



Sustainable EAF steel production (GREENEAF)

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EXECUTIVE SUMMARY

WP1 BIOMASS SELECTION FOR EAF CHAR PRODUCTION (TECNOCENTRO, CSM, IP)

WP is devoted to the analysis of availability of biomass in the area around the steel factories participating to the project. In fact, in order to make the biomass utilization economically convenient transportation costs must be reduced as much as possible.

The analysis of biomass availability has been carried out close to the steel plant of Ferriere Nord (Italy), DEW (Germany) and MH (Austria). Following Table reports the amount of total biomass amount close to the steel plants and the steel plant biomass demand.

In general, biomass is collected from agricultural residues, from forest residues, wood industry or can be cultivated.

Within this activity some biomass species have been selected for characterization activities:

- forest residues (including ligneous species as saw dust for pellets or pulp)
- grapewine and corn stalk as agricultural residues
- mischantus and sorghum as biomass from cultivation

Following Table summarises the main vantages and disadvantages of different biomass specie

Biomass	Advantages	Disadvantages
Forest residues	large amount available and well distributed during year	relatively high energy necessary for collection and transportation
Corn and grasewines	large amount; low cost	larger ash content and nitrogen (see analysis) respect other biomasses
Mischantus and sorghum	large amount available; present in both North Italy, Austria and Germany; high energy ratio. nitrogen and ash amount smaller than residues form cultivations	Need of dedicated cultivation, large productivity after second year of implantation; nitrogen and ash amount larger than forest residues

Summary of main characteristics of different types of biomass.

Samples of biomass of types described in Table 2 have been collected. The following characterization activities have been carried out on selected biomass:

1. Physico-Chemical characterization in terms of chemical composition, ash content, ash composition and properties, heating value;
2. Thermogravimetric tests

Table below summarizes performed characterization activities on selected biomass

Data*	Ligneous biomass (Forest residues)	Corn straw	grapewine	mischanthus
LHV* [kJ/kg]	20000	18000	18900	19100
Volatiles (%)	80	76-81	78	78
Ash (%)	1.1	5.5	3.9	3.5
C (%)	51.5	47.3	46.2	48.2
H (%)	6.7	5.4	5.5	5.4
N (%)	0.3	0.8	1.3	0.6
O (%)	39.7	43.2	37.7	42.1
S (%)	0.04	0.05	0.03	0.06
Cl (%)	0.05	0.2	0.05	0.2

* Lower Heating Value

Characterization activities performed on selected biomass

The performed analysis showed that the selected biomasses have very similar elemental analysis in terms of C/H/O and similar volatile matter content. Biomasses heating value is also very similar. Main differences can be found in minor elements (as N, S and Cl) and ash amount.

WP2 TAILORING OF BIOMASS PYROLYSIS (TECNOCENTRO, CSM, IP)

WP3 CHEMICAL AND PHYSICAL CHARACTERIZATION OF CHAR PRODUCED BY BIOMAS PYROLYSIS (IP, CSM, RWTH)

WP2 is devoted to the definition of the influence of the pyrolysis conditions in terms of temperature, residence time, material size, atmosphere composition on char and biogas yields and characteristics.

WP3 is devoted to define the yield and the quality of the char produced in terms of chemical composition, impurities content and relevant physical characteristics, as a function of pyrolysis conditions defined in WP2. Being the two WPs strongly connected, their activities are presented jointly in this same paragraph. Pyrolysis products are charcoal, condensable vapours and syngas. The percentages of formed products depends on pyrolysis heating rate, residence time and reaction temperature. Moreover the characteristics of formed products (in terms of composition, porosity, combustion behaviour and so on) are a function of pyrolysis conditions.

The following characteristics of char and syngas have studied:

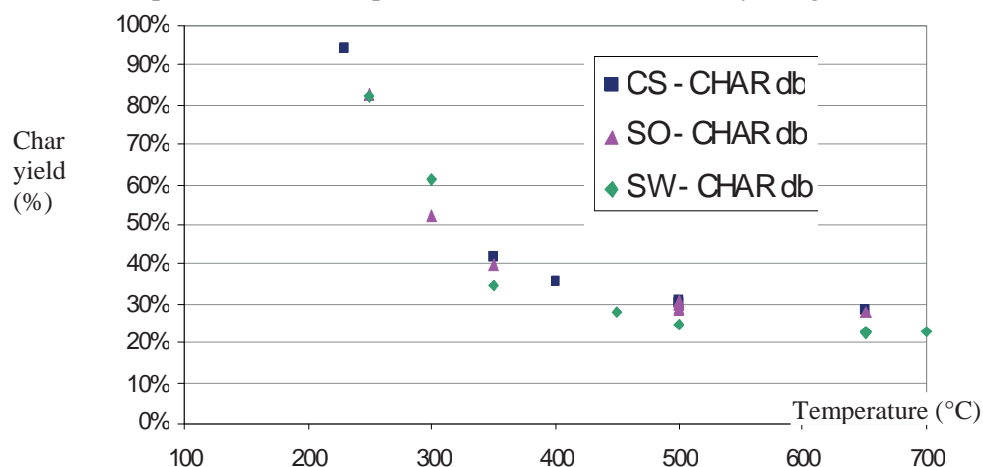
- Char/syngas yield as a function of different pyrolysis conditions and starting biomass
- chemical composition and porosity
- heating values of char as a function of different pyrolysis conditions and starting biomass
- syngas composition and heating value as a function of different pyrolysis conditions
- char reactivity
- comparison of char reactivity with coal reactivity
- Char proximate analysis

Laboratory tests are carried out with:

- thermobalance, to follow weight variation as a function of time and temperature (TG tests), using also different atmosphere and low heating rates (order of magnitude of 1-20 °C/min),
- Wire Mash Reactor, for high heating rate,
- Gray-King furnace, an apparatus used for testing coals according to the British Standard method-BS1016-107.2.

According to the performed tests the starting biomass particle size does not affect the general yield in terms of char, tar and syngas.

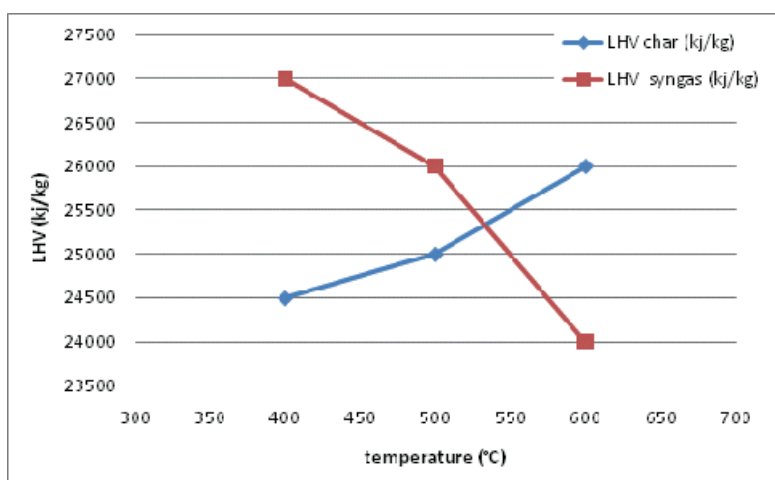
An important result is that, after 500°C, the char yield is almost stable, and this result does not depend on the biomass type. Figure below reports Char yield as a percentage of the original biomass (dry basis) as a function of temperature (°C) in experiments conducted in the Gray-King reactor.



Char yield for three different biomasses (CS: ligneous biomass, SO cultivated biomass, SW: biomass from residues)

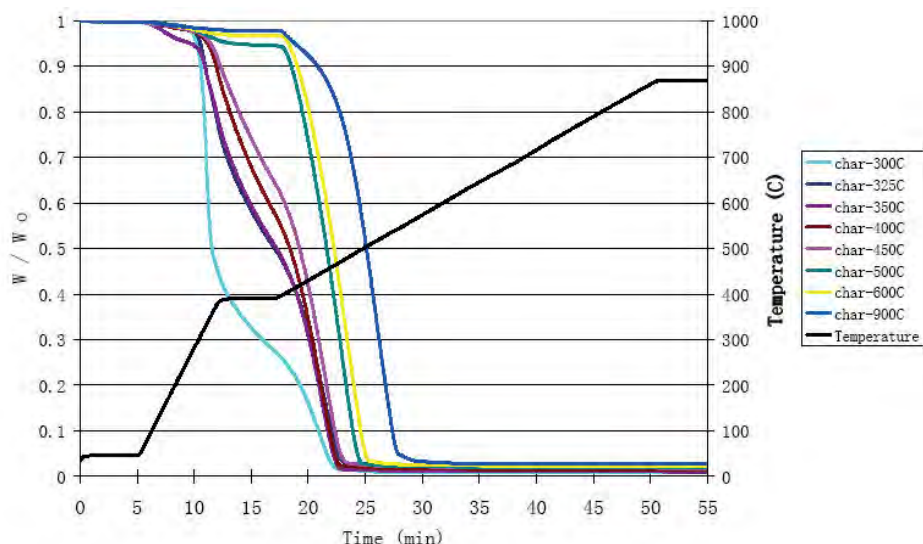
Syngas composition has been determined connecting a mass spectrometer As an example, following curve compare char and syngas heating value as a function of pyrolysis temperature. Char heating

values is measured, while syngas heating value is calculated from syngas composition measured with mass spectrometer during TG test (Figure below).



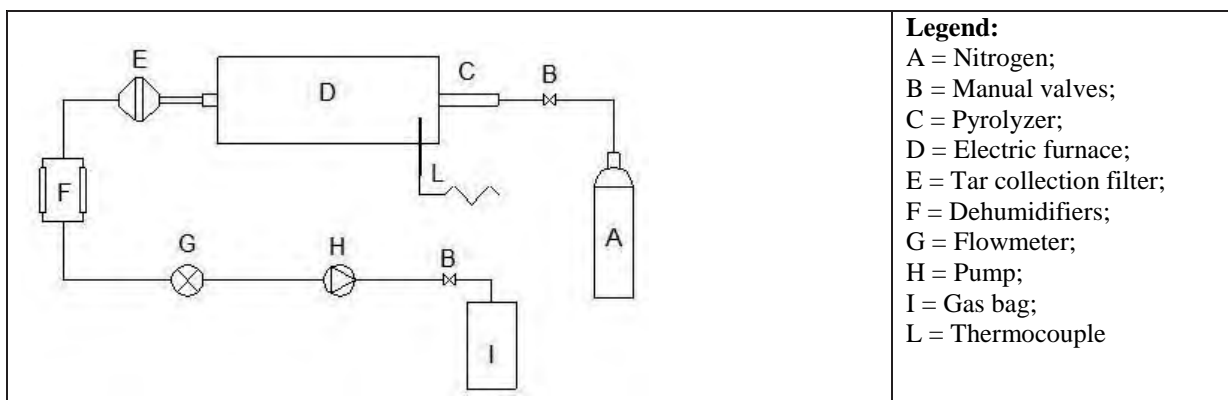
Heating value of syngas and char as a function of pyrolysis temperature

The reactivity of the chars was assessed in a thermogravimetric apparatus by both isothermal and non-isothermal methods. Below is reported result from non-isothermal determination. In this test, after an initial step in an inert atmosphere, the gas is switched to air at the beginning of the temperature ramp from 400 to 850°C. As expected, the chars produced at higher temperatures present lower reactivities. However, at the low end of the pyrolysis temperature range, there are marked differences between the behaviour of the 300°C char, which shows a high volatile content, and that of the chars produced between 325-450°C. There are as well significant differences between the latter and those chars generated at 500-600 °C, which present the same reactivity among themselves.



TGA non-isothermal char reactivity tests of beechwood chars produced in the Gray-King reactor. Curves of fraction of remaining weight for the different chars and temperature as a function of time are shown.

The tests performed by IP confirmed that char, gas and tar yield are almost stable after 500°C. A good compromise for pyrolysis temperature can be considered the value of 500°C. Validation of these results has been done by Tecnocentro, a by a small scale pyrolysis apparatus test. The laboratory system is composed by an horizontal electric furnace which works in nitrogen atmosphere. Scheme of the apparatus is reported below.



Scheme of laboratory pyrolysis furnace

Tests have been carried out with ligneous biomass and agricultural residues. Char, tar and gas percentage produced after different pyrolysis campaigns, were measured. Table 4 reports the amount of formed products for different biomass at 500°C, for a fixed residence.

BIOMASS	CHAR (% wt)	GAS (% wt)	TAR (% wt)
Sorghum pellet	35.9	52.8	11.3
Grape raspe	29.0	49.0	22.0
Dried wood	31.0	51.0	16.5

Char and gas percentage produced after different pyrolysis campaigns

After laboratory tests pyrolysis campaigns were carried out on demonstrative plant **to take char and pyrogas samples** in order to study their characteristics **varying process parameters** and define the best condition for char production from biomass.

The effect of the main process parameters, such as different combination of rate of heating, time of treatment and the rotation speed of pyrolysis reactor have been considerate.

The demonstrative pyrolysis plant can be fed with about 200 kg/h of fuel and the necessary heat energy for pyrolysis reactions is supplied by a gas burner of the maximum power of 500 KW.

The photo below shows the pilot plant: pyrolysis reactor, gas cleaning system and the microturbine.



Enerpol pyrolysis plant (Tecnocentro)

During the tests on different kind of fuel, the pyrogas has been burnt in the torch and sampled; the tar, which in biomass is in the percentage of 7-11% has been eliminated from the gas in the treatment section and collected in the tank with cooling and washing water.

So, for each test and different biomass, the yields have been sampled, weighed and analyzed to highlight the correlation between product characteristics and process parameters.

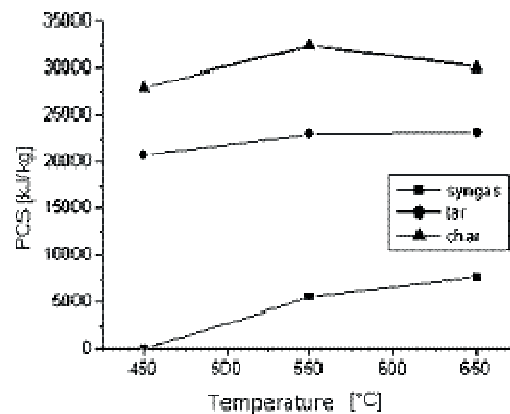
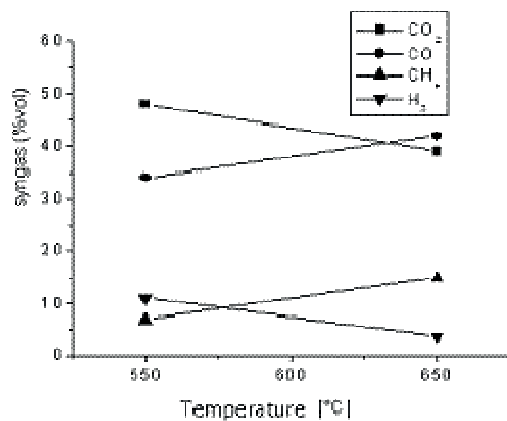
The main monitored and variable pyrolysis parameters are:

1. Pyrolysis temperature (optical pyrometer);

2. Gas temperature out from the reactor;
3. Gas pressure out from the reactor;
4. Internal reactor pressure;
5. Rotation speed of the reactor (residence time);
6. Feeding speed varying the rate of the feeding metering screw;
7. Chemical and physical properties of the feeding fuel;
8. Chemical - physical characteristics (density, elemental analysis, heavy metals), temperature and mass balances of char and gas obtained;

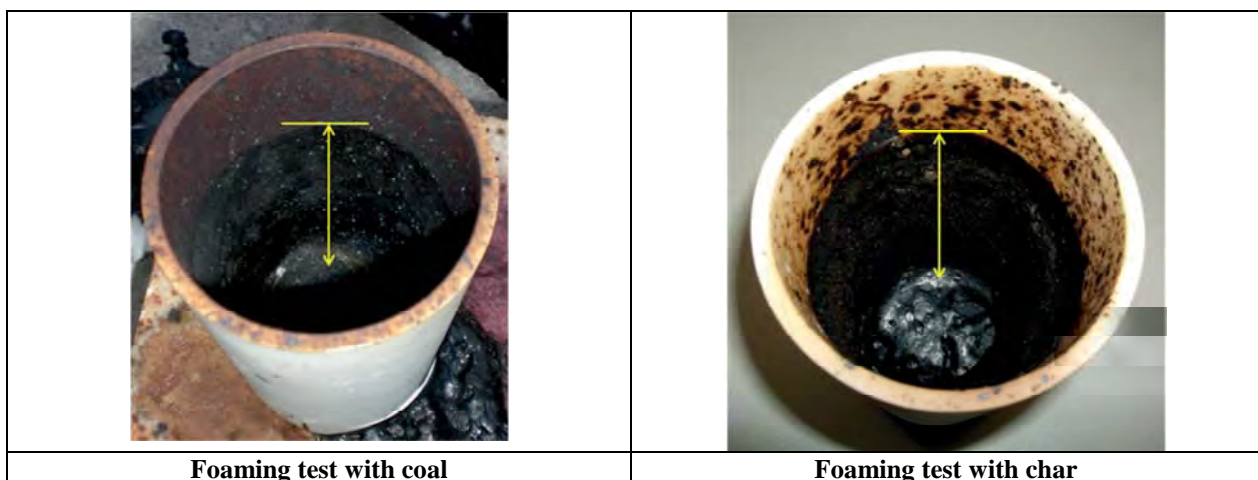
The **gas product** is typically a mixture of carbon dioxide (9-55% by volume), carbon monoxide (16-51%), hydrogen (2-43%), methane (4-11%) and small amounts of higher hydrocarbons.

Temperature affects char composition. Chars produced at higher temperatures having higher carbon contents both total- and fixed-carbon; **higher temperatures lead to lower char yield in all pyrolysis reactions.**



Influence of temperature on pyrogas composition and on Higher Heating Value of pyrolysis yields

Preliminary laboratory tests were carried out to have a first evaluation of char vs coal foaming behaviour. The trials have been conducted using slag sampled from the DEW EAF right before slag foaming. Foaming slag are carried into alumina crucible, filled with a mixture of pulverized char or coal and put into a furnace at 1600°C. The foamy slag is increasing the slag volume and leads to a freezing of slag to the inner crucible wall up to a height indicative of the maximum volume increase during the trial. Figure below shows pictures of the crucibles after the slag foaming trials. Within these pictures the foamy slag height reached during the trial is marked.



Crucible after laboratory foaming tests

The achieved volume increases clearly show the general suitability of the char for slag foaming.

WP4 DEFINITION OF THE EAF OPERATING PRACTICES (DEW, FENO, CSM, RWTH, MU, TECNOCENTRO, IP)

Activities preparatory to industrial trials have been performed consisting in:

1. To perform test in pilot plant of RWTH
2. Analysis of EAF cycle of the steelmakers, to design an operating practice

The pilot plant tests at RWTH have been started with trials investigating the slag foaming capability of the charcoal delivered by Tecnocentro and comparing it to conventionally used fossil coals.

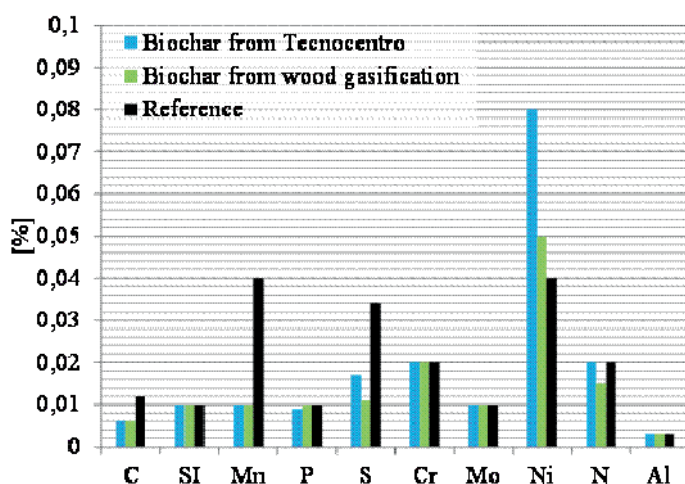
Regarding the tests into the pilot EAF plant of RWTH two types of biochar have been tested in the pilot plant as charge coal and as injection. Additionally tests with reference materials have been performed to compare the results from biochar tests with the standard situation in the industrial mills. As reference materials, anthracite coal and petrol coke presently used at DEW Siegen were used. The different compositions have been analyzed and the results are shown in **Table below**.

[%]	Biochar from grape seed (TC) ¹	Biochar from wood residues ²	Anthracite (DEW)	Petrol Coke (DEW)
Carbon	77.5	60	86	93
Ash	9	21	11.1	5.8
Volatiles	7.7	13.5	2.6	1
Humidity	5.6	5.2	-	0.2
Sulphur	0.3	0.06	0.3	1
Phosphor	0.5	0.4	-	-
Grain Size	<5 mm	<<1 mm	6-12 mm	<1 mm

¹: mean of 3 measurements; ²: mean of 24 measurements

Composition of different biochar and reference materials

As a basis the reference trials have been performed using an amount of 1 kg anthracite coal on 50 kg of scrap. Due to the lower heating value in comparison to the anthracite coal 1.6 kg of non-processed biochar from Tecnocentro and from wood gasification plants were charged to compensate the difference. Just before tapping at 1650°C, a melt sample was taken for chemical analysis to give information about possible negative effects of biochar use. After tapping all output fractions have been separated and the individual output masses were recorded. **Figure below** reports steel analysis after trial tests, comparing coal, and two char from two providers.



Steel composition after pilot trials

The evaluation of the pilot arc furnace trials shows no negative effects regarding the steel and slag analysis. Differences occur in terms of the Ni and Mn content. These differences can be explained by small fluctuations in the scrap composition and they are not addressed to pollution from char use. The reference trial shows a higher carbon content than the two biochar trials. This would imply a better carburization of the melt by the anthracite coal and would also be in agreement with the findings of the off-gas analysis. Considering the sulphur content of the steel, the effect is evident of the lower sulphur content of the biochar in relation to the reference materials. The steel produced by the biochar trials has only about half the sulphur content in relation to the reference trial. Despite the higher phosphor concentration in the different biochar on the other hand, the phosphor content in the steel is the same for all trials. So the use of biochar instead of fossil coal shows no negative impact on steel composition in the pilot trials. Also regarding the slag composition, these first preliminary results indicate no negative influence of the use of biochar with higher ash content on the general slag composition.

WP5 INDUSTRIAL EXPERIMENTATION (DEW, FERRIERE NORD, CSM, RWTH, MH, TECNOCENTRO, IP)

The use of char in EAF has been tested at industrial scale by the three industrial partners participating to the GreenEAF project. The industrial partners involved in this project have different EAF, which differs for size, capacity, and amount of chemical energy. Following Table reports the main EAF characteristics. Char industrial testing with these three furnaces will exploit a wide range of operational variability. Both char charging and injection have been tested. FENO uses coal charged and injected for respectively bath carburization and foaming. DEW uses coal mainly for bath carburization: coal is mainly charged and injected in a small amount. DEW and MH uses coal for foaming: coal only injected.

	Charge weight (TLS)	Num. buckets /heat	Electrical energy input [kWh/TLS]	CH ₄ [Nm ³ /TLS]	O ₂ [Nm ³ /TLS]	Coal lump [kg/TLS]	Injected Coal [kg/TLS]	Power on [min]	Tap to tap [min]
FENO	140	3	341	6	42	4	8	38	45
DEW	130	2	417,2	0	21,8	10.7	1,53	54	69
MH	40	3	375	7	45	0	12	31	45

FENO: Ferriere Nord

DEW: Deutsche Edelstahlwerke GmbH

MH: Marienhütte Ges. m.b.h.

Main characteristics of the electric furnaces of the industrial partners participating to the project

Charged char tests

Substitution of charged coal with char has been tested by Ferriere Nord and DEW. Charged coal can be needed to reach certain carbon levels in the steel depending on scrap qualities available. It can also be used to substitute electrical energy by chemical energy when oxygen is used to decarburize the melt and the carbon is burned to CO and CO₂ respectively.

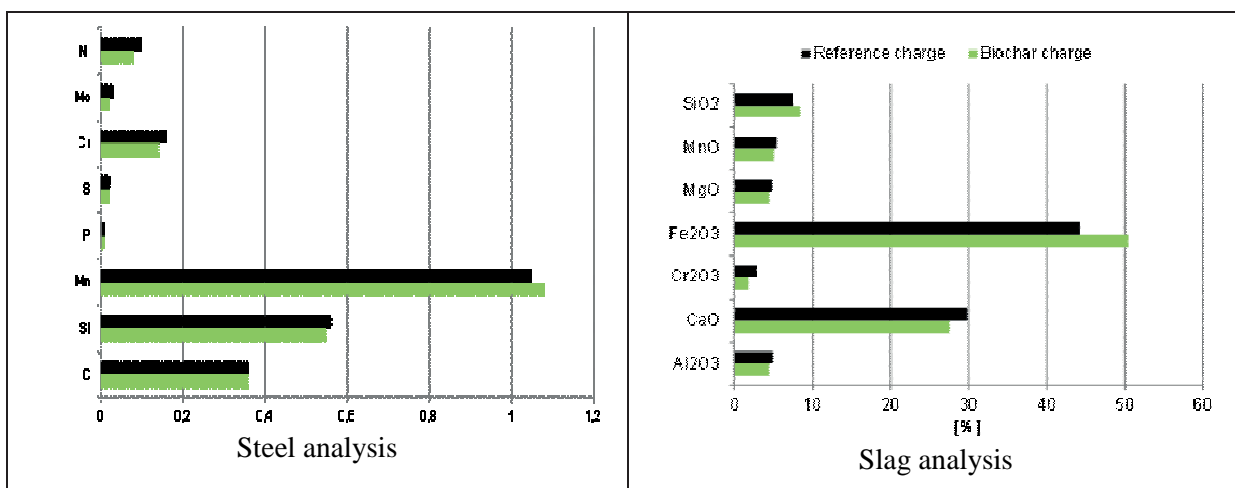
Ferriere Nord uses about 1 ton of charge coal per heat, while DEW about 1.4 tons of coal per heat. The Electric furnace of Ferriere Nord is equipped also with the offgas online monitoring system EFSOP™.

The average of steel and slag analysis with char charged in 5 heats has been compared with the average of 5 standard heats. As example Figure below reports the comparison of average values of steel and slag analysis measured at DEW in standard and trials heats. The results from steel and slag analysis show no significant differences.

Off gas analysis system (EFSOP analyzer) in Ferriere Nord has been used during tests. Measured data have been compared with data of the production of CO/CO₂/H₂ during standard operations.

The main difficulty in char charging is related to high char reactivity. Significant powder dispersion has been noticed during handling and charging operations and intense flame emissions were observed during trials with char.

This problem has been solved with preliminary material briquetting. New industrial tests performed with charcoal briquettes have been performed and confirmed the absence of anomalous flame emissions with briquetted material.



Comparison of steel and slag analysis of standard and trials heat measured at DEW

	CO/s*	CO ₂ /s*	H ₂ /s*	O ₂ /s*
Char Trials	16,07	17,34	9,85	0,39
Standard Trials	17,55	16,96	10,19	0,16

Average Values of offgas composition measured during industrial trials at Ferriere Nord

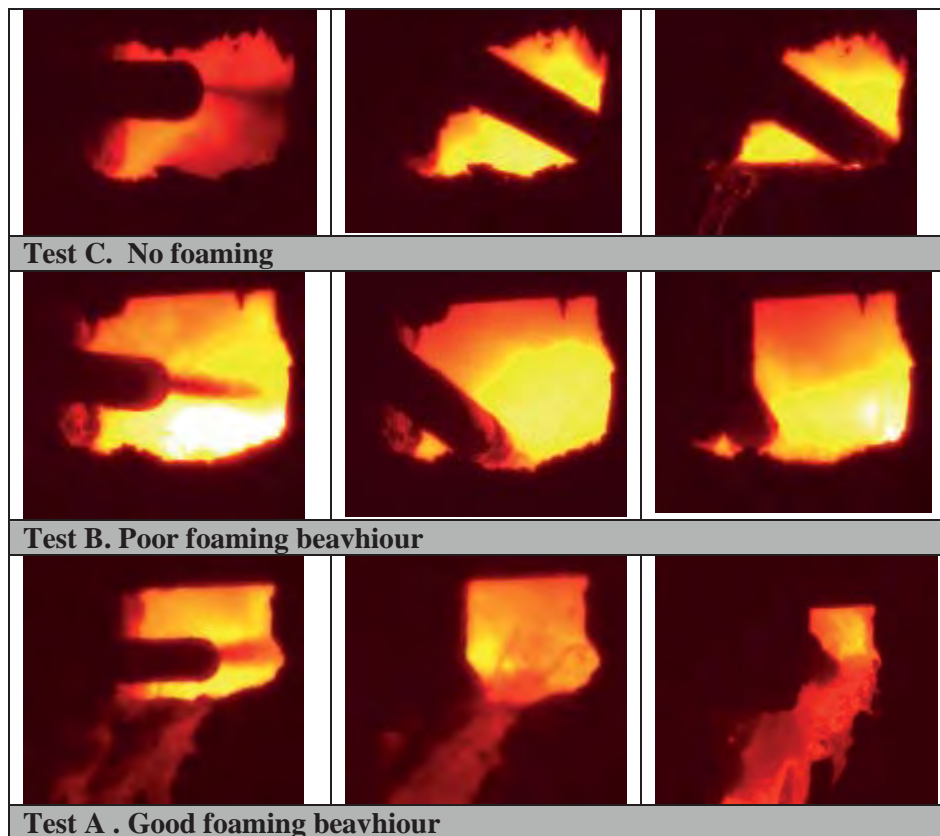
Injected char trials

Foaming trials were carried out by the three industrial partners. Slag foaming is a very complex equilibria depending on slag properties (mainly viscosity and surface tension), amount of injected coal (which affect the amount of gaseous species necessary to promote foaming) and also coal reactivity. So, beside the energetic input, the foaming behavior is an important process aspect which must be taken into account for industrial testing of char.

For a better control of foaming process Marienhütte developed together with VATRON GmbH an Optical Foaming Slag Management System (OFSM). The slag height is detected by a camera continuously. The camera is placed close to the slag door. Special image processing software calculates a slag index to be used for the injection of the carbon amount required. Due to the real-time monitoring of the slag level it is possible to adjust the C-contents by injection of the optimal quantity of carbon. Following figure reports the images of three foaming tests with char produced by Tecnocentro.

Injection tests were carried out also by DEW and Ferriere Nord.

Results obtained by the three partners were partially satisfactory, in the sense that in some trials good foaming behavior was observed, and in some trials no. These results indicate that injection system must be improved promoting the penetration of char into the slag.



Foaming tests recorded with Optical Foaming Slag Management System (OFSM installed at Marienhütte

Environmental monitoring at stack was carried out both by FENO and DEW and confirmed that char does not introduce any modification respect the historical plant trends.

Use of syngas in EAF

Due to the difficulty to produce syngas close to the steel plant for industrial trials, syngas utilization into the EAF burners has been simulated trough CFD modeling. Due to complexity of syngas composition the simulation of syngas industrial utilization has been carried out according to the following criteria:

- Definition of a quantitative criteria to compare natural gas burning with syngas burning
- CFD calculation with natural gas burning to be used as reference situation
- CFD calculation with the syngas and comparison with reference situation

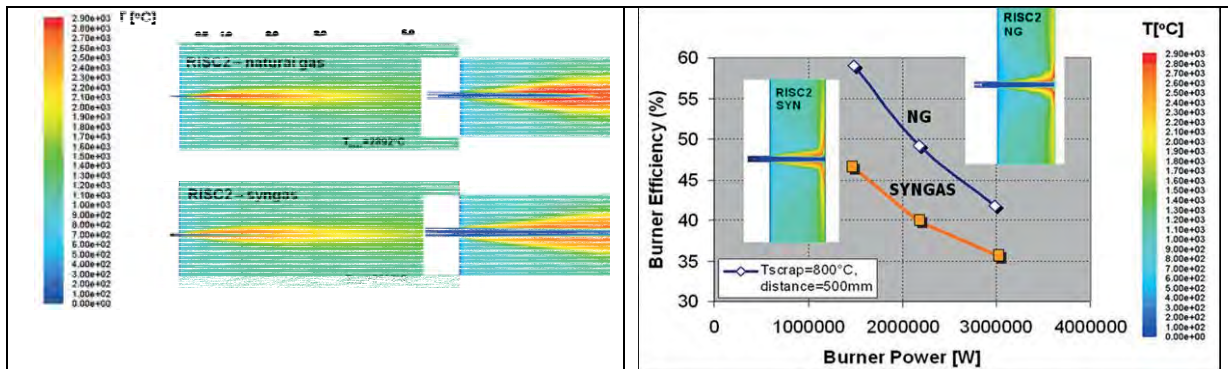
Calculation was set considering a bidimensional calculation domain having diameter of 2500 mm and length 6000 mm. The domain is surrounded on three sides by the furnace atmosphere (considered composition of the atmosphere is taken from measurement of offgas analysis system of FENO) at temperature of 1100°C. On one side (in which is present the burner in symmetric position) the temperature is fixed at 100°C (considering the temperature of water cooled panels)

Quantitative criteria to compare the standard and syngas situation must be introduced. The criteria selected to compare natural gas and syngas burning is the efficiency, defined as:

$$\frac{\text{kW} \cdot \text{to} \cdot \text{the} \cdot \text{scrap}}{\text{kW} \cdot \text{from} \cdot \text{the} \cdot \text{burner}}$$

The syngas composition used in the simulation has been measured during industrial char production. Due to the heating value of the obtained syngas, syngas composition has been enriched with methane up to obtain the value of 21 MJ/kg of heating value. This is the value which is compatible with the maximum flow rates available on the steel plant of Ferriere Nord.

Figures below report the temperatures of flames feed with natural gas and syngas and the efficiency of the burners.



Calculated flame temperature in case of natural gas burning and syngas burning and comparison of efficiency with syngas and natural gas.

The CFD calculation show that the shape of the flame of syngas is different, and the especially the temperature is lower respect natural gas burning. The efficiency also is lower of values ranging from 8 to 15% .

To recover the gap of efficiency following actions are possible:

- increase of amount of methane in the mix
- increase burned size and syngas flow rate
- modify burner geometry to increase combustion efficiency.

The design of new burner has been simulated and the increase of efficiency in about 10%.

WP6 TECHNO-ECONOMIC EVALUATION AND FINAL REPORT (FERRIERE NORD, CSM, TECNOCENTRO, IP, RWTH, DEW, MH)

Charcoal is a wood product that is made by heating wood in absence of sufficient air for full combustion to occur.

There is not a great deal of information available in literature on the cost of charcoal production. Charcoal cost can be grouped into three main issues:

1. wood/raw material (including cost of harvesting and collection of biomass up to the pyrolysis plant)
2. charcoal production
3. charcoal transport (to be intended as transportation from the pyrolysis plant to the steel factory)

where the first issue has the main weight.

The global cost of charcoal utilization can be decreased considering:

- carbon tax
- creation of local economy, optimising the process of biomass collection, transformation and transportation close (as much as possible) to the steel plant.

Literature reports charcoal prices ranging from 160 to 400 €/t of char [19,20].

General conclusions of the project

The global objective of the project is to investigate the partial or total substitution of coal and natural gas with charcoal and syngas produced from pyrolysis of biomass. The char is used as injectable powder or charged in the basket. The characteristics of char and syngas, and the related pyrolysis process, are tailored in order to match the requirements for their utilization in EAF.

The tests performed (both pilot and industrial) showed that coal can be replaced by char, both for charging and injection to promote foaming.

In case of charging the following aspects should be deeply investigated:

- char reactivity: char start burning during charging. Char reactivity depends on high surface area, volatile content and powders dispersion during charging. Proposed solution is a char pre-treatment with briquetting stage before charging;
- slag foaming: some trials showed good foaming behaviour, other trials were not satisfactory. Proposed solutions are improvement of injection system and utilization of additives together with char powder to increase char/slag wettability and promote reaction of char with iron oxide. The injection system must ensure char injection below the slag

Moreover, syngas utilization in EAF burners, instead of natural gas has been simulated by means of CFD calculations. The used syngas composition was that arising from the pyrolysis tests. Syngas utilization leads to a decrease of EAF efficiency.

Techno economic evaluation carried out considering char cost and CO₂ emission leads to the conclusion that:

- official market for biochar does not exist and which can be used in steel mills. Most part of biochar production is still in pilot scale state. So the prices per ton of produced biochar are not representative. Literature reports prices ranging from 160 to 400 €/t of produced char. Evaluation of Tecnocentro indicates a price of production in the range 200-250 €/t. The local availability of biomass is mandatory
- exemplary price of 18 € per ton of CO₂ partially compensate actually higher price of charcoal.

In the next few years the industrial scale production of different biochar qualities is expected and according to this the development of a market and a market price.

In Addition to that increases of the prices for fossil coal are expected, too. In general the use of biochar puts the electric steel mills in a position to avoid CO₂ emissions which are relevant for the EU ETS like the emissions from fossil carbon.

SCIENTIFIC AND TECHNICAL DESCRIPTION OF RESULTS

1 OBJECTIVES OF THE PROJECT

The ECSC project “Sustainable EAF Steel Production – GREENEAF” has the objective to study the EAF cycle in order to investigate the partial or total substitution of coal and natural gas with charcoal and syngas produced from pyrolysis of biomass.

Generally speaking, in the electric furnace coal (and consequently char) can be used as injected powder or charged into the basket. The syngas can be used for EAF burners.

The characteristics of char and syngas, and the related pyrolysis process, must be tailored in order to match the requirements for their utilization in EAF.

The feasibility of coal substitution has been tested with industrial trial.

2 COMPARISON OF INITIALLY PLANNED ACTIVITIES AND WORK ACCOMPLISHED

All project activities foreseen in the technical annex have been carried out without deviations.

3 DESCRIPTION OF ACTIVITIES AND DISCUSSION

WP1 BIOMASS SELECTION FOR EAF CHAR PRODUCTION (TECNOCENTRO, CSM, IP)

WP1 is devoted to the analysis of availability of biomass in the area around the steel factories participating to the project.

In general, biomass is collected from agricultural residues, forest residues, wood industry or can be cultivated.

These three species of biomass differ for:

- Amount
- Different expected characteristics of produced char in terms of size, shape, mechanical characteristics and pollutants emissions
- Availability during the year
- Different energetic balance [3,4,7], considering the heating values and the energetic expense for cultivation, collection and transportation.

In what follows, the local situation in Friuli (Italy), North Rhine-Westfalia (Germany) and Styria (Austria) has been analysed. In these three regions are located respectively the steel plant of Ferriere Nord, Deutsche Edelstahlwerke and Marhienutte.

The situation in Friuli (Italy)

The steel plant of Ferriere Nord steel plant is located in the region of Friuli, in the North of Italy.

Table 1 reports the amount and types of available biomass, the corresponding energy potential and an estimation of CO₂ amount which can be saved.

Biomass type	[t dry mass/a]
forest residues and ligneous species	284300
agricultural residues	355100
biomass from cultivations	300000
tot	939400

Table 1 Friuli Biomass amount and potential energy availability [1,2,3]

The biomass amount necessary to replace coal has been estimated in 100000 t/year (see WP 4 for details), so the amount of biomass available in the surrounding of the factory is largely enough. The amounts of biomass ensures also that material is available within the year.

The situation in North Rhine-Westfalia (Germany)

To complete the information on biomass availability at the different plant locations Deutsche Edelstahlwerke (DEW) and RWTH provided data about the situation for the DEW plant in Siegen, which is in the federal state of North Rhine-Westfalia (NRW) and the administrative district of Arnsberg respectively.

The two types of biomass which are mainly available in this area are dendro mass (fast growing tree species with short rotation) and agricultural residues like straw. Table 3 is showing the availability of dendro mass in the Arnsberg district as well as in the state of NRW. Table 4 is presenting the availability of straw in NRW and Germany.

