REDUCTION OF GOETHITIC IRON ORE USING THERMOGRAVIMETRIC METHOD

REDUKSI BIJIH BESI GUTIT DENGAN METODE TERMOGRAVIMETRI

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ABSTRACT

Compared to main iron ore minerals, either hematite or magnetite, Indonesian goethite is relatively abundant. However, this is not common to be used as feed material in iron making industries. Limitation in Indonesian high quality iron ore resources, the iron making industries have to seek another iron source such as the low grade iron ore of goethitic ore. Evaluation using thermogravimetric method was employed for analyzing behavior of goethitic composite pellet during reduction. The data show that reduction of goethitic iron ore is started by transforming goethite to hematite and then followed by iron reduction. The reduction was started by Fe_3O_4 formation at 442 °C and Fe at 910 °C. At those temperatures the composite pellet lost its weight. Identifying the FeO is hardly difficult due to the short range of phase existence.

Keywords: goethitic iron ore, iron reduction, thermogravimetric analysis.

SARI

Laterit merupakan cadangan terbesar bijih besi yang ada di Indonesia. Jenis ini umumnya bukan merupakan bahan baku utama dalam industri pembuatan besi namun karena keterbatasan dan semakin berkurangnya bijih besi primer, laterit diupayakan menggantikan bijih besi tersebut sebagai bahan baku terutama melalui pembentukan pelet komposit. Perilaku reduksi pelet komposit yang terdiri atas laterit dan batubara dikarakterisasi menggunakan metode termogravimetrik. Hasil menunjukkan bahwa proses reduksi pelet komposit didahului oleh proses awahidroksilasi yang mengubah gutit menjadi hematit, diikuti oleh reduksi hematit menjadi fasa besi lain. Reduksi dimulai pada 442 °C dengan pembentukan Fe_3O_4 dan Fe pada 910 °C. Proses reduksi pada pelet komposit diikuti dengan kehilangan berat. Identifikasi pembentukan FeO sulit dilakukan karena keberadaan fasa terjadi pada selang waktu yang pendek.

Kata kunci: bijih besi gutit, reduksi besi, analisis termogravimetri

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INTRODUCTION

Indonesia retains a lot of iron ore resources. However, such resources come mainly from lateritic ore. This ore consists of goethite mineral. Based on iron content, lateritic ore is classified as a low grade iron ore. This fact is contradictive with the primary iron ores, either hematite or magnetite, that have high grade of iron and commonly applied in iron making industries. As a result, the lateritic ores require different process when used for iron making.

Several researchers have studied the reduction of lateritic iron ore (Murakami et al., 2009; Kawigraha et al., 2013). Murakami et al. (2009) states that at fixed temperature the reduction degree of goethitic iron ore is higher than that of primary iron ore. It means that the energy for goethitic reduction is lower. Goethitic material will lose its hydroxide components during heating (Strezov et al., 2010; Gialanella et al., 2010)and weight in three stages (Strezov et al., 2010) Dehydration and dehydroxylation temperatures occur between 100 to 150 °C and 260 to 425 °C respectively while decomposition temperature for clay is between 540 to 605 °C. The three stages consecutively correspond to the loss of free water, hydroxide component and hydroxide available in clay. Reactions involve in second and third stages are :

$$2\ FeOOH \rightarrow Fe_2O_3 + H_2O. \quad (1)$$
$$Al_2Si_2O_5(OH)_4 \rightarrow Al_2O_3 + SiO_2 + 4H_2O \quad (2)$$

The change of Fe_2O_3 to Fe_3O_4 starts after dehydroxylation (Murakami et al., 2009; Kawigraha et al., 2013). Consequently, the H_2O gas is formed at early temperature (Jozwiak et al., 2007) and possibly there is H2 that will be generated from H2O dissociation. The two gases may influence reduction process at early stage. The reaction heats of dehydroxylation and clay decomposition range from 38 to 230 MJ/m^3 and from 2.4 to 28 MJ/m^3 respectively (Strezov et al., 2010).

The objective of this research is to analyze the reduction process of composite pellet containing goethitic iron ore and coal. It also discuss as characterization of composite pellet using thermogravimetric method to determine temperature of iron phases formation.

