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# Influences of pyrolysis parameters on the physical and chemical fuel qualities of pyrolyzed biomass briquettes for metallurgical use

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**Abstract.** The iron and steel industry needs for every ton of finished steel product a minimum of 250 kg of fossil coke. A CO<sub>2</sub>-neutral substitute of coke is biocoke to improve the carbon footprint of iron and steelmaking industry. Unused woody and straw-like biomass residue can be agglomerated to briquettes and using a pyrolysis technique transformed to biocoke. Objective of this study was the production and analysis of this biocoke regarding its possible use within the blast furnace by applying various pyrolysis temperatures of 200, 350, and 500 °C. Physical (mechanical strength) and chemical fuel qualities (proximate analysis, ultimate analysis, and calorific value) were investigated. It is asserted that with a rise in the pyrolysis temperature the physical fuel qualities are negative and the chemical ones positive effected. None of the used temperatures created a biocoke that can entire substitute the hitherto in the metallurgical industry used fossil coke with all its characteristics. Nevertheless, extensive knowledge about the behavior of various fuel qualities while rising the pyrolysis temperature was gained.

## 1. Introduction

During the era of climate change and exhaustion of resources, it is humanity's responsibility to reduce energy use and emissions. Energy is increasingly generated by renewable sources; however, this action is not sufficient to keep this planet within equilibrium for future generations.

The iron and steel industry is one of the most energy intensive industrial sectors. Each ton of produced crude steel consumes 20.6 GJ primary energy at an average [1]. In total 6% of the world's primary energy demand are used by this industry [1-3]. The global production of crude steel was 1,629.6 Mt in 2017 and the trend was increasing over the last two years [3, 4].

Every ton of finished steel product (blast furnace / BOF) needs a minimum of 250 kg fossil coke [3]. The coke functions in the blast furnace as a reduction agent, an energy source, a supporting framework with adequate gas permeability, and a carburizer [5]. Using this fossil resource a significant amount of CO<sub>2</sub> is emitted. 7% of the globally released greenhouse gases can be ascribed to the iron and steel industry [6].



A reduction of these emissions and a sustainable use of energy can be effectuated by a substitution of the fossil coke by a CO<sub>2</sub>-neutral biocoke. Brazil produced in 2003 28% of its pig iron in distinctive for charcoal designed blast furnaces. However, within the OECD Nations only 0.1% of the needed energy sources and reduction agents are deriving from renewable like regrowing resources [7]. Today and in future, there is a great demand of possible use of biocoke within the conventional blast furnaces.

A variety of biomasses within primary and secondary application can be used to produce biocoke. Biomass waste has the advantage of not being in competition with the food and feed industries. Residual materials can derive from different sectors, but are mainly originated within agriculture and forestry [8, 9].

Brazil and Germany, both among the top ten of steel producing nations, should focus on biomass, which is not used in any productive utilization hitherto [3]. Biomasses rich in lignin, such as woody and straw-like biomass, are suitable [10]. Lignin serves as a natural binder during previous briquetting and it is advantageous for the following pyrolysis because of its high carbon content [11]. Germany has an unused fresh biomass potential of approximately 50 Mt [12]. 15 Mt are straw-like material; other main residue is a variety of woody biomasses and excrements of animals [13, 14]. In Brazil, the unused biomass residue is about 600 Mt fresh biomass, whereas the main fraction of 150 Mt is originated from sugarcane bagasse [15]. During the last 20 years, the production of sugarcane increased explicitly.

The biomass potential of both nations, particularly Brazil, is available to produce biocoke. In one possible procedural method woody and straw-like material are first densified by agglomeration. Secondly the pyrolysis is performed. The biocoke should approximately have all aforementioned physical and chemical fuel qualities of a fossil coke. The briquettes should stay strong and stable during storage, transport, handling, and thermal treatment in the blast furnace. Therefore, the produced biocoke should have the highest possible mechanical strength to be functional. Additionally, for a use in the blast furnaces, the carbon content is to maintain high to have a high energy density and to work as a reduction agent.

