>
<tr>
<th>Component</th>
<th>Moisture (wt %)</th>
<th>Ash*</th>
<th>Volatile matter*</th>
<th>Fixed carbon*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PWS</td>
<td>-</td>
<td>0.3</td>
<td>99.7</td>
<td>-</td>
</tr>
<tr>
<td>Raw</td>
<td>8.5</td>
<td>0.87</td>
<td>87.5</td>
<td>11.6</td>
</tr>
<tr>
<td>Char</td>
<td>5.40</td>
<td>0.70</td>
<td>29.80</td>
<td>69.60</td>
</tr>
</tbody>
</table>

* By difference

TABLE 3: ASH ANALYSIS OF RAW CNS

<table>
<thead>
<tr>
<th>Component</th>
<th>Raw (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>37.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1.8</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1.8</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.29</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>3.1</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>0.07</td>
</tr>
<tr>
<td>CaO</td>
<td>6.2</td>
</tr>
<tr>
<td>MgO</td>
<td>4.2</td>
</tr>
<tr>
<td>Na₂O</td>
<td>3.7</td>
</tr>
<tr>
<td>K₂O</td>
<td>23.2</td>
</tr>
<tr>
<td>SO₃</td>
<td>5.2</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>1.7</td>
</tr>
<tr>
<td>ZnO</td>
<td>2.4</td>
</tr>
<tr>
<td>BaO</td>
<td>0.56</td>
</tr>
<tr>
<td>SrO</td>
<td>0.12</td>
</tr>
</tbody>
</table>

TABLE 4: ELEMENTAL ANALYSIS OF IRON OXIDE

<table>
<thead>
<tr>
<th>Component</th>
<th>Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>96.89</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.445</td>
</tr>
<tr>
<td>CaO</td>
<td>0.0225</td>
</tr>
<tr>
<td>MnO</td>
<td>0.020</td>
</tr>
<tr>
<td>ZnO</td>
<td>0.0115</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.134</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.257</td>
</tr>
<tr>
<td>LOI</td>
<td>2.22</td>
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</table>
**Thermal Decomposition Studies**

Pulverised PWS sample was mixed thoroughly with alumina powder and cylindrical pellets were formed from the resulting mixture by applying a load of 7.5 tonnes for 1 minute in a hydraulic press. The use of the alumina powder was to slow down the decomposition process (to enable gas measurements by the IR-analyser) as well as mimic the reduction environment through the cylindrical pellets. The alumina powder acted as a blank medium, since its reduction will be difficult at the selected temperature.

![Fig. 2: Composite pellet (of Al₂O₃ + PWS) utilized for thermal decomposition of PWS at 1500 °C](image)

The experimental apparatus consisted of two gas analysers connected to an electrically heated horizontal tube furnace and a data logging computer (Fig. 4). CO, CO₂ and CH₄ were monitored continuously by an IR gas analyser (Advance Optima model ABB® AO2020) while a GC analyser (SRI 8610C Multiple Gas Chromatograph #3 configuration, equipped with a thermal conductivity detector, TCD) monitored O₂, H₂, H₂O and CₙHₘ. 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 900 s. No appreciable change in gas composition was observed beyond 900 s.

**Reduction Studies**

The reduction experiments were conducted in a similar way as the thermal decomposition process, except that composite pellets in this case contained iron oxide instead of alumina. About 1.86 g of iron oxide was subsequently mixed with the carbonaceous blends (~ 30 wt %) and compacted in a die to produce cylindrical pellets (~ 14 mm thick and 15 mm diameter) (Fig. 3d), by applying a load of 7.5 tonnes for 120 s in a hydraulic press.

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 content was determined by the following chemical analysis methods:

- LECO Carbon/Sulphur analyser (model CS 230, LECO Corporation, Michigan, USA) for its C content and
- LECO Nitrogen/Oxygen analyser (model TC-436 DR 602-500-600, LECO
Proposed Mechanism of Reduction of Iron Oxide by Biomass/Plastics Blend

The reactions that take place in the furnace may be conveniently divided into the following four categories:

1) Conversion of the polymer into methane and other hydrocarbons.

\[ \text{Polymer} \rightarrow C_nH_m(g) \]

2) Thermal decomposition of methane (and other hydrocarbons) into carbon and
RESULTS AND DISCUSSION

