Influence of mineral matter on the gasification kinetics of coal chars in carbon dioxide stream

Paweł Torbus

ABSTRACT:

Literature reports that parent coal properties influence kinetics of coal gasification. The reactivity of coal chars towards CO_2 is influenced by coal rank, pyrolysis conditions (heating rate, holding time, final temperature), pressure, surface morphology, pore structure, particle size etc. The role of ash content, content and composition of inorganic constituents likely to catalyse oxygen exchange reactions is still under research. The main goal was to understand and predict the influence of mineral matter on kinetics of coal char gasification by carbon dioxide. In order to prove the role of certain compounds, they were additionally introduced into studied coals. Experiment results were used for structuring kinetic models. In this dissertation, integral and differential kinetic models were applied to describe the varying conversion rate: Flynn-Wall-Ozawa, Kissinger-Akahira-Sunose, and Freidman. Obtained from experimental part and further mathematical modelling results show significant influence of mineral matter compounds (iron oxides and limestone) on the kinetics of coal chars CO_2 gasification. Results show that at high conversions, exposure of included minerals on the char surface is mostly caused by fragmentation. In the later stage of gasification, the char particle fragmented into a few particles of *20–30 µm* as indicated by Scanning Electron Microscopes (SEM) pictures. Addition of limestone or iron (III) oxide catalyst does not promoted coal char gasification, but its particles conglomerated and blocked active sites.

Keywords: coal char, CO2 gasification, reactivity, isoconversional models, mineral matter

1. INTRODUCTION

The world of energy today, and coal industry in particular, is facing complex challenges. Global market becomes significantly more competitive and influenced by different regional approaches to environmental policies. Despite many negative factors and predictions, as it is visible in Figure 1, coal is and still will be in the near future one of the most important sources of energy in the world.
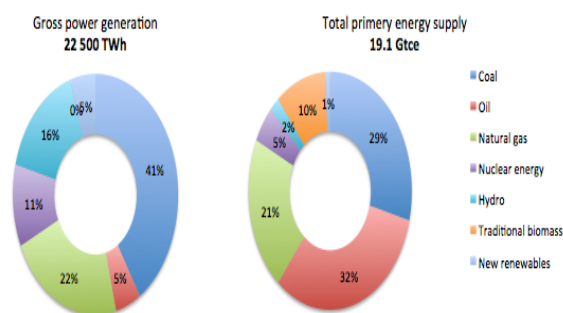

Figure 1. Global power generation and global primary energy mix by source 2012 [1].

Global energy use in *29%* depends on coal, and *41%* of gross power generation comes from coal-fired power plants. The European Union is the world's third largest coal consumer, after China and North America. In year 2013, *516.9* millions tones of coal and lignite were used, recalculated for tone of oil equivalent (*toe*). Moreover, coal remains the most abundant fossil fuel by global reserves-to-production (*R/P*) ratio. It appears that *88%* of Europe's fossil fuels reserves are to be found in a form of coal and lignite. Depending on actual usage they can provide energy security for the next *250* years [2].
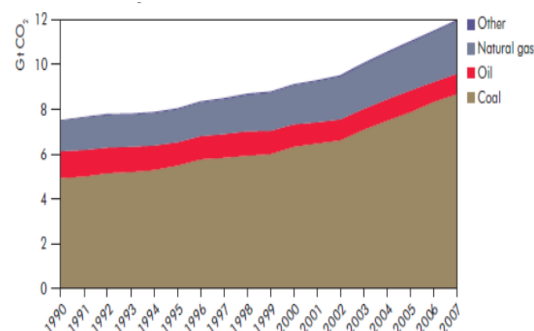

Figure 2. CO_2 emissions from global electricity generation [3].

At the same time, coal is the largest anthropogenic contributor to carbon dioxide emissions, shown above in Figure 2. Almost *87%* of European CO_2 emissions come from

coal-fired energy production or usage. Global green-house-gases emissions related with energy in 2012 reached a new historic high. There is a direct connection between coal technologies and environmental impact of human activity. European policies, due to agreed Kyoto Protocol [4], established the climate and energy package. It is a set of legal acts, which aims to ensure that the European Union meets its ambitious climate and energy targets in for 2020. These targets, known as the "*20-20-20*", establish three key objectives for 2020: a *20%* reduction in EU greenhouse gas emissions from 1990 levels; raising the share of EU energy consumption produced from renewable resources to *20%*; a *20%* improvement in the EU's energy efficiency. Moreover, European commission and national governments are working for upcoming EU 2030 energy and climate policy framework [5]. Finding the right balance between reducing environmental impact and energy strategy, that answers nowadays economic, social and industrial challenges, is essential for the further European development. Indeed, eco-friendly energy production and industry and available and safe energy should go hand in hand. Many factors show trends for increasing usage and significance of coal. New technologies of energy production like Carbon Capture and Storage (CCS) would allow European Union members, depending on coal, to fulfil environmental challenges without the prejudice to economy and labour market.

