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PRODUCTION OF IRON-CARBON NUGGETS DIRECTLY WITH SAWDUST IN AN EXPERIMENTAL ROTARY KILN AT 1773 K[1]

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Abstract

The growing demand for clean technologies is pushing the steel industry for alternatives to produce pig iron. One option is the use of biomass in substitution to mineral coke; however to spread this technology, the efficiency of the full process should be improved. On the case of mini-blast furnace for pig iron production, the volatile matters produced at charcoal plant are usually lost. This paper seeks to take advantage of these volatile matters by using it directly in production of iron-carbon nuggets. The biomass is sawdust of different types of wood, as it can be obtained in the sawmills. The raw material - sawdust was homogenized, dried and analyzed. A self-reducing mixture of low grade iron ore (43.5%) and sawdust (56.5%) was prepared and processed at 1773 K for 15 minutes in electric rotary kiln. Its atmosphere was enriched with argon (1NL/min.). The reaction fraction was measured, achieving 99.2% of reduction. The final product was carefully disaggregated to avoid any grinding of metallic phase. The particle size distribution of the iron-carbon nuggets was measured, showing that 50.5% of the product was larger than 7.93 mm, and 97.2% bigger than 0.84 mm. These results can open the way for the direct use of biomass as reducer of iron ore and a more energy efficient process can be born.

Keywords: Biomass; Sawdust; Self reducing mixture; Iron-carbon nuggets.

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1 INTRODUCTION

Since ancient time, charcoal was used for production of pig iron (bloomery smelting, Catalan forges). Price increase of coking coal, environment conscious policy, and the wasting of volatiles[1] in traditional charcoal plants are the driving forces for searching more efficient techniques for the reduction of iron ore.

Since 2004, a European research project, ULCOS,[2] is being carried out, with the target of halving the emission of CO_2 from steelworks. In this project, new techniques, such as melt reduction, new blast furnace techniques and steel production based on reduction agents other than coal (e.g. hydrogen gas and biofuel) are being investigated. Research on capturing of CO_2 is also included in the project.[3] The SOx emission is significantly reduced when the biomass fuels are used, but the NOx remains largely unaffected.[4]

1.1 Iron Ore Reduction by Biomass

Experiments with self-reducing mixture containing 10% w/w sawdust and 90% iron ore, processed at different temperatures, were reported. The results have shown that the hematite was partially reduced to magnetite (Fe_3O_4) and wustite (FeO). Increasing the biomass to 20% w/w, the product was predominantly wustite, with small amount of metallic iron. Addition of 30% w/w of biomass, the iron ore was predominantly reduced to metallic iron. Thermal analysis showed that for temperatures up to 670 °C the reactions in the 70:30 iron ore to biomass mixture were dependent on the properties and decomposition of the initial biomass and ore samples, while at temperature above 670 °C, the reactions were associated with the reduction. The reduction reactions were divided into three major temperature events with the first being exothermic while two higher temperature regions exhibited endothermic heat effects. The volatilization of organic matters of biomass is largely affected by the reduction process and is proportional to the reaction heat. The reaction degree of the three examined thermal regions followed the first-order kinetic mechanism.[5]

One paper presented a novel direct reduction technology using biomass as raw material in Fe_2O_3 self-reducing briquettes and using syngas made by steam gasification of biomass as reducing gas. The reduction of Fe_2O_3 briquette was carried out in a lab-scale reactor. The results showed that the Fe-content of the product reaches a maximum of 94.7%, at a reduction temperature and reaction time of 1373 K (1100 °C) and 60 min, respectively. The low C-content of the product (below 0.5%) meets the standard of crude steel, which could significantly reduce the steel making cost.[6]

Reducing gases such as CO and H_2 were generated by thermal decomposition of sawdust. Reduced iron was obtained by heating the mixture of sawdust and iron oxide, at the temperature from 1273 to 1573 K. The reaction fraction achieved 100% [7] .The H_2-generation was almost the same between thermal decomposition of sawdust and reduction of the mixture of sawdust and iron oxide. The H_2-generation reached about 50% at 1573 K. Furthermore, the CO-generation by reduction was larger than that by thermal decomposition. The CO-generation reached more than 80% at 1573 K.[7]

1.2 Process of Mixing and Coalescence in the Rotary Kiln

The smelting rotary kiln has the peculiarity to promote mixing of the charge and the coalescence of metallic phases, originated during the ore reduction.[8] Experiments with different particles size loads have shown that when there are very fine particles in the charge, two regions are formed in cross-section of the furnace: an active and a passive layer,[9] that is, the fine particles stay in the core of rotating charge surrounded by large particles as shown in the figure 1.

