



Utilization of rubber tree bark as a carbon source for electric arc furnace steelmaking: Carbon/slag interaction at 1550°C

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Abstract

Rubber tree bark (RTB) is a biomass that consists of wood and rubber parts, with high volatile and ash contents. This research reports the utilization of RTB as a carbon source in Electric Arc Furnace steelmaking processes. RTB was mixed with coal at a ratio of 1:1 by weight, and heated at 1000°C under an argon atmosphere for 1 h. The chars were brought to contact with Electric Arc Furnace slag (37.86 wt% Fe₂O₃) at 1550°C for 15 min to investigate their interaction and compared to coal. Coal showed short slag foaming behavior with a foaming time of 4 min, while complete FeO reduction was seen thereafter with the DOM of 65.14%. For RTB, slag foaming sustains over 15 min, but small extent of FeO reduction was observed with the DOM of 42.57%. For the Mixture, foaming time was 8 min, while iron droplets were seen since 8 min with the DOM of 54.63%. It was likely that interaction between the mixture and slag was due to the synergistic effect between coal and RTB. This research unlocks the potential of using RTB biomass for steelmaking process and the consumption of coal could be deducted by up to 50 wt%.

1. Introduction

The consumption of fossil fuels as a carbon source in steel industry is quite high, leading to greenhouse gas emission and various environmental problems. Due to the concerns about global warming and carbon releases, the reduction of fossil fuels consumption is necessary for sustainable steelmaking. During the scrap melting process, slag is floating on the top of liquid steel. Slag foaming practice is important for electric arc furnace (EAF) steelmaking. This practice starts by injecting oxygen into liquid steel to form FeO in the molten slag and followed by injecting solid carbon into the slag phase to reduce FeO dissolved in the slag. Thus, two important reactions that occur during carbon/slag interaction are the foaming of slag and the reduction of FeO in the molten slag. The reduction of FeO generates gas (CO/CO₂) in the slag layer, causing the expansion of molten slag [1]. The generation of CO/CO₂ from the oxidation of solute carbon by oxygen in molten steel can also promote slag foaming. Slag foam play vital roles in steelmaking processes, i.e. cover the arcs in EAF; improve steel quality by absorbing deoxidation products (SiO₂ and Al₂O₃) protect the steel from deoxidation; protect the steel from N₂ and H₂ absorption and insulate liquid steel to minimize heat loss [2].

Interactions between molten slag and various conventional fossil fuels, such as graphite, coal and coke had been reported previously [3-7]. Carbon/slag interactions had been studied in term of slag foaming and reduction of FeO in molten slag. For slag foaming, foaming index (Σ) was used to explain the foaming behavior, which correlates the foam height (H) with the superficial gas velocity (U),

as shown by $\Sigma = H/U$. It is related to physical properties of the slag such as viscosity (μ), density (ρ) and surface tension (σ) [3-4]. The physical properties depend on chemical composition of the molten slag, such as FeO, MnO, CaO and SiO₂. With an aim toward sustainable, several research works had shown that fossil fuels could be replaced by wastes polymer and rubber types [8-12]. The uses of high-density polyethylene (HDPE) and rubber tyres by blending with coke can improve carbon/slag interactions at 1550°C, in terms of higher levels of CO and CO₂ generation and associated slag foaming [8-10]. As compare to coke, the reduction of FeO in slag was also improve when using wastes polymer and rubber tyres as a reductant. This was attributed to the auxiliary FeO reduction by CH₄ and H₂ from volatiles, due to decomposition of polymers in addition to reduction by solid carbon [8-12]. Like polymeric materials, the use of biomass in ironmaking and steelmaking processes has been widely investigated as a solid fuel, FeO reductant in slag and iron ore reductant [13-16]. Typical biomass investigated include wood, saw dust, rice husk and palm shells. In Thailand, natural rubber is the major product obtained from latex. The latex is harvesting from rubber tree by making incision on the bark and then the milky latex flowing into the bowl hanging below the incision. Small piece of rubber tree bark (RTB) consisting of wood and rubber parts is generated after incising as a co-product. Due to the large planting areas of rubber tree, huge quantities of RTB are generating and considered as a biomass. The combination of cellulose and polymeric material made RTB different from the other well-known biomass. It has high volatiles and ash contents, which could have the possibility to be utilized in EAF steelmaking processes.