	Arnsberg [t dry mass/a]	Federal state NRW [t dry mass/a]
Theoretical potential	594,084	1,818,549
Sustainably mobilizable potential total	302,447	1,166,415
Sustainably mobilizable potential solid volume	254,426	977,613
Sustainably mobilizable potential brushwood	48,021	188,802

Table 2: Cultivated ligneous biomass (Dendro mass) availability in Arnsberg district and NRW [13]

	Federal state NRW [t dry mass/a]	Germany [t dry mass/a]
Acreage [ha]	630,000	8,100,000
Straw total [t _{wet mass} /a]	2,600,000	36 – 43 Mill.
Sustainably mobilizable potential for energetic use [t/a]	600,000	3,600,000
Energy equivalent	2,400 GWh/a	56.1 PJ/a

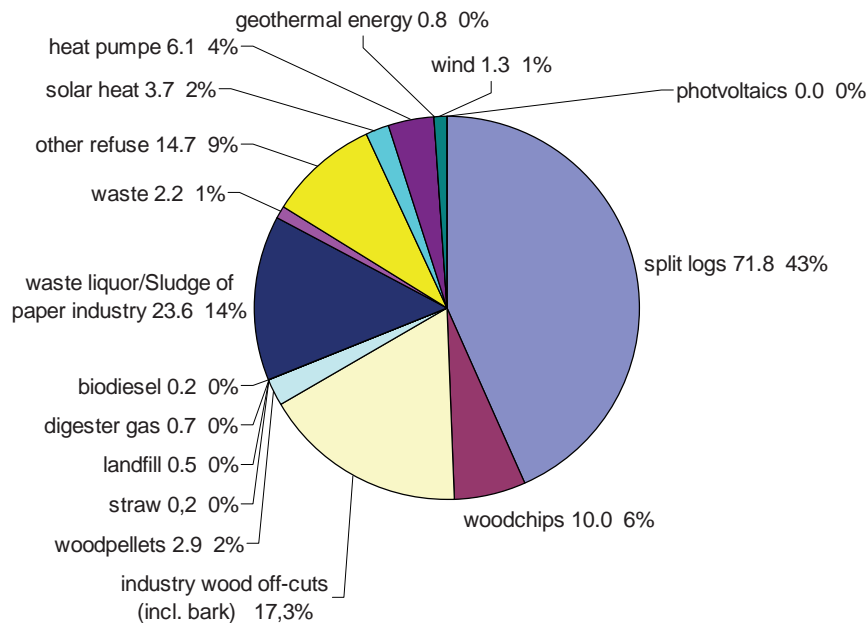
Table 3: Agricultural residues availability in NRW compared with availability in Germany [14]

In both cases sufficient potential is available to substitute the fossil fuel demand of the DEW plant in Siegen.

The situation in Styria (Austria)

Even if not directly involved in this WP, Stahl- und Walzwerk Marienhütte (MH) provided data about local situation of biomass availability in Austria, in order to have a reference situation to be compared with plant needs. Austria has a large amount of biomass availability, actually used for power generation (see Figure 1, (a)). The potential on wood is about 31 million solid cubic meters per year, wherefrom only 19 million are used at the moment. Most of this wood, with a still rising trend, is used for heat and energy production in different forms. In Styria the annual amount of wood used for energy production is about 1.2 million solid cubic meters (Steiermark Holzeinschlag, www.verwaltung.steiermark.at, Stand 21.1.2009).

(a)



(b)

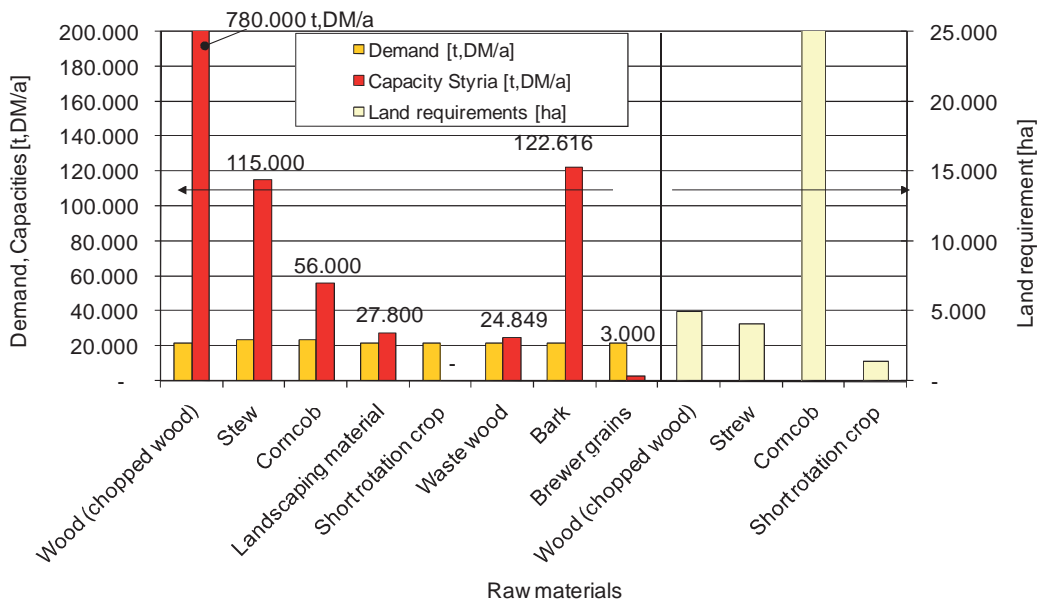


Figure 1 (a): Gross consumption of renewable energy sources in Austria in the year 2003
(b): Biomass potential in Styria

Due to the fact, that wood is a typically expensive biomass also some potentials of low priced biomasses were checked for the region Styria. One of these biomasses is stew from different origins,

which has a potential of about 115000 t per year. The actually used part of strew can only be estimated. One problem of strew is its seasonality, which would lead the high storage capacities.

In Styria also high amounts on corn are cultivated. This results in about 56000 t of cobs per year, which are also one potential feedstock material for charcoal production. The quantity of biomass arising at landscape conservation works is about 28000 t per year. In most cases this material is converted to woodchips. Bark, which is very often a by-product in wood industry, has a potential of about 123000 t per year. Also waste wood seems to be interesting for charcoal production. It accumulates in an amount of approximately 25000 t/a.

Two examples for very special but also interesting biogenic feedstock materials are brewer grains and sewage sludge with an occurring amount of 3000 t/a and 34000 t/a, respectively in Styria.

One additional option would also be the purchase of some agricultural areas and the cultivation of own biomass in form of e.g. short rotation crops or wood. The typical crop yield for such plantations in Styria is about 10 to 20 t/ha and year. This means, for the cultivation of reasonable amounts of biomass, huge areas of several km² would be needed.

Figure 1(b) gives an overview of the arising amounts of different biomasses in Styria. Comparable, the demand on injection coal at Marienhütte is about 5400 t per year, which gives a consumption of pure carbon of about 5000 t per year for slag foaming. To cover this demand by charcoal, approximately 20000 t/a of feedstock biomass would be needed, if a carbonization yield of 30 % and a carbon content of the charcoal of 80 % is taken as a base; this amount is largely available at the moment.

Main conclusions from the analysis carried out by all the partners are reported in Table 4, describing synthetically the main advantages/disadvantages of considered biomasses.

Biomass	Advantages	Disadvantages
Forest residues	large amount available and well distributed during year	relatively high energy necessary for collection and transportation
Corn and graspevines (agricultural residues)	large amount; low cost	larger ash content and nitrogen (see analysis) respect other biomasses. Seasonal
Mischantus and sorghum (cultivated biomass)	large amount available; present in both North Italy, Austria and Germany; high energy ratio. nitrogen and ash amount smaller than residues form cultivations	Need of dedicated cultivation, large productivity after second year of implantation; nitrogen and ash amount larger than forest residues. Seasonal

Table 4 Main advantages/disadvantages of considered biomasses

Task 1.2 Characterization activities (Tecnocentro, CSM)

Physico-Chemical characterization in terms of chemical composition, ash content, ash composition and properties, heating value have been carried out on the selected biomass. Results are presented in what follows

Physico chemical characterization of biomass

Representative samples of biomassess have been collected by Industrial partners and Tecnocentro and used for characterization activities and for further pyrolysis tests at lab scale..

Among the individuated categories of biomass (Table 5), the following representative samples were collected:

- Forest residues (with and without bark)
- Corn straw and Grapewine (residues from cultivations)
- Mischantus and sorghum (cultivated biomass)

Following Table summarises performed characterization activities of CSM and Tecnocentro

Data*	Forest residues	Wood+bark	Bark	Wood without bark	Corn straw	corn	grapewine	mischanthus	Sorghum pellet
Lower heating value (LHV) [kJ/kg]	20000	18100	16200	18500	18000	17500	18900	19100	18000
Volatiles (%)	80	82	76	85.0	76-81	76	78	78	81
Ash (%)	1.1	0.8	3	5.5	5.5	3.5	3.9	3.5	6.8
C (%)	51.5	47	47	51.0	47.3	45	46.2	48.2	43.7
H (%)	6.7	6	5.4	-	5.4	6	5.5	5.4	5.73
N (%)	0.3	0.3	0.4	0.16	0.8	1.8	1.3	0.6	1.07
O (%)	39.7	44	40		43.2	43	37.7	42.1	
S (%)	0.04	0.05	0.06	0.02	0.05	0.12	0.03	0.06	<0.1
Cl (%)	0.05	-	-	-	0.2	0.08	0.05	0.2	0.4

Table 5 Physico-chemical characterization of selected biomasses. Moisture content ranges form 10-12 % in all the samples

Following Table reports the characterisation of biomass ashes, in term of oxide content and also viscosity.

This data will be used to design the industrial tests. One representative example of ash for each category of biomass has been considered.

[%]	Forest residues	corn	Grape wine	mischantus
SiO ₂	5.6	1.4	22.03	71.7
K ₂ O	38	42	31.2	14.56
CaO	22.87	11.02	20.1	7.56
MgO	17.35	9	8.52	2.69
P ₂ O ₅	14.98	28.5	16.19	2
Na ₂ O	1.1	0.5	0.7	0.9
FeO	0.42	1.3	0.54	0.5
MnO	0	0.2	0.1	0
Al ₂ O ₃	0	1.06	0.1	0.93

Table 6 Biomass ashes composition

The performed analysis showed that the selected biomasses have very similar elemental analysis in terms of C/H/O and similar volatile matter content. Biomasses heating value is also very similar.

Main differences can be found in minor elements (as N, S and Cl) and ash amount. This means that the possible effects on EAF process, influence on steel and slag composition and environment pollution must be investigated and analysed in the industrial tests.

Ashes composition is very different from the four types of biomass: miscanthus has a very high silica content, while the other biomass have a significant content of potassium oxide. The effect on EAF slag composition and the subsequent effect of main slag physical properties (melting behaviour and viscosity) will be evaluated in WP4.

WP2 TAILORING OF BIOMASS PYROLYSIS (TECNOCENTRO; IP; CSM)

WP3 CHEMICAL AND PHYSICAL CHARACTERIZATION OF CHAR PRODUCED BY BIOMASS PYROLYSIS (CSM, IP, RWTH)

WP2 is devoted to the definition of the influence of the pyrolysis conditions in terms of temperature, residence time, material size, atmosphere composition on char and biogas yields and characteristics. WP3 is devoted to define the yield and the quality of the char produced in terms of chemical composition, impurities content and relevant physical characteristics, as a function of pyrolysis conditions defined in WP2. Being the two WPs strongly connected, their activities are presented jointly in this same paragraph.

In what follows the task activities are reported according to the following logical order:

1. Task 2.1: laboratory tests to define the pyrolysis kinetics of the selected biomass
2. Task 3.1: characterization of char and biogas
3. Task 3.2: process parameters
4. Task 2.2: definition of pyrolysis process parameters

Task 2.1: laboratory tests to define the pyrolysis kinetics of the selected biomass. (CSM, IP)

Laboratory tests have been carried out to determine:

- pyrolysis kinetic
- amount of char, biogas and tar produced under different pyrolysis conditions
- the chemical composition of biogas

Tests are carried out with thermobalance (TG tests), with low heating rates (order of magnitude of 1-20 °C/min) and with wire mesh reactor, for high heating rate and Gray-King furnace, an apparatus used for testing coals according to the British Standard method-BS1016-107.2

Experimental tests have been carried out by CSM and Imperial College. Descriptions

TG tests (CSM)

Laboratory tests have been carried out using a thermogravimetric apparatus (TG tests). Figure 2 reports a scheme of the laboratory apparatus. It consists of a vertical electric furnace, with heating rate in the range 1-20 °C/min, able to work under controlled Ar atmosphere. Sample is placed inside an alumina crucible of 20 cm³, which does not interact with sample or gaseous atmosphere during experimental test.

Sample is hang up to a balance, connected to a PC to continuously record weight variations during the test. The furnace is equipped also with a mass spectrometer to analyse gas composition evolution during test.

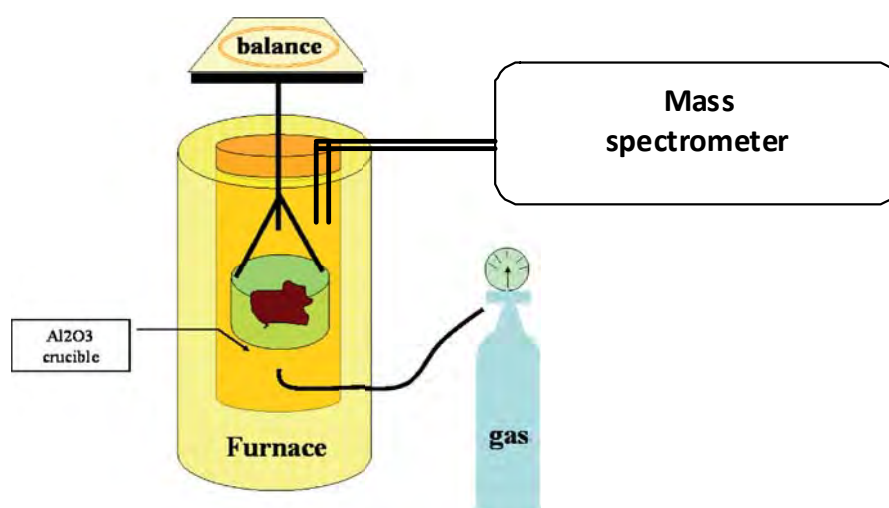


Figure 2 Scheme of laboratory thermogravimetric (TG) apparatus

Two types of tests have been carried out:

1. Tests under temperature gradient, to experimentally measure the characteristics temperature of starting of reactions. All the four selected biomass have been tested. The used temperature programme was: up to 900°C at 300°C/h, with continuous measurement of weight and gas evolution
2. Tests at constant temperature: to obtain the kinetic of pyrolysis process. All the four biomasses selected studied. Tested temperatures were: 400°C, 500°C and 600°C, and the Test duration was up to constant weight. Weight loss and gas evolution continuously measured during TG tests

Figure 3 reports an example of results from both type of tests.

From the analysis of the performed tests temperature of starting of pyrolysis, the temperature range of higher pyrolysis velocity and the pyrolysis kinetic (expressed as the time, as a function of temperature, of complete weight loss) have been measured. Table 7 reports the results of the both types of laboratory tests. Example is shown in Figure 3.

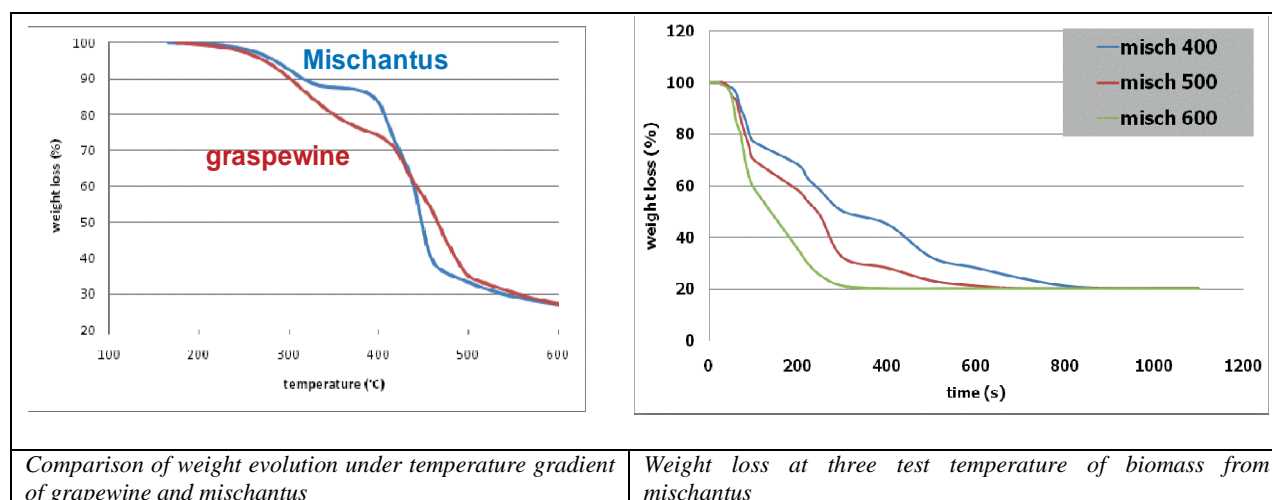


Figure 3 Example of thermogravimetric tests under temperature gradient and constant temperature

biomass	Starting of pyrolysis (°C)	Max range of dw/dt	Time for total weight loss at 400°C (s)	Time for total weight loss at 500°C (s)	Time for total weight loss at 600°C (s)
Forest residues	210	430-510	800	620	310
Corn	200	400-480	800	600	300
grapewines	190	420-500	800	610	320
Mischantus	200	400-470	800	600	280

Table 7 Results of laboratory thermogravimetric tests

Pyrolysis process starts at about 200°C for all the biomass samples, but reaction kinetic increases at temperature higher than 400°C; so the temperature of 400°C can be considered the minimum temperature for the biomass pyrolysis process.

The effect of temperature is also well visible in Table 7. In fact, in columns 3, 4 and 5 time necessary to complete pyrolysis (time for constant weight in TG test) is reported. Time to reach the final weight loss decreases inversely with temperature.

Test at imperial College

Biomass pyrolysis tests have been carried out in a Gray-King reactor using different types of biomass. Afterwards, char produced with these tests, together with chars received from project partners were then assessed in a thermogravimetric analyser (TGA) in terms of their reactivities and proximate analysis. Four samples of coal currently used in electric arc furnaces at Ferriere Nord were also analysed for comparison. A wire mesh reactor has been used to provide a further characterisation of some of the biomass-derived samples, in terms of their reactivity in comparison to that of coals industrially used.

A Gray-King furnace, which is an apparatus employed for testing coals according to the British Standard method-BS1016-107.2, was adapted to be used as a pyrolysis laboratory scale reactor (Figure 4).

Basically, it consists of a 30cm long, 2cm internal diameter quartz tube reactor, which is inserted in a furnace. 3-4g of sample is held by a wire mesh while a flow of gases removes the volatile matter generated as the sample is heated. The heating rate is approximately 30°C min⁻¹ and, after the heating up period, the sample is held at peak temperature for 15 minutes before the reactor is allowed to cool down.

Condensable materials are trapped with liquid nitrogen. Most of the studies carried out in this reactor focused on mischantus and beechwood (representing ligneous biomass) as raw materials, but other feedstocks including corn stalks, sorghum and switchgrass have also been analysed.

Objectives of these tests were to determine char, gas and tar yields of different biomass species.

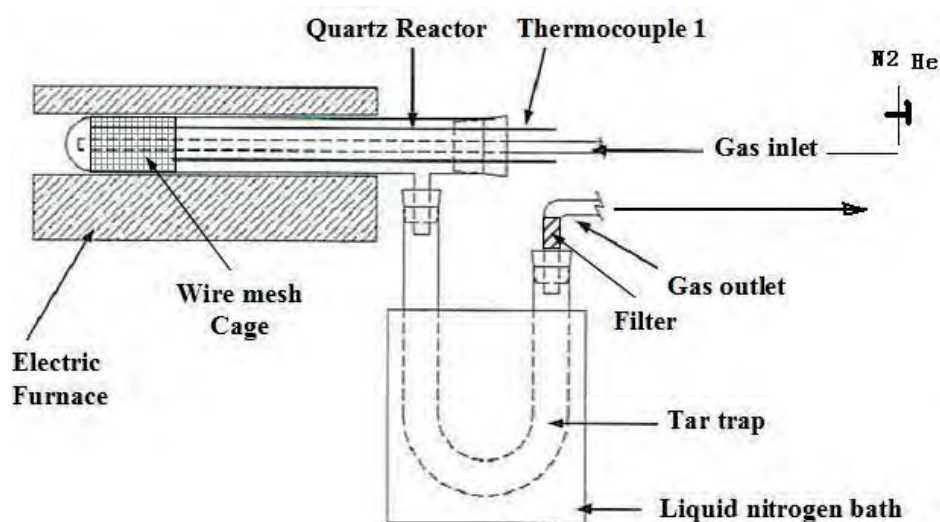


Figure 4 Pyrolysis reactor based on a Gray King Furnace

Beechwood (lignous biomass) was used as feedstock in pyrolysis experiments to determine the relative amounts of char, tar and gas recovered under different pyrolysis temperatures, ranging from 300 to 900°C. The char yield (Figure 5) was observed to decrease with temperature up to about 400°C and remain stable afterwards.

Tar and gas yields (not shown) also became stable after 400 °C with values in the region of 50-60% and 20-30% of the original biomass, respectively. These trends in char yields seem common to all different kinds of biomass studied, including miscanthus (Figure 6) and corn stalk (CS), sorghum (SO) and switchgrass (SW) (Figure 7).

In all cases, char yields did not show much change with temperature above 400°C and remained in the region between 20-30%. It can be observed that as for the beechwood and miscanthus samples discussed previously, the yield of char from these three biomass samples did not present significant variations for temperatures above 500°C. Variations in the particle size of the initial beechwood sample did not significantly affect the yield of char in the three particle size ranges studied, 0.212-0.5 mm, 0.85-1.7mm and 2.057-3.15mm, as shown in Figure 5.

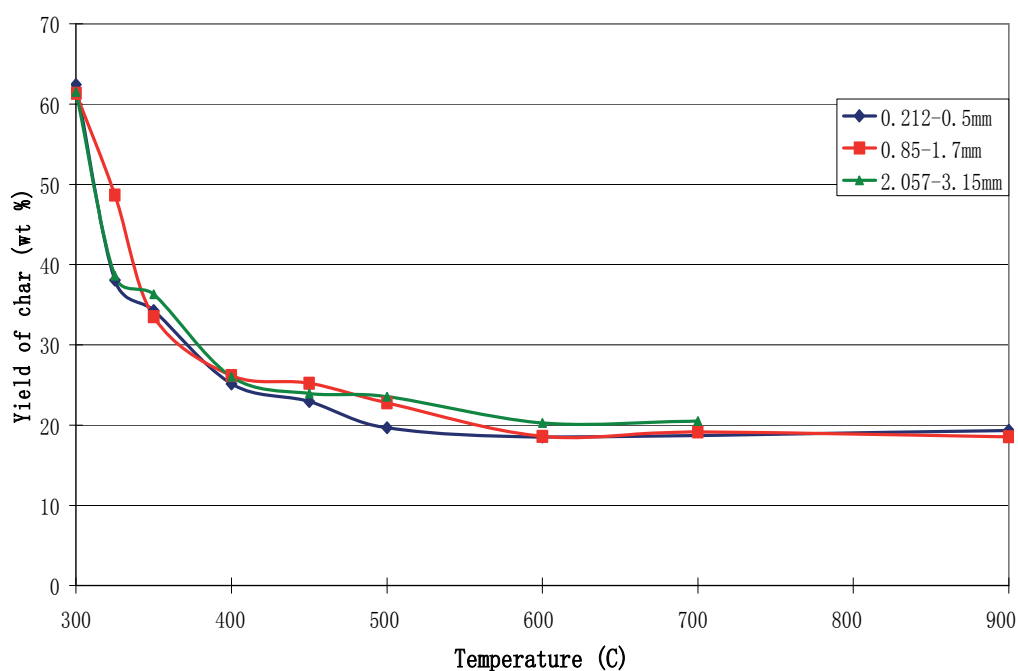


Figure 5. Char yields (as percentage of the original biomass in dry ash free basis) in the pyrolysis of beechwood in a Gray-King reactor as a function of temperature for three ranges of particle size.

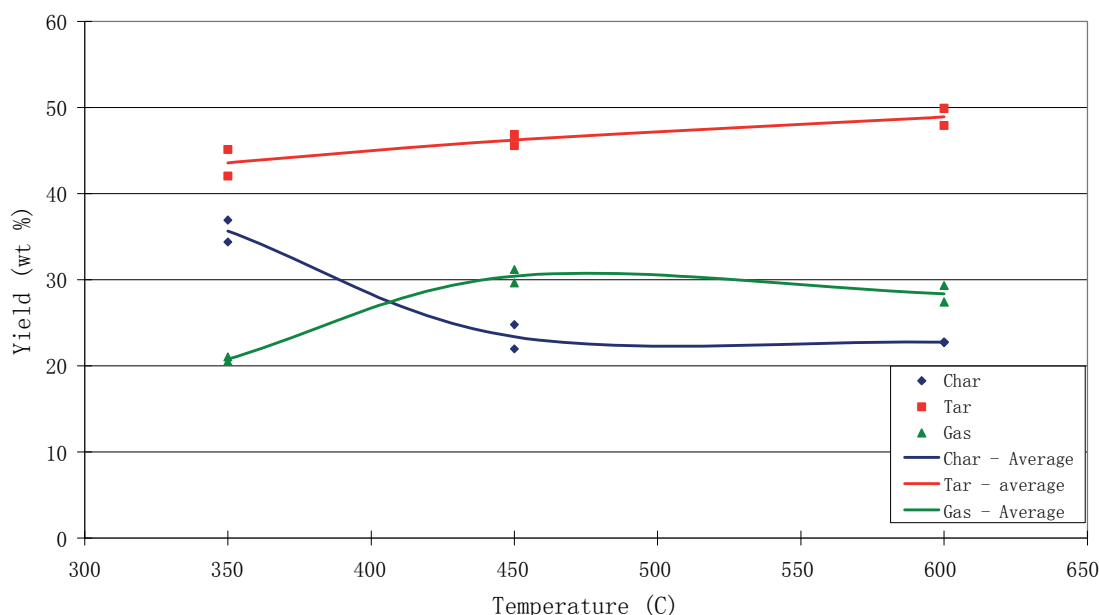


Figure 6. Char, gas and tar yields as a percentage of the original biomass (dry basis) in pyrolysis of miscanthus (particle size range: 0.212-0.5 mm) in a Gray-King reactor as a function of temperature.

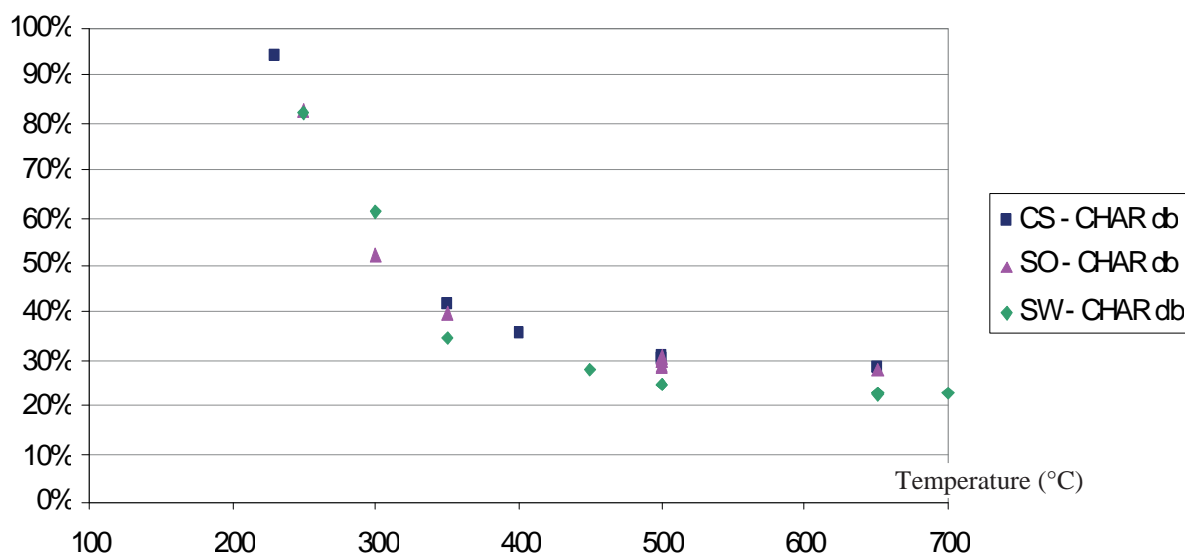


Figure 7. Char yield as a percentage of the original biomass (dry basis) as a function of temperature (°C) in experiments conducted in the Gray-King reactor. Three biomass samples were used: Corn Stalk (CS), Sorghum (SO) and Switchgrass (SW).

Char yields were observed to drop with temperature up to 500°C, after which the variations with increasing temperature were minor. Yields have been found to be similar across the range of biomass studied for equivalent pyrolysis conditions, which is promising in terms of flexibility of feedstock to supply electric arc furnaces. Particle size did not have a major effect on char yields for the range of particle sizes studied. The pyrolysis operating conditions had a strong effect on char reactivity and the volatile content of the chars. Reactivities similar to those of coals currently employed in electric arc furnaces have been found.

An important result is that, after 500°C, the char yield is almost stable, and this result does not depend on the biomass type and on the size of biomass particles.

Task 3.1 characterization of char and biogas produced

Production of char at laboratory scale, as function of temperature and residence time has been carried out.

CSM focused its attention to:

- Char chemical composition and porosity
- heating values as a function of different pyrolysis conditions
- syngas composition and heating value

Imperial College focused its attention to:

- char reactivity
- comparison of char reactivity with coal reactivity
- Char proximate analysis.

RWTH and DEW focused its attention on:

- Char and ash chemical composition
- Microscopic investigation

The results of the whole series of characterization activities gives indications to set the industrial pyrolysis process.

Char chemical composition and porosity

Among the tests at various temperatures, no significant differences have been found in the char chemical composition.

Table 8 reports, as representative example, the char characteristics after test at 500°C, with duration 700 s (complete weight loss).

	corn	grapewine	Forest residues	mischanthus
C %	70	70-81	75	73
H%	2	2	3	2
N (%)	1.8	2	0.3	1.2
S (%)	0.2	0.2-0.9	0	0.1
P(%)		0.48		
Ash (%)	23	10-16	3	10
LHV (kJ/kg)	23000	23000	27000	25000
Density (kg/m³)	280	270	300	270

Element(*)	K	Ca	P	S	Cl	Fe	Balance
Mass fraction	4.62	2.79	0.30	0.12	< LOD	0.21	91.93

Table 8 Char characteristics after test at 500°C, duration 700s, for the four biomasses tested (carried out by CSM; RWTH, DEW).

(*) Grapeseed Ash chemical composition by DEW/RWTH

Porosity and density resulted slightly affected by the temperature test. Char porosity has been observed to increase with increasing temperature, while density, as a consequence, decreases with temperature. No quantitative indication as been given about these variations, because the measurement of both quantities is affected by a large uncertainty.

Moreover, char structure (qualitative evaluation) appears very brittle and with low mechanical resistance (high porosity observed by OM), despite the starting biomass type and pyrolysis conditions.

Figure 8 reports the Optical image of char from grapewine, obtained at 500 and 600°C. The larger size of pores in the sample treated at 600°C, respect the one treated at 500°C is visible.

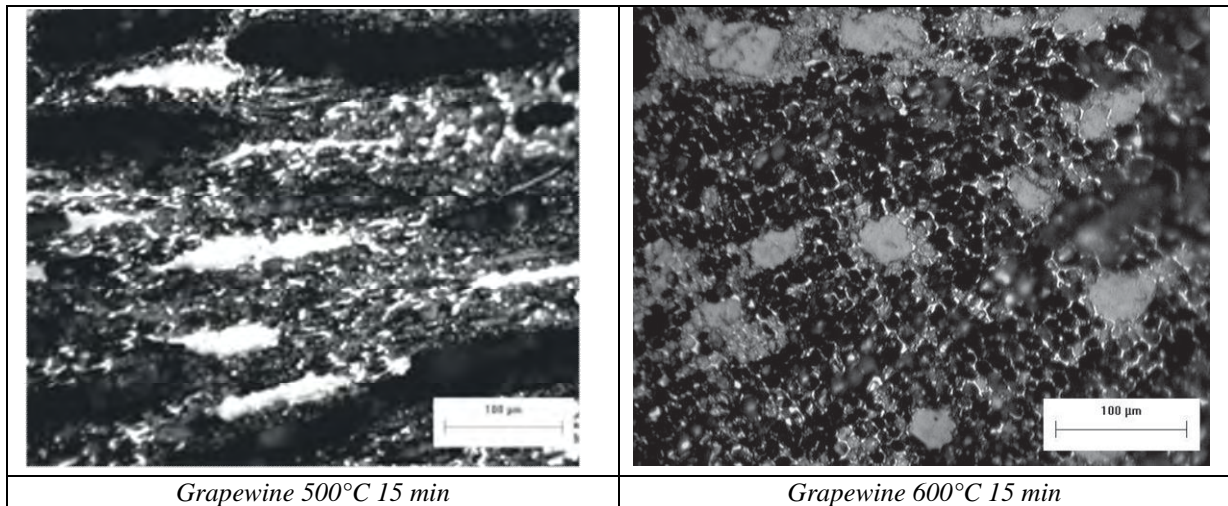


Figure 8 **Optical image of char sample from grapewine, after tests at 600 and 500°C**

The important aspect to be remarked for all types of biomass, is the low value of density (see Table 7 above) which may cause problems during injection, causing large dispersion of char particles into fumes instead penetrating into steel bath; in fact typical values of coal density are two or three times higher.

Figures 9 to 12 show the initial grape seed char and the effects of processing the char in form light-optical microscope images. Figure 10 shows the unprocessed char and the irregular form of the seeds is visible. The grain size of the unprocessed char is in the range of 2-4 mm. Figure 11 shows the result of a short processing of the char in a mortar. This result should be similar to the effect of transporting the char mechanically for example in a screw conveyor or similar. The Figure shows on one hand fragments of the char with sizes in the range of 0.5-1 mm and on the other hand a dust fraction which might be problematic in a conveying system. Figure 12 shows the result of short milling of the grape seed char. The resulting grain size is clearly below 50 µm.

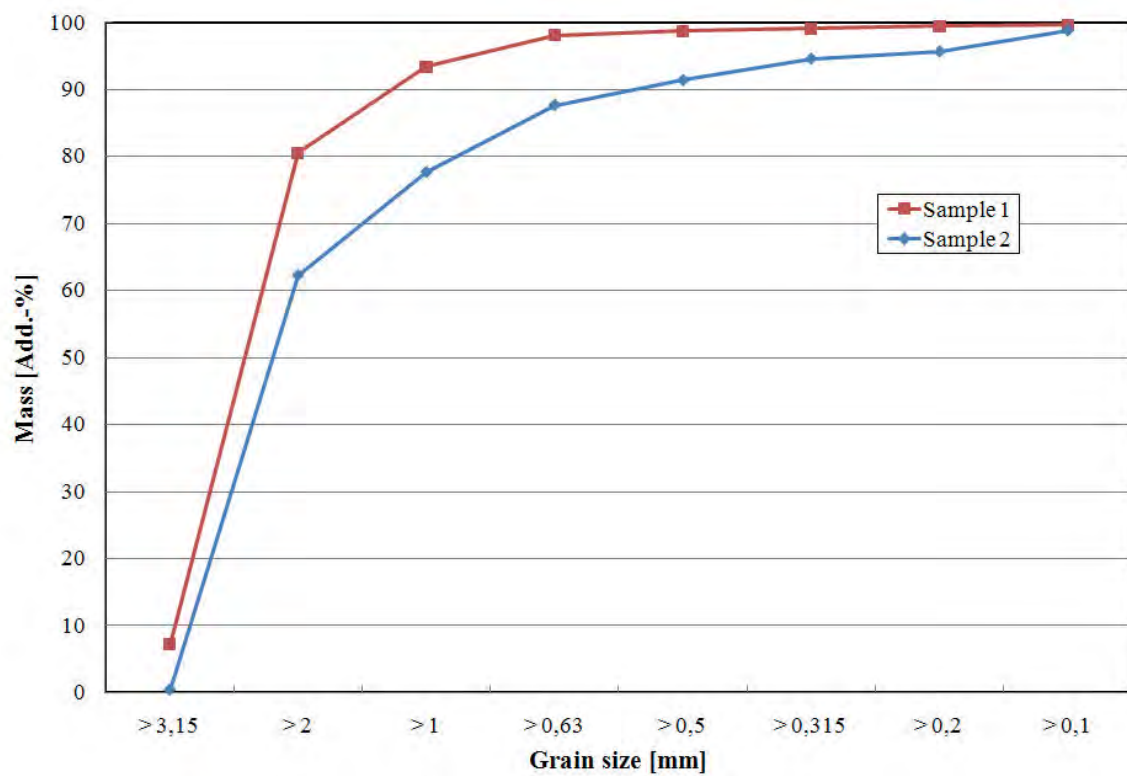


Figure 9 Grain size distribution of char samples

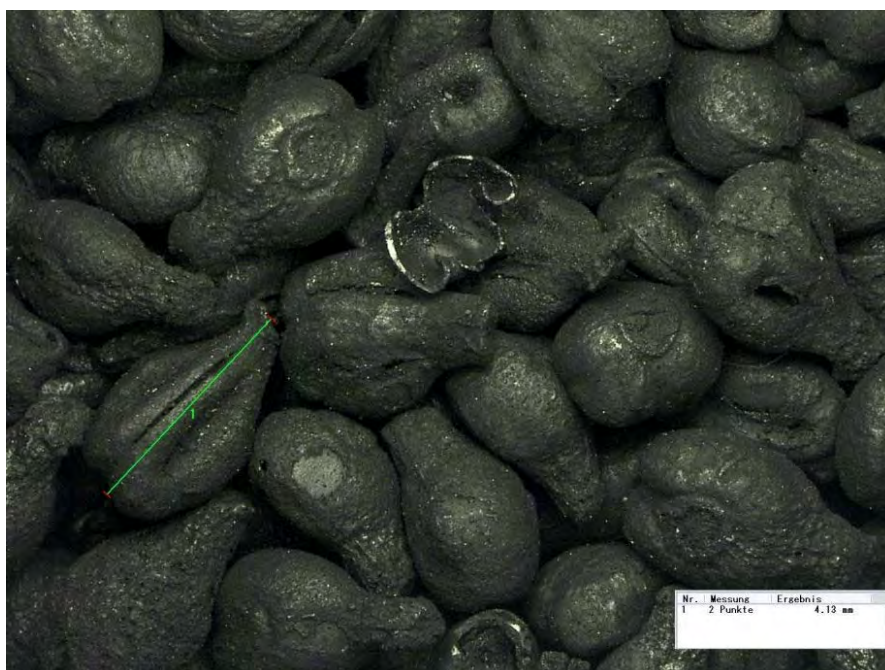


Figure 10 Light-optical microscope image of unprocessed grape seed char (magnification 20x)

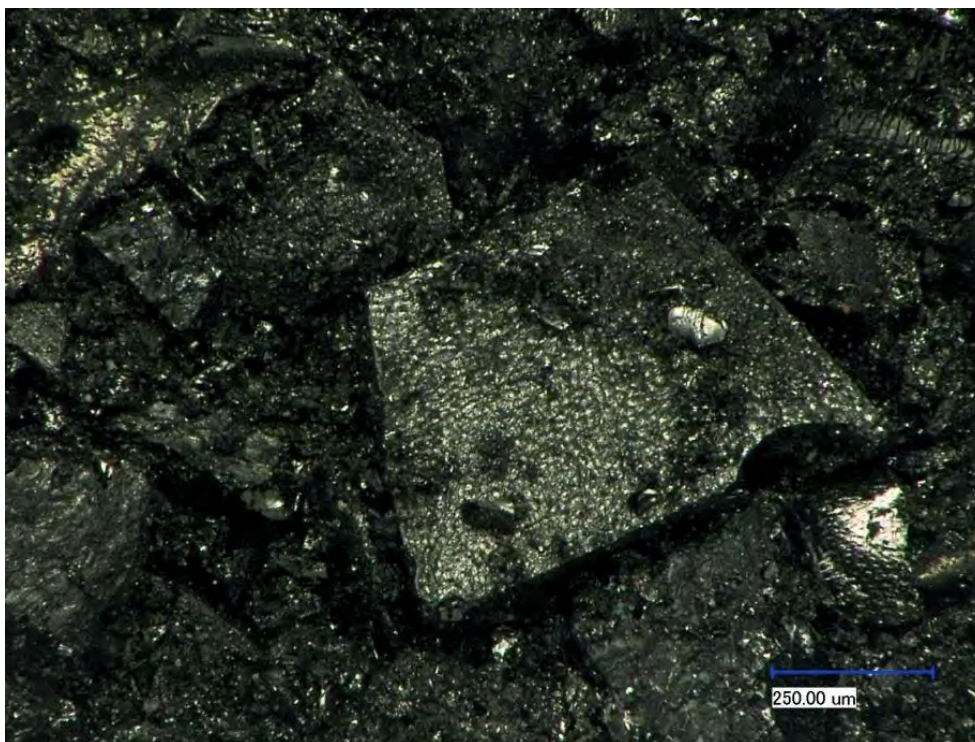


Figure 11. Light-optical microscope image of grape seed char after short processing in mortar (magnification 200x)

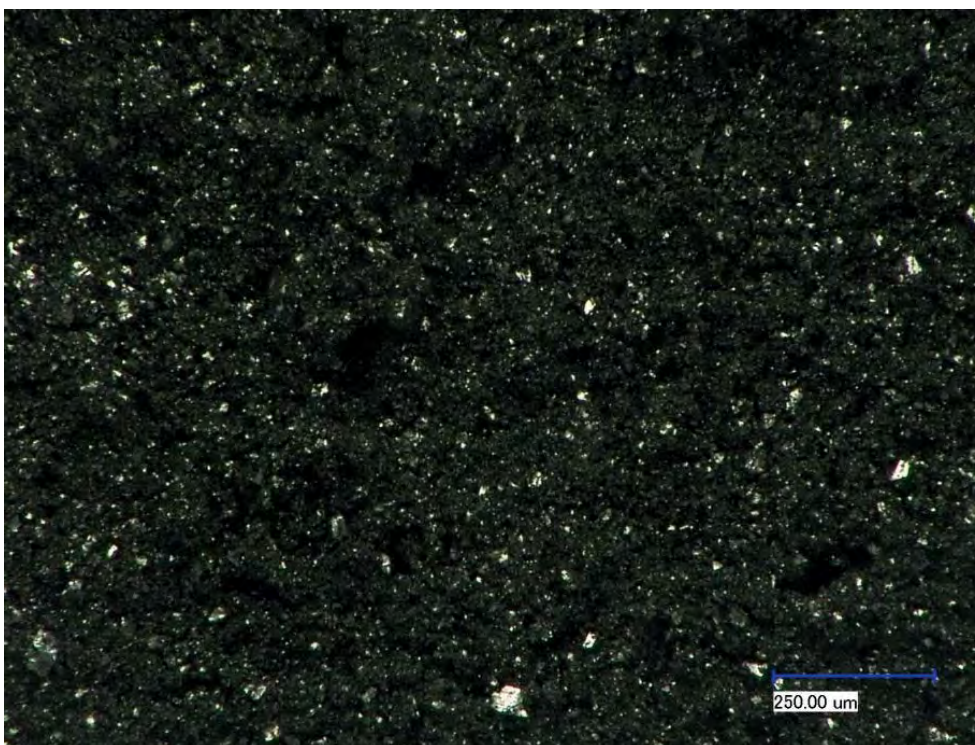


Figure 12: Light-optical microscope image of grape seed char after short milling (magnification 200x)

Heating values

Table 9 reports the measured values of heating values of chars obtained from four different biomasses, at three temperature. Heating values show increasing trend with temperature of pyrolysis. Obtained results indicate that the heating value of the char is lower than coal but in any case comparable. Among the different types of char, the one with highest heating value is, in according to literature obtained by

ligneous biomass, even if (see WP 1), forest residues requires a relatively large energy expense for collection and transportation.