## **2. Material and methods**

Twelve pyrolysis runs were performed. Each following mentioned material was pyrolyzed with three different temperatures (200, 350, and 500 °C). Ten pieces of fire wood respectively biomass briquettes with a diameter of 28 – 30 mm and a mass from 6 – 10 g were used in each pyrolysis.

### *2.1. Sample material*

The samples used for the pyrolysis were different wood and strawlike biomasses. First pure fire wood of beech (FWB) and pine (FWP) was used. Fire wood is traditionally used for charcoal production and the chosen materials are suitable references. Second briquettes of wood chips (BWC) and sugarcane bagasse (BSCB), which represent typical biomass residue of Germany and Brazil, were pyrolyzed and analyzed. The chemical composition of the samples is shown in Table 1.

**Table 1.** Chemical analysis of materials as received in [%].

	Beech	Pine	Sugarcane bagasse	Wood chips
Carbon	48.99	49.73	47.16	48.93
C <sub>fix</sub>	15.25	12.38	15.18	16.20
Ash	0.23	0.18	2.61	1.40
Volatile matter	84.52	87.44	82.21	82.40
Gross calorific value [MJ/kg]	20.4158	20.7915	18.69	21.1600
Hydrogen	6.14	6.22	5.92	6.79
Nitrogen	0.170	0.144	0.207	0.272
Sulfur	< LOD*	< LOD*	< LOD*	0.02
Oxygen	44.48	43.72	44.10	42.59

\*LOD = Limit of detection

### 2.2. Sample preparation

Wood chips (WC) and sugarcane bagasse (SCB) were milled with a shredding mill with a transmittance of 2 mm. The particles were agglomerated to cylindrical briquettes by a piston press using a matrix with a diameter of 30 mm, a pressure of 200 MPa and a temperature of 60 °C. Fire wood and briquettes were completely dried at 105 °C before pyrolysis.

### 2.3. Tumble test

The mechanical strength by tumble test (durability) was determined using a self-developed method which depends on DIN 51717 [16] and ISO 17831-2 [17]. Three briquettes or pieces of fire wood are tumbled for 100 revolutions with a velocity of 25.5 rpm. The tumble with a diameter of 244 mm has four lifters. The durability is calculated using equation (1).

$$DU = \frac{m_A}{m_B} * 100 \quad [17] \quad \begin{array}{l} DU = \text{mechanical durability [\%]} \\ m_A = \text{mass sieved, 16 mm sieve, after tumble test [g]} \\ m_B = \text{mass sieved, 16 mm sieve, before tumble test [g]} \end{array} \quad (1)$$

### 2.4. Chemical analysis

The chemical fuel analysis includes the determination of ash content, specific gross calorific value and ultimate analysis according to norms DIN EN ISO 18122 [18], DIN EN ISO 18125 [19] and DIN EN ISO 16948 [20]. Referring to norm DIN EN ISO 18123 [21] the content of volatile matter is determined. The fixed carbon C<sub>fix</sub> (DIN EN ISO 16599 [22]) and oxygen content is determined by calculation.

