Utilization of Waste Plastic for the Production of Metallic Iron, Hydrogen and Carbon Monoxide without Generating Carbon Dioxide

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National legislation within Japan has increased the need for the development of new process technologies that will utilise various waste materials. The present study is aimed at generating some fundamental data with respect to the application of waste plastic as a potential reductant for iron oxide. By using a high frequency induction furnace, mixtures of polyethylene+Fe$_2$O$_3$ were heated very rapidly to temperatures between 1 673 and 2 073 K in a stream of argon. Gas chromatography, chemical analysis and X-ray diffraction were used to detect reaction products, which consisted of metallic iron, ferrous oxide, char, CO, CO$_2$, H$_2$O, H$_2$ and CH$_4$ depending upon C/O mole ratios within the polyethylene+Fe$_2$O$_3$ mixture and the experimental temperature. The results were in good agreement with values calculated from thermodynamic equilibrium.

KEY WORDS: ironmaking; environmental control; CO$_2$ reduction metallurgy.

1. Introduction

Our daily life would depend very much upon various types of “new” materials. Upon such “new” materials are discarded as wastes, however, we often encounter a number of serious social problems. Plastic products are typical example of such wastes. In 1999, the volume of plastic disposed of as waste in Japan was about 8 million tons, 40% (3.2 million tons) of which was disposed of by landfill, 35% (2.8 million tons) by incineration, with the remaining 25% (2.0 million tons) being recycled for reutilization. Impetus for more recycling was proposed by national legislation that went into effect in April 2000.

The law for recycling plastic has increased the need for commercialized processes. It requires the recycling of all plastics except for polyethylene terephthalate (PET) bottles. Recently, the Japanese steelmaking industry has developed innovative technology for recycling various wastes at their iron and steelmaking complexes. For example, Wakimoto et al. pioneered the injection of waste plastic into blast furnaces through the tuyere system. Facilities for injecting various waste materials have now been installed at a number of blast furnaces in Japan.

Prior to this investigation, the present authors conducted an experimental study to elucidate a potential applicability of waste wood as a reductant for iron oxide. The work has now been extended to waste plastic: mixtures of polyethylene+Fe$_2$O$_3$ were heated very rapidly to temperatures between 1 673 and 2 073 K in a stream of argon, and the reaction products were analysed by using gas chromatography, chemical analysis and X-ray diffraction technique. The present paper is aimed at documenting the results obtained through such experiments.

2. Experimental Aspects

Polyethylene, (C$_2$H$_4$)$_n$, shown in Fig. 1(a), was mixed with reagent-grade Fe$_2$O$_3$ in a high-purity alumina mortar and pressed into a steel die of 12-mm diameter. The resulting mixture, shown in Fig. 1(b), had compositions given in Table 1. As indicated in this table, ratios of polyethylene/Fe$_2$O$_3$ within the mixtures were adjusted to yield carbon/
The experimental apparatus is shown schematically in Fig. 2. A high-frequency induction furnace was fitted with a silica reaction tube of 87-mm o.d., 80-mm i.d., and 500-mm in length. The reaction chamber consisted of an alumina protection crucible, a magnesia crucible of 35-mm o.d., 30-mm i.d. and 115-mm in length and a molybdenum tube of 45-mm o.d., 38-mm i.d. and 120-mm in length. The molybdenum tube served as a susceptor for induction heating. Temperatures were measured with a PtRh20–PtRh40 thermocouple placed alongside the magnesia crucible. The silica reaction tube containing the various crucibles was heated under a stream of purified argon at a flow rate of 1000 mL min⁻¹. During this period the samples were positioned within a horizontal glass tube. Samples of about 6-g were used for each run. After the temperature reached the desired value, the samples were charged into the reaction chamber with the aid of a molybdenum push rod for a period of 14 min. Upon being charged, the mixtures generated black smoke and the filter within the exhaust gas train trapped significant amounts of fine carbon particles. The exhaust gas leaving the furnace was collected in a Teflon bag via a three-way stopcock. Gas collection was continued for a period of 21 min.

After each experiment run, collections were also made on residues remained within the magnesia crucible. Residues were subsequently crushed and submitted to X-ray diffraction analysis, which eventually revealed the presence of metallic iron, iron oxide and relatively small amounts of char, depending upon C/O mole ratios and temperature. Thus it follows that

\[ W(\text{Residue}) = w(\text{metal}) + w(\text{oxide}) + w(\text{char}) \] ..............................(1)

where \( W(\text{Residue}) \), \( w(\text{metal}) \), \( w(\text{oxide}) \) and \( w(\text{char}) \) are the amounts (g) of residue, metallic iron, and iron oxide, respectively. Fine carbon particles were also observed on the inner wall of the reaction tube as well as within the gas trains. Hereafter such carbon particles are termed “tar”. Since direct determinations were not possible, the amount (g) of “tar”, \( W(\text{Tar}) \), was estimated from the relationship,

\[ W(\text{Tar}) = W(\text{Sample}) - W(\text{Residue}) - W(\text{Gas}) = W(\text{Sample}) - (w(\text{metal}) + w(\text{oxide}) + w(\text{char})) - W(\text{Gas}) \] ..............................(2)

where \( W(\text{Gas}) \) is the amounts (g) of gaseous products.