Rubber tree bark (RTB) is a carbon-based material, which is a local-based biomass in Thailand. The utilization of RTB is quite new and still in low level. With an aim to reduce the consumption of fossil fuels in steelmaking industries, the present study aims to evaluate the possibility for utilizing RTB as a carbon source for carbon/slag interactions in Electric Arc Furnace steelmaking process. RTB and its blend with coal will be heated to produce a char sample. Interactions between slag and the chars will be investigated in terms of slag foaming and FeO reduction behavior at 1550°C. Replacement of coal by using the local-based biomass was expected to reduce the consumption of fossil fuels in iron and steel industries.

2. Materials and methods

2.1 Sample preparation

Coal supported by Green Terminal Ltd., the solid fuels and biomass supplier in Thailand, is a conventional carbon source used in the present study for a sake of comparison. It was ground into a size of less than 1 mm. RTB in the form of scraps was crushed into small pieces (<5 mm). RTB was blended with the coal into the ratio of 1:1 using a rolling mill for 30 min, and named Mixture. Moisture removal was done by drying the prepared samples at 90°C in an oven for 48 h. RTB and Mixture were heated in a horizontal tube furnace at 1000°C under an argon atmosphere for 1 h. The obtained residual chars were ground in a ring mill and sieved into a powder of <106 µm. Composition of the char samples and the coal is given in Table 1.

Electric Arc Furnace slag used in this study was provided by UMC metal Ltd., EAF steel mill in Thailand. Its chemical composition given in Table 2. The slag contains 37.86 wt% of Fe₂O₃ (33.7 wt% of FeO) as a major component. The slag was ground and sieved into a size of <106 µm for the experiment. The saturation of slag with basic oxides is essential for good slag foaming, and this indicated by B_3 value [17]. B_3 value of the slag used in the present study is 1.1, which is suitable for good slag foaming.

2.2 Carbon/Slag interaction experiments

2.2.1 Slag foaming

Figure 1 shows the overall sample and experimental preparation. Two grams of the char powder was put in a refractory crucible and

then pressed to smooth the top surface. Same amount of slag was then put on the top surface of the char in the crucible. This provides an excess carbon in the system for carbon/slag interactions. The interactions were investigated through experiments in a tube furnace [21]. The prepared crucible was inserted into the cold zone of the furnace where the temperature was approximately 300°C for 5 min to prevent thermal shock. It was then inserted into the hot zone where the temperature was 1550°C, while high purity argon (99.99%) flowing through at the rate of 1 L·min⁻¹. The reaction time was noted to start when the slag had melted (~1 min), as referred to previous studies [8-10]. The crucible was quenched at 1, 2, 4, 8, 10 and 15 min. By this method, carbon/slag interactions as a function of time for all samples can be investigated and compared. Slag after quenched was mounted in a resin and cross-sectioned to observe the interaction inside the bulk slag using optical microscope.