## 3. Results and discussion

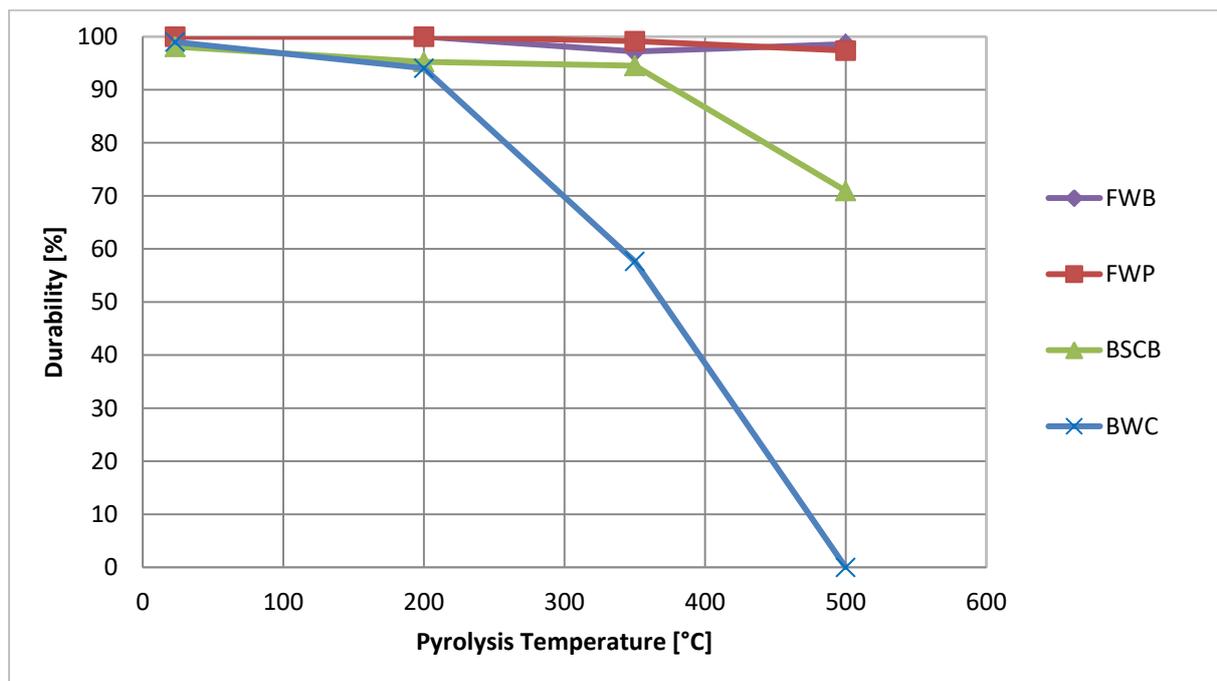
Briquettes and fire wood were analyzed by the methods previous mentioned with respect to different mechanical and chemical fuel qualities. A comparison of different materials and a comparison of the same material and different pyrolysis temperatures were performed.

### 3.1. Physical fuel qualities

Physical fuel qualities developed, with increasing pyrolysis temperature, contrary to the desired high mechanical strength in the blast furnace. The durability and the density decreased. The major change occurs from 200 to 350 °C, because of the pyrolytic decomposition during this temperature range.

The durability of all materials in its initial state is close to 100%, as shown in figure 1. This value changes marginal with a rise of pyrolysis temperature for FWB and FWP. At the contrary, the briquettes display a clearly decrease. BSCB had with 94.5% a barely higher durability than BWC with 94.0% at 200 °C. This difference increases with an increasing pyrolysis temperature. The durability of BWC is 0% (only undersized grain) and of BSCB it is 70.9% at the highest temperature of 500 °C. The reason for this is the particle size of the various materials. Fire wood consists of one natural grown piece. The impact forces cannot free singular particles. This possibility exists for briquettes. SCB consists of a very fibrous material. After milling some fibers were > 2 mm in length, but extremely thin, such that they could pass the sieve (mesh 2 mm) during milling. These longer particles lance through the major parts of the briquette. They have bondings, which connect the outer particles with the inner ones, and therefore, the particles cannot be easily removed by the impact forces. Contrary the wood chips had a great portion of very small, dust like particles. The smaller particles can be easily removed from the edges of the briquettes. Internal particles are increasingly exposed to the impact forces and the durability decreases.

The durability of the briquettes is insufficient for proper utilization in the blast furnace. A durability closes to the fire wood materials at 500 °C of 98 % is desirable.



**Figure 1.** Investigation of durability from various woody and straw-like biomasses in dependence on pyrolysis temperature.

The intermolecular hydrogen bonds are one main reason for the behavior of durability. They are broken during drying or latest during pyrolysis. Furthermore, hydrogen bonds are destroyed with a rise in pyrolysis temperature by elimination of oxygen. The mechanical strength decreases. The former elastic woody and straw-like material becomes brittle with an increasing carbonization.