LHV (kJ/kg)	Forest residues	corn	grapewine	Mischanthus
T=400°C	25000	23000	22000	25000
T=500°C	27000	23000	23000	25000
T=600°C	28000	25000	24000	26000

Table 9 Heating values of chars obtained from four different biomasses at three temperatures

Syngas composition

Gaseous evolution and composition has been measured in laboratory by mass spectrometer during thermogravimetric (TG) tests. Details of TG tests are reported in previous paragraph. Tests under temperature gradient have been used to characterise qualitatively the gas emission and to select a suitable number of gaseous species, to be measured quantitatively during isothermal tests. Tests are carried out under flowing Ar atmosphere. Figure 13 reports an example of gas concentration measured by mass spectrometer and Ar normalised.

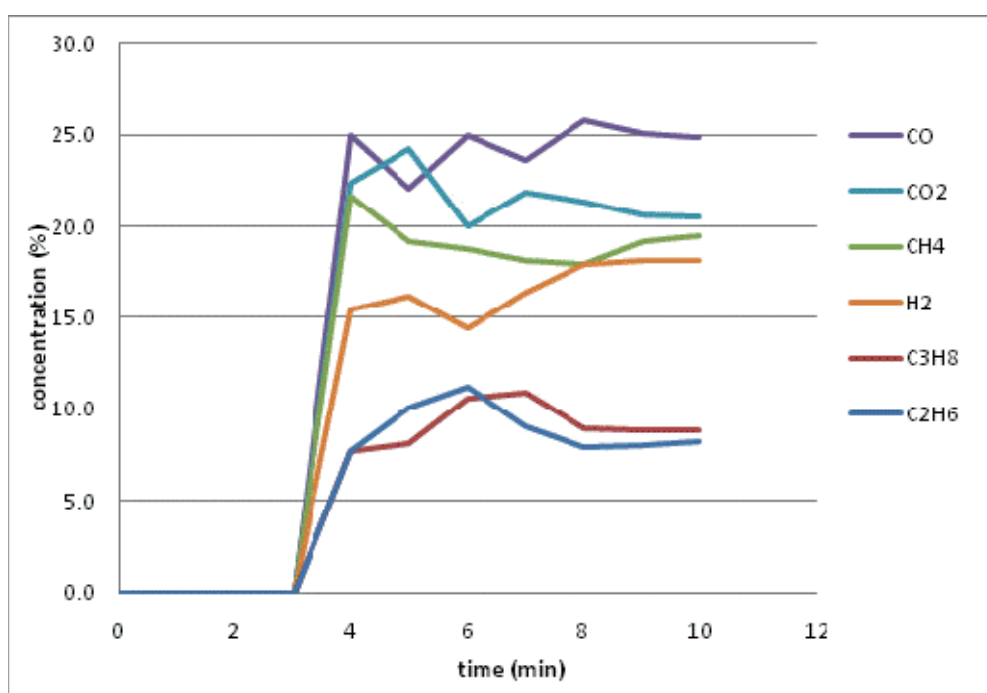


Figure 13. Gas concentration measured by mass spectrometer and Ar normalised.

Table 10 reports the syngas composition, measured during mischanthus pyrolysis. The syngas heating value, reported in the Table, has been calculated by the heating values of the single species, multiplied the molar ratio. The measurement of the gas evolution of the different considered biomass species did not show significant differences in syngas composition and heating values.

	C ₂ H ₆	C ₃ H ₈	CH ₄	CO	CO ₂	H ₂	Calc. LHV MJ/Nm ³
T=400°C	10.0	10.0	21	21	23	15	27
T=500°C	9	9	19	24	21	17	26
T=600°C	9.0	8.0	17	27	19	20	24

Table 10 Composition (%) and LHV of char and syngas as a function of temperature, for mischantus.

Figure 14 reports the heating values of syngas and char obtained in the same TG test. Depending from the main objective of the pyrolysis, the process conditions can be optimised to have higher heating value for char or syngas. If both products are required, a good compromise can be obtained at temperature of 500°C.

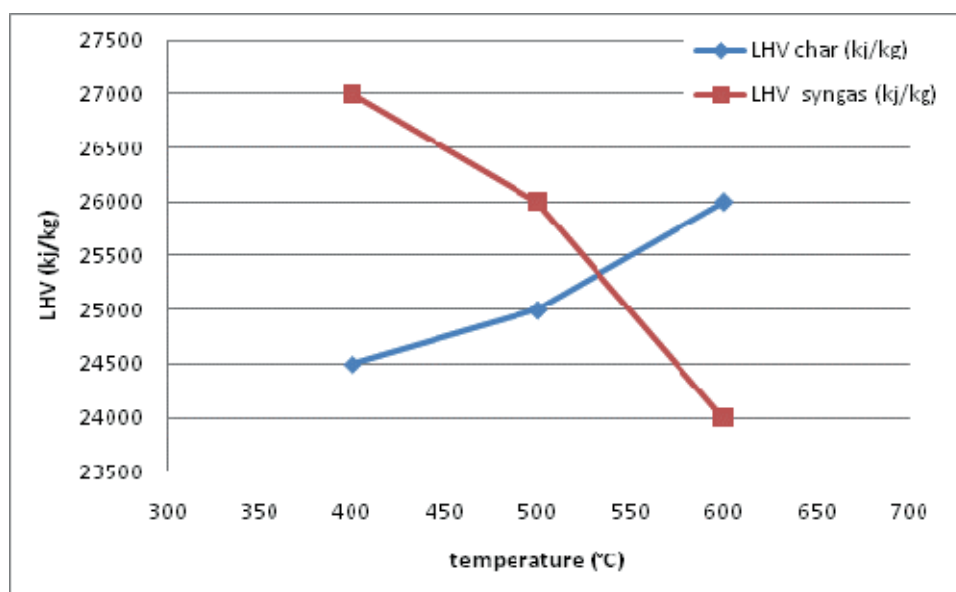


Figure 14. Heating values of syngas and char obtained in the same TG test

Char Reactivity Measurements

The reactivity of the beechwood chars was assessed in a TGA by both isothermal and non-isothermal methods. The results from the non-isothermal determination are shown in Figure 15 along with the temperature programme applied. Following an initial step in an inert atmosphere, the gas is switched to air at the beginning of the temperature ramp from 400 to 850°C. As expected, the chars that have been exposed to higher temperatures present lower reactivities. However, at the low end of the pyrolysis temperature range, there are marked differences between the behaviour of the 300°C char, which shows a high volatile content, and that of the chars produced between 325-450°C. There are as well significant differences between the latter and those chars generated at 500-600 °C, which present the same reactivity among themselves, while the 900°C char is clearly less reactive.

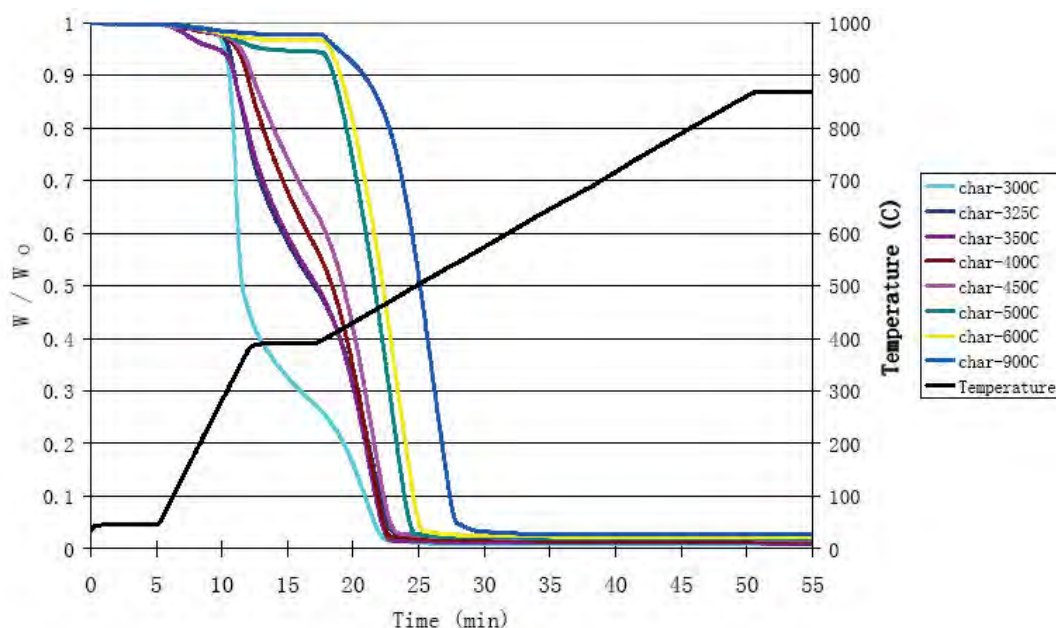


Figure 15. TGA non-isothermal char reactivity tests of beechwood chars produced in the Gray-King reactor. Curves of fraction of remaining weight for the different chars and temperature as a function of time are shown.
W: measured weight; **W₀:** starting weight

Proximate Analysis

Proximate analysis by TGA was performed on char samples in order to determine their remaining volatile content after the pyrolysis process. There was a progression in the amount of fixed carbon in the chars with the increase in pyrolysis temperature for both beechwood (Figure 16) and miscanthus (Figure 17) chars.

In the case of miscanthus, the char produced at 600°C showed a higher fraction of fixed carbon than those obtained at lower temperatures, 350 and 450°C. These two samples showed a similar amount of volatiles, although the latter lost them more slowly (at higher temperatures).

The grapeseed char sample produced at Tecnocentro (Figure 18) had a fixed carbon content slightly below 70%, which is not dissimilar from the fixed carbon content of beechwood pyrolysis char (65%) produced at the same temperature (500°C) in the Gray-King reactor. The grapeseed char also showed a higher ash content than the chars derived from beechwood and miscanthus.

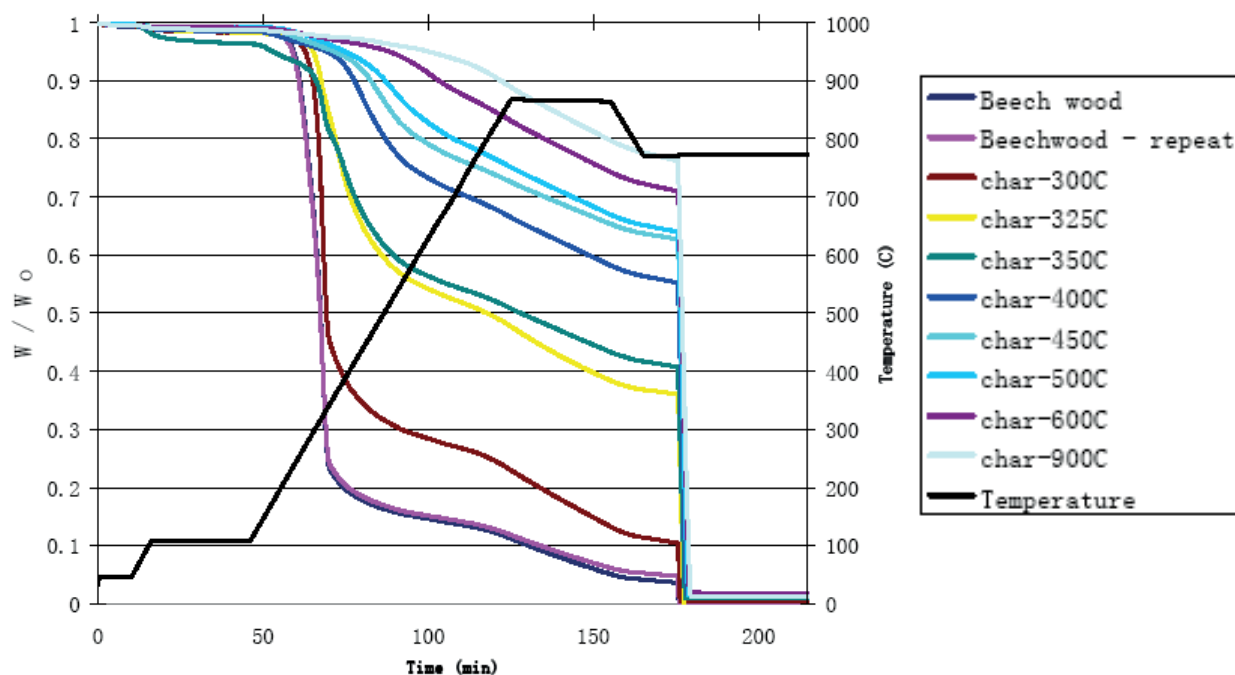


Figure 16. TGA proximate analysis of raw beechwood and beechwood chars produced in the Gray-King reactor. Curves of fraction of remaining weight of the different chars and temperature as a function of time are shown.

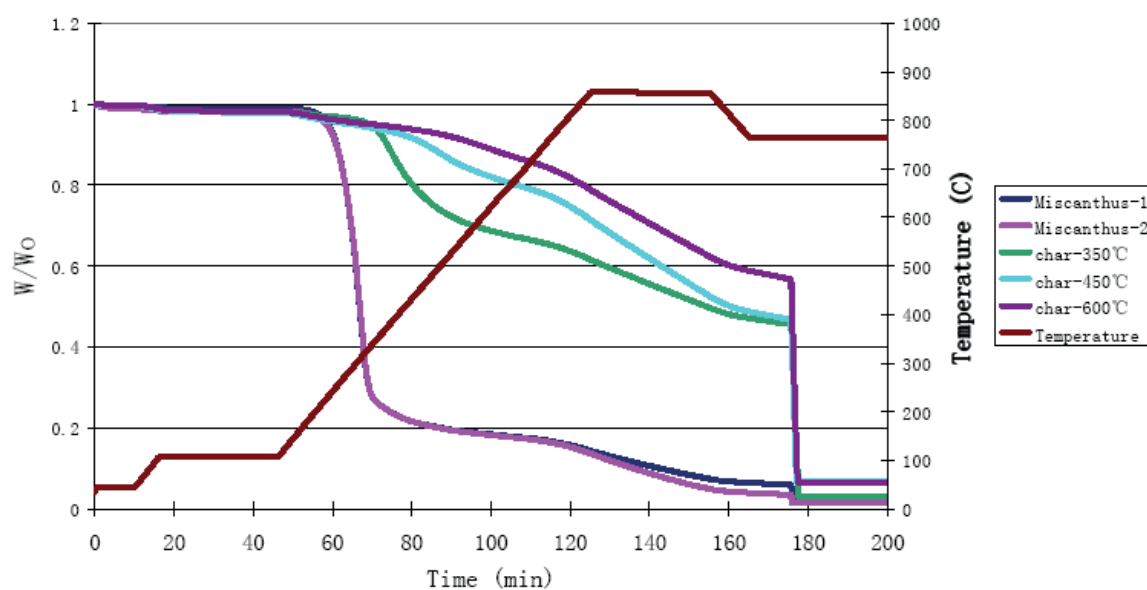


Figure 17. TGA proximate analysis of raw miscanthus and miscanthus chars produced in the Gray-King reactor. Curves of fraction of remaining weight of the different chars and temperature as a function of time are shown.

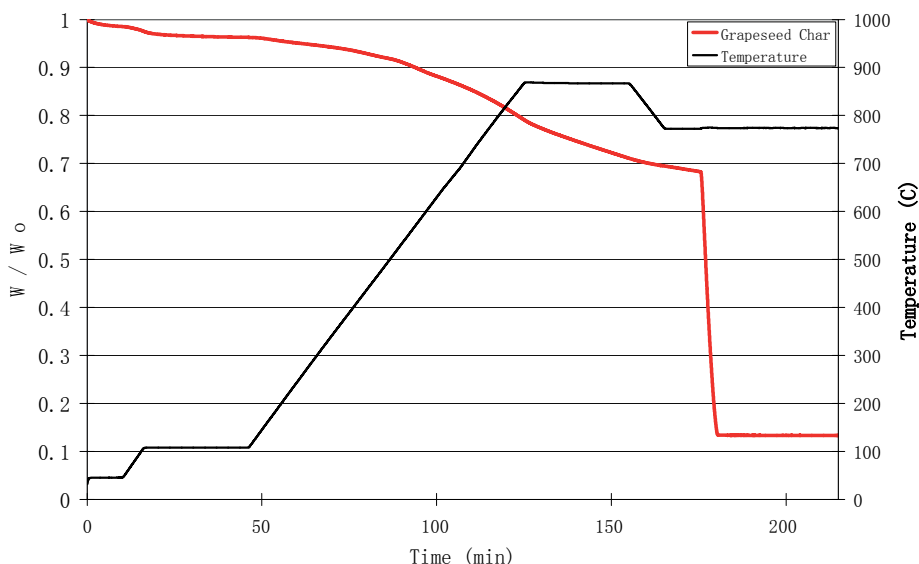


Figure 18. TGA proximate analysis of grapeseed char produced at Tecnocentro. Curves of fraction of remaining weight of the grapeseed char and temperature as a function of time are shown.

In order to compare these results with the coal currently used in electric arc furnaces, four samples supplied by Ferriere Nord have also been analysed. These comprise a metallurgical coke, two injected coals of different particle sizes and an anthracite, which is loaded in the basket. With the exception of the coke, the other three coals showed fixed carbon contents of nearly 90%. Their ash content was higher than that of the coke. In all cases these coal samples were less volatile than the biomass-derived chars, regardless of the conditions at which the latter were prepared.

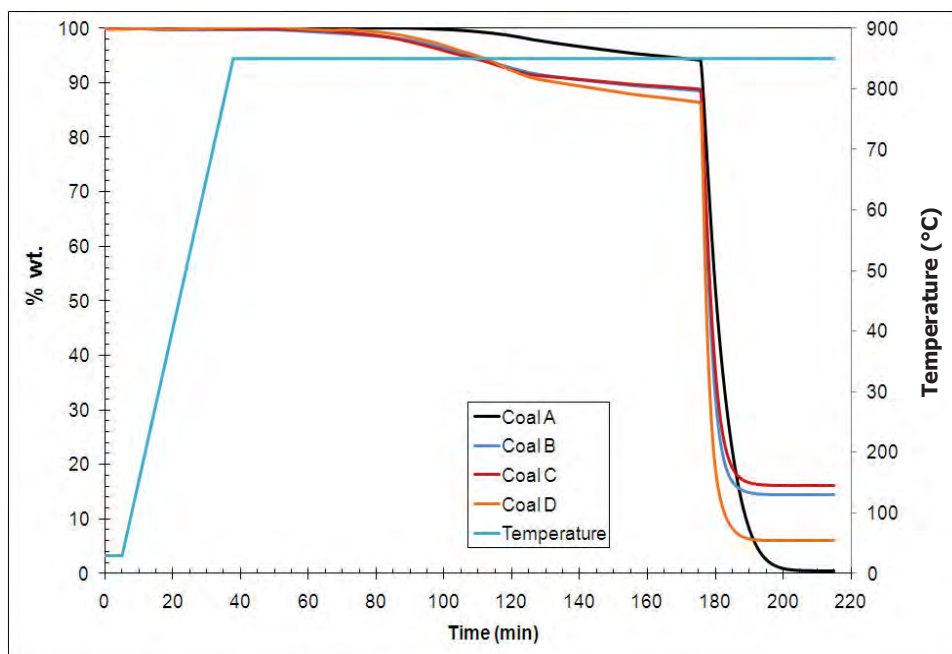


Figure 19. TGA proximate analysis of coal samples currently used at Ferriere Nord. Curves of fraction of remaining weight of the grapeseed char (as percentage of initial biomass, left axis) and temperature (°C, right axis) as a function of time are shown. Coal A: metallurgical coke; Coal B: injected coal (fine particles); Coal C: injected coal (coarse particles); Coal D: anthracite loaded in the basket.

Char reactivity tests (Wire Mesh Reactor Experiments)

A diagram of the reactor is shown in Figure 20. A full description of the reactor can be found elsewhere [Solid Fuels and Heavy Hydrocarbon Liquids, Kandiyoti, Herod and Bartle, Elsevier, 2006]. 5mg of sample are kept as a monolayer on a wire mesh, which is folded and placed between two electrodes. The sample is heated up by means of a current drawn between the electrodes and across the mesh while a carrier gas, which may also be reactive, sweeps the evolving volatiles away. This configuration suppresses any interactions between particles and between particles and evolving volatiles, and therefore it enables single-particle behaviour to be determined under certain conditions of temperature, heating rates and pressure.

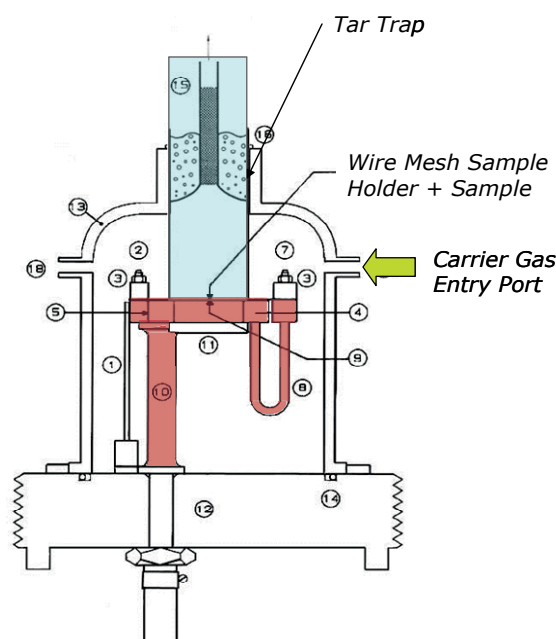


Figure 20. The atmospheric pressure *wire mesh* reactor.

In this study, experiments using this reactor have been carried out at atmospheric pressure, with a heating rate of 1,000°C/s and peak temperature of 850°C. The holding time at peak temperature was varied between 5 and 10 seconds. A CO₂ atmosphere was used to make the occurrence of gasification reactions possible to a certain extent. Two sets of experiments were performed at these conditions. Firstly, the set of coals from Ferriere Nord were analysed (Figure 21). Similarly to the outcome of TGA-based char reactivity experiments, the metallurgical coke showed very little conversion to volatiles, remaining almost 100% of the initial sample as coke. On the other hand, the two injected coals (both used in particle sizes between 106-150µm) had a significant release of volatiles, reaching nearly 18% after 10 seconds at peak temperature.

Three char samples were also studied in the wire mesh reactor, the miscanthus and grapeseed chars presented above, and a pumpkin seed char received from Marienhutte (Figure 22). At 5-second holding time, the pumpkin seed char showed very little release of volatiles, while the other two samples were more similar to the injected coals, with residual char in the range of 88-92%.

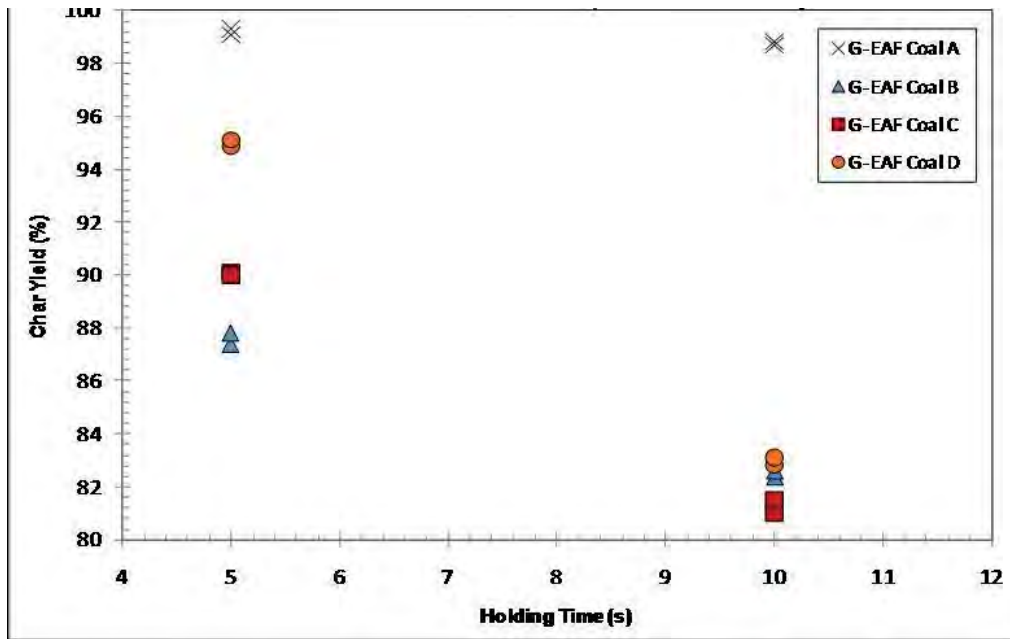


Figure 21. Char yield (as a percentage of initial sample weight in dry, ash free basis) as a function of holding time in wire mesh reactor experiments with CO₂ as carrier gas at atmospheric pressure, heating rate of 1,000°C/s and peak temperature of 850°C. Coal A: metallurgical coke; Coal B: injected coal (fine particles); Coal C: injected coal (coarse particles); Coal D: anthracite loaded in the basket.

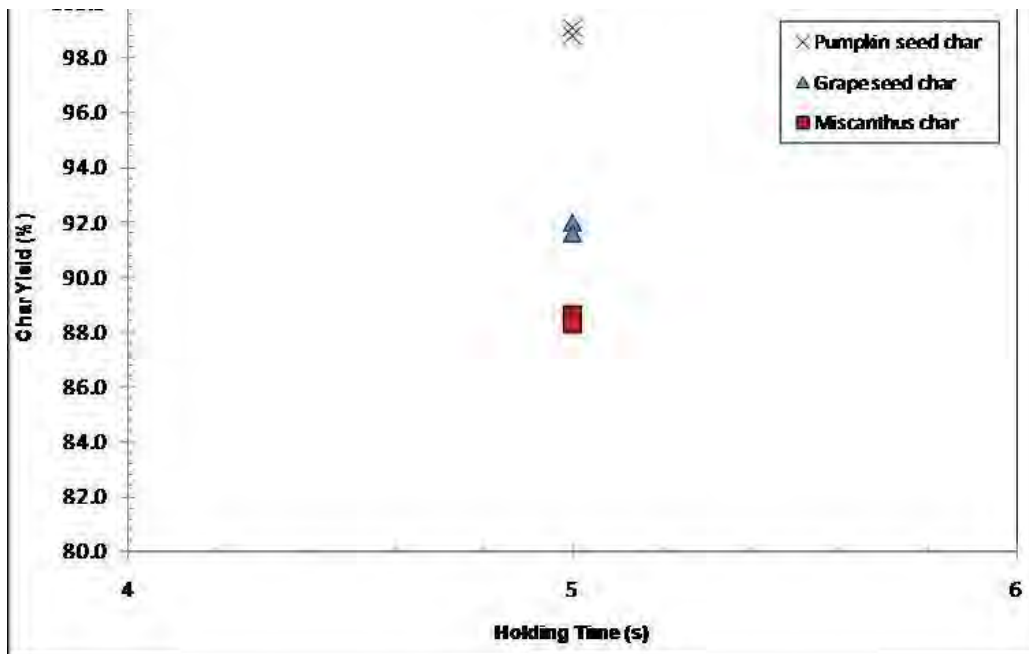


Figure 22. Char yield (as a percentage of initial sample weight in dry, ash free basis) as a function of holding time in wire mesh reactor experiments with CO₂ as carrier gas at atmospheric pressure, heating rate of 1,000°C/s and peak temperature of 850°C.

According to these tests, char (obtained from the different biomasses types) is expected to have similar reactivity behaviour inside the EAF.

In fact char produced at 500 and 600°C (see Figure 16) showed a similar weight loss trend of EAF coals (see Figure 19, in which coal from FENO are used).

Char from mischanthus and grape showed a reactivity beavhiour, in the wire mesh reactor (Figures 17 and 18), similar to EAF coal used in the MH steelplant.

Task 3.2 Definition of process parameters to optimize pyrolysis process (CSM, RWTH)

The industrial partners involved in the project use coal with different characteristics. The main distinguish aspect is the amount of volatile matter. Table 11 reports the characteristics (provided by the partners) of the coals currently used in the industrial practice.

		C %	S %	VM %	ash kcal/kg
FENO	charge anthracite	> 80%	< 1.5%	< 15%	< 15%
	injection anthracite 1	> 80%	< 1.5%	< 20%	< 20%
	injection anthracite 2	> 80%	< 1.5%	< 20%	< 20%
	injection met. Coke	> 85%	< 2.5%	< 20%	< 20%
DEW	Blow carbon	> 96 %	n. a.	< 3 %	< 3 %
	Anthracite	> 90 %	n. a.	< 8 %	< 8 %
	Petrol carbon	> 97 %	< 2 %	< 3 %	< 3 %
	Petrol carbon natural	> 98 %	< 1 %	< 1 %	< 1 %
	Petrol carbon low S	> 98 %	< 1 %	< 1 %	< 1 %
MH	Inj. Coal for foaming	99.7	< 1.26 %	0.15	0.15

Table 11 Characteristics of coals currently used by industrial partners

For this reason, in order to define target figures for the process parameters of the pyrolysis process RWTH did perform investigations regarding the requirements for carbon used in the EAF. The main differences between charcoal and fossil carbon where also investigated.

Of the two possible applications of char, the use as blow carbon for slag foaming is the more demanding application. The demands made by the steel plants regarding blow carbon are considerably higher than for charge carbon. A literature review led to the factors shown in Figure 23 influencing the foamy slag formation. Regarding quality requirements of the carbon source the important factors are the reactivity of the carbon influencing the chemical reactions creating the gas phase. On the other hand the ash content and its composition are influencing the slag phase and may change factors like slag viscosity and surface tension. Especially changes of the basicity and of the P_2O_5 content are possible.

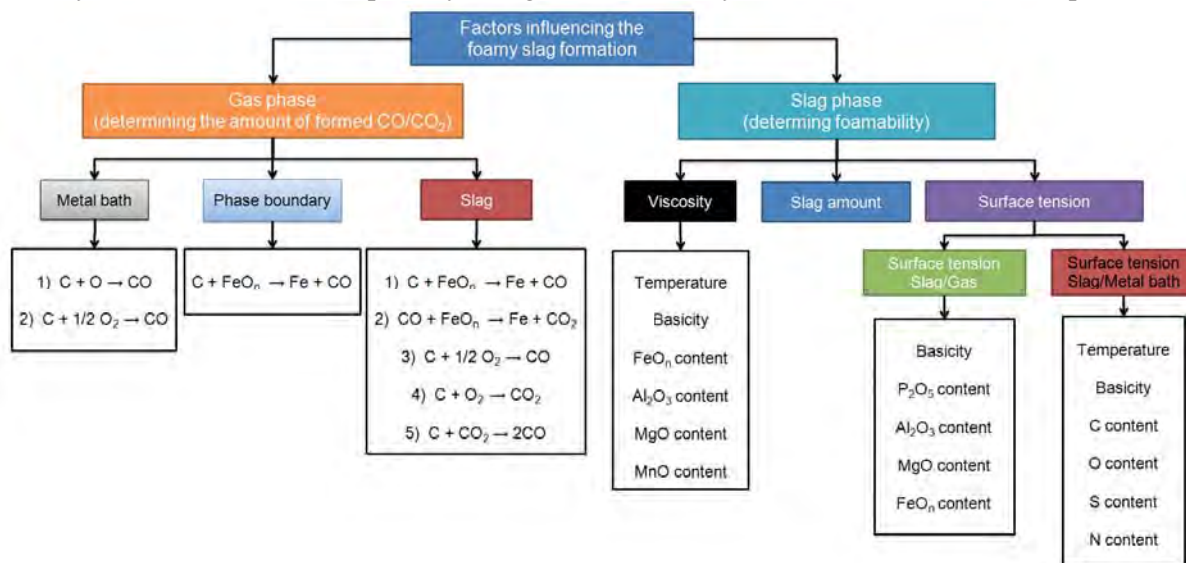


Figure 23: Factors influencing the foamy slag formation

Table 12 shows the main differences between carbon produced from biomass and fossil carbon concerning its use in the EAF. Additional physical differences like grain size distributions can be equalized by processing of the carbon.

	Fossil carbon	Carbon from biomass
Carbon content	> 80 %	lower – equal
Volatiles content	1-3 %	higher
Ash content	~ 10 %	lower
Sulfur content	~ 0.5 %	lower
Chloride content	n/a	ppm range
K ₂ O content	~ 2 % of ash	up to 20 % of ash
CaO content	~ 5 % of ash	up to 40 % of ash
P ₂ O ₅ content	~ 1 % of ash	up to 10 % of ash
Compressive strength [kgf/cm ²]	10-80	130-160
Density [kg/m ³]	550	180-350
Reactivity	lower	higher
Calorific value [MJ/kg]	29-33	25-35

Table 12. Characteristics of fossil carbon and charcoal [23,24]

Regarding its use in the EAF for example to foam the slag especially the carbon and volatiles content as well as the reactivity is of interest. The usually higher amount of volatiles in charcoal may be able to compensate for the often lower carbon content, which can also be seen by the higher reactivity of charcoal. Regarding its use as charge carbon to add chemical energy to the EAF mainly its calorific value is of interest which is usually similar for fossil carbon and charcoal.

Critical aspects of the use of charcoal in the EAF are the in relation to fossil carbon high concentrations of chlorine, potassium, calcium and phosphor. Chlorine and potassium may be problematic regarding corrosion within the off-gas dedusting system whereas the potassium, calcium and phosphor content may influence the slag composition and characteristics in the EAF negatively.

The differences in compressive strength should not be so important regarding the use in the EAF but may necessitate additional processing of the char like pelletizing or briquetting. The differences in density on the other hand may lead to longer blowing times if a fixed mass has to be charged with a given volume flow of gas. Moreover it has to be investigated whether the lower density has a negative effect on penetration depth into the slag.

Regarding the pyrolysis process its process parameters should be optimized in order to achieve a high carbon content and high reactivity respectively. On the other hand the amounts of alkali metals, phosphor and chlorine should be as low as possible.

Task 2.2 Design of industrial pyrolysis tests

On the basis of preliminary laboratory activities industrial pyrolysis process has been designed. According to coals characteristics reported in Table 9, different pyrolysis conditions can be used, depending on the final char end user. A good compromise for pyrolysis temperature can be considered the value of 500°C. According to CSM activity, this value is the best compromise for optimization of char and syngas heating value.

The tests performed by IP confirmed that char, gas and tar yields are almost stable after 500°C.

In case of pyrolysis process devoted to char production for char injection, the best temperature is 600°C, which allow to obtain a char with high heating values and low volatiles content, similar to used coals.

Globally, the carried out work have two principal objectives:

- To study the range of variability of the pyrolysis process parameters and how these variations affect yields and properties of products. The effect of different feedstocks on the process is also evaluated.
- Secondly, it is to understand how this range of control of pyrolysis may affect the overall energy and carbon balance of pyrolysis char and pyrogas systems, and so affect their industrial utilization.

Pyrolysis campaigns have been planned and implemented on laboratory and demonstrative scale that could reproduce, with different limits, but with the advantages of small-scale tests, the transformation process of the fuel gas, char and tar on industrial plant, taking into account the results obtained by the partners in the previous WPs.

Pyrolysis is thermochemical transformations which depend on thermodynamic parameters and operating conditions that determine the characteristics of final products; those parameters influence the choice of the industrial components plant. Three fractions are simultaneously present at the end of the pyrolysis process (char, tar and syngas) and the amount and characteristics can be varied, changing the process parameters governing the reactions of cracking, such as:

1. the temperature profile of the pyrolysis reactor;
2. the rate of heating of the material;
3. the residence time of material in the reactor;
4. the size of the pyrolyzed material;

Points (1), (2), and (3) are deeply investigated and results are shown below; point (4) has been largely investigated by Imperial college, which found out that, in slow pyrolysis the grain size of starting materials is not an influencing parameter.

Before making pyrolysis on demonstrative pyrolysis plant (named Enerpol) in Terni, a test system for small-scale has been set up to increase knowledge about the process of pyrolysis of different kind of materials and characterize the intermediate and final products of the pyrolysis process by simulating the operating conditions at laboratory scale. Figure 24 shows the laboratory scale pyrolysis apparatus.

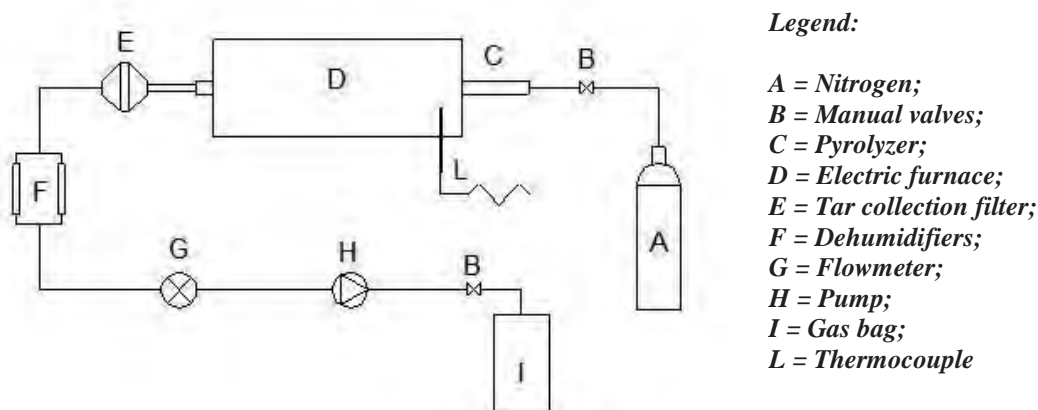


Figure 24 **Scheme of the demonstrative plant used by Tecnocentro to design industrial pyrolysis tests**

This demonstrative apparatus represent the link of the laboratory apparatus (used by CSM and Imperial College) and pilot plant which has been used for definite assessment, and industrial plant, which is used for industrial char production

Laboratory pyrolysis test have been useful to identify the char and gas percentage produced after different pyrolysis campaigns, as showed in the following Table.

BIOMASS	CHAR (% wt)	GAS (% wt)	TAR (% wt)
Sorghum pellet	35.9	52.8	11.3
Grape raspe	29	49	22
Dried wood	21	71	8
Underbrush virgin biomass	28	65	7

Table 13. Char and gas percentage produced after different pyrolysis campaigns

After laboratory pyrolysis test on different kind of biomass, pyrolysis campaigns were carried out on demonstrative plant **to take char and pyrogas samples** in order to study their characteristics **varying process parameters** and define the best condition for char production from biomass.

The effect of the main process parameters, such as different combination of rate of heating, time of treatment and the rotation speed of pyrolysis reactor have been considered.

The demonstrative pyrolysis plant can be fed with about 200 kg/h of fuel and the necessary heat energy for pyrolysis reactions is supplied by a gas burner of the maximum power of 500 KW.

Is it possible to vary the pyrolysis temperature (monitored continuously by a pyrometer) by means of burner thermal power variation.

The photo below shows the pilot plant: pyrolysis reactor, gas cleaning system and the microturbine.



Figure 25 Enerpol pyrolysis plant (Tecnocentro)

The pyrolyzer rotation speed is variable by inverter. During the tests on different kind of fuel, the pyrogas has been burnt in the torch and sampled; the tar, which in biomass is in the percentage of 7%-11% (see Table 13) has been eliminated from the gas in the treatment section and collected in the tank with cooling and washing water.

