CONSUMPTION OF COALS AND CHARCOAL BY SECONDARY REACTIONS AT THEIR INJECTION INTO BLAST FURNACES[1]

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Abstract

For about 10 years the steel industry in Brazil has used pulverized coal injection (PCI) technology in the blast furnaces based on imported coals. In order to decrease the dependence on imported coals, the conversion behaviour and properties of a Brazilian sub-bituminous coal, to be used as feed coal for PCI in the blast furnace tuyeres, have been examined in the current study and compared to imported coals and charcoal. This study has been focused on reactions of secondary gasification in the blast furnace shaft in order to estimate the possibility of consumption of unburnt in the raceway materials. Simultaneous thermal analyses and Tammann furnace experimental set were used to evaluate the reactivity of Brazilian and imported coals as well as charcoal. Tests carried out at LASID / UFRGS, Porto Alegre, Brazil and at IEHK / RWTH Aachen University, Germany showed that the reactivity of the Brazilian coal occupies an intermediate position between the reactivity of the imported coals and the reactivity of the charcoal. However, it is characterized by high ash, sulphur and alkali contents. It was concluded that the Brazilian coal itself is not appropriate for PCI. One way for its utilization could be injection of blends of Brazilian coal with imported coals or charcoal. The charcoal use in the steel industry contributes to the CO_2 emission reduction, since it represents a renewable source of energy. Therefore, reactivity of various mixtures of coals and charcoal has been investigated as well. Results of this study are presented and discussed.

Key words: Brazilian coal; Charcoal; Pulverized coal injection; Reactivity; Solution loss

CONSUMO DE CARVÕES E BIOMASSA PELAS REAÇÕES SECUNDÁRIAS QUANDO DA INJEÇÃO NOS ALTOS-FORNOS

Resumo

Há cerca de 10 anos, a indústria siderúrgica implantou a técnica de injeção de carvão pulverizado (PCI – pulverized coal injection) nos altos-fornos (AFs) e esta se baseia na utilização de carvões importados. Visando diminuir a dependência dos mesmos, neste trabalho será investigado o comportamento de conversão e as propriedades de um carvão brasileiro sub-betuminoso para ser utilizado em PCI. O carvão brasileiro será comparado com carvões importados e biomassa, tipo carvão vegetal. Este estudo está focado nas reações secundárias de gaseificação que ocorrem na cuba do AF quando partículas de char não reagidas saem da zona de combustão do AF. Análise termogravimétrica e forno Tammann serão usados para avaliar a reatividade do carvão brasileiro, carvões importados, biomassa e misturas. Testes realizados no Brasil, na UFRGS/LASID e na Alemanha, na Universidade Técnica de Aachen RWTH/IEHK mostraram que a reatividade do carvão brasileiro ocupa uma posição intermediária entre a reatividade dos carvões importados e a reatividade da biomassa. Entretanto, este é caracterizado por alto teor de cinzas, enxofre e alcális. Conclui-se que o uso individual de carvão brasileiro em PCI não é adequado. Uma forma de utilização seria através de misturas com carvões importados e biomassa. O uso de biomassa na indústria siderúrgica contribui para a minimização das emissões de CO_2, desde que ele representa uma fonte renovável de energia. Também nesse estudo os resultados das reatividades das misturas com os carvões e biomassa serão apresentados e discutidos.

Palavras-chave: Carvão brasileiro; Biomassa; PCI; Reatividade; Reação de Boudouard.

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1 INTRODUCTION

Around 60% of raw steel production worldwide is based on blast furnace (BF) ironmaking. In Brazil, in 2007 approximately 74% of raw steel was made using this way;(1) hot metal production made up 32.45 Mt in 2007.(1) Increasing demand on steel is forcing BF plants to improve their performance in order to reduce operating costs and, at the same time, to increase productivity and to mitigate pollution emissions.

The BF route is based on coke use which is the most expensive feed material used in the process. Besides this, the use of coke is associated with the release of significant amounts of carbon dioxide (CO_2). One way to decrease the coke rate and CO_2 emissions is the injection of auxiliary reducing agents like coals, natural gas, biomass, organic wastes etc. through the BF tuyeres. Pulverized coal injection (PCI) into the BFs tuyeres is a commonly used effective cost saving technique.(2)

In Brazil, about 10 years ago, the steel industry started to use this technology in the BFs. Brazil is one of the biggest coal importers; it imports all the coal used in the BF ironmaking: about 17 million ton per year including 14 million for cokemaking and 3 million for PCI.(3) The use of national coals for PCI would reduce the dependence on expensive imported coals. The measured coal reserves in Brazil are about 10 Gt.(4) This sub-bituminous coal has a low rank, high contents of inert components, non-coking properties and a high reactivity. Studies on properties of this coal have shown that it could be injected into BFs in blends with imported coals.(5)

Besides national coal, other promising fuels in Brazil are biomass and charcoal. Charcoal plays an important role in Brazil's iron and steel industry. In 2006 about one third of total hot metal production, i.e. 10.7 million ton was made in 153 small charcoal blast furnaces.(1) The production is located in two regions: Minas Gerais and Carajás. Approximately, 85% of this HM was produced by the independent producers and 15% by the Integrated Steelworks.(6) In the mini BFs where HM based on charcoal is produced, the injection of charcoal fines has been used for many years. In 2005 around 193.000 ton of charcoal fines were injected in these BFs. Injection rates makes up 100 to 150 kg/tHM. Nowadays, technology for charcoal use as a renewable energy source in the large modern blast furnaces is being developed in the scope of a European steel industry initiative to reduce the CO_2 emissions to the level where this might be needed in the post-Kyoto period.