METHODOLOGY

Laterite ore used in this experiment is derived from South Kalimantan that consists of goethitic iron ore. The material shows a porous iron character and easy to crush using a crusher and a milling instrument. A 140-mesh powder is used for the experiment while its reductant is subbituminous coal that comprises 41.53 % fixed carbon and 38.23 % volatile matter.

The ore is then analyzed using Rietveld method to quantify all of major Fe phases such as FeOOH, Fe_2O_3 and Fe_3O_4. The quantification using Rietveld method is based on XRD difractogram.

Instrument

The main apparatus in this experiment are simultaneous thermal analyzer (STA) Perkin Elmer, tube furnace which has ability to heat the composite pellet from 25 to 1000 °C, Vario gas analyzer and XRD. The heating rate and temperature of tube furnace can be controlled after introducing the parameters before experiment.

RESULTS AND DISCUSSION

Quantification of lateritic iron ore shows that the ore consist of 70.25 % FeOOH 1.49 % Fe_2O_3, 1.47 % Fe_3O_4, and 6.78 % gangue. The powder is then analyzed using Simultaneous Thermal Analysis to elaborate its thermal properties. Chemical analysis of the ore is shown in Table 1.

Iron ore is mixed with coal in order to analyze their heat content by thermal analyzer. Iron ore to coal ratio in the mixture is fixed to 1:3 for Fe to C ratio. The mixture is then pelletized around 12 mm to 15 mm in diameter. A chopped pellet is introduced into Perkin Elmer STA equipment to observe its thermal properties during reduction

Table 1. Chemical composition of lateritic iron ore used in this experiment.

Component	Fe_{total}	FeO	Fe_2O_3	TiO_2	SiO_2	Al_2O_3	CaO	MgO	S_{total}	SO_3	Cr_2O_3	Ni	LOI
%	53.62	-	79.3	0.84	2.26	4.03	0.04	0.08	0.14	0.84	2.39	0.09	9.58

process. The experiment is accomplished from 25 to 1000 °C with the heating and nitrogen flow rates of 10 °C/minute and 20 ml/minute respectively. The obtained thermogravimetric curve is then analyzed using exel program to obtain Differential Thermogravimetric Curve.

Some pellets are also reduced in a tube furnace using temperature of 350 , 460, 680, and 980 °C. Furnace heating rate is 10 °C/minute until reaches the desired temperature and then is hold for 20 minutes. The nitrogen is flowed during reduction process to carry the produced gasses during pellet heating. The gases are identified using gas analyzer. The reduced pellet is then analyzed by X-Ray Diffraction to examine its phases.

Thermogravimetric and heat curves of iron ore is shown in Figure 1. The iron loses more than 14 % of total weight from 25 to 1000 °C. It releases gases at 301.9 °C performing ore lost around 7 % of its weight.

During heating, there are three endothermic peaks while the heat curve itself can be divided into three regions. The first region is between 160 and 370 °C which Corresponds to hydroxide release (Strezov et al., 2010). The endothermic peak occurs at 301.9 °C. In the second region which ranges between 370 and 640 °C, there is only low endothermic peak and after 640 °C the heat curve has another endothermic peak near 900 °C.

Thermogravimetic characterization of coal is represented in Figure 2. The curve can be divided in to three regions, the first one corresponds to a free water release and it covers from 25 to 195 °C. The second region takes place between 195 to 350 °C and the curve is relatively stable. In the third region the weight curve decrease quickly which means that weight loss is erraticaly after 350 °C. Moreover the coal lost of weight continuously until high temperature. During heating, the heat curve shows that there are only four peaks of endothermic at around 100 °C, 550 °C, 750 °C and 900 °C. The heat curve also shows an exothermic peak at around 500 °C. The heat curve diminishes quickly after 350 °C to a minimum endothermic peak.