Thermal Decomposition Behaviour of PWS at 1500°C

The gas generation behaviour during the thermal decomposition of PWS-alumina at 1500 °C is illustrated in Fig. 4. The predominant gases from the thermal decomposition of PWS are the reducing gases CH₄ and H₂ (peak identified in Fig. 5). Minor amounts of CO and CO₂ were detected as indicated in Fig. 4. As alumina was unlikely to have been reduced by PWS (and the PWS had no oxygen), the only probable source of CO and CO₂ could be from partial oxidation of the PWS by trapped oxygen in the pores of the PWS-alumina compact and/or minor reformation of CH₄ by H₂O and/or CO₂ (equations 10-12).

\[
\frac{1}{2}(C_2H_4)_n + O_2 = nCO_2 + nH_2O
\]

\[
\begin{align*}
\text{CH}_4 + \text{CO}_2 & = 2\text{CO} + 2\text{H}_2 \\ 
\text{CH}_4 + \text{H}_2\text{O} & = \text{CO} + 3\text{H}_2 
\end{align*}
\]

However, the contents of CO and CO\(_2\) were negligible compared to \(\text{H}_2\) and \(\text{CH}_4\) when PWS-alumina was heated at 1500 °C.

![Fig. 4: Gas generation behaviour during the thermal decomposition of PWS from a PWS-alumina compact](image)

![Fig. 5: Gas chromatogram obtained after 60 s of heating PWS-alumina compact](image)

Direct ingress of oxygen into the furnace was unlikely as the furnace was purged continuously with argon. After 60 s of heating the compact, the area ratio \(\text{H}_2/\text{CH}_4\) was approximately 1.0 but this gradually increased to about 2.5 after 300 s, implying that \(\text{CH}_4\) undergoes cracking to generate more \(\text{H}_2\) and nascent C in the course of heating, probably through equation 13, which is spontaneous above 550 °C.

\[
\text{CH}_4 = \text{C} + 2\text{H}_2 \\
\Delta G^\circ = 91,040 - 110.7 \text{ T [J mol}^{-1}\text{]} 
\]

It is clear from Figs 4 and 5 that the main reductants produced from the thermal decomposition of PWS are \(\text{H}_2\), \(\text{CH}_4\), and minor amounts of CO and C. The generated
carbon particles are present at the Nano-scale level. The potential for PWS to function as a reductant for iron oxide reduction therefore exists, as indicated by the formation of Nano-scale solid carbon and gaseous H₂ and CH₄.

**Nature of Metal Produced**

Samples of reduced metal were obtained for all blend proportions and the result for PWS as the reducing agent is shown in Fig. 6. The vigorous nature of the reaction is apparent from Fig. 6, where several small droplets of metallic iron are seen distributed across the entire volume of the crucible.

![Fig. 6: Droplets of metallic iron and char obtained after 600 seconds of reduction of iron oxide by a) PWS and b) CNS](image)

The particles could not coagulate into one big lump because of the excess amount of carbonaceous materials (1.45 ≤ C/O ≤ 1.68) utilised in this investigation, the essence of which was to ensure that enough carbonaceous material was available for the reaction to go to completion.

**IR Gas Analyses**

The contents of CO and CO₂ in the off-gas were measured continuously by an IR gas analyser from which the rates of gas evolution (µmol/s.g-Fe) were calculated for each carbonaceous blend. The results are shown in Fig. 7. The rates of evolution of CO and CO2 increase slowly for the first 200 seconds for PWS (Fig. 7a), followed by a sharp rise, attaining maximum values of 154.4 and 16.6 µmol/s.g-Fe after about 230 and 220 seconds, respectively. Fig. 7b illustrates the gas generation behaviour of CNS. Active gas generation commences after 180 seconds, and attains maximum values of 96.7 and 26.4 µmol/s.g-Fe after about 330 and 210 seconds for CO and CO₂, respectively. CO₂ generation for CNS is quite significant, unlike PWS, which has almost negligible generation. Gas generation for PWS-CNS blends (Figs. 7c-e) commenced earlier than PWS or CNS, indicating that blending promotes gasification and/or reduction of iron oxide.

