Article

Utilization of Rubber Tree Bark for Reduction of Mill Scale at 1550 °C: Implication for Sustainable Wastes Recycling in Steelmaking Process

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Abstract: Utilization of local-based waste materials can be a challenge due to the resource's limitations. This study investigated the utilization of rubber tree bark (RTB) as a reductant for mill scale. RTB was blended with coal into five ratios, namely RTB#1–RTB#5. The blends were heated at 1000 °C under argon for 1 h. The char was mixed with scale to produce a carbon-mill scale composite pellet (CCP) with a 1.5 C/O molar ratio. The reduction of CCP was carried out in a tube furnace at 1550 °C for 30 min under argon flowing at 1 L/min. The reduced Fe droplets separate clearly from the residues. The CCP produced from blends RTB#1–RTB#5 shows better reduction with metal of 35.28–39.82 wt.%. The degree of metallization (DOM) ranges between 75.25–84.51%, which is two times higher than that of coal. RTB#3 shows the optimum condition with the highest DOM. CaO in RTB plays a role in forming an ash layer on the metal surface and reacting with Fe₂O₃ to form a new phase. Utilization of our local-based biomass, such as RTB as a reductant for mill scale, is possible. The consumption of fossil fuel in the process could be decreased by 30%, thus also the production cost.

Keywords: mill scale; rubber tree bark; reduction reaction; steelmaking

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1. Introduction

Metal sources, carbonaceous materials, and limestone are the major charged materials for the melting process in EAF steelmaking. The metal sources can be iron scrap, direct reduced iron (DRI), hot briquetted iron (HBI), and pig iron. The carbonaceous materials used in the process can be coal, coke, and anthracite. Limestone in the form of CaCO₃ or CaO can be used as a fluxing agent in the melting process. The quality of the charged materials is important for controlling the quality of steel production; a high amount of carbon consumption and the high extent of carbon footprint emission are also typical problems for the steel industry in Thailand and worldwide. In view of the circular economy, the replacement of conventional charges materials by alternative materials is essential for increasing the sustainability of steel industries. One of the possible solutions is to utilize the end-of-life or waste materials that are available in the local steel industry area, which is a challenging process due to the limitations of the resources.

Coal and coke are conventional carbon sources used in ironmaking and steelmaking industries as a fuel, FeO reductant, slag foaming and liquid steel carburizing agents. The consumption of these fossil fuels worldwide in these industries is quite high, leading to greenhouse gas emissions and various environmental problems. Thus, several research studies have been conducted toward the reduction of fossil fuels consumption [1–6]. The uses of high-density polyethylene (HDPE) plastic and rubber tires by blending with metallurgical coke as FeO reductant and slag foaming agent at 1550 °C have been investigated [1,2]. It was reported that the carbon/slag interactions could be better in terms of higher levels of CO and CO₂ generation and associated slag foaming as compared to that in

the case of coke [1,2]. The reduction of FeO in slag was also improved when using polymer and rubber tires waste as a reductant—this is due to the auxiliary FeO reduction by CH₄ and H₂ from the decomposition of polymers, in addition to reduction by solid carbon [3,4].

Biomass is one of the popular alternative sources of carbon. The utilization of biomass as a solid fuel, e.g., FeO reductant in slag and iron ore reductant in ironmaking and steelmaking processes, has been widely investigated [7–9]. The typical biomass investigated depends on the available local based resources of each area such as wood, saw dust, rice husk, and palm shells. Ueki et al. [7] utilized woody biomass as a fuel by mixing with coal to produce coke. The effect of the woody biomass addition on the coke properties was studied and found that the strength of the produced coke decreased extremely by adding woody biomass to caking coal. However, the coke properties could be improved by partially removing volatile matter from woody biomass at temperatures of more than 500 °C before mixing with caking coal [7]. Yunos et al. [8] used palm shell biomass as a slag foaming agent by blending with metallurgical coke. The foaming behavior of electric arc furnace slag during the interaction with palm shell/coke blends at 1550 °C was studied. It was found that the high amount of gases evolved from the biomass blends at temperatures higher than 1000 °C might participate in the slag foaming and the FeO reduction in the molten slag. This was indicated by the entrapment of gas bubbles in the bulk slag along with the reduced Fe droplets. It was concluded that partial replacement of coke by palm shell biomass leads to improved/sustained interactions with EAF slag [8]. Baganiti et al. [9] investigated the reduction of iron ore using the volatiles evolved from biomass pyrolysis between 200–1000 °C. It was reported that volatiles from biomass could be utilized as a reducing agent for iron ore. At low temperatures, the reduction occurred mostly by the non-condensable gases (CO and H₂) from biomass pyrolysis and tar cracking reactions. For the temperatures higher than 800 °C, carbon deposited in the system promoted the reduction of iron ore [9].