Differential Thermogravimetric (DTG) curve of goethitic iron ore can be seen in Figure 3. The curve, derived from thermogravimetric curve, shows

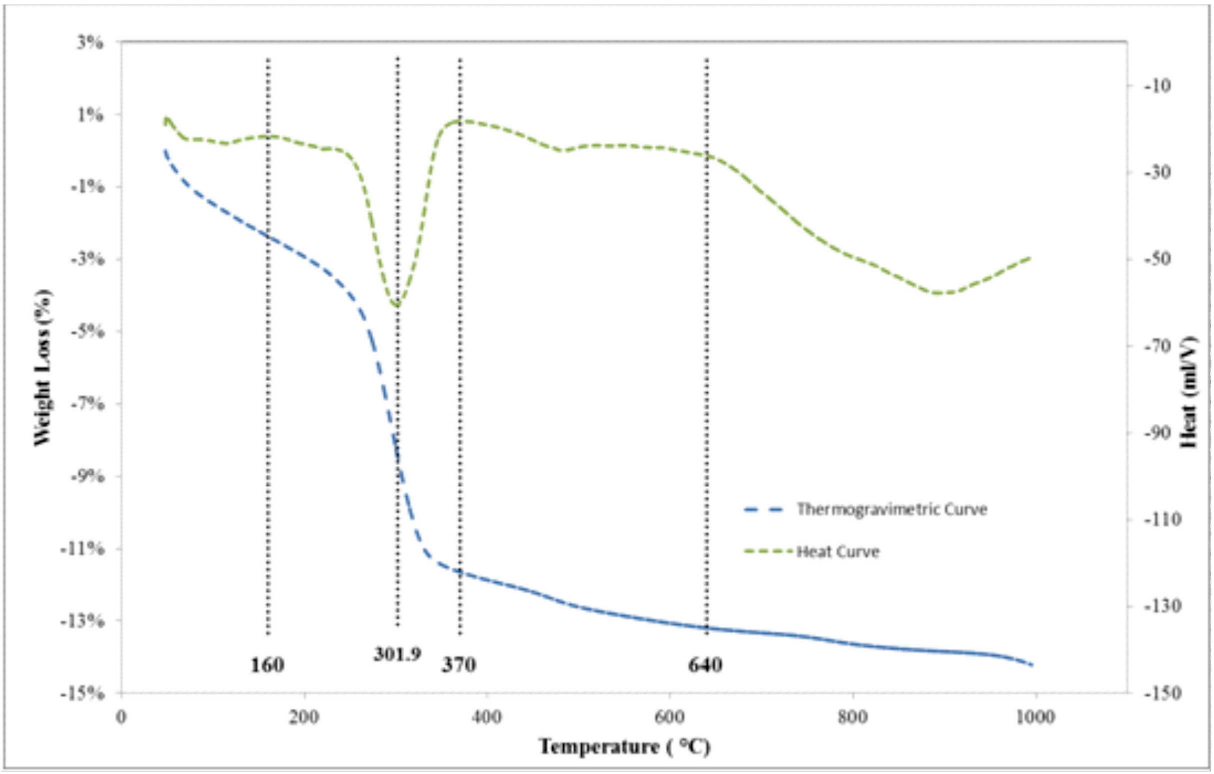

Figure 1. Thermogravimetric and heat curves of goethitic iron ore.

