

# Recycling Blends Of HDPE And Coconut Shells As Reducing Agent For The Production Of Metallic Iron From Iron Oxide ( $\text{Fe}_2\text{O}_3$ )

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**Abstract:** Laboratory studies on the production of metallic iron from iron oxide using blends of coconut shells (*cocos nucifera*) and high density polyethylene (HDPE) as reducing agent have been performed through experiments conducted in a horizontal resistance heating tube furnace. Composite pellets were formed from mixtures of iron oxide and carbonaceous materials consisting of chars of coconut shells (CNS), HDPE and three blends of CNS-HDPE. 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, HDPE and blends of these carbonaceous materials as reductants. It was revealed that the extent of reduction improved significantly when CNS was blended with HDPE. The results also revealed that blending of the carbonaceous materials has a beneficial effect on the environment through decreasing carbon dioxide emissions.

**Index Terms:** Coconut shells, High density polyethylene, Composite pellets, Infrared gas analyser, Gas chromatographic analyser, LECO carbon/sulphur analyser, LECO oxygen/nitrogen analyser, Extent of reduction, Carburisation

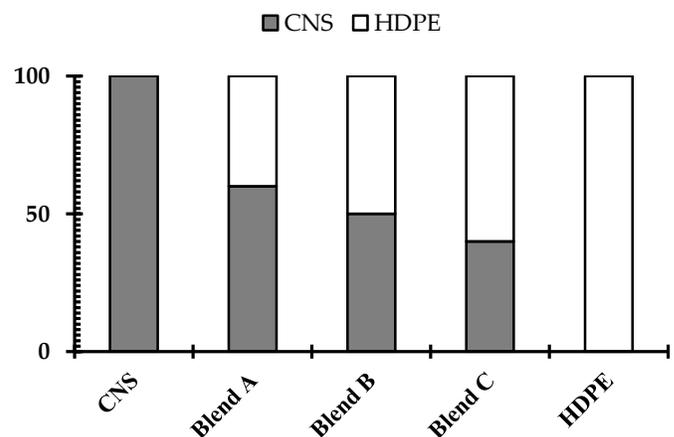
## 1 INTRODUCTION

23% of HDPE was recycled in Australia in 2011-2012 [1]. The rest was either landfilled or dumped illegally. This category of waste stream occupies large landfill space and is not biodegradable. HDPE, a thermoplastic polymer contains high levels of carbon and hydrogen and its thermal decomposition at high temperatures generates large amounts of the gaseous reducing species  $\text{H}_2$  and  $\text{CH}_4$  [2], 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. 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 [3], [4], [5], [6], [7], [8], [9], [10], [11], [12]. However, not much is known about the use of blends of CNS/HDPE as reductants or carburisers in iron and steelmaking technologies. In the present work, the potential for producing metallic iron from hematite using blends of CNS and HDPE as reducing and carburising agents is investigated under inert atmosphere in a custom made horizontal tube furnace.

## 2 EXPERIMENTAL

### 2.1 Raw Materials

CNS (collected from Koforidua, Ghana) and its blends in three different proportions (Fig. 1) with granulated HDPE (obtained from Qenos Pty. Ltd., Victoria, Australia) 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%  $\text{Fe}_2\text{O}_3$ ) was obtained from Ajax FineChem Pty Ltd, Taren Point, NSW, Australia; its composition (determined by XRF analysis) is given in Table 4.



**Fig. 1:** Blend compositions of the different carbonaceous materials utilised in this study

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Samples of CNS were ground and sieved to particle size in the range of -470 +450  $\mu\text{m}$  while samples of granulated HDPE were crushed to smaller sizes by using a cutting mill "Pulverisette 15" (Fritsch GmbH, Idar-Oberstein, Germany). By means of a sieve insert with 0.5 mm trapezoidal perforations in the cutting mill a particle size -470 +450 $\mu\text{m}$ , similar to that of CNS was obtained. Blends of CNS/HDPE were prepared in

three different proportions.