In Thailand, a large number of agricultural products are traded globally. Agricultural wastes are a significant problem as a result of the high production rates and require a suitable management method. Natural rubber is the major product obtained from latex. The latex is harvested from rubber trees by making an incision on the bark, allowing the milky latex to flow into a bowl hanging below the incision. A 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 rubber tree planting areas, huge quantities of RTB are generated and can be considered as a local biomass. The production of RTB in Thailand is 2890 tons a day, which could be adequate for the demand for carbon in the metallurgical process of steel production. The utilization of RTB as a carbon resource is quite new and has not been utilized in the metallurgical process. The combination of cellulose and rubber make RTB unique from the other well-known biomass types. It has high volatiles and ash oxide (CaO) content that could have the possibility to be utilized as a carbon and limestone resource.

Mill scale is a by-product of rolling mills, generated from the hot rolling of semi-finished and finished steel productions. Due to the high amount of iron oxide content, the utilization of mill scale has a wide interest [10–25]. However, mill scale has been considered as an industrial waste, and thus the movement or transfer of mill scale waste between nations needs to comply with the Basel Convention [26]. Recycling techniques for mill scale depend on several factors such as the technologies available, economics, and the policies of each nation. Mill scale can be recycled via the smelting process to obtain iron-bearing compounds using graphite and coke [10]. It is used to produce pellets for iron and steelmaking processes [11–13]. Recently, mill scale has been utilized via direct reduction techniques by using various reducing agents, such as conventional solid carbon [14–16], reducing gas [17–22] and biomass [23–25]. Products from the direct reduction of mill scale were mostly iron-bearing compounds and iron powder. Table 1. shows some of the previous research on utilizing of mill scale via direct reduction techniques. Benchibeub et al. [18] synthesized iron powder from mill scale via the direct reduction using CO as a reducing agent at 750 °C and 1050 °C for 40–180 min; under these conditions, a powder

of 98.4% total Fe was obtained [18]. Sista et al. [22] studied the recycling of mill scale to obtain iron powder via direct reduction techniques at a temperature of 600–1300 °C in an H₂ atmosphere. The degree of metallization ranged from below 10% to over 99%. It was reported that mill scale iron powder with more than 99% degrees of metallization, 97% total Fe, and more than 96% metallic Fe was synthesized after 4 h of reduction at 1200 °C and 1300 °C [22]. Direct reduction of mill scale using biomass as a reducing agent, such as wood charcoal and coconut fiber, has also been investigated [23–25]. Khaerudini et al. [25] utilized coconut fiber biomass as a reducing agent for mill scale direct reduction at 900 °C and 1000 °C under an N₂ atmosphere for 1 and 2 h. The mill scale was composed of FeO, Fe₂O₃, and Fe₃O₄. The mill scale and coconut fiber were mixed with 3 wt.% polyvinylidene fluoride (PVDF) as a binder to produce a composite pellet with a diameter of 20 mm. The formation of 80 wt.% metallic Fe was reported at the reduction temperature of 1000 °C for 2 h. It was concluded that coconut fiber biomass could be used as a carbon source for composite pellet production [25]. In Thailand, a considerable amount of mill scale can be found mostly in the eastern industrial provinces near steel plant area, which has not been widely utilized.

Table 1. Previous research work on reduction of mill scale.

Experimental Technique	Experimental Parameter	Reducing Agent	Product	Literatures
Direct Reduction	1050–1150 °C 3–12 h	Coke	Fe powder	Martin et al. [15]
Direct Reduction	900 °C 30–90 min	Low grade coal	Fe powder	Sen et al. [16]
Direct Reduction	750–1050 °C 20–60 min	Carbon monoxide	Fe powder	Benchiheub et al. [18]
Direct Reduction	600–1300 °C 1–4 h	Hydrogen	Fe powder	Sista et al. [22]
Direct reduction	1050–1150 °C 20–60 min	Wood char coal	Fe powder	Ye et al. [23]
Direct reduction	900–1000 °C 1 and 2 h	Coconut fiber	Fe powder	Khaerudini et al. [25]

With an aim to utilize the available local-based resources in the steelmaking process, rubber tree bark (RTB) was used as a reductant for the reduction of mill scale. RTB was used as carbon source by partially blending with coal. The RTB/Coal blends were mixed with mill scale to produce a carbon-mill scale composite pellet (CCP). The reduction of mill scale was studied via high-temperature interaction of the CCP at 1550 °C in an argon atmosphere. The effect of RTB content in the carbonaceous blends on the interaction with mill scale was determined and the possibility of utilizing rubber tree bark biomass as a carbon source in steelmaking process was evaluated.