The bulk concentrations (mass %) of carbon within the residue, \([%C]_{\text{Residue}}\), were determined by using the LECO carbon analyzer. In addition, in order to determine the concentrations (mass %) of carbon in metallic iron, \([%C]_{\text{Fe}}\), the residues were dissolved into HCl and then filtered. By knowing the amounts of solid carbon remained on the filter, it was possible to determine the total quantities of char within the residue, \( w(\text{char}) \). Values for, \([%C]_{\text{Fe}}\), were then derived from the relation,

\[ w(\text{metal}) /[%C]_{\text{Fe}}/100 = W(\text{Residue}) /[%C]_{\text{Residue}}/100 - w(\text{char}) \] ..............................(3)

With samples of C/O ≤ 1 and \( T \leq 1773 \) K, however, values for \([%C]_{\text{Fe}}\) thus obtained did not have satisfactory accuracy. On the other hand, with C/O ≥ 2 and \( T \geq 1873 \) K, it was possible to confirm the presence of metallic iron even by naked eyes; direct determinations of \([%C]_{\text{Fe}}\) could be made on such metallic iron with satisfactory accuracy.

Values for \( w(\text{metal}) \) and \( w(\text{oxide}) \) were based upon the bulk concentrations (mass%) of oxygen and iron in residue, \([%O]_{\text{Residue}}\), and \([%Fe]_{\text{Residue}}\), respectively. LECO oxygen analyzer and conventional chemical analysis, respectively, were used to determine values for \([%O]_{\text{Residue}}\) and \([%Fe]_{\text{Residue}}\).

Exhaust gas collected within the Teflon bag was analyzed for Ar, CO, CO₂, H₂ and CH₄ by means of gas chromatography, while other gaseous hydrocarbons rather than CH₄ were not detected. The amounts of H₂O generated were determined by knowing the quantity of water condensed within the cold trap. The concentrations of gaseous species, \( i \) (i=CO, CO₂, CH₄, H₂O, H₂), as determined by gas chromatography, \([\%i]\)*, are related to the volume of \( V_i \), collected within the Teflon bag, through the relationship:

\[ V/V_{Ar} = ([\%i])*/([\%Ar])* \] ..............................(4)

Table 1. Compositions of the polyethylene+Fe₂O₃ mixtures.

| Mole ratio of CO in mixture | Compositions of mixture** (mass%) | Compositions of mixture* (mass%) |
|-----------------------------|-----------------------------------|---------------------------------|
| \( \text{C}_3\text{H}_8 \) | \( \text{Fe}_2\text{O}_3 \) | Fe | C | H | O |
| 11.64                       | 88.36                            | 61.80 | 9.98 | 1.66 | 26.56 | 0.50 |
| 15.57                       | 84.43                            | 59.05 | 13.35 | 2.22 | 25.38 | 0.70 |
| 20.86                       | 79.14                            | 55.35 | 17.88 | 2.98 | 23.79 | 1.00 |
| 34.51                       | 65.49                            | 45.81 | 29.58 | 4.93 | 19.68 | 2.00 |
| 51.32                       | 48.68                            | 34.05 | 43.99 | 7.33 | 14.63 | 4.00 |

* Mixtures are considered to consist of (C₃H₈)ₙ and Fe₂O₃.

** Mixtures are considered to consist of Fe, C, H and O.
where \((\%i)^*\) is defined as,
\[
(\%i)^* = 100V_i/(V_{Ar} + V_{CO} + V_{CO_2} + V_{H_2} + V_{CH_4}) .......(5)
\]
Values for \(V_{Ar}\) are obtainable by knowing the flow rate of argon and the duration of the experiment, while \(V_i\) \((i \neq Ar)\) is deduced from Eq. (4). Hence one can obtain values for \((\%)\) as defined below,
\[
(\%) = 100V_i/(V_{CO} + V_{CO_2} + V_{H_2} + V_{CH_4} + V_{H_2O}) .....(6)
\]
where values for \(V_{H_2O}\) could separately be determined by knowing the amount of water collected within the cold trap. The partial pressures (atm) of \(i\), \(P_i\), at a total pressure of 1 atm were then defined as
\[
P_i = (\%)/100 ................................(7)
\]

3. Experimental Results

The experimental results are summarised in Tables 2 through 6.

3.1. Gas, Metal, Oxide, Char and Tar

In Fig. 3, the amounts (g) of metal + oxide, gas, and char + “tar” in relative to initial sample weight, \([w(\text{metal}) + w(\text{oxide})]/W(\text{Sample})\), \([W(\text{Gas})]/W(\text{Sample})\) and \([W(\text{Tar}) + w(\text{char})]/W(\text{Sample})\), respectively, are plotted against temperature. Solid, broken and dotted lines in Fig. 3 indicate the theoretical values derived from thermodynamic calculations. Details of such thermodynamic calculations will be described in a later section. As shown in Fig. 3, by taking account of the uncertainties in the values of \(W(\text{Tar})\) agreements between observed and calculated values would not be disappointing.

3.2. Gaseous Reaction Products

Partial pressures of gaseous products are plotted against temperature in Fig. 4, where various lines indicate thermodynamically calculated values. The partial pressures of CO were much greater than those of \(H_2O\). This implies that, apparently, reduction of iron oxide would be attributed to carbon rather than hydrogen in polyethylene. It is also noted that the gaseous reaction products consist of highly reducing gases: \((\%CO) + (\%H_2) \approx 92\). The authors’ previous

Table 2. Experimental results with polyethylene + Fe_2O_3 mixture with C/O mole ratios of 0.50.

