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A Novel Slag Carbon Arrestor Process for Energy Recovery in Steelmaking Industry

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ABSTRACT

A novel slag carbon arrestor process (SCAP) was proposed to improve the heat recovery in energy-intensive steelmaking process, which typically has a low heat recovery. The proposed SCAP process introduces a tar reformer to utilise the slag - a by-product from steelmaking process - as the catalyst to convert coke oven gas and tar into hydrogen-enriched fuel gas. This is achieved by making use of the valuable carbon and/or energy contained in the coke oven gas, which otherwise being wasted, to assist

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in tar reforming and produce hydrogen-enriched gas. Such concept is expected to reduce the undesired tar formation in steelmaking process along with improved heat recovery efficiency and higher quality coke oven gas production. Both simulation and experimental studies on the slag carbon arrestor process were performed. The preliminary thermodynamic analysis carried out using Aspen Plus v8.4 indicates that with the tar reformer the energy content of coke oven gas was found increased from ~34.6 MJ/kg to ~37.7 MJ/kg (or by 9%). Also, with the utilisation of carbon deposition on the slag, a reduction of up to 12.8% coke usage in the steelmaking process can be achieved. This corresponds to an energy saving of 4 % and a carbon emission reduction of 5.7 % compared with the conventional steelmaking process. Preliminary experimental TGA-FTIR investigations revealed a reduction in the aromatic and aliphatic hydrocarbon groups and an increase in the production of CO_2 and CO, attributed to the tar cracking abilities of slag.

KEYWORDS: slag carbon arrestor process (SCAP), steelmaking, carbon deposition, tar, coke oven gas.

1 INTRODUCTION

Steel production is a major indicator for economy growth especially for developing countries. However, steel making is a highly energy intensive process accounting for nearly 5% of the world's total energy consumption and approximately 6.7% of total world CO_2 emissions. Also, the heat recovery in a steel making process is typically low at only ~17% [1]. The rising cost of energy and

high demand for greenhouse gas emission reductions represent major challenges for the steel industry.

Currently, approximately 17% of the operating cost of the steelmaking industry is energy. This energy originates from multiple sources, such as coal, electricity, natural gas, recycled coke oven gas (COG) and blast furnace gas (BFG) [2]. Recycling of waste heat and recovery of energy rich by-products from these energy sources are identified as key measures to improve energy efficiency and reduce costs and emissions of the modern-day steelmaking process. It is estimated that the energy recycled from COG supplies ~20% of the total energy consumed in the present steelmaking process, with potential of increasing to 40% if fully utilised. BFG, on the other hand, has the potential to supply up to another 40% of the total plant energy consumption despite its low energy density (~ 1/3 of that of COG) [3].

Motivated by this path, our research team at the University of Newcastle, Australia developed a novel Slag Carbon Arrestor Process (SCAP) to improve the energy recovery of the steelmaking industry. The work is also part of a major research theme on low-emission energy technology options [4-10] being developed at the University of Newcastle, Australia. The SCAP process is to be introduced in the following texts.

Figure 1 shows the conventional steel production process which primarily consists of two integrated unit operations: coke production and iron ore reduction. The coke making process involves carbonization of coal at high temperatures (800 - 1200°C) in an oxygen deficient atmosphere in order

to concentrate the carbon. During the coke making process, hot COG along with unwanted aromatic hydrocarbon compounds (i.e. tar) are generated, which contain valuable carbon and energy [1]. The produced COG is considered to be a good fuel source [11]. However, to ensure effective utilisation of COG, tar must be removed as it can create operational problems such as condensation and pipe blockages [11, 12]. To achieve this, the hot COG, at temperatures between 800 and 850°C, emitted from coke ovens is spray cooled with an aqueous ammonia solution in order to remove most of the higher hydrocarbons in the tar, such as benzene (C_6H_6), toluene (C_7H_8), and naphthalene ($C_{10}H_8$) etc. In addition, complex processing plants are required for the conversion of tar into valuable chemical by-products [13]. These processes, as mentioned by Yue et al. [14], cause significant heat losses and serious secondary pollution due to tar losses in the waste water. Therefore, instead of physically and chemically separating tar from COG, it would be highly beneficial if the tar could be decomposed into light fuel gases in-situ with the assistance of a catalyst. The heat and chemical energy embodied in the hot COG can also be used in this process.

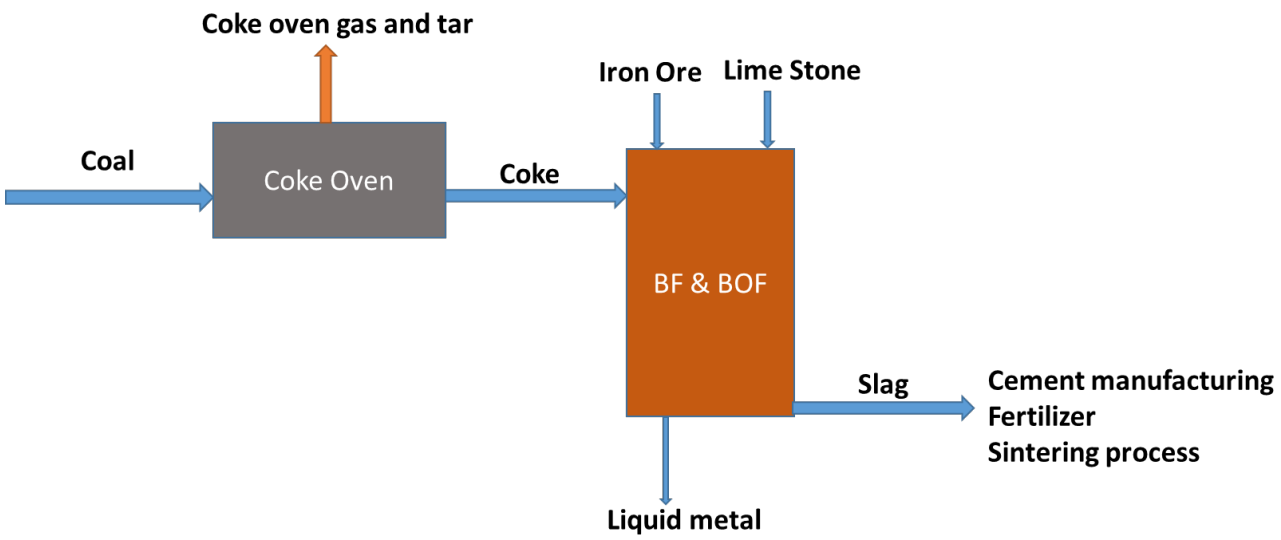

Figure 1: Process flow diagram of a conventional steelmaking process (BF & BOF: blast furnace & basic oxygen furnace).

After the coke making process, iron ore reduction and steel production occur in the blast furnace (BF) and basic oxygen furnace (BOF), respectively. Coke, sinter, and limestone are added in these two furnaces. The purpose of the blast furnace is to chemically reduce iron oxides into liquid metal and physically separate the liquid metal from slag. The operation of the blast furnace and basic oxygen plant usually results in the production of a high amount of slag, containing high amounts of CaO, FeO, SiO_2 and Al_2O_3 [15]. The majority of slag produced is currently used in the cement industry or as a fertilizer, while a fraction of the slag is recycled in the sintering process and in the blast furnace for supplying limestone and iron [16]. Heat recovery from slag is generally low and difficult due to its low thermal conductivity between 0.1 - 3 W/mK [17]. In general, this contributes to the low heat recovery of the steelmaking industry.

To overcome the aforementioned issues such as low heat recovery, high heat losses, and possible secondary pollution, several options have been suggested in the literature such as hot-slag heat recovery and more efficient process design [18]. Nonetheless those options are not fully developed for commercial implementation. As a step change solution, a novel Slag Carbon Arrestor Process (SCAP) was developed.

