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STUDY ON COAL AND COAL BRIQUETTES PYROLYSIS AND CONVERSION[1]

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Abstract

The efficiency of ironmaking processes depends largely on the conversion behaviour of used carbonaceous reductants. Systematic kinetics data of pyrolysis and conversion of reducing agents needed for process description and modelling are often missing. Within the scope of the Austrian K1-MET programme this work aims to investigate the char conversion behaviour by its usage under conditions in Corex®/Finex® smelting reduction processes. Char samples were produced by pyrolysis of two coals and four coal briquettes; the thermo shock conditions at 1,000°C were simulated. This contribution reports experimental results on the reaction kinetics of pyrolysis, gasification via solution loss reaction and the combustion of the examined substances gained from the tests. The equipment used for the investigation was Simultaneous Thermal Analysis (STA), Tammann furnace experimental set and several analytical methods. Microscopic examination was performed before and after the tests. The tests were conducted in five scenarios simulating the above-mentioned conversion steps. Reaction velocity coefficients for each substance were determined for various reaction steps according to the running scenarios. The reaction enthalpy was quantified by the DTA method. By looking at the microscopic study on the development of total porosity and the pore distribution of samples in the test scenarios leads to the conclusion that the increase of large pores and their size causes higher coal reactivity. Besides lump materials, conversion behaviour and the kinetics data of fine coal for injection were studied using a lab injection rig and the thermo-gravimetric equipment, STA.

Key words: Corex/Finex process; Coal conversion; Injection.

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1 INTRODUCTION

The smelting reduction aims at production of hot metal without the need of using coke. The Corex® process is the most advanced smelting reduction process.(1)
Coal and coal briquettes should meet special requirements.(2,3)
During the journey through the Melter Gasifier mechanical, physical and chemical factors causes coal degradation. The coal is directly without pre-treatment charged into the Melter Gasifier. Within this step it is exposed to an atmosphere with high CO and H_2 content and a temperature of about 1,000°C. The coal directly starts to pyrolyse and so contributes to the indirect reduction of iron oxides. The coal has to offer a high strength after the pyrolysis to guarantee high gas permeability through the fixed bed of the Melter Gasifier.(4)
After the pyrolysis the coal is exposed to high temperature CO_2 attack, the Boudouard-reaction, in the fixed bed. The residuals are burned in front of the Corex raceway.
In this study, the behaviour of coal materials under simulated conditions of the different zones of the Melter Gasifier was investigated.

2 COALS AND MANUFACTURING OF THE BRIQUETTES

Coals and coal briquettes as well as coke (for reference) were examined. Two different coals were used: coal 1 is a low volatile and weak-baking coal and coal 2 is a high volatile and baking coal (Table 1).
Four different types of briquettes were produced using various ratios of these coals and two types of binders, molasses and bitumen. For one type of briquette, a third coal, coal 3, was added.

Table 1. Proximate analysis of coals

sample	water	ash	C-fix	volatile
Coke	0.6	13.6	84.8	1.0
Coal 1	5.2	4.9	64.3	25.6
Coal 2	1.7	10.7	53.2	34.4
Coal 3	8.4	6.3	59.8	25.5

3 INVESTIGATION OF MASS AND HEAT FLOW CHANGE WITH THERMO-GRAVIMETRIC ANALYSER

The aim of this study was to gain information about the reaction behaviour of coal and coal briquettes in the different zones of the Melter Gasifier.
Therefore three different steps of the conversion are investigated accumulative:

1. the pyrolysis simulating the reactions in the dome,
2. gasification in CO_2 simulating the conditions in the fixed bed upper region,
3. combustion in oxygen simulating the conditions in front of the Corex® raceway.

To enable these accumulated scenarios, the samples with a grain size of 1-2 mm were heated up in argon atmosphere with a heating rate of 5 K/min until 1,000°C. By reaching 1,000°C, CO_2 is purged for 30 minutes. Then the atmosphere is set with a mixture of 40 % oxygen and 60% nitrogen for 30 minutes.
The measured weight loss for the whole scenario is shown in Figure 1. During the pyrolysis in argon atmosphere, coke and coal 1 show different reaction behaviour due to the lower content of volatile matter (Table 1). The coke, which is already pyrolysed shows only weight loss in cause of the vaporization of water and little

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amount of volatile matter. The Coal 1 has a lower content of volatile matter in contrast to coal 2 and the briquettes so that the weight loss is lower.

The biggest differences between the samples can be observed during the second step of the conversion, the gasification in CO_2. The coke shows the lowest weight loss, followed by coal 1, then the coal 2 and the briquette bound by bitumen. The briquettes bound by molasses show the highest weight loss. The weight loss of the coke, the coals and the briquette 4 Bitumen can be approximated by a linear function. The weight losses of the briquettes 1-3 molasses show an exponential curve progression. For the comparison of all samples in CO_2 atmosphere an exponential fit was used.

