Investigation of Polyethylene and Paper as Blast Furnace Injectant

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ABSTRACT

National legislation within Japan has increased the need for the development of new process technologies that will utilize waste wood materials. In order to generate some fundamental data with respect to the possible injection of such materials into blast furnaces, a study has been made of the decomposition and gasification reactions that take place when biomass material, in this case Japanese cypress chips, are exposed to temperatures between 1673 and 2073K using a high frequency induction furnace. The relative amounts of gas, char and tar were determined as well as the concentration of the various species present in the gas phase. The results obtained from gas analysis were in good agreement with values calculated from thermodynamic equilibria.

1. INTRODUCTION

Recently, the Japanese steelmaking industry has developed innovative technology for recycling various wastes at their own iron and steelmaking complexes. For example, facilities for injecting waste plastic through the tuyere system have been installed at a number of blast furnaces owned by JFE steel (Former NKK /1,2,3/ and Kobe Steel. It is believed that such facilities would also be appropriate for injecting waste wood and paper. When such organic compounds are injected to blast furnace, decomposition and gasification will take place extremely rapidly. By using a high-frequency induction furnace, the present authors /4/ investigated the gasification reactions of wood at temperatures closer to those encountered within the tuyere zone of the blast furnace. The work has now extended to plastic (polyethylene) and paper.

2. EXPERIMENTAL ASPECTS

The compositions of the polyethylene and paper are given in Table 1. Figure 1 shows polyethylene, \([C_2H_2]_n\), supplied from Nakarai Chemicals Inc. This polyethylene did not contain any plasticizer. Paper used for conventional photo-copy was first shredded and then compacted into a steel die as shown in Figures 2(a) and 2(b). Prior to experiments, samples were dried at 343 K.

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Table 1
Compositions of polyethylene and paper used in this study (pct by weight).

<table>
<thead>
<tr>
<th></th>
<th>Plastic</th>
<th>Paper</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>85.6</td>
<td>43.6</td>
</tr>
<tr>
<td>H</td>
<td>14.4</td>
<td>6.02</td>
</tr>
<tr>
<td>O</td>
<td>0</td>
<td>47.9</td>
</tr>
<tr>
<td>Ash</td>
<td>0</td>
<td>3.2</td>
</tr>
<tr>
<td>CaO</td>
<td>0</td>
<td>0.35</td>
</tr>
</tbody>
</table>

The experimental apparatus is shown in Figure 3. A high-frequency induction furnace fitted with a silica reaction tube of 87 mm o.d., 80 mm i.d., and 500 mm in length. The reaction chamber for gasification consisted of an alumina protection crucible, a magnesia crucible 35 mm o.d., 30 mm i.d. and 115 mm in length and a molybdenum tube 45 mm o.d., 38 mm i.d. and 120 mm in length; the latter served as a susceptor for induction heating. Temperatures were measured by either a Pt-PtRh13 or 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 1,000 cc/min. During this period the samples were positioned within a horizontal glass tube. After the temperature reached the desired value, the samples were charged into the reaction chamber, with the aid of a molybdenum push rod over a period of 14 minutes. About 6 g of samples were used for each run. The exhaust gas leaving the

Fig. 1: Polyethylene used in this study.

Fig. 2: (a) Paper used in this study was first shredded, and then (b) compacted in a steel die.
furnace was collected in a Teflon bag via a three-way stopcock for a period of 21 minutes. The exhaust gas collected within the Teflon bag was analyzed for Ar, CO, CO₂, H₂, and CH₄ by means of gas chromatography, while the amounts of water vapor generated were determined by knowing the quantity of water condensed within the cold trap. Char remaining within the magnesia crucible was weighed, crushed and then submitted to X-ray diffraction analysis. In addition to chars obtained in this study, X-ray diffraction analysis was also made on wood-char obtained through the authors' previous study /4/ for the sake of comparison. Tar was also observed on the wall of the reaction tube as well as within the gas trains. Since direct determination of the amount of tar formed was not possible, the amount formed was estimated from the relationship:

\[ W(Tar) = W(Sample) - W(Char) - W(Gas). \]  

where \( W(i) \) corresponds to the weight of the various species \( i \).

The concentrations of gaseous species, \( i \), as determined by gas chromatography, \( (%i)^* \), are related to the volume of \( i \), \( V(i) \), collected within the Teflon bag, through the relationship:

\[ \frac{V(i)}{V(Ar)} = \frac{(%i)^*}{(%Ar)^*}. \]

where \( (%i)^* \) is defined as:

\[ (%i)^* = 100\frac{V(i)}{V(Ar) + V(CO) + V(CO₂) + V(H₂) + V(CH₄)}. \]

Fig. 3: Experimental apparatus used in this study,
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 Equation (4).

$$\frac{100V(i)}{V(CO) + V(CO_2) + V(H_2) + V(CH_4)}$$ (4)

3. RESULTS and DISCUSSION

3.1 Reaction Products

The experimental results for polyethylene and paper, respectively, are given in Tables 2 and 3. Values for $(%i)$ given in this table are based upon equation (4).