Figure 2 shows the proposed SCAP process in which a tar reformer is introduced to the conventional steelmaking process. It is essentially the integration of a conventional steelmaking process and a tar

reforming/hydrogenation process. In the tar reformer, tar decomposes under a catalytic reaction with steelmaking slag (see reaction R1) while COG is converted into a hydrogen-enriched gas [19],

$$\text{Tar} \rightarrow H_2 + CO + CO_2 + CH_4 + \text{other light hydrocarbon} + C \qquad \text{(R1)}$$

Normally very high temperatures are required for tar decomposition; catalysts such as steelmaking slag can help to reduce such temperatures. Generally, calcium and iron are considered to be favourable catalyst materials for pyrolysis, reforming or decomposition of coal and/or tar as well as hydrogen-enriched gas production [20]. The innovativeness of the SCAP process is that the tar reforming process makes use of slag, which is rich in calcium and iron oxides, in the place of traditional calcium/iron oxide catalysts.

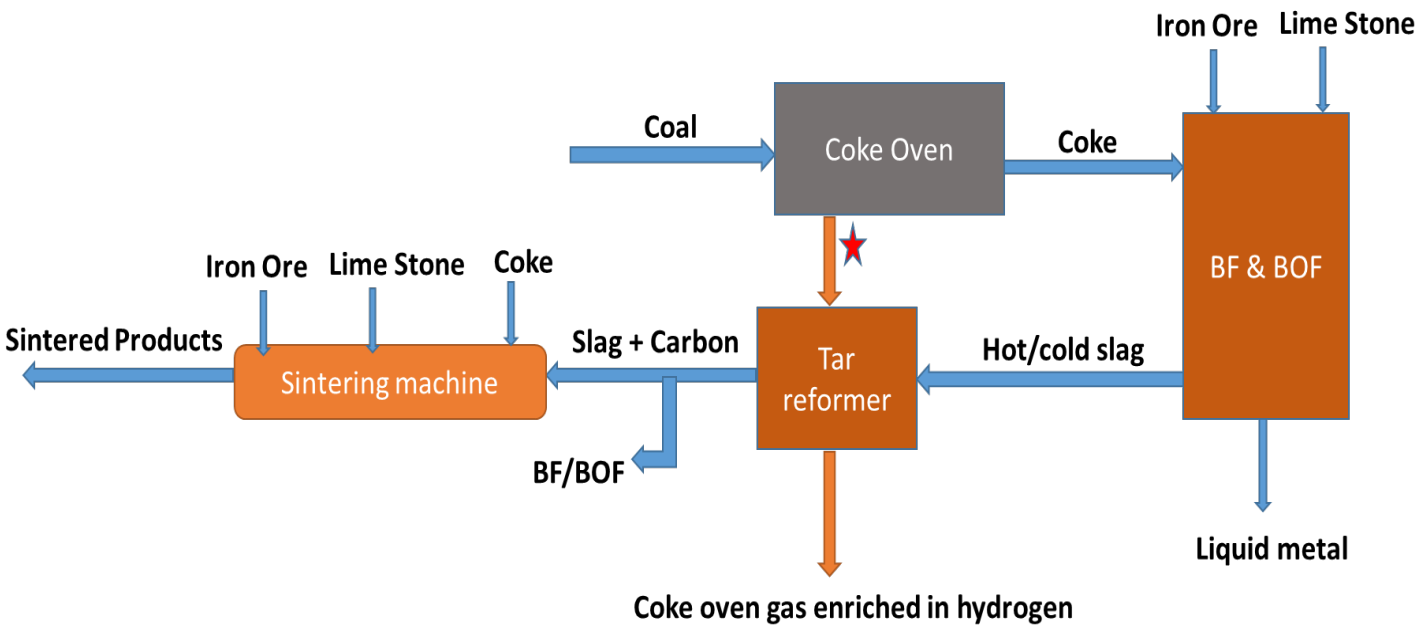

Figure 2: Process flow diagram of the Slag Carbon Arrestor process for steelmaking (BF & BOF: blast furnace & basic oxygen furnace; the star sign: potential energy recovery point).

The slag entering into the tar reformer is best in the form of granulated slag (providing more surface area for catalytic reaction), which is a sand-like product produced using instant quenching of molten slag. Nevertheless, hot molten slag / rock type slag (produced by slowly cooling the molten slag) should not be excluded for future study. Also generated along with the tar reforming process is a possible soot formation/carbon deposition on the surface of slag, which can then be recycled back to the sinter machine and blast furnace. With such carbon recycling, the SCAP process is expected to not only reduce coke consumption in the steelmaking process, but also eliminate tar associated problems as well as the production of a hydrogen-enriched COG. Another advantage of SCAP process is that it can be readily retrofitted to existing steel production plants.

The objective of this paper was to study the feasibility of the SCAP process by (i) investigating via simulations the extents of COG quality improvement, carbon deposition and tar decomposition (ii) conducting energy and mass balance analyses of the process, (iii) examining the effect of tar decomposition extent on carbon deposition, energy saving, and emission reduction potentials, and (iv) using preliminary experiments to confirm the concept and verify simulation results.

2 METHODOLOGY

2.1 Process Simulation

The process simulation was carried out using the process simulation package - Aspen Plus v8.4. The Aspen model solves all the equilibrium constant equations simultaneously and calculates the equilibrium conditions by minimizing the total Gibbs free energy of the system. Moreover, thermodynamic database - HSC chemistry (developed by Outotec) - was also used as an assisting tool. With the above tools, energy and mass balance analyses were performed for the SCAP process.

Figure 3 shows the process flow diagram of the SCAP model. The SCAP model was developed and designed at a steel production rate of one tonne/hr and based on the typical conditions of the conventional steelmaking process. Specifically, in the simulation it was assumed that for the production of one tonne of steel it requires 243 kg of coke and 140 kg of sinter in the blast furnace for iron production [21]. To produce the 140 kg of sinter, approximately 3.9 kg of recycled BOF slag and 5 kg of coke breeze was consumed [22], whilst the production of 243 kg of coke generates approximately 66.6 kg of hot raw COG (excluding tar) and 13.3 kg of tar [23]. The production of one tonne of steel also generates about 180 kg of BOF slag and 375 kg of blast furnace slag [24]. However, due to the harmful constituents (Na_2O, K_2O and S) in the blast furnace slag, it is not recycled in the steelmaking process while up to 25% of BOF slag can be recycled back to the sinter machine, basic oxygen plant and blast furnace [25]. These data are based on and crosschecked with multiple literature [24, 26, 27].

The above data also indicates that the typical coke consumption of a sinter machine is only ~2% of the total coke usage for the steelmaking process, and thus coke saving in the sinter machine has a practical limit on the maximum saving that could be achieved. In contrast, the major energy saving that may be contributed by the SCAP process is more related to the recycled BOF slag in the basic oxygen plant and blast furnace. Here, the carbon-deposited BOF slag may help reduce coke usage in the blast furnace and the potential for this saving is far greater than the coke saving in the sinter machine. Based on the above discussion, the amount of BOF slag used in the simulation was fixed at 45 kg per tonne of steel production, including 41.1 kg of recycled BOF slag to the blast furnace [24, 25] and 3.9 kg to the sinter machine [22].