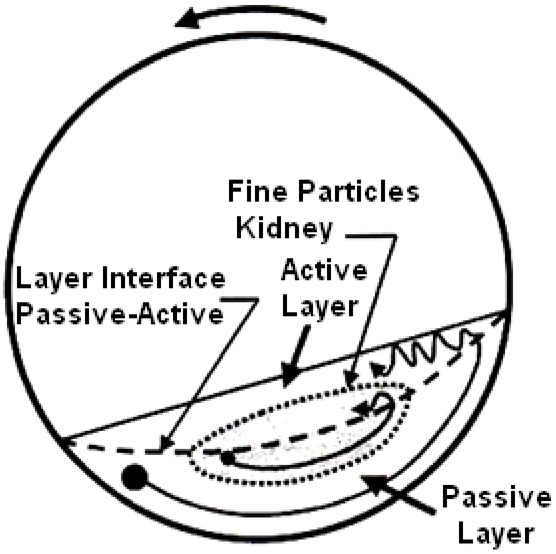


Figure 1. Aspects of segregation of the charge when the load contains large difference of particles sizes [9].

2 MATERIALS AND METHODS

2.1 Characterization of Raw Materials

The chemical analysis of iron ore is shown in Table 1. It is a low grade ore, containing 16.3% gangue.

Table 1. Chemical analysis of iron ore (% mass)

Fe_2O_3	CaO	Al_2O_3	SiO_2	MnO_2
83,7	1,7	8,3	3,7	2,6
ASTM E 135-08				

The sawdust is basically composed of volatile matters. Its C_{fix} is around 15%, as shown in Table 2.

Table 2. Sawdust characterization (% mass)

C_{fix}	Volatile matters	Ash
15.4	83.2	1.4
ASTM D 1102-84, ASTM E 872-82		

The chemical analysis of sawdust ash is shown in Table 3. It is rich in iron, calcium and magnesium oxide.

Table 3. Sawdust ash chemical analysis (% mass)

Component	% mass	Component	% mass
Na_2O	1.91	K_2O	5.20
MgO	27.07	CaO	20.40
Al_2O_3	3.88	MnO	2.50
SiO_2	10.06	Fe_2O_3	28.98

2.2 Self-reducing Mixture

The composition of self-reducing mixture is shown in Table 4. Low grade iron ore was chosen by purpose, to check the feasibility of this technique in adverse conditions. The amount of sawdust was calculated, considering C_{fix}/O unitary ratio with 5% excess. There are large amount of volatile matters, which are mostly released at temperature close to 873 K (600°C). Around this temperature, hematite can hardly been reduced to iron. Excess of biomass was considered to guarantee the full reduction of iron ore.

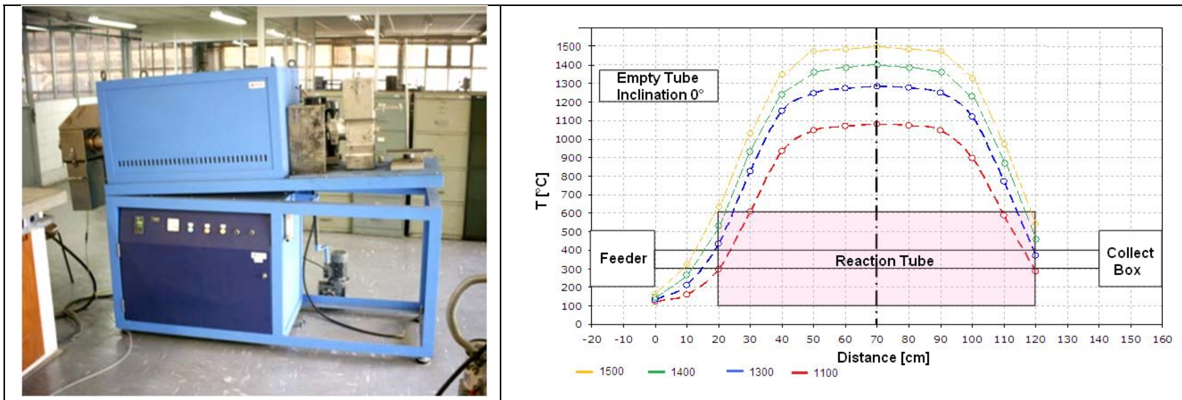
Table 4. Composition of self-reducing mixture (% mass)

% Low grade iron ore	% Sawdust
43.5	56.5

The raw materials were dried at 120 °C for 2 hours. They were loaded into Turbula mixer to be homogenized.