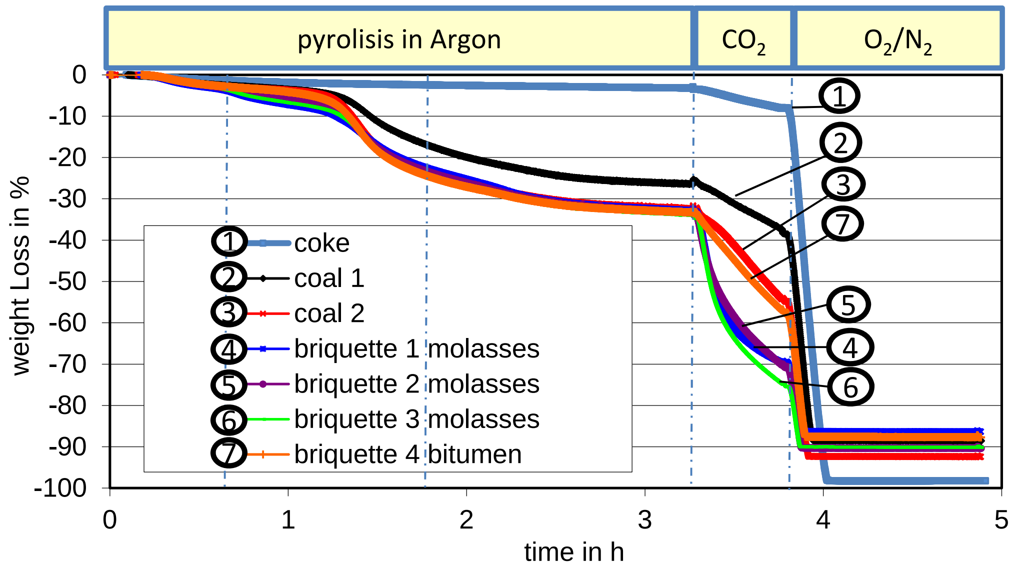

Figure 1. Weight loss of coals and coal briquettes during pyrolysis, gasification and combustion.

In Figure 2 the third step of the scenario, the combustion in oxidising atmosphere, is shown. All samples have a weight loss with a slope according to a linear approximation. After the combustion the remaining weight corresponds to the ash of the samples.

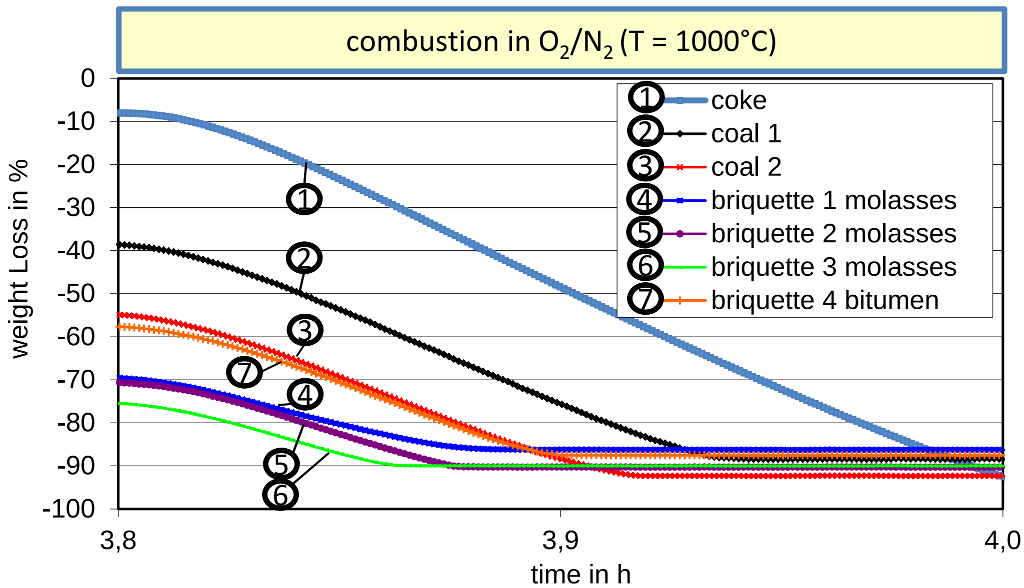

Figure 2. Combustion of coals and coal briquettes in O_2 atmosphere.

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From Figure 1 and Figure 2 the reaction coefficients for the gasification in CO_2 and combustion in oxygen were calculated (Table 2).