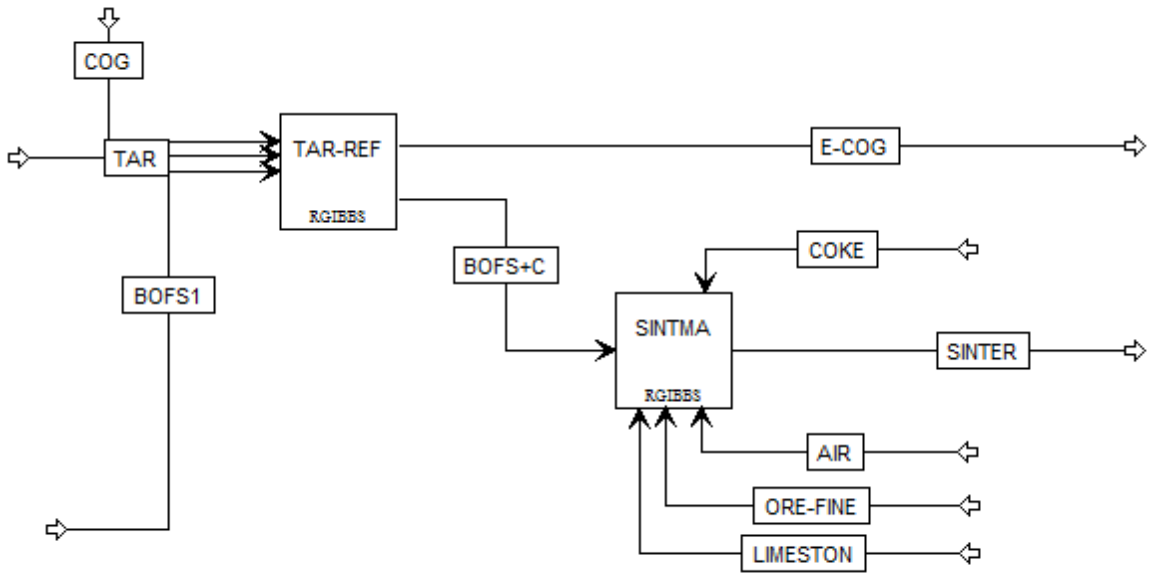

Figure 3: Aspen Plus process flow diagram of the proposed SCAP concept (E-COG: hydrogen-enriched COG; TAR-REF: tar reformer; SINTMA: sinter machine).

The operating temperature of the tar reformer was fixed at 600°C with an inlet COG temperature at 800°C. These temperatures were chosen based on the literature which suggests the optimum

temperatures of coal pyrolysis and tar decomposition for achieving the maximum carbon deposition [28]. Table 1 gives the detailed compositions of the hot raw COG (excluding tar) and BOF slag used in this study. It should be highlighted that the hot raw COG used in this study is the uncooled raw oven gas emitted directly from the coke oven battery, rather than the conventional cooled COG obtained from the gas collection main after tar removal. The hot raw COG composition in Table 1 however does not include tar, the composition of which is to be identified separately. Before simulating the tar component in the COG, it should be noted that coal tars are extremely complex mixtures consisting of greater than 400 components. These components again vary considerably according to the nature of the coal charge and the coal carbonisation conditions [29]. A simple yet effective way to simulate coal tar in Aspen Plus was reported by Hamelinck et al. [30] based on the C:H atomic ratio of most coal tar (1.4:1) [11]. In his approach (also adopted in this study) the composition of tar was represented by phenanthrene ($C_{14}H_{10}$) which has a similar C:H atomic ratio and thermo-physical properties with tar [30]. The yield of tar per tonne of dry coal is about 30-50 litres (or 3.5 - 5.9 wt% of dry coal) [27], whilst the yield of tar per one standard m^3 of hot raw COG (without tar) is typically 100 g/m^3 [26]. In this study the tar content of the hot raw COG (excluding tar) was fixed at the typical value of 100 g/m^3 or 20 wt%. A tar conversion rate of 0 - 100% in the tar reformer was examined. Further, a cold granulated BOF slag with a temperature of 25°C was used. Utilising the heat from the hot slag directly for tar reforming reactions is expected to further improve heat recovery. However, this aspect was not examined in the present study.

Table 1: Composition of hot raw COG and BOF slag.

Hot raw COG* (excluding tar)	Fraction (vol%)	BOF slag**	Composition (wt%)
H_2O	10.41	$Ca_2Fe_2O_5$	10
H_2	49.28	Ca_2SiO_4	45
CH_4	26.75	FeO	25
CO	5.50	CaO	5
CO_2	2.28	Ca_3SiO_5	15
N_2	2.19	-	-
C_2H_4	1.61	-	-
C_2H_6	0.82	-	-
C_3H_6	0.05	-	-
H_2S	0.47	-	-
NH_3	0.66	-	-
Total	100	Total	100

*. Based on reference [11]; **.Based on reference [31].

2.2 Experimental

A series of preliminary coal and coal-slag pyrolysis experiments were completed. The apparatus, presented in Figure 4, consisted of a thermo-gravimetric analyser coupled with a Fourier Transform Infrared Spectrometer (TGA-FTIR) to allow for online mass loss and gas evolution characterisation. An Australian bituminous coal was used in all experiments, with proximate and ultimate analyses of the coal presented in Table 2. A synthetic slag, with a composition of CaO: FeO: SiO_2:Al_2O_3 = 0.45:0.3:0.2:0.05 and particle size of 75-212 μm, was used in experiments and was calcined in nitrogen at 800°C for 1 hr prior to experiments.

Table 2: Proximate and ultimate analysis of coal used in this study

	Proximate Analysis[a]				Ultimate Analysis				
	M (%)	A (%)	VM (%)	FC (%)	C (%)	H (%)	N (%)	S (%)	O[b] (%)
coal	3.7	8.9	32.7	58.4	77.2	5.2	2.0	0.7	15

a - On a dry basis, with M, moisture; A, ash; VM, volatile matter; and FC, fixed carbon.

b - O calculated by difference.

TGA conditions for all experiments consisted of a nitrogen sweep gas flow rate of 100 mL/min, ramp rate of 10°C/min and final pyrolysis temperature of 900°C. FTIR scans were taken at 10°C intervals and operating conditions consisted of a gas cell length of 10 cm and temperature of 240°C, transfer line temperature of 240°C, 32 scans per spectra for a scan range of 500 – 4000 cm^{-1} and resolution of 4 cm^{-1}. Experimental scenarios examined were coal pyrolysis without slag and coal pyrolysis with slag at mass ratios of 6.75:1 (the same ratio used in the simulation), 1:1 and 1:3 of coal to slag respectively.

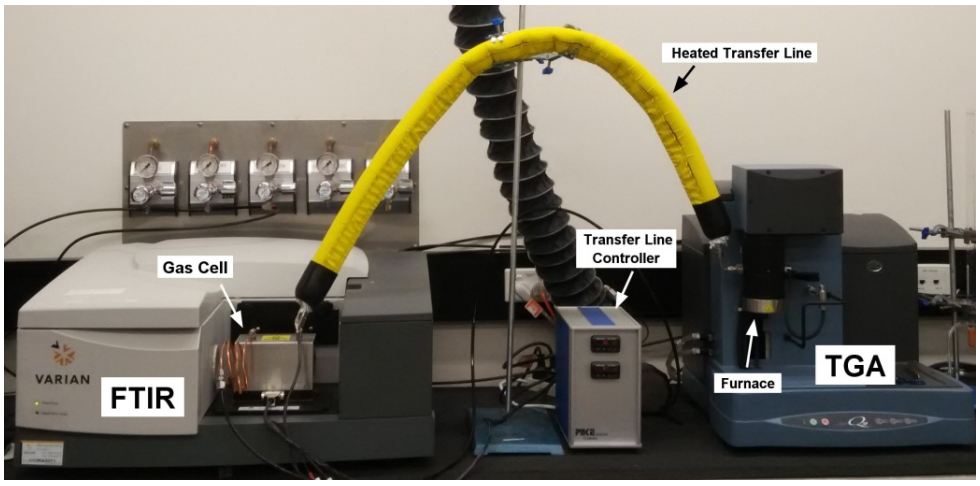

Figure 4: Experimental TGA-FTIR setup.

2.3 Performance Indicators

The advantages of the proposed SCAP process over the conventional steelmaking process were investigated by evaluating some of the key performance indicators, including COG quality improvement, carbon deposition and coke reduction rate, energy saving, and emission reduction.

2.3.1 COG quality improvement

Depending on the extent of COG reforming and the tar decomposition reaction, the energy content of the reformed COG varies accordingly. To quantify such improvement, Equation (1) was used, namely,

$$COG\ quality\ improvement = \frac{E_{COG}}{E_{COG,0}} - 1 \quad (1)$$

where $E_{COG,0}$ denotes the energy content of the hot raw COG (excluding tar) and E_{COG} denotes the energy content of the reformed COG.

