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The application of simultaneous TG–DTA to the determination of the fate of injected coal in a pilot-scale blast furnace simulation rig[1]

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Abstract

Coal injection is an important technique for increasing the efficiency of blast furnaces, although the required optimum properties of injectant coals have not yet been fully identified. The Single-Tuyere Coal Injection Investigation Rig at the British Steel Teesside Technology Centre is a pilot-scale blast furnace simulation operated without iron ore so that the combustion (and gasification) of the injected coal can be studied in isolation. About two tonnes of coke are used to create a realistic simulation of the blast furnace raceway. Coal is injected into the hot air blast, and changes in the raceway conditions observed. Carryover fines from the waste gas are collected during the trial, and at the end of the trial, the coke bed is cooled, and coke samples dug out. These solid materials are analysed for traces of the injected coal, in order to assess the efficiency with which the injected coal is combusted.

The determination of the proportion of injected coal char present in these samples was originally carried out by point-counting particles using optical microscopy. This technique is labour-intensive and subjective. An alternative technique has therefore been devised, employing simultaneous thermogravimetry–differential thermal analysis (TG–DTA). The technique gives good agreement with optical microscopy, whilst being considerably faster and less subjective. © 1997 Elsevier Science B.V.

Keywords: Blast furnace; Coal injection; TG–DTA

1. Introduction

1.1. Blast furnace coal injection

The main features [1] of a typical blast furnace are shown schematically in Fig. 1. It is continuously "charged" at the top with iron ore, coke and a flux. The iron ore is reduced to metallic iron by CO and hydrogen gases formed inside the furnace.

Using magnetite (Fe_3O_4) as an example, the overall process can be expressed as:

$$Fe_3O_4(s) + 2CO(g) + 2H_2(g) \rightleftharpoons 3Fe(l) + 2CO_2(g) + 2H_2O(g) \qquad (1)$$

The flux removes impurities in the liquid iron, producing the waste product *slag*, which floats on the surface of the liquid metal, from where it can be easily removed via the *slag notch.* CO is produced by the reaction (combustion) of coke with the hot (ca. 1000°C) air blast:

$$2C(s) + O_2(g) \rightleftharpoons 2CO(g) \qquad (2)$$

CO production occurs primarily in the *raceway* region of the blast furnace (Fig. 2). The reaction is highly exothermic, producing raceway temperatures >2000°C.

In a blast furnace fuelled solely by coke, hydrogen is usually present in small, although important quantities, since it is a much better reducing agent than CO. Hydrogen can also be 'regenerated' by the reaction of

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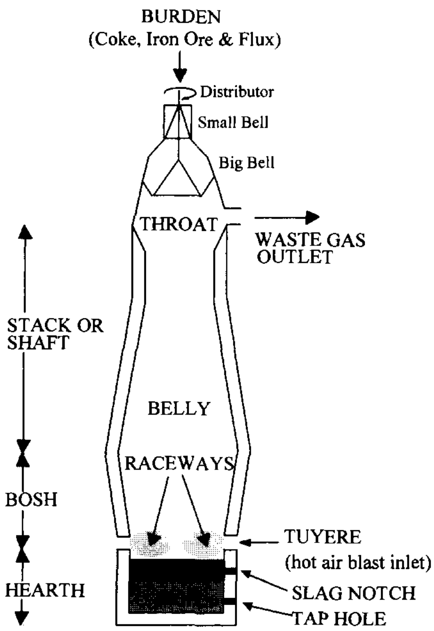

Fig. 1. The blast furnace.

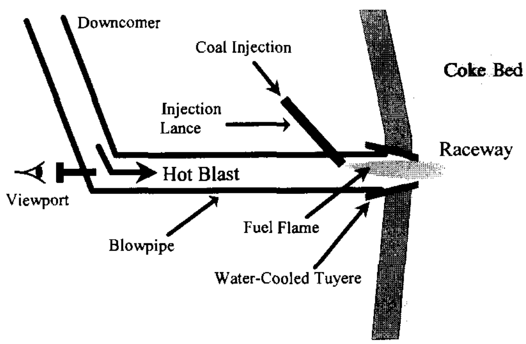

Fig. 2. The blast furnace raceway (after Hutney et al. [3]).

water vapour with the hot coke:

$$C(s) + H_2O(g) \rightleftharpoons H_2(g) + CO(g) \qquad (3)$$

Modern blast furnaces often use an "auxiliary fuel" such as coal, which is injected along with the hot blast. Coal injection has several advantages over "coke-only" operation:

1. Coal is about half the price of coke [2].
2. Coal injection increases the amount of hydrogen in the raceway. This is advantageous, since the reduction of iron ore by hydrogen is more effective than reduction by CO [3].
3. Coal injection can be used to control the raceway temperature [3].