A part of coal or charcoal injected which was not gasified in the raceway by oxygen of the blast, can be utilised by reactions of secondary gasification (2). Examples of these reactions are direct reduction of iron oxides (injected via the tuyeres or contained in the slag passing through the tuyere zones) and reaction of char with carbon dioxide (Boudouard reaction). Char generation and its behaviour in the blast furnace are very important.(7) Char affects the BF operation (gas permeability, drainage of liquid products, slag viscosity, and, finally, furnace productivity and reducing agent consumption) and the coke properties and its degradation behaviour.(2,8)

This work aims is to evaluate the reactivity of coals, charcoal and their mixtures towards carbon dioxide using thermogravimetrical and tammann furnace experimental sets. A Brazilian coal from Leao Mine, two high-rank imported coals and a biomass type charcoal were examined under conditions that simulate the reactions when unburnt coal or charcoal char leave the raceway and passes up the furnace shaft.

2 MATERIALS, METHODS AND EQUIPMENT

2.1 Samples and their Characterization

The Brazilian coal used in this work is from Leão-Butiá mine. The imported coals and charcoal were supplied by a Brazilian steel company. Binary blends were prepared in the proportions 50–50% (wt.%).

Proximate analyses (ash, volatile matter, moisture), ultimate analyses and calorific values were determined according to ASTM standards. Ash composition was determined by X-ray fluorescence (SIEMENS-BRUKER-AXS Model D5000). Investigations of the charcoal and coal microstructure were done using scanning electron microscopy (SEM).

2.2 STA and Test Procedure

The reactivity towards carbon dioxide was evaluated in a thermogravimetric analyzer NETZCH - STA 409. In the first phase of the test (pyrolysis), 30 mg of sample sieved under 75 μm was heated to 1050 °C with a heating rate of 30°C/min in nitrogen atmosphere (50ml/min). After the removal of volatile matter, the gas atmosphere was switched to CO_2 (50 ml/min); the test was finished after the complete reaction. Conversion degree, i.e, the fraction of the carbon matter that reacts with CO_2 and generates CO, was calculated as follows:

$$X = \frac{(m_0 - m)}{(m_0 - m_c)} x100$$

The reactivity was evaluated according to: $R = -1/m_0 (dm/dt)$, where R is the maximum reactivity, m_0 is the initial ash free weight and dm/dt is the maximum rate of fixed carbon loss.

2.3 Tammann Furnace Experimental Set and Test Procedure

The Tammann furnace laboratory rig (Figure 1) described in (9) was used to simulate solution loss of coals and charcoal. Coal samples (grain size <45μm) were heated in alumina crucible. Reaction temperature was 1100°C. In the first phase of the test the samples were maintained at the reaction temperature under argon (200 l/min) for 5 min. After this, the gas atmosphere was changed to CO_2 (200 l/min) and the duration of the second test phase was 1 hour.

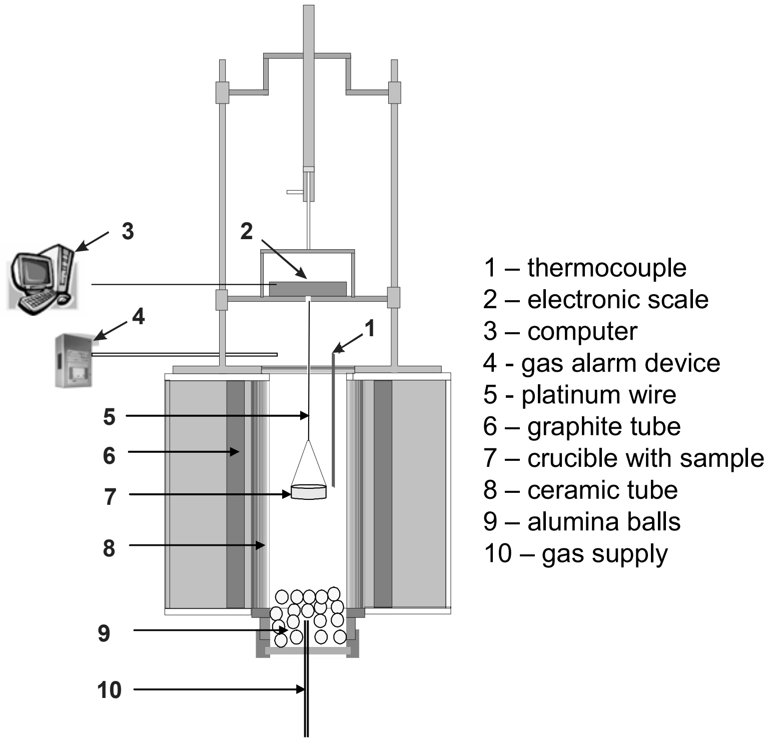


Figure 1. Scheme of the Tammann furnace experimental rig.