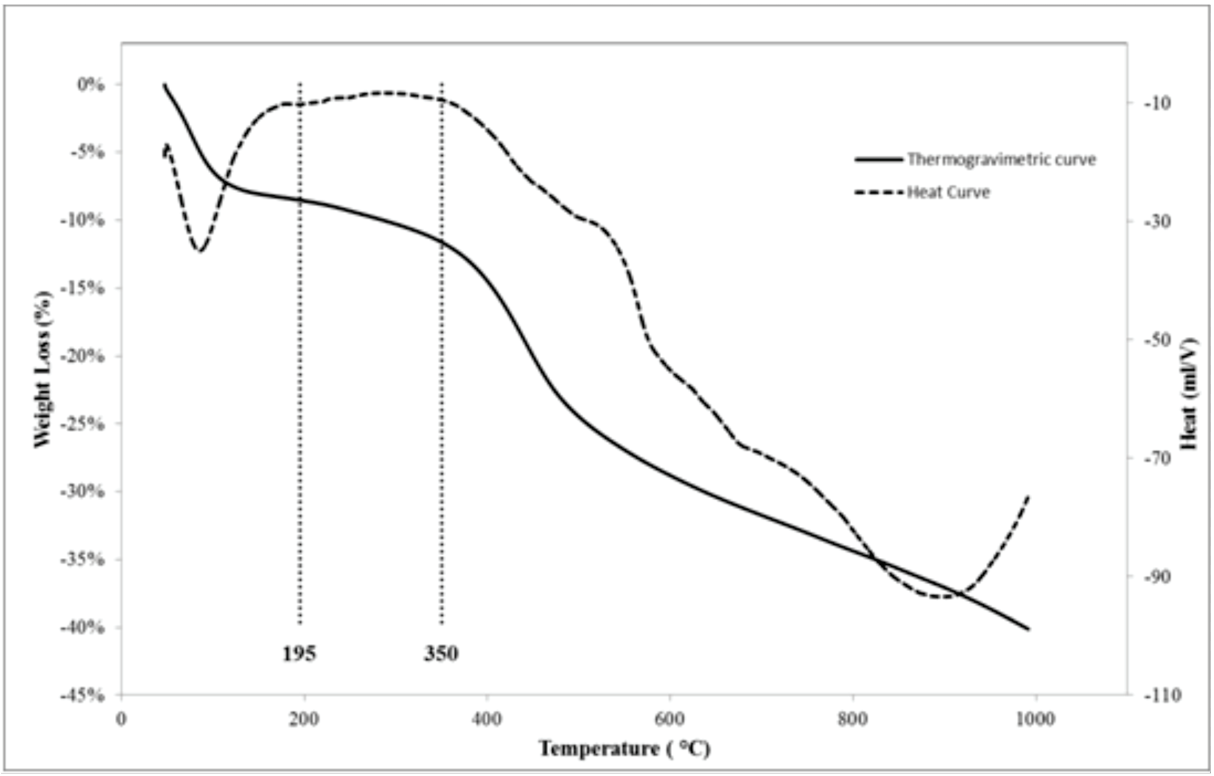

Figure 2. Thermogravimetric and heat curves of coal

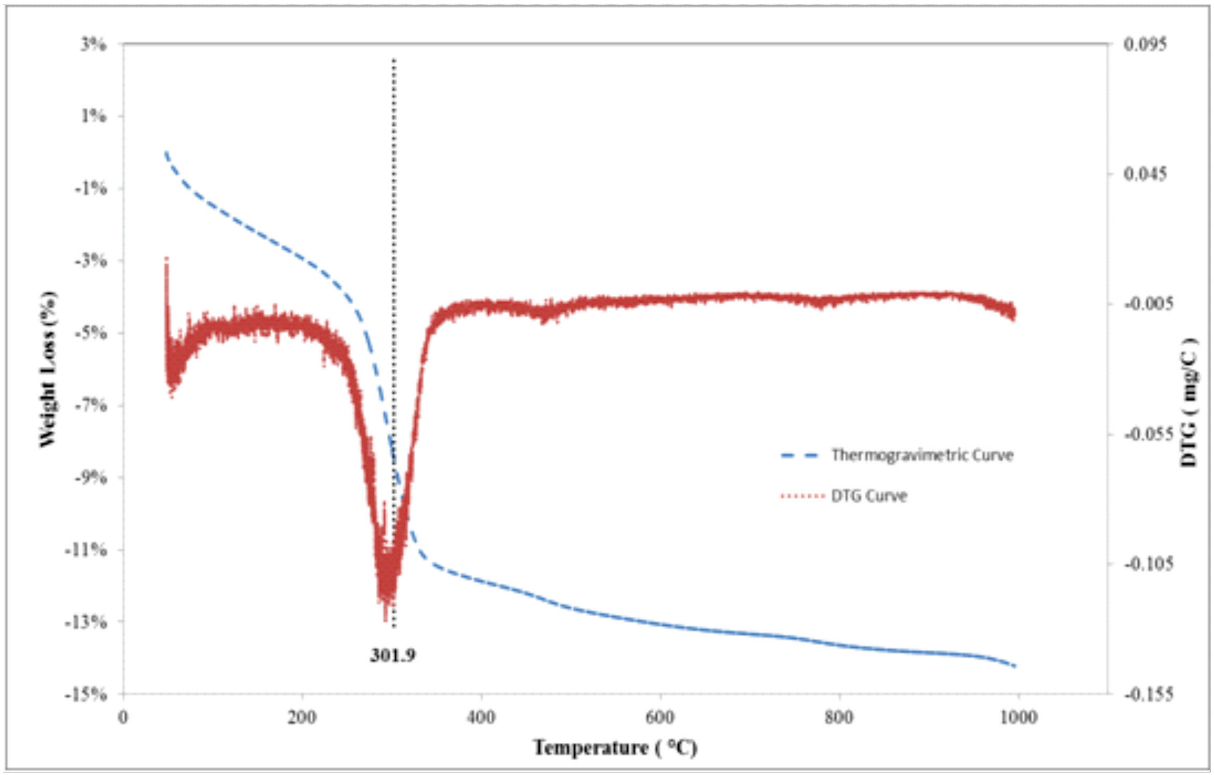

Figure 3. Thermogravimetric and DTG curve of lateritic ore.

that at least there are four peaks. Two peaks can be identified easily whereas the third and fourth peaks are low minimum peaks. The first two peaks correspond to dehydration and dehydroxylation whereas the second two peaks correspond to clay decomposition. Clay decomposition temperature is similar to the data reported by other researcher (Strezov et al., 2010). At 301.9 °C, the ore has a significant loss of weight. The loss component is the OH available within goethite.

DTG curve of coal is shown in Figure 4. The curve is characterized by two significant peaks. The first one corresponds to hydration of free water whereas the second one corresponds to dissociation of carbon. The first is at 78.8 °C and the second is at 439.9 °C.

Thermogravimetric curve of composite goethitic iron ore-coal is shown in Figure 5. It shows that weight loss occurs continuously from low to high temperatures. Significant slope occurs at around 285 °C shows that the composite pellet loses weight significantly in a short time. It indicates that the dehydroxylation of lateritic iron ore occurred. There are at least 3 other slopes that indicate the loss of composite weight. The two peaks after 285 °C-peak can easily be identified at 442 and 625 °C. However, the last peak cannot easily be determined due to the limitation of STA performance. The 825 °C-peak is not really a peak because the DTG decreases continuously from 700 to 1000 °C.

DTG curve analysis shows that at least there are five peaks. All peaks correspond to slope at thermogravimetric curve. The first and second slope corresponds to dehydration and dehydroxylation process. The third, fourth and fifth peaks of DTG have low loss of weight compared to the first and second slope. After the fourth peak the DTG curve has a tendency to decrease.

Measurement of gases, released by composite pellet, is shown in Figure 6. Heating the pellet was conducted at 1 atmosphere. The identified gases are CO, CO_2 and CH_4 that are responsible for iron reduction. The Figure 6 shows that CO has two peaks, small and high ones. They are at 630 and 920 °C. However, the CO starts to be detected at 300 °C. CO_2 has two peaks, namely a low one at 450 °C and a high peak at 880 °C. The ratio of two gases reach maximum before decreases indicated the gasification of coal in