2.   COAL GASIFICATION IN CO_2 ATMOSPHERE

Coal gasification is the key enabling technology in future of low emissions power generation and high efficiency energy systems. Moreover, it is a flexible core technology with many possible applications, like hydrogen, chemicals and liquid fuels production. Current gasification research builds on a strong Research & Development base progression from extended use of combustion technologies. Coal gasification in CO_2 atmosphere is based on the Boudouard reaction. There were performed thermodynamic calculations for coal gasification at the temperature of *1000°C*, which results are

presented in Figure 3 [6]. Its use may lead to the increase in process efficiency and economic enhancement of syngas production, due to reduction of feedstock coal and oxidizing medium consumption.
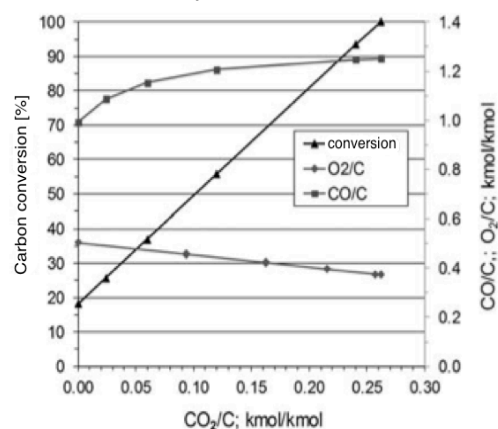

Figure 3. Effect of CO_2 introduction in the gasification of solid fuels on relative increase in the CO production, and CO_2 consumption reduction. CO/C, CO_2/C, O_2/C [6].

Moreover, it can decrease environmental footprint, provoked by carbon dioxide emitted into the atmosphere. Comparing classic gasification to one with carbon dioxide, CO_2 implementation into chemical reactor enhances carbon conversion with the following increase of carbon monoxide fraction in process syngas. Effective carbon dioxide introduction to coal gasification process requires several fundamental conditions. One of the most important is the requirement of high process temperature. Chemical reactor with circulating fluidized bed (CFB), as one presented in Figure 4 below, guarantees proper conditions of mass and heat exchanges, that is the second important factor of coal gasification by CO_2.
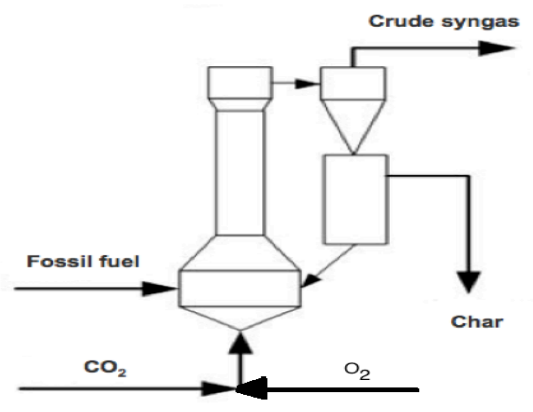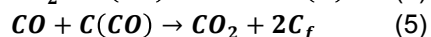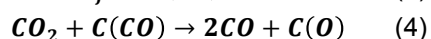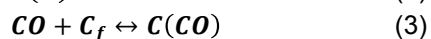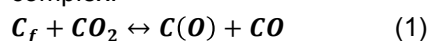

Figure 4. Installation for CO_2 coal gasification [7].

Recycle of partial converted coal char (separated from crude syngas in the preliminary cyclone), establishes conditions of high concentration of solid phase (coal char and coal), well mixed in gas flow. Occurring in reactor, reactive, high carbon-content coal char allows at its surface conversion of feed CO_2 into carbon monoxide, so desired in syngas composition. Moreover, produced in circulating fluidized bed (CFB) reactor coal char, may be used for energetic purposes. Oxygen is fed to the reactor to provide proper temperature, due to the coal combustion.