Table 2. Reaction coefficient in h^{-1} for the gasification and combustion of coals and coal briquettes

sample	gasification in CO_2	combustion in O_2/N_2
Coke	0,11	470,59
Coal 1	0,35	426,52
Coal 2	0,82	394,91
Briquette 1 molasses	1,53	308,91
Briquette 2 molasses	1,53	248,63
Briquette 3 molasses	1,81	280,20
Briquette 4 bitumen	0,91	373,07

The reaction coefficient clearly indicates the ranking of the reactivity. In CO_2-atmosphere the briquettes bound with molasses react most fast, followed by the briquette 4 bound with bitumen, coal 2, coal 1 and coke.
In oxidising atmosphere the opposite result is observed: the coke reacts fastest, followed by coal 1, coal 2, briquette 4 and the molasses bound briquettes. In oxidising atmosphere the difference between the samples is not as high as in CO_2 atmosphere. Figure 3 shows the visualisation of the reaction constants from Table . The trend can clearly be seen.

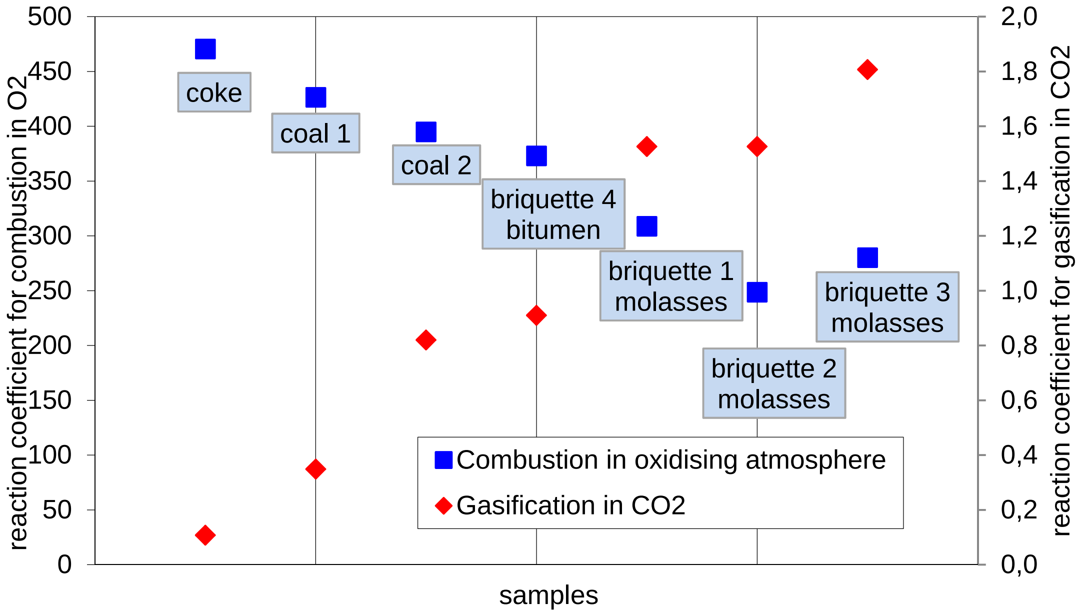

Figure 3. Reaction constant k in h^{-1} for the gasification in CO_2 and the combustion in oxygen 40%.

4 INVESTIGATION OF MASS CHANGE WITH A TAMMANN FURNACE EXPERIMENTAL SET

In contrast to the investigations with the thermo balance the investigations with the Tammann furnace experimental set are conducted with samples of original size.
The samples are hold by a Pt-Rh-wire, which is connected to a balance measuring the weight loss (Figure 4). With a pneumatic cylinder the sample can be lifted up and down within seconds into the Tammann furnace. The heat is mainly transferred

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through radiation to the sample from each side except from the bottom. From the bottom the set atmosphere is purged.

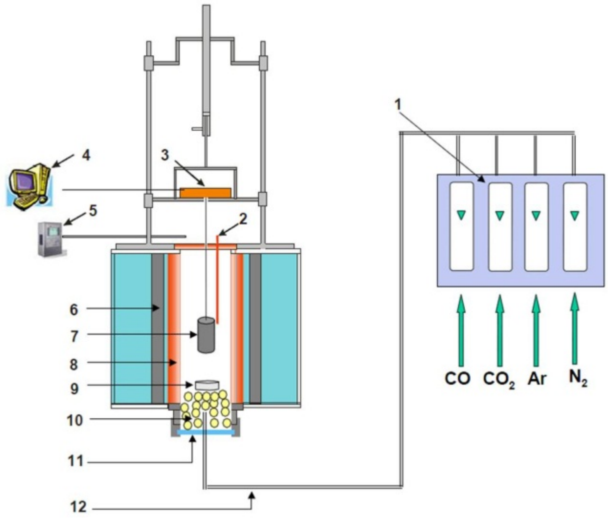

Figure 4. *Scheme of the Tammann furnace experimental set.*[(5)] *1: flow controller; 2: thermocouple; 3: electronic scale; 4: computer; 5: gas analyser; 6: graphite tube; 7: sample; 8: ceramic tube; 9: potassium carbonate, not in use at these trials; 10: alumina balls; 11: quartz glass; 12: gas supply*

Figure 5 shows results of the accumulative scenario for all samples. The biggest differences in the reaction behaviour also appear during the gasification in CO_2. In contrast to the investigations with the thermo balance the distinctions are not as high.