The char, conveyed by a screw, is usually discharged from the reactor at 500 ° C. The continuous rotating movement of the reactor contribute to the degradation of biomass into powder.

The main monitored and variable pyrolysis parameters are:

- Pyrolysis temperature (optical pyrometer);
- Gas temperature out from the reactor;
- Gas pressure out from the reactor;
- Internal reactor pressure;
- Rotation speed of the reactor (residence time);
- Feeding speed varying the rate of the feeding metering screw;
- Chemical and physical properties of the feeding fuel;
- Chemical - physical characteristics (density, elemental analysis, heavy metals), temperature and mass balances of char and gas obtained;

The main values of pyrolysis parameters during the tests have been:

- O₂ content in the rotary kiln: 2-3 %;
- Internal reactor depression: -2/ -3 mmH₂O;
- Biomass feeding to the reactor: 100 kg/h;
- Pyrolysis temperatures for the tests: 450°C, 550°C, 650°C;
- Residence time for different tests: 30, 40, 50 min

During the tests, gas and char produced have been sampled to analyze the influence of process parameters variation on their weight percentage and on their energy characteristics and chemical composition.

The gas product is typically a mixture of carbon dioxide (9-55% by volume), carbon monoxide (16-51%), hydrogen (2-43%), methane (4-11%) and small amounts of higher hydrocarbons. The gases are usually present with nitrogen introduced to inert the pyrolysis equipment, this can be treated as a diluent and ignored for material balancing but will affect the heating value of the syngas.

Gases analyses show high rates of nitrogen and oxygen, due to such infiltrations; additional calculations are needed to verify the real mass and energy balances.

Figure 26 reports the chemical composition of syngas obtained with different starting biomasses

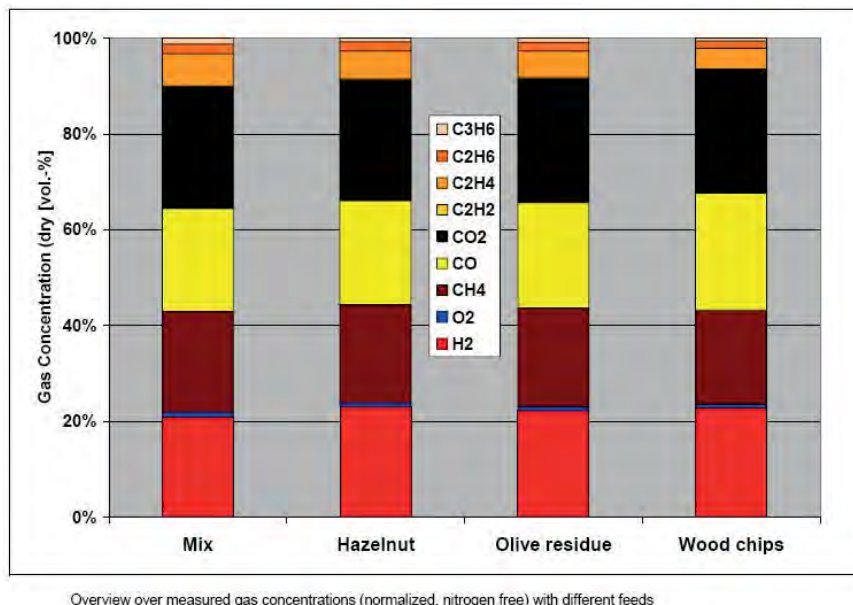


Figure 26 Syngas composition obtained during preliminary pyrolysis test at 550°C, with rotating speed of 3 rpm

In agreement with laboratory tests performed by CSM and Imperial College (results described in task 3.1) syngas composition is dependent mainly on pyrolysis conditions than biomass types.

Table 14 report the detail of the syngas composition, obtained with sorghum, at the pyrolysis temperature of 600°C.

specie	[%vol]
H ₂	6.5
CH ₄	7.6
CO	21.7
CO ₂	23.6
O ₂	6.6
N ₂	31.8
C ₂ H ₆	0.7
C ₃ H ₈	0.6

Table 14. Syngas composition, obtained with sorghum, at the pyrolysis temperature of 600°C.

This syngas composition, if normalised by nitrogen, is similar to what obtained in laboratory tests. Table 15 reports char characteristics.

	Char from forest residues	Char from agric. residues
C	39.12	75.06
H	1.87	1.84
S		<0.1
N	1.30	2.02
O		5.78
Ash	55	7.6
HHV (kcal/kg)	2548.5	5450.7
LHV (kcal/kg)	2548.1	5450.7

Table 15. Char characteristics obtained with forest residues (underbrush) and grapewine.

Temperature also has an effect on char composition; chars produced at higher temperatures having higher carbon contents both total- and fixed-carbon. Higher temperatures lead to lower char yield in all pyrolysis reactions.

When temperature increasing it's pointed out that:

- Tar decreases
- Pyrogas increases
- Substantial stability of the char

With increasing residence time:

- Tar decreases
- Pyrogas increases
- Char decreases
- Char LHV increases with the residence time

Feedstock humidity control is a parameter of great importance for optimizing the efficiency of the process, because if the level increases, the heat necessary for pyrolysis of biomass is no longer sufficient as used for evaporating the water in the fuel. For good process performances, fuel moisture contents of 15-20% are typical. In all pyrolysis reactor, water is also a product and is usually collected together with other condensable vapours in the liquid product.

Chars formed under low flow, high pressure conditions with consequent higher char yields also have higher fixed-carbon yields.

As with the biomass feed, the char and liquid products have energy values roughly related to their carbon contents.

For any given feedstock it is possible to vary the product distribution between char, liquid and gas, within limits, by choice of process type and operating conditions. Higher char yields are obtained by slow pyrolysis processes with lower temperatures and low flow rates; higher liquid yields arise from fast pyrolysis processes, specific temperatures and high flow rates. The gas yield is not usually the focus of slow or fast pyrolysis and is generally not actually measured but calculated by difference in mass balance.

Similarly, for any given process and equipment set-up, different product distributions will arise from different feedstocks depending on their composition. However, this should not be a major factor in choice of feedstock for pyrolysis, as controllable operating conditions, such as temperature, generally have a larger effect and could be changed to adjust product distributions. Choice of feedstock is more likely to be dependent on factors such as availability, cost and sustainability considerations. Variation in biomass feedstock, even if nominally a single source, is likely to be one of the main causes of variability. The exact composition of a type of biomass will vary depending on many factors relating to when, where and how it was grown, for instance the weather, soil type and agricultural regime.

Figures for carbon contents in nominally the same type of biomass may differ by as much as 10% relative. The composition of a single supply of a particular biomass type should be more consistent but is not likely to be truly homogenous, except at small scale, unless special provisions for mixing and blending are made. Feedstock moisture content and particle size may vary within and between loads and affect process yields.

Temperature control is also likely to be an important cause of variability, particularly for slow pyrolysis. The lower heat fluxes and longer residence times of slow pyrolysis give scope for variation in heating rate and peak temperature. Yields from traditional charcoal kilns are known to be affected by weather conditions, due to the effect on temperature control and fuel-wood consumption.

As general conclusion, it can be stated that char yield is about 20% of weight of starting biomass, and this value decreases with temperature; yield is almost constant at temperatures higher than 500°C. Pyrolysis at temperatures higher than 500°C and longer residence time are necessary to obtain charcoal with low values of volatile matter (suitable for charging); pyrolysis temperatures lower than 500°C permit to obtain charcoal with higher volatile matter content, suitable for injection and foaming. Regarding the amount of char, tar and syngas obtained after pyrolysis process, values are reported in Table 13. Increases of temperature and residence time determines the reduction of Tar and increases of syngas amount.

WP4 DEFINITION OF THE EAF OPERATING PRACTICES (DEW, FENO, CSM, RWTH, MU, TECNOCENTRO, IP)

Task 4.1 EAF cycle Analysis (RWTH, Ferriere Nord, DEW and MH)

An analysis of the EAF cycle of the three steelmakers participating to the project has been carried out. The analysis was aimed at:

- collect data of amount of coal used
- collect data about coal utilization (charge/injection)
- modification of current operating practices of coal utilization

- Definition of burners working conditions (geometry, furnace atmosphere, burners powers, inlet gas flow rate) to simulate biogas use

FENO EAF cycle analysis

FENO EAF is an AC furnace with capacity of 140 tons. The global energy consumption is of 80 Mwh. Almost 50% of energy demand is provided by chemical energy, (coal and natural gas burning, and from exothermic reactions oxidation of charge material as Fe, Si and Mn). Energy from coal represents almost 17% of total energy demand of the furnace.

Coal and natural gas burning is managed through ten burners. Seven burners are natural gas fed (CH_4) and are installed in tangential position, and three are oxygen lance installed in radial position.

Figure 27 reports a general view of the EAF with the position of the installed burners.

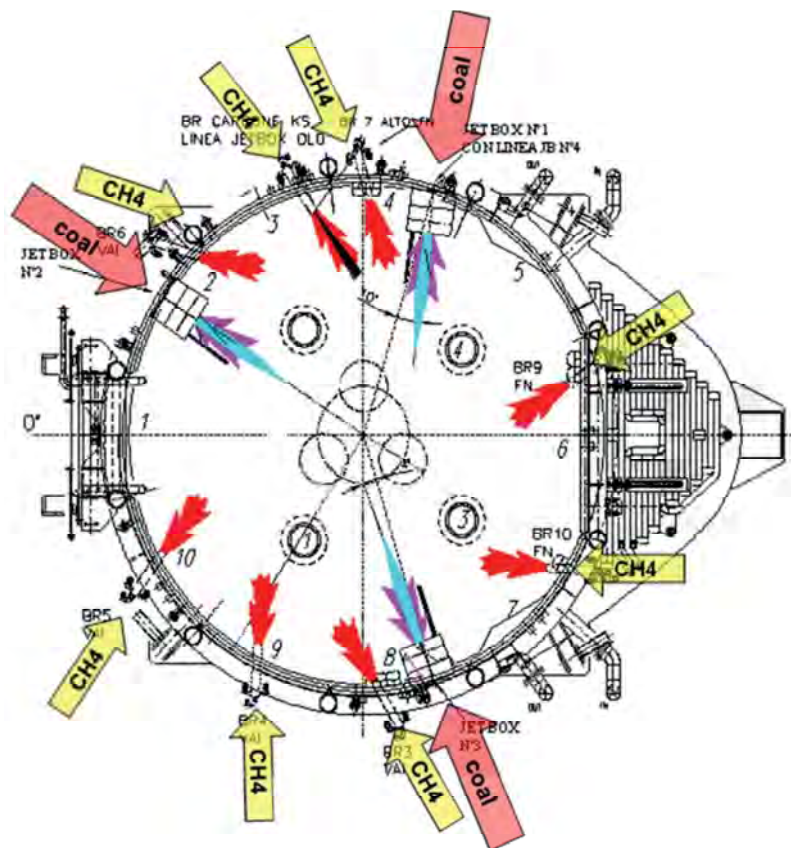


Figure 27. General view of the EAF with the position of the installed burners

Table 16 and 17 report the global energy input distribution of the furnace.

EAF Total energy input		
total EAF energy input	80	Mwh
electrical Energy	42	Mwh
chemical Energy	38	Mwh

Table 16 Energy input of and chemical energy distribution of EAF of Ferriere Nord

Chemical energy distribution		
energy from carbon (pulv. + inject.)	13.4	Mwh
natural gas energy	8.7	Mwh
remaining chemical energy (Fe, Al, Si, Mn oxidation)	13.8	Mwh
% of EAF energy input from carbon	16.8	%

Table 17 Chemical energy distribution of EAF of Ferriere Nord

The amount of chemical energy which potentially can be replaced by biomass (charcoal charged and injected and syngas burning) is 28% of the total EAF energy input.

An estimation of the amount of biomass yearly necessary to replace coal and natural gas has been carried out and compared with regional amount of available biomass (described in WP1).

Table 18 reports the calculation of biomass necessary to replace coal; for this evaluation, average values of heating values and pyrolysis char yield have been used.

Charcoal heating value (average value among measured and literature data [3])	20.000	kJ/kg
char per heat	2.000	kg
% char from biomass pyrolysis (average value [3])	20	%
Calculated biomass per heat	8.066	kg
average year steel production	1.2	Mt
biomass consumption per year	100.000	t

Table 18 Mass Balances to estimate biomass necessary to replace coal in Electric Furnace of Ferriere Nord.

According to the study of biomass availability it can be concluded that the amount of available biomass is enough for Ferriere Nord EAF use.

According to the performed analysis syngas amount produced by pyrolysis is in the range 30-40% respect the starting amount of biomass.

Considering that the current consumption of natural gas is 840 m³ per heat, which correspond to an energy input of 30,24·10⁴ kJ per heat. The global energy input due to natural gas burning is 3,024·10¹¹ kJ/year, with the productivity of FENO EAF. If a relatively low value of heating value of syngas (15.000kJ/kg, for a prudential evaluation) is considered, 20160 tons of syngas are theoretically necessary to replace natural gas burning. Having estimated that 100.000 tons of biomass produces 30.000-40.000 tons of syngas, this amount is largely available

Design of industrial tests: char utilization in EAF

Coal is both charged in the bucket and injected. Both ways of utilisation have been tested in the industrial tests. In the current operating practice, the amount of used coal is:

Charged 4 kg/t → 550 kg per heat

Injected 8 kg/t → 1100 kg per heat

Steel and slag composition, offgas composition, oxygen and power consumption and gaseous emission at stack (including dioxin monitoring) are monitored during industrial trials with char utilization and compared with average current values.

The effects of char utilization on the process have been preliminarily analysed before making industrial trials. The following aspects have been considered:

1. Effects of char ash on slag composition and on slag properties (viscosity and melting point)
2. Effects on steel composition
3. Effects on environmental pollution

Effects of char ash on slag composition and on slag properties (viscosity and melting point)

Table 19 reports the calculated amount of formed ashes due to char injection

	kg charg. char (per heat)	kg inject. char (per heat)	kg of formed ash (per heat)
corn	600	1200	414
grapewine	600	1200	432
Forest residues	600	1200	54
mischanthus	600	1200	180

Table 19. Mass (kg) of formed ashes which derives from char charge and injection. Data refers to single heat

Ashes dissolves into the slag and modifies its composition. The ash addition in case of forest residues and mischanthus addition can be simply neglected, due to the low amount of ashes formed. In case of ashes from corn and grapewine biomass, the modification of slag composition and the subsequent modification on viscosity and melting behaviour (whim variation may affect EAF process) have been evaluated with models available in literature. To calculate the variation of slag composition it has been considered an average value of slag composition and a slag mass of 10 tons. Table 20 reports the starting slag composition and the modification with ashes

	Slag [%]	slag+corn ash [%]	slag+grapewine ash [%]
FeO	39.6	39.3	37.8
MnO	4.1	4.1	3.9
SiO ₂	13.4	13.3	13.7
P ₂ O ₅	0.1	1.2	1.8
S	0.1	0.1	0.1
Al ₂ O ₃	6.1	6.1	5.9
MgO	3.2	3.5	3.7
CaO	29.1	29.3	28.9
Cr ₂ O ₃	1.0	0.9	0.9
TiO ₂	0.4	0.4	0.4
K ₂ O	0.0	1.7	2.8
Na ₂ O	0.0	0.0	0.0

Table 20. Starting slag composition and the modification with ashes

On the basis of the chemical composition of starting and modified slag, viscosity and melting behaviour have been calculated with Urbain model [9] and with Thermocalc [26].

Figure 28 reports the viscosity of starting and modified slag.

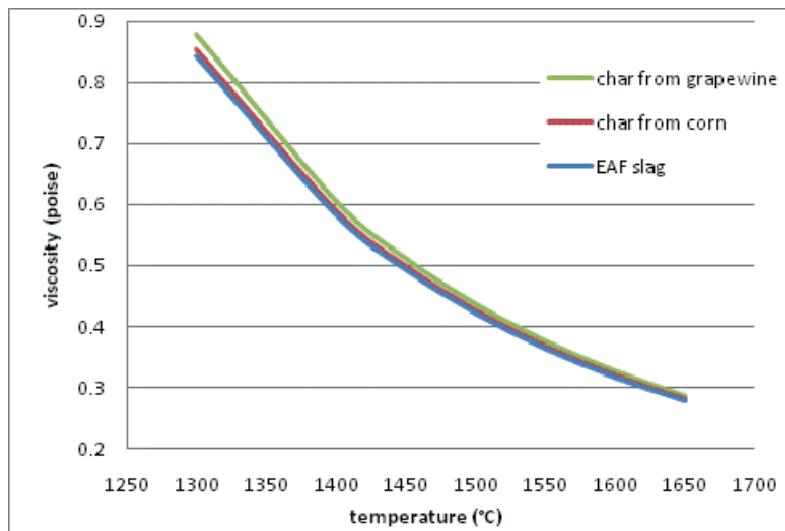


Figure 28 Viscosity of starting and modified slag. Viscosity is calculated with Urbain model [9].

Slag viscosity remain practically constant after char ashes dissolution. The characterization of melting behaviour calculated with ThermocalcTM did not show a significant modification respect the starting composition.

- Effect on steel composition

The presence of metal impurities inside char is of the same order of magnitude of coal. Moreover all these metals are oxidized during injection and are entrapped by slag. Steel and slag samples will be collected during industrial tests to verify that steel quality and slag characteristics are not affected by char utilization.

- Environmental pollution

Char utilization may affect environmental pollution for the following reasons:

1. presence of Cl (even if at low level) may affect dioxin formation
2. large amount of pulverised char in the EAF dust (due to low density of material)
3. presence of P and S in the slag may restrict further slag re-utilization

An estimation of the amount of Cl in the fumes, considering the actual situation and the eventual increase (min and max values are indicated) compared with optimal range of working defined by BATs [10] indicates that char contribution to dioxin formation is low (see Table 21), and in any case is close to the lower limit of the range defined by the BATs, considering both offgas and dust content (Best Available Technologies).

Chlorine added with char	Cl in char [%]	char Kg/heat	Cl kg/heat
Max	0,2	1600	3,2
Min	0,05	1600	0,8

Dust FENO (current situation)	Cl in EAF dust [%]	Dust kg/heat	Cl in dust kg/heat
	1,5	1650	24,75

BATs Chlorine content in Off gas	HCl mg/t steel	t.steel/heat	Cl kg/heat
Max	9600	120	1,15
Min	800	120	0,10

BATs Chlorine content in Dust	Cl % in Dust	Dust kg/heat	Cl kg/heat
Max	1,5	1650	24,75
Min	4	1650	66

Table 21. Estimation of Cl presence into fumes and comparison with acceptability range of BATs [10]

DEW EAF cycle analysis

At DEW coal is used in the EAF cycle in two ways. Blow carbon is used to foam the slag when producing carbon steel qualities. Blow carbon is injected in order to foam the slag after melting down the 2nd bucket. The carbon is lanced with air (carrier gas) in the layer between melt and slag. The slag foaming procedure is used to shield the electric arc so that less energy is radiated onto the sidewalls of the furnace and therefore to lessen energy losses and to improve the heat transfer from the arc into slag and steel. Up to now there are no known foamable slags for the produced stainless steel grades. Therefore the EAF in the steelworks Siegen utilise no blowing carbon for stainless steel grades.

Another way to use coal in the EAF cycle at DEW is to charge the coal together with the scrap in the bucket. The coal used this way is also called charge coal at DEW. Charge coal can be needed to reach certain carbon levels in the steel depending on scrap qualities available. It can also be used to replace electrical energy by chemical energy when oxygen is used to decarburize the melt and the carbon is burned to CO and CO₂ respectively.

At the moment DEW is using fossil coal only. The characteristics of the used coal species are shown in **Table 22**. The specific amounts of coal used at DEW are shown in **Figure 29**. According to this data for the years 2006-2009 the mean amount of blow carbon used per ton of steel produced is about 3.1 kg. The mean amount of charge carbon is 10.7 kg/t_{Steel}.

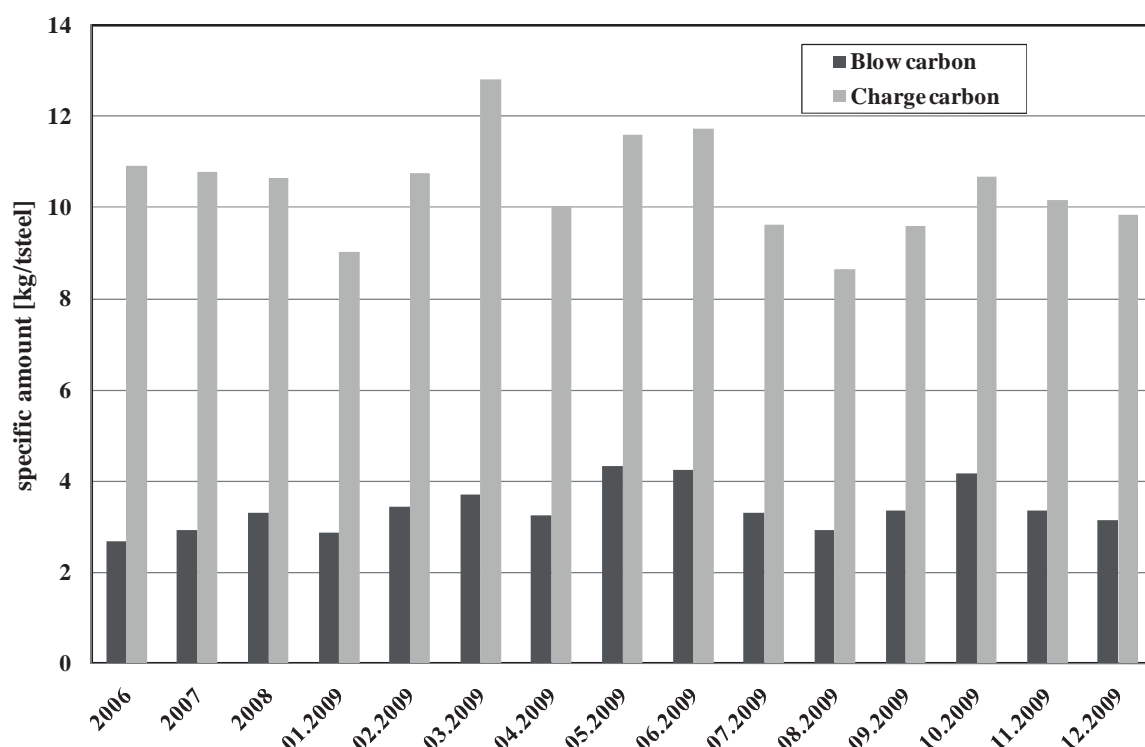


Figure 29. Specific amounts of carbon used at DEW (2006-2009)

At DEW, per heat of carbon steel (140 t), are used on average 434 kg of blow carbon and 1498 kg of charge carbon.

Based on the average carbon usage per heat and per ton of produced steel the annual demand for biomass has been established for DEW. Taking the differences in carbon content into account and assuming that there are no further differences in the quality of charcoal and fossil coal regarding reactivity and therefore the ability to foam the slag the amounts of biochar and biomass needed have been calculated. Table 22 reports the amount of biomass necessary to replace fossil carbon at DEW.

Annual carbon demand	5000 - 8000 t/a
CO ₂ emissions	~ 18000 – 30000 t/a
Annual biochar demand	6000 – 9600 t/a
Average yield for biomass pyrolysis	20 %
Biomass demand	30000 – 48000 t/a

Table 22: Annual carbon and biomass demand at DEW Siegen EAF

Within the scope of the cycle analysis at DEW also reference values for the foamy slag composition have been established. These values will be used to investigate the influence of the charcoal and its ashes on the composition of the EAF slag. Table 23 reports slag compositions and average values of the slag composition for a series of heats at DEW.

The industrial trials planned at DEW will start with the partial to total substitution of fossil charge coal with charcoal. Especially mass and energy balances will be used to investigate to influence of the charcoal use on EAF operations.

In a further stage the substitution of blow carbon by charcoal was investigated. To prevent a negative impact of possible problems like line clogging on the production, a redundant carbon blowing system will be installed temporarily at the DEW EAF. The slag foaming capability of charcoal will be studied qualitatively in comparison to fossil blow carbon.

The influence of char composition, especially the ash, on slag and steel composition will be investigated for all trials by according analyses.

Heat	FeO _n [%]	CaO [%]	SiO ₂ [%]	MgO [%]	MnO [%]	Al ₂ O ₃ [%]	Cr ₂ O ₃ [%]	TiO ₂ [%]	S [%]
1	30,2	20,7	13,4	8,8	6,3	3,5	2,7	2,0	0,2
2	36,8	24,6	12,8	7,8	7,0	3,6	3,8	0,6	2,5
3	44,9	18,9	8,5	6,9	5,3	4,0	4,1	0,7	-
4	30,3	25,5	12,0	8,4	5,9	4,9	5,5	0,8	-
5	52,6	16,8	10,0	7,1	3,5	3,5	1,3	1,0	-
6	42,5	23,1	8,5	8,0	4,3	4,7	3,7	1,2	-
7	48,4	23,2	7,0	5,4	4,2	3,9	2,9	0,8	-
8	37,8	26,6	8,8	8,7	5,4	3,9	4,4	0,8	-
9	36,5	26,3	10,7	9,7	6,0	4,2	2,8	1,0	-
10	22,2	38,3	15,0	8,0	5,0	6,3	2,1	1,0	-
11	42,6	18,8	13,5	7,4	6,5	5,3	3,6	1,0	-
12	47,9	20,5	7,4	6,9	4,2	3,3	5,1	0,5	-
average	39,4	23,6	10,6	7,8	5,3	4,2	3,5	1,0	-
st. dev.	8,8	5,6	2,7	1,1	1,1	0,9	1,2	0,4	-

Table 23. Composition of foamy slag at DEW Siegen EAF

MH EAF cycle analysis

In case of Marienhütte steel plant, coal is injected by a lance. So, beside the energetic input, the foaming behavior is an important process aspect which must be taken into account for industrial testing of char. Slag foaming is a very complex equilibria depending on slag properties (mainly viscosity and surface tension), amount of injected coal (which affect the amount of gaseous species necessary to promote foaming) and also coal reactivity. Comparison of coal and char reactivity (works carried out in WP3) studied at laboratory scale indicated that a similar behaviour is expected.

For a better control of this process Marienhütte developed together with VATRON GmbH an optical foaming slag management system (OFSM [24]). The slag height is detected by a camera continuously. The camera is placed close to the slag door. A special image processing software calculates a slag index to be used for the injection of the carbon amount required (Figure 30). Due to the real-time monitoring of the slag level it is possible to adjust the C-contents by injection of the optimal quantity of carbon.

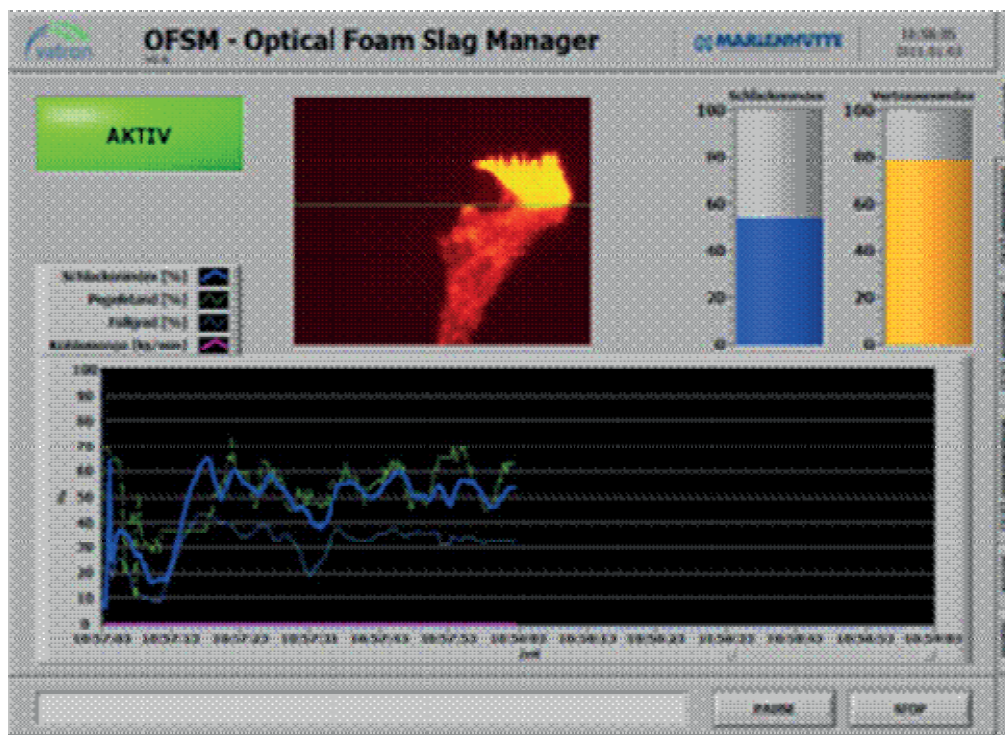


Figure 30 Optical Foaming Slag Management (OFSM)

Due to the Optical Foaming Slag Management the overall efficiency of the melting process can be increased significantly. Moreover a reduction of total carbon added could be achieved.

The OFSM was used for further assessment of the EAF cycle and for assessment of the charcoal injected.

Task 4.2 Pilot plant tests

Before performing trials at the EAF pilot plant of RWTH, slag foaming capability of the charcoal delivered by Tecnocentro and comparing it to conventionally used fossil coals has been carried out. These trials have been conducted using EAF slag samples from the DEW and MH.

To determine the minimum amount of carbon needed to reduce the iron oxides in the slag, the slag has been analysed using XRF. Table 24 shows the result of the XRF analysis of the slag of DEW. Table 25 shows the oxidic slag composition deducted from the XRF analysis and assuming that the balance consists of oxygen. The amount of carbon needed for a stoichiometric reduction of the FeO and Fe₂O₃ in 100 g of slag has been determined to be about 14 g. Because of the lower carbon content of the char this equates to 17.2 g of char.

Element	Fe	Ca	Mn	Cr	Si	Mg	Al	Ti	S	P	Bal.
Mass fraction [%]	25.71	16.65	3.80	1.25	0.83	0.38	0.35	0.15	0.12	0.04	50.38

Table 24: XRF analysis of the slag used for foaming trials at RWTH, with EAF slag from RWTH

Slag composition	CaO	MnO	Cr ₂ O ₃	SiO ₂	Al ₂ O ₃	MgO	TiO ₂	P ₂ O ₅	S	FeO	Fe ₂ O ₃
Mass fraction [%]	23.3	4.9	3.6	1.8	1.3	0.6	0.2	0.2	0.1	7.9	55.9

Table 25. Oxides species composition derived from X ray analysis

A defined amount of slag and carbon have been mixed and charged into alumina crucibles. The crucibles have then been put into a furnace heated by a natural gas/oxygen burner. The furnace has been heated to temperatures of up to 1600°C. Figure 31 shows a charged crucible und the crucibles inside the furnace.



Figure 31: Crucible filled with slag and carbon mixture (left) and crucibles in the furnace (right) in lab experiment carried out by RWTH.

During the trial after the melting of the slag the formation of gas and the foaming of the slag can be observed. The foamy slag is increasing the slag volume and leads to a freezing of slag to the inner crucible wall up to a height indicative of the maximum volume increase during the trial. Figure 32 and 33 show pictures of the crucibles after the DEW slag foaming trials. Within these pictures the foamy slag height reached during the trial is marked. Table 26 reports measured slag height in the crucible and relative volume increase for the different trials.

Trial	Foamy slag height [mm]	Volume increase [%]
Injection coal FENO	50	250
Injection coal DEW	76	378
Grape seed char 1	98	491
Grape seed char 2	82	421

Table 26: Results of slag foaming trials

The achieved volume increases show the general suitability of the char for slag foaming.

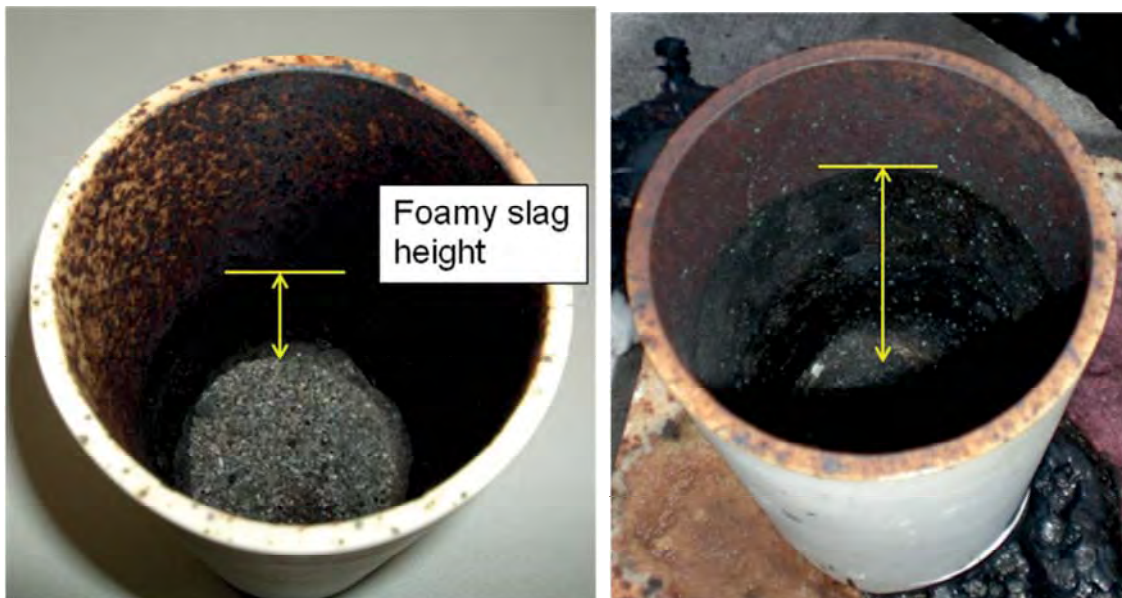


Figure 32: Slag foaming with injection coal from FENO (left) and DEW (right)

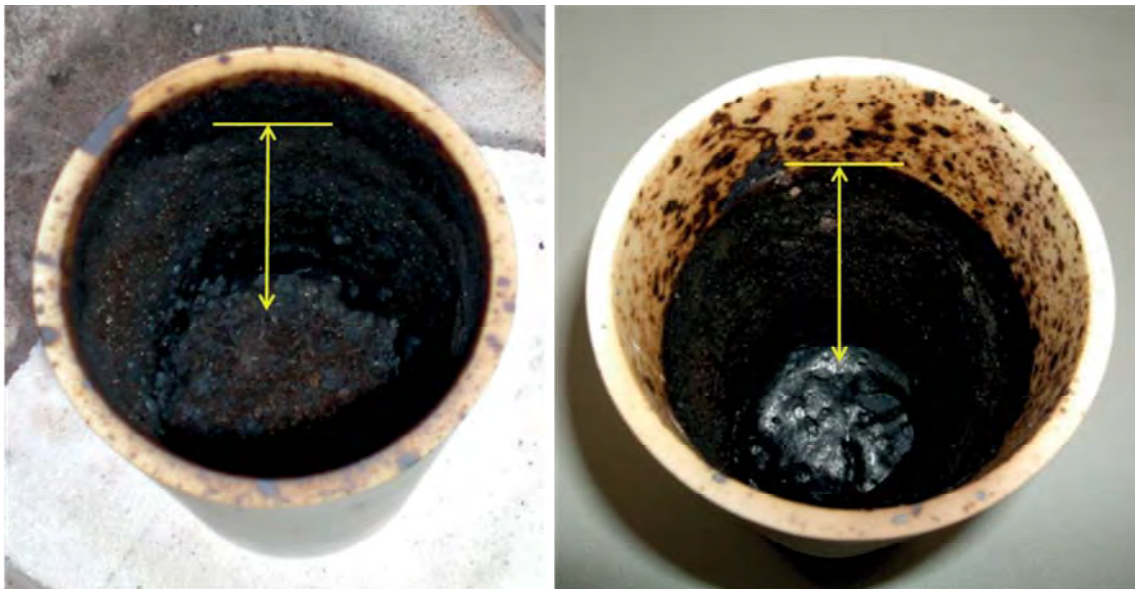


Figure 33: Slag foaming trials with grape seed char

Similar experiment has been repeated with MH EAF slag, the same charcoal from Tecnocentro and compared with char samples produced from a laboratory reactor and with petroleum coke. Especially the influence of the volatile components on the slag foaming should be investigated. Also the reactivity and the specific surface area are very important factors, which could influence the foaming of the slag. For the reason, Table 27 gives an overview of these parameters of the tested materials. The reactivity was measured with a TGA at 1300 °C under CO₂ atmosphere, whereas the porosity and surface area was measured with a gas sorption sampler using the BET-method.

	Reactivity	Surface area	Pore volume
	[%/min]	[m ² /g]	[cm ³ /g]
Calcined petroleum coke	1,51	2,34	0,002
Charcoal Tecnocentro	3,28	165,75	0,069
Charcoal 064/KO/07	6,96	327,69	0,135

Table 27 Reactivity, specific surface area and pore volume of the tested materials

It is obvious that charcoals have much higher porosity and therefore surface areas than petroleum coke, which leads to their higher reactivity.

The investigations of the influence of these differences on the foaming behaviour were performed with the so called “sessile drop test” as well as with some foaming test in small scale¹.

The results of the “sessile drop tests” are illustrated in Figure 34, where some exemplary pictures are picked out. These pictures are only a part of the whole video but visualize the sequence of the slag foaming very clear. The first picture of each row gives the melting beginning of the slag which is at about 1300 °C. The formation of a spherical form of the slag is obvious which indicates the non-wettable character of carbon. The next pictures show the reaction of the FeO in the liquid slag with the carbon of the substrate with increasing temperature. In dependence of the carbonaceous material the intensity of the reaction differs, which results in varying CO bubble formation and therefore slag foaming.

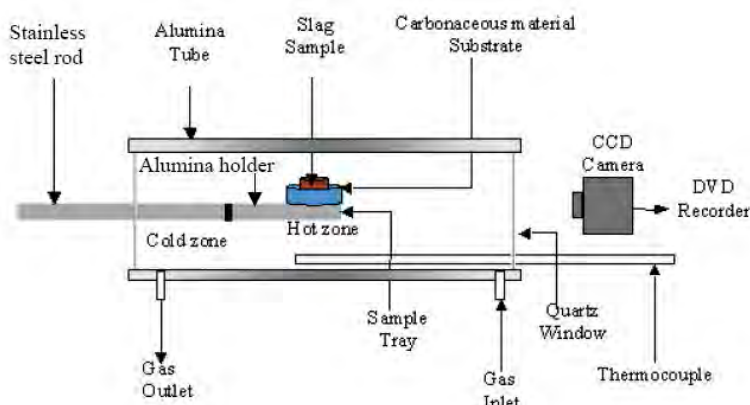
The calcined petroleum coke forms very rapidly a foamed slag due to a fast slag-carbon-reaction. This foamy slag stays stable very a long time period. The specimen pulsates during this period due to the permanent new CO bubble formation.

At the test with charcoal from Tecnocentro it can be seen, that at the beginning only a slightly foamed slag specimen is formed which also collapses very fast. The CO bubble formation in combination with slag foaming starts not before the slag is spread over the substrate by a strong reaction

Charcoal 064/KO/07 is, in contrast, absolutely unwettable. Here the liquid slag drop stays absolutely unchanged and stable on the carbon substrate and does not react. Only a kind of explosion leads to a changed situation. However, no slag foaming could be observed.

In conclusion, the “sessile drop test” represents a good tool to estimate the foaming behaviour of different carbonaceous materials. Clear differences can be seen between the three tested materials.

¹ The principle of the sessile drop test is illustrated in figure below. Here, a slag sample in cylindrical form is put on a crucible filled with the carbonaceous material which should be tested. Both are put on a ceramic holder and pushed in a furnace at 1500 °C under nitrogen atmosphere. There the slag liquefies and the FeO in the slag reacts with the carbon below forming CO-bubbles which foam the slag. These reactions are recorded by a CCD-camera and analyzed afterwards.



Scheme of a sessile drop test

Whereas petroleum coke formed a well and stable foamed slag, the tested charcoals provided only bad foaming results. The most evident difference is the varying wettability which, in case of charcoals, prevents the reaction between FeO in the slag and the carbon and therefore the formation of CO bubbles. The content of the volatile components in the carbonaceous material has in these trials absolutely no influence on the slag foaming.