**TABLE 1: ELEMENTAL ANALYSIS OF HDPE AND CNS**

Component	C	H	S	N	O*
HDPE (wt %)	85.5	14.2	0.3	-	-
CNS Raw (wt %)	52.4	5.72	0.03	0.11	41.77
CNS Char (wt %)	78.1	3.49	0.01	0.15	17.55

\* By difference

**TABLE 2: PROXIMATE ANALYSES OF HDPE AND CNS**

Component	Moisture	Ash*	Volatile matter*	Fixed carbon*
HDPE (wt %)	-	0.3	99.7	-
Raw (wt %)	8.5	0.87	87.5	11.6
Char (wt %)	5.40	0.70	29.80	69.60

\*Dry basis

**TABLE 3: ASH ANALYSIS OF RAW CNS**

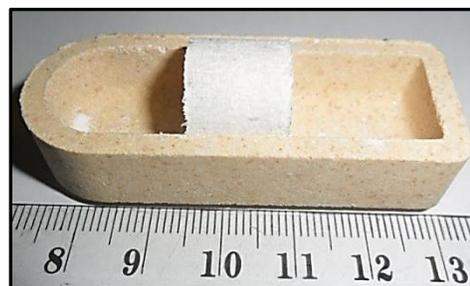
Component	Raw (wt %)
SiO <sub>2</sub>	37.5
Fe <sub>2</sub> O <sub>3</sub>	1.8
Al <sub>2</sub> O <sub>3</sub>	1.8
TiO <sub>2</sub>	0.29
P <sub>2</sub> O <sub>5</sub>	3.1
Mn <sub>3</sub> O <sub>4</sub>	0.07
CaO	6.2
MgO	4.2
Na <sub>2</sub> O	3.7
K <sub>2</sub> O	23.2
SO <sub>3</sub>	5.2
V <sub>2</sub> O <sub>5</sub>	1.7
ZnO	2.4
BaO	0.56
SrO	0.12

**TABLE 4: ELEMENTAL ANALYSIS OF HDPE AND CNS**

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

## 2.2 Thermal Decomposition Studies

Pulverised HDPE sample (particle size below 1 mm) 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. The experimental apparatus consisted of two gas analysers connected to an electrically heated horizontal tube furnace and a data logging computer (Fig. 4). CO, CO<sub>2</sub> and CH<sub>4</sub> 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 O<sub>2</sub>, H<sub>2</sub>, H<sub>2</sub>O and C<sub>n</sub>H<sub>m</sub>.



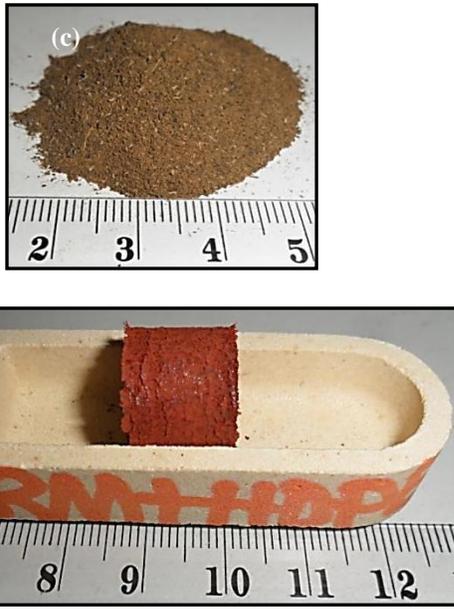
**Fig. 2:** Composite pellet (of Al<sub>2</sub>O<sub>3</sub> + HDPE) utilized for thermal decomposition of HDPE at 1550 °C

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.

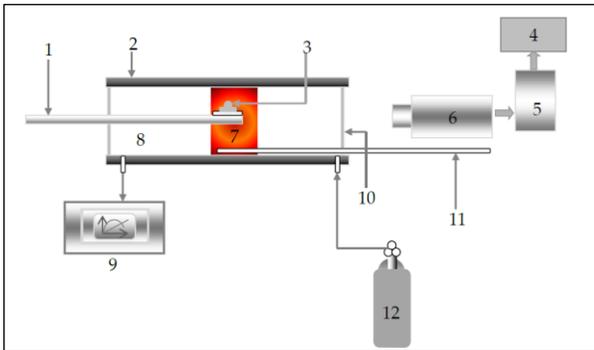
## 2.3 Reduction Studies

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.