2.3 Processing of Self-reducing Mixture in the Rotary Kiln

The self-reducing mixtures were processed in a laboratory rotary kiln at 1773 K (1500 °C). The view of this electric furnace is shown in Figure 2a the internal temperature profiles are shown in Figure 2b. Argon was injected at a rate of approximately 1NL/min to reduce the O_2-content due leakage of air (guarantee positive pressure inside the kiln). The mixture was loaded into the rotary kiln by vibrating feeder. The reduction time was set at 10 minutes, time enough for full reduction of hematite, carburization and coalescence of iron-carbon particles. The residence time was achieved by controlling the slope of the furnace (5 [deg] for self-reducing mixtures), at 5 rpm. Graphite tube with internal diameter of 48 mm was inserted into the mullite tube with 1500 mm length.



(a)

(b)

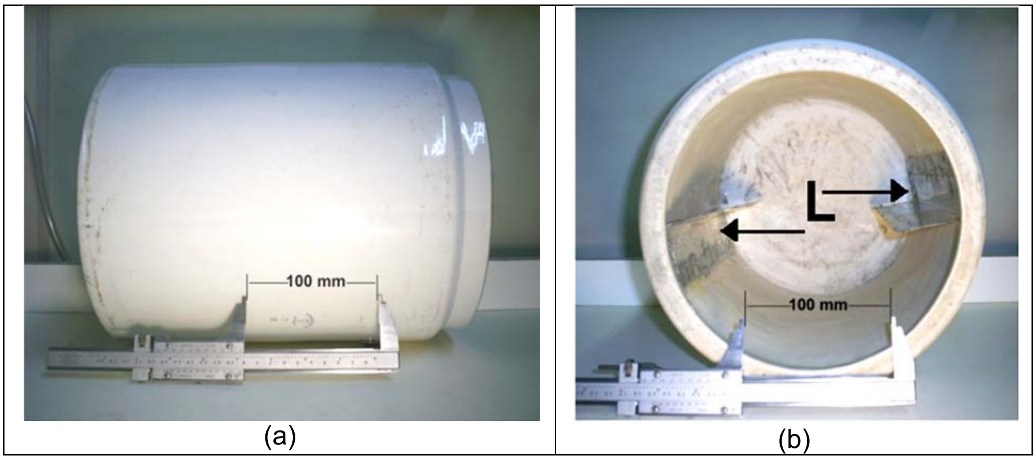
Figure 2. (a) View of the rotary kiln (b) Internal profile temperature [° C] of the rotary kiln.

2.4 Measurement of Coalescence Degree

The coalescence degree is proportional to the diameter of the iron-carbon nuggets obtained. The metallic phases were liberated after the products of reduction were carefully disaggregated. For this purpose, it was used the drum test method, ASTM E 279-97. This method was validated, after comparing the results obtained in manual grinding in porcelain mortar and the drum test.
The particle size of the grinded material was measured, according to ASTM B 214-76. Two sets were used. The first one was to measure the particle size distribution of non-metallic phase, with a very broad distribution of sieves in order to get the average distribution: 0.84 / 0.50 / 0.30/ 0.149 and 0.106 mm. The second one was to measure the particle size distribution of the iron-carbon nuggets: 7.93 / 5.66 / 4.76 / 2.83 and 0.84 mm.

2.5 Disaggregation of the Reduced Material

One charge of the rotary kiln is around 1000 g of self-reducing mixture. The amount of the reduced material is generally less than 300 g, which is much smaller than 11 kg, defined in ASTM E 279-97; therefore the drum has to be resized to accommodate this situation. The high density alumina drum has 300 ± 1 mm in length and 200 ± 1 mm in diameter, as shown in Figure 3. There are two lifters in L, which dimensions are 50.8 X 50.8 x 1.0 mm. The previously dried reduced material was submitted at 200 revolutions with a rotation of 24 ± 1 RPM and subsequently its particle size distribution was measured. Simultaneously, similar reduced material was carefully handy grinded to avoid any crushing of the iron-carbon nuggets. The particle size distribution was measured, and compared with previous one.



(a) (b)

Figure 3. Alumina jar used in the drum test (ASTM E 279-97. (a) Side view. (b) Front view, showing the lifters in L.