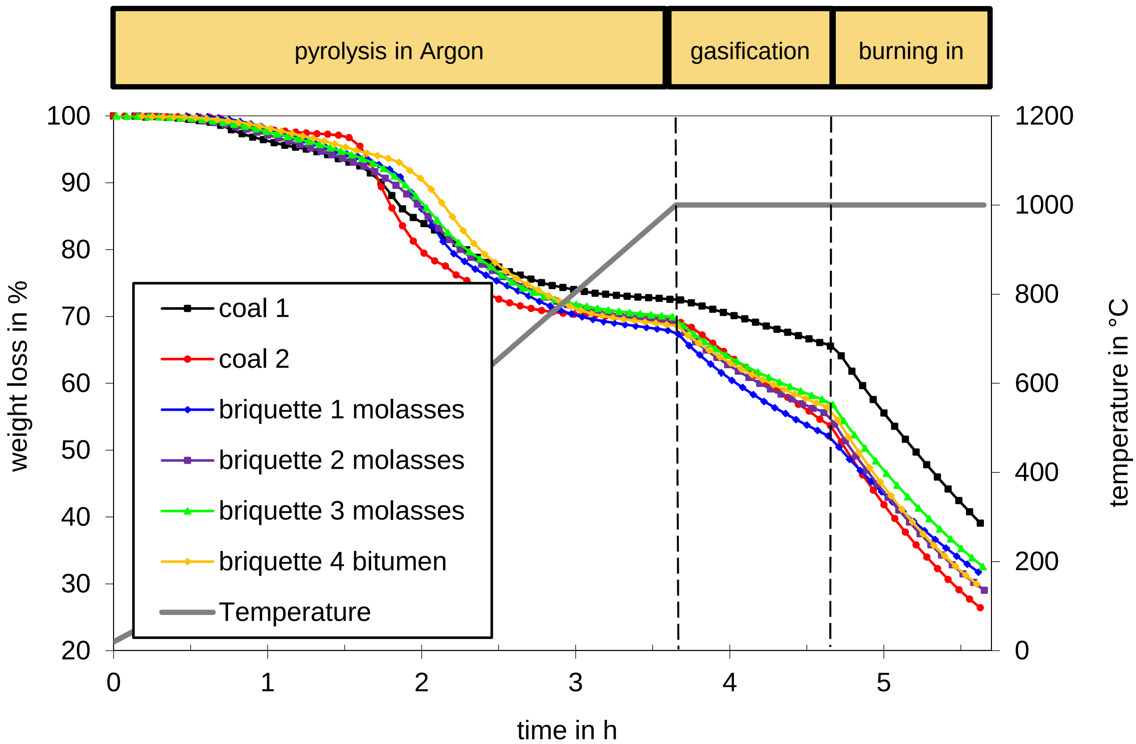

Figure 5. Weight loss of coals and coal briquettes in Tammann furnace trials for pyrolysis, gasification and combustion

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The pyrolysis in Figure 5 clearly points out similar behaviour of the different samples in inert atmosphere. The coal 1 differs a little from the other samples due to the lower content of volatile matter.

Figure 6 shows the gasification results for 1 hour in CO_2 atmosphere and 1 hour in air atmosphere. During the gasification in CO_2 atmosphere it can be observed that the coal 1 reacts slower than coal 2 and much slower than the briquettes. During the gasification in air atmosphere the coals 1 and 2 show the highest and fastest weight loss. All different types of briquettes show nearly the same conversion behaviour.