**Fig. 3:** (a) HDPE, (b) iron oxide, (c) CNS (raw) and (d) cylindrical pellet of iron oxide-HDPE



**Fig. 4:** Schematic of the horizontal tube furnace and IR gas analyser system. (1 Sample Rod; 2 Alumina tube; 3 Reaction mixture; 4 PC; 5 DVD; 6 CCD Camera; 7 Hot Zone; 8 Cold Zone; 9 Gas analyser; 10 Quartz window; 11 Thermocouple; 12 Argon gas)

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 Corporation, Michigan, USA) for its O content.

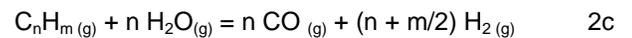
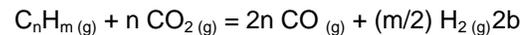
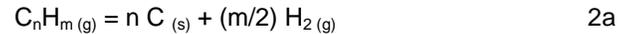
## 2.4 Proposed Mechanism of Reduction of Iron Oxide by Biomass/Plastics Blend

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

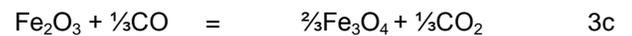
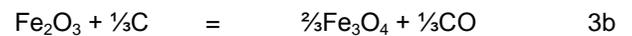
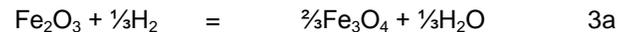
1) Conversion of the polymer into methane and other hydrocarbons.



2) Thermal decomposition of methane (and other hydrocarbons) into carbon and hydrogen or reformation into CO and H<sub>2</sub>:



3) Reduction of Fe<sub>2</sub>O<sub>3</sub> by hydrogen, carbon and carbon monoxide to produce Fe<sub>3</sub>O<sub>4</sub>:



4) Reduction of Fe<sub>3</sub>O<sub>4</sub> by hydrogen, carbon and carbon monoxide to produce FeO

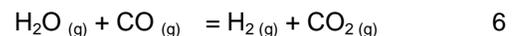


5) Reduction of FeO by hydrogen, carbon and carbon monoxide to produce Fe

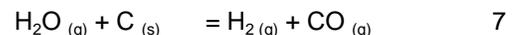


6) Auxiliary reactions 13, 14)

i. Water gas shift reaction:



ii. Gasification of C by H<sub>2</sub>O:



iii. Gasification of C by CO<sub>2</sub> (Boudouard reaction):



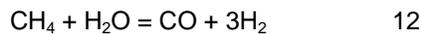
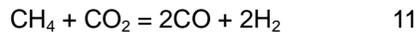
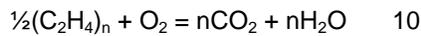
iv. Carbon dissolution into molten metal:

$$C_{(s)} = \underline{C} \quad 9$$

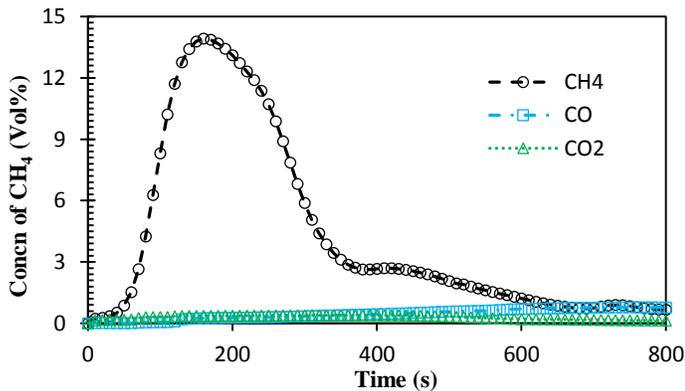
### 3 RESULTS AND DISCUSSIONS

#### 3.1 Thermal Decomposition Behaviour of HDPE at 1500°C

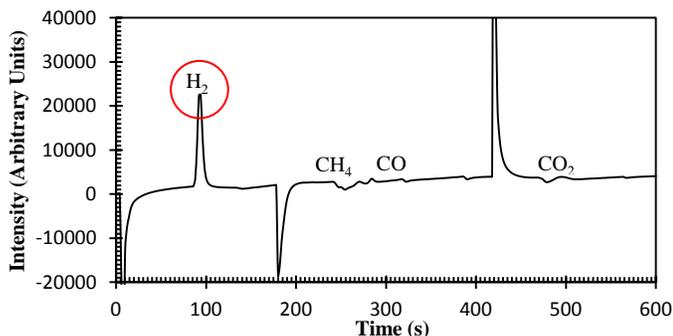
The gas generation behaviour during the thermal decomposition of HDPE-alumina at 1500 °C is illustrated in Fig. 4. The predominant gases from the thermal decomposition of HDPE are the reducing gases CH<sub>4</sub> and H<sub>2</sub> (peak identified in Fig. 5). Minor amounts of CO and CO<sub>2</sub> were detected as indicated in Fig. 4. As alumina was unlikely to have been reduced by HDPE (and the HDPE had no oxygen), the only probable source of CO and CO<sub>2</sub> could be from partial oxidation of the HDPE by trapped oxygen in the pores of the HDPE-alumina compact and/or minor reformation of CH<sub>4</sub> by H<sub>2</sub>O and/or CO<sub>2</sub> (equations 10-12).



However, the contents of CO and CO<sub>2</sub> were negligible compared to H<sub>2</sub> and CH<sub>4</sub> when HDPE-alumina was heated at 1500 °C.

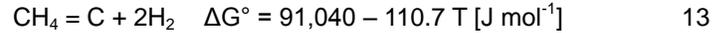


**Fig. 4:** Gas generation behaviour during the thermal decomposition of HDPE from a HDPE-alumina compact



**Fig. 5:** Gas chromatogram obtained after 60 s of heating HDPE-alumina compact

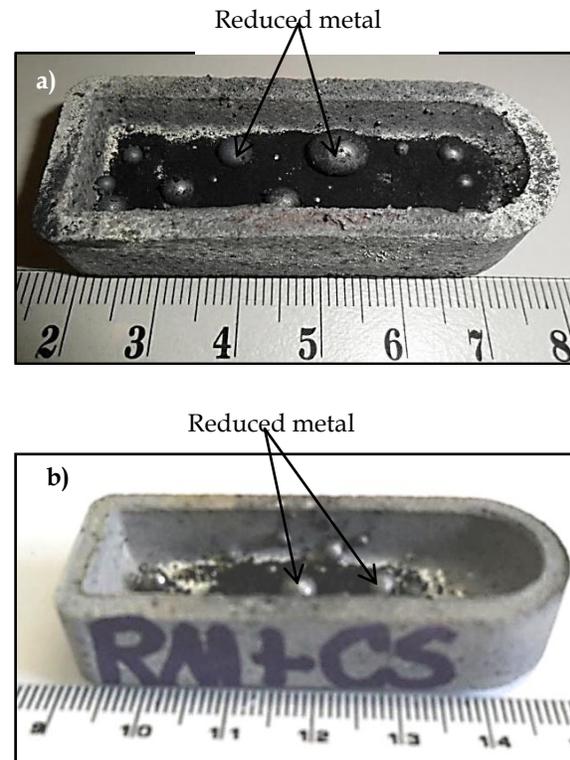
Direct ingress of oxygen into the furnace was unlikely as the furnace was purged continuously with argon. After 60 s of heating the compact, the area ratio H<sub>2</sub>/CH<sub>4</sub> was approximately 1.0 but this gradually increased to about 2.5 after 300 s, implying that CH<sub>4</sub> undergoes cracking to generate more H<sub>2</sub> and nascent C in the course of heating, probably through equation 13, which is spontaneous above 550 °C.



It is clear from Figs 4 and 5 that the main reductants produced from the thermal decomposition of HDPE are H<sub>2</sub>, CH<sub>4</sub>, and minor amounts of CO and C. The generated carbon particles are present at the Nano-scale level. The potential for HDPE to function as a reductant for iron oxide reduction therefore exists, as indicated by the formation of Nano-scale solid carbon and gaseous H<sub>2</sub> and CH<sub>4</sub>.

#### 3.2 Nature of Metal Produced

Samples of reduced metal were obtained for all blend proportions and the result for HDPE 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.