2.1. CHARACTERIZATION OF THE BOUDUARD REACTION MECHANISM

The Boudouard reaction is a main reaction of uncatalysed carbon gasification involving CO_2. It is an endothermic reaction, resulting in a production of carbon monoxide. Due to the large positive enthalpy (c.a. *172 kJ/mol* under standard conditions), thermal equilibrium does not favour CO production until the temperature range over *700 ^{o}C*, when the entropic term, $-T\Delta S$, begins to dominate and the Gibbs free energy becomes negative. Several carbon – carbon dioxide reactions mechanisms have been proposed in the literature [8], however there seems to be a common attitude towards it. Those reactions listed below are complex, partially reversible. The mechanism is given in 5 steps, of which two are assumed reversible. Oxygen and carbon monoxide can appear in a form of complexes at the carbon surface [C(O) and C(CO)]. The rate-limiting step is the desorption of the carbon–oxygen surface complex.

$$C_f + CO_2 \leftrightarrow C(O) + CO \qquad (1)$$
$$C(O) \rightarrow CO \qquad (2)$$
$$CO + C_f \leftrightarrow C(CO) \qquad (3)$$
$$CO_2 + C(CO) \rightarrow 2CO + C(O) \qquad (4)$$
$$CO + C(CO) \rightarrow CO_2 + 2C_f \qquad (5)$$

Firstly, carbon dioxide dissociates at free active site, releasing carbon monoxide and forming and oxidized surface complex C(O). Secondly, the carbon-oxygen complex produces a molecule of CO, intrinsic decomposition rate constant and active site density product characterize Boudouard rate constant. Under steady conditions, in the atmosphere of CO_2,

the reaction is driven to the right, production of one carbon monoxide's molecule for each active site is reached. Second molecule of CO is formed due to complex decomposition.
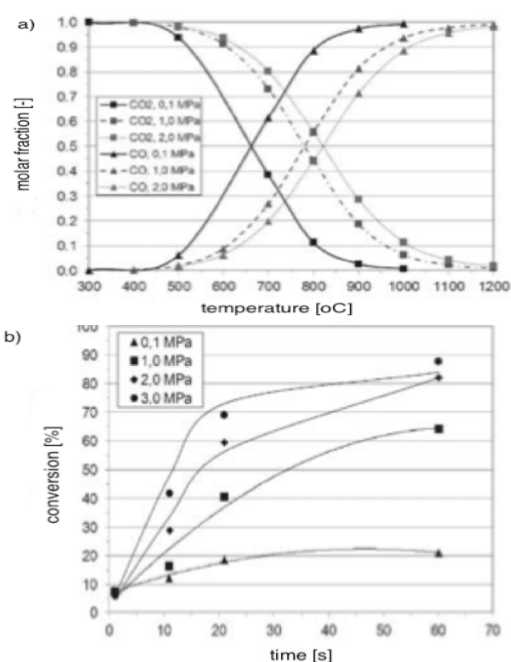

Figure 5. a) Boudouard equilibrium in a function of temperature and pressure, b) char conversion versus time and pressure [9].

As seen in Figure 5, high temperatures, above *650 ^{o}C* promote Boudouard reaction direction to the carbon monoxide production. Increasing pressure causes the need of higher temperature, as may be seen in Figure 5a, to obtain the same mole fraction of carbon monoxide. Despite the thermodynamic limitations (influence of pressure on the temperature), as seen in Figure 5b, elevated pressures promote the Boudouard reaction and enhance carbon conversion. For the reaction to be performed properly several factors are necessary to be provided: reactive coal char, reaction time (determined by kinetic conditions) and intensive contact gas-solid surface.

2.1.2.1. ALKALI AND ALKALINE EARTH METALS

Alkali and alkaline earth metals (AAEM) mainly occur as organically associated cations or in discrete minerals. For low rank coals, these highly dispersed metals are forming the mineral matter naturally present in the carbon matrix, they also act as catalysts for the gasification reaction. An Argentinian group of scientists

J.Ochoa [10] performed research on influence of mineral matter occurring in coal matrix on gasification kinetics of the Argentinean subbituminous (SB) and high volatile bituminous (HVB) coal chars.
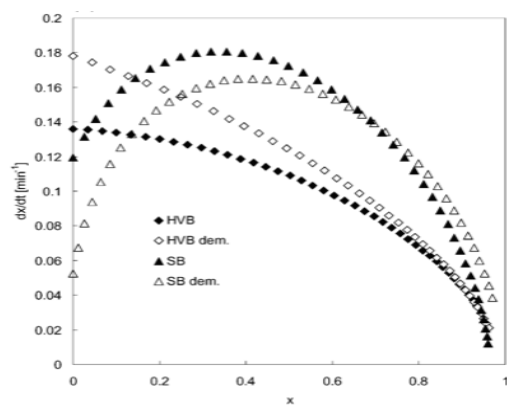