Coke is necessary as a gas-permeable support for the iron ore, so it can only be partially replaced by coal. Maximising the *coke replacement ratio* is therefore a prominent research goal.

One of the difficulties encountered when trying to increase the coke replacement ratio is that of incomplete combustion. This creates problems [3], since:

1. Expensive fuel is being wasted.
2. The products of incomplete combustion reduce the permeability of the coke bed to carbon monoxide.
3. The "waste gas" from the blast furnace often contains solid carbonaceous residues ("carryover fines") as a result of incomplete fuel combustion, which must be removed before the gas can be used for heating, etc.

1.2. The British Steel Single-Tuyere Coal Injection Investigation Rig

The *Single-Tuyere Coal Injection Investigation Rig* [4] ("single-tuyere rig") at the British Steel Corporation Teesside Technology Centre is a pilot-scale blast furnace simulation rig, operated without iron ore so that the combustion of injected coal can be studied in isolation. A full description of the rig is given by Atkinson et al. [4].

Approximately two tonnes of coke are used to create a realistic simulation of the blast furnace raceway. Once a stable raceway has been obtained, granular (< 2 mm) coal is injected into the hot (950–1100°C) air blast at injection rates ≤ 3 kg min^{-1}, and changes in the raceway conditions observed. Carryover fines from the waste gas are collected via cooling towers and a cyclone, and at the end of the trial, the coke bed is cooled and samples dug out. These solid materials are then analysed for traces of the injected coal. The path of the injected coal from the raceway to the "receiving box" is shown schematically in Fig. 3.

The determination of the proportion of injected coal char in the single-tuyere rig samples was originally

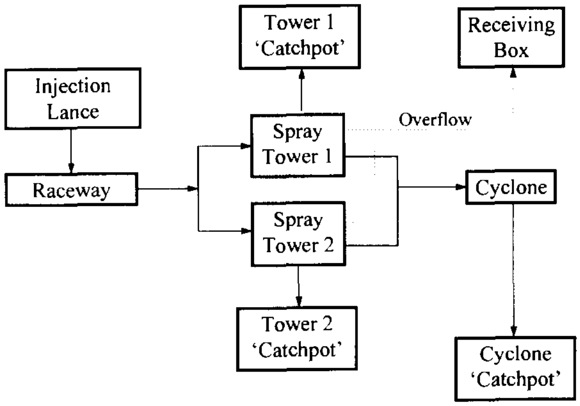

Fig. 3. Path of injected coal in the British Steel single-tuyere rig.

carried out by point-counting particles using an optical microscope. This type of analysis is extremely slow and subjective. An alternative technique was therefore required to distinguish between combustion residues originating from injected coal and those originating from coke. This is not a simple task, since both materials are produced by the pyrolysis of coal and are essentially very similar. The problem was eventually solved using simultaneous TG–DTA to distinguish between the two materials.

2. Experimental

2.1. Simultaneous TG–DTA of single-tuyere rig samples

Combustion residues from the single-tuyere rig were supplied by the British Steel Teesside Technology Centre. These were mixed thoroughly, and representative samples (ca. 5 mg) of each of the residues were heated to 1273 K in flowing (50 $cm^3\ min^{-1}$) air at a rate of 10 K min^{-1}, using a Stanton Redcroft STA 780 series simultaneous TG–DTA unit. The combustion of each of the components in the sample was monitored using differential thermal analysis (DTA) and derivative thermogravimetry (DTG). The reference material was calcined alumina (5 mg). The DTA signal was recorded using an analogue-to-digital converter (adc) and the results plotted on an arbitrary scale.

The ordinate scale of the DTG curves was defined as dX/dt, where X is given by:

$$X = \frac{m_0 - m}{m_0} \qquad (4)$$

where m is the sample mass at time t, and m_0 the initial sample mass. This produced positive-going peaks for mass loss.

The mass fraction of each of the components in the sample was determined by Gaussian fitting of the DTG curve, followed by numerical integration of each of the resolved peaks. This was carried out using MicroCal Origin™ software for Microsoft Windows®.

2.2. Optical microscopy

Analysis of the combustion residue samples by optical microscopy was carried out at the British Steel Corporation Teesside Technology Centre, as described by Atkinson et al. [4].