2.3.2 Carbon deposition and coke saving

The amount of deposited carbon on the slag was expressed in terms of a mass fraction of the reacted slag/hot raw COG. The associated coke saving that may be achieved directly in the SCAP process was calculated by,

$$Direct\ coke\ saving = \frac{m_{coke,0} - m_{carbon} \times E_{carbon}/E_{coke}}{m_{coke,0}} \quad (2)$$

where $m_{coke,0}$ is the conventional coke consumption, m_{carbon} is the amount of deposited carbon, E_{carbon} and E_{coke} are respectively the energy contents of pure carbon and coke, taken as 33 MJ/kg and 29 MJ/kg, respectively.

In addition, there may also be some forms of indirect coke saving that may be achieved in the SCAP process owing to the improved energy recovery, which is quantified by,

$$Indirect\ coke\ saving = \frac{m_{coke,0} - Q_{saving}/E_{coke}}{m_{coke,0}} \quad (3)$$

where Q_{saving} is the thermal energy saving that may be achieved in the SCAP process yet is generally unavailable for recovery in the conventional steelmaking process.

2.3.3 Energy saving and emission reduction

The total energy saving of the SCAP process per tonne of steel was calculated against the average energy intensity of the conventional steelmaking process at 21 GJ/tonne of steel. The associated emission reduction was estimated by converting both direct and indirect coke savings to an equivalent CO_2 saving, which were then compared with the typical emission intensity of the conventional steelmaking process at 1.8 tonne CO_2/tonne of steel.

3 RESULTS AND DISCUSSION

The simulation and experimental results are presented in Sections 3.1 and 3.2, respectively.

3.1 Simulation

3.1.1 Energy and mass balance

Figure 5 shows the heat and mass balance analysis of the SCAP process, designed based on a capacity of one tonne/hr of steel production. A quick mass balance analysis shows that at a tar reformer temperature of 600°C and assuming a complete tar conversion, the weight of BOF slag was found to increase from 45 kg/hr to 69 kg/hr while the amount of COG reduced from 67 kg/hr to 56 kg/hr. These changes were confirmed to be owing to carbon deposition on the slag. The heat balance analysis shows that a noticeable part of the sensible and chemical energy stored in the hot raw COG and tar was transformed into the chemical energy in the deposited carbon, whilst the rest was kept with the reformed COG, the sensible heat of the hot reacted slag, and in the form of reaction heat. A more detailed analysis of the energy flows in the SCAP process is presented in Figure 6 via a Sankey chart.

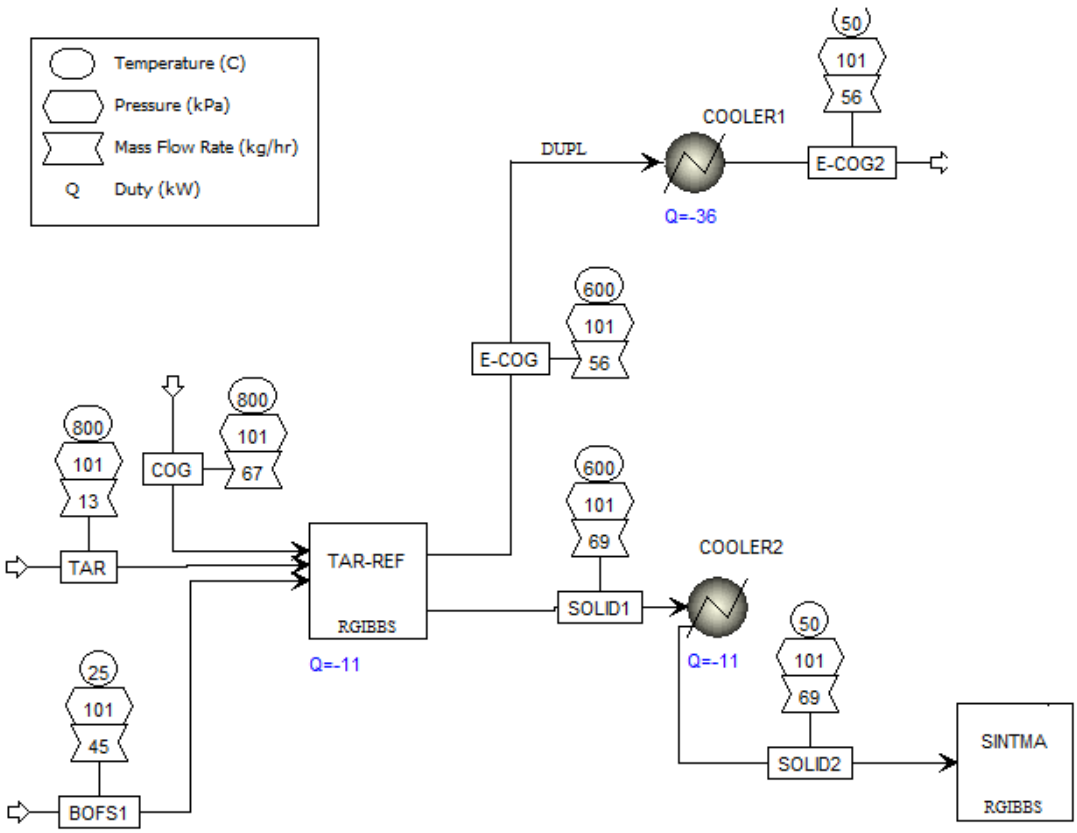

Figure 5: Heat and mass balance of SCAP process at a tar reformer temperature of 600°C and assuming 100% tar conversion (E-COG: hydrogen-enriched COG; TAR-REF: tar reformer; SINTMA: sinter machine).

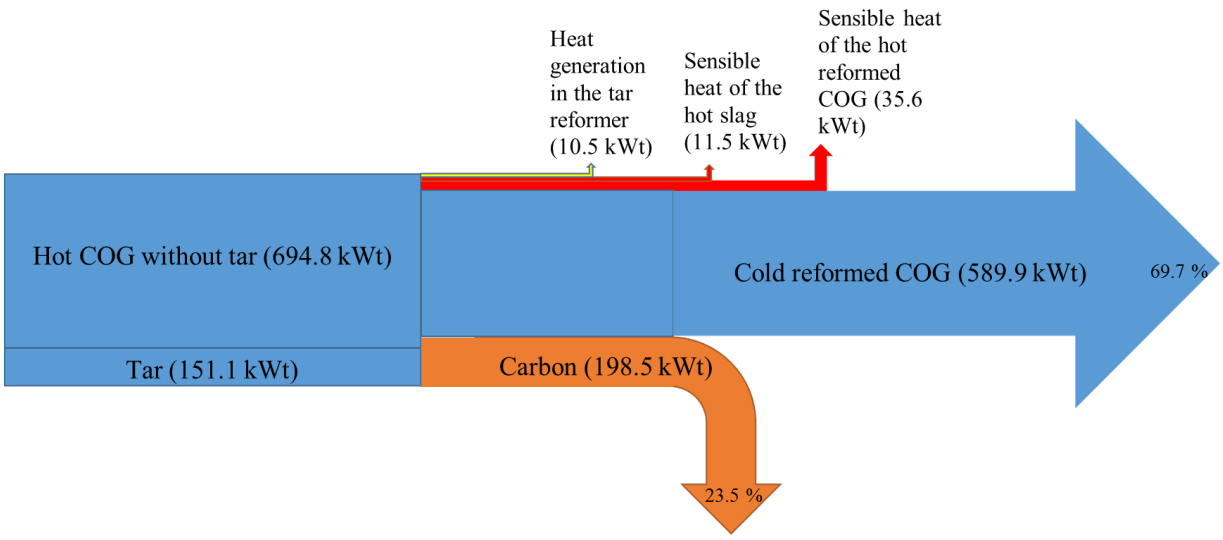

Figure 6: Sankey diagram of the energy flows in SCAP process at a tar reformer temperature of 600°C.