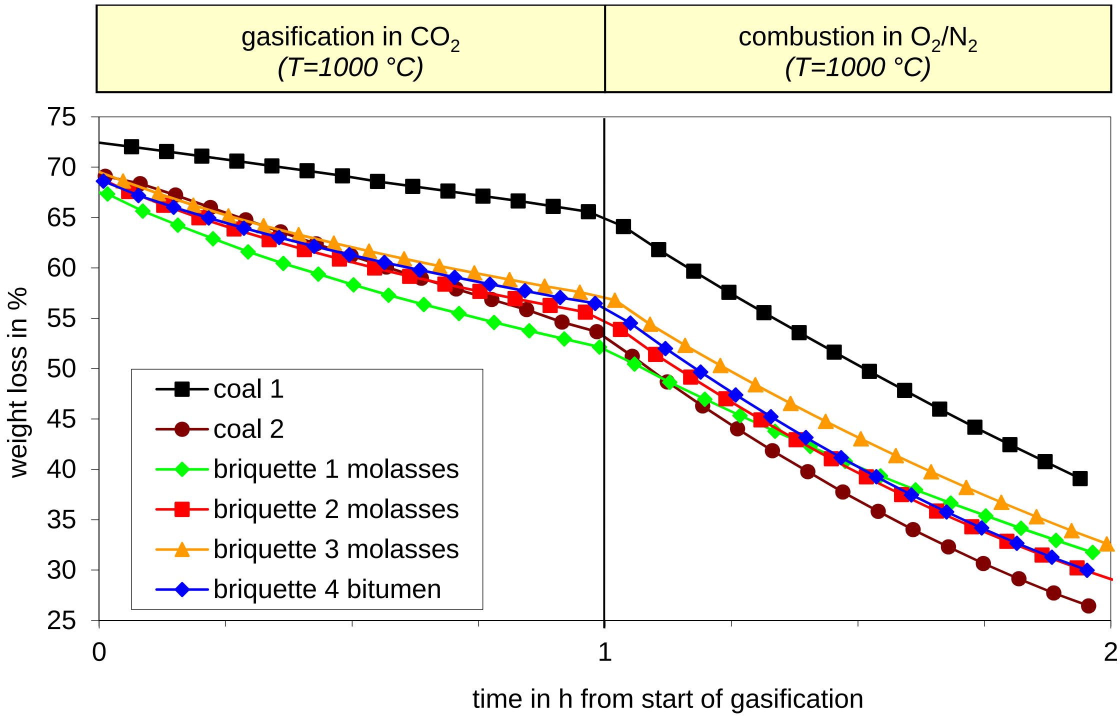

Figure 6. Weight loss during gasification in CO_2 and combustion in air atmosphere.

Table 3 shows the samples of the Tammann furnace trials before and after the reaction from the outside and from the inside with a cut and view of an optical microscope. The photographs from the optical microscope show much higher porosity from the state after the reaction than from the sample before the reaction. In the initial state the samples are dense in their structure with a lot of small pores. After the trials the samples show a high porosity with almost only big pores. Coal 1 is the only sample which shows a high amount of middle big pores.

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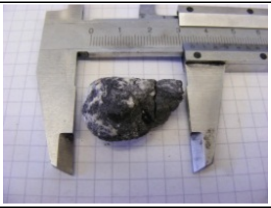
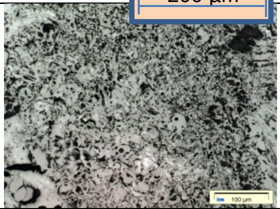
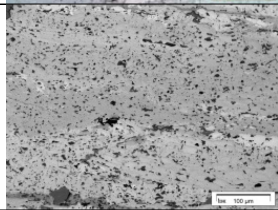
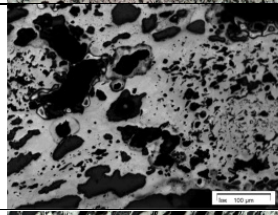
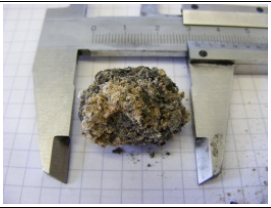
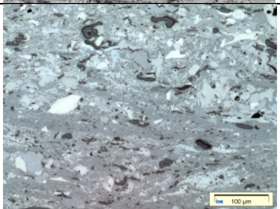
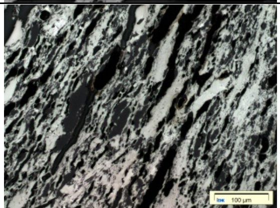
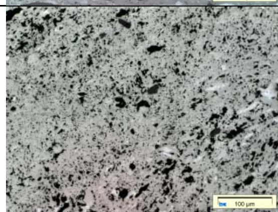
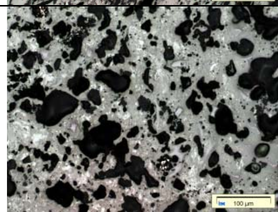
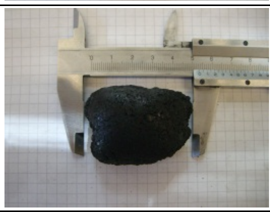
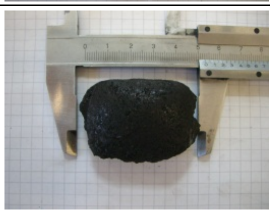
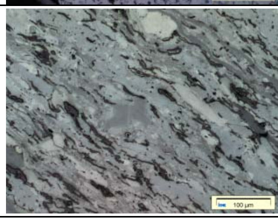
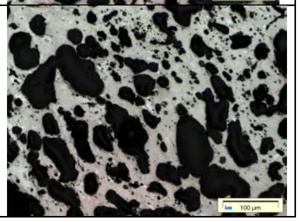
Table 3. Coal and coal briquette sample before and after Tammann furnace trials

sample	initial state	after trials	Optical microscope initial state 200 µm	Optical microscope after trials 200 µm
Coal 1				
Coal 2				
Briquette 1 100% coal 2 Molasses				
Briquette 2 50/50 coal1/coal 2 Molasses				
Briquette 3 33/33/33 Coal 1/2/3 Molasses				
Briquette 4 50/50 coal 1/2 Bitumen				

From the graphs of the gasification in CO_2-atmosphere and from the combustion in air-atmosphere the slope, reaction constant, is calculated. For the Tammann furnace trials with the assumption that the reaction is a first order reaction the mass loss can be described by an exponential fit for both reactions in CO_2 and air.

