Recycling Waste Bakelite As A Carbon Resource In Ironmaking

James Ransford Dankwah, Emmanuel Baawuah

Abstract: Bakelite is a 3-dimensional cross-linked network structured thermosetting polymer which is difficult to recycle after use. However, it contains high levels of carbon and $CaCO_3$ that can be recovered for use as reductant and fluxing agent in ironmaking. In this work we report the use of post-consumer bakelite as reductant for the production of metallic iron from iron oxide in a horizontal tube furnace through the composite pellet approach.Gas emission studies were conducted by pyrolysing raw bakelite at different temperatures within the temperature range 1200-1600 °C in a horizontal tube furnace. Following this,composite pellets were then formed from mixtures of iron oxide and post-consumer bakelite.The iron oxide-bakelite 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 after ten minutes was determined from the oxygen content. Gas emission studies revealed the emission of large volumes of the reductant gases CO and CH_4along with CO_2.It is further demonstrated that post-consumer bakelite is effective at reducing iron oxide to produce metallic iron.

Key Words: Bakelite, Composite pellets, Infrared gas analyser, LECO carbon/sulphur analyser, LECO oxygen/nitrogen analyser, Extent of reduction.

1 INTRODUCTION

Bakelite ($[C_7H_8O_2]n$) is an amorphous polymer with a 3-dimensional cross-linked network structure, that imparts high hardness, rigidity, and strength along with good thermal and electrical insulating properties and chemical resistance. It is a material based on the thermosetting phenol formaldehyde resin, andconsists principally of C, H and O atoms. Calcium carbonate ($CaCO_3$) is usually added as a filler to commercially used bakelite. As a thermosetting polymer it is difficult to recycle because it does not lend itself to remoulding when heated. Accordingly, conventional methods for recycling have concentrated largely on disposal in landfill sites. Decreasing landfill space along with increasing landfill costs call for novel ways for its recycling.Bakelite contains moderate levels of carbon and hydrogen and its thermal decomposition at high temperatures generates large amounts of the gaseous reducing species CO and CH_4 along with solid C which are known reductants of metal oxides. The use of waste polymeric materials as chemical feedstock in iron and steelmaking is currently gaining the attention ofresearchers [1-7].However, not much is known about the use of bakelite as reductant in iron and steelmaking technologies. In the present work, the potential for producing metallic iron from hematite using bakelite as a reducing agent is investigated under inert atmosphere in a custom made horizontal tube furnace.

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2 EXPERIMENTAL

2.1 Raw Materials

Commercial grade bakelite (pulverised to 125 µm using a ring mill) containing about 30 wt %$CaCO_3$ (as filler)was employed in this study as carbonaceous material. The chemical composition (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% Fe_2O_3) was obtained from Ajax FineChem Pty Ltd, Taren Point, NSW, Australia; its composition (determined by XRF analysis) is given in Table 2.

TABLE 1: CHEMICAL COMPOSITION OF RAW BAKELITE

	Elements				Ash		
Component	C	H	O	S	$CaCO_3$	SiO_2	SO_3
wt %	53.4	4.0	11.6	0.017	30.03	0.91	0.06

TABLE 2: ELEMENTAL ANALYSIS OF Fe_2O_3

Component	Composition (wt %)
Fe_2O_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

2.2 Thermal Decomposition Studies

The experimental apparatus consisted of a gas analyser connected to an electrically heated horizontal tube furnace and a data logging computer (Fig. 1). CO, CO_2 and CH_4 were monitored continuously by an IR gas analyser (Advance Optima model ABB^® AO2020). Pulverised raw bakelite was placed in a LECO crucible prior to being pyrolysed. 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.

