



Research Article

Production of Bio-Carbon Materials from Animal Manure That Can Be Used in Iron Reduction

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ABSTRACT

The material obtained from cow manure is rich in carbon and has good heat capacity. Its characteristic feature is its predominantly cellulose composition. Research shows that the carbon contained in manure makes it usable as fuel. The use of bio-carbon materials, which have valuable features in terms of renewable and rich resources to replace fossil materials, is important in the metallurgical industry. In this study, the functional group containing carbon and the thermal carbon, hydrogen and nitrogen values of cow manure dry at 105 °C (QD105) and pyrolyzed cow manure dry and at 350 °C (QD350) were investigated using FTIR and CHNS analysis. The study shows that the product of slow pyrolysis (10°C/min) up to 350°C of dry cow manure powder has C, H and N values of equivalent carbon content of 29.77, 2.45 and 2.11%, respectively. Reactions and thermal decomposition of cow manure reduce the CO₂ gas present in its charcoal. The highest heating value (HHV) is 19.82 kJ/Kg. Cow dung charcoal creates different properties in terms of temperature, storage time, heating rate and efficiency. At a temperature of 325–500 °C, CO and CH₄ gases have the highest efficiency.

1. Introduction

Reducing the carbon footprint is a necessity for many researchers in the fields of iron and steel production [1]. Hydrogen technology is expanding in steel production [2] Blast furnaces, electric arc furnaces, and the reduction process are among the situations where hydrogen is used [3]. Zero carbon emissions are targeted for 2050 [4].

Carbon plays a key role in the iron and steel production chain, from generating the required electrical energy to raw materials for reduction reactions and metal extraction. It is mainly obtained from fossil fuels and materials. In a situation where steelmaking is responsible for 6% of global CO₂ emissions [5].

In 2006, the IPCC examined the axes of reducing greenhouse gas emissions and achieved international agreement in this regard, and in this regard, it has set an eight-part breakdown structure [6]. In the first and second parts, metal and mineral industries are mentioned. The IPCC treaty emphasizes the replacement of fossil carbon with biological materials and industrial waste. In Appendix A, it is mentioned that in calculating greenhouse gas emissions, if CO₂ and CH₄ gas emissions are due to the consumption of fossil materials, the emission factor is calculated otherwise, and the use of organic biological resources, the emission factor is not taken into

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account [7, 8]

Carbon is obtained from fossil coal resources and the conversion of low-enriched carbon (about 10-20%) to high-enriched carbon (0.9-80%) is carried out in coking plants. This process requires energy consumption, including extraction from mines, transfer to coking, energy consumption for coke production, etc. Greenhouse gas emissions in this process are significant [10, 9].

The charcoal from Brazil was used as reductant in the smelting experiment to produce Fe-Si 75%. The furnace performed well, and we obtained a metal yield of 89.3% as an average for the last 10 hours with stable production [11]. An increasing focus on sustainability issues in the minerals and metal production industry means that the sustainability of these processes must be assessed at the earliest possible stage in their development. In this paper, life cycle assessment methodology has been used to assess the environmental sustainability of various processing routes for nickel laterite ores in terms of embodied energy and greenhouse gas emissions [12].

Biochar is expensive, but its use provides advantages. By increasing the carbon content of the pyrolysis method, its cost can be justified [15]. Producing biochar from cheap and disposable resources is one known route [16]. Corn waste [17], fruit pulp [18], coffee grounds [19], wheat stalks [20], animal manure [19, 20], and sugarcane bagasse [21] are examples of carbonaceous charcoal used in research. Slow pyrolysis of bamboo at 300 °C under nitrogen has shown the highest efficiency (74%) [22]. Microwave, wet pyrolysis, and fast pyrolysis are among the charcoal production methods [23]. Environmental conditions [24] (heating rate and target temperature) and storage time at high temperature are effective variables in the charcoal production path. Results have shown that the maximum pyrolysis temperature has the maximum decomposition of polymers (cellulose, hemicellulose, and lignin) [25]. Biochars are produced at temperatures below 500 °C, and longer storage time leads to increased ash and decreased hydrogen and nitrogen [26]. The growth of the livestock industry and the demand for milk, for example in Australia, have increased from 3791 kg in 1991 to 6227 kg in 2011. This has led to an increase in manure waste, and the accumulation of cow manure has caused pollution, disease and environmental problems and is responsible for the emission of the greenhouse gas CH₄ at a rate of, 397609 m³/year [27, 28]. Pyrolysis is a rapid and efficient thermochemical process for the clean conversion of manure [29]. The material obtained from cow manure is rich in carbon and has good heat capacity. Its characteristic feature is its mainly cellulose composition. Research shows that the carbon contained in the manure makes it usable as fuel [30]. Each cow produces an average of 30 kg of manure per day, and each kg of it emits the equivalent of 312 kg of greenhouse gases when combined with water [31]. Charcoal production from animal waste has been tested, and hydrothermal