| Temperature (K)   | 1673 | 1773 | 1873 | 1973 | 2073 |
|-------------------|------|------|------|------|------|
| \(W(\text{Sample})(g)\) | 5.994 | 5.937 | 6.001 | 5.909 | 5.847 |
| \([w(\text{metal}) + w(\text{oxide})]/W(\text{Sample})\) (g) | 4.466 | 4.245 | 4.332 | 4.271 | 4.160 |
| \(W(\text{Gas})/W(\text{Sample})\) | 1.515 | 1.645 | 1.652 | 1.588 | 1.655 |
| \(W(\text{Tar})/W(\text{Sample})\) | 0.013 | 0.047 | 0.017 | 0.050 | 0.033 |
| \[%Fe_{\text{oxide}}\] | 84.0 | 82.4 | 83.1 | 83.7 | 81.8 |
| \[%CO_{\text{oxide}}\] | 15.9 | 17.5 | 16.8 | 16.1 | 18.1 |
| \[%CO_{\text{char}}\] | 0.05 | 0.09 | 0.08 | 0.24 | 0.14 |
| \([w(\text{metal})]/[w(\text{metal}) + w(\text{oxide}) + w(\text{char})]\) | 0.286 | 0.294 | 0.246 | 0.278 | 0.188 |
| \([w(\text{oxide})]/[w(\text{metal}) + w(\text{oxide}) + w(\text{char})]\) | 0.714 | 0.706 | 0.754 | 0.722 | 0.812 |
| \([w(\text{char})]/[w(\text{metal}) + w(\text{oxide}) + w(\text{char})]\) | 0 | 0 | 0 | 0 | 0 |
| \[%CO\] | 0.17** | 0.2** | 0.32** | 0.85** | 0.77** |
| \[%CO_2\] | 41.8 | 40.5 | 43.3 | 42.8 | 42.4 |
| \[%H_2\] | 6.5 | 10.1 | 5.9 | 7.2 | 9.1 |
| \[%H_2O\] | 46.2 | 40.6 | 45.5 | 44.7 | 43.1 |
| \[%CH_4\] | 41 | 3.3 | 2.5 | 1.5 | 0.5 |
| \[%H_2O\] | 1.4 | 5.4 | 2.8 | 3.8 | 4.9 |
| \(w(\text{CO})/W(\text{Gas})\) | 0.714 | 0.626 | 0.734 | 0.706 | 0.671 |
| \(w(\text{CO}_2)/W(\text{Gas})\) | 0.175 | 0.246 | 0.157 | 0.186 | 0.226 |
| \(w(\text{H}_2)/W(\text{Gas})\) | 0.056 | 0.045 | 0.055 | 0.053 | 0.049 |
| \(w(\text{CH}_4)/W(\text{Gas})\) | 0.040 | 0.029 | 0.024 | 0.015 | 0.005 |
| \(w(\text{H}_2O)/W(\text{Gas})\) | 0.015 | 0.054 | 0.030 | 0.040 | 0.049 |
| \(w(\text{metal})/W(\text{Sample})\) | 0.212 | 0.21 | 0.178 | 0.201 | 0.134 |
| \(w(\text{oxide})/W(\text{Sample})\) | 0.532 | 0.505 | 0.544 | 0.522 | 0.578 |
| \(w(\text{char})/W(\text{Sample})\) | 0 | 0 | 0 | 0 | 0 |
| \(W(\text{Tar})/W(\text{Sample})\) | 0.002 | 0.008 | 0.003 | 0.008 | 0.006 |
| \(w(\text{Gas})/W(\text{Sample})\) | 0.253 | 0.272 | 0.275 | 0.269 | 0.283 |
| \(w(\text{CO})/W(\text{Sample})\) | 0.180 | 0.174 | 0.202 | 0.190 | 0.190 |
| \(w(\text{CO}_2)/W(\text{Sample})\) | 0.044 | 0.068 | 0.043 | 0.050 | 0.064 |
| \(w(\text{H}_2)/W(\text{Sample})\) | 0.014 | 0.012 | 0.015 | 0.014 | 0.014 |
| \(w(\text{CH}_4)/W(\text{Sample})\) | 0.010 | 0.008 | 0.007 | 0.004 | 0.001 |
| \(w(\text{H}_2O)/W(\text{Sample})\) | 0.004 | 0.015 | 0.008 | 0.011 | 0.014 |

* \(W(\text{Tar}) = W(\text{Sample}) - [w(\text{metal}) - w(\text{oxide}) + w(\text{char})] - W(\text{Gas})\)

** These values were not based upon direct determinations on metallic iron, hence accuracy was not satisfactory.
Table 3. Experimental results with polyethylene + Fe₂O₃ mixture with C/O mole ratios of 0.70.