The pyrolytic degradation of biomass rises with an increase of the pyrolyzing temperature. Parallel occurring change in volume are less distinctive, consequently density decreased. The density of the materials is between 319 and 476 kg/m<sup>3</sup> at 500 °C, in contrast the average density of a fossil coke is

about 1,000 kg/m<sup>3</sup>. A low density degrades the productivity of the blast furnace. Simultaneously the connection of a low density of a pyrolyzed biomass briquette leads to a low mechanical strength.

### 3.2. Chemical fuel qualities

An increase of pyrolysis temperature leads the chemical fuel qualities towards the standard of fossil coke used in blast furnaces, except of the ash content, as shown in table 2. The major change occurs for the same reasons previously mentioned, between 200 °C to 350 °C.

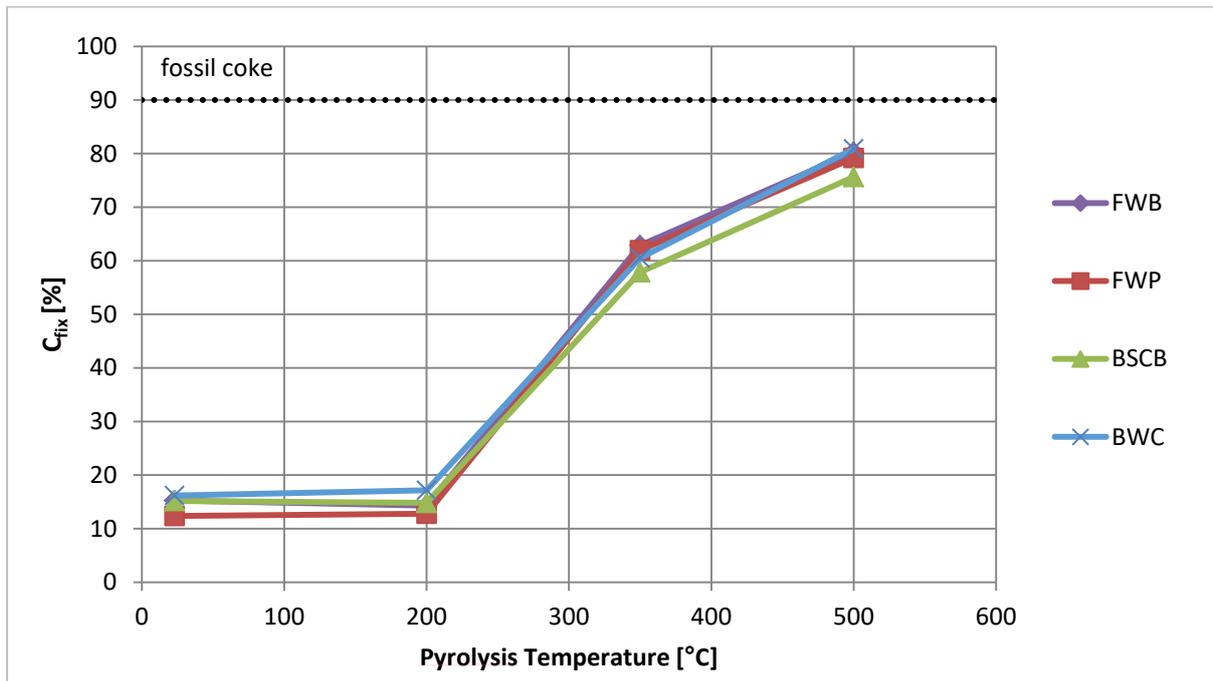
**Table 2.** Chemical fuel qualities of the materials after pyrolysis of 500 °C in [%].