carbonization (HTC), roasting, slow and fast pyrolysis, gasification and combustion are some of the methods for producing biochar [32–34]. In this study, the physical, chemical and thermal properties of cow manure were investigated as a symbolic proposal for other industrial animal wastes, such as poultry. Fourier transform infrared spectroscopy (FTIR), thermal and derivative thermal gravimetric analysis (DTG, TGA), elemental analysis (determining the amount of carbon, hydrogen and nitrogen), and proximate analysis of cow manure were investigated.

2. Materials and Methods

Cow manure was sampled from the industrial manure storage area of the Zara Company in Golpayegan. The sample preparation steps were carried out according to ASTM D 1762-84 standard, including grinding and sieving No. 100 (150) to reach a size of 0.1 mm according to ASTM E11 and Method D 410. The sample was weighed in an amount of 1 gram with a scale with an accuracy of 0.000 and dried in an oven for 24 hours at a temperature of 105 °C in a ceramic crucible with a capacity of 50 cc. Approximate analysis to determine the content of the sample was carried out according to ASTM E872-82 standard to determine the percentage of moisture in the oven and ash and volatile matter according to D 1102-84 standard in a muffle furnace and repeated three times, and the average of the results was taken. A 5-gram amount of manure sample was subjected to slow pyrolysis at a rate of 10 °C / min to produce charcoal in an oxygen-free atmosphere up to a temperature of 350 °C. (The pyrolysis sample and the dried sample were named.) FTIR analysis was performed in the range of 400 to 4000 cm⁻¹ on dry manure and pyrolysis coal samples in a few milligrams using a Bruker instrument to identify organic functional groups according to ASTM E168 and E1252 standards. In order to more precisely identify the type of carbon structures including amorphous (D) and graphite (G), RAMAN spectroscopy analysis was performed separately on QD105 and QD350 in the range of 4000-400 cm⁻¹ using a Thermo Scientific Nicolet instrument according to the ASTM E1683-02 standard. Carbon, hydrogen and nitrogen content of pyrolysis coal. Final analysis according to standard D 3176-89. CHNS analysis of 3.7840 mg of pyrolysis coal (QD350) fertilizer sample was performed using a Perkin-Elmer 2400 II. Investigation of the thermal properties of the sample and the phase transition temperature and thermal stability was performed using a TG-DTG analysis of 5.3340 mg of coal sample from ambient temperature 25 to 800 °C in a nitrogen atmosphere with a temperature increase rate of 50 mL/min and a temperature increase rate of 10 °C/min according to the ASTM E1131 standard using a Metler Toledo device. For DSC calorimetry of QD105 and QD350 samples in controlled environmental conditions under a nitrogen gas atmosphere with a temperature increase rate of 50 mL/min

from 25 to 453 °C with a temperature increase rate of 10 °C/min, a DSC302 device was used.

3. Results and Discussion

3.1. Proximate Analysis

An approximate analysis was performed to show the amount (moisture, volatile matter and ash). According to Table 1. fixed carbon was identified as 11%, residual ash was 11%, and volatile matter was calculated as 57%. In this table, by comparing the results, it can be seen that the fixed carbon content of Dry cow manure is close to FCM and its residual ash is more than FCM and close to the content of Cattle Droppings. The estimated HHV was calculated according to [35]. The HHV obtained based on the approximate analysis data for QD was higher than Cattle Droppings [28].

3.2. Ultimate Analysis

Table 2. shows the results of CHNS analysis of a sample of cow manure pyrolyzed to 350 °C at a rate of 110 °C min (QD350). A comparison of the carbon content of BC300 and BC400 shows that QD350 has a lower carbon concentration, which can be affected by several variables such as season and animal feeding regimen [37]. By performing pyrolysis at a higher temperature and retention time, higher carbon can be achieved. As can be seen, in the sample BC300–10–60 [36], the retention time was 60 min and the carbon content reached 45%.

3.3. FTIR Analysis

FTIR infrared spectroscopy was performed based on the characteristic infrared absorption of the structure by the functional group containing carbon-hydrogen, oxygen and nitrogen. The results are shown in Fig. 1. a and b. in the cases of dry powder QD105 and charcoal QD350. According to the Beer-Lambert law, the higher the wave absorption in the characteristic peak, the higher the concentration of the substance belonging to the characteristic peak [38]. The main gaseous compounds that decompose upon heating are H₂O (3900–3500 and 1800–1300 cm⁻¹), CH₄ (3130–3050), CO₂ (2400–2250, 780–600 cm⁻¹) and [39] CO (2250–2000 cm⁻¹).