2. Materials and Methods

2.1. Sample Preparation

2.1.1. Mill Scale

Mill scale was collected from UMC Metal Co., Ltd. (Bangkok, Thailand), the EAF steel mill located in Klongtoey, Thailand. It was ground in a ring mill and sieved into a powder of <180 µm. As shown in Figure 1, the major component of the mill scale is iron oxide in the forms of Fe₃O₄, Fe₂O₃, and FeO. XRF analysis of the mill scale, showing iron oxides in the form of hematite, is given in Table 2.

Figure 1. XRD pattern of mill scale used in the present study.

Table 2. Chemical composition of the mill scale used in the present study.

Oxides (wt.%)								
Fe(T)	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	CaO	SO ₃	TiO ₂	K ₂ O	P ₂ O ₅
69.70	93.66	0.82	1.42	0.17	0.08	0.04	0.02	0.04

2.1.2. Carbonaceous Samples

Rubber tree bark (RTB) was collected from the southern province of Thailand. It was crushed into small pieces (<5 mm). Coal was supported by the solid fuels and biomass supplier, Green Terminal Ltd, Ayutthaya province, Thailand. It was ground into a size of less than 1 mm. RTB was blended with coal into five different ratios (10–50 wt.% of RTB with coal) using a rolling mill for 30 min and named blends RTB#1–RTB#5. The blends were dried at 90 °C in an oven for 48 h to remove moisture and then heated in a horizontal tube furnace at 1000 °C for 1 h under an argon atmosphere, with a gas flow rate of 1 L/min. The obtained chars were ground in a ring mill and sieved into a powder of <106 µm. Raw coal and RTB char were also employed for the sake of comparison. All carbonaceous samples will be used as a reducing agent for the mill scale, and their chemical analysis is given in Tables 3 and 4.

Table 3. Composition of the carbonaceous samples as a reductant.

Reductants Name	Composition (wt.%)					
	Fixed C *	Volatile *	Ash *	S **	H	N
Coal	84.74	9.96	5.30	0.56	1.86	1.13
RTB#1	85.27	6.46	8.27	0.51	0.97	0.99
RTB#2	82.79	8.19	9.01	0.50	0.81	0.94
RTB#3	81.39	8.03	10.58	0.45	0.88	0.88
RTB#4	79.68	10.25	10.07	0.46	0.92	0.85
RTB#5	80.03	9.52	10.45	0.45	0.91	0.77
RTB	56.76	24.48	18.76	0.02	0.7	0.75

* ASTM D7852-15 and ** ASTM D4239-14.

Table 4. Composition of ash in the coal and RTB samples (wt.%).

Reductants	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	SO ₃	TiO ₂	K ₂ O	P ₂ O ₅
Coal	53.55	34.12	7.15	1.10	1.26	1.42	1.01	0.39
RTB	3.19	3.98	0.22	75.94	2.10	0.06	13.8	0.70

2.1.3. Carbon-Scale Composite Pellet (CCP)

To prepare the composite pellet, the chars that were produced from RTB/Coal blends were mixed homogeneously with mill scale according to the C/O molar ratio of 1.5 to

provide an excess carbon in the system, see Table 5. The molar of C is the total moles of carbon in the carbonaceous blends. The molar of O is the total moles of oxygen from Fe_2O_3 in the scale. A half percentage of bentonite was added into the mixtures as a binder. By adding some water, the spherical composite pellet can be produced by hand with a weight of ~5 g. The CCP was air-dried in the oven at 90 °C for 48 h and named the same as the carbonaceous reductant.

Table 5. Carbon and scale in the CCP at the C/O molar ratio of 1.5.