	FWB	FWP	BSCB	BWC	Standard fossil coke
Carbon	86.73	85.61	75.54	81.64	
C <sub>fix</sub> (calculated)	80.26	79.2	75.65	80.88	90 [23, 24]
Ash	1.52	0.79	10.77	4.37	<9[7, 23]
Volatile matter	18.22	20.01	13.58	14.75	<1[7, 24]
Gross calorific value [MJ/kg]	33.3873	32.7383	30.1820	32.1810	29.7 [25]
Hydrogen	3.12	3.30	2.73	2.95	
Nitrogen	0.344	0.145	0.407	0.558	0.8 [26]
Sulfur	< LOD*	< LOD*	< LOD*	< LOD*	<1 [23, 24]
Oxygen (calculated)	8.28	10.15	10.55	10.48	

\*LOD = Limit of detection

An increase of pyrolysis temperature results in an increase of pyrolytic degradation. The total mass decreases and the percentage of ash within the total mass increases. Ash is ballast, which produces slag within the melt and has to be removed with an energy consuming procedure. A low ash content of < 9% [7, 23] is needed for the use in the blast furnace. The industries except sometimes an ash content up to 15% [26]. According to this characteristic, the tested materials can be used in the blast furnace. Fixed carbon functions as a reduction agent, energy source, and it is an important characteristic of the coke substitute. An increase in pyrolysis temperature leads to an elevated fixed carbon, as shown in figure 2. The standard of fossil coke of 90% fixed carbon is not reached [24]. A higher temperature raises the degree of coalification. Volatile matter desorbs by pyrolysis and do not stay or do stay in a very low percentage within the product. Consequently, fixed carbon is increasing. C<sub>fix</sub> correlates to the ash content. BSCB had a very high ash content of 10.77% and therefore, it cannot reach the standard of 90% fixed carbon. A substitution in the blast furnace as a partial substitute using different burden proportions is possible.

The high gross calorific value supports the partial or full substitution by biocoke pyrolyzed at 500 °C. All materials exceed the standard value of a fossil coke of 29.7 MJ/kg, as shown in table 2.



**Figure 2.** Investigation of  $C_{fix}$  from various woody and straw-like biomasses in dependence on pyrolysis temperature.

*3.3. Correlation of physical and chemical fuel qualities*

There is a contrary behaviour of the physical and chemical fuel qualities while increasing the pyrolysis temperature. The chemical characteristics display possible use of the product, pyrolyzed at 500 °C, in the blast furnace. In contrast, the physical characteristics preclude that use. This phenomenon is reversed at low pyrolysis temperatures. The charcoal-like materials of beech and pine are an exception.

**4. Conclusion and future prospects**

The development of a high-quality biocoke with equally satisfying physical and chemical fuel qualities that correspond to standards of a fossil coke which is currently used in the iron and steel industry, was not achieved. Contrary correlation while increasing the pyrolysis temperature prevented that. Following insights were obtained:

- Negative development of physical fuel qualities while increasing pyrolysis temperature.
- Positive development of chemical fuel qualities (except ash content) while increasing pyrolysis temperature.
- Particle size and particle shape is essential for the mechanical strength of pyrolyzed biomass briquettes. Fibrous materials have a higher mechanical strength than materials with a great quantity of small particles.
- Qualitative statements about the tendentious behavior can be based on the pyrolysis temperature and / or on the trend of other fuel qualities.
- The major change of the analyzed characteristics occurs between the pyrolysis temperatures of 200 °C to 350 °C.
- A partial substitution of fossil coke is possible. Further preliminary tests or a general improvement of physical and chemical fuel qualities are necessary to achieve a full substitution.

The obtained results can be used to concretize and develop new methods of in future performed analyzes:

- Analysis with the mentioned methods of a fossil coke used in the industry to achieve a better benchmark
- Series of tests with more woody and strawlike materials
  - o Investigation of different material behavior and their relationships
- Performing pyrolysis with smaller temperature intervals ( $\Delta$  50°C) and expansion of the temperature range (200 - 600 °C)
  - o Development of qualitative and quantitative statements of pyrolysis temperature and of the development of other fuel qualities.
- Analyzing mechanical strength applying a typical blast furnace atmosphere.
- Melting test to control the applicability

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