It is apparent from Fig. 7 that all the blends showed lower CO₂ evolution compared to CNS. The relatively low values recorded for CO₂ compared to CO may be an indication of direct
reduction of Fe$_2$O$_3$ by C or a dominant carbon gasification by CO$_2$ (Boudouard reaction, equation 8) and/or by water (equation 7). Equations 7 and 8 are highly endothermic and occur above 1000 °C. Another possible reaction is the direct reduction of Fe$_2$O$_3$ by CH$_4$, which was the predominant gaseous hydrocarbon detected in the off-gas in the initial stages of the reaction.

$$3\text{CH}_4 + \text{Fe}_2\text{O}_3 = 2\text{Fe} + 6\text{H}_2 + 3\text{CO}$$ (14)
Fig. 7: Change in the rate of generation of CO and CO$_2$ with time for each carbonaceous reductant

**Extent of Reduction**

The extent of reduction (after 600 s) was calculated from the oxygen content of the reduced metal produced from the reaction of the iron oxide with each carbonaceous reductant. The results are shown in Table 5.

**Table 5: Extent of Reduction Attained After 600 s of reduction of Fe$_2$O$_3$ with various Carbonaceous Reductants**

<table>
<thead>
<tr>
<th>Carbonaceous Reductant</th>
<th>CNS</th>
<th>Blend A</th>
<th>Blend B</th>
<th>Blend C</th>
<th>PWS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extent of reduction (%)</td>
<td>73.9</td>
<td>79.6</td>
<td>82.8</td>
<td>86.8</td>
<td>84.7</td>
</tr>
</tbody>
</table>

Blending of CNS with PWS resulted in improved extent of reduction because more hydrogen was released into the reaction system as indicated by the improved peak of hydrogen in the chromatogram of PWS compared to that of CNS (Fig. 8). This results in an increase in the H$_2$/CO ratio in the system. Work done by Alamsari *et al.* (2011) has shown a significant improvement in iron oxide reduction with an increase in the H$_2$/CO ratio. Similar observations were reported by other researchers (Bonalde *et al.*, 2005; Pineau *et al.*, 2006)

Fig. 8: Gas chromatogram obtained after reduction of iron oxide by (a) PWS and (b) CNS for 1 minute at 1500 °C
Environmental Considerations: CO₂ emission

The rate of CO₂ generation in the first ten minutes by each carbonaceous reductant is plotted in Fig. 9 whilst the accumulated amount of CO₂ generated (μmol) is shown in Fig. 10. It is clear from Figs (9 and 10) that the highest rate (26.4 μmol/g.s Fe) and highest accumulated amount (~3257 μmol) of CO₂ was produced from the reaction involving CNS. Blending of CNS with PWS resulted in a decrease in the rate and amount of CO₂ evolved up to Blend B, which recorded the lowest rate and accumulated amount of 11.5μmol/g.s Fe and 853 μmol, respectively. The significantly high value of CO₂ recorded for CNS as opposed to that for PWS and the blends is attributed to the high oxygen content of CNS char (17.55 wt %).

![Fig. 9: Concentration of CO₂ generated by reactions of iron oxide with each carbonaceous reductant](image)

The observed decrease in CO₂ emissions with PWS addition agrees with the observation by Matsuda et al. (2008) that it is possible to utilise waste plastics to produce metallic iron without generating CO₂. Singh et al. (2010) observed a 6.5% reduction in CO₂ emissions when coal was fired with 25% PWS (measured in terms of thermal energy). They attributed this to the higher heating value of HDPE (46.2 MJ/kg) compared to that of the coal.

![Fig. 10: Amount of CO₂ generated by reactions of iron oxide with each carbonaceous reductants](image)
Since biomass is considered as a CO$_2$-neutral material, achieving further reduction in gaseous emissions through blending with postconsumer plastics would be a great step towards ultralow CO$_2$ emissions in iron and steel production technologies.

CONCLUSION
A laboratory investigation has been conducted on the possibility of a coke-free iron making utilising postconsumer PWS, chars of waste CNS and their blends as reducing agents. Major findings of this investigation are:

1) Blends of postconsumer PWS with waste CNS could be used effectively as reducing agents in ironmaking.
2) The extent of reduction after ten minutes of reaction showed an improvement with the amount of PWS blended with CNS.
3) Although biomass is considered as a CO$_2$-neutral material, this investigation has shown that it is still possible to achieve further reduction in gaseous emissions through blending the biomass with postconsumer plastics, a measure that would be a great step towards ultralow CO$_2$ emissions in iron and steelmaking technologies.

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REFERENCES