| Temperature (K) | 1673 | 1773 | 1873 | 1973 | 2073 |
|-----------------|------|------|------|------|------|
| W(Sample) (g)   | 5.840| 5.900| 5.876| 5.952| 5.836|
| [w(metal) + w(oxide) + w(char)] (g) | 4.132| 3.956| 3.795| 3.963| 3.913|
| W(Gas) (g)      | 1.555| 1.661| 1.505| 1.651| 1.703|
| W(Tor) (g)*     | 0.174| 0.283| 0.576| 0.338| 0.219|
| [%Fe] in oxide  | 87.4 | 88.8 | 99.9 | 99.7 | 100.0|
| [%O] in oxide   | 12.5 | 11.1 | 0.14 | 0.26 | 0.00 |
| [%C] in oxide   | 0.08 | 0.10 | 0.08 | 0.08 | 0.00 |
| w(metal) / [w(metal) + w(oxide) + w(char)] | 0.439| 0.502| 0.994| 0.988| 1.000|
| w(oxide) / [w(metal) + w(oxide) + w(char)] | 0.561| 0.498| 0.006| 0.012| 0.000|
| w(char) / [w(metal) + w(oxide) + w(char)] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| [%C₁₂]         | 0.18**| 0.20**| 0.00 | 0.00 | 0.00 |
| [%CO]          | 40.6 | 44.3 | 42.7 | 42.7 | 44.1 |
| [%C₂O]         | 3.9  | 3.2  | 3.1  | 3.2  | 2.8  |
| [%CH₃]         | 49.9 | 49.9 | 50.4 | 49.4 | 49.4 |
| [%H₂O]         | 4.4  | 2.3  | 3.5  | 3.1  | 2.3  |
| [%H₂O]         | 1.1  | 1.3  | 1.6  | 1.3  | 1.3  |
| w(CO) / W(Gas) | 0.758| 0.814| 0.803| 0.790| 0.813|
| w(C₂O) / W(Gas)| 0.115| 0.093| 0.091| 0.094| 0.081|
| w(H₂) / W(Gas) | 0.067| 0.066| 0.068| 0.065| 0.065|
| w(CH₃) / W(Gas)| 0.047| 0.024| 0.037| 0.032| 0.024|
| w(H₂O) / W(Gas)| 0.013| 0.004| 0.004| 0.019| 0.016|
| w(metal) / [w(metal) + w(oxide) + w(char)] | 0.310| 0.336| 0.642| 0.658| 0.671|
| w(oxide) / W(Sample) | 0.397| 0.334| 0.004| 0.008| 0.000|
| w(char) / W(Sample) | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| W(Tor) / W(Sample) | 0.030| 0.048| 0.098| 0.057| 0.038|
| w(Gas) / W(Sample) | 0.263| 0.281| 0.256| 0.277| 0.292|
| w(CO) / W(Sample)| 0.199| 0.229| 0.205| 0.219| 0.237|
| w(C₂O) / W(Sample)| 0.030| 0.026| 0.023| 0.026| 0.024|
| w(H₂) / W(Sample) | 0.017| 0.018| 0.017| 0.018| 0.019|
| w(CH₃) / W(Sample)| 0.012| 0.007| 0.010| 0.009| 0.007|
| w(H₂O) / W(Sample)| 0.004| 0.001| 0.001| 0.005| 0.005|

* W(Tor) = W(Sample) – [w(metal) + w(oxide) + w(char)] - W(Gas)
** These values were not based upon direct determinations on metallic iron, hence accuracy was not satisfactory.

Table 4. Experimental results with polyethylene + Fe₂O₃ mixture with C/O mole ratios of 1.00.

| Temperature (K) | 1673 | 1773 | 1873 | 1973 | 2073 |
|-----------------|------|------|------|------|------|
| W(Sample) (g)   | 5.998| 5.976| 5.917| 5.983| 5.907|
| [w(metal) + w(oxide) + w(char)] (g) | 3.626| 3.363| 3.570| 3.495| 3.268|
| W(Gas) (g)      | 1.737| 1.977| 1.832| 1.887| 1.677|
| W(Tor) (g)*     | 0.635| 0.636| 0.515| 0.601| 0.961|
| [%Fe] in oxide  | 88.8 | 95.8 | 99.9 | 99.8 | 99.6 |
| [%O] in oxide   | 11.0 | 3.8  | 0.12 | 0.23 | 0.36 |
| [%C₁₂]         | 0.25 | 0.41 | 0.00 | 0.02 | 0.00 |
| w(metal) / [w(metal) + w(oxide) + w(char)] | 0.506| 0.829| 0.995| 0.990| 0.984|
| w(oxide) / [w(metal) + w(oxide) + w(char)] | 0.494| 0.171| 0.005| 0.010| 0.016|
| w(char) / [w(metal) + w(oxide) + w(char)] | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| [%CO]          | 38.2 | 42.8 | 38.8 | 41.7 | 38.4 |
| [%C₂O]         | 1.9  | 1.0  | 0.9  | 0.8  | 0.0  |
| [%H₂]          | 54.9 | 53.4 | 53.7 | 54.8 | 57.7 |
| [%H₂O]         | 4.5  | 2.3  | 6.5  | 2.5  | 3.6  |
| w(CO) / W(Gas) | 0.797| 0.859| 0.811| 0.861| 0.858|
| w(C₂O) / W(Gas)| 0.061| 0.032| 0.030| 0.025| 0.000|
| w(H₂) / W(Gas) | 0.082| 0.077| 0.080| 0.081| 0.092|
| w(H₂O) / W(Gas)| 0.053| 0.027| 0.078| 0.079| 0.046|
| w(Metal) / W(Sample) | 0.007| 0.005| 0.002| 0.004| 0.004|
| w(oxide) / W(Sample) | 0.306| 0.467| 0.600| 0.578| 0.544|
| w(char) / W(Sample) | 0.299| 0.096| 0.003| 0.006| 0.009|
| W(Tor) / W(Sample)| 0.106| 0.106| 0.087| 0.101| 0.163|
| W(Gas) / W(Sample)| 0.290| 0.331| 0.310| 0.315| 0.284|
| w(CO) / W(Sample)| 0.231| 0.284| 0.251| 0.272| 0.244|
| w(C₂O) / W(Sample)| 0.018| 0.011| 0.009| 0.008| 0.00 |
| w(H₂) / W(Sample)| 0.024| 0.025| 0.025| 0.026| 0.026|
| w(CH₃) / W(Sample)| 0.015| 0.009| 0.024| 0.009| 0.013|
| w(H₂O) / W(Sample)| 0.002| 0.002| 0.001| 0.001| 0.001|