For this study, five main functional groups, including (1025cm⁻¹) CO, (991cm⁻¹) NH₃, (11721cm⁻¹) KETONE, (1771cm⁻¹) CARBOXYL and (2211cm⁻¹) CO₂ were compared and investigated. Table 2. shows the percentage reduction in infrared absorption by the QD350/QD105 sample. So that CO₂>CO>NH₃>CARBOXYL>KETONE had the highest reduction, which indicates that the most decomposition and destruction due to pyrolysis occurred in them. The small change in ketone absorption indicates the higher resistance to decomposition of this material to decomposition, and therefore the temperature of 350°C is not sufficient for its destruction and degradation. This change shows that the gases produced and released during pyrolysis are useful and valuable gases, so by designing a suitable process, they can be collected

Table 1. Results of proximate analysis of QD beef dry powder.

RAW	VM	M	FC	ASH	HHV/ Calorific value (J·g ⁻¹)
QD	57.77±2.21	61.55± 5.11	11.71± 0.44	22.23± 1.26	19.82±0.23
FCM[21]	78. 86 ± 1.42	88.40 ± 4.21	9. 94 ± 0.26	11. 20 ± 0.57	-----
Cattle Droppings[22]	64.67±2.08	77.00±0.73	13.02±4.06	22.31±2.52	18.12±0.18
Sheep droppings[22]	53.33±0.58	38.71±3.50	25.72±1.32	20.94±1.29	17.59±0.32
Goat droppings[22]	55.67±0.57	33.30±2.01	22.10±1.20	22.23±1.34	17.46±0.06

Table 2. The results of the final analysis of CHN.

QD350	C	H	O	N	H/C	O/C
	29.33±1.35	2.51±2.17	16.11±0.87	7.16±0.98	0.034	0.220
BC300–10- 60[21]	45.75 ± 1.28	4.01 ± 0.62	19.44 ± 1.23	2.52 ± 0.64	0.087	0.424
BC400–10- 60[21]	45.75 ± 1.28	3.05 ± 0.47	12.97 ± 0.92	2.15 ± 0.58	0.066	0.283

and used in different stages, such as reduction in the blast furnace.

3.4. Raman Analysis

Raman is a standard and non-destructive tool for identifying crystalline, non-crystalline and amorphous carbon structures. To further understand the morphology of carbon in charcoal and the changes caused by pyrolysis, Raman analysis was performed. Fig. 2 (b, a). shows the Raman spectra of QD105 and QD350. In Raman analysis, we look for two main structures, graphitic G and disordered amorphous D [40]. Four Lorentzian ($D_1 \sim 1360$, $D_2 \sim 1620$, $D_4 \sim 1180$, $G \sim 1580$) and Gaussian (D_3 1500) [41] bands were recorded. Examination of the intensity of the D_2 , D_3 , and D_4 peaks showed that there was no noticeable change in these positions. Given that the two structures have Raman absorption oscillations approximately at 1580G (ideal graphite lattice) and 1320 D_1 (disordered graphite lattice) and are present in the range of 800 to 2000 cm^{-1} , the rest of the spectra were ignored. A decrease in the total absorption value was observed in QD350 compared to QD105. Fig. 2 (d, c). shows the change in the amount of D, G structure present in QD350 compared to QD105. It can be seen that the intensity of the absorption peak of the I_G structure has a major contribution in both cases. By performing pyrolysis, the amount of I_G has decreased and the amount of I_D has increased. Therefore, it can be seen that pyrolysis has caused an increase in carbon in the disordered amorphous form D_1 .

3.5. TG-DTG Analysis

The thermal stability of QD350 charcoal was evaluated by TG-DTG analysis. The reaction atmosphere was maintained by nitrogen gas injection and a heating rate of 10 °C/min starting from ambient temperature to 800 °C. Three stages of mass reduction of charcoal material were observed during TG. According to Table 4. from 25 to 207 °C, the main factor of reduction in this stage is evaluated as 4.28% due to water removal during evaporation. In the DTG results (Fig. 3.), an endothermic peak is observed at 71 °C. 12.49% of the total residue is reduced by 95.72% in the temperature range of 209–504 °C. The

DTG results showed an endothermic peak of charcoal at 446 °C. The cause associated with this stage is the destruction and decomposition of aliphatic structures, cellulose and hemicellulose, and parts of lignin [38]. With the passage of time and continued heating to a temperature of 800 °C, a mass reduction of 15.85% of the remaining 83.23% occurs. The maximum endothermic peak at 675 °C in the DTG diagram shows the endothermic of charcoal at this stage. When the temperature reaches 800 °C, 67% of the mass of the raw material remains. This can be from fixed carbon and lignin residues.