CCP Name	Composition		Total Weight (g)
	Carbon (g)	Scale (g)	
Coal	3.74	10	13.74
RTB#1	3.72	10	13.72
RTB#2	3.83	10	13.83
RTB#3	3.89	10	13.89
RTB#4	3.98	10	13.98
RTB#5	3.96	10	13.96
RTB	5.58	10	15.58

2.2. High-Temperature Interaction

Figure 2 shows the research overview for the present study. The prepared CCP was firstly analyzed using the thermal gravity analysis (TGA) technique, METTLER TOLEDO, Columbus, OH, USA, to determine its thermal stability and the reaction at high temperature. The high-temperature experiments were conducted in a horizontal tube furnace; the experimental approach is shown in Figure 3. The CCP was put in a refractory crucible and then 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%) flowed through at a rate of 1 L/min. The crucible was quenched at 1, 2, 5, 10, 15, and 30 min. The metallic reduced Fe droplets after 30 min of reaction were collected and weighed manually in order to determine the degree of metallization for each CCP sample. SEM and EDS analysis were used to investigate the interfacial phenomena at the surface of the reduced Fe droplets. By these, the reduction of mill scale by the different carbonaceous reductants can be compared in order to evaluate the possibility of utilizing rubber tree bark and mill scale as charged materials in the steelmaking process.

Figure 2. Research overview for the present study.

Figure 3. High-temperature experimental approach.

3. Results and Discussion

3.1. TGA Analysis of Carbon Composite Pellet (CCP)

Thermal gravity analysis (TGA, METTLER TOLEDO, Columbus, OH, USA) was used for investigating the thermal stability of the CCP samples. It was carried out from room temperature to 1550 °C with a heating rate of 20 °C/min in nitrogen atmosphere. Figure 4 shows the TGA analysis for scale used in the present study. It was observed that the scale could withstand at 1550 °C with the total weight loss of about 6 wt.%. The first step of weight loss occurred by about 2 wt.% between 200–400 °C, which possibly due to the decomposition of an iron oxyhydroxide or goethite [27]. The second step decreased by 1 wt.% at 600 °C and then withstood until about 1300 °C before a further decrease of 3 wt.% at 1550 °C.

Figure 4. TGA analysis of raw scale used in the present study.

For carbon-scale composite pellets, TGA curves of the CCP in the cases of RTB/Coal blends compared to that of coal are shown in Figure 5, and data obtained from the TGA curves are given in Table 6. For CCP from coal, the major weight loss of 43.46 wt.% was observed to start from about 1000 °C to the inflection temperature of 1223.33 °C. The further weight loss was seen until 1550 °C with a final value of 53.98 wt.%. For CCP from RTB, the major weight loss of 46.52 wt.% was observed to start earlier from 800 °C to the inflection temperature of 1120.33 °C. The weight continued to decrease to 53.08 wt.% until 1550 °C.

In the cases of CCP from blends RTB#1–RTB#5, the thermal decomposition behavior was different. The major weight loss ranged between 31.98–43.96 wt.% and was seen to start from about 1000 °C to the inflection temperature of about 1220 °C. The weight of the CCP was observed to stabilize from about 1220 °C, and no further weight loss occurred until 1550 °C for all cases (26.92–44.36 wt.%). Among the blends, RTB#3 showed the highest weight loss of 43.96 wt.% at the inflection temperature of 1220 °C and then withstood until 1550 °C with no significant weight change (44.36 wt.%).

Figure 5. TGA analysis of raw carbon composite pellet (CCP) for all samples compared to that of coal.

Table 6. TGA data of the carbon composite pellet (CCP) for all samples.

Samples	Input (mg)	Inflection Point, I.P. (°C)	% Output at I.P.	% Wt. Loss at I.P.	% Output at 1550 °C	% Wt. Loss at 1550 °C
Coal	9.736	1223.33	56.54	43.46	46.02	53.98
RTB#1	12.362	1225.00	68.02	31.98	73.08	26.92
RTB#2	11.898	1223.00	62.46	37.54	62.97	37.03
RTB#3	11.392	1220.00	56.04	43.96	55.64	44.36
RTB#4	9.282	1217.67	60.30	39.70	61.91	38.09
RTB#5	13.145	1224.33	57.35	42.65	57.25	42.75
RTB	10.651	1120.33	53.48	46.52	46.92	53.08

From the TGA results, it was found that the reduction of mill scale by all carbonaceous samples occurred at about 1100–1200 °C, but the reduction behavior was different. The CCP weights in the cases of coal and RTB keep decreasing till 1550 °C due to the incomplete reduction reaction, indicating a slow reduction behavior. However, the CCP weights in the cases of RTB#1–RTB#5 stabilized until 1550 °C, which was expected due to the completion of the reduction reaction, showing a faster reduction behavior.