Figure 4 shows the relative amounts of gas and char + tar, $W(Gas)/W(Sample)$ and $W(Char+Tar)/W(Sample)$, respectively, in comparison with those of wood reported by Takekawa et al. As shown in Figure 4, with polyethylene, $W(Char+Tar)/W(Sample) > 0.8$; major reaction products are solid carbon rather than gases. On the other hand, with paper and wood, $W(Gas)/W(Sample) > 0.65$. Thus major reaction product of polyethylene is quite different from those of wood and paper. With respect to this, it is noted that polyethylene does not contain oxygen; hence any oxygen-bearing gases cannot be produced from polyethylene. Solid and broken lines given in Figure 4 indicate calculated values based upon thermodynamic equilibrium. The details of such calculations will be described in a later section. Satisfactory agreements between calculations and observations were obtained with polyethylene and wood, while slight disagreement with paper might be attributed, to some extents, to ash.

In Figure 5, concentrations of the various gaseous components, $(%i)$, are plotted against temperature. Solid lines in these figures indicate calculated values based upon thermodynamic equilibrium. For paper and polyethylene, satisfactory agreements were observed for $(%CO)$, $(%H_2)$ and $(%H_2O)$. Although observed values for $(%CH_4)$ with paper, polyethylene and wood were greater than the calculated ones at lower temperature, they approached equilibrium with an increase in

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Experimental results for polyethylene.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K</td>
<td>W(Sample)</td>
</tr>
<tr>
<td>1673</td>
<td>5.996</td>
</tr>
<tr>
<td>1773</td>
<td>6.017</td>
</tr>
<tr>
<td>1873</td>
<td>6.001</td>
</tr>
<tr>
<td>1973</td>
<td>5.994</td>
</tr>
<tr>
<td>2073</td>
<td>6.005</td>
</tr>
</tbody>
</table>

* Calculated from the relationship: $W(Tar) = W(Sample) - W(Char) - W(Gas)$.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Experimental results for paper.</th>
</tr>
</thead>
<tbody>
<tr>
<td>T/K</td>
<td>W(Sample)</td>
</tr>
<tr>
<td>1673</td>
<td>5.923</td>
</tr>
<tr>
<td>1773</td>
<td>6.029</td>
</tr>
<tr>
<td>1873</td>
<td>6.002</td>
</tr>
<tr>
<td>1973</td>
<td>6.052</td>
</tr>
<tr>
<td>2073</td>
<td>5.726</td>
</tr>
</tbody>
</table>

* Calculated from the relationship: $W(Tar) = W(Sample) - W(Char) - W(Gas)$. 
Fig. 4: Relation between \( W(Gas)/W(Sample) \) and \( W(Char+Tar)/W(Sample) \), respectively, and temperature for paper, polyethylene and wood, respectively. Solid and broken lines indicate, respectively, the calculated values for \( W(Gas)/W(Sample) \) and \( W(Char+Tar)/W(Sample) \).

Fig. 5: Concentrations of CO, CO\(_2\), H\(_2\) and CH\(_4\) generated during gasification of paper, polyethylene and paper as a function of temperature.
temperature. Major gaseous reaction products with paper and polyethylene are $H_2$ and $H_2 + CO$, respectively. In both cases the ratios of such highly reducing gases were in excess of 90% of the gaseous components.

Figures 6 through 10 show the XRD spectra of char obtained with gasification of wood, polyethylene and paper at 1673K, 1773K, 1873K, 1973K and 2073K, respectively. Attention would be focused on (002) peak of $2\theta \approx 25^\circ$, which corresponds to the inter-layer of graphite /5/. A sharp and narrow peak with graphite indicates highly ordered structures. In other words, at 1673 K, all chars showed very much disordered structure; the crystallinity increased in an order, paper < wood < polyethylene << graphite. With an increase in char-making temperature from 1673 K to 1873 K via 1773K, the (002) the peak of paper-char became slightly sharper. With further increase in temperature from 1873 K to 1973 K, however, a drastic change in X-ray intensity profile was observed with paper-char, while such changes were not distinctly obtained for wood- and plastic-char. For polyethylene-char the X-ray spectra were fairly independent of temperature. Following the
extensive research works of Sahajwalla's 6 group, char structure would be strongly related to char reactivity. Detailed investigations on such correlation would be a subject of future publications.