3 RESULTS AND DISCUSSION

3.1 Samples Characterization

Proximate and ultimate analysis as well as calorific values of the coals and charcoal are shown in Table 1. The result of ash composition of major elements is shown in Table 2.

Table 1 – Analysis of materials.

	Proximate analysis, wt. %		**Ultimate analysis, wt. %**					**CV kcal/kg**
Sample	Ash	VM	C	H	N	S_t	O	-
Charcoal (CC)	4.64	20.77	79.77	2.96	1.07	0.08	11.48	7165
Brazilian coal (BC)	15.68	32.60	62.96	4.22	1.19	0.88	15.07	6110
Imported coal A (ICA)	9.48	25.05	78.16	4.46	1.91	0.58	5,41	7545
Imported coal B (ICB)	10.27	15.34	80.53	3.86	1.75	0.48	3.11	7635

VM = volatile matter; CV = calorific value; S = Sulfur; C = Carbon; H = Hydrogen; N = Nitrogen; O=Oxygen

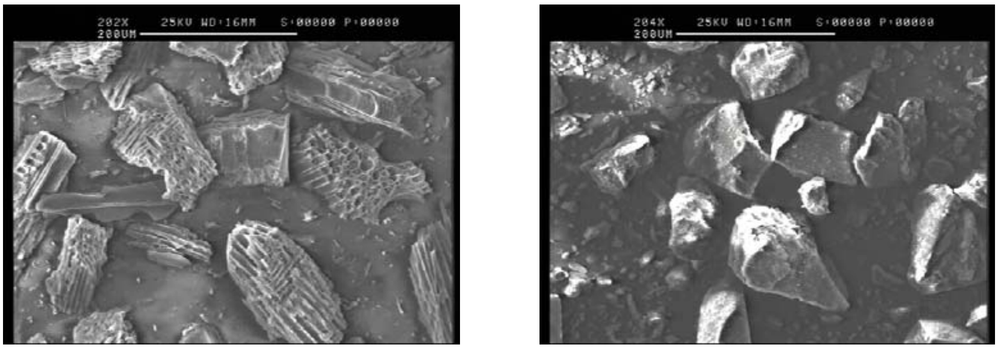
Table 2 – Chemical analises of major elements in coals and charcoal ashes.

	CC	BC	ICA	ICB
Ash (wt%)	4,64	15,68	9,48	10,27
SiO_2	28,45	43,64	46,84	50,95
Al_2O_3	3,96	18,59	25,65	27,16
TiO_2	0,23	1,81	1,26	1,35
Fe (total)	1,95	4,94	14,88	9,18
MnO	0,62	0,06	0,14	0,09
MgO	4,32	1,01	1,72	1,55
CaO	39,45	3,52	4,19	3,97
Na_2O	0,12	3,88	0,21	0,42
K_2O	2,40	1,15	1,24	1,06
P_2O_5	1,29	0,04	1,67	1,58
SO4	1,91	1,75	1,22	0,79

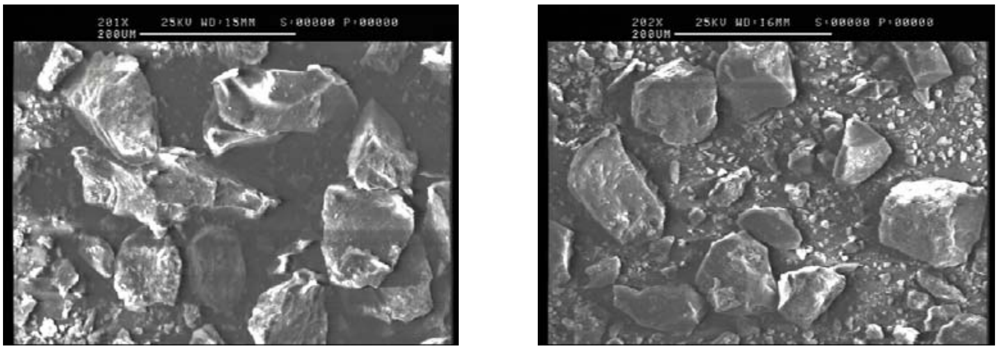
In Table 1 it can be seen Brazilian coal is characterized by high level of ash (15,68 wt.%) and sulphur (0,88 wt.%); it makes its individual use not feasible for PCI. Brazilian coal is a sub-bituminous coal, so it is characterized by a high volatile matter content, low elementary carbon, and high O contents. The imported coals A and B have low volatile matter and high elementary carbon contents. The ash content of charcoal is considerably lower than the one of coals. The low ash content of the charcoal affects positively the blast furnace operation. Ash must be collected in the slag, which requires heat for slag forming and overheating and this increases the coke consumption. Charcoal has a lower sulphur content compared with coals. Content of sulphur is of a high interest for blast furnace process since about 70-95% of sulphur input comes in the furnace from fuel. Metallurgical work must be done to reach low S- content in hot metal. These results show that the low ash and sulphur content of the charcoal make its use attractive when mixing with Brazilian and imported coals.