3. Results

A typical TG–DTA trace from the temperature-programmed combustion of a sample of carryover fines from the "receiving box" of the single-tuyere rig is shown in Fig. 4. The maximum rate of mass loss of each of the components occurs at different temperatures, resulting in two peaks in both the DTA and DTG curves. The peaks can be readily identified by analysis of samples obtained by operating the single-tuyere rig without coal injection, or by using different coal injection rates to systematically vary the amount of coal char in the combustion residues. Cokes are generally seen to combust at higher temperatures [5] than coals and rapid pyrolysis chars because of their decreased reactivity to air (due to a more ordered structure) compared to these materials. The mass fractions of each of the components in the sample can be readily determined by Gaussian fitting of the DTG curve (Fig. 5), followed by numerical integration of each of the resolved peaks.

TG–DTA analysis of samples from the single-tuyere rig was found to give excellent agreement with point-counting, and a comparison between the results produced by the two techniques is given in Table 1. It should be noted that while point-counting is carried

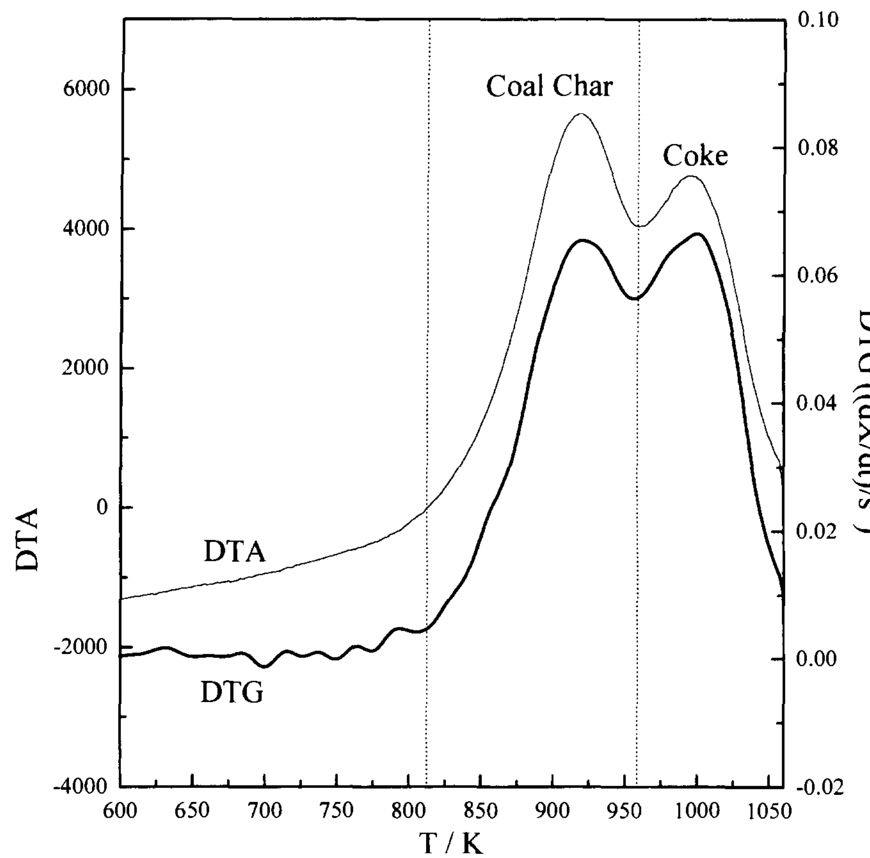

Fig. 4. Typical DTG and DTA traces produced by the temperature-programmed combustion of a single-tuyere rig 'receiving box' sample (Trial 68).

out on a particle number basis, integration of DTG curves produces a mass ratio. Peak maxima and widths (full width at half-height) for the data presented in Table 1 are given in Table 2.

4. Discussion

Good agreement between DTG and point-counting was achieved for samples from spray tower 1, the receiving box, and the cyclone. Samples from tower 2 were not in close agreement, with a discrepancy of ca. 20%. This was attributed to a high degree of char heterogeneity, which is reflected in a large DTG (and DTA) peak width for the char component (see Table 2). Samples taken from the raceway were notable for their narrow coke DTG peaks, which was ascribed to thermally induced ordering (annealing) of the constituent lamellar molecules in the coke as a result of the high (ca. 2000°C) raceway temperature. The coke peak maxima were also observed at slightly higher temperatures than for the other coke DTG peaks, which is consistent with thermal annealing.

The presence of char (ca. 15%) in the raceway samples (which were dug out at the end of the trial) is direct evidence for the 'blocking up' of coke due to incomplete combustion of the injected coal. This has important applications for the development of coal injection technology.