2.6 Reaction Fraction

The reaction fraction was calculated using the equations 1 and 2.

$$fr = \frac{m_1}{m} \quad (1)$$

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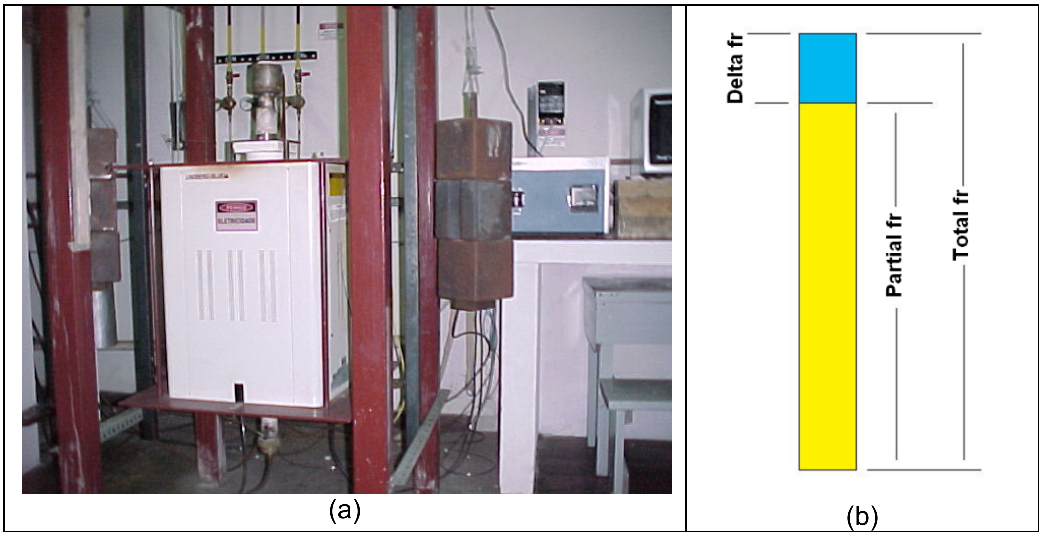
$$m_1 = \frac{M_i - M_t}{M_i} \quad (2)$$

Where:
f_r = reaction fraction in the instant t.
M_i = initial mass of the sample, dried [g].
M_t = mass of the sample in instant t [g].
m_1 = mass loss relatively to initial mass [g].
m = maximum reduction fraction, obtained by the step method.[10]

2.7 Measurement of Reaction Fraction by Indirect Method

The self-reducing mixture contains large amount of sawdust, which can be carried out by off gas and argon flow. Furthermore, there are losses due to the vibratory feeder. Significant error is achieved if the equation 1 is simply applied. Indirect method was designed to estimate the reaction fraction.

The procedure: the collected material from the exit of rotary kiln is blended with 10% graphite; graphite with no volatile matters was used as reducer; the absence of oxygen inside the termogravimetric furnace (figure 4a) was guaranteed with flow of argon 2NL/min; alumina crucible containing the reduced material was hung with a Cr-Ni wire, as shown in Figure 5 and heated at 1673 K, during 10 minutes, at an inert atmosphere. The result of reduction degree is then calculated, that is, if no weight loss is observed means that the material from rotary kiln is completed reduced. The figure 4b shows graphically the reaction fraction by indirect method.



(a) (b)

Figure 4. (a) Lindberg / Blue vertical furnace adapted to thermogravimetric tests. (b) Schematic representation of the measurement of the reaction fraction by indirect method.