3.2. High-Temperature Interaction of the Carbon-Scale Composite Pellet (CCP)

The high-temperature interaction was studied in terms of the reduction reaction of iron oxides at 1550 °C, which is higher than the inflection point observed from the TGA results. Figure 6 shows the CCP produced from different reductants after interaction at 1550 °C, as a function of time. It can be observed that the reduction of iron oxides in the mill scale occurred from the first minute for all cases, excepted RTB. The formation of metallic Fe droplets was observed in the crucible and found to separate clearly from the black residues. The remaining black residues might compose of ash oxides and/or unreacted carbon-scale.

Figure 6. Carbon-mill scale composite pellet (CCP) after interaction at 1550 °C for 30 min.

The conversion of iron oxides into metallic Fe or Fe_3C by removal of oxygen using a reductant can be measured in terms of metallization. In this study, the degree of metallization (DOM) is the extent of iron oxide reduction in the CCP. DOM is calculated as a percentage of the mass of metallic iron ($\text{Fe}(\text{Met})$) divided by the mass of total iron ($\text{Fe}(\text{T})$), Equation (1).

$$\text{DOM}(\%) = \frac{\text{Fe}(\text{Met})}{\text{Fe}(\text{T})} \times 100 \quad (1)$$

By considering the ratio of carbon and scale in Table 5, percentages of fixed carbon, Fe_2O_3 , and total iron in 5 g of each CCP sample before high-temperature interaction are calculated and shown in Table 7. After 30 min of interaction at 1550 °C, reduced metallic Fe droplets for all cases were separated and weighted manually and are shown in Table 7. Unreacted iron oxides and the residue in the crucible were excluded. By these, the degree of metallization (DOM) for all CCP samples can be determined. The trend of DOM as a function of RTB concentration in the reductants used in the CCP are presented in Figure 7.

Table 7. Composition in the CCP (5 g) for each reductant before and after the interaction at 1550 °C for 30 min.

CCP Name	Before			% Fe(Met)
	% Fixed Carbon	% Fe_2O_3	% Fe(T)	After 30 min
Coal	23.07	68.17	47.64	23.05
RTB#1	23.12	68.27	47.70	36.49
RTB#2	22.93	67.72	47.33	39.24
RTB#3	22.79	67.43	47.12	39.82
RTB#4	22.68	67.00	46.82	38.47
RTB#5	22.70	67.09	46.88	35.28
RTB	20.33	60.12	42.01	6.09

Figure 7. Degree of metallization (DOM) for all CCP samples.

For coal, a small amount of reduced Fe droplets was seen in the first min of reaction and then no significant change was observed until 30 min with 23.05 wt.% of metallic Fe. This indicates the small extent of iron oxides reduction in mill scale by the coal with the DOM of 48.38%. In the case of RTB alone, the reduction of iron oxides was likely to be incomplete within 30 min and occurred with the lowest DOM of 14.49% only. The CCP was seen to collapse after the first minute of reaction. The residue with red and black color was seen in the crucible for over 30 min of reaction along with the tiny metallic Fe droplets (6.09 wt.% Fe).

By blending RTB with coal, carbon that was prepared from the blends enhanced the interaction with mill scale as compared to its parent coal and RTB. The CCP produced from blends RTB#1–RTB#5 showed a higher extent of iron oxide reduction as a number of big Fe droplets found in the crucibles (35.28–39.82 wt.% Fe). The reduction of iron oxides in the CCP was likely to complete rapidly due to no significant change in amount of the Fe droplets seen after 2 min of reaction. The DOM after 30 min were in the range of 75.25–84.51%, which was about two and six times higher than that in the cases of coal and RTB, respectively. From visual observation, the characteristic of the metallic Fe droplets was different. In the cases of RTB#1–RTB#3, the reduced Fe was in the form of one or two huge droplets, while it was in the form of many smaller droplets for blends RTB#4–RTB#5. From Figure 6, the separation between Fe droplets and residues in the crucible was seen clearly. Among the blends, RTB#2–RTB#4 showed an almost similar reduction behavior with the DOM higher than 82%. However, with the increased RTB content in the blends up to 50 wt.% (RTB#5) was the decrease in DOM of the CCP.