Samples taken from the cyclone (which is used to remove very small particles from the waste gas) were found to be more heterogeneous than the other samples, and a small secondary DTG peak overlapping the

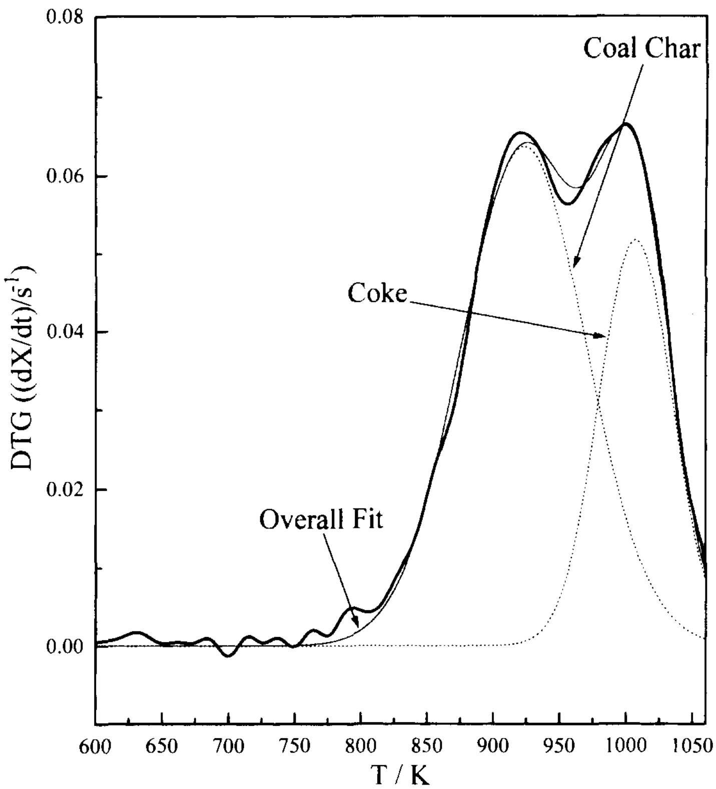

Fig. 5. Gaussian curve-fitting to typical DTG trace.

Table 1
Comparison of TG–DTA and point-count data (single-tuyere rig trial number 68)

Sampling location	Run	TG–DTA data [a]		Point-count data [a,b]	
		% char	% coke	% char	% coke
	1	76	24		
Tower 1	2	72	28		
	Mean	74	26	75	25
	1	53	47		
Tower 2	2	57	43		
	Mean	55	45	33	67
	1	58	42		
Receiving box	2	60	40		
	Mean	59	41	70	30
	1	85	15		
Cyclone [c]	2	81	19		
	Mean	83	17	89	11
	1	16	84		
Raceway	2	14	86		
	Mean	15	85	Not determined	

[a] All values shown to nearest 1%. Mean values calculated using data precise to 2 decimal places.
[b] Courtesy of British Steel Teesside Technology Centre. Converted to ash-free basis for comparison.
[c] Two char peaks observed (see text).

Table 2
DTG peak widths and centres (single-tuyere rig trial number 68)

Sampling location	Run	Char peak(s) [a]		Coke peak [a]	
		maximum/K	width/K	maximum/K	width/K
Tower 1	1	908	62	992	59
	2	910	63	996	58
Tower 2	1	933	89	1019	54
	2	915	81	1001	54
Receiving box	1	919	76	1006	60
	2	915	73	1005	56
Cyclone	1	(a) 885	(a) 77	992	61
		(b) 935	(b) 24		
	2	(a) 881	(a) 62	975	77
		(b) 931	(b) 31		
Raceway	1	968	56	1043	43
	2	967	55	1049	45

[a] All values shown to nearest 1%.

major char peak was observed. The areas of these two peaks were added together to produce the total char figure in Table 1. It is clear that TG–DTA produces additional information on sample heterogeneity which cannot easily be obtained using microscopy.

5. Conclusions

Simultaneous TG–DTA is considerably more efficient than optical microscopy for analysing the carry-over fines from blast furnaces and blast furnace simulation rigs. The main advantages of the technique over optical microscopy are speed and the provision of quantitative information on sample heterogeneity. The rapidity of the technique means that many samples can be analysed within a short period of time, and it is hoped that the technique will enable the production of a larger database of injected coal combustion efficiencies than would otherwise have been possible. The technique also provides information on the combustion efficiency of injected coal which is known to cause operational problems by reducing the permeability of the coke bed (especially in the raceway region).

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