Ash composition of Brazilian and imported coals are dominated by SiO_2 and Al_2O_3, reflecting the high contributions of quartz and clay minerals to the inorganic portion of these coals (Table 2). The high content of these compounds indicates an acid character of ashes of these coals. On the other hand, ash composition of charcoal shows high amount of CaO and indicates a basic character of these ashes. The total alkalis content (Na_2O+K_2O) for Brazilian coal is higher than the ones for imported coals and charcoal. Phosphorous, another undesirable element for the steel production, is found in acceptable low amounts for Brazilian coal (0.04%). For the imported coals and charcoal, P_2O_5 level is much higher (1,3-1,7%).

Figure 2 shows the charcoal and coals surface at magnification 200. It can be observed that all examined coals have a dense and compact surface. In contrast to this, the charcoals are characterised by highly porous structure.



CC microstructure BC microstructure



ICA microstructure ICB microstructure

Figure 2. Charcoal and coal surface, grain size 90-125μm, SEM, 200x.

3.2 Study on Behaviour of Coals, Charcoal and Mixtures Using STA at LASID/ UFRGS, Brazil

A representative graph showing the thermogravimetric curves (TG) is given in Figure 3.

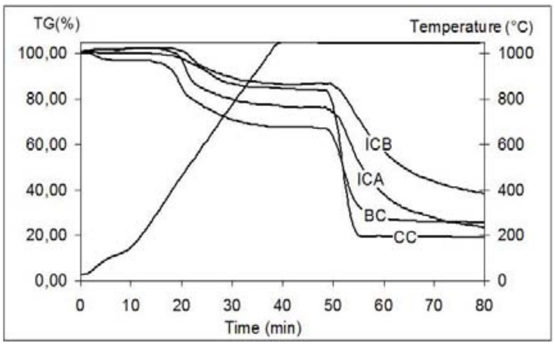


Figure 3. TG curves for coals and charcoal.

TG curves show an initial decrease in the weight of samples for the BC and CC due to release of the moisture remaining in the sample. At the beginning of the experiment with samples ICA and ICB, slight weight increase was observed. This effect is associated with chemosorption processes(10) and occurred in all tests, but with moisture release it was compensated.

Due to the high VM content in BC, the weight loss during the pyrolysis stage was the highest, followed by ICA, CC and ICB (Figure 3). The temperature of pyrolysis rises from 396°C for BC over 438°C for ICA to 450°C for CC and 480°C for ICB. BC is a low rank coal and consequently its pyrolysis temperature is low. The pyrolysis temperature increases with higher coal rank.(11) In the case of charcoal, its pyrolysis temperature is similar to a coal with equivalent VM content.

The weight loss that begins in around 50 min is referring to the solution loss reaction. The derivative TG curve (DTG) provides the maximum reaction rate of the samples. The maximum reaction rate and the conversion curves for coals and charcoal vs. time are given in Figure 4.

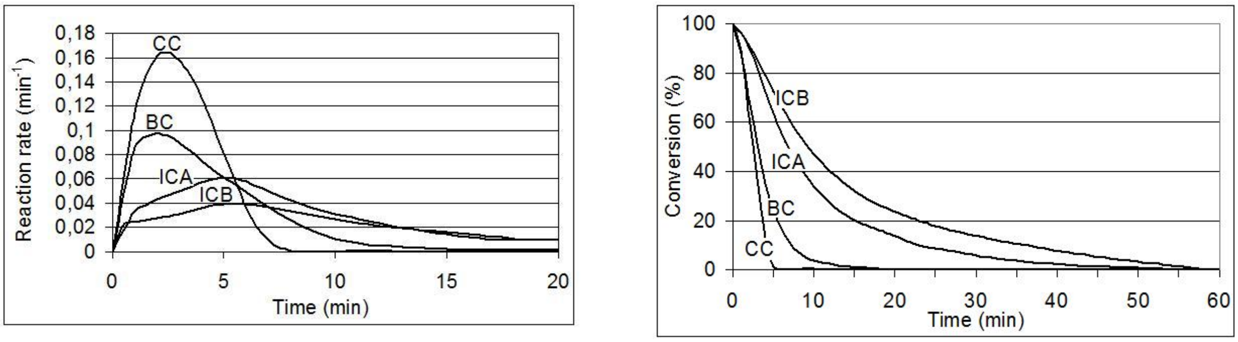
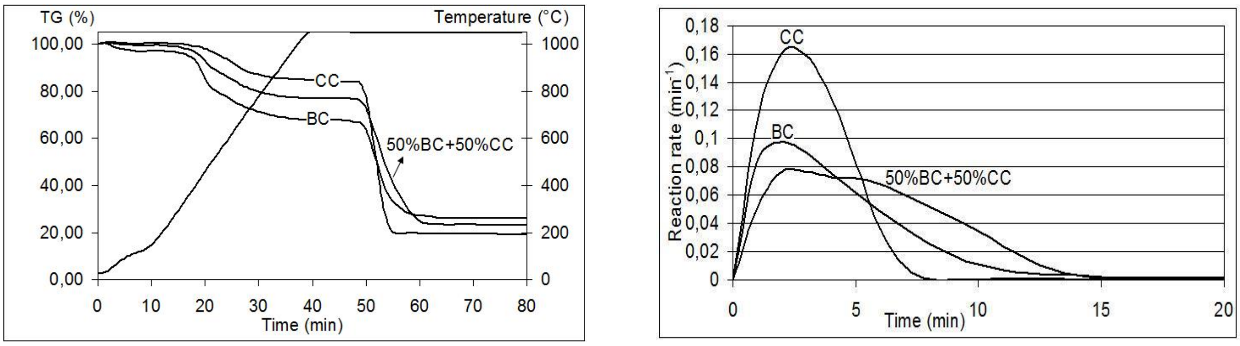


Figure 4. DTG and conversion for coals and charcoals.