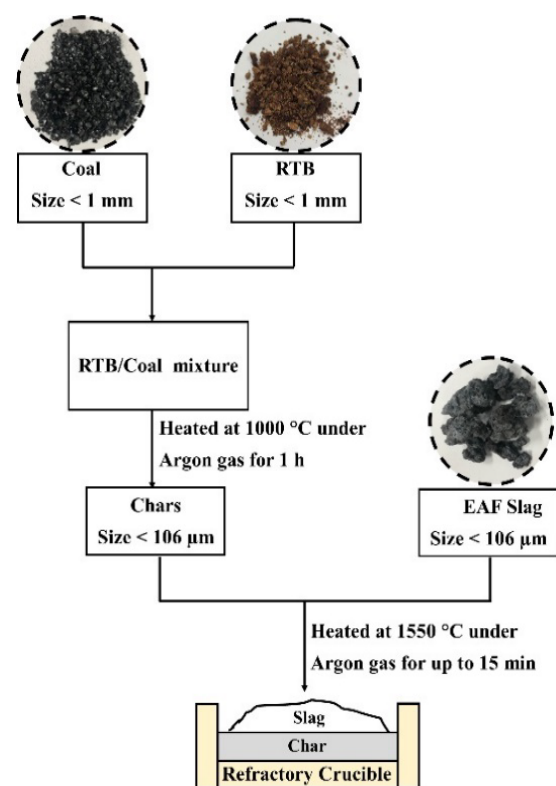


Figure 1. Overall samples and experimental preparation.

Table 1. Composition of the carbonaceous samples.

Samples	Composition (wt%)			
	Fixed C	Volatile	Ash	S
Coal	84.74	9.96	5.30	0.56
Mixture	80.03	9.52	10.45	0.45
RTB	56.76	24.48	18.76	0.02

Table 2. Composition of EAF slag (wt%).

FeO	Al ₂ O ₃	SiO ₂	CaO	MgO	MnO	$B_3 = \frac{\%CaO}{(\%SiO_2 + \%Al_2O_3)}$
33.7	8.41	16.43	27.49	4.98	4.83	1.1

2.2.2 FeO reduction

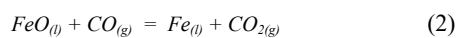
The char powder was mixed with slag according to the C/O molar ratio of 2 to provide an excess carbon in the system. The molar of C is the total moles of carbon in the carbonaceous sample. The molar of O is the total moles of oxygen from Fe₂O₃ in the slag. Amount of slag-coal in the mixture was 83.1 wt% to 16.9 wt%, while it was 82.2 wt% to 17.8 wt% and 76.7 wt% to 23.3 wt% for slag-Mixture and slag-RTB, respectively. By adding some water, approximately 5 g of spherical composite pellet can be produced. The pellet was then air dried in the oven at 90°C for 48 h. The composite pellet was put in a refractory crucible and followed the procedure in slag foaming sections.

3. Results and discussion

3.1 Slag foaming

Slag after contacted with coal, RTB and Mixture at 1550°C as a function of times are shown in Figure 3. For coal, the molten slag was observed to foam for 4 min of reaction and totally die down thereafter. The huge Fe droplets were clearly observed after 4 min at the bottom of the crucible; with a glassy slag phase adhere in the crucible. For RTB, in contrast, the molten slag was seen to foam since first min of reaction and sustains over 15 min. Reduced iron droplets cannot be observed clearly, which expected to be trapped in the bulk slag. For Mixture, a better slag foaming behavior was observed as compared to that of the coal. The fluctuation in size of slag foam was observed for 8 min, and then the foam dies down until 15 min of reaction. Similar to coal, the huge Fe droplets were clearly observed after 8 min along with a glassy slag phase. Based on visual observations, RTB alone shows the longest slag foam life followed by Mixture and coal.

The possible reactions occurring when the carbonaceous material contacted with molten slag at 1550°C for our experimental approach are described in Figure 4. During carbon/slag interactions, FeO in molten slag will be firstly reduced by solid carbon at the carbon/slag interface (Step I). This reaction produces Fe in the form of spherical droplet and CO gas into the molten slag, Equation (1). The produced CO gas entrapped in molten slag can react with FeO to form Fe and CO₂ into the system (Step II), Equation (2). The CO₂ can react with solid carbon and produce CO back to the system as in Equation (3), which could further reduce FeO in the molten slag (Step III). Standard Gibbs free energy (ΔG°) at 1550°C for Equations (1-3) are -124.46, -276.71 and -145.63 kJ, respectively [10]. The produced CO/CO₂ gas bubbles could entrap or escape from the molten slag and this cause the molten slag to foam. Ability of molten slag to hold CO/CO₂ gas bubbles depends on its physical properties, such as viscosity, surface tension and density [18,19].