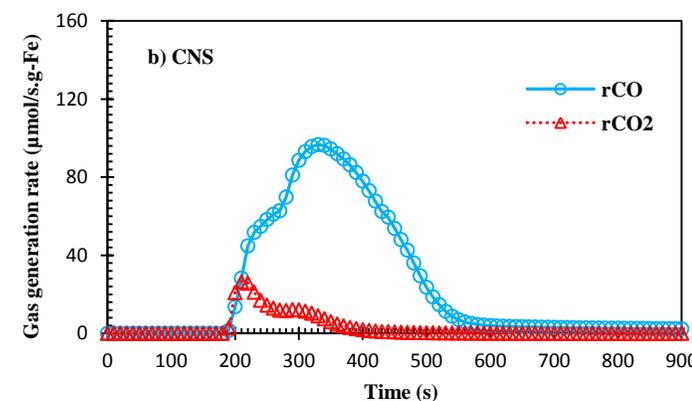
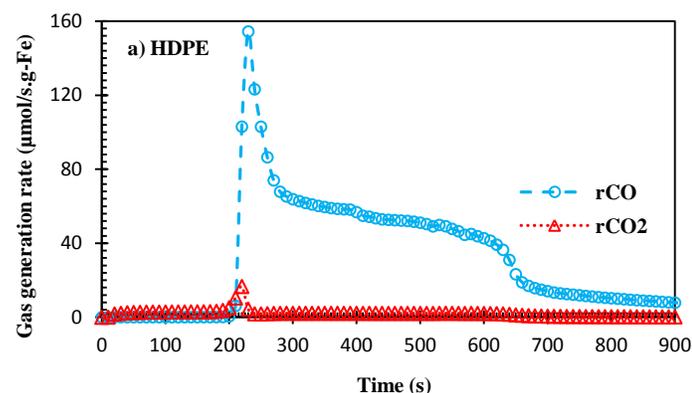
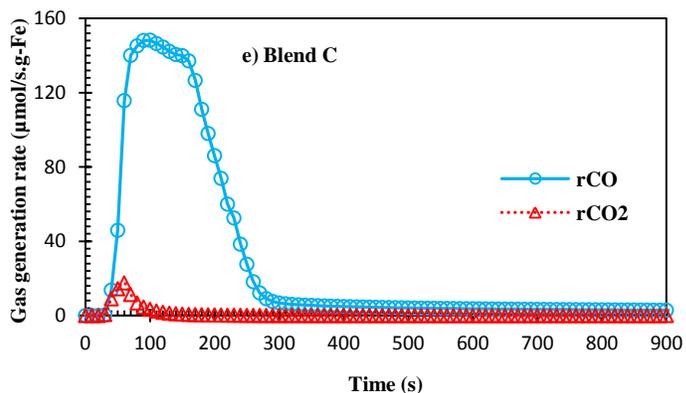
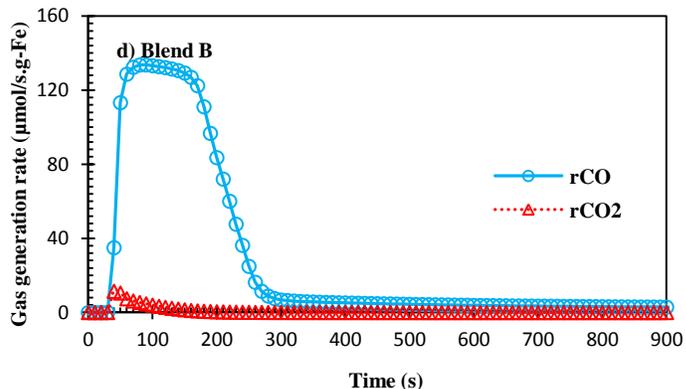
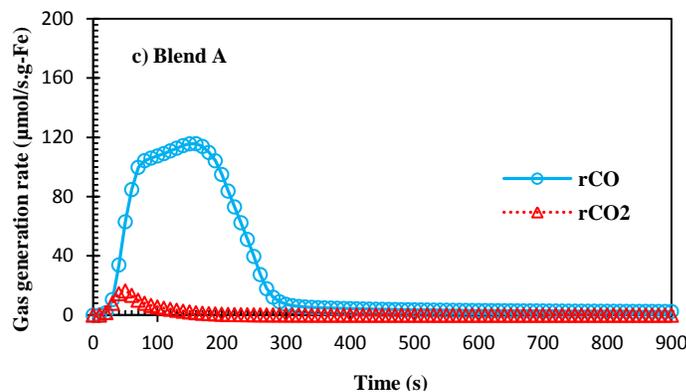