Figure 6 shows that ~19% of the total energy input of the process comes from tar. Upon successful conversion and utilisation, such energy can be recovered and transformed into energy in the form of

238 carbon to be more effectively utilised. Some carbon also derives from the methane content of the COG,
239 which in total contributes to a net carbon energy output of ~23.5% of the total energy input (see Figure
240 6). This portion of energy can be directly used to offset coke usage in the sinter plant and blast furnace.
241 The reformed COG was found to contain ~69.7% of the total energy input, which is believed to be a
242 more valuable fuel than the conventional COG as it is now hydrogen-enriched. Also, the sensible heat
243 contained in the hot COG and slag, although insignificant and mostly wasted in the conventional
244 steelmaking process, may easily find a recovery path in the proposed SCAP process.

245 3.1.2 COG quality improvement

246 Table 3 gives the gas composition of COG before and after the tar reformer at a reforming temperature
247 of 600°C for both 0% and 100% tar conversion rates. The results show that with the newly installed tar
248 reformer, the SCAP process can greatly increase the hydrogen content of the COG from about 49% to
249 63% assuming that the tar remains intact (i.e. 0% tar conversion) while 64% assuming that the tar was
250 completed decomposed (100% tar conversion). This indicates that COG reforming was the main reason
251 for hydrogen enrichment instead of tar decomposition. The decreasing methane content from about 27%
252 to 18% was attributed to the reaction converting methane into the deposited carbon on the slag and H_2.
253 On the other hand, the decreasing CO_2/CO contents can be mainly attributed to the carbonation of free
254 CaO contained in the slag. C_2 and C_3 hydrocarbons were also found completely reacted in the tar
255 reformer. The above changes in the gas composition of COG are expected to result in an improved
256 energy quality of the COG, which was quantified in the following study.

Table 3: Gas composition of COG before and after tar reformer at a reforming temperature of 600°C.

Gas composition (vol%)	Raw COG (tar excluded)	Reformed COG 0% tar conversion	Reformed COG 100% tar conversion
H_2O	10.41	10.25	10.05
H_2	49.28	63.30	64.36
CH_4	26.75	17.50	18.09
CO	5.50	3.67	3.54
CO_2	2.28	1.60	1.49
N_2	2.19	2.27	2.20
C_2H_4	1.61	0.00	0.00
C_2H_6	0.82	0.00	0.00
C_3H_6	0.05	0.00	0.00
H_2S	0.47	0.25	0.25
NH_3	0.66	0.01	0.01
Tar	0.0	1.14	0.0

Table 4: Gas composition of the reformed COG and deposited carbon on the slag as a function of the amount of slag participating in the reaction (100% slag = 45 kg/hr, tar reforming temperature: 600°C, tar conversion rate: 100%).

COG composition (vol%)	150% slag	100% slag	50% slag
H_2O	9.7	10.0	10.3
H_2	64.7	64.4	64.0
CH_4	18.3	18.1	17.9
CO	3.4	3.5	3.7
CO_2	1.4	1.5	1.6
N_2	2.2	2.2	2.2
C_2H_4	0.00	0.00	0.00
C_2H_6	0.00	0.00	0.00
C_3H_6	0.00	0.00	0.00
H_2S	0.25	0.25	0.26
NH_3	0.01	0.01	0.01
Tar	0.0	0.0	0.0
Deposited carbon (kg per tonne of steel)	21.7	21.6	21.6

Table 4 shows the gas composition of the reformed COG and the amount of deposited carbon on the slag for different amounts of slag participating in the reaction and assuming 100% tar conversion. The simulation results, however, are based on pure thermodynamics, rather than kinetics, of the tar reforming reaction and thus should be interpreted accordingly. Indeed, the results indicate no

significant change to the COG composition or carbon deposition for varied amounts of slag. This suggests that from a purely thermodynamic point of view, the amount of slag has little effect on the COG quality and extent of carbon deposition. This is partly explained by the low free CaO content in the slag which leads to low absorption rates of CO_2/CO in the COG and thus a limited variation in the COG composition. Nevertheless, due to the catalytic effect of the slag on tar reforming, literature has shown that the extent of carbon deposition was significantly affected by the amount of slag present in the reaction [19]. The quantification of such effect was investigated by experimental studies, the results of which are presented in section 3.2.

Figure 7 shows the improved energy content of the COG in the SCAP process compared with that of the reference case (i.e. the COG before entering the tar reformer). It was found that the energy content of COG increased by up to ~9% using the SCAP process, of which only 1.5% of the increase is attributed by tar decomposition. The low increment of COG energy content contributed by tar decomposition can be explained by the relatively low fraction of tar (~13 wt%) in the raw COG. It implies that the expectation of solely relying on tar decomposition to improve COG quality is impractical. Instead, COG reforming assisted with tar decomposition and carbon deposition is the main route for obtaining a hydrogen-enriched COG. The above discussion is also supported by the literature [21] which reports that only 2.3% of the total exergy input of the steel making process is retained in the tar, while a significant fraction (about 24%) of the total exergy is found in the combustible off-gases (mainly COG and BFG). Thus, this leads future research efforts to examining the effect of COG

reforming temperature on carbon deposition and gas quality (to be studied in our future journal publications).

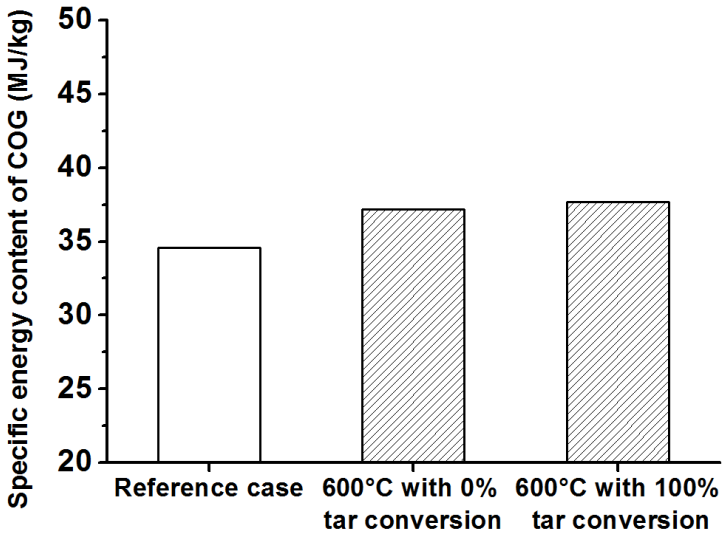

Figure 7: Specific energy content of COG before (i.e. the reference case) and after the tar reformer at a reforming temperature of 600°C.

3.1.3 Carbon deposition

Figure 8 gives the extent of carbon deposition in terms of weight fraction of the reacted slag/raw COG as a function of tar conversion rate at a reforming temperature of 600°C. It can be seen that with nil tar conversion the carbon derived solely from the COG can reach approximately 12.5 wt% of the raw COG or 18.1 wt% of the reacted slag. Increasing the tar conversion rate from 0 % to 100 % was found to yield nearly 100 % more carbon. This indicates that tar decomposition is another significant source of carbon despite its minimal contribution to the improved COG quality. In addition, to validate our simulation results against the experimental data presented in the literature, we found that at a reforming temperature of 600°C and a tar conversion rate of ~26% the simulation predicted a similar amount of deposited carbon (~16 wt% of the raw COG) with experimental data [19] (see the black dot in Figure 8

at 600°C and 40 mins). For the readers' information, other literature experimental data obtained at 500°C and 900°C for a reaction period of 40 mins are also presented in Figure 8.