Amount of CO/CO₂ produced in the system is significant as it indicates the extent of FeO reduction reactions during the carbon/slag

interaction in the system [8-12]. In the present study, the measurement of CO/CO₂ gas produced in the experimental system cannot be conducted due to the limitation of our laboratory. However, the quenched slag after reaction with coal, Mixture and RTB were selected to investigate the entrapment of gas bubbles and reduced Fe droplets in the bulk slag. The optical micrographs of the cross-sectioned bulk slag are shown in Figure 4. The black circle areas represent gas bubbles entrapped in the bulk slag, while the shiny white and gray regions represent reduced iron and slag phases, respectively. For coal, the presence of gas bubbles in the bulk slag indicates the FeO reduction reaction and gas generation, leading to a foaming of slag within 4 min. Thereafter, the generation of gas could slow down due to the completion of FeO reduction in molten slag and thus, no slag foaming was observed. For Mixture, similar volume of gas bubbles entrapped in the bulk slag were seen, and could occur until 8 min before the completion of FeO reduction. In the case of RTB, the volume of entrapped gas bubbles in the bulk slag within the first 4 min was similar to the other cases. However, it could occur until 15 min of reaction due to the expected slow rate of FeO reduction and the sustain slag foaming behavior.

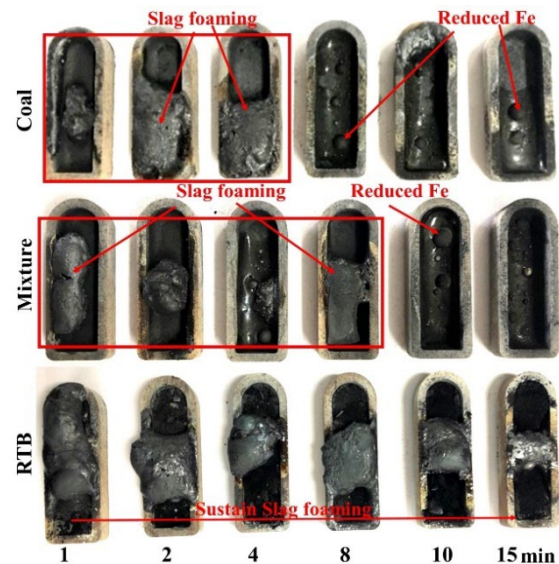


Figure 2. Slag foaming behavior after contact with coal, RTB and Mixture at 1550°C.

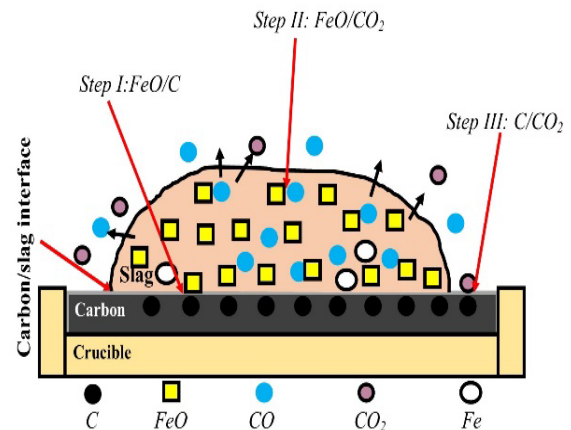


Figure 3. Schematic describes the possible reactions for the carbon/slag experiment.