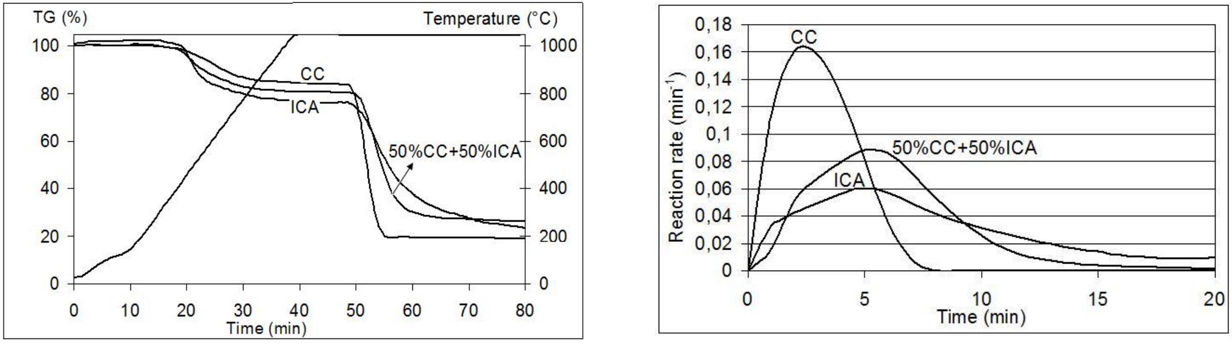
It is evident from Figure 4 that CC has the highest reaction rate. It reacts with CO_2 faster than the Brazilian and imported coals. The time to reach the maximum rate was similar for CC and BC, around 2 minutes. The right graph on Figure 4 shows that CC reacts quickly with CO_2 and in about 5 min all carbon reacted. For BC the time to reach all carbon conversion was around 15 min. For the imported coals, ICA and ICB, the times were significantly higher, around 47 and 60 min respectively.

The high reactivity of CC can be explained by its porous and highly disordered carbon structure. Charcoal char belongs to the most reactive carbon materials. The high reactivity of BC is due to its minor rank.

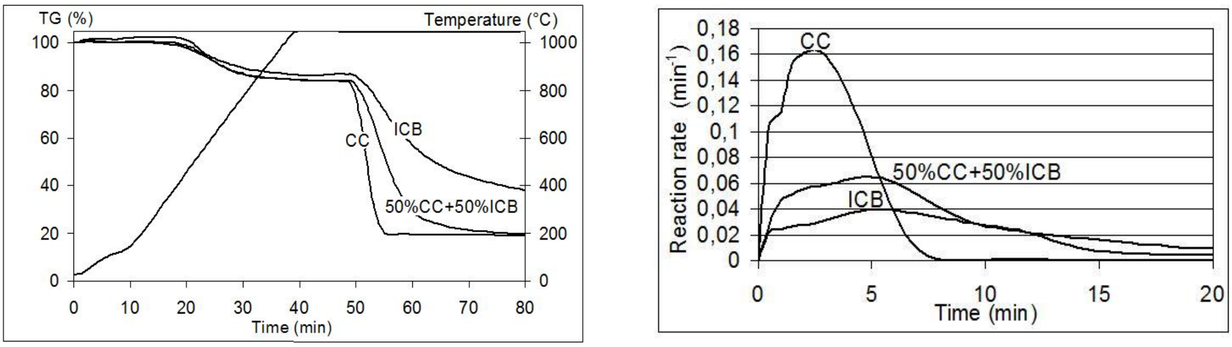
The TG and DTG curves for the blends as well as for the coals and charcoal for purposes of comparison are shown in Figure 5.