Table 4. Reaction coefficient k in h^{-1} for the gasification in CO_2 and the combustion in air

sample	k_{CO2} in h^{-1}	k_{air} in h^{-1}
Briquette 3 molasses	0.191	0.568
Briquette 1 molasses	0.258	0.511
Briquette 2 molasses	0.217	0.641
Briquette 4 bitumen	0.193	0.665
Coal 1	0.032	0.526
Coal 2	0.151	0.768

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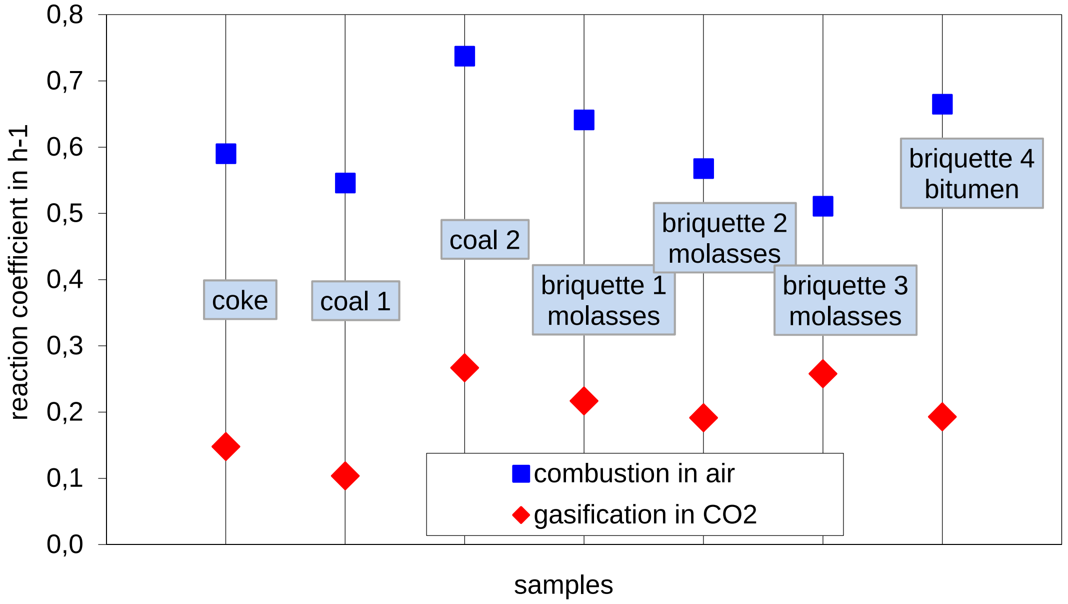

Figure 7. Reaction coefficient k in h^{-1} for the gasification in CO_2 and the combustion in air.

5 INVESTIGATION ON PC CONVERSION WITH THERMO BALANCE AND LABORATORY INJECTION RIG

The pilot trials on the reaction behaviour of the coals and coal briquettes and their interaction with PC are being performed and are out of the scope of this contribution. Here the conversion of three different PCs was investigated using the thermo-balance (STA) and the lab injection rig. Table 5 shows the proximate and ultimate analysis of the investigated pulverised coals. The biggest difference is the volatile matter and the oxygen content. PC 2 has the highest content of V_M and oxygen followed by PC 1 and at least PC 3.

Table 5. Composition of the investigated coals for injection

	proximate analysis (%db, waf)			Ultimate analysis (%wf)			
	ash (wf)	C-Fix (waf)	Volatile (waf)	C(wf)	H(wf)	N(wf)	O(wf)
PC 1	14,4	65,4	34,6	69,4	4,3	0,87	10,2
PC 2	15,7	61,3	38,7	74,7	5,0	1,4	17,9
PC 3	10,3	81,5	18,5	89,8	4,3	2,0	3,5

The samples underwent following scenario: heating up in inert atmosphere (Ar) until 1,500°C with heating rate of 15 K/min. After reaching 1,500°C the atmosphere is switched to air and the burning of the samples at high temperatures is measured. In Figure 8 the weight loss and the derivation of the weight loss against the time is shown. The conversion in inert atmosphere shows the characteristic steps of the pyrolysis, the vaporisation of moisture, the primary and the secondary pyrolysis. The weight loss in air atmosphere, the combustion, shows a linear curve progression.