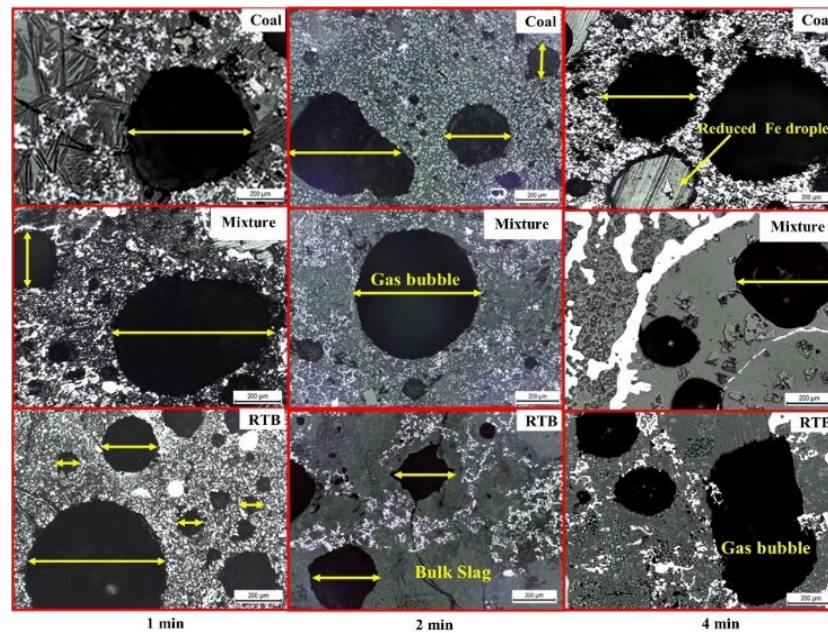


Figure 4. Optical micrographs showing the cross-sectioned of bulk slag after interacted with coal, Mixture and RTB at 1550°C for up to 4 min.

Several previous studies had investigated slag foaming behavior during the interactions between EAF slag and various types of carbonaceous materials at 1550°C [10]. Sessile drop technique was employed to investigate carbon/slag interactions at 1550°C, using coke (~80 wt% fixed carbon) and the PET/Coke blend (~71 wt% fixed carbon) as the carbonaceous samples [10]. It was found that coke showed a higher rate of gas generation than that of PET/Coke blend. But, PET/Coke blend showed a good and sustain slag foaming for all reaction times, while coke showed a good slag foaming only first min of reaction and the foamy slag died down thereafter. It was concluded that the slower rate of CO and CO₂ generation allowed for greater gas entrapment in the slag sample, and resulting in better slag foaming [10]. *Rahman* studied interaction between FeO rich slag with coke and graphite at 1550°C using a sessile drop technique [20]. Coke showed fast FeO reduction with high rates of gas generation but poor slag foaming behavior. On the other hand, graphite showed slow rate of FeO reduction but good slag foaming. This was due to the slower rate of gas generation in the case of graphite, made it easier for gases entrapment in slag phase [20]. The ability of molten slag to enfold the gases bubbles could responsible for the different results between previous studies. In the present study, the rate of CO and CO₂ generation for RTB was expected to be lower than that in the case of coal due to its smaller extent of FeO reduction. This might responsible for the last longer gas entrapment in the molten slag, and thus sustains slag foaming. These agree with the previous studied [10,20]. Carbon/slag interactions for Mixture are likely to be a favorable synergistic effect between coal and RTB.

3.2 FeO reduction

The slag-carbon composite pellet was produced according to the C/O molar ratio of 2. Figure 5 show the composite pellets after reaction at 1550°C. TGA analysis was not employed in the present study due to the limitation in our laboratory. In the present study, the reduction

extent of Fe₂O₃ in the slag is represented by degree of metallization (DOM), Equation (4). Fe(Met) is mass of metallic iron after reduction, while Fe(T) is mass of total iron in the slag before interaction at 1550°C.