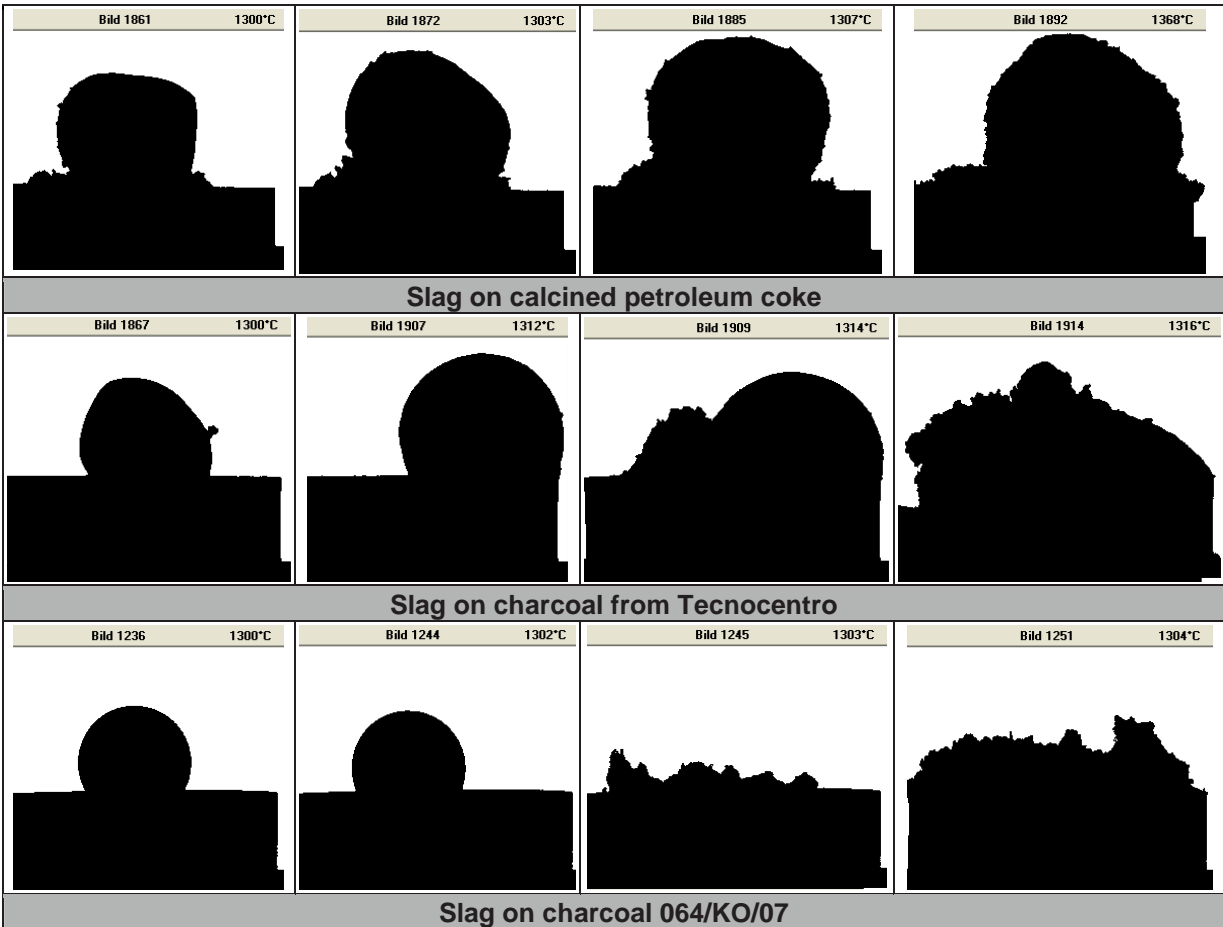


Figure 34 Sequence of the slag-carbon-reaction with different carbonaceous materials as a subject to the temperature (at the upper right corner in each picture)

To verify the results of the “sessile drop test” some additional foaming trials in a lab furnace were performed. Due to the fact that the injection of carbon in a liquid slag in lab scale is far too complex, a mixture of slag with 10 % carbon was produced. This mixture was then filled in a ceramic crucible and put in a resistance heated furnace at 1400 °C. The furnace was flushed with nitrogen and monitored with a camera from the top. The foaming of the slag was recorded by the camera and afterwards checked by the slag height of the crucible (see Figure 35).

The best foaming performance shows, once again, petroleum coke. Here the slag even reaches the rim of the crucible. The slag heights at the experiments with charcoals were very low.

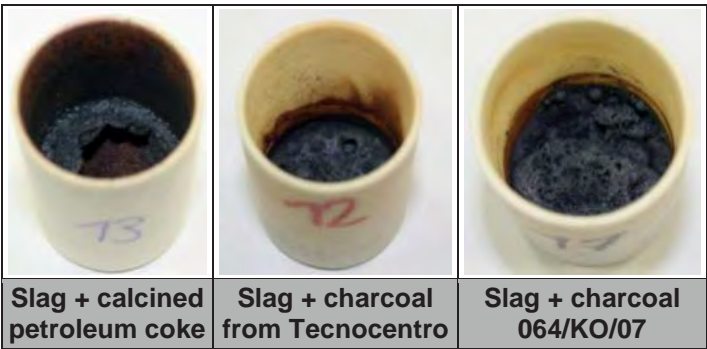


Figure 35 Comparison of the foaming height with different carbonaceous materials

Some pictures of the video recording are shown in Figure 36. With these recordings especially the way and the rate of the CO bubble formation could be investigated.

At the mixture with petroleum coke the bubble formation starts immediately after slag smelting and stays constant over a long time period which leads to a perfect foamy slag. The bubbles rise to the slag level and are obvious as dark points in the pictures.

In contrast, at the experiments with charcoal hardly any bubble formation is recognizable. Only some but in this case very big bubbles were detectable. However, such big bubbles do not really foam the slag. Once again, charcoals showed a worse performance.

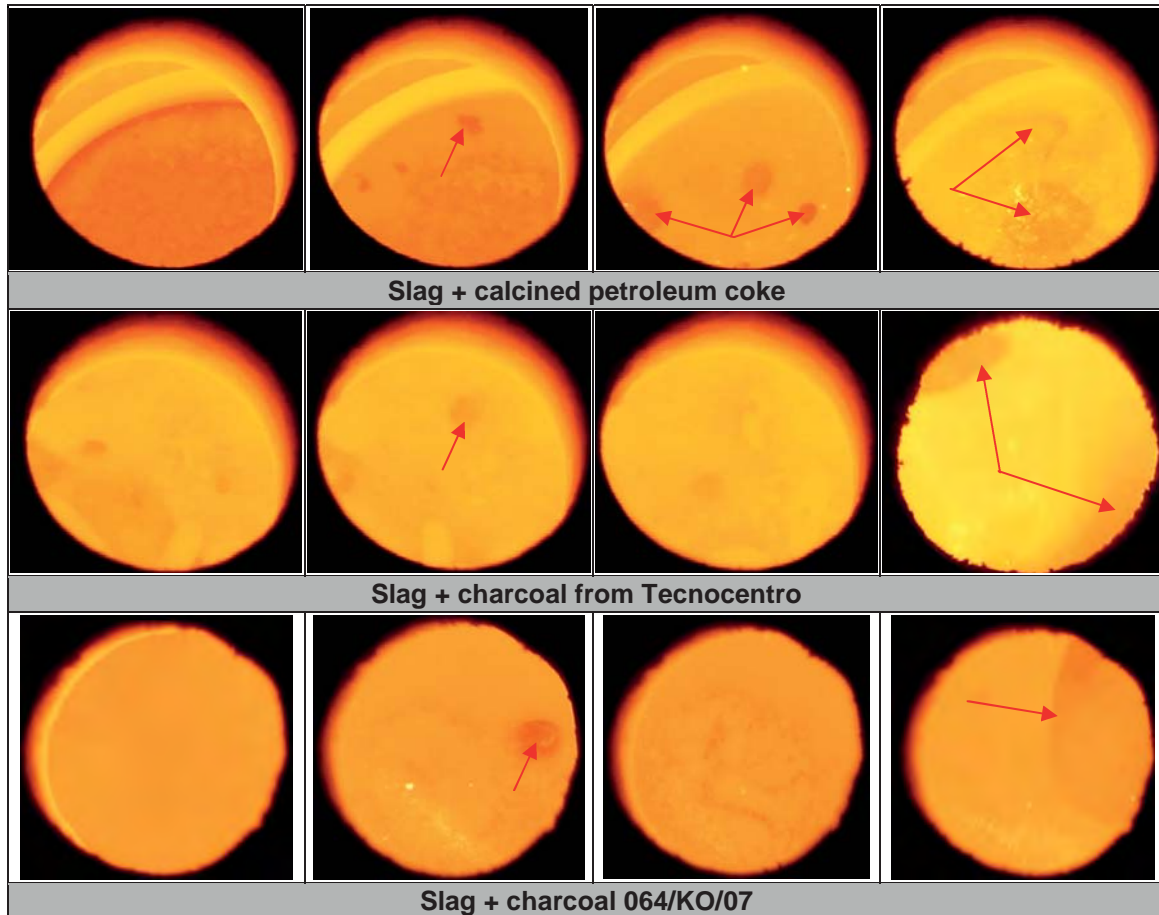


Figure 36 Pictures from the video recording of the slag foaming trials in a lab furnace; CO bubbles (dark spot with arrow)

In conclusion, the small scale tests gave a good overview about the foaming behaviour of different carbonaceous materials. In all trials petroleum coke delivered the better performance in case of slag foaming and stability, whereas the slag foaming with charcoals was hardly recognizable in most cases. The reason for this seems to be the different wettability of fossil coke and charcoal. Nevertheless, it has to keep in mind that these small scale experiments can only give tendencies. It is nearly impossible to reproduce the industrial process in lab scale due to the endless parameters. This is why in the next step the foaming behaviour of charcoals is tested in industrial scale.

Pilot plant tests at RWTH Aachen

The pilot EAF tests were performed at the airtight pilot arc furnace of the department for industrial furnaces and heat engineering (IOB). Figure 37 shows the furnace (left) and a schematic representation of the pilot furnace (right). The water cooled furnace consists of a fixed top reactor and a moveable crucible with a maximum capacity of about 200 kg of steel melt. It is possible to operate in AC-mode with two electrodes or in DC-mode with one top electrode and an anode in the bottom of the crucible. In AC-mode the maximum active power is 600 kW and in DC-mode it is 300 kW. The biochar and reference material tests were performed in DC-mode. It is possible to take a sample of melt for

chemical analysis and the actual melt-temperature. Through the three front windows the arc and the bath level can be monitored during the melting phase.

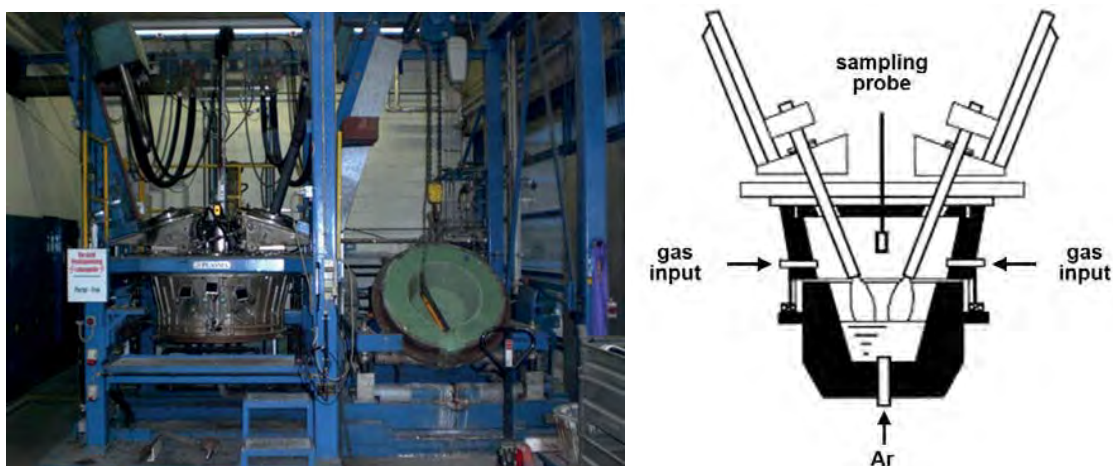


Fig. 37. Pilot Arc Furnace (left) and schematic representation (right)

For determination of the off gas composition during the tests an off gas analysis system is installed. The off gas sample and off gas temperature are taken directly at the reactor-room outlet. The analysis of the exhaust gases was conducted with regard to CO, CO₂ and H₂ levels.

In the first experimental series RWTH Aachen tested two types of biochar in the pilot EAF plant as charge coal and as injection coal. On one hand the biochar produced by Tecnocentro and on the other hand waste products from wood gasification plants were tested.



Figure 38 Biochar from Tecnocentro (left); Biochar from wood gasification plants (right)

Additionally tests with reference materials have been performed to compare the results from biochar tests with the standard situation in the industrial mills. As reference materials anthracite coal and petrol coke which are presently used at DEW Siegen were used. The different compositions have been analyzed and the results are shown in Table 28.

[%]	Biochar from grape seed (TC) ¹	Biochar from wood residues ²	Anthracite (DEW)	Petrol Coke (DEW)
Carbon	81	72.3	86	93
Ash	9	21	11.1	5.8
Volatiles	7.7	13.5	2.6	1
Humidity	5.6	5.2	-	0.2
Sulphur	0.3	0.06	0.3	1
Phosphor	0.5	0.4	-	-
Grain Size	<5 mm	<<1 mm	6-12 mm	<1 mm

¹: mean of 3 measurements; ²: mean of 24 measurements

Table 28. Composition of different biochar and reference materials

Due to the relatively high ash content of the biochar from wood gasification plants the ash composition has been analyzed to get information about the possible influence on the slag composition. Figure 39 shows the results of the ash analysis.

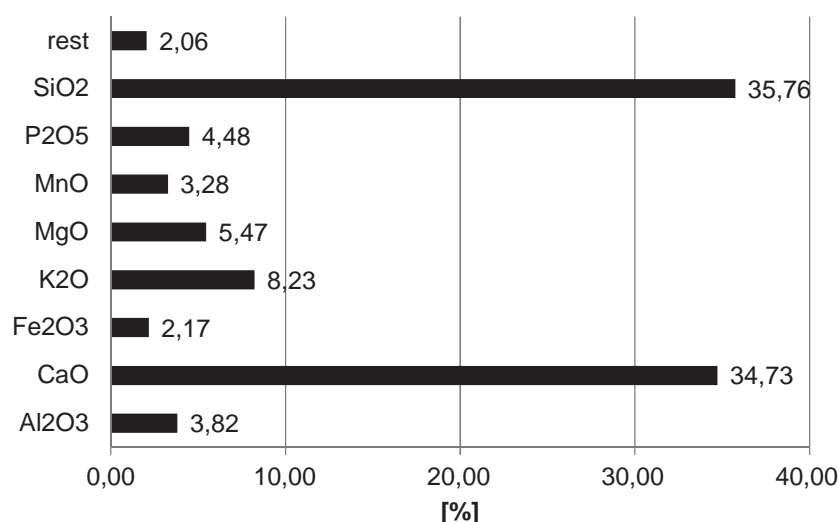


Figure 39. Results from ash analysis of biochar from wood gasification plants.

As a basis the reference trials have been performed using an amount of 1 kg anthracite coal on 50 kg of scrap. Due to the lower heating value in comparison to the anthracite coal 1.6 kg of non-processed biochar from Tecnocentro and from wood gasification plants were charged to compensate the difference. Figure 40 illustrates the significant difference in density of the biochar fines (left) and the anthracite coal (right).



Figure 40. 1.6 kg of biochar fines (left) and 1 kg of anthracite coal (right)

Figure 41 (left) illustrates the process of lancing coal and oxygen through one of the front windows directly into the slag using the IOB pilot lancing system (right) after reaching the liquid phase. While lancing coal and oxygen by hand the furnace power had to be turned off.



Figure 41. Lancing operation of coal and oxygen (left) and IOB pilot lancing system (right)

Just before tapping at 1650°C a melt sample was taken for chemical analysis to get information about possible negative effects of biochar use. After tapping all output fractions have been separated and the individual output masses were recorded. Table 29 gives an overview of the conducted trials in the pilot plant.

Input [kg]	1	2	3	4	5	6	7	8
Scrap I	50	50	50	40	36	25	25	25
Scrap II				25	25	25	25	25
Σ Scrap	50	50	50	65	61	50	50	50
Lime				0,5	1,5	1,5	2	2
Dolomite lime	0,5	1,5		1,5	0,5	0,5	1,5	1,5
Slag			4					
Σ Slag Former	0,5	1,5	4	2	2	2	3,5	3,5
Anthracite (DEW)	1	1						
Biochar from wood gasification			1,6	1,6		1,6	1,6	1,6
TC biochar					1,6			
Petrol Coke (DEW)				0,10				
Biochar from wood gasification as injection coal						0,10	0,25	0,15
Σ Coal	1	1	1,6	1,7	1,6	1,7	1,85	1,75
Oxygen					1,23	1,1	1,71	2,89
Electrode Consumption	0,18	0,24	0,28	0,48	0,23	0,3	0,29	0,31

Table 29. First conducted trials at pilot plant

Results of first trials

The evaluation of the first pilot arc furnace trials shows no negative effects regarding the steel and slag analysis. The comparison of the steel analysis of different trials is shown in Figure 42. Differences occur in terms of the Ni and Mn content. These differences can be explained by small fluctuations in the scrap composition. The reference trial shows a higher carbon content than the two biochar trials. This would imply a better carburization of the melt by the anthracite coal and would also be in agreement with the findings of the off-gas analysis. Considering the sulphur content of the steel, the effect of the lower sulphur content of the biochar in relation to the reference materials can be seen. The steel produced by the biochar trials has only about half the sulphur content in relation to the reference trial. Despite the higher phosphor concentration in the different biochar on the other hand, the phosphor content in the steel is the same for all trials. So the use of biochar instead of fossil coal shows no negative impact on steel composition in the pilot trials.

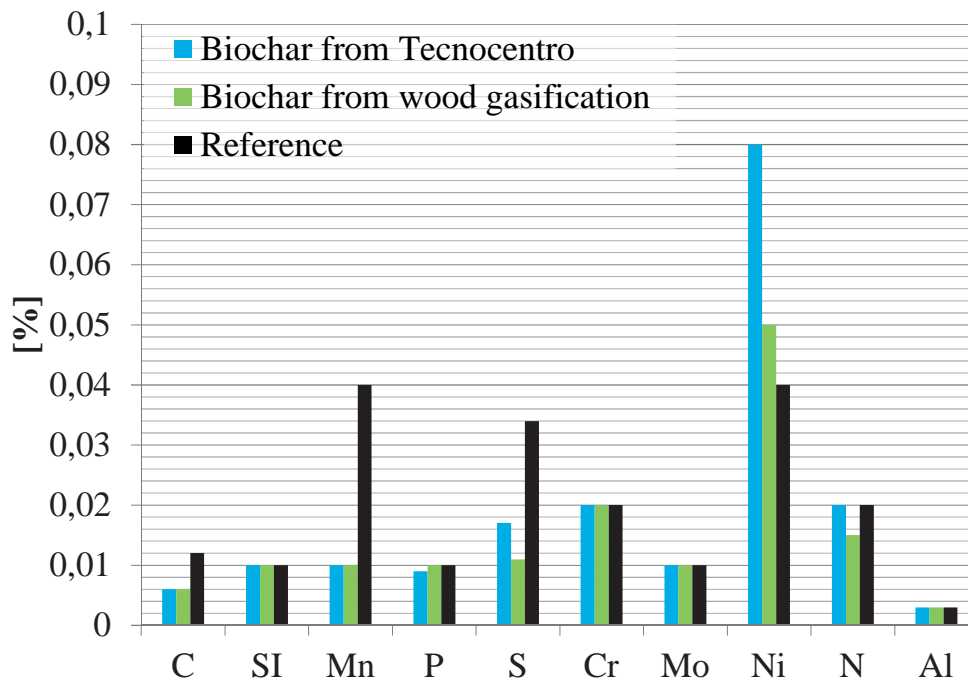


Figure 42. Steel composition after pilot trials

In Figure 43 the slag composition for the trials is shown to investigate a possible influence of the biochar ash content on slag chemistry. The striking differences between biochar from Tecnocentro and the reference e. g. in the Fe_2O_3 or CaO content of the slag cannot be explained by the use of biochar, since the biochar produced by Tecnocentro has similarly high ash content as the fossil anthracite coal. Between biochar from wood gasification and the reference trial the difference in the ash content is almost factor 2 (cf. Table1), but the slag compositions show only small differences. Further this issue has to be investigated, but these first preliminary results indicate no negative influence of the use of biochar with higher ash content on the general slag composition.

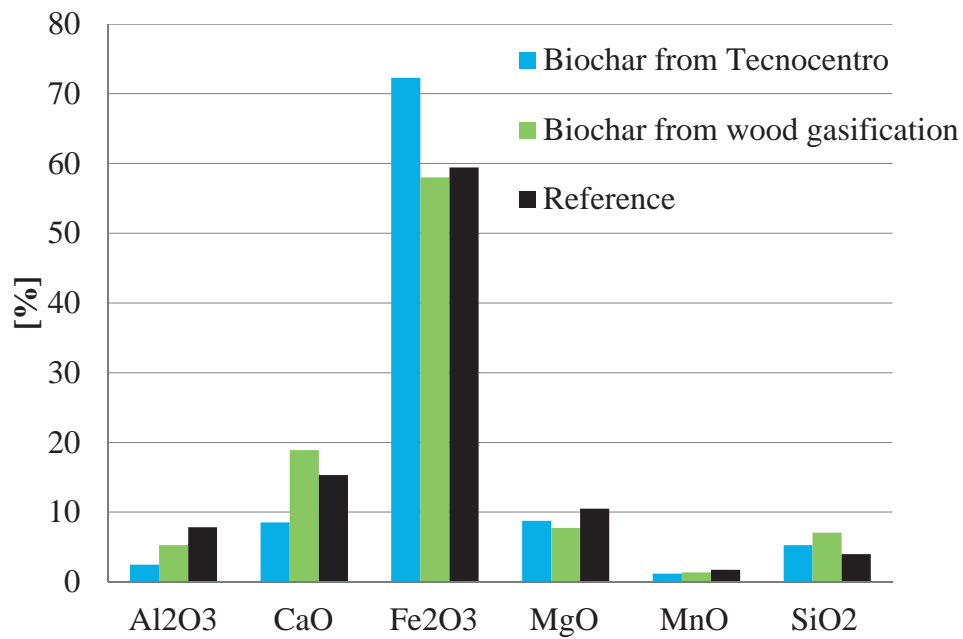


Figure 43. Slag compositions of pilot furnace trials

Agglomeration of biochar

Due to the handling problems using the biochar fines as charge coal in pilot scale at RWTH and industrial tests at DEW agglomeration tests have been performed. The aim of the tests was to find suitable binders and to establish the right blend to produce stable biochar agglomerates. At first some tests have been carried out to agglomerate the biochar fines without binders. An agglomeration was not possible (Fig. 44 a)). Also a blend using 30 % of molasses and 20 % of water did not provide stable agglomerates (Fig. 44 b)). First stable agglomerates have been produced using 30 % of molasses and 15 % of water and a forge pressure of 100 MPa (Fig. 44 c)). These agglomerates had a green strength of 0.87 MPa and strength after 2 days of drying of 1.73 MPa.



Figure 44: First agglomeration tests (a-c)

On this basis further tests have been performed to increase the strength of the biochar agglomerates. Table 30 gives an overview of produced blends that have been tested.

blend no.	biochar [%]	water [%]	molasses [%]	green strength [MPa]	fatigue strength [MPa]
1	85	5	10	-	-
2	78	5	17	-	-
3	71	5	24	-	-
4	65	5	30	-	-
5	80	10	10	-	-
6	73	10	17	-	-
7	66	10	24	-	-
8	60	10	30	1,16	-
9	75	15	10	0,78	-
10	68	15	17	1,27	3,12
11	61	15	24	1,73	6,13
12	55	15	30	0,92	-
13	70	20	10	0,69	-
14	63	20	17	1,16	4,91
15	56	20	24	1,30	-
16	50	20	30	-	-

Fatigue strength measured after 3 days of drying

Table 30. Produced and tested blends for agglomeration tests

Blend no. 11 showed the best performance and was elected to perform further pilot scale briquetting tests. The comparison of most stable blends is shown in Figure 45.

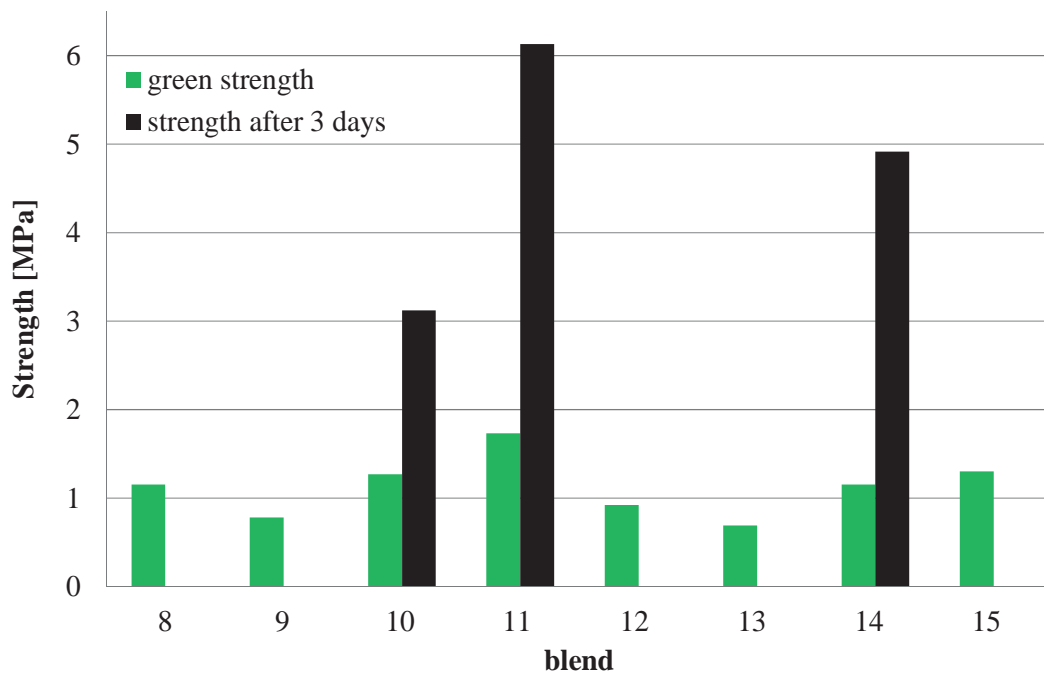


Figure 45. Comparison of green strength and strength after 3 days of drying

Further an amount of about 30 kg of biochar briquettes was successfully produced on a pilot scale double roll press. Figure 46 shows a briquette (left) for comparison a piece of anthracite coal from DEW (right).

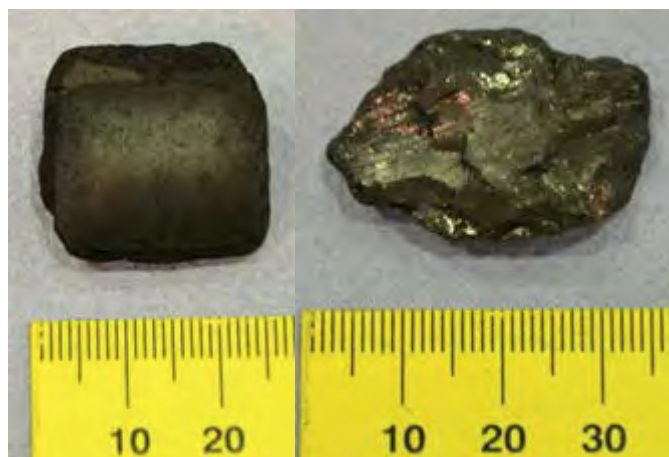


Figure 46. Biochar briquette (left) and anthracite coal (right)

For the use of the agglomerates to replace anthracite as charge coal it is important to know the bulk behavior and the abrasion resistance. To compare the behavior of the agglomerates to the behavior of the anthracite coal, tests in a vibrating sieve and drop tests have been performed. For vibrating sieve tests 1 kg of biochar briquettes and anthracite have been tested for abrasion resistance. The results of vibrating sieve tests (Figure 47) show nearly equal grain size distributions.

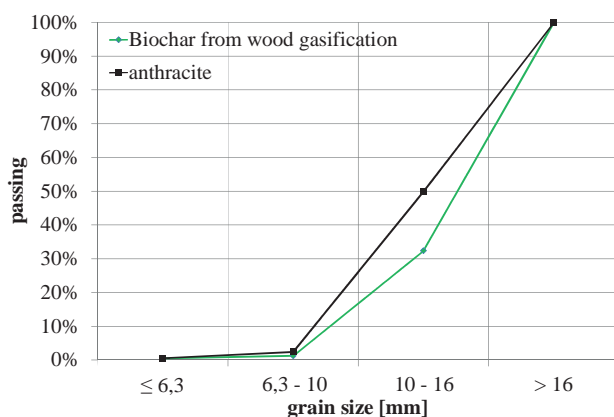


Figure 47. Grain size distributions (left) and mass fractions (right) after vibrating sieve tests

Additionally drop tests in a closed tube of 150 mm diameter and 2 meter length have been performed to simulate transportation and charging behavior. Also the results of the drop test below show that there are only minimal differences between biochar briquettes and anthracite coal.

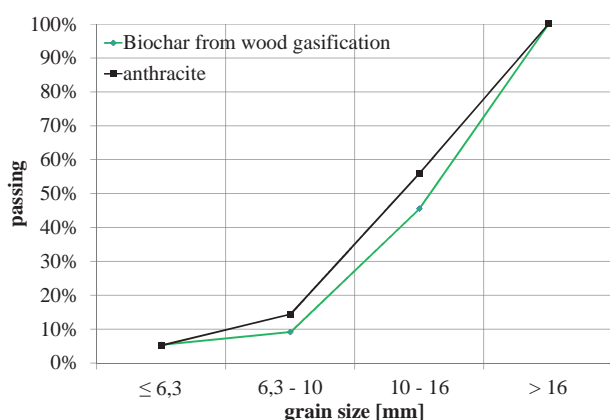


Figure 48. Grain size distributions (left) and mass fractions (right) after drop tests

In summary it can be stated that the biochar could be briquetted successfully. The briquettes show good strength and resistance behavior. The handling of the biochar briquettes in the same way as the

anthracite coal in the steel mills should be possible. In addition, a better combustion behavior due to the smaller surface area is expected in further trials.

In secondary trials the briquettes of the biochar from wood gasification were used as charge coal. The composition of the biochar briquettes is shown in the following Table.

[%]	Biochar briquettes from wood gasification (BCB)
Carbon	55,9
Ash	21,6
Volatiles	23,6
Humidity	7,7
Sulphur	0,09
Phosphor	0,317
Grain Size	6-12 mm

Table 31. Chemical composition of biochar briquettes from wood gasification

The trials have been performed similar to the previous trials where the fines have been charged with the scrap. An amount of 1.6 kg of briquettes was charged with scrap and slag formers in the crucible of the pilot furnace. Figure 49 shows the crucible charged with the briquettes.



Figure 49. Crucible of pilot furnace charged with a first scrap layer and biochar briquettes (BCB)

The results of the steel analysis of the biocoal briquettes (BCB) trials is shown in Figure 50 compared to the results of the reference coal (RC) steel analysis. Like the previous trials using the biochar fines the steel analysis regarding the carbon content shows that the carburization of melt by the reference coal is higher than using the agglomerates. Also the contents of phosphor and sulphur show the same behaviour as in the previous trials and there is no discernible negative influence on the steel composition from the higher phosphorus content of the agglomerates in comparison to the phosphorus content of the reference anthracite coal from DEW (130 ppm) The very low silica content (<0.0015 %) and other deviations can be explained by fluctuations in the scrap composition or by errors in the measurement.

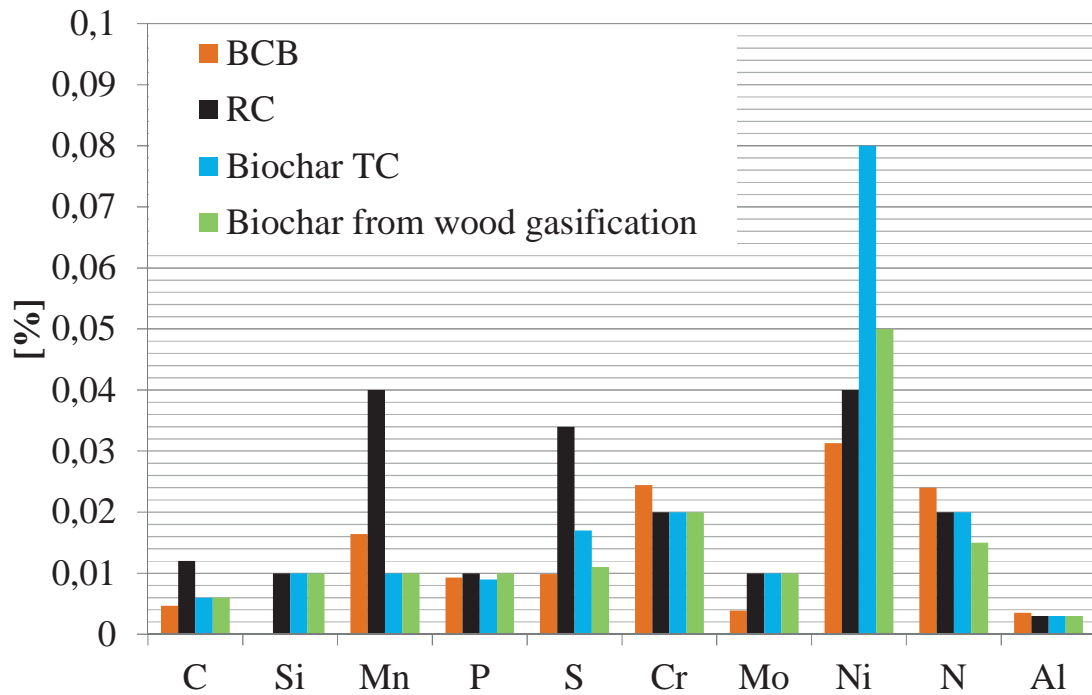
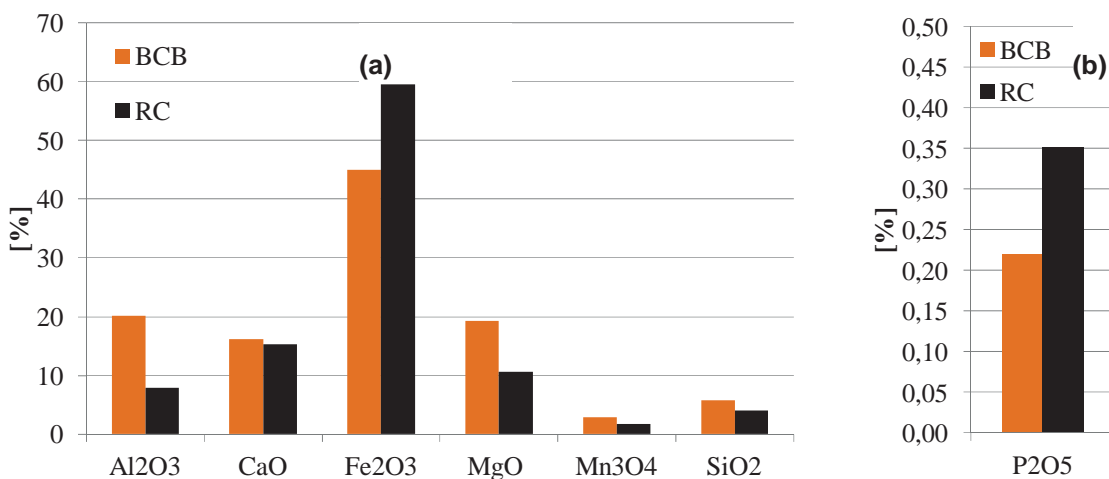


Figure 50. Steel compositions of BCB and RC trials

During the BCB trials a dislodging of the refractory of the crucible was observed. Considering the significant higher Al_2O_3 and the MgO -content of the BCB slags, a dissolving of the dislodged refractory could be the reason for this phenomenon. The wear layer of the crucible mainly consists of MgO and when this wear layer is damaged the acid permanent lining (93 % Al_2O_3) reacts with the alkaline slag and dissolves. Moreover there is no other explanation for the additional input of Al_2O_3 and MgO in this case. Looking at the P_2O_5 content, it is obvious that the content is even lower by using the briquettes in comparison to the reference material. Even the lower P_2O_5 level indicates that there must have been a dilution effect caused by the refractory material dissolved in the slag. Because of the considerable higher phosphorus content of the BCB a higher P_2O_5 content of the slag was expected. However the results of the slag analysis in general show that there is no negative effect detectable by using the BCB.



**Fig. 51: (a) Slag compositions of BCB and RC trials
(b) P_2O_5 content of BCB and RC slag**

Task 4.3 To evaluate the effects on the pollutants emission from the EAF

Effects of char on the formation of polluting species was investigated both in pilot trial and industrial trials. Here are reported the results obtained with pilot plant. Results obtained with industrial tests are reported in WP5.

Effects of pollutants emission from RWTH pilot plant

The effects of using biochar instead of fossil coal on pollutants emissions have been recorded during the pilot plant tests and have been analyzed and evaluated. The results of evaluation are shown in the following Figures. In Figure 52 the off gas composition of the reference trial is shown when coal from DEW was used. Comparing Figure 52 with Figure 53, where the biochar from Tecnocentro was used, a flatter curve of CO formation can be noticed using the coal from DEW. In addition the significantly lower reactivity of the anthracite coal can be ratified. The reaction of oxygen with the carbon from anthracite coal starts at a later point (≈ 600 s after power on) and extends over a period of about 2100 s with a constant CO formation of about 4 to 5 vol.-% in the off-gas. The formation of CO in the trial where the biochar from Tecnocentro was used already starts ≈ 400 s after power on and it largely ends up after a period of ≈ 1400 s.

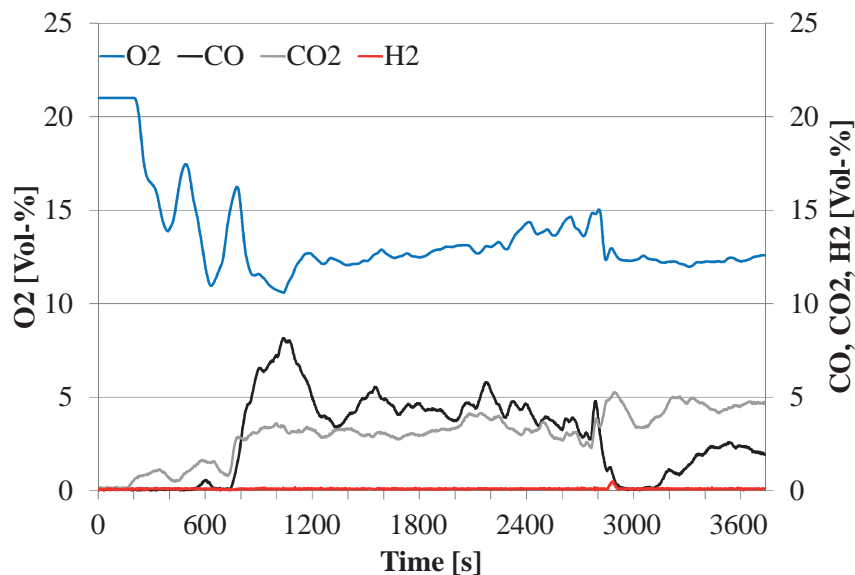


Figure 52 Off gas composition using anthracite coal

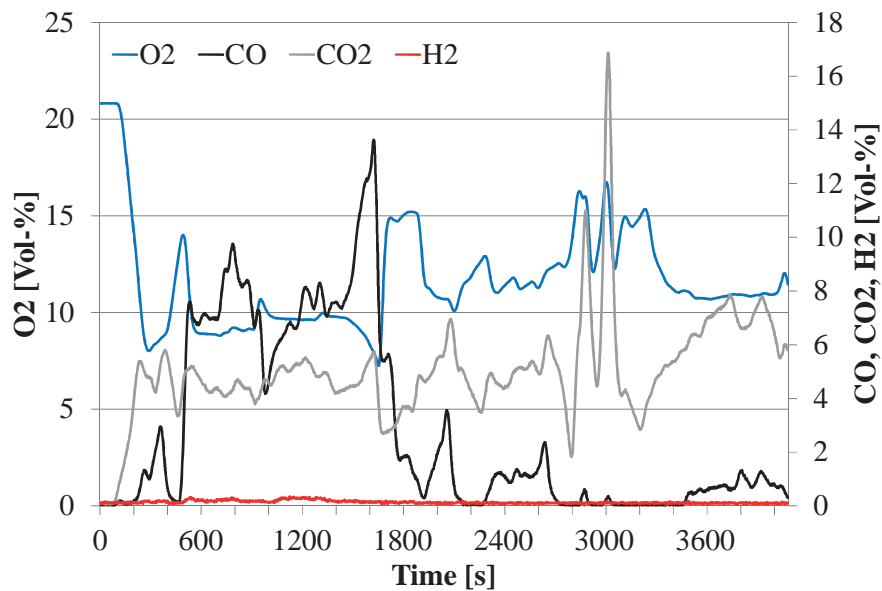


Figure 53 Off gas composition using biochar from Tecnocentro

By using the biochar fines from wood gasification plants, the combustion starts directly after ignition of the arc. The off gas composition (Figure 54) shows the highest formation rate and the shortest time period to generate the main amount of CO.