3.6. DSC Analysis

Differential scanning calorimetry was performed in vitro with a nitrogenization rate of 50 ml/min and a heating rate of 10 °C.min⁻¹ from ambient temperature to 453 °C. Fig. 4 (a, b). shows the curves of changes in the endothermic and exothermic reactions during heating that occurred in QD105 and QD350. The dip in the graph from 68 to 200 °C indicates maximum endothermic loss due to water loss and evaporation [42].

Starting at a temperature of 210°C, the decomposition and destruction of cellulose, hemicellulose, and lignin structures, which will generate heat, continues heating up to 453°C. In the QD105 sample at 253 °C, fluctuations occur that could be due to cellulose decomposition and aromatization. The enthalpy of the reaction of QD105 was measured to be 173.421 J/g in the temperature range of 240 to 350 °C (at a heat flow of 0-1.5 mW). While the enthalpy of QD350 in the same range and heat flow was 215.511 J/g. Therefore, pyrolysis has caused a change in enthalpy (increase). In the study of Powell et al. [43], DSC analysis on elephant manure reported two endothermic reactions at 37-146, 158-252 °C. The exothermic reaction in this study was located in the range of 252–300 °C. Considering this, we know [44] that the degradation of hemicellulose ($C_5H_8O_4$, $C_6H_{10}O_5$) at The temperature (225-325°C) and cellulose ($C_6H_{10}O_5$ - $C_6H_{12}O_6$) at temperatures (305-375°C). With increasing temperature to 207°C in sample QD105, the endothermic to exothermic reaction change occurs, while in sample QD350, the reaction change occurs at 192°C. The peak observed at 251°C in sample QD105 is related to the degradation of hemicellulose, while in QD350, the fluctuation occurred at 245°C.

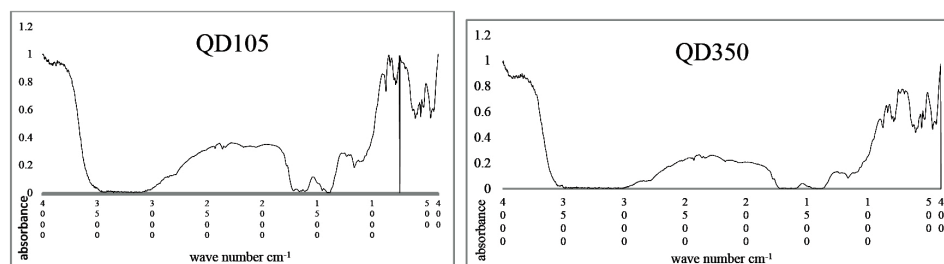


Fig. 1. FTIR spectra of different QD105, QD350.

Table 3. The absorbance change in compounds.

CO ₂ (221cm ⁻¹)	68.75161
CO (1025cm ⁻¹)	66.07094
NH ₃ (991cm ⁻¹)	63.80427
CARBOXYL (1771cm ⁻¹)	39.74469
KETON (11721cm ⁻¹)	16.90418