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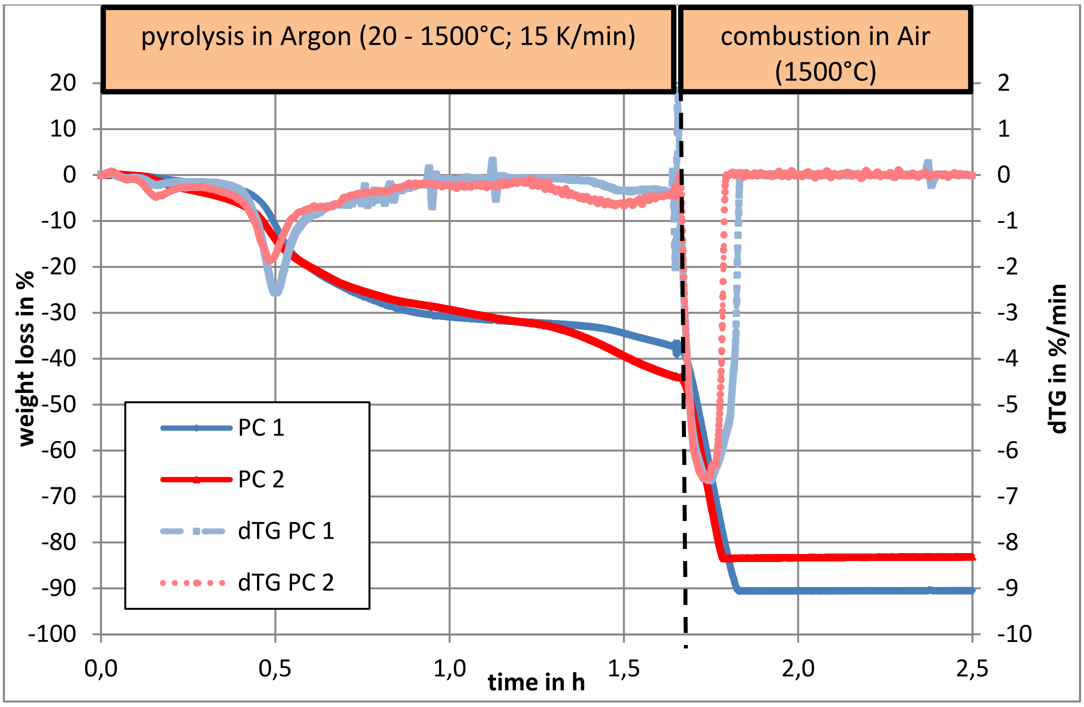

Figure 8. PC conversion in inert and oxidising atmosphere at high temperatures.

The laboratory injection rig simulates the conversion behaviour of solid injectants in the blast furnace tuyères and oxidising part of the raceway (Figure 9).
The high pressure part simulates the conditions in the injection lance; the low pressure part simulates the situation in the blast furnace tuyère and oxidising part of the raceway. The reaction gas is collected in a gas mouse and analysed. The conversion degree can be defined as the amount of analysed carbon containing product gas (CO and CO_2) divided by the theoretically possible CO_2-product.[6]

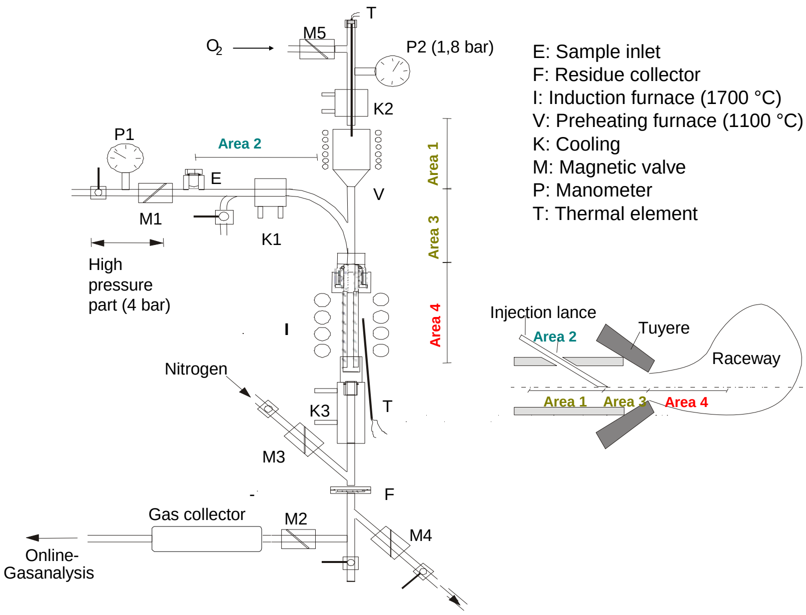

Figure 9. Scheme of the Batch Injection Rig at the IEHK.[6]