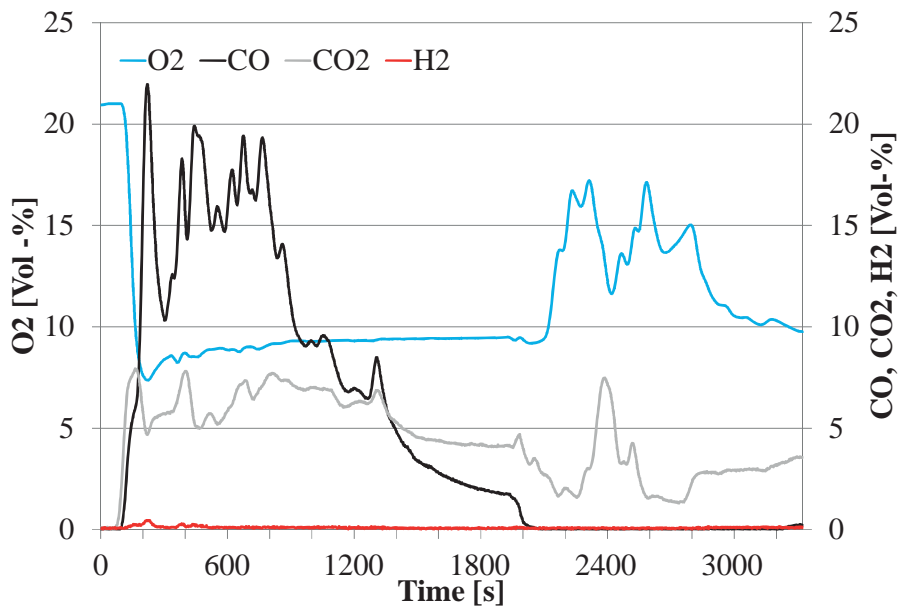


Figure 54. Off gas composition using biochar from wood gasification plants

In the evaluation of the off gas composition of secondary trials where the biochar briquettes were used it was found that the use of briquetted biochar (BCB) has a positive influence on the combustion behaviour. In comparison to Figure 54 the direct CO peak is missing and the reaction of oxygen and coal starts at a later point. Generally it can be determined that the combustion behaviour of the briquettes is closer to the combustion behaviour of the reference coal (Figure 52), excepting the higher CO formation rate.

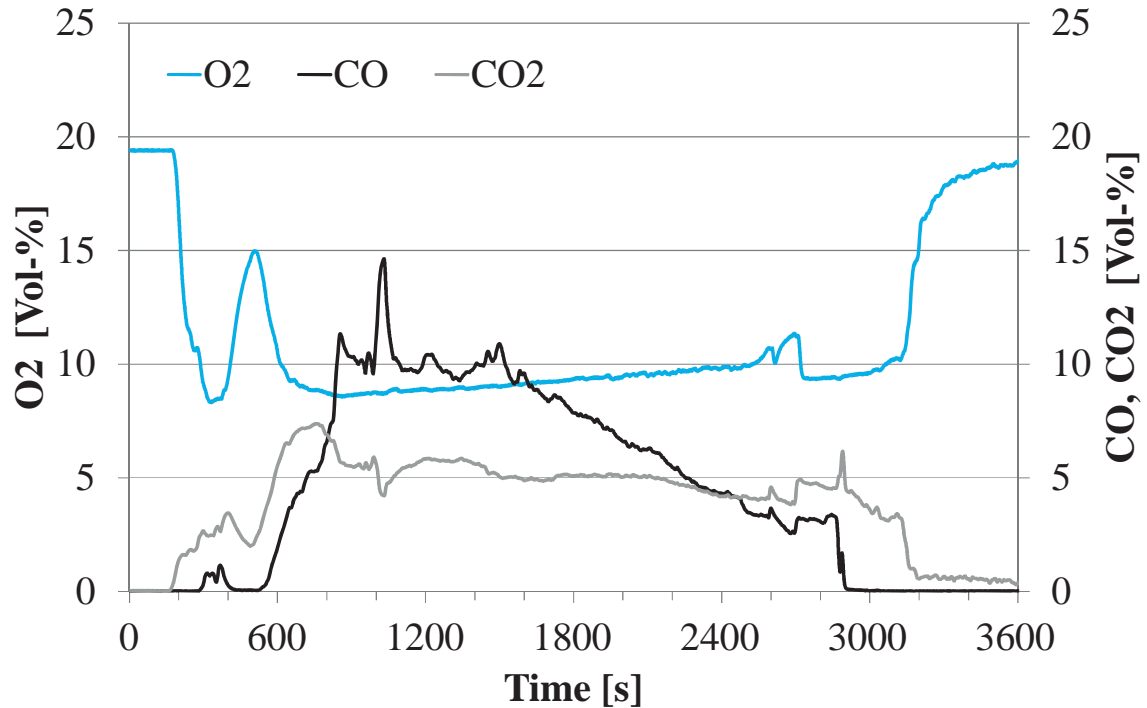


Figure 55. BCB: Off gas composition using biochar briquettes (BCB)

In summary the results of the investigations regarding the pollutant emissions from biochar in comparison to the fossil coal show that the combustion behaviour of the fines is completely different from using the reference material. Because of the large surface scale of the fines it comes to a direct combustion right after arc ignition. This may indicate problems by using the biochar fines in industrial scale trials to replace charge carbon. There will be the danger of explosive combustion by charging the bucket within the biochar together with scrap into the hot furnace. Only the briquetted char shows a combustion behaviour which is comparable to the combustion behaviour of the anthracite.

WP5 INDUSTRIAL EXPERIMENTATION (DEW, FERRIERE NORD, CSM, RWTH, MH, TECNOCENTRO, IP)

Task 5.1 Definition of the EAF operating practices

Char utilization into the EAF has been tested at industrial scale by the three industrial partners participating to the GreenEaf project. The industrial partners involved in this project have different EAF, which differs for size, capacity, amount of chemical energy. Following Table reports the main EAF characteristics.

	Charge weight (TLS)	Num. buckets /heat	Electrical energy input kWh/TLS	CH ₄ Nm ³ /TLS	O ₂ Nm ³ /TLS	Coal lump kg/TLS	Injected Coal Kg/TLS	Power on (min)	Tap to tap (min)
FENO	140	3	341	6	42	4	8	38	45
DEW	130	2	417,2	0	21,8	10.7	1,53	54	69
MH	40	3	375	7	45	0	12	31	45

FENO: Ferriere Nord

DEW: Deutsche Edelstahlwerke GmbH

MH: Marienhütte Ges. m. b. h.

Table 32. Main characteristics of the electric furnaces of the industrial partners participating to the project.

FENO EAF uses coal for both carburization and foaming; coal is both charged and injected.

DEW uses coal mainly for bath carburization: coal is mainly charged and injected in a small amount.

MH uses coal for foaming; coal is only injected.

The results of the investigations on the use of biochar instead of fossil coal in the EAF steelmaking process in comparison to reference material showed that in general there are no significant negative impacts on the steel or slag compositions. Problems occurred regarding the handling of fine-grained carbonaceous materials with a high specific surface in the presence of liquid steel and oxygen. First tests showed the direct combustion of the highly reactive biochar fines right after arc ignition in the pilot EAF.

In order to solve these problems, investigations on the agglomeration behaviour of biochar have been made. The biochar was briquetted successfully. A stable briquette from a fully biogenic blend has been created with characteristics which are comparable to the characteristics of the anthracite coal that is presently used in electric steel mills.

These biogenic briquettes have been used as charge carbon in the pilot EAF of the department for industrial furnaces and heat engineering (IOB). The evaluation of the results of these trials regarding steel, slag and off gas composition shows no negative impact on the slag and steel chemistry. Concerning the off gas composition it could be shown that the combustion behaviour of the briquettes is close to the combustion behaviour of the anthracite coal.

Char industrial testing with these three furnaces exploited a wide range of operational variability. Moreover, the utilization of syngas in EAF has been simulated through CFD modeling.

Task 5.2 Industrial tests with char and biogas.

Industrial tests at FENO – charge trials

The Electric furnace of Ferriere Nord has a capacity of 120 t, with almost 50% of energy provided by chemical reactions. Coal is used both as charge material in the bucket and also as powder for slag foaming. The furnace is equipped also with the offgas online monitoring system EFSOP™. Both char charging and injection have been tested.

Three industrial campaigns were carried out:

- first campaign: charge test
- Second campaign: charge tests with preliminary char briquetting
- Third campaign: Injection tests

In the charge test, five heats have been tested with char charging and compared with five subsequent standard heats. Charging conditions and steel analysis at tapping are reported in **Table 33**.

In the first five consecutive heats, anthracite in the bottom of the first basket, has been partially or completely replaced with CHAR. The material was loaded into the basket after two layers of fine material using a scrap yard crane equipped with grabbers.

Off gas analysis system (EFSOP analyzer) has been used during tests. Measured data have been compared with data of the production of CO/CO₂/H₂ during standard operations.

Heat ID	Grade	Char/Coal	C % x100	Mn % x100	Si % x100	P % x1000	S % x1000
4349	Fe50	Char+Coal	14,00	62,60	11,60	14,10	20,10
4350			14,60	65,60	11,70	11,90	16,70
4351		Char	14,60	64,60	14,30	15,50	18,40
4352			14,30	65,70	13,70	16,30	21,60
4353			14,90	65,70	12,70	15,50	13,70
Average			14,48	64,84	12,80	14,66	18,10
4354	Fe50	Coal	14,90	63,60	12,80	14,50	16,60
4355			14,60	61,00	13,70	14,30	18,70
4356			14,40	65,00	14,40	11,50	27,70
4357			14,40	63,80	13,80	13,80	17,40
4358			13,70	66,80	14,50	19,20	14,40
Average			14,40	64,04	13,84	14,66	18,96

Table 33 Trials and standard heats with steel analysis after EAF cycle (average values measured during test heats are compared with average values of standard heats)

Table 34 shows the values of offgas composition measured.

	CO/s*	CO ₂ /s*	H ₂ /s*	O ₂ /s*
4349	17,61	17,47	10,56	0,28
4350	12,83	17,15	7,66	1,10
4351	16,79	17,41	10,10	0,41
4352	16,69	17,68	9,85	0,02
4353	16,42	16,99	11,08	0,15
Average	16,07	17,34	9,85	0,39
4354	19,01	16,33	10,35	0,23
4355	16,57	16,79	10,20	0,11
4356	16,54	16,71	8,84	0,40
4357	17,65	17,75	10,28	0,01
4358	17,98	17,21	11,28	0,04
Average	17,55	16,96	10,19	0,16

Table 34. Values of offgas composition measured during industrial trials at Ferriere Nord

The results achieved showed that:

1. Difficulties occur in handling and loading in bucket due to material conditions (fine grain).
2. Combustion occurs during the charging of the bucket in EAF (fine grain).
3. Main process parameters (including steel/ slag analysis) are comparable with standard values.

The main difficulty in char charging is related to high char reactivity. Significant powder dispersion has been noticed during handling and charging operations and intense flame emissions were caused during trials with char.

Second industrial campaign

The main difficulty in char charging is related to high char reactivity. A possible countermeasure can be to transform char into mechanically stable briquettes. Briquetting tests were performed both at laboratory and semi-industrial scale, before performing industrial trials at EAF. The objective of the *laboratory activity* was to define the best mix of materials in order to obtain briquettes with good mechanical properties (able to resist to handling operations into a steel plant).

Satisfactory results were obtained with the following mix:

- 90% char,
 - 5% flour,
 - 5% bentonite,
- flour and bentonite being the binding agents.

Addition of ladle slag (in the range 10-15%) did not change briquettes properties. The briquettes were characterized by drop tests (based on drops number from 50 cm on flat metallic surface).

After the laboratory activity a *semi industrial* activity has been carried out at Ferriere Nord. A semi-industrial apparatus has been purposely set for briquettes production. Figure 56 shows a picture of the apparatus used at FENO for briquetting tests.



Figure 56. Semi industrial briquettes production

Five tests have been carried out using the same blend developed at laboratory scale. The material mixing and the low grain size of the binding agents seem to be determinant in briquettes strengthening. In tests no. 4 and 5, the EAF dust have been mixed with char to increase the density of the material and to recover the powder. From a qualitative point of view, the addition of this powders seems to improve the product stability. Briquettes have been characterized with drop tests from 1 m height. The presence of powder fraction after drop formation was evaluated. Relevant data are shown in **Table 35**.

Test	Char/%	Bent/%	Flour/%	Filter dust/%	LF slag/%	Drop test
N1	90	5	5	-	-	negative
N2	90	5 (finer powder)	5	-	-	Partially positive
N3*	90	5 pure bent.	5	-	-	
N4*	85	5 pure bent.	5	5		positive
N5*	85	5 pure bent.	5	-	5	Partially positive

Table 35. Results of the briquetting tests at Ferriere Nord.

Obtained results indicates that materials can be pressed into briquettes with good mechanical resistance. In order to perform a long duration test (six heats), and to have enough material available in a short time, briquetted material has been acquired from the market. A market research has been carried out in order to acquire a charcoal having same physic chemical characteristics of one used in first campaign. Another important characteristic which has been considered selecting the provider was the mechanical stability of briquettes, measured with drop test carried out according to ISO 4700 (Table 36)

	Char Briquettes %	Wood residues %
C	55.1	60
H	2.1	
N	0.7	
S	0.052	0.06
P	0.099	0.4
Cl	0.084	
ash	19.3	21

volatile matter	260	13.5
Higher Heating* value	20 MJ/kg	20 MJ/kg
H ₂ O	7	5.2
Drop test- Numb. Of drops (ISO 4700)	31	

Table 36. Characteristics of char briquettes used in the second testing campaign at FENO, compared with char used in this project

The testing campaign has been carried out charging 850 kg of char briquettes in the first bucket for six heats. Subsequent six heats are carried out in standard mode and used as comparison.

In the trials heats the following parameters are monitored:

- Steel and slag analysis at tapping
- Slag analysis in subsequent ladle
- Off gas composition
- Power on time
- Productivity
- Gas analysis in the stack (including dioxin)

Results about gas analysis are reported in task 5.3

Tables 37 and 38 reports the results of industrial trials. The results are expressed as percentage variation respect subsequent standard heats. Even if FeO variation may look as significant, it is in range usually observed with coal practice.

FeO	MnO	SiO₂	CaO	IB2
+19.2%	-4,2%	-14,9%	-8.2%	+17,8%

(a)

CO	CO₂	H₂
-2.9%	-4.8%	+0.3%

(b)

**Table 37 (a) variation of slag composition
(b) Variation of offgas composition during industrial trials with char at FENO**

Steel prod. (t)	productivity (t/h)	Power On (min)	Electrical consumption (kwh/t)
-1,1%	-2,0%	+2,1%	+3,5%

Table 38 **Variation of main production parameters recorded during industrial trials with char at FENO**

Char addition as substitute of charge coal did not modify steel and slag characteristics; also the main process parameters did not show relevant deviation from standard situation.

The intense flame emissions during char charge in bucket, observed in first campaign tests disappeared with performing a preliminary briquetting stage.

Third industrial campaign at FENO: injection tests

Pulverised char has been injected by a secondary lance modified for industrial tests. This lance is currently used to spray refractory cement for furnace walls maintenance. Injection of 500 kg char was made with a mass flow rate within the range 12÷16 kg/min.

The first results showed that the injected char did not penetrate inside the slag. In order to increase the efficiency of the char penetration into the slag, two possible solutions were individuated:

- injection below the slag level;
- use of a double jet to improve the injection system (see Figure 54).

The double jet is achieved with one lance for oxygen and one lance for pulverized char with a carrier gas. The jet penetration inside the slag can be calculated and it is mainly a function of lance distance from the slag and gas velocity.

Calculation of jet penetration into the bath as a function of distance of lance from the bath and gas velocity [23] has been carried out. The calculation takes as data input:

- distance to the bath: S_0 (see Figure 57)
- coal/char flow rate
- angle: α (see Figure 54)
- jet angle: θ (see Figure 54)
- carrier gas velocity
- slag density

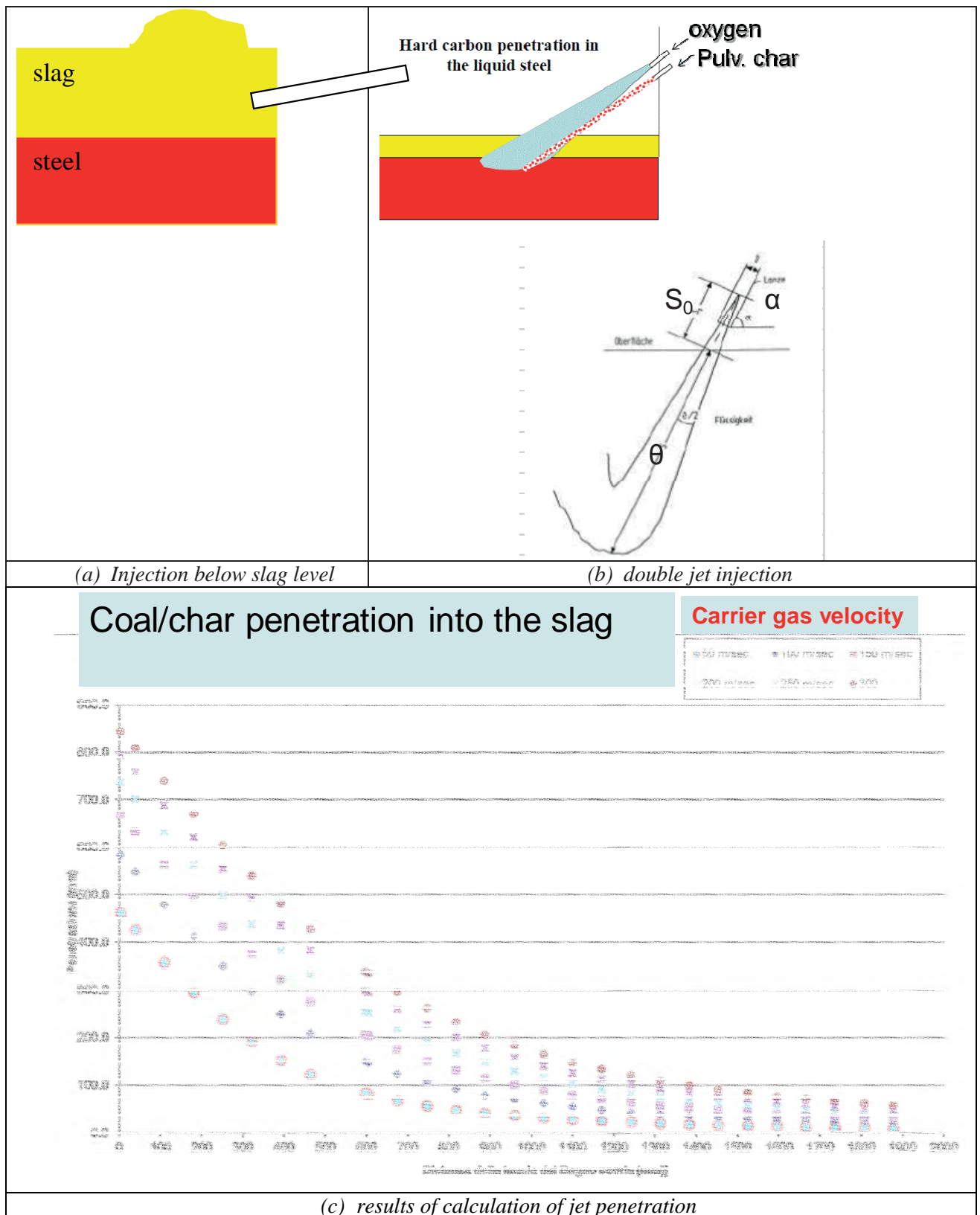


Figure 57 Improvement of char injection: (a): installing a lance for under slag injection; (b) using a double jet for slag penetration; (c) results of calculation of jet penetration

Industrial tests at DEW – charge and injection trials

The biochar has been tested at DEW as charge coal and as injection coal.

Biochar as charge coal

The biochar fines from wood gasification plants were directly charged by the grabber into the scrap buckets in big bags because of the low grain size. Figures below show the charging procedure. The generation of dust caused by the damage of the big bags by sharp-edged scrap is enormous.



Figure 58. Charging of biochar fines at DEW Siegen

Directly after charging the bucket into the furnace it came to an undesirable rapid combustion of the biochar fines. For this Reason, it was only possible to replace the charge carbon from one charge partially with the biochar fines. The Tables below show the feedstock quantities of the reference charge (Table 39) and of the biochar charge (Table 40).

Feed	Mass	Feed	Mass
Scrap [kg]	141120	Blow carbon [kg]	391
Lime [kg]	3520	Sublimed sulfur [kg]	78
Dolokalk [kg]	1500	Oxygen [m ³]	2930
Anthracite [kg]	1320	Spez. energy [kWh/t]	421
Biochar [kg]	0	Heat duration [min]	55

Table 39. Feedstock quantities of the reference charge

Feed	Mass	Feed	Mass
Scrap [kg]	149100	Blow carbon [kg]	388
Lime [kg]	3520	Sublimed sulfur [kg]	105
Dolokalk [kg]	1400	Oxygen [m ³]	3032
Anthracite [kg]	800	Spez. energy [kWh/t]	433
Biochar from wood gasification [kg]	720	Heat duration [min]	58

Table 40. Feedstock quantities of biochar charge

After evaluating the steel and slag analysis of the biochar and the reference charge the results have been compared. Regarding Figure 59 there are no significant differences in the slag compositions that can be referred to the use of biochar in the process. The basicity value of the reference slag is 2.63 and 2.93 is the basicity value of biochar slag. The difference between these two values is small.

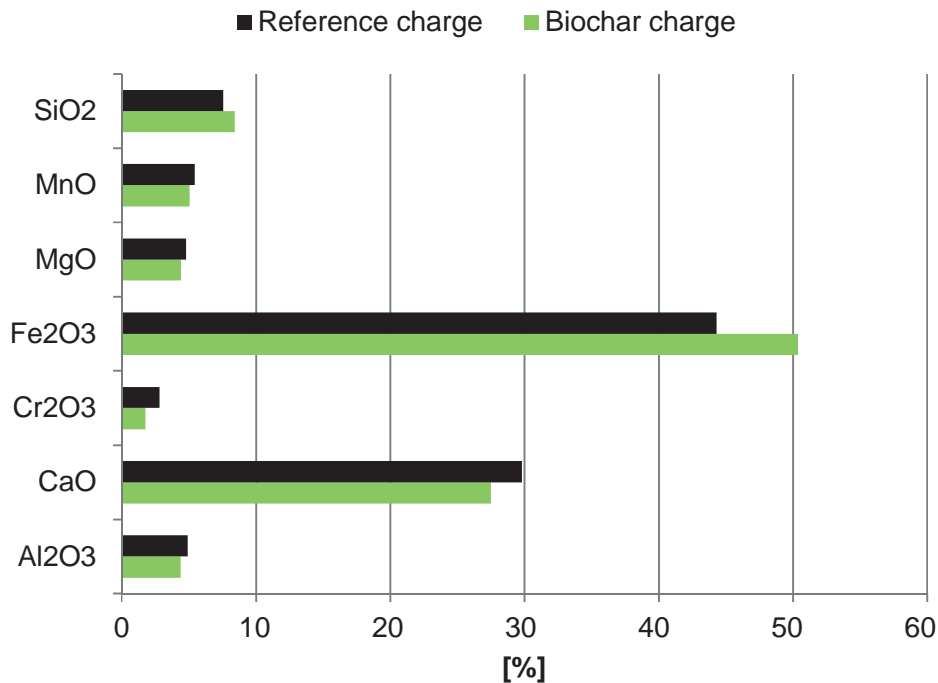


Figure 59. Slag analysis of reference and biochar charge (left) and basicity (right)

Considering the results from the steel analysis (Figure 60) there are also no significant differences.

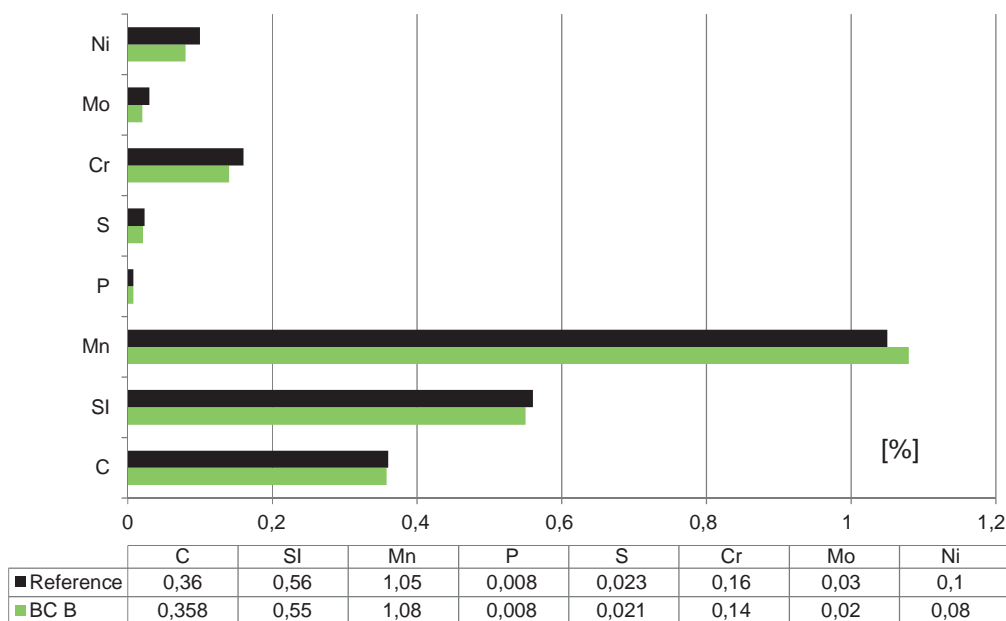


Figure 60. Steel analysis of reference and biochar charge

Industrial scale trials using biochar to replace charge coal have been performed with success. In summary the industrial scale trials using biochar as charge coal showed no negative influences on slag and steel compositions. The results regarding the off-gas evaluation will be discussed in task 5.3. Problems occurred by the handling of the biochar fines (charging of buckets). Due to the very large surface area the biochar fines combust directly by/after charging into the furnace. Using biochar fines as charge coal seems not to be successful without a prior agglomeration step

Biochar as injection coal

For the industrial experiments of using biochar as injection coal DEW Siegen installed a secondary coal injection system (Figure 61). The injection machine can directly be charged by big bags.

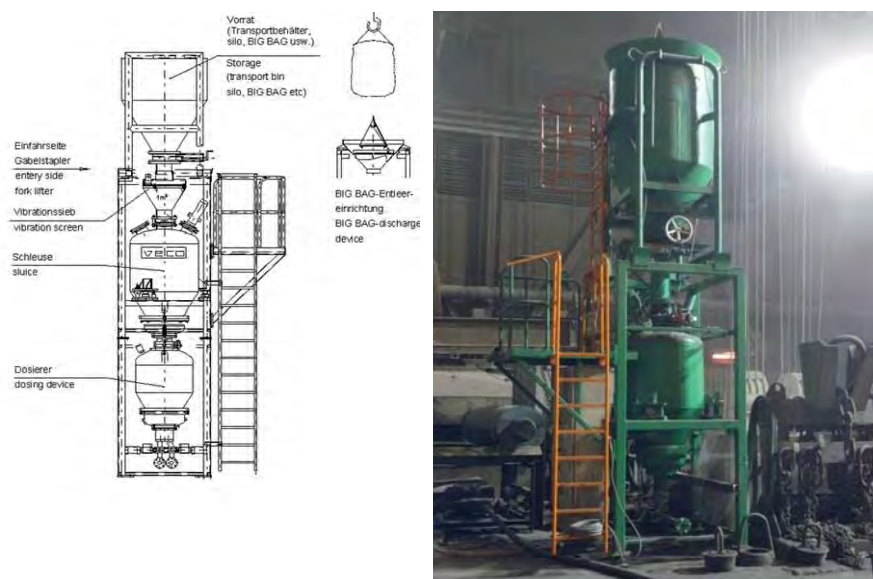


Figure 61. Secondary injection system for biochar fines

The following illustration shows the filling procedure of the injection system.

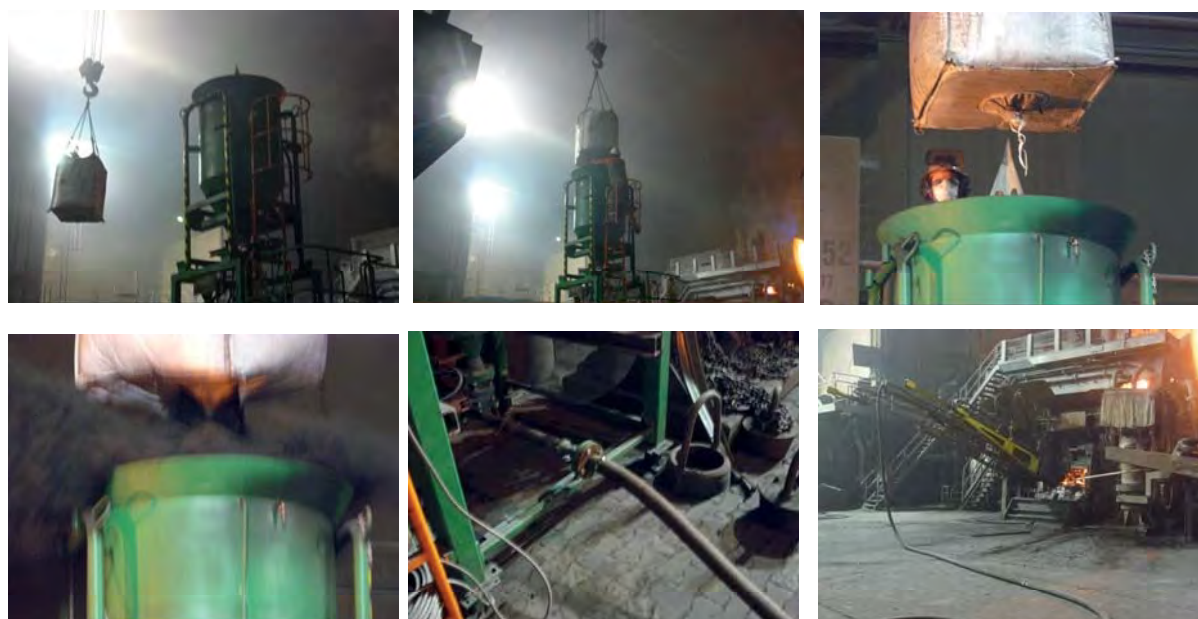


Figure 62 Charging the injection machine at DEW Siegen

Two trials have been performed using biochar fines as injection coal to foam the slag. The feedstocks of the two charges are shown in Table 41.

Feed	Charge 1	Charge 2
Scrap [kg]	139920	145000
Lime [kg]	3060	2020
Dolokalk [kg]	1300	600
Anthracite [kg]	2000	180
BC B as blow carbon [kg]	420	440
Oxygen [m ³]	2867	2912
Spez. energy [kwh/t]	407	415
Heat duration [min]	52	59

Table 41 Feedstock of trial charges using biochar as injection coal

The foaming of slag using biochar fines from wood gasification plants was successful. The slag compositions of the two trial charges have been analysed and evaluated. Regarding slag chemistry and basicity no significant differences occur by using biochar instead of petrol coke to foam the slag.

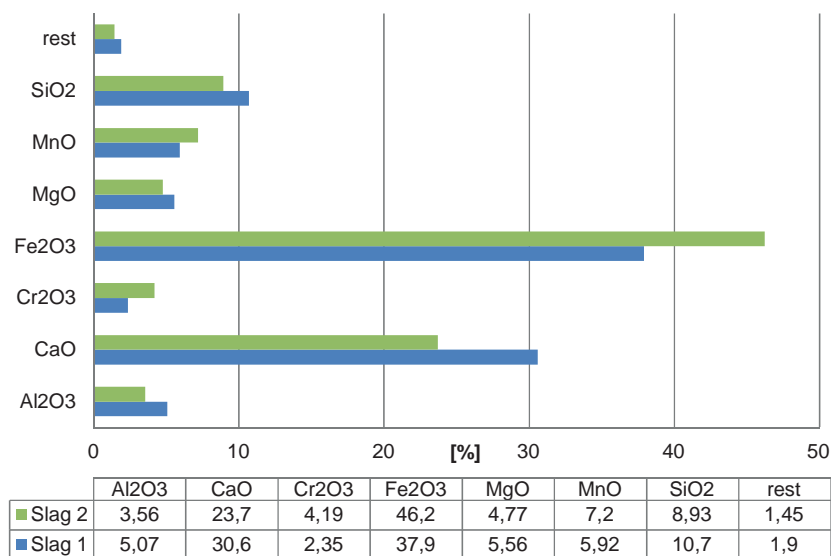


Figure 63. Slag composition of biochar trials

Regarding the basicity of the reference and the biochar trial Figure 64 shows that the difference is marginal.

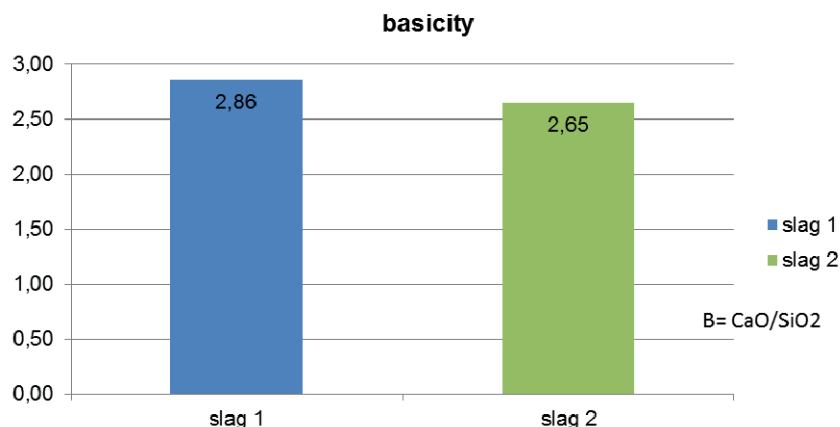


Figure 64. Slag basicity of biochar trials

Industrial scale trials using biochar fines as injection carbon have been carried out successfully. The results showed no negative influences on slag composition and basicity. Additionally the foaming of slag could be achieved.

Problems appeared by the discharging of big bags into the injection system (Enormous dust emissions). In addition problems came up by plugging of the fine material in the pneumatic conveying system. Because of all these problems it came to delays in the logistics of the melting shop.



Figure 65. Problems occurring while using biochar fines as injection coal

MH industrial trials – injection trials

In order to evaluate the substitution of petroleum coke by charcoal as injection coal into the electric arc furnace (EAF) large-scale experiments were performed. Different carbon sources provided by Tecnocentro were tested for their slag foaming ability.

The charcoal samples with different moisture contents were injected via the door lance manipulator. The reference material was calcined petroleum coke used at Marienhütte as standard carbon for slag foaming purpose.

The electric arc furnace has a diameter of 4700 mm, a height of 1870 mm and a capacity of around 40 tonnes. Additionally to the door lance the KT system (Köster Technology) is installed at the water-cooled side wall panels near the "cold spots". The system combines three natural gas / oxygen-carbon blocks, with burner function, lance function in the supersonic range and coal injection, distributed evenly around the circumference.

The injection of carbon sources with compressed air for experimental purposes is possible only through the door lance manipulator (see Figure 66). The injection started after melt down period of the scrap at the beginning of the flat bath at a bath temperature of about 1540 °C. The carbon flow rate was about 20 kg/min. Compressed air was used at 6 bar for this application. The experimental evaluation and documentation was done by the foaming slag management system OFSM (Optical Foaming Slag Management), which determines the slag index. The slag index is a measure of the slag height. Additionally, a video camera for visual assessment of foaming effect was installed. Furthermore, slag samples were taken.

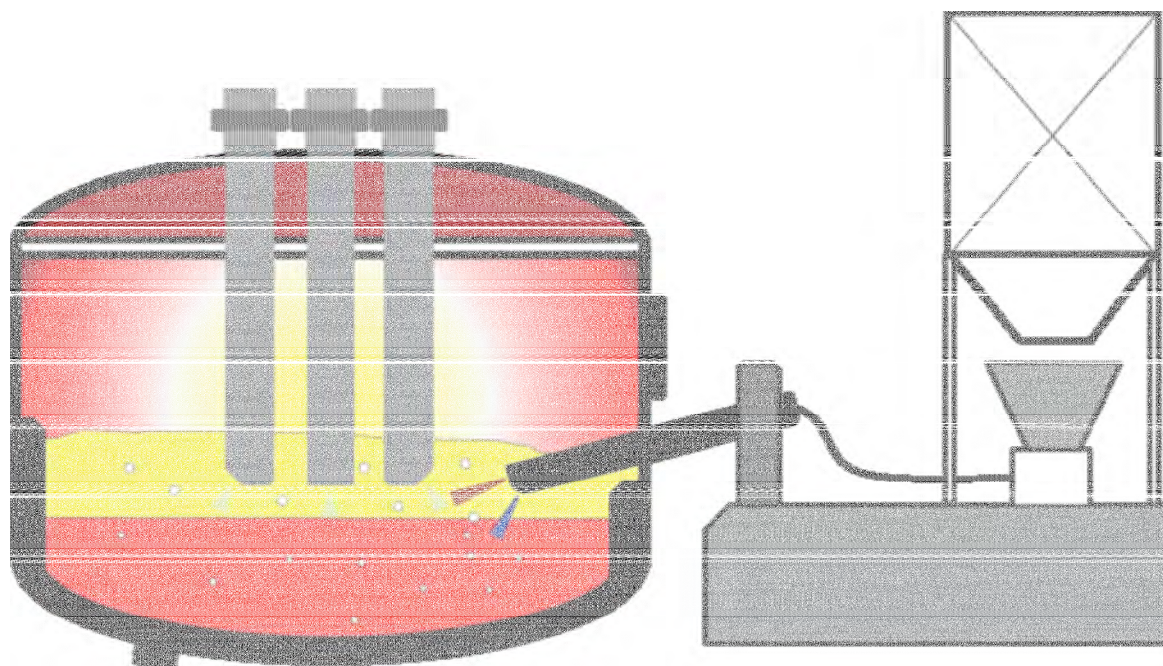


Figure 66 Electric Arc Furnace and Injection Equipment at MH EAF.

The images of the video recording during the injection of three different char coals supplied by Tecnocentro are illustrated in Figure 67. In the first field left the starting of the injection through the door lance is shown, while the second and third Figure represents the injection itself. The last picture right shows part of the slag foaming after the start of the KT-lances with petroleum coke. It can be seen that with exception of the charcoal sample with the highest moisture content (50 %) any of the coals tested even caused a foamy slag formation. Only with injection of calcined petroleum coke a slag foaming and an overflow were achieved. Despite the injection time of about two minutes no improvements were observed. Only the wet charcoal led the slag to overflow the furnace wall. In comparison, after the start of the KT system with petroleum coke a strong reaction deployed and the slag immediately flow out of the furnace door. This shows evidence that the slags were foamable. The corresponding slag analysis shows Table 42. The compositions are in typical ranges but without particular correlation.

char	FeO	Fe ₂ O ₃	Al ₂ O ₃	CaO	SiO ₂	MgO	MnO	Cr ₂ O ₃	S
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
Sample C	25,45	4,08	17,79	24,56	12,64	8,42	4,38	1,34	0,09
B Tecnocentro	34,45	5,58	9,25	28,85	9,34	4,59	4,58	2,29	0,12
A Tecnocentro	38,53	7,52	8,41	21,65	9,42	6,10	4,24	2,91	0,13

Table 42 Slag analysis after char injection tests at MH

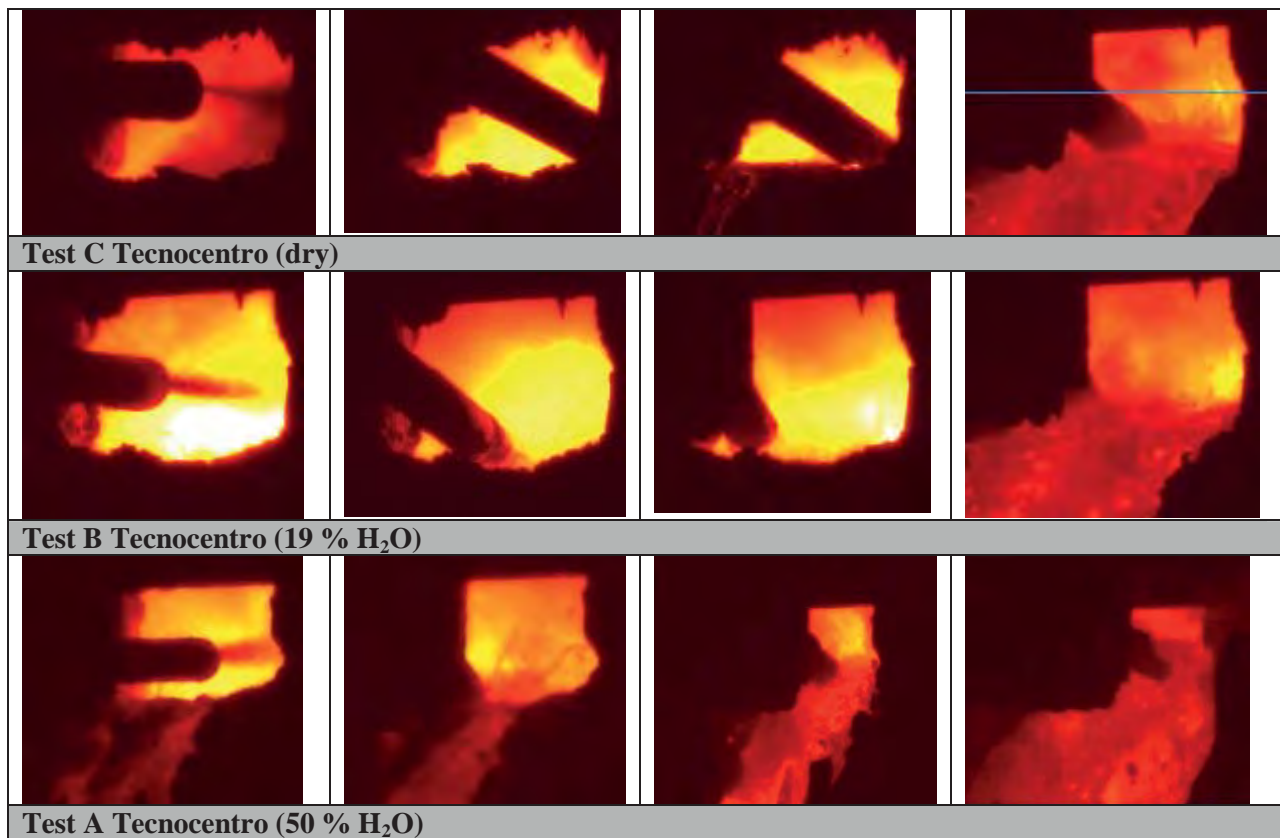


Figure 67 video images of Injection tests with different char samples

The low bulk density of the charcoal samples had a negative effect on the flow rate and the higher moisture contents led to blockages in the delivery system. After elimination of these technical difficulties the injection experiments were carried out as planned. This was, as already mentioned, the injection of char into the liquid slag through the door lance. The lance was submerged into the slag. The KT-lances were not used during injection of char because petroleum coke injected via the KT-system would falsify the test results. Only at the end of the refining period, the KT-lances were used to show the differences between the slag formation caused either by char or by petroleum coke. The injection procedure of test A with the wet char is illustrated in **Figure 68** and **69**.