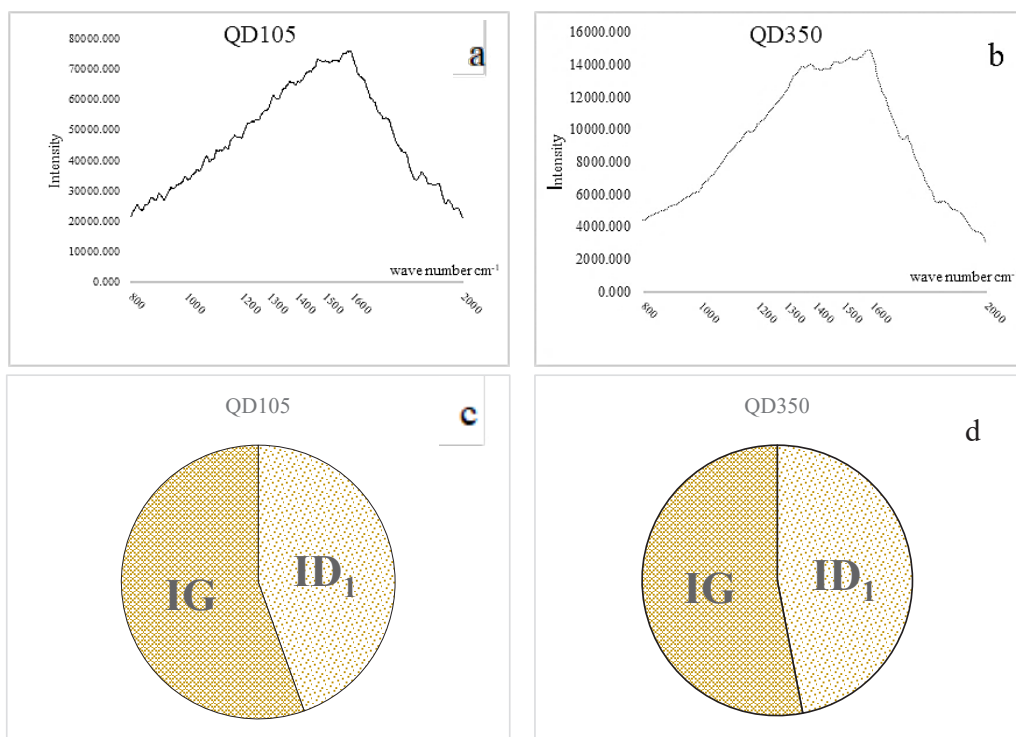


Fig. 2. Raman spectra: a) QD105 ,b) QD350 ,c) I_{D1}/I_G(QD105) , d) (QD350).

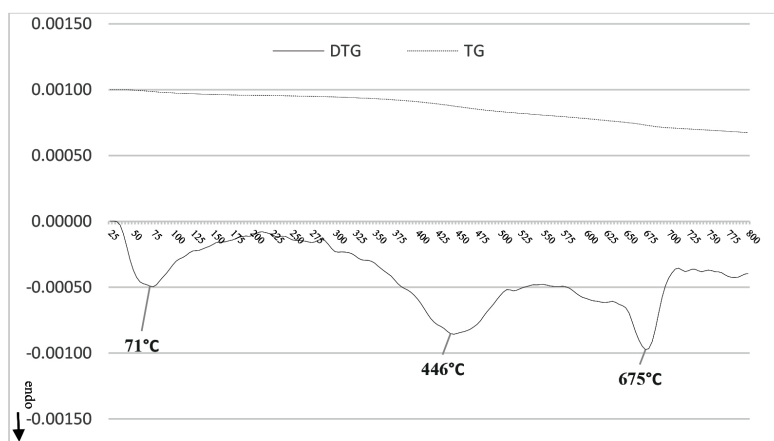


Fig. 3. TG/DTG curve of sample QD350.

Table 4. Mass reduction stages at different temperatures of QD350.

	STEP I	STEP II	STEP III	RESIDUE
TEMPERATUR	25-207	209-504	504-800	
QD350	4.28%	12.49%	15.80%	67.37%

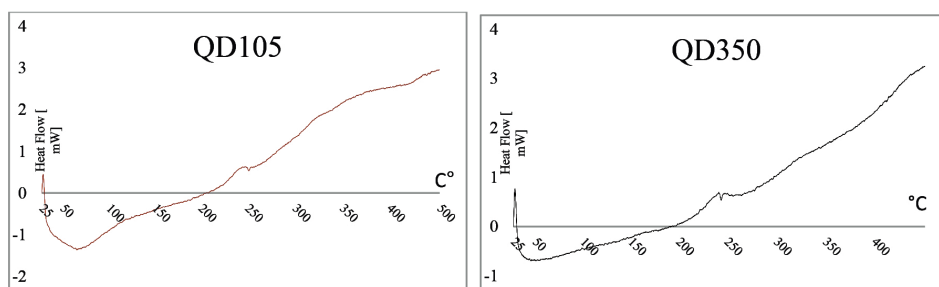


Fig. 4. DSC calorimetry a) QD105 and b) QD350.

4. Conclusions

The final analysis of the CHNSO results showed that the amount of carbon in animal manure was justified for extraction and that the pyrolysis method was an effective method for producing charcoal, green steelmaking, and green regeneration.

FTIR results of studying the changes in absorption in biomass and biochar showed that, based on the functional group, the gases released during pyrolysis were mainly CO₂ and CO and could be sources of green gas supply for regeneration.

RAMAN The changes in the carbon structure from graphitic to amorphous form were investigated in this analysis.

TG/DTG The thermal stability of the charcoal was shown based on the residual amount after 800 °C.

DSC Enthalpy was investigated in a specific temperature range and heat flow of 1-1.5 mW, and endothermic and exothermic reactions were determined.

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