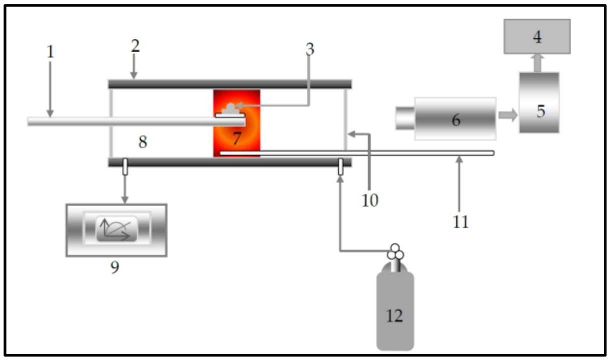

Fig. 1 *Schematic of the horizontal tube furnace and IR gas analyser system (1 Sample Rod; 2 Alumina tube; 3 Reaction mixture; 4 PC; 5 DVD; 6 CCD Camera; 7 Hot Zone; 8 Cold Zone; 9 Gas analyser; 10 Quartz window; 11 Thermocouple; 12 Argon gas)*

2.3 Reduction Studies

Spherical pellets were formed from pulverised iron oxide andbakelite (~ 30 wt %) with about 2 wt % flour as binder without flux addition **(Fig. 2)**.

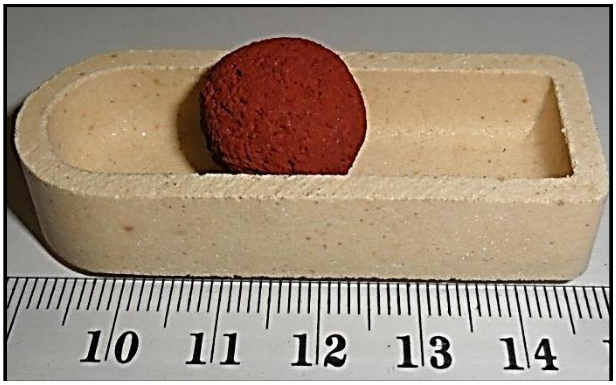

Fig. 2 *Spherical pellet of iron oxide-bakelite composite*

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 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.

3.0 RESULTS AND DISCUSSIONS

3.1 Thermal Decomposition Behaviour of Bakelite

The gas generation behaviour during the thermal decomposition of bakeliteis illustrated in Figs. 3, 4 and 5.The predominant gases from the thermal decomposition of bakelite are the reducing gases CH_4 and CO along with CO_2.

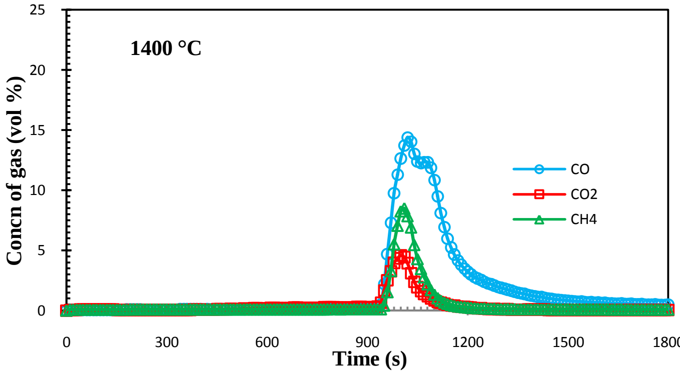

Fig. 3 *Gas generation behaviour during the thermal decomposition of bakelite at 1400 °C*

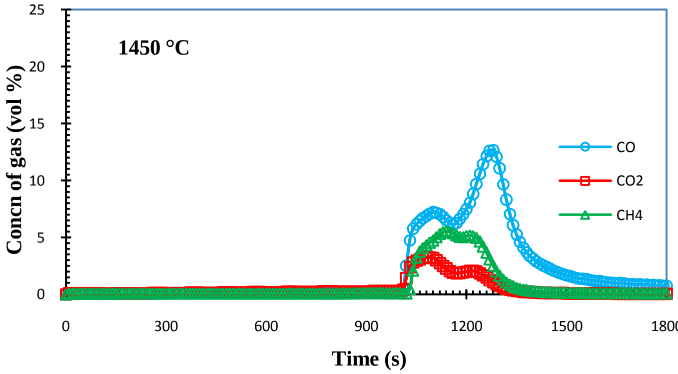

Fig. 4 *Gas generation behaviour during the thermal decomposition of bakelite at 1450 °C*