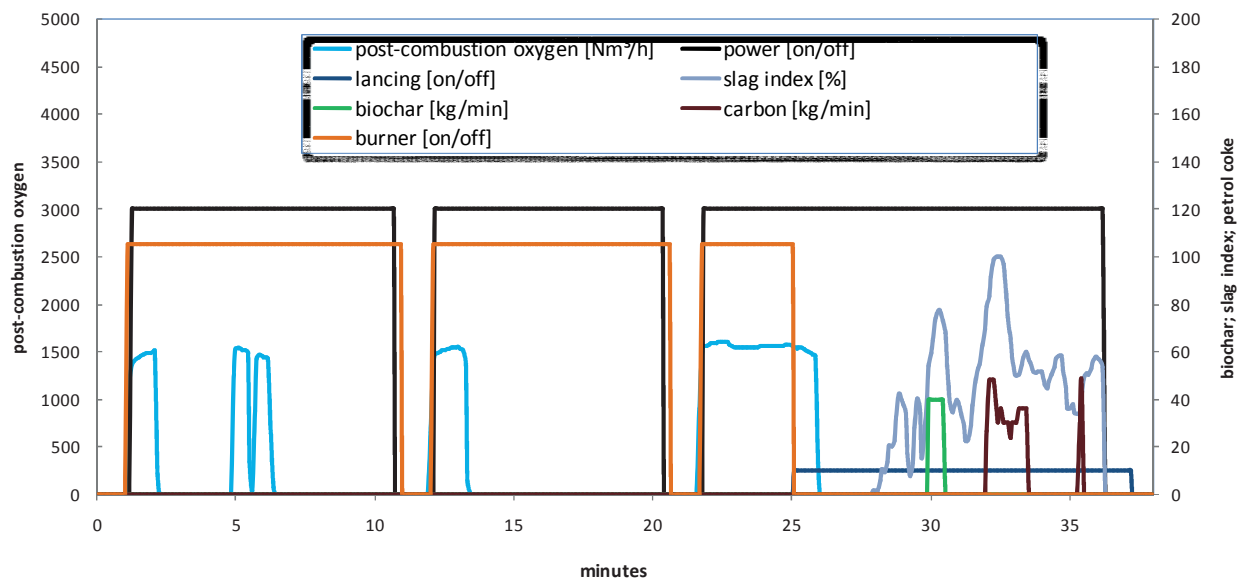


Figure 68. EAF cycle of injection Test A

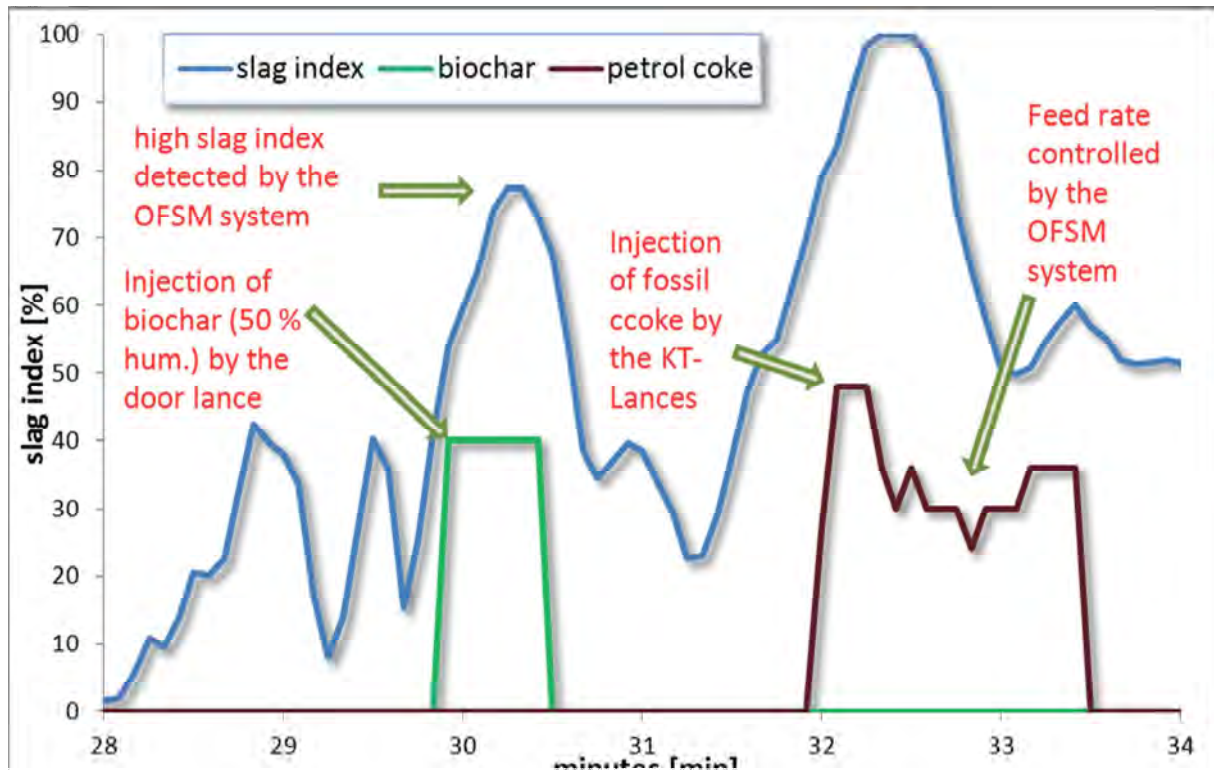


Figure 69. Slag Index detected by the OFSM system

Figure 70 summarizes theoretical mechanism for slag foaming using char.

- CO formation by reduction of FeO
- Volatiles
- Moisture

The contribution of the CO bubbles formed by reduction of FeO to the slag foaming is called into question.

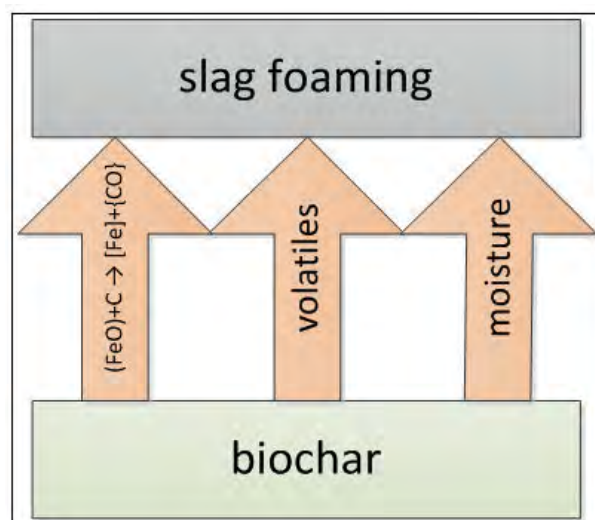


Figure 70. slag foaming mechanism using char

The result of the injection tests of charcoal in the EAF at MH shows that charcoal doesn't cause or if any a very slight foaming of the slag. The reason for this could be a low wettability of charcoal by the liquid slag, which prevents a reaction of carbon with FeO of the slag to form enough CO bubbles. This

was demonstrated by a sessile drop test. The low bulk density of the charcoal bears a risk of floating on the slag layer, which reduces the penetration in the slag significantly. Only the experiment with moist charcoal led to the formation of an acceptable slag foam. Here, the resulting water vapour at the high temperatures $> 1500\text{ }^{\circ}\text{C}$ due to the water-shift equilibrium resulted in formation of high quantities of gas which lead to slag foaming, but without effect on reducing FeO. This is of course undesirable. In addition, high humidity in combination with liquid metal and / or slag bears the risk of explosive gas formation.

Syngas utilization in EAF

Syngas produced during biomass pyrolysis can be used in EAF burners instead of natural gas. Due to the difficulty to have pilot syngas production close to the steel plant, according to the technical annex the syngas use has been simulated through CFD calculations. Considering the situation of FENO EAF, the simulation has been designed according to the following steps:

- i) Definition of a reference EAF situation with natural gas burners configurations.
- ii) Definition of quantitative criteria to compare burner performances with natural gas and syngas.
- iii) Definition of syngas characteristics and simulation with syngas burner feeding.
- iv) Global evaluation about syngas utilization in EAF. Definition of a reference EAF situation with actual burners configurations with natural gas.

i) Definition of a reference situation. CFD simulation has been carried out in order to set a reference situation, to be compared with subsequent simulations with syngas. The reference situation consider the design of the current used burner, the burners operating parameters and the EAF atmosphere composition . **Figure 71** shows the burner geometry.

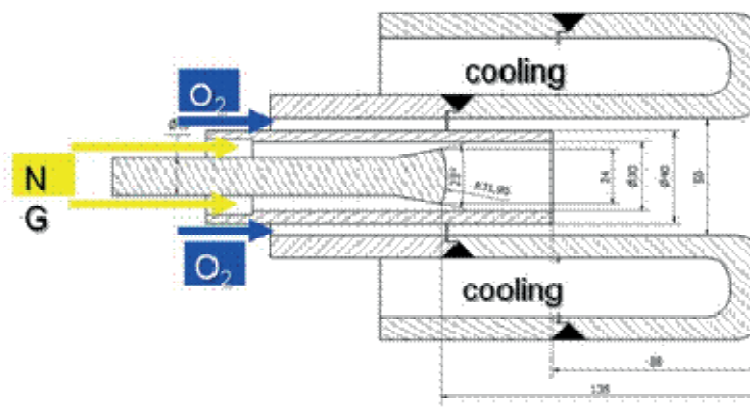


Figure 71. Scheme of burner currently used at FENO steelplant

The calculation domain considers a cylinder with 2500 mm diameter and 6000 mm length. Atmosphere composition is defined based on average values measured by EFSOP sensor. The burner is placed in symmetric position in one side of the domain, as indicated in **Figure 72**, where boundary conditions are also shown.



Figure 72. Boundary conditions used for CFD calculations

Being the final objective of the calculations the syngas simulation, a detailed kinetic combustion model has been chosen. This model includes 16 species and 42 reactions.

ii) Definition of quantitative criteria to compare burner performances with natural gas and syngas.

Once the flow field and flame temperature has been calculated for the current process working conditions, in order to simulate the EAF syngas utilization a quantitative criterion has been defined. The criterion is based on the comparison of the burners efficiencies, calculated with natural gas and with syngas. Such efficiency is defined as:

$$\frac{\text{kW} \cdot \text{to} \cdot \text{the} \cdot \text{scrap}}{\text{kW} \cdot \text{from} \cdot \text{the} \cdot \text{burner}}$$

Figure 73 reports the results of the calculations of the burner efficiency, for three different standard working conditions (corresponding to three burner powers).

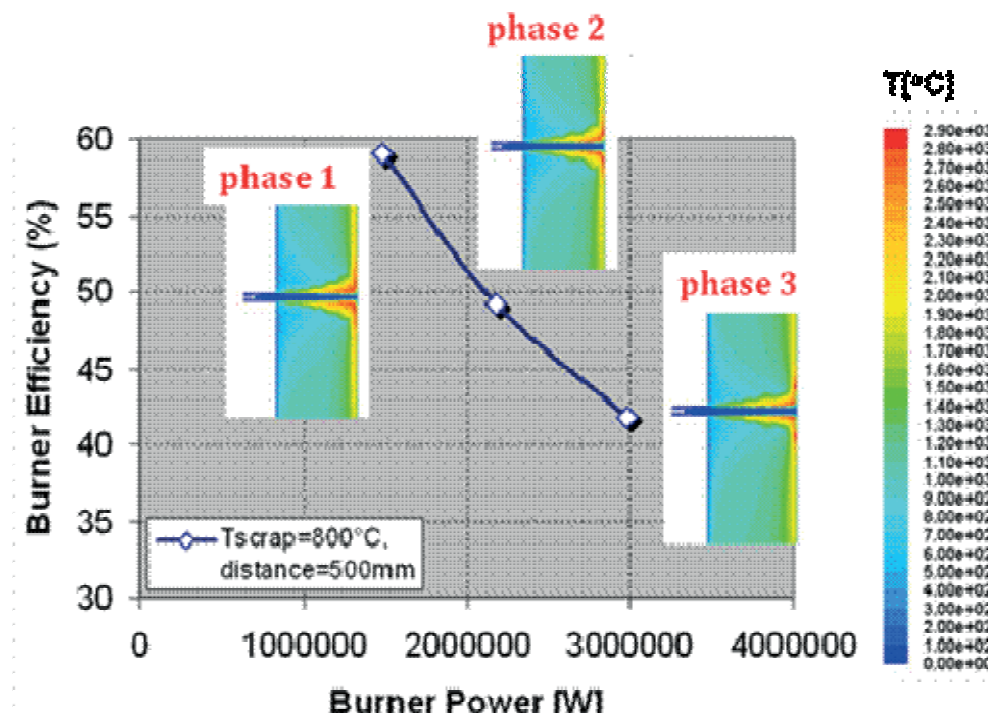


Figure 73 Calculation of the burning efficiency, for the three working conditions with natural gas.

The same calculation has been performed using syngas instead of natural gas.

iii) Definition of syngas characteristics and simulation with syngas burner feeding.

Syngas composition has been taken from the industrial trials of char production as follows:

Component	%
C ₃ H ₈	0.9
C ₂ H ₆	0.7
CH ₄	4.1
CO ₂	35.1
CO	20.6
O ₂	7.1
H ₂	0.5

Based on these data, the calculated syngas heating value is 7.15MJ/Nm³.

Due to the low value of such heating value it was necessary to increase gas flow rate in the burner. In Ferriere Nord steelplant gas flow rates higher than 500Nm³/h are not available.

For this reason, syngas has been mixed with natural gas, in order to obtain the target heating value of 21 MJ/Nm³, to stay within the feeding steelplant constraints. The same CFD calculations have been then carried out with syngas.

iv) Global evaluation about syngas utilization in EAF.

Figure 74 compares the flame temperature and the heat flux in case of syngas and natural gas. As a result, the burner fed with syngas produces a flame with lower temperature respect natural gas and lower heat flux on the scrap.

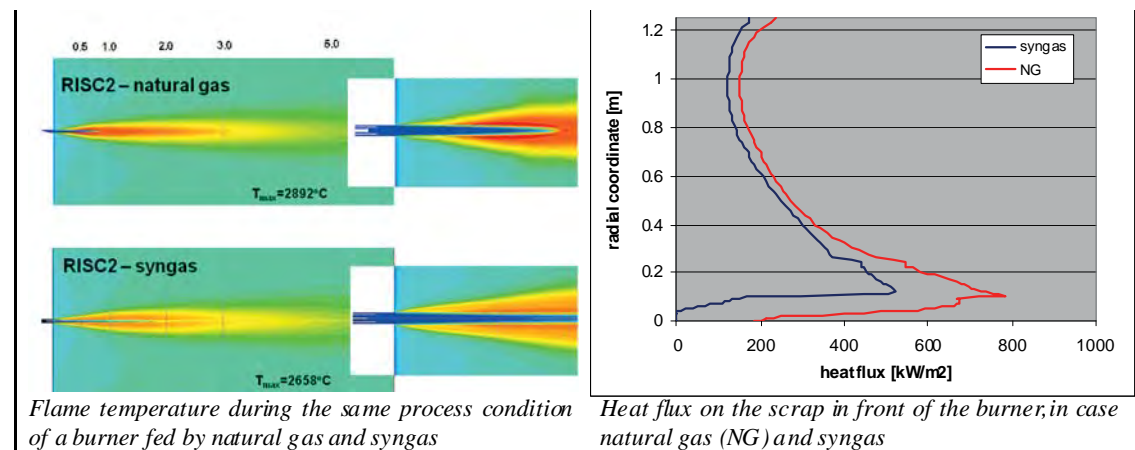


Figure 74. Comparison of flame temperature in case of natural gas and syngas burning.

Comparing the performances of the burners in term of efficiency (Figure 75), it has been found that the use of syngas determines a decreasing of efficiency of about 10%.

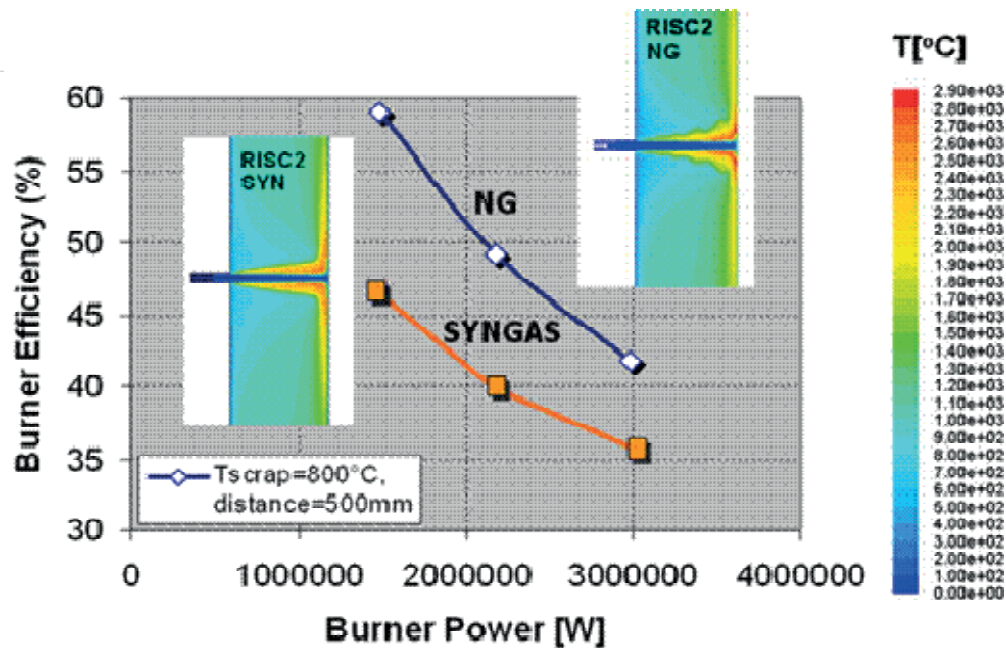


Figure 75. Difference of efficiency of burner in case of natural gas (NG) and syngas

To recovery the efficiency lost by syngas utilization, different burner configurations have been simulated. Figure 76 reports the results on a simulation showing the flame aspect and temperature in case of feeding with syngas the current burner, a burner modified with swirl motion on oxygen and swirl motion on oxygen and syngas.

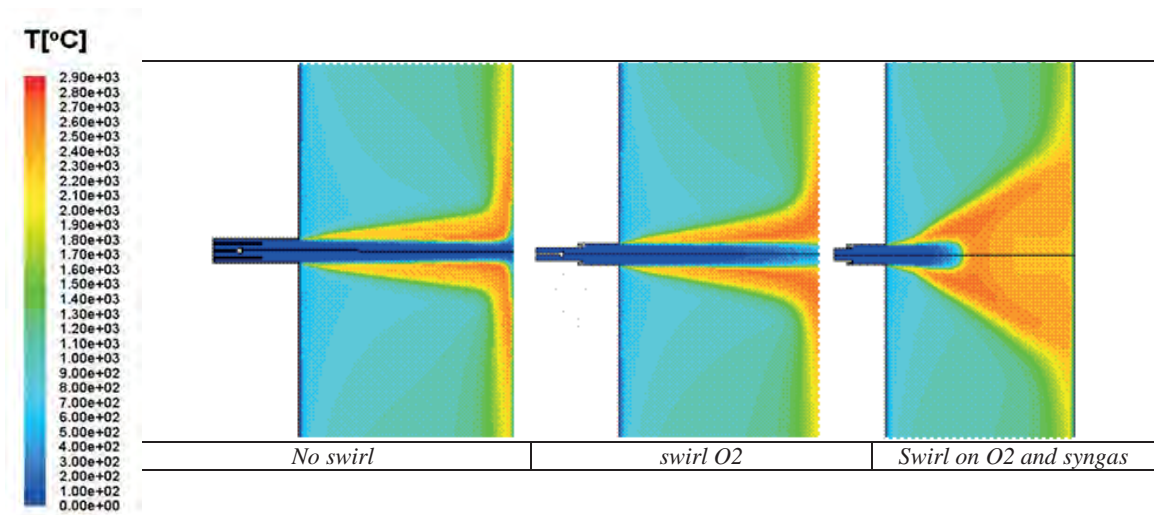


Figure 76. Flame aspect and temperature in case of feeding with syngas the current burner, a burner modified with swirl motion on oxygen and swirl motion on oxygen and syngas.

The calculation of efficiency in case of swirl motion did not a significant gain. Simulation show a larger portion of scrap heated by burner improved with swirl, but the global increase of efficiency is small. Summarising, the simulations showed a decreasing of efficiency of burner fed with syngas. In order to

keep the plant productivity at the same level, it is necessary to enrich the mix of natural gas, or to increase the gas flow rate. This calls for plant modifications.

Task 5.3 Evaluation of the variations of pollutants emissions from the plant.

Environmental monitoring during industrial trials has been carried out at Ferriere Nord and DEW. MH uses a smaller amount of char/ton of steel, respect the two other industrial partners, because carbon is used only as foaming agent, and not as charge material for steel recarburization of energy input.

Ferriere Nord, beside the current off gas analysis carried out with patented online installed system (EFSOPTM), performed extra analysis at the stack.

The results coming from stack analysis are compared with plant historical data.

Following species have been analysed.

- Powders
- Metals (Pb, Cd, Cu, Zn, Cr, Cr(VI), V, Ni, Mn, Sn)
- HCl
- PAH
- PCDD/PCDF

Below results of stack monitoring are reported and compared also with historical plant data:

	measured	historical
Powders (mg/Nm ³)	<0.5	<0.5
HCl (mg/Nm ³)	<0.5	<0.5
Dioxin (ng/Nm ³)	0.004	0.005
PAH (mg/Nm ³)	0.008	0.002

The analysis at Ferriere Nord indicate that fumes chemical analysis is not modified by char utilization, compared to average historical data.

Pollutant emissions and off gas temperature of biochar and reference trials at DEW have been measured, analyzed and evaluated. The measurements were carried out in the exhaust system of the arc furnace. Figure 77 shows a drawing of the exhaust system. The measuring point is marked. At this position, there are openings in the pipe, which were used to install the measurement equipment.

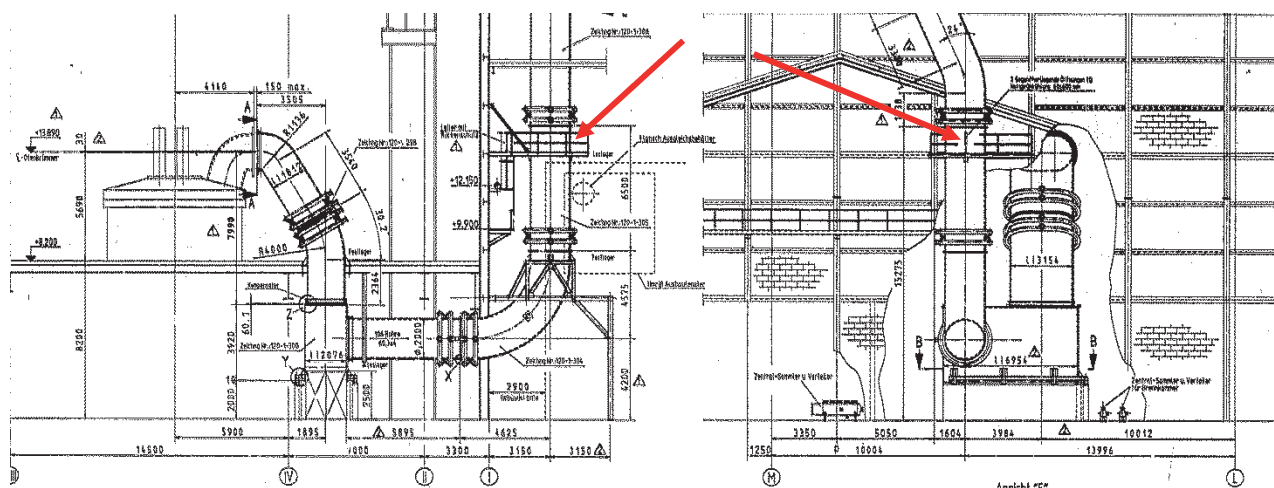


Figure 77. Points of off gas measurement

In the opening a thermocouple type K (range 0-1000°C) for the measurement of the exhaust gas temperature and a gas sampling probe was installed. From the gas sampling probe the exhaust gas was filtered and was conducted in a gas analysis unit. The analysers are listed with their relevant technical data in Table 43.

gas component	measuring principle	response delay	measuring range
CO ₂	infrared radiation absorption	3 s - 7 s	0 % - 20 %
O ₂	O ₂ -para-magnetism	< 4 s	0 % - 25 %
CO	infrared radiation absorption	3 s - 7 s	0 % - 2500 ppm

Table 43. Technical data off gas analyzers

The continuously recorded data were analysed using the operating data of the electric arc furnace.

Reference Charge

The operating data of an exemplary reference charge is listed in Table 44. The measurement data of temperature and gas composition is shown in the time course of the charge in Figure 78.

Material	1.5231
charge time [s]	4800
melting time [s]	3300
tapping temp. [°C]	1691
energy input [kWh]	60660
specific energy input [kWh/t]	421
<i>feedstock</i>	
scrap weight bucket I [kg]	82760
scrap weight bucket II [kg]	61180
injection coal [kg]	391
lime [kg]	3520
SBLU [kg]	78
blow oxygen [m ³]	2930
<i>output</i>	
tapped steel [kg]	139389
slag weight [kg]	1862

Table 44. Operating data of an exemplary reference charge

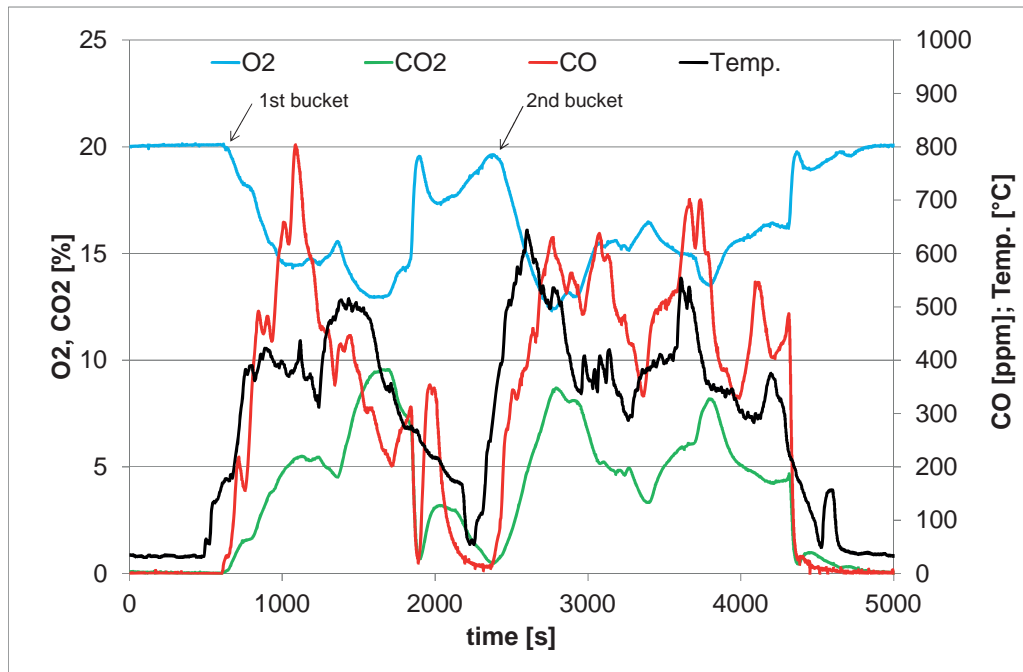


Figure 78. Off gas composition of an exemplary reference charge

As expected for the measurement point, the exhaust temperature peaks at a maximum of 650°C. Also expected and in agreement with previous measurements on this furnace, and this point the contents of carbon monoxide in the exhaust gas are in a range up to 800 ppm. The CO₂ content of the exhaust gas varies in a range of about 0-10 vol -%.

Biochar charge

The operating data from the experimental operation with biochar as charge coal in the arc furnace is listed in Table 45. The measurement data of temperature and gas composition are shown in the time course of the charge in Figure 79. The temperature measurement shows temperature peaks up to 620°C a very similar picture to the results from reference charge. Differences occur considering the measured values for the CO content of exhaust gas. As for the reference batch, the CO content only from time to time shows more than 500 ppm, for the biochar trials, especially during the melting of the second bucket, significantly higher CO values of 500-1500 ppm in peaks and even up to full scale value of 2500 ppm have been measured.

material	1.5231
charge duration [s]	4500
melt duration [s]	3480
tapping temp. [°C]	1641
energy input [kWh]	65180
specific energy input [kWh/t]	433
<i>feedstock</i>	
scrap weight bucket I [kg]	80820
scrap weight bucket II [kg]	69680
injection coal [kg]	388
lime [kg]	3520
SBLU [kg]	105
blow oxygen [m ³]	3032
<i>output</i>	
slag weight [kg]	not specified
tapped steel [kg]	not specified

Table 45. Operating data of biochar charge

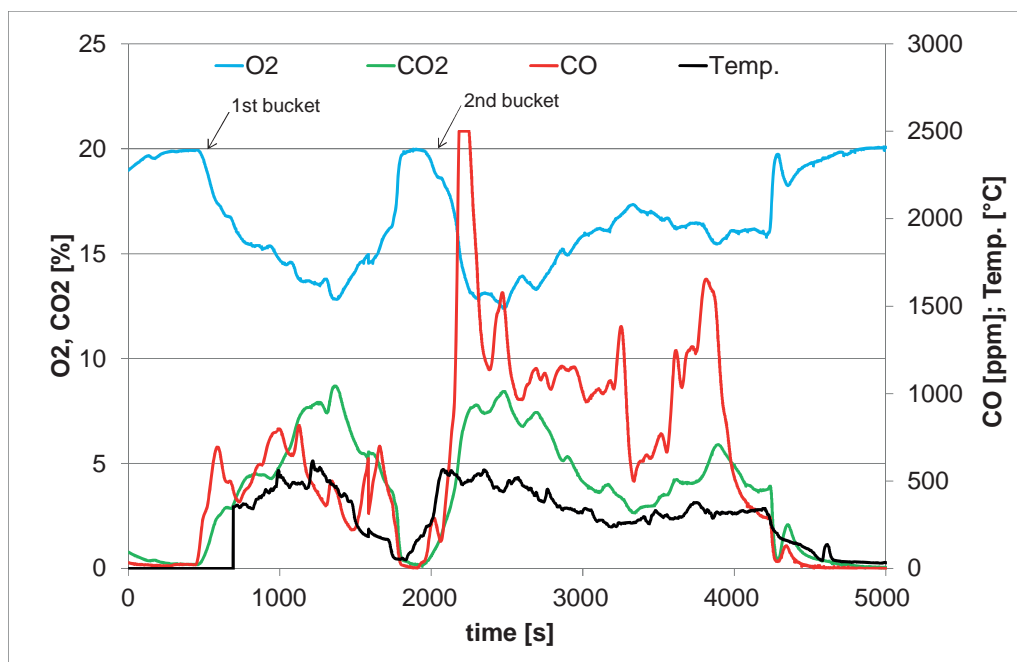


Figure 79. Off gas composition of biochar charge

The Measurements at the electric arc furnace at DEW in Siegen have been performed successfully. Off-gas data of both reference and biochar charges could have been recorded, evaluated and compared to each other. The comparison of the data sets shows higher CO levels in the off-gas composition while using biochar fines as charge coal.

As general conclusion from both monitoring activities at Ferriere Nord and DEW, the following indications can be drawn:

- the CO increase in the second bucket observed with char utilization (20% in the off gas respect 16%) is not a dramatic value which can be controlled optimising the operating practice and with a longer industrial testing
- char does not contribute to dioxin formation or increase of powder dispersion into fumes.

From the environmental point of view char can be used as charge material in electric furnace

WP6 TECHNO-ECONOMIC EVALUATION AND FINAL REPORT (FERRIERE NORD, CSM, TECNOCENTRO, IP, RWTH, DEW, MH)

Task 6.1: Techno economic evaluation of the project results

This project has exploited the possibility to use biomass products (char and syngas) in electric arc furnaces, replacing fossil sources. Environmental benefits deriving from biomass utilization instead of fossil fuels has been widely described in literature [1,2,3,22]. The main advantage derive from being neutral respect CO₂ emission.

Below techno-economic evaluations are reported; the project showed that charcoal utilization is technically feasible in shorter time respect syngas. For this reason most of considerations and simulations are devoted to charcoal, even if economic aspect bond with syngas are taken into considerations.

Charcoal is a wood product that is made by heating wood in absence of sufficient air for full combustion to occur. Heating releases wood volatile compounds leaving behind a relatively light weight and clean burning fuel that is 70-90% carbon. Tecno-economic evaluation of charcoal utilization has to consider two aspects:

- char costs
- cost savings from reduction of CO₂ emission

There is not a great deal of information available in literature on the cost of charcoal production. Schematic diagram [19] in Figure below shows the phases of char production; each step contributes to the global char cost.

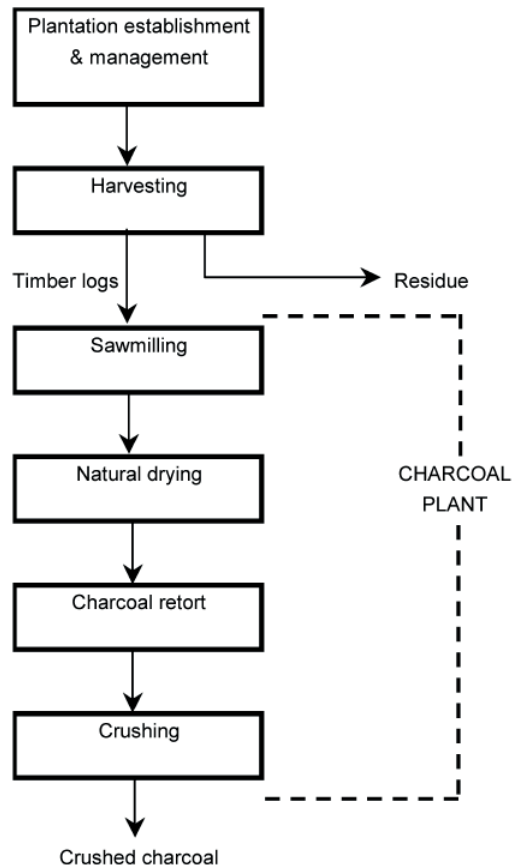


Figure 80 Schematic flowsheet of charcoal production

All the steps of production of Figure 80 can be grouped into three main issues:

1. wood/raw material (including cost of harvesting and collection of biomass up to the pyrolysis plant)
2. charcoal production
3. charcoal transport (to be intended as transportation from the pyrolysis plant to the steel factory)

Figure 81 reports the contribution of these three various issues [19] to the global cost of charcoal. According to this Figure, charcoal cost is estimated with an order of magnitude of 400 €/t, but about 70% is due to the cost of biomass. Inside this cost is included cost for biomass production, cultivation or collection and transportation to the pyrolysis plant. In Figure 81, with the term transportation is intended only the delivery of produced charcoal from the production pyrolysis plant to the utilization 1 plant.

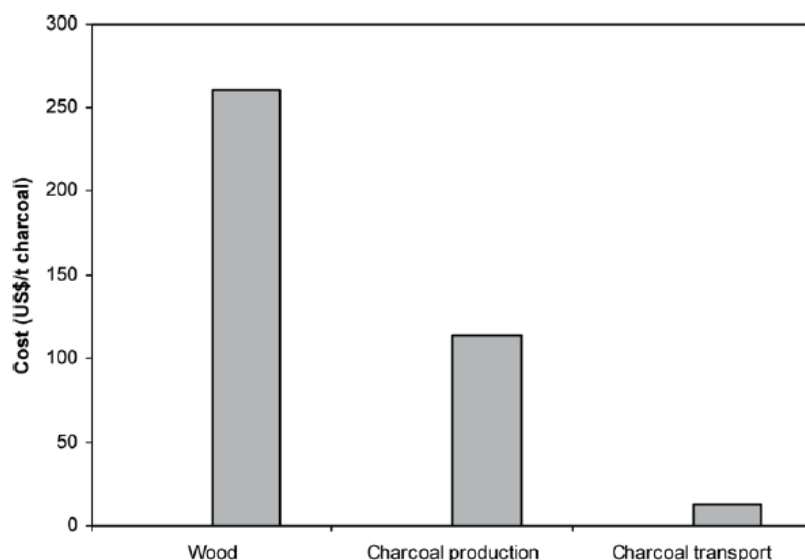


Figure 81. Contribution of stages to global charcoal cost.

In literature, smaller costs (in the order of magnitude of 160 €/ton) are reported [22] for specific situations with large amount of biomass available in the surroundings.

In order to get an idea about the economics of charcoal, case study of char production for MH steelplant in Austria has been considered. Raw material prices and costs, investigations concerning costs for transport as well as the conversion of biomass (including potentially drying) into charcoal have been taken into account. Due to the fact, that the biomass market in most cases is not a typical market with standardized products, it is impossible to get detailed and totally comparable prices for different biomasses. This is why always price ranges dependent on quality, region etc. are referred. However, the listed prices can change very quickly. Especially a big demand for certain biomasses can lead to a radical price increase.

The only biomass which is a more or less standardized product with an existing trading is wood chips. For bulk consumers the prices are in the range of 80-100 €/t dry matter. However, also bark is very often traded as biogenic energy source. The prices for bark are at about 25-40 €/t dm and therefore still attractive at the moment.

In case of strew the mentioned prices differ a lot. Realistically the price for strew is between 65 and 100 €/t dm, but has to be fixed individually with the partners or farmers. The prices for cobs are similar in the area of 43 to 89 €/t dm. In general, the prices for agricultural products are a combination of harvesting costs and collecting costs and are often declared as prices ex works.

The costs for waste wood also have a wide range depending on the degree of contamination. Untreated waste wood realizes prices of up to 40 €/t dm, whereas for contaminated waste wood you will even get up to 30 €/t dm for disposal. The problem in case of the utilization of waste wood is the legal situation.

The cost situation for short rotation crops including land purchasing, crop cultivation and harvesting including chipping is about 110 €/t dm.

To calculate the real charcoal costs, beside the costs for the feedstock material there are several other things which have to be considered. E.g., the demand on biomass for every ton of charcoal is approximately 4 tons. Further, charcoals typically have a carbon content of 80-85 %. This means, that about 4 to 5 tons of biomass are needed to deliver the same carbon amount as with 1 ton of petroleum coke. This is why in Table 46 the relative prices for petroleum coke as standard injection coal and those of the comparable amount of several biomasses are listed.