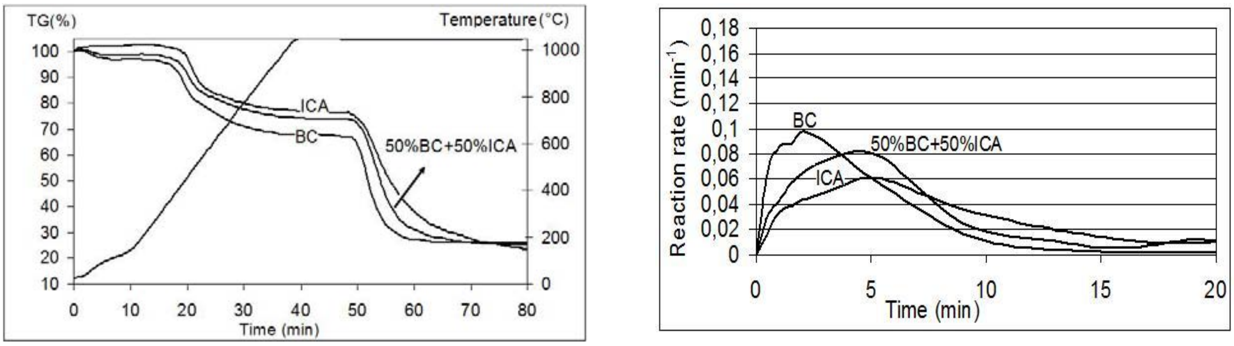
CC, BC and mixture



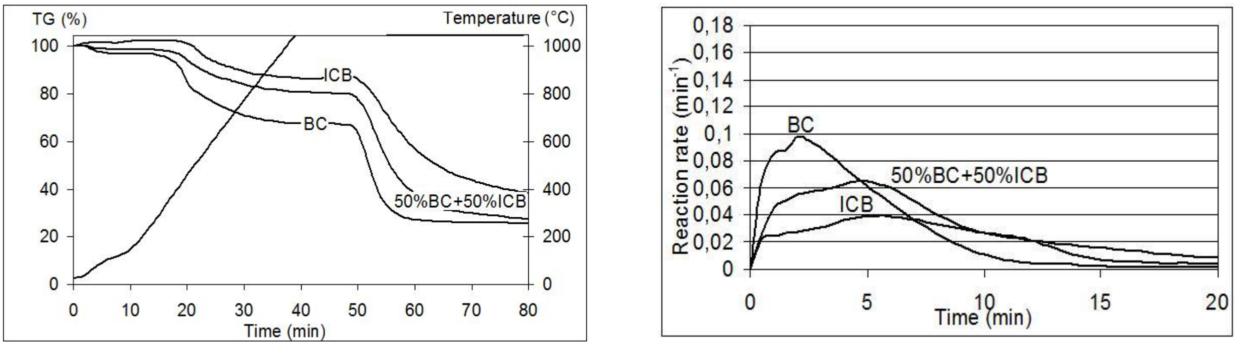
CC, ICA and mixture



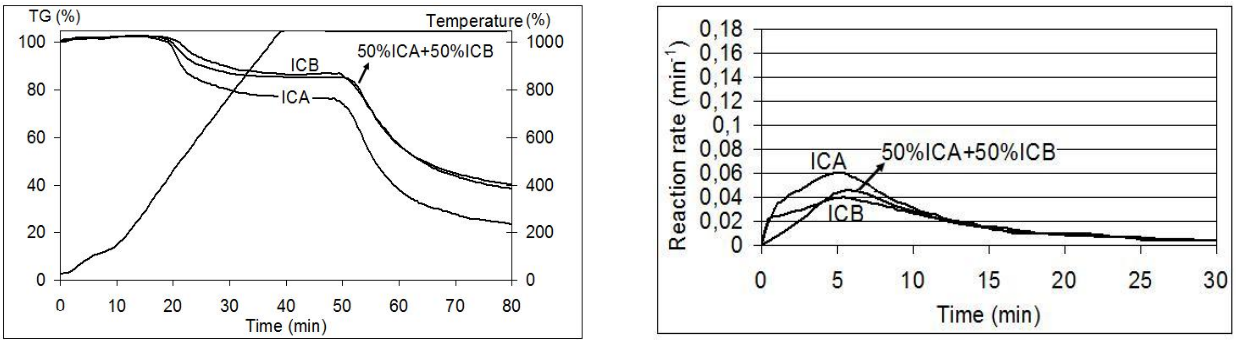
CC, ICB and mixture



BC, ICA and mixture



BC, ICB and mixture



ICA, ICB and mixture

Figure 5. TG and DTG curves for coals, charcoal and mixtures.

Analysis of TG curves shows that during the pirolysis the percentages of volatiles released in the mixtures were between those for the individual samples. This fact allows supposing that there are no synergetic effects (lack of chemical interactions) between the fuels. Similar pyrolytic behaviours of coal/coal and coal/charcoal mixtures have been reported in the literature.(12,13)

As to the char reaction with CO_2, DTG curve for CC, BC and blend, show that the maximum reaction rates of CC (0,1634 min^{-1}) and BC (0,0976 min^{-1}) were higher than the one of the mixture 50%CC-50%BC (0,0790 min^{-1}). It was expected that the reactivity of the mixture would be between the ones of the individual materials. Despite the fact that CC and BC are high reactive fuels in comparison with the imported coals, there mixture does not confirm the highest reactivity. The time to reach the maximum rate for the mixture was similar to the CC and BC, about 2 min. Both fuels react quickly and practically at the same time. Probably the CO_2 amount was locally minimized due to generation of CO and this might inhibits the solution loss reaction**.** Reported results are preliminary and more research is needed for final conclusions.

The blend ICA-ICB showed the lowest maximum reaction rate (0,0455 min^{-1}) and this rate was similar to the one for the higher rank coal, i.e. ICB. The other blends showed intermediate maximum reaction rate in comparison with the individual materials. The mixture CC-ICA presents the higher reactivity (0,0890 min^{-1}) and it was followed by the following mixtures: BC-ICA (0,0822 min^{-1}) CC-ICB (0,0651 min^{-1}) and BC-ICB (0,0646 min^{-1}). It was observed for the mixtures, that the time to reach the maximum reaction rate was about the same of the one shown by the component with lower reactivity.