* W(Tor) = W(Sample) – [w(metal) + w(oxide) + w(char)] - W(Gas)
** These values were not based upon direct determinations on metallic iron, hence accuracy was not satisfactory.
Table 5. Experimental results with polyethylene + Fe2O3 mixture with C/O mole ratios of 2.00.

| Temperature (K) | 1673 | 1773 | 1873 | 1973 | 2073 |
|-----------------|------|------|------|------|------|
| \(W(Sample)(g)\) | 5.981 | 6.021 | 5.945 | 6.011 | 5.916 |
| \(\text{w(metal)} + \text{w(oxide)} + \text{w(char)}\) (g) | 2.793 | 2.783 | 2.574 | 2.488 | 2.755 |
| \(W(Gas)(g)\) | 2.172 | 2.406 | 2.268 | 2.374 | 2.362 |
| \(W(Tar)(g)\)* | 1.016 | 0.832 | 1.103 | 1.189 | 0.830 |
| \%Fe2O3 | 96.9 | 98.9 | 99.9 | 99.7 | 100.0 |
| \%O2 | 3.0 | 1.4 | 1.0 | 0.3 | 0.2 |
| \%C | 0.04 | 0.09 | 0.03 | 0.06 | 0.03 |
| \(w(\text{metal}) + w(\text{oxide}) + w(\text{char})\) | 0.864 | 0.994 | 0.994 | 0.987 | 0.999 |
| w(\text{oxide}) / (w(\text{metal}) + w(\text{oxide}) + w(\text{char})) | 0.136 | 0.006 | 0.006 | 0.013 | 0.001 |
| w(\text{char}) / (w(\text{metal}) + w(\text{oxide}) + w(\text{char})) | \(= 0\) | \(= 0\) | \(= 0\) | \(= 0\) | \(= 0\) |
| \%C_{\text{tot}} | 0.05** | 1.00** | 0.00 | 0.04 | 0.03 |
| \%CO | 31.8 | 53.2 | 34.2 | 34.6 | 34.4 |
| \%CO2 | 0.2 | 0.2 | 0.1 | 0 | 0.2 |
| \%H2 | 60.7 | 61.0 | 60.9 | 61.0 | 59.2 |
| \%CH4 | 7.1 | 3.3 | 4.6 | 4.4 | 5.9 |
| \%H2O | 0.2 | 0.2 | 0 | 0.2 | 0.3 |
| w(CO) / W(Gas) | 0.781 | 0.840 | 0.823 | 0.834 | 0.810 |
| w(CO2) / W(Gas) | 0.009 | 0.007 | 0.005 | 0 | 0.007 |
| w(H2) / W(Gas) | 0.107 | 0.104 | 0.105 | 0.105 | 0.100 |
| w(CH4) / W(Gas) | 0.100 | 0.045 | 0.064 | 0.060 | 0.079 |
| w(H2O) / W(Gas) | 0.003 | 0.004 | 0.003 | 0.004 | 0.000 |
| w(CH4) / W(Sample) | 0.403 | 0.459 | 0.430 | 0.402 | 0.460 |
| w(\text{oxide}) / W(Sample) | 0.064 | 0.003 | 0.003 | 0.005 | 0 |
| w(\text{char}) / W(Sample) | \(= 0\) | \(= 0\) | \(= 0\) | \(= 0\) | \(= 0\) |
| w(Tar) / W(Sample) | 0.170 | 0.138 | 0.186 | 0.198 | 0.140 |
| w(Gas) / W(Sample) | 0.363 | 0.400 | 0.381 | 0.395 | 0.399 |
| w(CO) / W(Sample) | 0.284 | 0.336 | 0.314 | 0.330 | 0.324 |
| w(CO2) / W(Sample) | 0.003 | 0.003 | 0.002 | 0 | 0.003 |
| w(H2) / W(Sample) | 0.039 | 0.041 | 0.040 | 0.041 | 0.040 |
| w(CH4) / W(Sample) | 0.036 | 0.018 | 0.024 | 0.024 | 0.032 |
| w(H2O) / W(Sample) | 0.001 | 0.001 | 0.001 | 0 | 0.002 |

* \(W(Tar) = W(Sample) - [w(\text{metal}) + w(\text{oxide}) + w(\text{char})] - W(Gas)\)
** These values were not based upon direct determinations on metallic iron, hence accuracy was not satisfactory.

Table 6. Experimental results with polyethylene + Fe2O3 mixture with C/O mole ratios of 4.00.