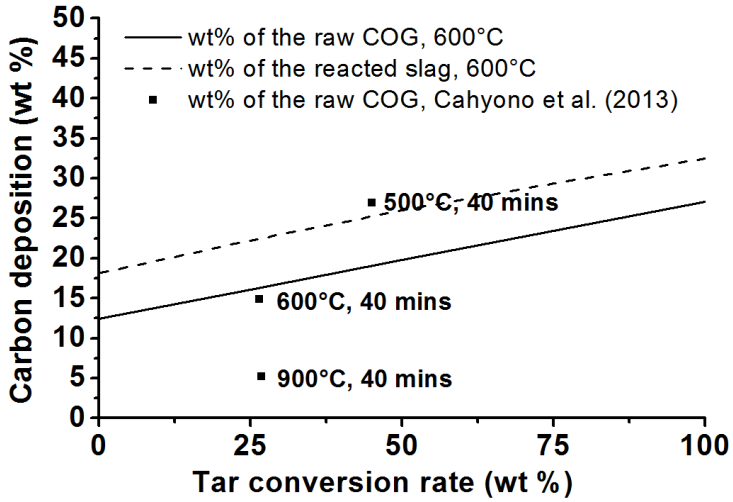

Figure 8: Carbon deposition as a function of tar conversion rate at a reforming temperature of 600°C, compared with some experimental data in the literature.

Table 5 shows the coke saving potential per tonne of steel production due to the recycling of the deposited carbon in the SCAP process at a tar reforming temperature of 600°C. It shows that compared to the conventional steelmaking process, the SCAP process can directly help reduce coke usage by 4.6 - 9.9 wt% depending on the tar conversion extent. Upon full utilisation of the excess heat generated in the SCAP process, a further indirect coke saving of 2.7 – 2.9 wt% can be achieved. The total maximum amount of coke saving per tonne of steel production was thus estimated to be 12.8 wt%, namely 31.7 kg coke per tonne of steel.

Table 5: Direct and indirect coke saving potentials per tonne of steel produced in SCAP process compared to the conventional steelmaking process (tar reforming temperature: 600°C).

Tar conversion rate (%)	Conventional coke usage (kg)	Carbon deposition (kg)	Direct coke saving per tonne of steel* (wt%)	Indirect^ coke saving per tonne of steel (wt%)	Total maximum coke saving per tonne of steel (wt%)

100	248	21.6	9.9	2.9	12.8
75	248	18.7	8.6	2.8	11.4
50	248	15.8	7.3	2.8	10.0
25	248	12.9	5.9	2.7	8.6
0	248	10.0	4.6	2.7	7.2

*. Assuming the energy contents of coke and carbon are 29 MJ/kg and 33 MJ/kg, respectively.

^. Indirect coke saving is related to the equivalent amount of coke that may be saved if the total thermal energy excess generated in the SCAP process is fully recycled back to the process. The thermal energy excess includes heat production in the tar reformer and heat embedded in the hot slag product and the reformed COG, which are generally not available for recovery in the conventional steelmaking process.

3.1.4 Energy saving and emission reduction

To better understand the advantages of the SCAP process, here we calculated the theoretical maximum energy saving and emission reduction of the SCAP process compared to those of the conventional steelmaking process (i.e. ~21 GJ and 1.8 tonne CO_2 emissions per tonne of steel) (see Figure 9). Figure 9 shows that at a tar reforming temperature of 600°C, the maximum energy saving of the SCAP process was between 480 MJ and 850 MJ per tonne of steel depending on tar conversion extent. This equates to approximately 2.3 – 4 % of the total energy intensity of conventional steelmaking process. The associated maximum carbon emissions reduction was calculated to be about 3.2 % to 5.7 %.

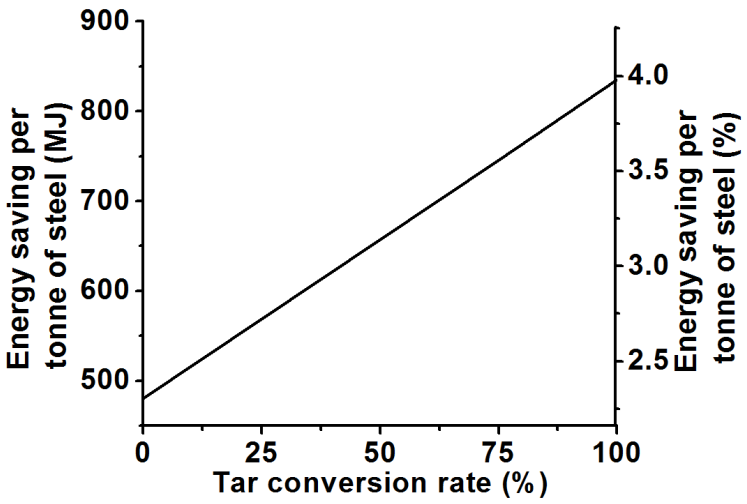

Figure 9: Energy saving potential of SCAP process per tonne of steel production for a tar reforming temperature of 600°C.

3.2 TGA-FTIR evaluation of coal and slag mixtures

The differential thermo-gravimetric (DTG) curves for each of the different coal to slag ratios are presented in Figure 10. It can be seen that pyrolysis of coal alone resulted in a single peak in the DTG curve at approximately 450°C attributed to primary devolatilisation of coal due to thermal decomposition of its structure. For the coal and slag mixtures, this same peak was also apparent at approximately 450-455°C but with decreasing intensity as the amount of slag increased. This may be caused by an increasing amount of chemical adsorption of CO_2 via carbonation reactions on the surface of the slag components as the amount of slag increases, which leads to less volatile weight losses as coal decomposes. The amounts of CO_2 adsorbed by free CaO and FeO components of the slag start to release this CO_2 at approximately 500°C and 650°C and peak at approximately 570°C and 800°C, respectively. The peak at ~340-350°C may be attributed by the liberation of inter-molecular water formed during hydration of CaO in the presence of wet coal at lower temperatures [32].

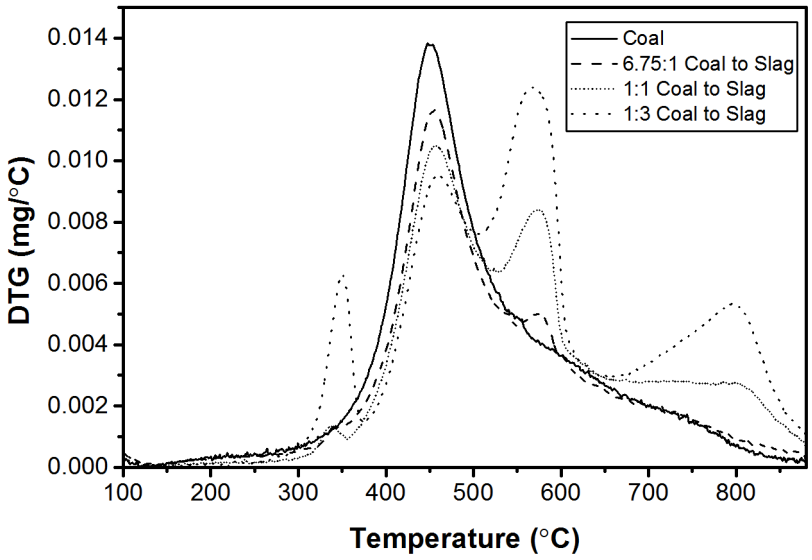

Figure 10: DTG curves for coal and three different coal to slag ratios.

For each of the significant peaks in the DTG curves presented in Figure 10 at temperatures of 450, 570 and 800°C, the corresponding FTIR spectra for each of the different coal/slag treatments are presented in Figure 11, Figure 12 and Figure 13 respectively. At 450°C (Figure 11), the primary volatile constituents observed were CO_2 (~2400 cm^{-1}), CO (~2100 cm^{-1}), H_2O (~3700 cm^{-1}) as well as aliphatic and aromatic C-H (~2900-3200 cm^{-1}). At 570°C (Figure 12), the primary volatile constituents observed were CO_2 (~2400 cm^{-1}), CO (~2100 cm^{-1}), and to a lesser extent aliphatic and aromatic C-H (~2900-3200 cm^{-1}). At 800°C (Figure 13), the primary volatile constituents observed were CO_2 (~2400 cm^{-1}), and CO (~2100 cm^{-1}), with the aliphatic and aromatic C-H (~2900-3200 cm^{-1}) compounds no longer observed in the gaseous phase. These findings are expected as more tar components will decompose as temperature increases. For a more complete view of FTIR spectra variation as a function of temperature, the overall volatile evolution profile via FTIR is presented in Figure 14 for the coal to slag ratio of 1 to 1.