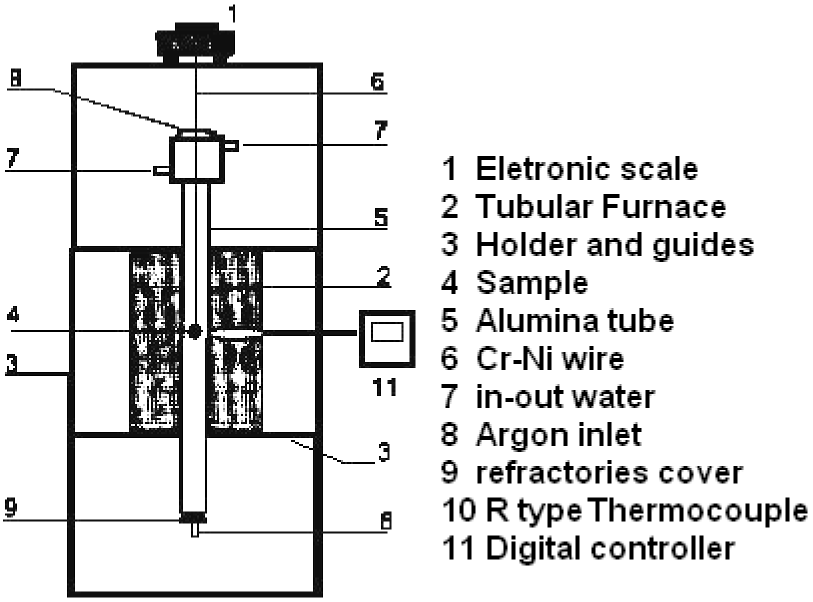


Figure 5. Lindberg / Blue vertical furnace adapted to thermogravimetric measurements (schematic representation).

Therefore the fractional reduction was calculated by equation (3). Where fr_{delta} was estimated assuming that weight loss is due to CO, since the temperature was 1673 K. From this loss is enable to estimate the C and reduced iron.

$$fr=1-fr_{delta} \quad (3)$$

$$\%fr=fr*100 \quad (4)$$

3 RESULTS AND DISCUSSION

3.1 Reduction and Fusion in the Rotary Kiln

When the self-reducing mixture of the low grade iron ore and sawdust is fed into the rotary kiln (figure 6), the material is preheated, followed by the volatilization of organic compounds of sawdust. The off gas has shown the presence of volatile matters, some of them condensable (eg tar) organic compounds.

At higher temperature, the generation of gases is high enough to fluidize the mixture. The sawdust is converted in charcoal; CO and CO_2 are generated by Boudouard reactions. Iron oxide is reduced to metal, subsequently the process of carburization takes place, coalescence of metallic particles and phase separation of metal and slag are observed. The final products are iron-carbon nuggets of different sizes, agglomerated slag containing metallic phases, and small pieces of charcoal, as shown in Figure 7a. Metallic nuggets as large as 15 mm (Figure 7b), not shown in Figure 7a, were obtained at the same experiment after processing the self reducing mixture for 10 minutes at 1773K (1500° C). The reaction fraction by indirect method is around Fr ≈ 99% indicating the high efficiency of the process.

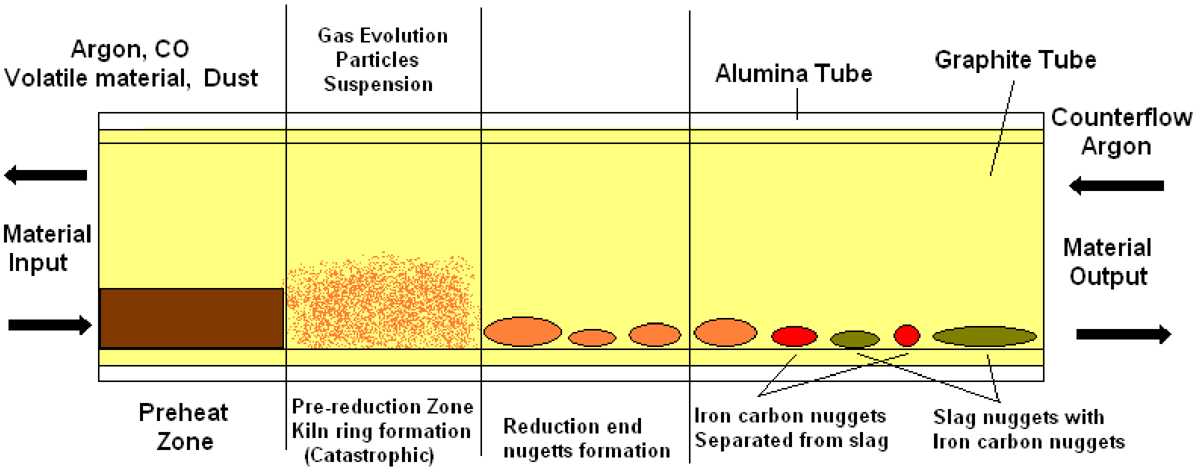
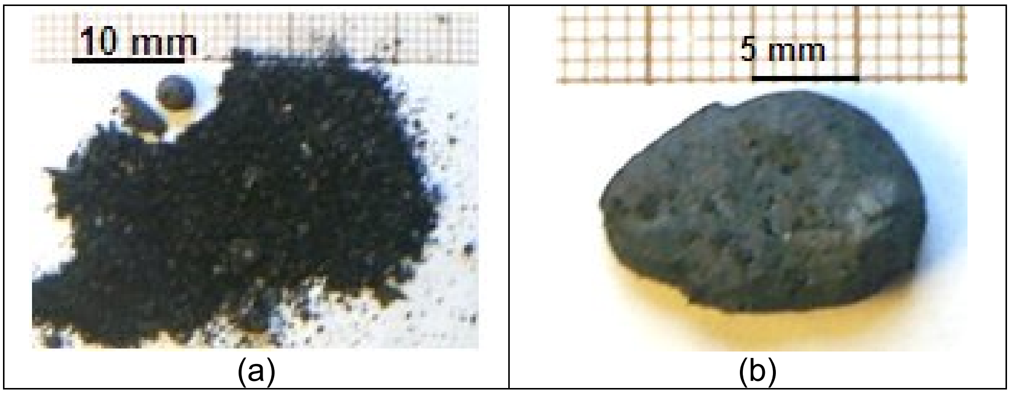