| Temperature (K) | 1673 | 1773 | 1873 | 1973 | 2073 |
|-----------------|------|------|------|------|------|
| \(W(Sample)(g)\) | 5.884 | 5.886 | 5.118 | 5.525 | 5.887 |
| \(\text{w(metal)} + \text{w(oxide)} + \text{w(char)}\) (g) | 2.678 | 2.341 | 1.619 | 1.725 | 1.578 |
| \(W(Gas)(g)\) | 2.052 | 2.362 | 1.847 | 2.042 | 2.163 |
| \(W(Tar)(g)\)* | 1.004 | 1.183 | 1.652 | 1.758 | 2.146 |
| \%Fe2O3 | 95.7 | 98.0 | 99.3 | 98.9 | 94.6 |
| \%O2 | 0.49 | 0.14 | 0.03 | 0.03 | 2.67 |
| \%C | 3.78 | 1.9 | 0.64 | 1.1 | 2.69 |
| \%CO | 21.3 | 24.1 | 19.7 | 23.1 | 22.3 |
| \%CO2 | 0 | 0 | 0 | 0 | 0 |
| \%H2 | 71.3 | 67.7 | 69.7 | 70.3 | 71.8 |
| \%CH4 | 7.4 | 8.2 | 10.3 | 6.4 | 5.9 |
| \%H2O | 0 | 0 | 0.2 | 0.2 | 0 |
| w(CO) / W(Gas) | 0.696 | 0.717 | 0.641 | 0.725 | 0.724 |
| w(CO2) / W(Gas) | 0 | 0 | 0 | 0 | 0 |
| w(H2) / W(Gas) | 0.166 | 0.144 | 0.162 | 0.157 | 0.166 |
| w(CH4) / W(Gas) | 0.138 | 0.139 | 0.192 | 0.115 | 0.110 |
| w(H2O) / W(Gas) | 0 | 0 | 0.004 | 0.003 | 0 |
| w(metal) / W(Sample) | 0.460 | 0.395 | 0.316 | 0.312 | 0.236 |
| w(\text{oxide}) / W(Sample) | 0.010 | 0.003 | 0 | 0 | 0.032 |
| w(\text{char}) / W(Sample) | \(= 0\) | \(= 0\) | \(= 0\) | \(= 0\) | \(= 0\) |
| W(Tar) / W(Sample) | 0.181 | 0.201 | 0.323 | 0.318 | 0.365 |
| w(Gas) / W(Sample) | 0.349 | 0.401 | 0.361 | 0.370 | 0.367 |
| w(CO) / W(Sample) | 0.243 | 0.288 | 0.231 | 0.268 | 0.266 |
| w(CO2) / W(Sample) | 0 | 0 | 0 | 0 | 0 |
| w(H2) / W(Sample) | 0.058 | 0.058 | 0.058 | 0.058 | 0.061 |
| w(CH4) / W(Sample) | 0.045 | 0.056 | 0.069 | 0.062 | 0.040 |
| w(H2O) / W(Sample) | 0 | 0 | 0.002 | 0.001 | 0 |

* \(W(Tar) = W(Sample) - [w(\text{metal}) + w(\text{oxide}) + w(\text{char})] - W(Gas)\)
** These values were not based upon direct determinations on metallic iron, hence accuracy was not satisfactory.
study also reported generation of such highly reducing gases through gasification of waste wood and polyethylene. The partial pressures of CO2 showed significant dependence upon C/O mole ratios rather than temperature. As can be seen from Fig. 4, the CO2 emission decreased with an increase in temperature and C/O ratios. On the other hand, the observed values for $P_{\text{CH}_4}$ were greater than the theoretical values, and increased with an increase in C/O ratios.

### 3.3. Metallic Iron and Iron Oxide

Figures 5(a) and 5(b), respectively, show the values for $w(\text{metal})/W(\text{Sample})$ and $w(\text{oxide})/W(\text{Sample})$ as the function of C/O mole ratio.

Fig. 4. Partial pressures of CO, H2, H2O, CO2 and CH4 as the function of temperature.

Fig. 5. Values of (a) $w(\text{oxide})/W(\text{Sample})$ and (b) $w(\text{oxide})/W(\text{Sample})$ as the function of C/O mole ratio.

4. Discussion

#### 4.1. Thermodynamic Considerations

The reduction of iron oxide by polyethylene can be interpreted through thermodynamic calculations. Consider polyethylene + Fe2O3 mixture which consists of $n_0^\text{Fe}$ moles of Fe, $n_0^\text{C}$ moles of carbon, $n_0^\text{H}$ moles of atomic hydrogen and $n_0^\text{O}$ moles of atomic oxygen. The reaction products formed at elevated temperatures would depend upon C/O atom ratios. In the subsequent thermodynamic calculations, we consider three cases.

Case (1) For relatively low C/O atom ratios, e.g., C/O=0.5, proportions of carbon in polyethylene+Fe2O3 of a reaction;

$$\text{Fe}_2\text{O}_3 + 3\text{C} = 2\text{Fe} + 3\text{CO} \quad \text{..........(8)}$$

Figures 6(a) through 6(e), respectively, show the residues remained within magnesia crucible at 1873 K for example, with C/O mole ratios of 0.5, 0.7, 1.0, 2.0 and 4.0. With C/O=0.5 and 0.7, particularly 0.5, the reaction products contained significant amounts of ferrous oxide, which penetrated into the magna crucible. On the other hand, with C/O mole ratios=2.0 and 4.0, droplets of metallic iron were obtained, and direct determinations of $[%\text{C}]_\text{Fe}$ through LECO analyser could be made on such droplets with satisfactory accuracy. Figure 7 shows the concentrations of carbon in metallic iron, $[%\text{C}]_\text{Fe}$, within metal droplet as the function of temperature. This figure is superimposed on the phase diagram of the binary system Fe–C. As already mentioned, at C/O=1 and $T=1773 K$, values for $[%\text{C}]_\text{Fe}$ were not in satisfactory accuracy, hence not given in Fig. 7. For C/O=2 and 4, theoretical values based upon thermodynamic calculations were identical to the solubilities of carbon in metallic iron. The observed values for $[%\text{C}]_\text{Fe}$ were, however, fairly lower than the calculated ones, implying that equilibrium would not be attained for carbon dissolution. With respect to this, it is to be noted that carbon dissolution has to be accompanied with relatively slow diffusion process.
mixture would not be large enough to complete the reduction of Fe$_2$O$_3$ to metallic iron. Hence, in addition to metallic Fe, ferrous oxide would be present within the reaction products, while solid carbon is absent. In this case, oxygen potential would be prevailed by equilibrium between metallic iron and ferrous oxide.