It was found that the high-temperature interaction results agreed with the corresponding thermal analysis in Section 3.1. The possible reactions of mill scale with solid carbon from coal and RTB at 1550 °C are Equations (2)–(4). These reactions produce CO in the system that can participate in the reduction of mill scale, as in Equations (5)–(7). Due to the excess solid carbon in the pellet, it can react with the produced CO₂ gas to give CO back to the system, Equation (8). At 1550 °C, the standard Gibbs free energy (ΔG°) for Equations (4), (7) and (8) are −124.46 kJ, −276.71 kJ, and −145.63 kJ, respectively. These reactions occur like a cycle, which could further enhance the reduction of mill scale. The measurement of CO and CO₂ evolved from the system is needed in order to determine the extent of iron oxide reduction by our reduction. However, it cannot be done due to the limitation of our laboratory. Weight loss of the CCP from the TGA results could be due to the reduction reactions of mill scale.

3.3. Effect of RTB on the Formation of Metallic Iron Droplets

3.3.1. Carbon Structure

XRD patterns of the carbonaceous samples are presented in Figure 8. Coal used in the present study is characterized as an amorphous to semi-crystalline carbon, which the observed broad 002 carbon peaks. The char produced from RTB is characterized as an amorphous carbon in nature, in which a 002-carbon peak cannot be clearly observed. The Crystallite size (L_C) of the reductant was calculated using Scherrer's equation and is given in Table 8. The wavelength of 0.15418 nm was used for Cu K α filament. It was found that the addition of rubber tree bark into coal was found to insignificantly effect the carbon structure. The RTB/coal blends are amorphous to semi-crystalline carbon like the parent coal. L_C of coal was 1.1893 nm, while it was slightly lower for that of RTB#1-RTB#5. In the present study, the structure of the carbonaceous reductant was not expected to be a dominant factor affecting the reduction of mill scale.

Figure 8. XRD patterns of coal, RTB, and its blends.

Table 8. L_C of the reductant used in the present study.

CCP Name	L_C (nm)
Coal	1.1893
RTB#1	1.1453
RTB#2	1.1432
RTB#3	1.0310
RTB#4	0.9960
RTB#5	1.0078
RTB	-

3.3.2. Volatiles

Kongkarat et al. [5] investigated the interactions of EAF slag with polyethylene terephthalate (PET) and polyurethane (PU) blended with metallurgical coke at 1550 °C to determine the role of additional chemical elements in the polymers on the carbon/slag interactions, PET (C-H-O), and PU (C-H-O-N). It was reported that chemical composition in the polymers play a critical role in the gasification behavior of the blends, and this, in turn, modified the slag foaming behavior. O_2 released from the polymers led to the combustion of CH_4 . N_2 from PU was found to affect the foaming behavior by diluting the concentration of the other gaseous species in the system, and thereby caused a hindrance to the reactions with molten slag [5]. Rubber tree bark (RTB) is a biomass that composes of wood and natural rubber, which makes RTB differ from the other biomass. RTB char contains a high amount of volatile (24.48 wt.%), which could be CO_2 , CO , CH_4 [28]. These gaseous species may participate in high-temperature interaction with mill scale as the auxiliary reducing agents. The fresh Fe surface that is produced in the system acts as a catalyst to aid the decomposition of CH_4 , Equation (9). This further reacts with Fe_2O_3 in the scale, as Equations (10)–(12) [29]. The reaction between H_2O and CO through the water gas shift reaction is not likely to occur at 1550 °C [30]. On the other hand, H_2O can react with solid carbon through carbon gasification by water vapor, Equation (13). This reaction occurs above 1000 °C and is spontaneous at 1550 °C [31]. At 1550 °C, ΔG° for Equations (9), (12), and (13) are -110.82 kJ, -21.39 kJ, and -125.21 kJ, respectively. However, the experimental results in the present study have shown that volatile matter from RTB has an insignificant effect on improving the reduction of mill scale. RTB shows the lowest degree of metallization.

Figure 9 shows SEM micrographs ($\times 350$) of metallic Fe droplets surface obtained from the CCPs after high-temperature interaction at 1550 °C for 30 min. It was observed that the metal droplet surface was covered by ash oxides layer for all cases with the difference in morphology.

The metal surfaces for the CCPs produced from RTB#1–RTB#4 were observed to be partially covered by the ash layer, while full coverage was seen in the cases of coal, RTB, and RTB#5. The major source of ash oxides in the CCP was RTB and coal, with an ash content of 18.76 and 5.3 wt.%, respectively. Apart from iron oxides, the amount of the other oxides in the mill scale were small and can be neglected (see Table 2). The major component of ash oxides in RTB was CaO (75.94 wt.%), while it was SiO_2 (53.55 wt.%) and Al_2O_3 (34.12 wt.%) for that of the coal. By blending RTB with coal, the difference in ash composition and concentration was expected to vary and compromise between that of the parent coal and RTB. The difference in ash chemistry of each carbonaceous sample could affect the formation of metallic Fe droplets and the formation of ash layer on the

metal droplets surface, and thus the separation between metallic Fe and unreacted slag (oxides) phases.