Figure 6. Schematic representations of the process: reduction of iron ore, carburizing the iron metal, formation of iron-carbon and slag nuggets.

The carbon content in metal was analysed by LECO and the results indicate around 5% w/w. The particle size distribution of processed mixture, after disaggregation, is shown in Table 5 and Figure 8. More than 97% of nuggets are bigger than 0.84 mm; furthermore more than 50% are larger than 7.93 mm. These results show that the reduction of low grade iron ore by using sawdust itself as reducer is technically feasible.



(a) (b)

Figure 7. a) Products obtained after processing the self-reducing mixture 43,5% w/w of low-grade iron ore and 56,5% w/w of sawdust at 1773 K (1500 ° C) for 10 minutes. b) iron-carbon nugget obtained in the same sample.

Table 5. Particle size distribution of the processed mixture after its disaggregation

Mesh [mm]	0	<0,84 mm	0,84 mm	2,83 mm	4,76 mm	5,66 mm	7,93 mm
Retained [%w/w]	0	2,8	1,2	9,9	14,8	20,9	50,5
Accumulated [% w/w]	0	2,8	4	13,9	28,8	49,5	100

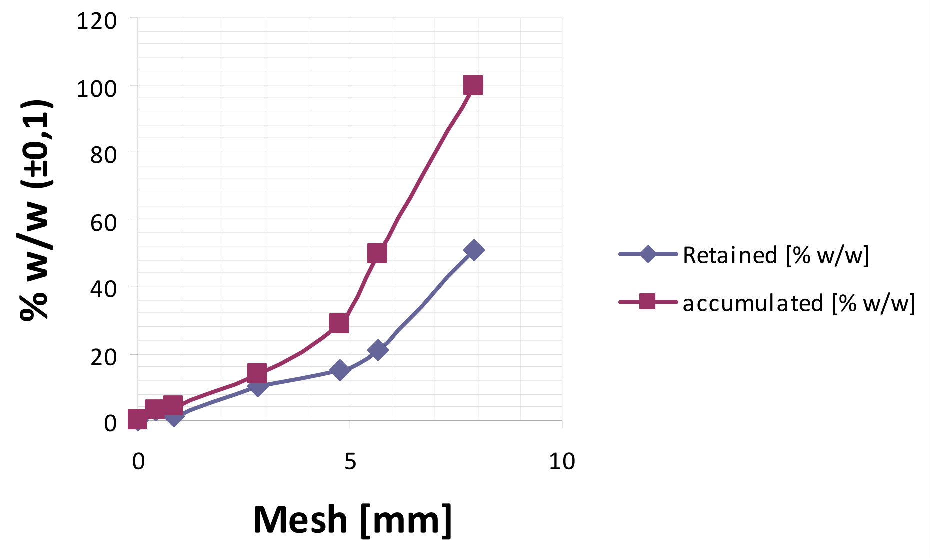


Figure 8. Particle size distribution of the processed mixture after its disaggregation.

4 CONCLUSIONS

Within the experimental conditions used, at laboratory scale rotary graphite kiln, the conclusions were**:**

1. It's possible to reduce directly low grade iron ore with sawdust in rotary kiln at 1773 K (1500 ° C) for 10 minutes.
2. The particle size distribution of iron-carbon nuggets shows that 97.2% is larger than 0.84 mm and more than half is greater than 7.93 mm, showing that reduction of low grade iron ore by using sawdust is technically possible and could be economically feasible.
3. The carbon content of the nuggets is in the range of 5.0% w/w.

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