Considering the conversion degree of 50%, time to reach this value for the mixtures is given in Table 4.

Table 4 – Time to reach 50% of conversion.

Sample	t (min)	Sample	t(min)	Sample	t (min)
CC	2,5	CC	2,5	CC	2,5
BC+CC	**4,4**	**CC+ICA**	**5,2**	**CC+ICB**	**5,3**
BC	3,1	ICA	6,8	ICB	9,3
Sample	t(min)	Sample	t(min)	Sample	t (min)
BC	3,1	BC	3,1	ICA	6,8
BC+ICA	**4,6**	**BC+ICB**	**5,7**	**ICA+ICB**	**9,3**
ICA	6,8	ICB	9,3	ICB	9,3

It was observed that all the mixtures, except for ICA-ICB, reached 50% of conversion in around 5 min. In the case of mixture of coals with lower reactivity, ICA-ICB, the time was higher, about 9 min.

3.3 Study on Coals, Charcoal and Mixture Behavior Using Tammann Furnace Experimental Set At Lehk / Rwth Aachen University, Germany

The weight loss curves of the studied coals and charcoal are presented in Figure 6.

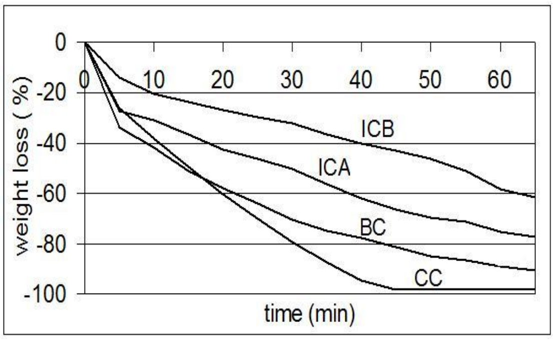
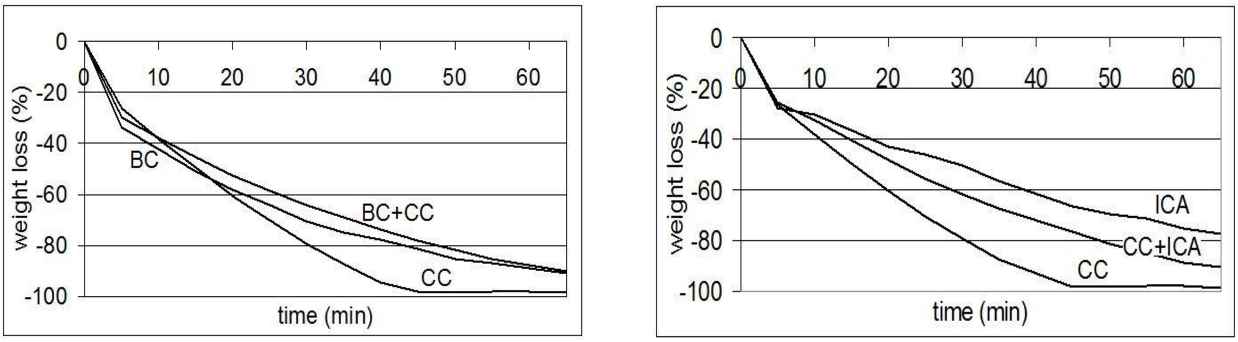


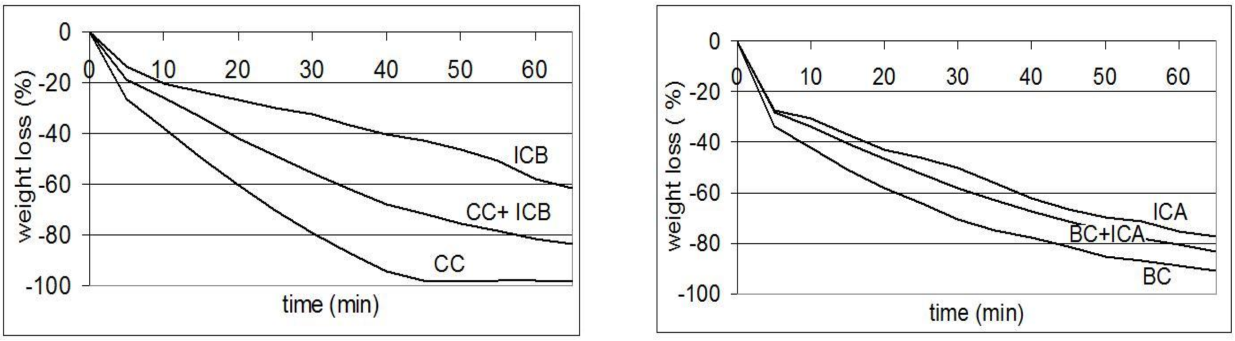
Figure 6. Weight loss curves of the studied coals and charcoal at 1100°C.