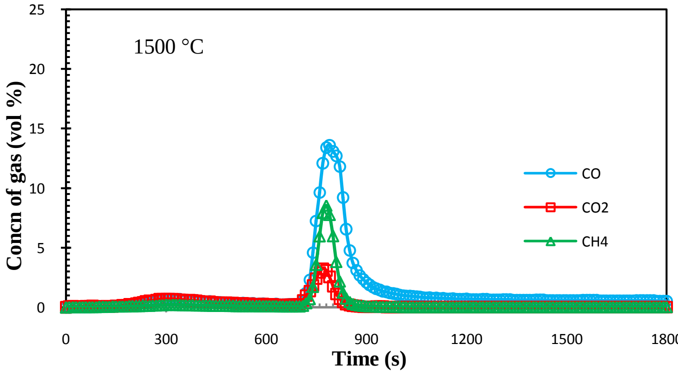

Fig. 5 *Gas generation behaviour during the thermal decomposition of bakelite at 1500 °C*

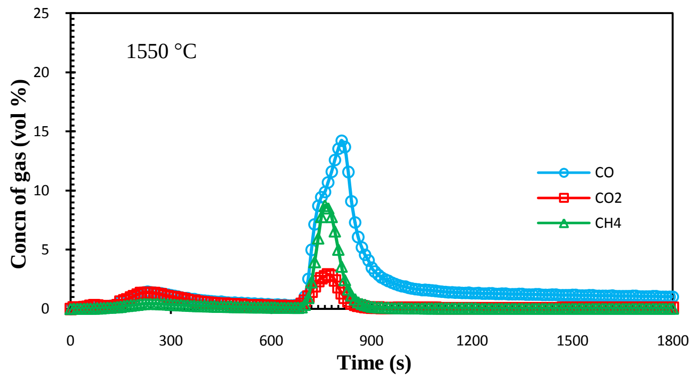

Fig. 6 *Gas generation behaviour during the thermal decomposition of bakelite at 1550 °C*

The potential for bakelite to function as a reductant for iron oxide reduction therefore exists, as indicated by the formation of solid carbon and gaseous CO and CH_4.

3.2 Reduction Studies

3.2.1 Mass loss and gas generation behaviour during heating of Fe_2O_3-bakelite composite from room temperature to 1200 °C

The mass loss and gas generation behaviour of Fe_2O_3-bakelite composite during heating from room temperature to 1200 °C is illustrated as a function of temperature in **Fig. 7**.

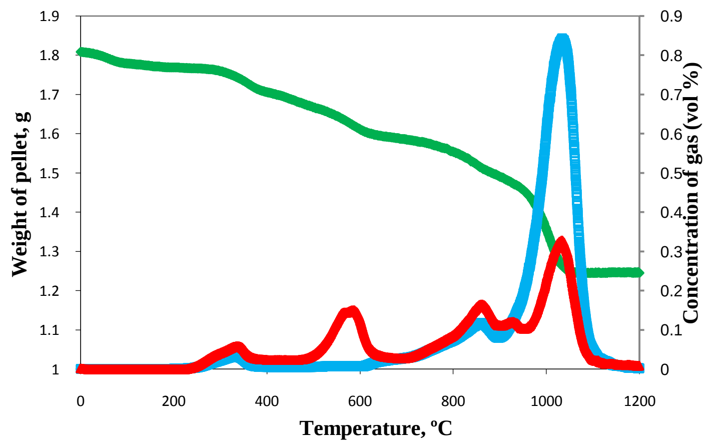

Fig. 7*Weight loss and gas generation behaviour during heating of Fe_2O_3-bakelite from room temperature to 1200 °C*

The weight of the pellet decreased from 1.806 g at room temperature to 1.245 g at 1200 °C, representing a weight loss of about 31 wt %. Three minor peaks (at 320, 570 and 850 °C) are observed in the gas emission plot before the major peak at 1030 °C.The minor peak at 320 °C corresponds to the devolatilisation of bakelite, while that at 570 °C corresponds to the reduction of Fe_2O_3 to Fe_3O_4 by CO and H_2. As pointed out by Wagner *et al.* [8], the temperature 570°C is important in the reduction of Fe_2O_3 to Fe_3O_4 by both CO and H_2. For temperatures higher than 570°C, hematite (Fe_2O_3) is first transformed into magnetite (Fe_3O_4), then into wustite ($Fe_{1-y}O$), and finally into metallic iron whereas at temperatures below 570°C, magnetite is directly transformed into iron since wustite is not thermodynamically stable [8]. The third peak at 850 °C is attributed to the calcination of $CaCO_3$, which constituted about 30 wt % of bakelite. This calcination process results in the emission of CO_2 along with some CO. The major peak around 1030 °C occurs in the main reduction region where the oxides are transformed into metallic iron.