Figure 9. SEM micrograph ($\times 350$) at the surface of the metallic Fe droplets obtained after high-temperature interaction of the CCP for 30 min for all cases.

Figures 10–12 show the SEM micrographs ($\times 5000$) and EDS spectra of the reduced Fe droplets surface obtained from the CCPs at $1550\text{ }^{\circ}\text{C}$ for 30 min in the cases of coal, RTB, and RTB#3, respectively. The chemistry of the metallic Fe droplets' surface was determined using EDS point analysis (JEOL USA Inc., Peabody, MA, USA) and is given in Table 9. With higher magnification, the Fe surface in the case of coal was found to be fully covered by ash in the form of layers and lumps (Figure 10). The ash layer is composed of Fe and O, which are expected to be unreacted iron oxide in the system. The formation of SiO_2 and Al_2O_3 at the metal surface were not observed, even though they are the major oxides in coal ash. Carbon that appeared in the EDS spectra was expected to be unreacted carbon that adhered on the ash layer due to its excess amount in the system. In the case of RTB, the reduced iron surface was completely covered by a dense and rough ash layer (Figure 11). The composition of the ash layer was C, Fe, O, Ca, and S, which could be iron oxides, CaS complex. During the formation of reduced iron droplets, the carbon and sulfur atoms will transfer into the liquid iron concurrently [32]. RTB contains high amounts of CaO as a

major ash component, thus the presence of solid CaS on the iron surface could come from the desulfurization reaction of liquid iron by CaO in the ash and solute carbon atom, as in Equation (14) [32]. For RTB#3, the Fe surface was partially covered by iron oxides, as shown in Figure 12, point#2. No CaS complex was detected. The metal surface can be observed at point#1, which indicates the higher degree of metal separation from slag phase. CaO in RTB ash can act as a fluxing agent or a catalyst and help in scavenging sulfur [16,33]. High amount of CaO in RTB ash could retard the reduction mill scale [33], leading to the lowest extent of reduction. However, the optimum of CaO content in the system for RTB#3 could be responsible the greater extent of mill scale reduction.

Figure 10. SEM micrograph ($\times 5000$) on the surface of the metallic Fe droplets obtained after high-temperature interaction of the CCP for 30 min in the case of coal.

Figure 11. SEM micrograph ($\times 5000$) on the surface of the metallic Fe droplets obtained after high-temperature interaction of the CCP for 30 min in the case of RTB.

Figure 12. SEM micrograph ($\times 5000$) on the surface of the metallic Fe droplets obtained after high-temperature interaction of 30 min in the case of RTB#3.

Table 9. EDS point analysis on the surface of the metallic Fe droplets obtained after high-temperature interaction of the CCP for 30 min in the case of coal, RTB#3, and RTB.

Samples	Point	Element (Atomic %)				
		C	Fe	O	Ca	S
Coal	1	16.74	68.55	14.70	-	-
	2	27.92	26.20	45.88	-	-
RTB#3	1	92.27	7.73	-	-	-
	2	8.52	38.25	53.23	-	-
RTB	1	7.69	37.52	54.01	0.46	0.32
	2	9.35	33.14	56.65	0.47	0.39

In the present study, the use of pure RTB as a reductant could retard the direct reduction of mill scale at 1550 °C. For the CCP from mill scale-RTB, the major oxides in the system were Fe_2O_3 from the scale and CaO from RTB ash. CaO could react with Fe_2O_3 to form spinel compounds in the system, such as CaFe_2O_4 [34]. The formation of these spinel compounds occurred below 1000 °C (Equation (15)), and were in the form of solid residues in the crucible. Standard Gibbs free energy (ΔG°) for Equation (15) was provided as $\Delta G^\circ = -31512 - 3.211T \pm 425$ [35]. At 1550 °C, ΔG° for CaFe_2O_4 is in between -36.06 to -36.91 kJ. The consumption of Fe_2O_3 by CaO could hinder the reduction of mill scale with solid carbon from RTB, thus being responsible for the lower extent of iron oxide reduction reaction compared to the other cases. When using RTB/Coal blends as a reductant, the reduction of mill scale was observed to be much better than that of the parent coal and RTB. This expected due to the compromise between ash oxides content in the carbon and the synergistic effect between coal and RTB.