	Material costs	Annual demand	Annual costs
	[%]	[t/a]	[%]
Petroleum coke	100	5400	100
Wood chips	30	24300	135
Strew	26,7	24300	120
Bark	10	24300	45
Cobs	20	24300	90
Waste wood	3,3	24300	15

Table 46 Cost comparison of different feedstock for injection coal

It is obvious, that in most cases even the raw material price for the biomass is nearly the same or even higher as the one for the standard injection coal, petroleum coke. Only really low priced biomass is an economically attractive alternative to fossil coke. However, the availability of such biomasses is not the best one. Nevertheless, additionally to the feedstock prices also transportation costs, storage costs operating costs of the carbonization plant etc. have to be considered. Table 47 shows a rough estimation for total costs of injection chars of different origin, which are between 220 and 580 €/t and therefore up to the double price of typical injection coals.

	Raw material costs	Transport	Conversion costs	Storage and handling	Total costs
	€/t charcoal	€/t biomass	€/t charcoal	€/t charcoal	€/t
Wood chips	405	10	150	15	580
Strew	360	20	150	15	545
Bark	135	15	150	15	315
Cobs	270	20	150	15	455
Waste wood	45	10	150	15	220

Table 47 Cost comparison of total costs for charcoals from different origins

The range of costs for charcoal production individuated is in agreement with what reported in literature [19, 22]

Cost saving from reduction of CO₂ emission

The economical evaluation about to biomass utilizations needs to consider also the advantage deriving from the reduction of CO₂ emissions.

The CO₂ sources from the EAF process are shown in Figure 82. The main proportion of the total CO₂ sources is provided by the injected/charged carbon. This calculation is tailored on the EAF of Ferriere Nord, but the order of magnitude can be considered valid for most of EAFs.

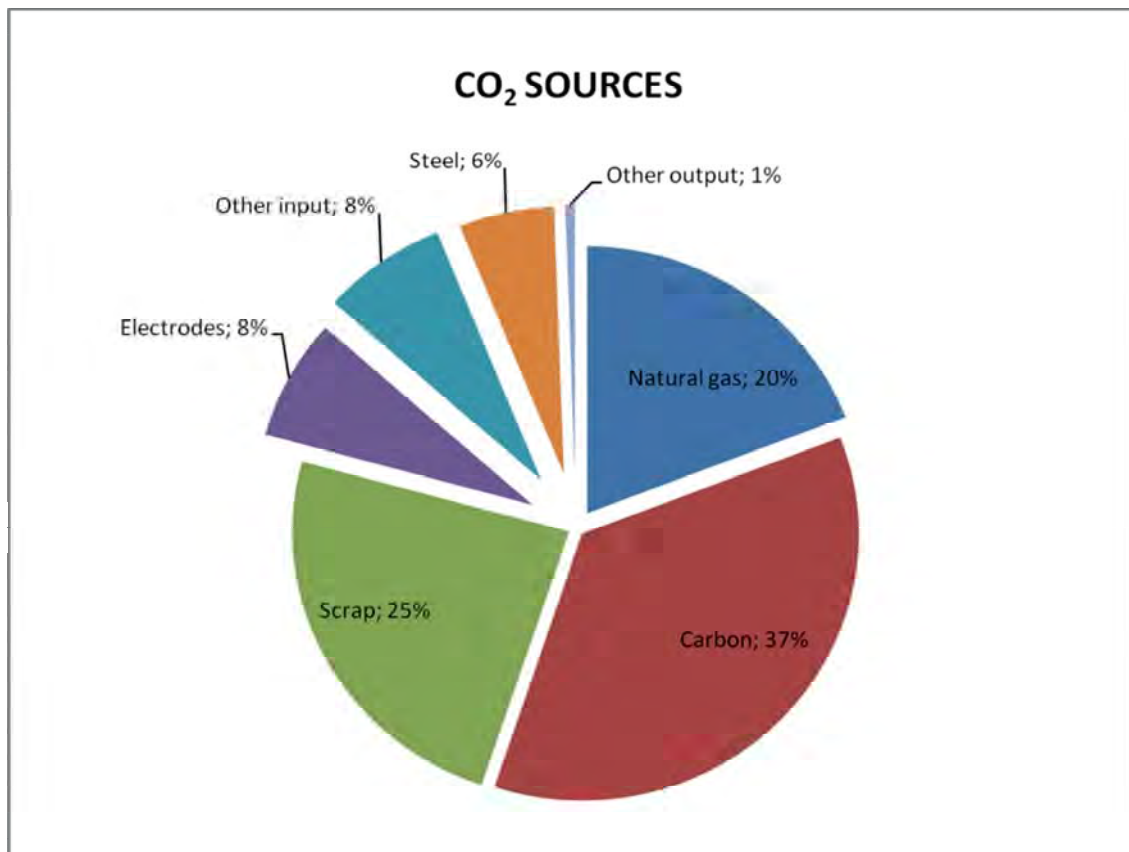


Figure 82 Percentage of CO₂-sources of an EAF process

In order to reduce the CO₂ emission from the electric steel production, the main issue is to reduce the coal consumption.

CO₂ emissions are calculated with the mass balance approach that considers all the carbon entering and leaving the installation.

The following formula is applicable for mass balance:

$$EM_{MB} = \sum (f \times AD_i \times CC_i)$$

where:

- EM_{mb} emissions from all source streams included on the mass balance [ton CO₂];
- f factor for converting the molar mass of carbon to CO₂. The value is 3.664 tonCO₂/tonC;
- i index for the material or fuel under consideration;
- AD_i activity data of the material or fuel under consideration. Ingoing materials or fuels are taken into account as positive, outgoing are taken into account as negative.
- CC_i the carbon content of the component under consideration;

Figure 83 represents CO₂ emissions for Ferriere Nord SPA for year 2011, a total amount of 92.804 tons of CO₂ have been generated. The specific emissions were 78 Kg of CO₂ / ton of steel produced by EAF.

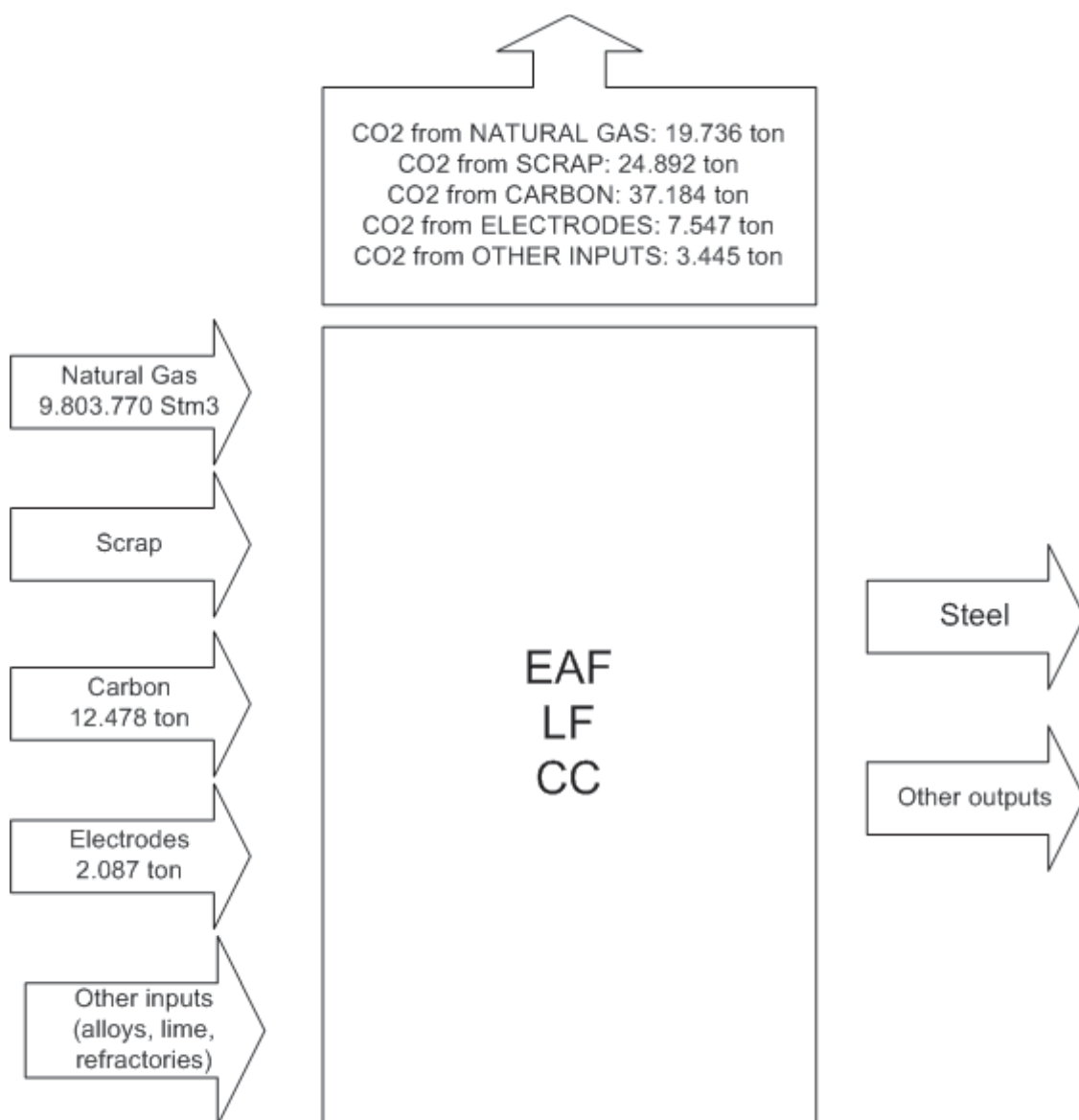


Figure 83. CO₂ emissions for Ferriere Nord SPA for year 2011. The specific emissions were 78 Kg of CO₂ / ton of steel produced by EAF.

Figure 84 reports the scheme of CO₂ emission from DEW Siegen.

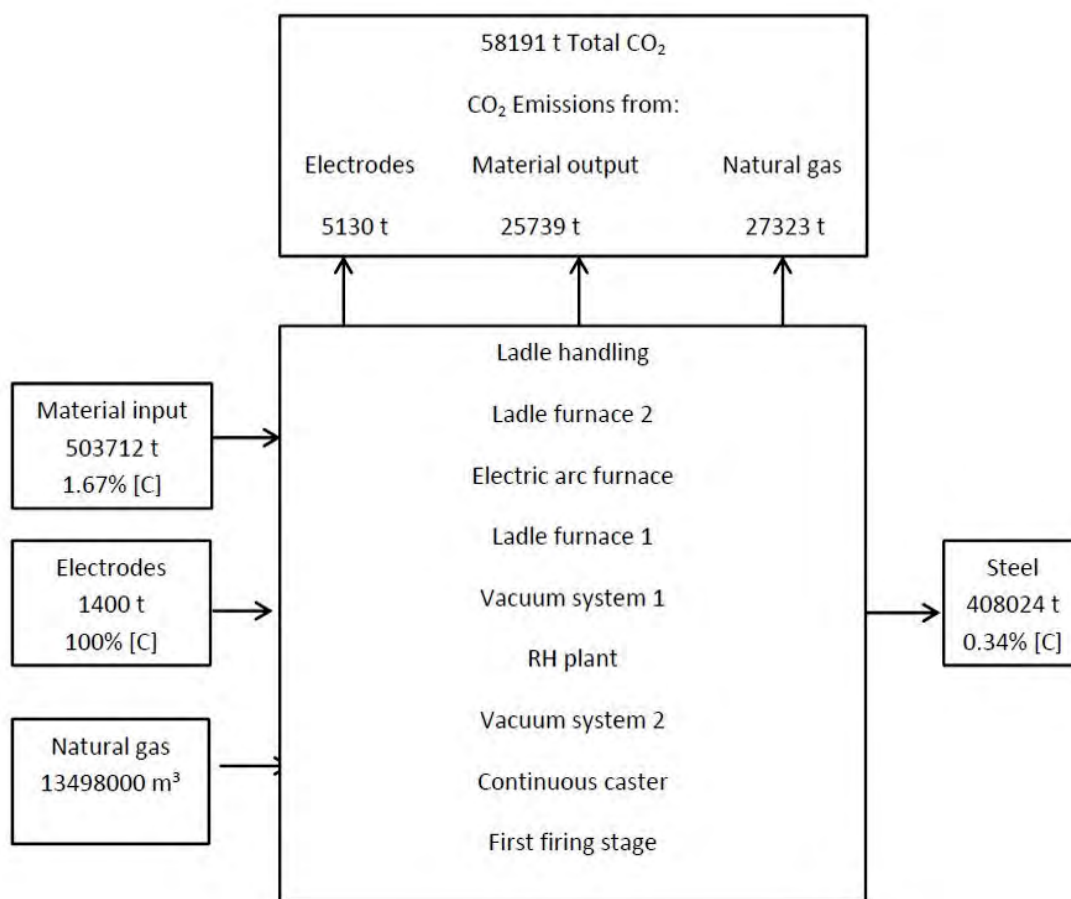


Figure 84. DEW CO2 emission balance of a given year

Details of the calculations of the CO₂ emissions for DEW steelplant are reported in Annex 2.

Once the CO₂ emission is calculated, it is possible to estimate the advantages deriving from reduction of CO₂ emissions, and also make some hypothesis varying the amount of substitution, coal price, and values of CO₂ quotes.

In these calculations biomass is considered neutral respect the CO₂ emission.

Figure 85 reports, for Ferriere Nord, global cost for CO₂ emission from steel plant, in four cases:

1. Actual situation with fossil fuels
2. Substitution of charge coals
3. Substitution of injected coals
4. Substitution of syngas

For the calculation, three possible values of CO₂ are considered:

- 10 €/t, of the order of magnitude of current values
- 18 €/t, a value higher
- 100 €/t, the fine value, according to ETS, for missing EUA - European Union Allowances (assumed as maximum value in the EU ETS market)

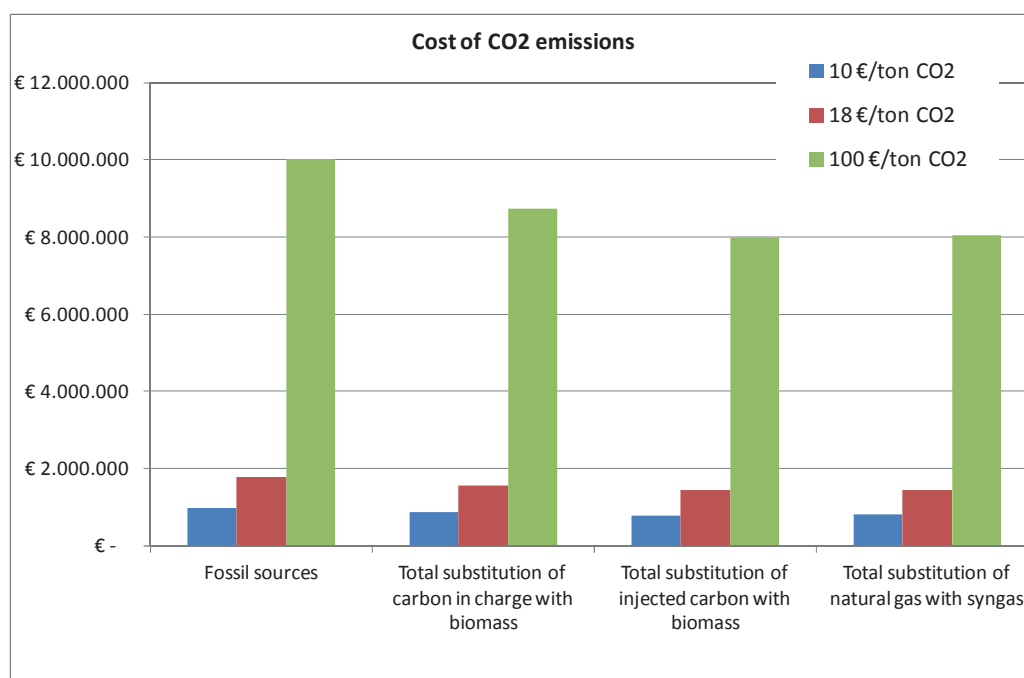


Figure 85 Global cost for CO₂ emission from steel plant (Ferriere Nord), in four cases:
 1. Actual situation with fossil fuels
 2. Substitution of charge coals
 3. Substitution of injected coals
 4. Substitution of syngas

Figure 86 reports the difference between the costs, calculated as a sum of supplying costs and CO₂ emission costs, using only fossil carbons and using biomass as a total substitute for carbon in charge and injection, in seven different market conditions.

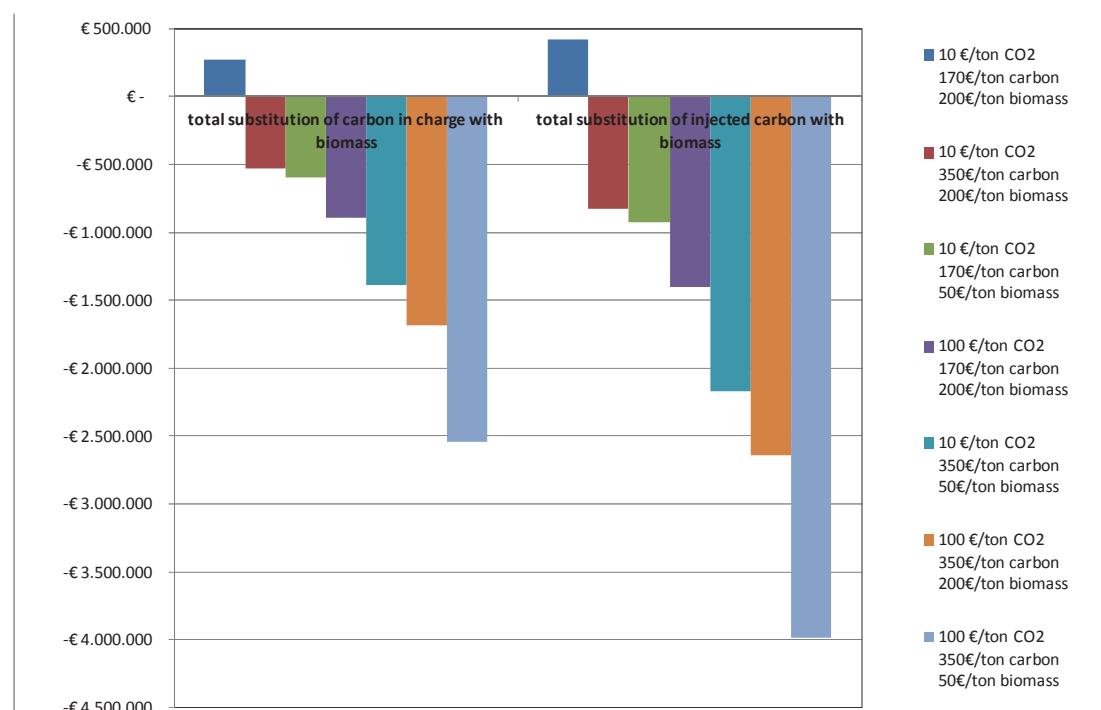


Figure 86 Difference between costs (supplying + CO₂ emissions) using onlys fossil carbons and using biomas as total substitute for carbon in charge and injection, in seven different market conditions

The actual market conditions indicates that globally a small global cost increases can be expected, but realistic future scenario indicate that an economical convenience in biomass utilization can be foreseen.

The diagram in Figure 87, calculated for MH steel plant, shows a rough overview about the necessary CO₂-prices to make a usage of biomass in form of charcoal economically attractive for the production of steel in an electric arc furnace, considering a value of 170 €/ton for coal.

In the end, from the quantitative point of view, including the availability of biomass, and also the qualitative point of view, almost entirely woody biomass like wood chips are eligible feedstock materials for charcoal production. If this is the case, politically driven costs like CO₂-taxes have to rise to a level of about 50-100 €/t to make these CO₂-neutral alternatives also economically competitive.

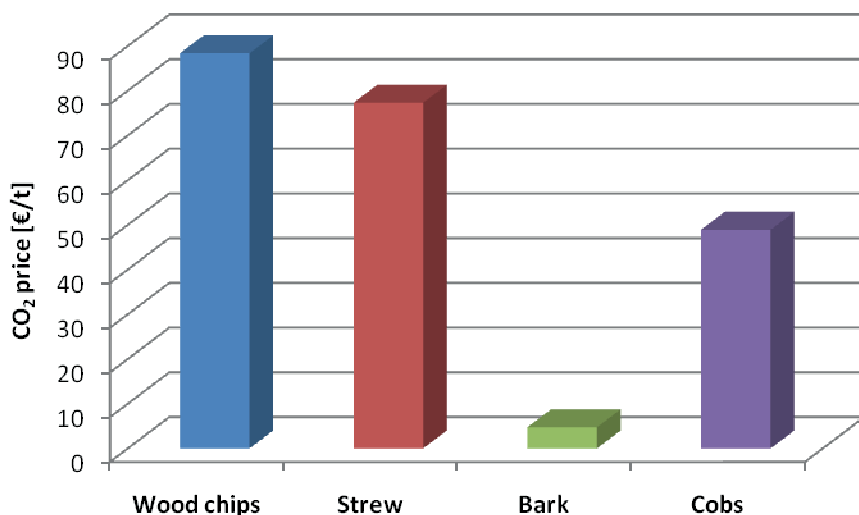


Figure 87 Necessary CO₂-price for economical biomass utilization in electric steel production (calculated for MH steel plant)

Besides the increase of costs of CO₂ certificates, the need to acquire CO₂ quotes has been also considered. For example, the DEW in Siegen has an annual allocation of 48,150 CO₂ certificate. Experience shows that, depending on the annual production output, more CO₂ certificates would be needed. This yields a missing quantity of about 10,000 CO₂ certificates per year. In This case a partial substitution may be enough to avoid increases of costs. Following table reports, the global reduction of CO₂, depending on the amount of coal substitution.

Depending on the substitution, it is possible to reduce the total CO₂ emissions by 19 %.

Substitution [%]	Operational CO ₂ -Reduction [%]	Total Reduction [%]
0	0	0
20	12	6
40	24	13
60	36	19

Table 48. CO₂-Reductions

In order to calculate the monetary value of the CO₂ certificate, the highest spot market prices for emission allowances from 2008 to 2011 are being considered

A price of 18 € – 35 € is assumed for the year 2013, this lies above the average price in the last 3 years (16.40€). The results of these calculations are summarized in Table 49. The case of non-substitution with bio carbon yields additional cost of about 181,000 € to 351,000 €. On the other hand, using 60% substitution could yield additional revenue between 18,000€ and 37,000 €.

Substitution [%]	ΣCO_2 [t]	allocated certificates [t]	ΔCO_2 certificates [t]	18 €	25 €	35 €
0	58,192	48,150	-10,042	-180,748	-251,038	-351,454
20	54,493	48,150	-6,343	-114,173	-158,574	-222,003
40	50,794	48,150	-2,644	-47,599	-66,109	-92,553
60	47,096	48,150	1,054	18,976	26,355	36,898

Table 49. Additional cost in the third trading period

Figure 88 shows the price variation as a result of substitution. Positive results are yielded from 54% Substitution.

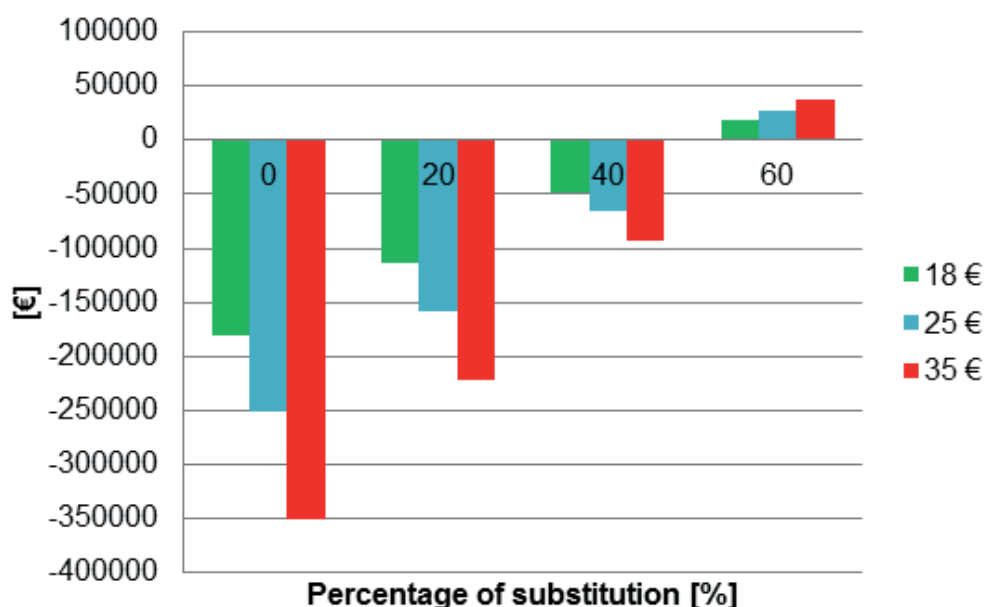


Figure 88. Price Variation

This techno economic evaluation on the basis of the data from DEW Siegen shows for an exemplary price of 18 € per ton of CO₂ that the total savings for the steel plant by a replacement of 60 % of the common anthracite coal by biochar would be about 11,000 € per year. Assuming a price of 35 € per ton of CO₂ that would mean even savings up to 388,000 € per year.

These calculations are based on assumptions and the price for biochar is unaccounted. Up to now there does not exist an official market for biochar which can be used in steel mills. Most part of biochar production is still in pilot scale state. So the prices per ton of produced biochar are not representative. Industrial scale production and the development of different production processes for different qualities of biochar is currently under construction. In the next few years the industrial scale production of different biochar qualities is expected and according to this the development of a market and a market price.

However, rising prices for additional CO₂ certificates are expected for the future. In Addition to that increases of the prices for fossil coal are expected, too.

Moreover, in these evaluations possible savings from syngas can be considered. These project showed the problems arising with syngas utilization in electric arc furnaces. Syngas can be used as fuel for other type of furnace, as re-heating furnaces, or can be used for power generation, directly inside the pyrolysis plant.

Another by-product from pyrolysis which can be used to save cost from biomass utilization is tar. Tar can be mixed with charcoal itself as binding agent for char briquettes production, or can be sold as *chemical*.

Syngas and tar utilization would increase the economical advantages from charcoal practice.

In general the use of biochar puts the electric steel mills in a position to avoid CO₂ emissions which are relevant for the EU ETS like the emissions from fossil carbon. Therefore, depending on prices for biochar and its processing, the use of biochar instead of fossil carbon should, apart from the positive ecological effects, also have a positive effect on the economics of the electric steelmaking process.

CONCLUSIONS

The global objective of the project is to investigate the partial or total substitution of coal and natural gas with charcoal and biogas produced from pyrolysis of biomass. The char is used as injectable powder or charged in the basket.

The characteristics of char and biogas, and the related pyrolysis process, are tailored in order to match the requirements for their utilisation in EAF.

- Optimization of pyrolysis process and production of char according to the indication obtained from laboratory and pilot activities performed in the first half of the project.
- Laboratory tests were carried out to study under controlled conditions char reactivity and slag foaming promoted by char
- Pilot EAF tests before industrial tests revealed that steel and slag composition are not altered by coal substitution by char
- Industrial tests have been performed replacing coal with char. Both char charging and injection have been tested
- Syngas utilization in EAF burners, instead of natural gas has been simulated by means of CFD calculations. The used syngas composition is the one from pyrolysis tests (WP5).

The tests performed (both pilot and industrial) showed that coal can be replaced by char, both for charging and injection to promote foaming.

In case of charging the following aspects should be deeply investigated:

- char reactivity: char start burning during charging. Char reactivity depends on high surface area, volatile content and powders dispersion during charging. Proposed solution is a char pre-treatment with briquetting stage before charging;
- slag foaming: some trials showed good foaming behaviour, other trials were not satisfactory. Proposed solutions are improvement of injection system and utilization of additives together with char powder to increase char/slag wettability and promote reaction of char with iron oxide. The injection system must ensure char injection below the slag

Moreover, syngas utilization in EAF burners, instead of natural gas has been simulated by means of CFD calculations. The used syngas composition was that arising from the pyrolysis tests. Syngas utilization leads to a decrease of EAF efficiency.

Techno economic evaluation carried out considering char cost and CO₂ emission leads to the conclusion that:

- official market for biochar, which can be used in steel mills, does not still exist. Most part of biochar production is still in pilot scale state. So the prices per ton of produced biochar are not representative. Literature reports prices ranging from 160 to 400 €/t of produced char.
- exemplary price of 18 € per ton of CO₂ partially compensate actually higher price of charcoal.

In the next few years the industrial scale production of different biochar qualities is expected and according to this the development of a market and a market price.

However, rising prices for additional CO₂ certificates are expected for the future. In Addition to that increases of the prices for fossil coal are expected, too. In general the use of biochar puts the electric steel mills in a position to avoid CO₂ emissions which are relevant for the EU ETS like the emissions from fossil carbon.

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26 Thermocalc

EXPLOITATION AND IMPACT OF THE RESEARCH RESULTS

Application: the project results can be applied in all EAFs. Project results that coal substitution by char is feasible: the steel, slag and furnace operating parameters are not modified significantly. Also the absence of environmental increase of pollution due to char has been verified. The utilization of char as charge material, on a routine basis needs industrial experimentation to optimize the operating practices. The application as foaming agent (injection) needs also further experimentation to stabilize the foaming process and modify the injection system and injection practice in general.

Advantages: char eliminate the dependency from fossil coal and reduces the CO₂ emissions.

Patent: project results can not be transformed into a patent. The eventual modification of the injection system may be protected by a patent, but further research activities is necessary and also subsequent industrial validation is necessary

Publications: during the project have been produced five publications.

Other aspects: the possibility to use char from biomass to replace fossil coal is strongly related to the local availability of biomass. The availability of biomass in the surrounding of the steel plant, and the reduce of the CO₂ emission increase the economicity of this technology. Moreover the utilization and transformation of biomass into charcoal can generate new local economies.

LIST OF SYMBOLS AND ABBREVIATIONS

BCB	biochar briquettes
CSM	Centro Sviluppo Materiali SpA - partner
DEW	Deutsche Edelstahlwerke GmbH, Deutsche Edelstahlwerke, - partner
FENO	Ferriere Nord - coordinator
HHV	higher heating value
IP	Imperial College - partners
LHV	lower heating value
MH	Stahl- und Walzwerk Marienhütte Ges. m. b. h.- partner
RC	reference coal
RWTH	Rheinisch Westfälische Technische Hochschule Aachen, - partner
TG	termogravimetric apparatus

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ANNEX 1- SLAG FOAMING

By creating a foamy slag the following main benefits can be achieved: improvement of the heat transfer, better arc stability, and protection of refractory material inside the furnace. Because of better arc stability and less radiation losses, foaming slag practice leads to reductions in energy consumption, electrode, consumption, noise level, and an increase in productivity. The foaming capability of the slag depends on several parameters. The relationship of most important parameters is shown in Figure A1.

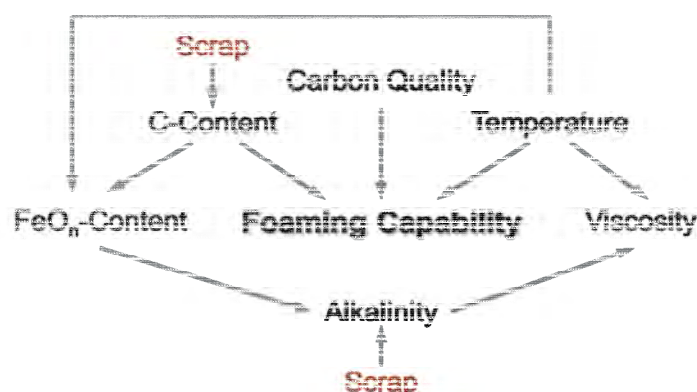


Figure A1 Parameters affecting the foaming capability [18]

The melting of scrap necessarily generates slag with a high level of silica from soil or sand inevitably adhering to the scrap surface. Sulphur and phosphorus are usually present in the scrap as well. To reduce their transfer to the steel it is necessary to employ a basic slag by adding lime and/or dolomite. Good foaming capabilities can be achieved with a basicity CaO/SiO_2 between 2 and 2.5. Desulphurization and dephosphorization are the main metallurgical tasks for the slag. For example high sulphur contents in the scrap/melt requires an higher amount of lime and carbon as well as higher energy consumption and processing time. Slag is foamed by the rising of CO bubbles from the bath or the generation of such bubbles directly in the slag. The generation scheme is illustrated in Figure A2.

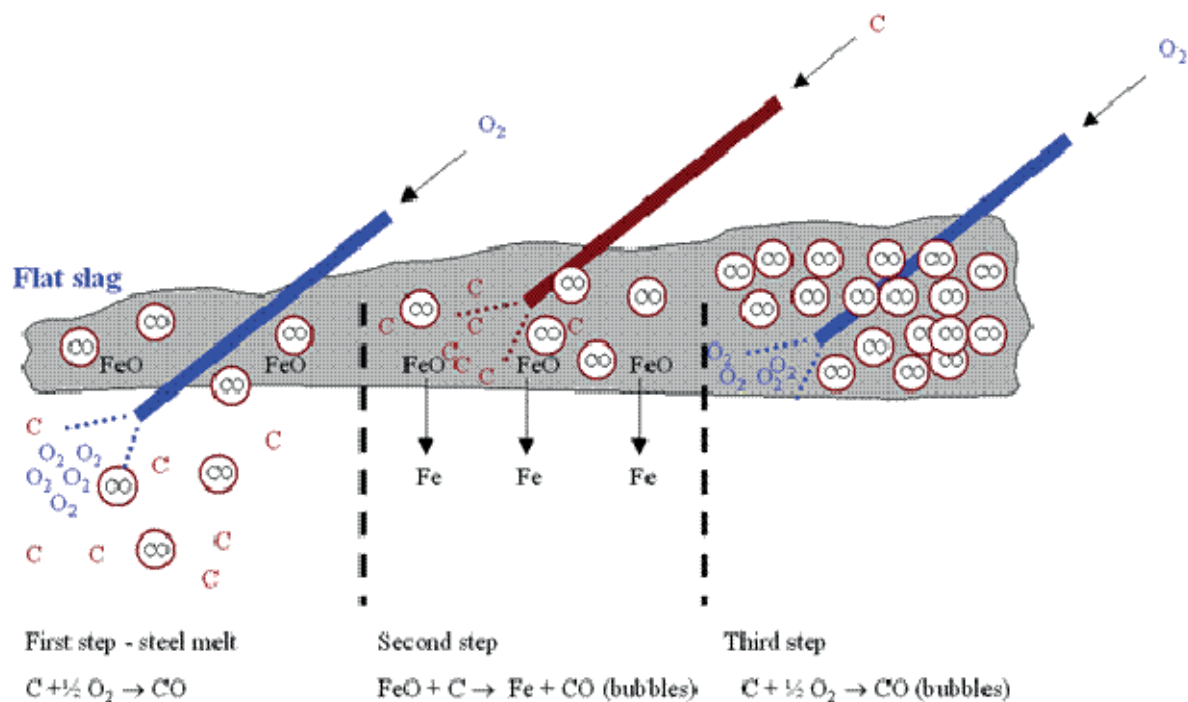


Figure A2 Process of elaboration of foamy slag [19]

During the initial foaming period the carbon content predominantly determines the process of generation a foamy slag. This carbon content of the melt depends on the different scrap grades charged to the furnace. To keep the C-content within the desired range for each single melt a constant mixture of different scrap grades has to be obtained. According to the scrap mixture the necessary carbon is to be injected or added as lump coke. In the second period carbon is injected in to the slag to reduce FeO and to create CO bubbles leading to a further increase of the slag height.

ANNEX 2

CALCULATION OF CO₂ EMISSIONS FROM DEW STEELPLANT

According to Figure 80, the electrode and stock input are considered as operational (process related) CO₂ emission. The calculation of operational CO₂ emissions of the electrodes is done according to equation (1.1). The operational CO₂ emission is the product of the annual electrode consumption, the emission factor and reaction factor of the electrodes.

$$m_{C, \text{Electrodes}} * \text{conversion factor} = m_{\text{CO}_2, \text{Electrodes}} \quad (0.1)$$

$$m_{\text{CO}_2, \text{Electrodes}} = 1400t * 3.667 = 5130t$$

For the process of steel production in the electric steel plant, the entire operational annual CO₂ emission on the raw material input, as well as a carbon balance for the input and output of carbon on scrap, steel and other materials are calculated according to equation (7.4).

$$\left[m_{\text{material input}} * (C \%) - m_{\text{Stahl}} * (C \%) \right] * \text{conversion factor} = m_{\text{CO}_2, \text{Output}} \quad (0.2)$$

$$m_{\text{CO}_2, \text{Output}} = \left[503712 \text{ t} * (1.67\%) - 408024 \text{ t} * (0.34\%) \right] * 3.667 = 25739 \text{ t}$$

The monthly material consumption is listed in Table below. The material input includes scrap, alloys, coal and slag former. The material input yields an average of 1.67% for C-concentration value per year. According to DEW, the average C- concentration value for produced steel is 0.34%.

	Material Input	C in Input	Portion
	[kg]	[kg]	[%]
January	48,996,019	786,237	1.60%
February	49,602,327	854,427	1.72%
March	34,436,328	517,907	1.50%
April	50,149,661	828,786	1.65%
May	47,005,128	794,885	1.69%
June	49,197,936	813,560	1.65%
July	42,702,569	732,714	1.72%
August	43,945,440	734,344	1.67%
September	38,452,922	671,336	1.75%
October	31,214,081	551,218	1.77%
November	28,045,043	466,197	1.66%
December	39,964,360	682,265	1.71%
Total	503,711,814	8,433,876	1.67%

C-concentration per batch

The annual energy related CO₂ emissions of the combustion are the product of the fuel consumption, the net calorific value, the calorific value related emission factor and the oxidation factor of the fuel.

$$\left(V_{\text{natural gas}} \right) * (\text{net calorific value}) * (\text{conversion factor}) = m_{\text{CO}_2, \text{natural gas}} \quad (0.3)$$

$$m_{\text{CO}_2, \text{ natural gas}} = \left(13498000 \text{ Nm}^3\right) * \left(10.121 \frac{\text{kWh}}{\text{Nm}^3}\right) * \left(0.2 \text{ kg} \frac{\text{CO}_2}{\text{kWh}}\right) = 27323 \text{ t}$$

For the case of substitution the operational CO₂ emissions and the total CO₂ emissions are calculated on the basis of the available process data: A production quantity of 60% carbon steel and 40% stainless steel is considered in this example.

Carbon Steel:

$$\left[503712 \text{ t} * (1.67\%) * (100\% - 60\%) - 408024 \text{ t} * (0.34\%)\right] * 3.667 * (60\%) = 4347 \text{ t}$$

Stainless steel

$$\left[503712 \text{ t} * (1.67\%) - 408024 \text{ t} * (0.34\%)\right] * 3.667 * (40\%) = 10295 \text{ t}$$

The dependency of the balance of CO₂ emissions is shown in table below.

Substitution [%]	Structural Steel [t]	Stainless steel [t]	Electrodes [t]	Σ [t]	Natural gas [t]	ΣCO2 [t]
0	15,443	10,295	5,130	30,869	27,323	58,192
20	11,745	10,295	5,130	27,170	27,323	54,493
40	8,046	10,295	5,130	23,471	27,323	50,794
60	4,347	10,295	5,130	19,773	27,323	47,096

The balance of CO₂ emissions

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In the modern electric arc furnace (EAF) more than 40 % of energy comes from chemical sources by fossil fuels: natural gas is used in dedicated burner during the melting of the scrap while coal (mainly anthracite), lump in the basket and pulverised by wall injector, is used as foaming agent. In the frame of the European Research Fund for Coal and Steel (RFCS), project GREENEAF was carried out with the objective to replace coal and natural gas in EAF with char and syngas produced by biomass pyrolysis.

Generally speaking, in the electric furnace, coal (and consequently char) is used as injected powder or charged into the basket. The syngas can be used for EAF burners.

The characteristics of char and biogas, and the related pyrolysis process, are tailored in order to match the requirements for their utilisation in EAF. The following activities have been carried out within the project:

- Biomass selection and classification respect their origin and characterisation activities;
- Tailoring of biomass pyrolysis: Laboratory tests to define the pyrolysis kinetics of the selected biomass, and on the basis of these results design of industrial pyrolysis; then chemical and physical characterisation of char produced by biomass pyrolysis has been carried out to define pyrolysis plant process parameters. About 15 tons of char has been produced for industrial trials;
- EAF pilot plant experimentation: First tests of char utilisation have been carried out in the pilot Furnace;
- Industrial experimentation: industrial tests with char have been carried out.

Simulation of syngas utilisation: due to the difficulties in having syngas available close to the steel plant syngas utilisation for EAF burners has been simulated by CFD calculation. In this paper the simulation of syngas utilisation into the EAF burners are not described.

The use of syngas by biomass pyrolysis in the wall-mounted burner has been investigated in this stage of the project by calculation based on CFD analysis due to the difficulty to produce syngas directly close to the EAF.

The results obtained have demonstrated the technical feasibility of the approaches used while the economical evaluation has showed the sustainability of replacing the coal with char from biomass, in addition to environmental benefits due to CO₂ reduction, even if at the moment there is not a real assessed market of charcoal for steelmaking purposes.