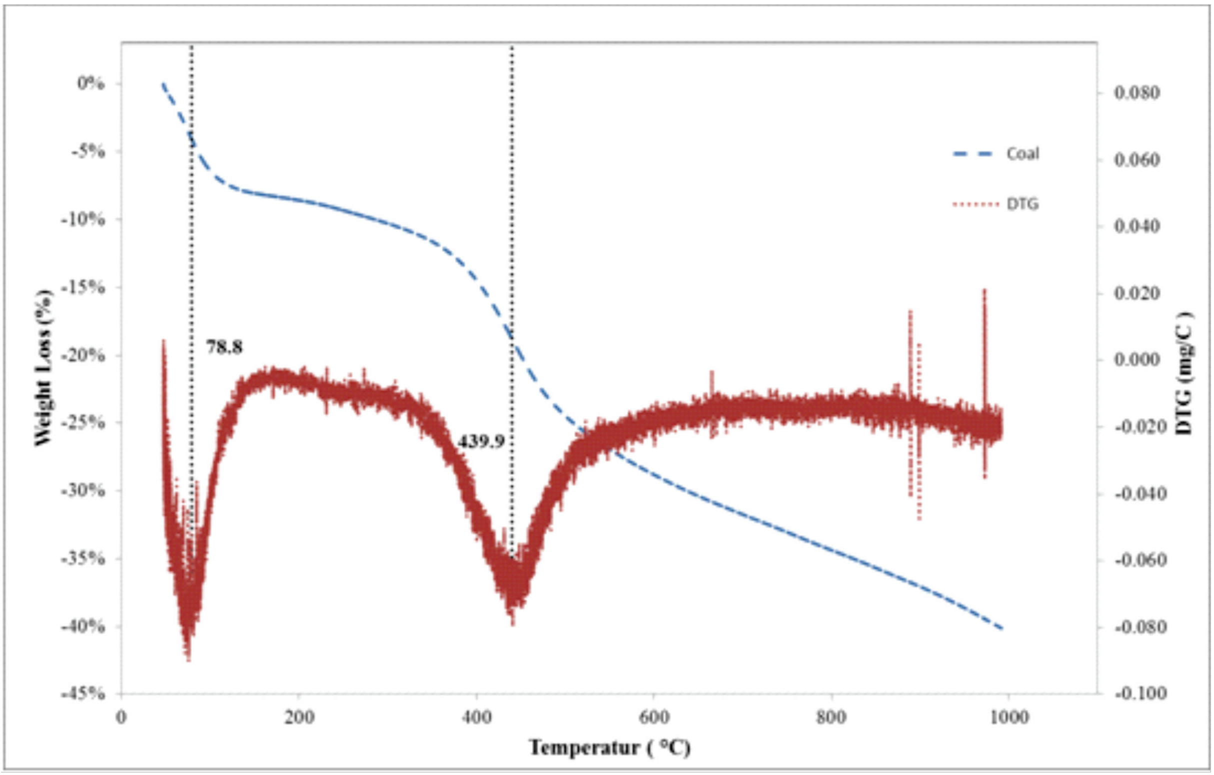

Figure 4. Thermogravimetric and DTG curve of coal.

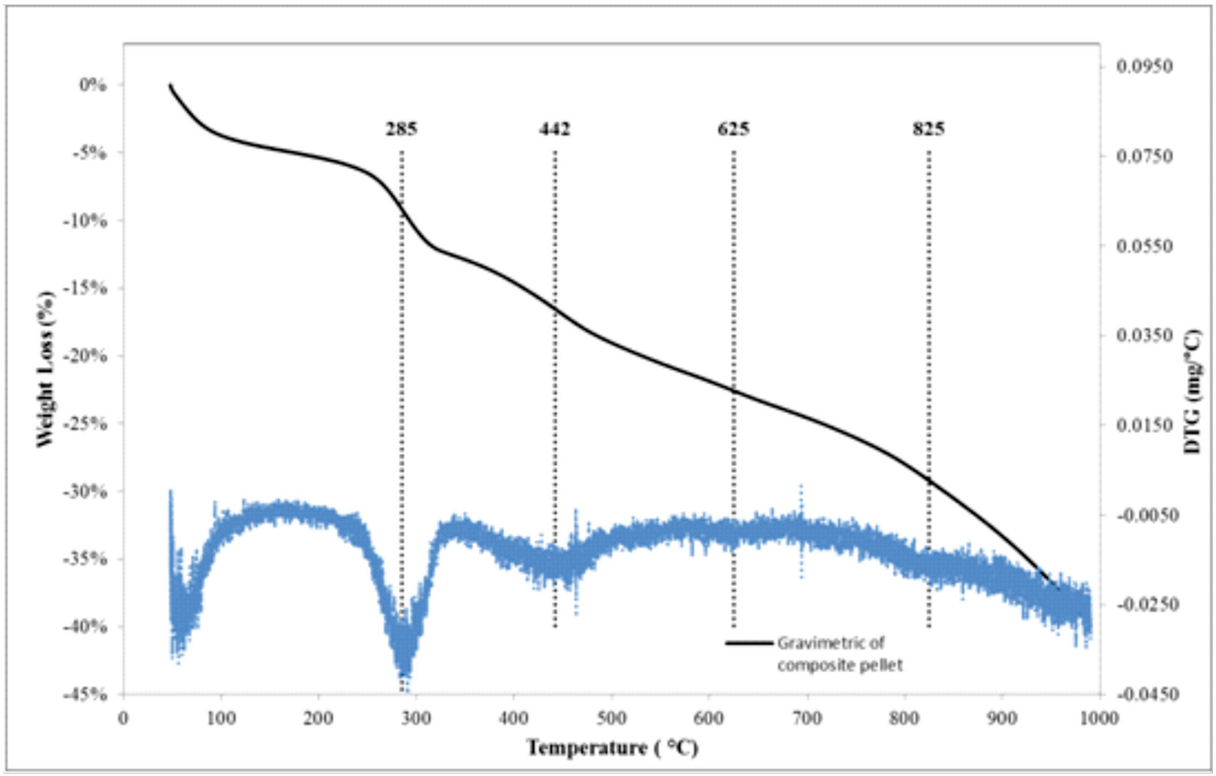

Figure 5. Thermogravimetric and DTG curves of composite pellet.