First five minutes of the experiment are related to the volatile matter loss. As it can be seen, BC shows higher volatile matter loss followed by ICA, CC and ICB. After five minutes, gas atmosphere was switched to CO_2 and the Boudouard reaction started. It was observed that only CC was consumed completely during the experiment time. In about 44 minutes CC reached 100% of weight loss. Considering the same time, BC reached 80%. For the imported coals the weight losses were lower, around 66% for ICA and 43% for ICB. These results are in agreement with the ones using STA, i.e, a higher reactivity of CC followed by BC, ICA and ICB.

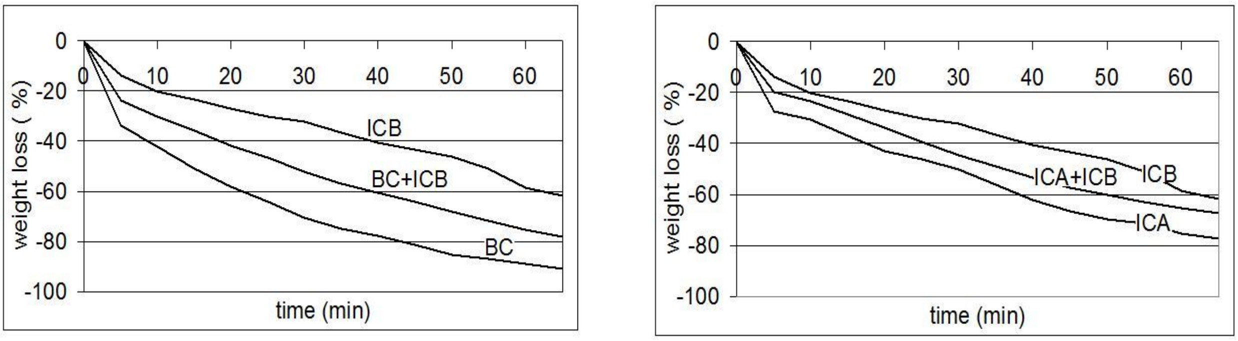
The weight loss curves of the coals and charcoal mixtures are given in Figure 7.



CC, BC and mixture
CC, ICA and mixture



CC, ICB and mixture
BC, ICA and mixture



BC, ICB and mixture
ICA, ICB and mixture

Figure 7. Weight loss curves of the coals and charcoal mixtures at 1100°C.

It could be observed that after the volatiles release, the weight loss for CC-BC mixture was not between the ones of the individual materials. The same behaviour was also noted in the TGA tests.

On the other hand, the weight loss of ICA-ICB mixture was between the ones of the individual samples. However, this behaviour was not noted in TGA tests, which showed that the maximum reaction rate for the mixture was similar to the higher rank coal, i.e. ICB. The tests in Tammann furnace rig were performed with a smaller particle size (<45µm) in comparison with TGA tests. Probably the increase of particle surface area facilitated the gas diffusion into the pore and accelerated the reaction. The difference in particle size may have affected more significantly the mixture of coals with lower reactivity.

The other blends showed intermediate weight losses in comparison with the individual samples and similar behaviour of the one seen in TGA tests.

4 FINAL REMARKS

- BC presents high level of ash and sulphur content: its ash has acid character and high alkali content; phosphorous content is low. CC has low ash and sulphur content; its ash has basic character, lower alkali and higher phosphorous content in comparison with BC. The imported coals present higher calorific value and intermediate ash contents in comparison with CC and BC; their ash is acid; content of alkali is low and phosphorous is high.
- The TGA tests for the individuals fuels showed: the starting temperature of pyrolysis was lower for high ranking coal BC and followed by the ICA, CC and ICB. Considering the solution loss reaction, CC has the highest reaction rate. It reacts with CO_2 faster than the Brazilian and imported coals. In about 5 min CC reached 100% of conversion. For BC the time was around 15 min. For the imported coals, ICA and ICB, this time was significantly higher, around 57 and 60 min respectively.
- The TGA tests for the mixtures showed: it was surprising that the maximum reaction rate for CC-BC mixture was lower than the maximum reaction rate for single substances. Both fuels react quickly and practically at the same time. Probably the CO_2 amount was locally minimized due to the CO generation and this might inhibits the solution loss reaction. More research is needed to confirm these results. The mixtures CC-ICA and ICA-ICB presented the highest (0,0890 min^{-1}) and the lowest (0,0455 min^{-1}) reactivity respectively. The other blends showed intermediate reactivity: BC-ICA (0,0822 min-1), CC-ICB (0,0651 min-1) and BC-ICB (0,0646 min-1). It was observed that all the mixtures, except ICA-ICB, reached 50% of conversion in around 5 min. In the case of mixture of lower reactivity coals, ICA-ICB, the time was higher, about 9 min.
- The Tammann furnace tests for the individual substances showed the same behaviour like TGA tests, i.e. a higher reactivity for CC followed by BC, ICA and ICB.
- The Tammann furnace tests for the mixtures showed: reactivity of CC-BC mixture was lower than the ones for the individual substances, as observed in TGA tests. The weight loss of ICA-ICB mixture was in between of the ones observed for the individual substances. Probably the difference in particle size of the samples used in both tests, Tammann furnace and TGA, was responsible for this effect.

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