Figure 10 shows the conversion degree of the three injection coals. The conversion degree rises with the O/C ratio due to the fact that with higher O/C ratios less amount of coal is injected and so more oxygen is available for the reaction. The coal with the

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lowest content of V_M PC 3 shows the lowest conversion degree. PC 2 has the highest conversion degree, but the difference to PC 1 is not very high.
In the industrial practice the conversion degree should be higher due to following facts: the injection rig only simulates the oxidising part of the raceway, so that the solution loss reaction is not taken into account, as well as possible secondary reactions in slag or by Boudouard-reaction in upper part of the melter gasifier. The samples were sieved and the investigated grain size was 90-125 µm. This was done to minimize the factor of different corn distributions. Often used pulverised coals have a high fraction of particles with a grain size < 90 µm, which leads to a higher conversion degree due to the higher specific surface they offer.

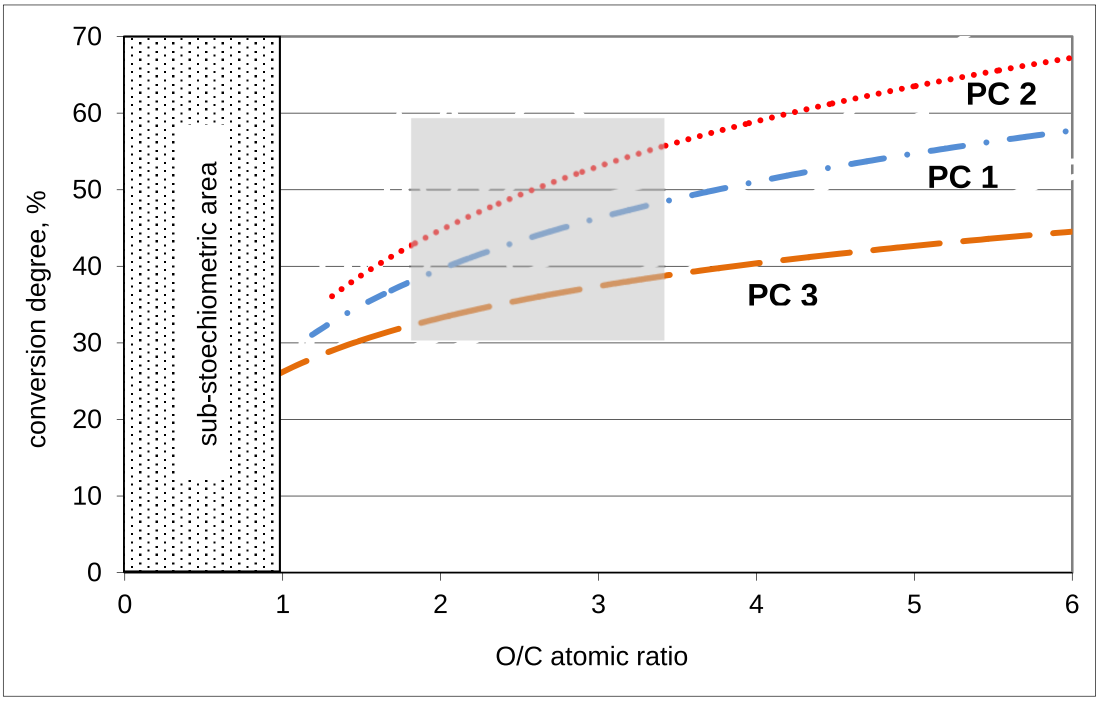

Figure 10. Conversion degree against O/C ratio for the 3 pulverised coals

6 CONCLUSION

Pyrolysis, gasification and combustion behaviour of different coals and coal briquettes were examined.
The results from the investigations in the simultaneous thermal analysis point out differences in the conversion behaviour during the pyrolysis. They reflect the differences in content of volatile matter in the corresponding coals and briquettes. The biggest difference occurs during the gasification in CO_2 atmosphere, here the chemical reaction is a dominating factor and the briquettes bound by molasses react much faster than the briquettes bound with bitumen. During the combustion the samples again show only little differences.
The results from the Tammann furnace trials show not such high differences during the conversion in CO_2. In contrast to investigation with the STA (grain size of samples 2-3 mm), samples of original size (about 35 mm) were investigated. Here the chemical reaction is not as important as with the STA. The dominating factor is the diffusion of the reaction gas through the ash layer of the sample. The conversion in oxygen atmosphere confirms the results from the STA.

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The microscopic investigations show that the amount and size of pores in all samples increases in high amount. And the sample with a low reactivity show less pores than the other.
The investigation on the conversion of PC showed the clear correlation between volatile matter and conversion degree. The more volatile matter and the more bound oxygen is in the sample, the higher is the conversion degree.

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