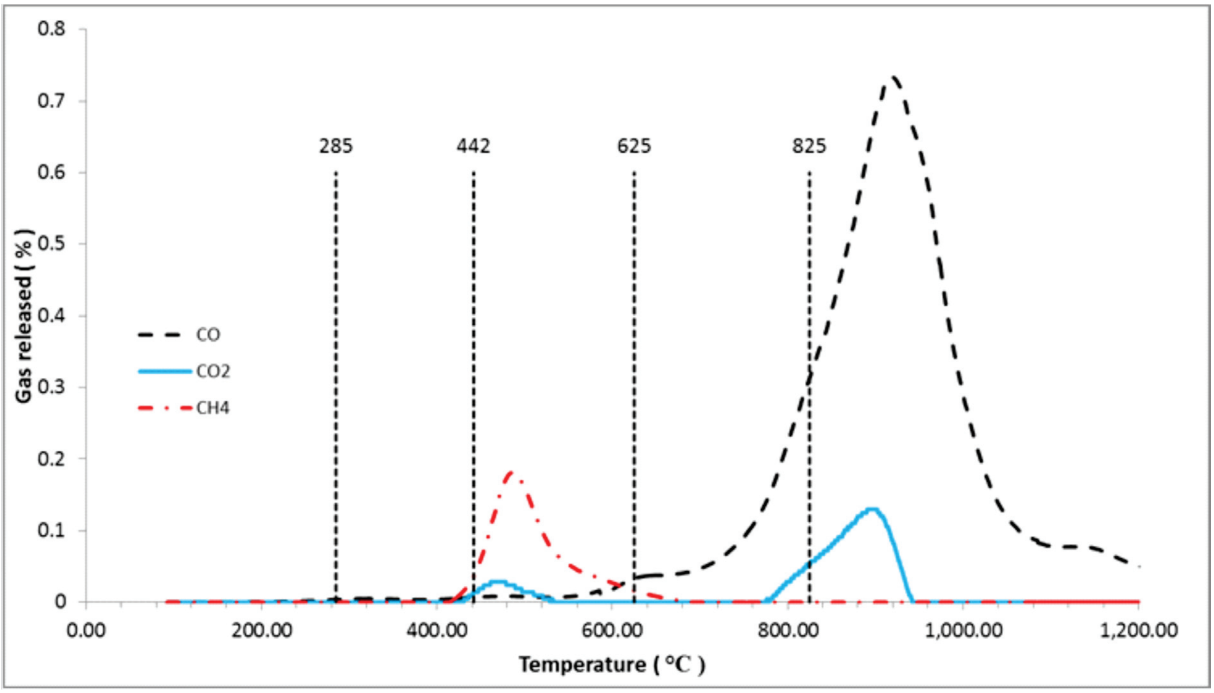

Figure 6. Released gas occurs during heating the composite pellet.

the pellet completed. There are only one peak of CH_4 namely at 470 °C. The gas is released at early temperature.

CO curve shows that iron reduction starts at above 442 °C. Around such a temperature, composite pellet loses its carbon and transforms to CH4, CO and CO2. Reduction process may increase with the increase of CO formation. After 700 °C, the quantity of released CO increases with temperature. At early temperature, CH_4 also plays as reductant, confirmed by DTG curve. After that, DTG curve decreases rapidly.

XRD data confirms DTG analysis explaining that FeOOH disappears at 350 °C (Figure 7). At such a temperature, there are only Fe_2O_3 and Fe_3O_4. At higher temperature (470 °C), almost all of Fe_2O_3 has been reduced to Fe_3O_4. In fact, Figure 6 shows that at 442 °C, composite pellet releases CH4 gas. It is probably the CH_4 is a reduction agent for Fe_2O_3 transformation. Formation of CH_4 is supported by Figure 5 that at 442 °C, the composite loses significant weight.