**Fig. 6:** Droplets of metallic iron and char obtained after 600 seconds of reduction of iron oxide by a) HDPE and b) CNS

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

### 3.3 IR Gas Analyses

The contents of CO and CO<sub>2</sub> 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 CO<sub>2</sub> increase slowly for the first 200 seconds for HDPE (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 CO<sub>2</sub>, respectively. CO<sub>2</sub> generation for CNS is quite significant, unlike HDPE, which has almost negligible generation. Gas generation for HDPE-CNS blends (Figs. 7c-e) commenced earlier than HDPE 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 CO<sub>2</sub> evolution compared to CO. The relatively low values recorded for CO<sub>2</sub> compared to CO may be an indication of direct reduction of Fe<sub>2</sub>O<sub>3</sub> by C or a dominant carbon gasification by CO<sub>2</sub> (Boudouard reaction, equation 8) and/or by water (equation 7). Equations 7 and 8 are highly endothermic and occur above 1000 °C [15]. Another possible reaction is the direct reduction of Fe<sub>2</sub>O<sub>3</sub> by CH<sub>4</sub>, which was the predominant gaseous hydrocarbon detected in the off-gas in the initial stages of the reaction.



**Fig. 7:** Change in the rate of generation of CO and CO<sub>2</sub> with time for each carbonaceous reductant

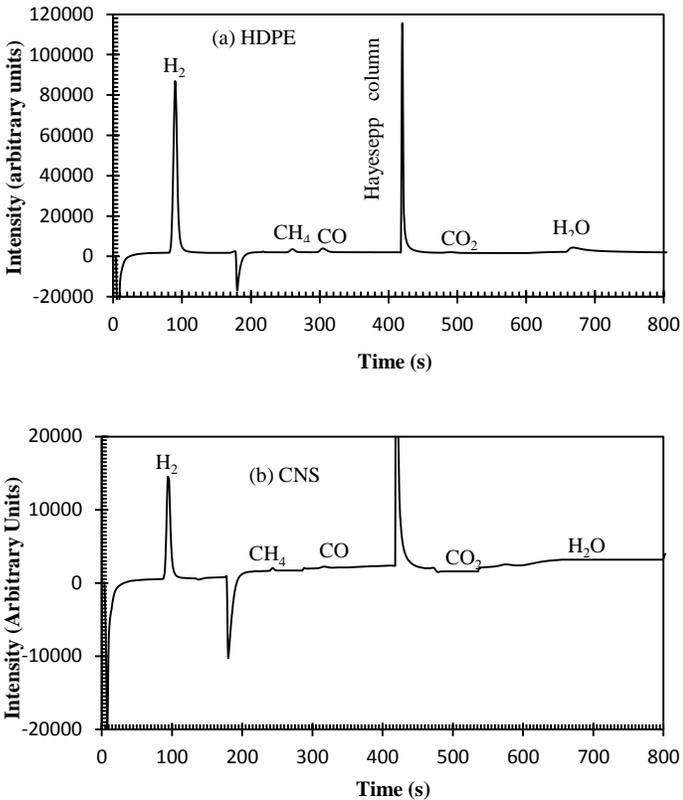
### 3.2 Extent of Reduction

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<sub>2</sub>O<sub>3</sub> WITH VARIOUS CARBONACEOUS REDUCTANTS

Carbonaceous Reductant	CNS	Blend A	Blend B	Blend C	HDPE
Extent of reduction (%)	73.9	79.6	82.8	86.8	84.7