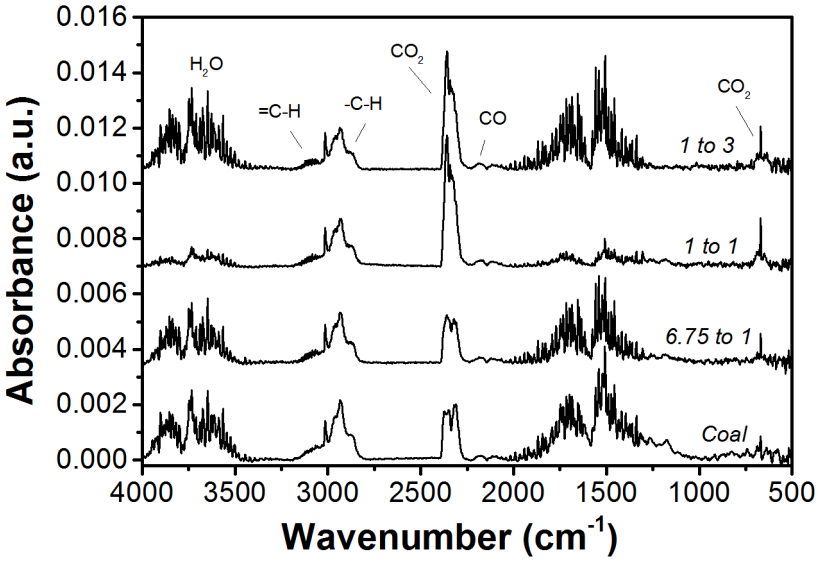

Figure 11: Online-FTIR gas analysis of three different coal to slag ratios at 450°C; Coal pyrolysis alone, 6.75:1 coal to slag, 1:1 coal to slag and 1:3 coal to slag.

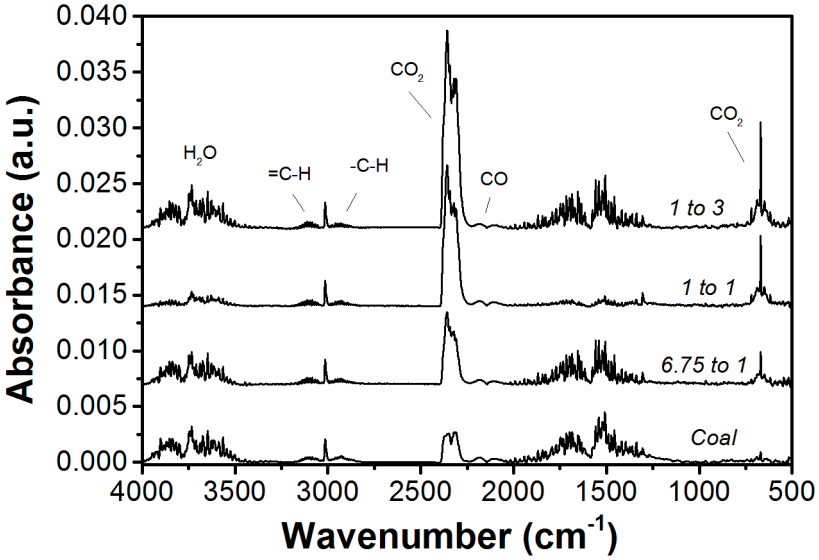

Figure 12: Online-FTIR gas analysis of three different coal to slag ratios at 570°C. Coal pyrolysis alone, 6.75:1 coal to slag, 1:1 coal to slag and 1:3 coal to slag.

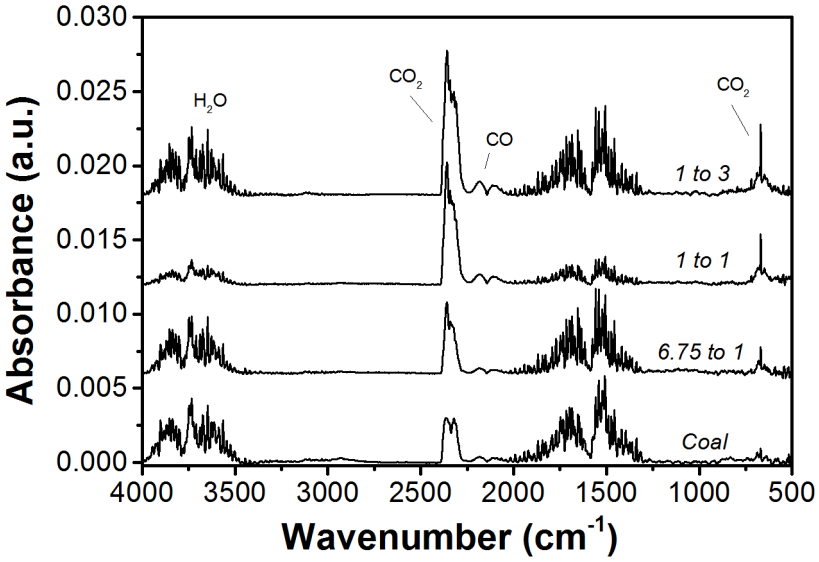

Figure 13: Online-FTIR gas analysis of three different coal to slag ratios at 800°C. Coal pyrolysis alone, 6.75:1 coal to slag, 1:1 coal to slag and 1:3 coal to slag.

Over the entire temperature range it can be see that the primary volatile constituents observed were CO_2 (~2400 cm^{-1}), CO (~2100 cm^{-1}), and aliphatic/aromatic C-H (~2900-3200 cm^{-1}) compounds. This figure

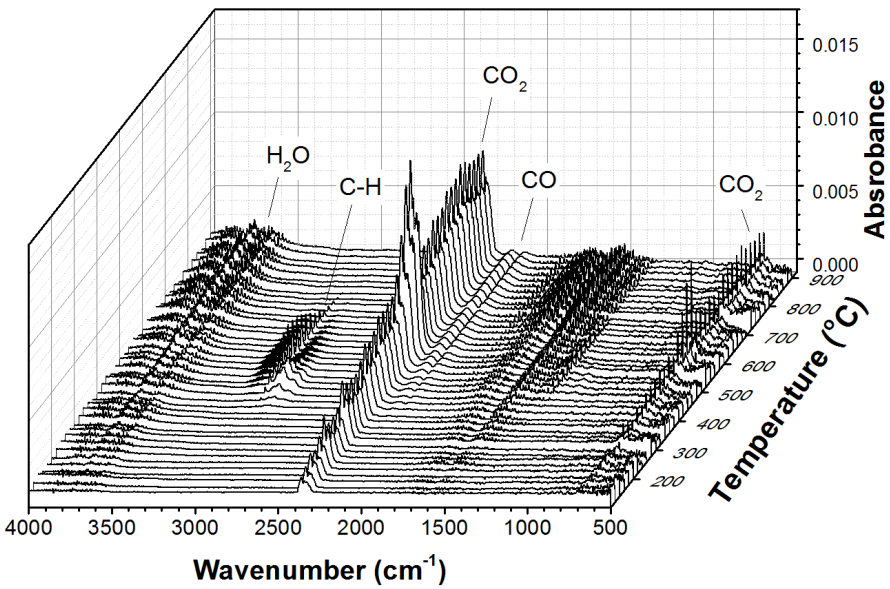

Figure 14: FTIR volatile evolution profile for a coal to slag ratio of 1:1.