3.2.2Gas generation behaviour during heating of Fe_2O_3-bakelite composite between 1400-1550 °C

The gas generation behaviour in the preheated furnace at various temperatures is illustrated in **Figs 8-11.**

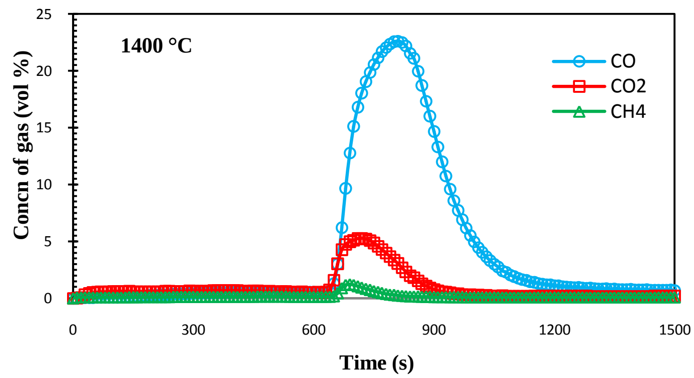

Fig. 8 *Gas generation behaviour during heating of Fe_2O_3-bakelite composite at 1450 °C*

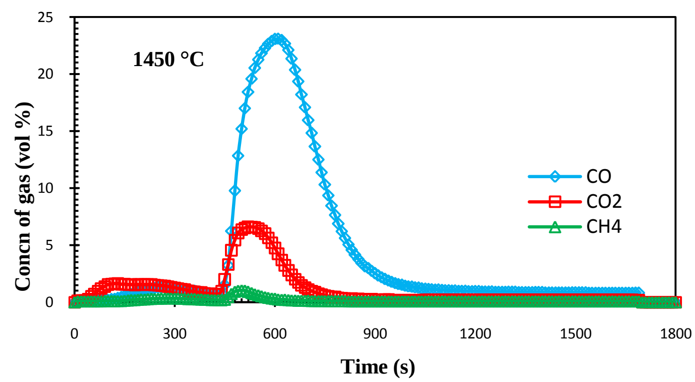

Fig. 9 *Gas generation behaviour during heating of Fe_2O_3-bakelite composite at1500 °C*

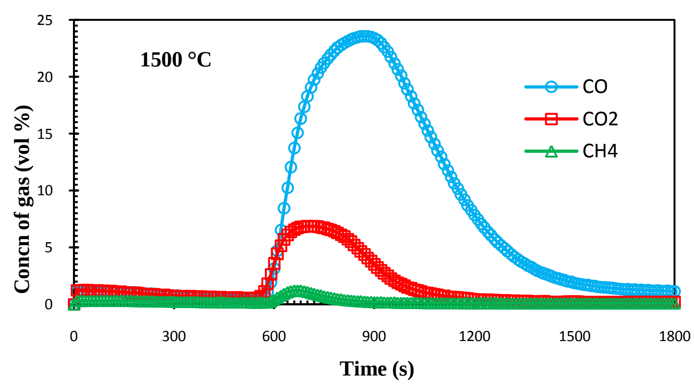

Fig. 10 *Gas generation behaviour during heating of Fe_2O_3-bakelite composite at 1550 °C*