Case (2) For medium C/O mole ratios, e.g., C/O=0.7, FeO would completely be reduced to metallic iron, and excess amount of carbon can result in dissolution of carbon into metallic iron. The concentrations of carbon in metallic iron, however, would be less than the solubility limits. It is supposed that oxygen potentials are governed by equilibrium between metallic iron and ferrous oxide.

Case (3) With high C/O ratios, e.g., C/O>~1.0, the reaction products would be carbon-saturated liquid iron, while excess amounts of solid carbon would be present at unit activity. Oxygen potentials are prevailed by equilibrium between pure solid carbon of unit activity and carbon monoxide in gas phase.

Table 7 summarises chemical species in condensed-phase reaction products, carbon activity and reaction prevailing oxygen potential used for thermodynamic calculations.

4.2. Case (1)

At temperature, $T$, polyethylene+Fe$_2$O$_3$ mixture would generate $n_{i(Fe)}$, $n_{i(C)}$ and $n_{i(O)}$ moles of iron, carbon and oxygen, respectively, in liquid iron, $n_{i(FeO)}$ moles of {FeO}, and gas of volume, $V$, containing $n_{i(CO)}$, $n_{i(CO_2)}$, $n_{i(H_2)}$, $n_{i(CH_4)}$, $n_{i(H_2O)}$, and $n_{i(O_2)}$ moles of each species. At one atmospheric pressure, the partial pressures, $P_j$, of gaseous components, $j$, $(j=CO, CO_2, H_2, CH_4, H_2O$ and $O_2$) are related to $n_j$ and $V$ through the relationship:

$$P_j=n_jRT/V............................(9)$$

The mass balance for iron, carbon, hydrogen and oxygen, respectively, is given as follows:

$$n_{i(Fe)}=n_{i(Fe)}+n_{i(FeO)}=(2/3)n_i^C..........................(10)$$

$$n_i^C=n_{i(C)}+n_{i(CO)}+n_{i(CO_2)}+n_{i(CH_4)}.............(11)$$

$$n_i^H=2n_{i(H_2)}+4n_{i(CH_4)}+2n_{i(H_2O)}..................(12)$$

$$n_i^O=n_{i(CO)}+2n_{i(CO_2)}+2n_{i(O_2)}+n_{i(H_2O)}+n_{i(FeO)}+n_{i(O)}............(13)$$

By combining Eq. (9) with Eqs. (11), (12) and (13), respectively, one obtains the followings:

$$n_i^C=n_{i(C)}+(V/RT)\{P_{i(CO)}+P_{i(CO)}+P_{i(CH_4)}\}...........(14)$$

$$n_i^H=(V/RT)\{2P_{i(H_2)}+4P_{i(CH_4)}+2P_{i(H_2O)}\}.............(15)$$

$$n_i^O=n_{i(FeO)}+n_{i(O)}+(V/RT)\{P_{i(CO)}+2P_{i(CO)}+2P_{i(O_2)}+P_{i(H_2O)}\}...............(16)$$

At high temperatures, reactions between the various species can be expressed as:

$$2\{C\}+2\{O_2\}=2\{CO\}....................(17)$$

$$K(17)=P_{i(CO)}/a_i^C\cdot P_{i(O)}..........................(18)$$

$$\{C\}+\{O_2\}=\{CO_2\}........................(19)$$

$$K(19)=P_{i(CO)}/a_i^C\cdot P_{i(O)}..........................(20)$$

$$\{C\}+2\{H_2\}=\{CH_4\}..................(21)$$
where \( \{C\}_{Fe} \) and \( \{O\}_{Fe} \) denotes, respectively, carbon and oxygen dissolved in liquid iron, and other symbols have the usual meanings. Hereafter Kubaschewski–Alcock notation\(^7\) is be used. The activities of Fe and C in liquid iron referred to pure iron and carbon, respectively, are expressed as \( a_{Fe} \) and \( a_{C} \), respectively, and \( h_{o} \) is the Henrian activities of oxygen referred to 1 wt% solution in liquid iron. Values for equilibrium constants were taken from Elliott and Gleiser\(^8\), or Kubaschewski and Alcock.\(^9\) By assuming ideal behaviours for iron and carbon in liquid \( \{Fe–C–O\} \) alloys, we have;

\[
K(21) = \frac{P_{CH_4}}{a_C n^{2}_{CH_4}} \tag{22}
\]

\[
2(H_2) + (O_2) = 2(H_2O) \tag{23}
\]

\[
K(23) = \frac{P_{H_2/O}}{P_{H_2} P_{O_2}} \tag{24}
\]

\[
2\{Fe\} + (O_2) = 2\{FeO\} \tag{25}
\]

\[
K(25) = 1/a_{Fe} P_{O_2} \tag{26}
\]

\[
(1/2)(O_2) = \{O\}_{Fe} \tag{27}
\]

\[
K(27) = h_{O}/P_{O_2}^{1/2} \tag{28}
\]

where \( \{C\}_{Fe} \) and \( \{O\}_{Fe} \) denotes, respectively, carbon and oxygen dissolved in liquid iron, and other symbols have the usual meanings. Hereafter Kubaschewski–Alcock notation\(^7\) is be used. The activities of Fe and C in liquid iron referred to pure iron and carbon, respectively, are expressed as \( a_{Fe} \) and \( a_{C} \), respectively, and \( h_{o} \) is the Henrian activities of oxygen referred to 1 wt% solution in liquid iron. Values for equilibrium constants were taken from Elliott and Gleiser\(^8\), or Kubaschewski and Alcock.\(^9\) By assuming ideal behaviours for iron and carbon in liquid \( \{Fe–C–O\} \) alloys, we have;