3.2 Thermodynamic calculations

Based upon consideration that the paper used in this study would consist of $X_C$ moles of carbon, $X_H$ moles of atomic hydrogen and $X_O$ moles of atomic oxygen, it follows that one mole of sample can be represented by:

$$1 = X_C + X_H + X_O$$  \hspace{1cm} (5)

On the assumption that at temperature $T$, one mole of paper generates $n_C$ moles of char, and gas of volume $V$ containing $n_{CO}, n_{CO_2}, n_{H_2}, n_{CH_4}$ and $n_{O_2}$ moles of each species, then at one atmospheric pressure, the partial pressures, $P_j$, of gaseous components, $j$ ($j = CO, CO_2, H_2, CH_4$ and $O_2$) are related to $n_j$ and $V$ through the relationship:

$$P_j = n_j RT / V$$  \hspace{1cm} (6)

The mass balance for carbon, hydrogen and oxygen, respectively, is given by the following expressions:

$$X_C = n_C + n_{CO} + n_{CO_2} + n_{CH_4}$$  \hspace{1cm} (7)

$$X_H = 2 n_{H_2} + 4 n_{CH_4}$$  \hspace{1cm} (8)

$$X_O = n_{CO} + 2 n_{CO_2} + 2 n_{O_2}$$  \hspace{1cm} (9)

Combining Equation (6) with Equations (7),(8) and (9), yields the relationships:

$$X_C = n_C + (V/RT) \{ P_{CO} + P_{CO_2} + P_{CH_4} \}$$  \hspace{1cm} (10)

$$X_H = (V/RT) \{ 2 P_{H_2} + 4 P_{CH_4} \}$$  \hspace{1cm} (11)

$$X_O = (V/RT) \{ P_{CO} + 2 P_{CO_2} + 2 P_{O_2} \}$$  \hspace{1cm} (12)

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

$$<C> + 2O_2 = 2CO$$  \hspace{1cm} (13)

$$<C> + 2H_2 = CH_4$$  \hspace{1cm} (15)

for which the respective equilibrium constants are:
\[ K(13) = \frac{P_{CO}^2}{P_{CO_2}} \]  \( (16) \)
\[ K(14) = \frac{P_{CO_2}}{P_{O_2}} \]  \( (17) \)
\[ K(15) = \frac{P_{CH_4}}{P_{H_2}^2} \]  \( (18) \)

Combining Equations (10), (11) and (12) with (16), (17) and (18), respectively:

\[
X_C = n_C + \frac{(V/RT)}{\{P_{CO} + P_{CO_2}^2/K(13) + P_{H_2}^2 K(15)\}}
\]
\( (19) \)

\[
X_H = \frac{(V/RT)}{\{2P_{H_2} + 4P_{H_2}^2 K(15)\}}
\]
\( (20) \)

\[
X_O = \frac{(V/RT)}{\{P_{CO} + 2P_{CO_2}^2/K(13) + 2P_{CO_2}^2/K(13) K(14)\}}
\]
\( (21) \)

Since the gas phase is present at one atmosphere pressure,

\[
1 = P_{CO} + P_{CO_2} + P_{H_2} + P_{CH_4} + P_{O_2} = P_{CO} + P_{CO_2}^2/K(13) + P_{H_2} + K(15) P_{H_2}^2 + P_{CO_2}^2/K(13) K(14)
\]
\( (22) \)

Equations (19), (20), (21) and (22) involve four unknown quantities, \( n_C, V, P_{CO} \) and \( P_{H_2} \). Hence values for \( n_C, V, P_{CO} \) and \( P_{H_2} \) can be obtained by solving these four equations simultaneously for a given temperature, \( T \), and known initial compositions, \( X_C, X_H \) and \( X_O \). Using this information, values for \( P_{CO_2}, P_{O_2} \) and \( P_{CH_4} \) are obtainable from Equations (16), (17) and (18), respectively. In comparison with the partial pressures of the other species, the values for the partial pressures of \( O_2 \) were negligible.

For polyethylene, thermodynamic calculations become much easier, since polyethylene does not contain oxygen. By putting \( P_{CO_2} = P_{CO_2} = P_{H_2} = 0 \) into Equation (19) and (22), we have

\[
X_C = n_C + \frac{(V/RT)}{\{P_{H_2}^2 K(15)\}}
\]
\( (19') \)

\[
1 = P_{H_2} + P_{CH_4} + P_{H_2} + K(15) P_{H_2}^2
\]
\( (22') \)

Values for \( P_{H_2} \), \( n_C \) and \( P_{CH_4} \) are obtainable by solving simultaneously equations (19'), (20) and (22').

The calculated values for the equilibrium partial pressures of \( CO, CO_2, H_2 \) and \( CH_4 \) are included in Figure 5 as a function of temperature, together with the experimental data. It is evident that for the temperature range investigated, the results obtained from gas analysis are in satisfactory agreement with the values calculated from considerations of thermodynamic equilibria.

**4. CONCLUSION**

Based on the results of the present study, at temperatures between 1673 K and 2073 K, corresponding to those encountered in the blast furnace raceway, there is a good thermodynamic foundation for the injection of waste paper and polyethylene through the tuyeres of the blast furnace as a partial replacement for coke. In addition to preservation of a limited natural resource, metallurgical coal, the environmental benefits include utilization of waste polyethylene and paper material as well as a reduction of \( CO_2 \) added to the atmosphere.

**REFERENCES**