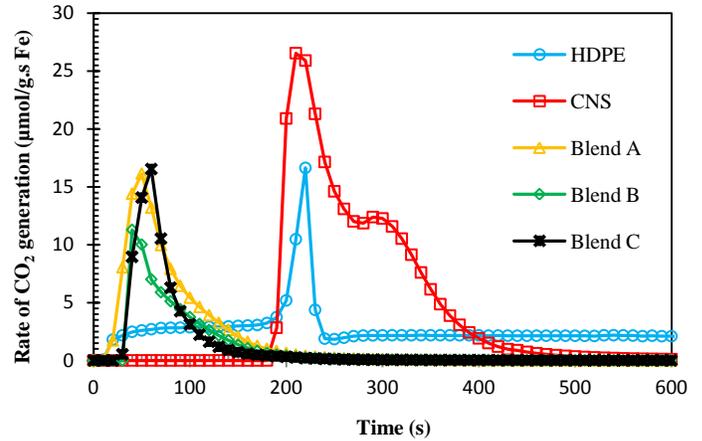
Blending of CNS with HDPE resulted in improved extent of reduction because more hydrogen was released into the reaction system as indicated by the improved peak of hydrogen in the chromatogram of HDPE compared to that of CNS (Fig. 8). This results in an increase in the  $H_2/CO$  ratio in the system. Work done by Alamsari *et al.* [16] 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 [17], [18], [19].



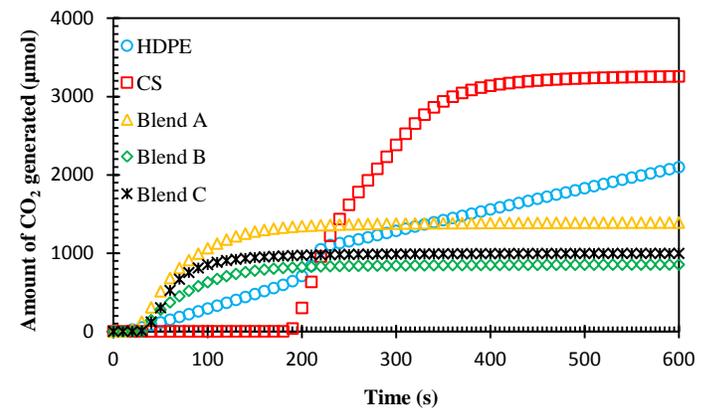
**Fig. 8:** Gas chromatogram obtained after reduction of iron oxide by (a) HDPE and (b) CNS for 1 minute at 1500 °C

### 3.3 Environmental Considerations: CO<sub>2</sub> emission

The rate of CO<sub>2</sub> generation in the first ten minutes by each carbonaceous reductant is plotted in Fig. 9 whilst the accumulated amount of CO<sub>2</sub> generated ( $\mu\text{mol}$ ) is shown in Fig. 10. It is clear from Figs (9 and 10) that the highest rate (26.4  $\mu\text{mol/g.s Fe}$ ) and highest accumulated amount ( $\sim 3257 \mu\text{mol}$ ) of CO<sub>2</sub> was produced from the reaction involving CNS. Blending of CNS with HDPE resulted in a decrease in the rate and amount of CO<sub>2</sub> evolved up to Blend B, which recorded the lowest rate and accumulated amount of 11.5  $\mu\text{mol/g.s Fe}$  and 853  $\mu\text{mol}$ , respectively. The significantly high value of CO<sub>2</sub> recorded for CNS as opposed to that for HDPE and the blends is attributed to the high oxygen content of CNS char (17.55 wt %). The observed decrease in CO<sub>2</sub> emissions with HDPE addition agrees with the observation by Matsuda *et al.* [20] that it is possible to utilise waste plastics to produce metallic iron without generating CO<sub>2</sub>. Singh *et al.* [12] observed a 6.5% reduction in CO<sub>2</sub> emissions when coal was fired with 25% HDPE (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. 9:** Concentration of CO<sub>2</sub> generated by reactions of iron oxide with each carbonaceous reductant



**Fig. 10:** Amount of CO<sub>2</sub> generated by reactions of iron oxide with each carbonaceous reductants

Since biomass is considered as a CO<sub>2</sub>-neutral material, achieving further reduction in gaseous emissions through blending with postconsumer plastics would be a great step towards ultralow CO<sub>2</sub> emissions in iron and steel production technologies.

## 4 CONCLUSIONS

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

- (1) Blends of postconsumer HDPE 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 HDPE blended with CNS.
- (3) Although biomass is considered as a CO<sub>2</sub>-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<sub>2</sub> emissions in iron and steelmaking technologies.

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