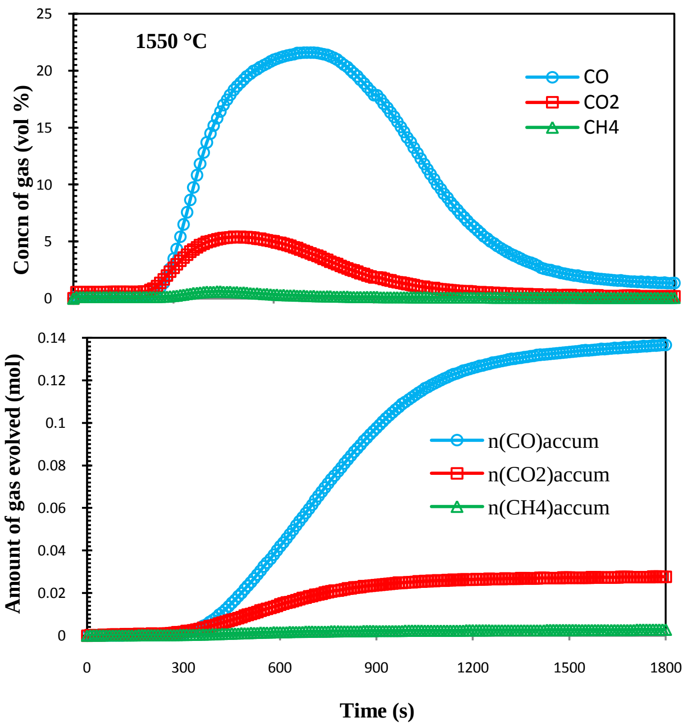

***Fig. 11**Gas generation behaviour during heating of Fe_2O_3-bakelite composite at1600 °C*

Comparing**Figs 8-11** to **Figs 3-6**, it is apparent that the concentration of CO and CO_2 increase while that of CH_4 decreases, implying that CO and especially CH_4 were actively involved in the reduction process. However, the levels of CO attained in the reduction process give an indication that although over 80% of CH_4 could have been converted into CO, the residual carbon from the thermal decomposition process was also an active reductant. Possible reactions for the reduction of Fe_2O_3 to Fe are:

$Fe_2O_3 + 3\ CH_4 = 2\ Fe + 3CO + 6\ H_2$ 1
$Fe_2O_3 + 3\ CO = 2\ Fe + 3CO_2$ 2
$Fe_2O_3 + 3\ C = 2\ Fe + 3CO$ 3
$Fe_2O_3 + 3\ H_2 = 2\ Fe + 3H_2O$ 4
$CO_2 + C = 2CO$ 5
$H_2O + C = CO + H_2$ 6

3.2.3 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. The SEM of the reduced pellet is shown in **Fig. 13.**

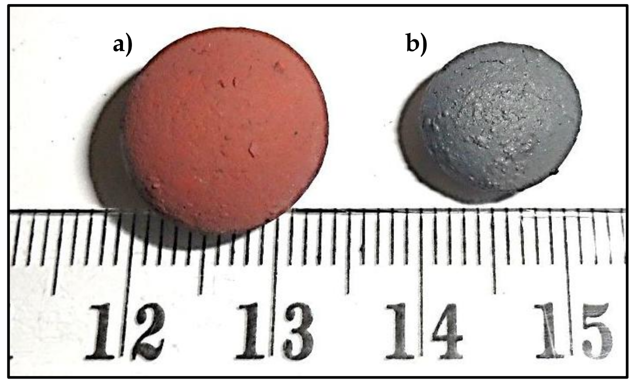

***Fig. 12**a) Fe_2O_3-bakelite composite b)Droplet of metallic iron obtained after 1200 seconds of heating Fe_2O_3-bakelite composite at 1200 °C*

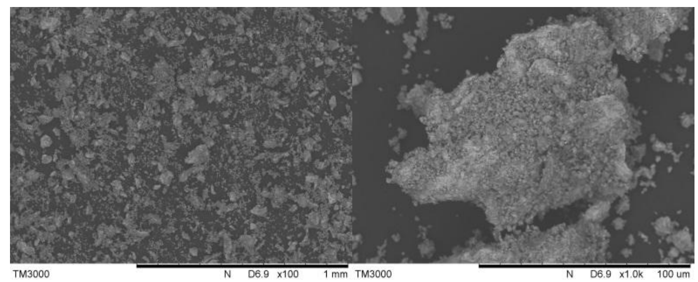

***Fig. 13** SEM of reduced Fe_2O_3-bakelite composite pellet at 1200 °C*

At 1550 °C a clear separation of reduced metal from the slag layer was observed, as shown in **Fig. 14.** 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.