Fe_3O_4 is stable at least until 680 °C due to not enough reduction agents at this temperature. Figure 6 confirms that at that temperature CH_4 and CO present at the same time. However, CH_4 will disappear and CO will increase for a maximum concentration.

The Fe presents when composite pellet is reduced at 980 °C as shown in Figure 7. Fe formation occurs due to Fe_3O_4 and FeO reductions by CO (Figure 6)., CO reaches maximum at around 920 °C. Reduction is followed by loss of weight continuously until temperature above 1000 °C.

CONCLUSION

Reaction of composite pellet consists of dehydration, dehydroxylation, Fe_2O_3, Fe_3O_4, FeO and Fe formation. The reaction characterized by weight loss at temperature below 100, 285, 442, 625, and above 700 °C. Reduction of goethitic iron ore is started by Fe_2O_3 formation above 350 °C followed by forming Fe_3O_4. The formation of FeO and Fe occur above 680 °C.

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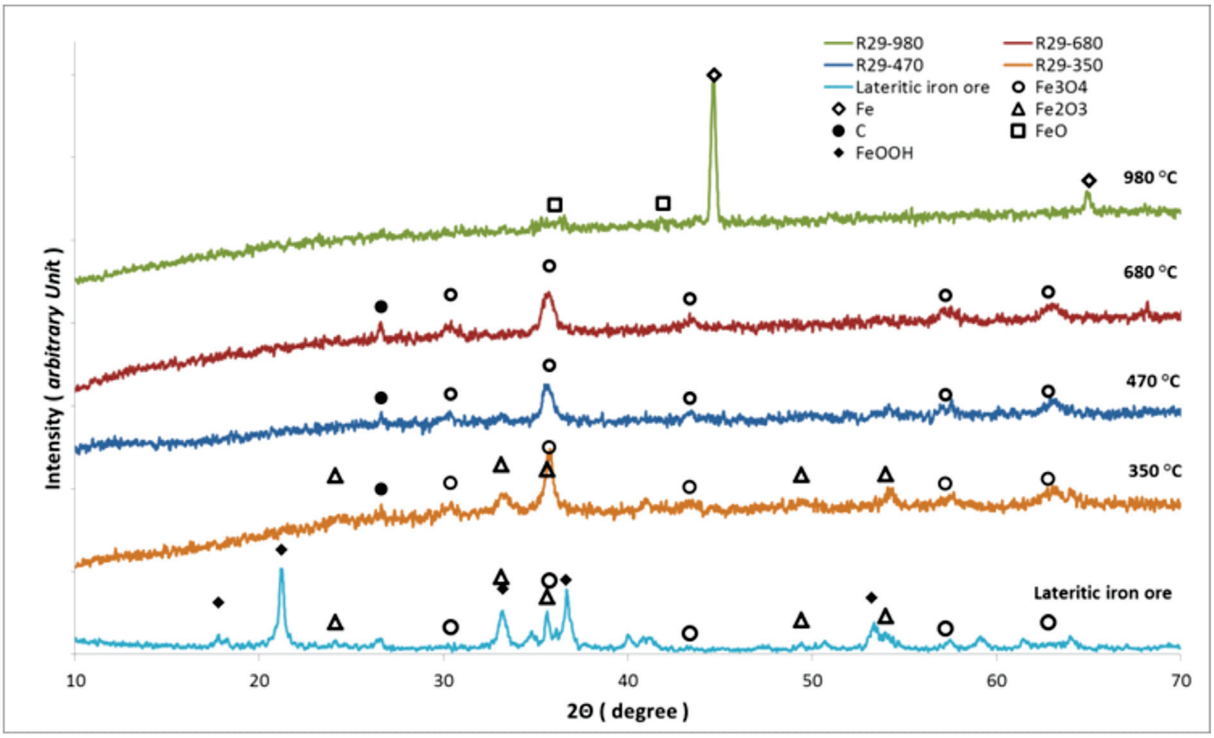

Figure 7. X-ray Diffraction of lateritic iron ore and composite pellets at 350, 470, 680, and 980 °C.

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