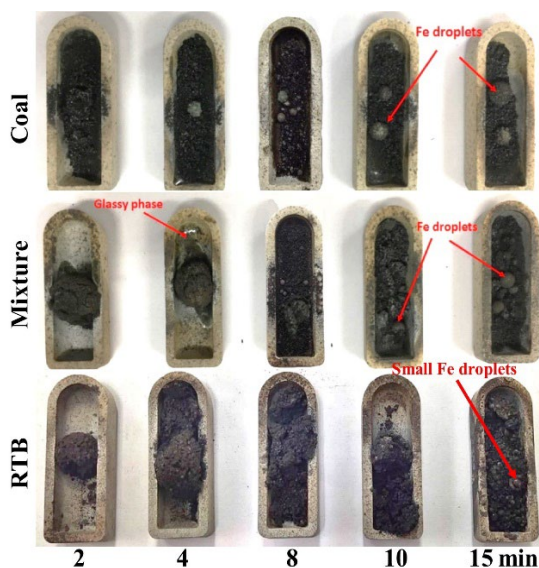
$$\%DOM = \frac{Fe(Met)}{Fe(T)} \times 100 \quad (4)$$

By removal of metal droplets from the slag phase, Fe(Met) after 15 min of reaction for coal, Mixture and RTB can be obtained. According to C/O ratio in the slag-carbon composite pellet, percentages Fe₂O₃ and total iron in 5 g of each pellet were calculated. Unreacted slag and the residue in the crucible were excluded. By these, the DOM for all composite pellets can be determined and showed in Table 3. For coal, the pellet decomposes at 2 min and the reduced Fe droplets can be observed after 4 min with the DOM of 65.14%. For RTB alone, the pellet was seen to decompose slowly with small Fe droplets observed at 15 min with the DOM of 42.57%. For Mixture, the pellet decomposes at 8 min and the reduced Fe droplets was seen thereafter with the DOM of 54.63%. The highest extent of iron oxides reduction in molten slag was in the case the coal, followed by Mixture and RTB, respectively. This indicates the existence of favorable synergistic effect between coal and RTB. These results are in agreement with the slag foaming results in section 3.1.

The ability of molten slag to trap the gases bubbles influence foamability of molten slag. Foamability of the molten slag is controlled by the slag phase physical properties, including surface tension, density and viscosity. These properties vary with slag chemical composition. RTB used in the present study contain high amount of ash oxides (18.76 wt%), while it was 10.45 wt% and 5.3 wt% for the mixture and coal, respectively. The replacement of coal by RTB could modify and vary chemical composition of molten slag, and thus in turn effect the foamability and other carbon/slag interactions. To prove that chemical composition of the molten while reacting with the carbonaceous materials need to be analyse as a function of time.

Table 3. Composition in 5 g of slag-carbon composite pellets before interaction at 1550°C for 15 min and the metallic iron obtained.

CCP Name	Before			Obtained	%DOM
	Slag (g)	Fe ₂ O ₃ (g)	Fe(T) (g)	Fe(Met) (g)	
Coal	4.12	1.56	1.09	0.71	65.14
Mixture	4.11	1.55	1.08	0.59	54.63
RTB	3.84	1.45	1.01	0.43	42.57

**Figure 5.** Slag-carbon composite pellets after reaction at 1550°C for coal, Mixture and RTB.

4. Conclusions

The possibility of utilizing rubber tree bark (RTB) as a carbon source in Electric Arc Furnace steelmaking had been investigated in term of carbon/slag interaction at 1550°C. The experimental results can be concluded as below.

Based on visual observations, coal shows a rapid FeO reduction with slag foaming life time of 4 min and totally die down. The huge Fe droplets and a glassy slag phase were observed at the bottom of the crucible, which the degree of metallization of 65.14%.

In contrast, RTB shows a sustain slag foaming over 15 min. But, reduced iron droplets cannot be observed clearly, which expected to be trapped in the bulk slag. The degree of metallization in the case of RTB was of 42.57%.

For Mixture, slag foaming behavior and iron oxide reduction level was in between the cases of coal and RTB. The fluctuation in size of the slag foam was observed with the slag foaming life time of 8 min, and the degree of metallization of 54.63%.

Carbon/slag interaction in the case of Mixture was likely to be the favorable synergistic effect between coal and RTB.

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