On the other hand, Figures 11-13 also show that as more slag is introducing into the system the peaks of major tar components (aliphatic and aromatic C-H) slightly decrease while that of CO_2 greatly increases. This indicates that a greater amount of tar was decomposed into lighter components (e.g. CO_2) as more slag was presented. To investigate this effect in a more quantitative manner, we used similar methods to those presented in literature [33-35] and calculated the integrated absorbance under the curve for different components in the gaseous phase (i.e. quantifying the changes in species concentration). The definitions of the wavelength intervals for each of the species are detailed in Table 6.

Table 6: Wavenumber interval definitions for integrated area plots.

Species	**Wavenumber range (cm^{-1})**
CO	2140 - 2240
CO_2	2241 - 2400
-C-H (aliphatics)	2800 - 3024
=C-H (aromatics)	3025 - 3200

Using the wavenumber assignments (Table 6), the area under the curve for each of the intervals was calculated for each species as presented in Figure 15. In Figure 15, the curves for =C-H and CO have been multiplied by a factor of five, while the –C-H curve has been multiplied by a factor of two in order to discern the trends in the curve with increasing temperature.

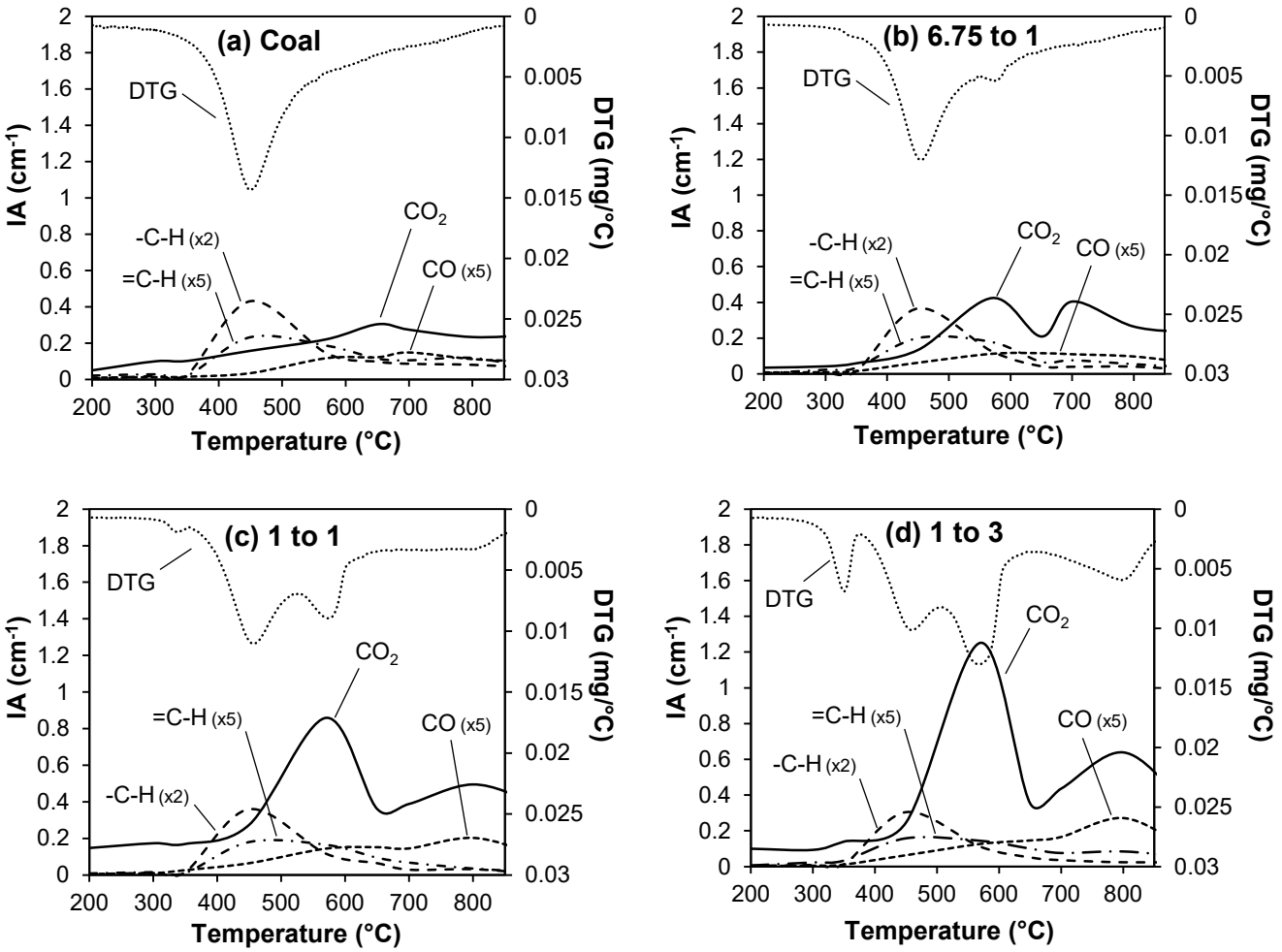

Figure 15: Qualitative gaseous product evolution via integrated absorbance and derivative weight for four different coal to slag ratios; (a) coal pyrolysis, (b) coal to slag ratio of 6.75:1, (c) coal to slag ratio of 1:1 and (d) coal to slag ratio of 1:3.

For coal pyrolysis alone (Figure 15a), the release of aromatic (=C-H) and aliphatic (-C-H) hydrocarbons and CO_2 were primarily observed at the single peak in the DTG curve at 450°C. As the temperature increased the release of –C-H and =C-H groups decreased, while CO_2 and CO release increased, reaching maximums at 650°C and 700°C respectively.

In Figure 15a, b &c it can be seen that the addition of slag to the pyrolysis process had a direct effect on the gas evolution profile. The evolution of aromatic (=C-H) and aliphatic (-C-H) hydrocarbons occurred at approximately the same temperature, 450°C, for all coal to slag ratios, however the peak

394 intensity slightly decreased with increased slag content, signifying the catalytic effects of the slag. The
395 total amount of CO_2 and CO released dramatically increased with the introduction of slag. The peak in
396 CO evolution at approximately 800°C for coal to slag ratios of 1:1 (Figure 15c) and 1:3 (Figure 15d)
397 were attributed to the higher concentrations of CO_2 reacting with carbon contained in char or deposited
398 on the surface of slag via the following reaction:

399 $$C + CO_2 \leftrightarrow 2CO$$

400 The increase in CO_2 observed is indicative of slag reacting with hydrocarbon and oxygenated
401 compounds released during primary devolatilisation to form CO_2. At temperatures below 500°C, this is
402 then trapped by the CO_2 scavengers in the slag i.e. calcium and iron. As the temperature increased, the
403 CO_2 initially captured was released due to changes in the CO_2 equilibrium partial pressure. The release
404 of CO_2 occurred primarily at 570°C and above 700°C, which is characteristic of the calcination of the
405 calcium and iron rich components of the slag respectively. The absence of similar quantities of CO_2 and
406 CO for the pyrolysis of coal alone (Figure 15a) compared to other figures clearly indicates that the
407 presence of slag has the ability to catalyse tar cracking reactions to form the lower molecular weight
408 species identified such as CO_2 and CO. The greatest extent of catalysis was observed for the highest
409 slag to coal ratio of 3:1 where the greatest amount of CO_2 and CO were released.

410

4 CONCLUSION

A novel slag carbon arrestor process using steelmaking slag was proposed for energy recovery in the steelmaking industry. In the SCAP process energy recovery can be achieved by utilising the energy embedded in the hot raw COG while the tar reforming process is able to produce a carbon-rich slag and a higher quality COG product. The results indicate that with SCAP process the COG energy content can be increased from ~34.6 MJ/kg to ~37.7 MJ/kg (or by 9%). Also, recycling the carbon-rich slag in the sinter machine and blast furnace can help reduce coke usage in the conventional steelmaking process by up to ~12.8 wt%. This translates into a theoretical maximum energy saving of 4 % and a carbon emission reduction of 5.7 % of the conventional steelmaking process. Moreover, our preliminary experimental investigations have provided first-hand evidence of the catalytic ability of slag for use in the SCAP process.

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