\[
av_{Fe} = a_{Fe} (n_{Fe}) (n_{C} + n_{O}) \tag{29}
\]

\[
av_{C} = a_{C} (n_{Fe} + n_{C} + n_{O}) \tag{30}
\]

where \( X_{sat}^c \) is the solubility limit of carbon in iron in mole fraction. Although the Fe–C system would deviate from ideality,\(^9\) Eq. (30) would be good enough for the purpose of this study. The Henrian activities of oxygen can be expressed as;

\[
\log h_{o} = \log[\%O] + e_{O}^{c} [\%O] + e_{C}^{c} [\%C] = \log \{1.600 n_{O}/(55.85 n_{Fe} + 12 n_{C} + 16 n_{O})\}
\]

\[
+ e_{O}^{c} [1.600 n_{O}/(55.85 n_{Fe} + 12 n_{C} + 16 n_{O})]
\]

\[
+ e_{C}^{c} [1.200 n_{C}/(55.85 n_{Fe} + 12 n_{C} + 16 n_{O})] \tag{31}
\]

where \( [\%O] \) and \( [\%C] \) denote, respectively, the concentrations of oxygen and carbon in percent by weight in liquid iron, and \( e_{O}^{c} \) and \( e_{C}^{c} \) are the interaction parameters.\(^8\)

When the gas phase is present at one atmospheric pressure, then we have;

\[
1 = P_{CO} + P_{CO_2} + P_{H_2} + P_{H_2O} + P_{CH_4} + P_{O_2} \tag{32}
\]

Attention is now focussed on Eqs. (10), (14), (15), (16), (18), (20), (22), (24), (26), (28), (29), (30), (31) and (32). These 14 equations involve 14 unknowns, i.e., \( V, P_{CO}, P_{CO_2}, P_{CH_4}, P_{H_2}, P_{H_2O}, P_{O_2}, n_{Fe}, n_{C}, n_{O}, n_{FeO}, a_{Fe}, a_{C} \) and \( h_{o} \). Hence values for these unknowns can be obtained by solving these equations simultaneously for a given temperature, \( T \), and known initial values for \( n_{Fe}^{0}, n_{C}^{0}, n_{O}^{0} \) and \( n_{O} \).

### 4.3. Case (2)

For medium C/O mole ratios, e.g., \( \sim 0.7 < C/O < 1.0 \), ferrous oxide would not be present within the reaction products, corresponding to \( n_{FeO} = 0 \). Hence, attention is now focussed on 13 equations, i.e., Eqs. (10), (14), (15), (16), (18), (20), (22), (24), (28), (29), (30), (31) and (32), rather than Eq. (26). These equations involve 13 unknowns, i.e., \( V, P_{CO}, P_{CO_2}, P_{CH_4}, P_{H_2}, P_{H_2O}, P_{O_2}, n_{Fe}, n_{C}, n_{O}, a_{Fe}, a_{C} \) and \( h_{o} \). Values for these unknowns, hence, can be obtained by solving these equations simultaneously.

### 4.4. Case (3)

For relatively high C/O mole ratios, e.g., \( C/O > 1.0 \), pure solid carbon (char) would present at unit activity; \( a_{C} = 1 \). Hence, instead of Eq. (14), we have;

\[
n_{C}^{0} = n_{C} + (V/RT)(P_{CO} + P_{CO_2} + P_{CH_4}) \tag{14'}
\]

where \( n_{C} \) is the number of moles of carbon (char and “tar”) in residue. For the iron activity at carbon saturation, instead of Eq. (29), we have;

\[
1 - X_{C}^{sat} = a_{Fe} \tag{29'}
\]

Attention is now focussed on 12 equations, i.e., Eqs. (10), (14'), (15), (16), (18), (20), (22), (24), (28), (29), (30), (31) and (32), rather than Eqs. (26) and (30). These 12 equations involve 12 unknowns, i.e., \( V, P_{CO}, P_{CO_2}, P_{CH_4}, P_{H_2}, P_{H_2O}, P_{O_2}, n_{Fe}, n_{C}, n_{O}, a_{Fe}, a_{C} \) and \( h_{o} \). Again, values for these unknowns can be obtained by solving these equations simultaneously.

### 5. Conclusions

Polyethylene consists of carbon and hydrogen. Hence there is a possibility to use such plastic as a reducing agent for production of metallic iron. In this study, mixtures of polyethylene+Fe\(_2\)O\(_3\) were heated very rapidly to temperatures of 1673 K, 1773 K, 1873 K, 1973 K and 2073 K under argon atmosphere. The reaction products were collected and submitted to X-ray diffraction, chemical analysis and gas chromatography. Observations through such experiments can be summarised as follows.

1. Potential feasibilities on the reduction of iron oxide with waste plastic were confirmed.
2. The gaseous reaction products through such reduction processes contained very small proportions of carbon dioxide, while highly reducing species could be obtained; \( (C/O) + (H_2) > 92 \).
3. The metal yield, \( \% (metal)/W(Sample) \), showed maximum with C/O ratio \( \sim 1.0 \), in conforming to the stoichiomet-
etry of a reaction, Fe$_2$O$_3$ + 3C → 2Fe + 3CO.

(4) The emission of carbon dioxide can be lowered by increasing C/O ratio and temperature.

(5) These behaviours could be well interpreted through thermodynamic calculations, except for the dissolution of carbon into metallic iron and partial pressures of CH$_4$.

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