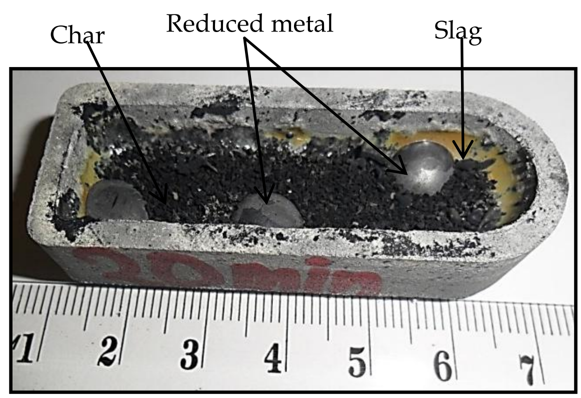

***Fig. 14**Droplets of metallic iron obtained after 1200 seconds of heating Fe_2O_3-bakelite composite at 1550 °C*

The XRDs of the raw Fe_2O_3 and the clearly separated reduced metal are shown in **Figs** (**15** and **16**), respectively. The sharp peaks of Fe_2O_3 in **Fig 15**are observed to disappear completely after reduction and are replaced by sharp peaks that correspond to Fe and Fe_3Cin **Fig 16**. Waste bakelite is therefore able to reduce Fe_2O_3 to produce highly carburised metallic iron.

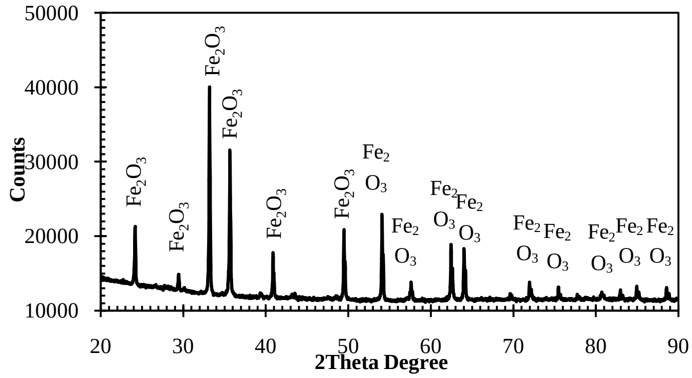

Fig. 15 *XRD of reagent grade Fe_2O_3 before reaction*

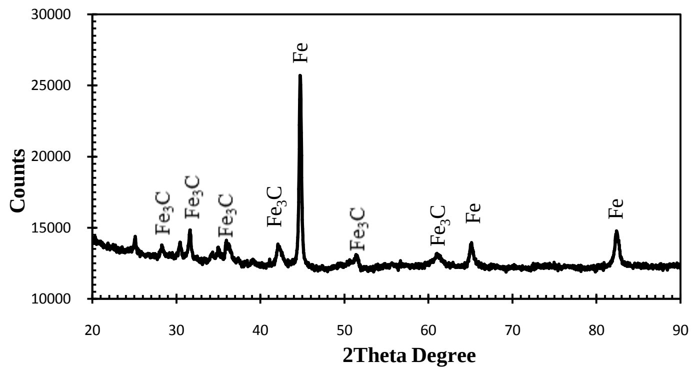

Fig. 16 *XRD of reduced pellets of Fe_2O_3-bakelite composite pellets at 1550 °C*

4 CONCLUSIONS

A laboratory investigation has been conducted on the recycling of post-consumer bakelite as a carbon resource in ironmaking. Major findings of this investigation are:

1) Thermal decomposition studies revealed the generation of large volumes of the reductant gases CO and CH_4, indicating the potential of post-consumer bakelite as a reductant in ironmaking.
2) Metallic iron was produced after heating Fe_2O_3-bakelite composite.
3) Up to 1200 °C, the metal was not separated from the slag layer.
4) Slag-metal separation improved with temperature, with complete slag-metal separation being attained at 1550 °C.

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