3.4. Preliminary Cost Analysis for Using RTB as a Carbon Source in Steelmaking Process

UMC Metals Ltd. is a steel mill located at Chonburi, the eastern industrial province of Thailand. UMC operates an electric arc furnace steelmaking for the production of billet, deformed bar and round bar, producing approximately 130,000 tons per annum. Details for carbon consumption in the process for the UMC are presented in Table 10. The consumption of coal (anthracite) in the process was approximately 5330 tons per annum, with an average carbon consumption of 41 kg per ton of steel. The average price for carbon

is 6700 Thai baht per ton. In September 2021, the exchange rate was 1 US dollar to about 31.43 Thai baht.

Table 10. The consumption of carbon in the process for UMC Metals Ltd.

Size (Nm)	Price (Thai Baht/Ton)	Quantity (Kg/Ton of Steel)	Location
1–3	6000	24	EAF
3–6	7500	14	EAF
10–15	9000	3	Ladle furnace

RTB is a biomass that has had no commercial price available before. The assumed price for RTB is 2000 Thai baht per ton, which is close to that of well-known biomass likes palm shell. Table 11 shows the estimate price of RTB and its blends with coal used in this study. From the high-temperature interaction experiment, RTB#3 shows a rapid FeO reduction with the highest degree of metallization. The composition of RTB#3 is in between that of the parent coal and RTB (see Table 3). Therefore, the blending of rubber tree bark with coal up to 30 wt.% (RTB#3) could replace the use of coal in the EAF steelmaking process. This could help UMC steel mill to reduce the consumption of coal in its processes by up to 30%. Thus, the steel mill could deduct its carbon cost by 2350 Thai baht per ton (21%) or over 7 million baht per annum, compared to the use of coal alone.

Table 11. Estimate price of the samples used in this study.

Samples	Coal (wt.%)	RTB (wt.%)	Price (Thai Bath/Ton)
Coal	100	0	6700
RTB#1	90	10	6230
RTB#2	80	20	5760
RTB#3	70	30	5290
RTB#4	60	40	4820
RTB#5	50	50	4350
RTB	0	100	2000

4. Conclusions

With an aim to utilize the local-based resources, the reduction of mill scale using rubber tree bark (RTB) as a reducing agent was investigated at 1550 °C. It was found that rubber tree bark biomass can be successfully utilized as a reductant for mill scale. The experimental results can be concluded as below.

- From the TGA results, the reduction of mill-scale in the CCP occurs at about 1100–1200 °C for all cases. The weight of CCP in the cases of coal and RTB keeps decreasing until 1550 °C with the weight loss of 53.98 and 53.08 wt.%, respectively. This indicates a slow reduction behavior and incomplete reduction. For blends RTB#1–RTB#5, the CCP weight stabilizes until 1550 °C due to the complete reduction, with the weight loss ranging between 26.92–44.36 wt.%.
- The reduction of mill scale in the CCP at 1550 °C occurs after the first min for all cases, except for RTB. The reduced Fe droplets were found to separate clearly from the black residues in the crucible. The degree of metallization (DOM) of the CCP produced from coal and RTB was 48.38% and 14.49%, respectively, and the metallic iron obtained was 23.05 wt.% for coal, while it was only 6.09 wt.% for RTB.
- On the other hand, the CCP produced from blends RTB#1–RTB#5 shows higher extent of iron oxides reduction with the metallic iron of 35.28–39.82 wt.%. The DOM ranges between 75.25–84.51%, which is about two and six times higher than that in the cases of parent coal and RTB, respectively.
- Among the blends, RTB#3 showed the maximum DOM of 84.51%. The increase of RTB content in the blends up to 50 wt.% (RTB#5), caused the decrease in DOM of the CCP.

- The addition of RTB into coal was not found to significantly change the composition and carbon structure of chars produced compared to the parent coal, but rather for the ash chemistry. CaO in rubber tree bark played a role in forming ash layer as the interfacial product on the metal surface, and thus the separation between metallic Fe and slag phases. The excess of CaO content in the system hinders the reduction of mill scale, thus the optimum CaO content is essential.
- Rubber tree bark, which is a local-based resource, can be used as a reductant for mill scale at 1550 °C by optimally blending with coal up to 30 wt.%. This can reduce the consumption of fossil fuel by 30 wt.% and reduce the production cost in steelmaking industries.

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