Figure 6. Gasification rate vs. conversion for the raw and demineralized chars SB, HVB at:1413K,70%CO_2

To achieve the test goals, they investigated differences in kinetics of raw coal char and chars that were demineralized. As presented in Figure 6, subbituminous char with mineral matter has higher reaction rate then the demineralized one in the initial conversion range. The reaction rate of demineralized coal decreases steadily, which is a quite different behaviour from raw coal, which discloses a maximum. It is clearly seen that ash in coal needs time to be activated as catalyst and this results in a increasing rate and in a later stage the catalytic effect becomes weaker because ash layer blocks reaction surface.

A Japanese Koichi Matsuoka's research group [11] reported that the alkali and alkaline earth metal AAEM species in SB coals, used in the tests, occur mostly in a form of dispersed species. The way that AAEMs were released from coal matrix during gasification process depended on the type of metals. Sodium and Potassium vaporized during the gasification and their interaction with other materials was very weak. The main part of Calcium and Magnesium remained in the residue char, despite the fact that the major part of carbon underwent gasification reaction. Calcium has the biggest share in the alkali and alkaline earth metal species. It has a great influence on the formation of low temperature melting ash. Dispersed species of Calcium were converted

into submicron particles during pyrolysis and then they reacted with clay minerals to form alumni-silicates complexes. Most of coal ash is composed of silica, aluminium, iron and calcium oxides (total $73.7\%_{wt}$), but there also occur magnesium, titanium, sodium, phosphorus oxides and several others, not mentioned in a table below.
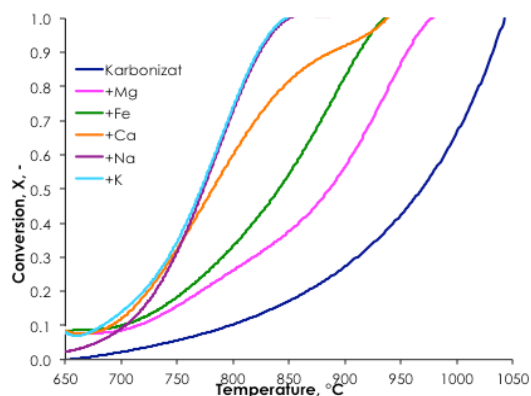

Figure 7. Catalytic effects of different compounds addition on coal char conversion during CO_2 gasification [12].

Literature reports that metals catalysing the Boudouard reaction are: Potassium (K), Sodium (Na), Calcium (Ca), Iron (Fe), Magnesium (Mg), Vanadium (V), Lithium (Li), Cesium (Cs), Chromium (Cr), Manganese (Mn), Barium (Ba), Strontium (Sr), Nickel (Ni), Copper (Cu). [12] As presented in Figure 7, those metals decrease activation energy and in the same time decrease gasification temperature. Those catalysts cause an increase of coal char conversion at the same temperature, for example: for presented results at the temperature of *800 ^{o}C*, the conversions obtained are *0.22, 0.4, 0.65, 0.83, 0.84* and for coal char with addition of Magnesium (Mg), Iron (Fe), Calcium (Ca), Sodium (Na), and Potassium (K) compounds respectively, comparing to the *0.1* conversion for pure coal char.

2.1.2.2. SODIUM AND POTASIUM CARBONATES

Chinese scientists Shufen Li and Yuanlin Cheng [13] investigated the catalytic effect of Na_2CO_3 and K_2CO_3 addition on the rate of the coal char CO_2 gasification. The catalytic effect of K_2CO_2 is greater that of Na_2CO_3. As presented in Figure 9, for CO_2 gasification at

790-1020 °C and *0.2 MPa* catalyst additions is enhancing gasification reaction rate up to the certain loading level (*5-20%_{wt}* for K_2CO_2 and *9-25%_{wt}* for Na_2CO_3) after reaching this point it drops again. Below *9%_{wt}* for Na_2CO_3 and *5%_{wt}* for K_2CO_3 the loading has little effect.
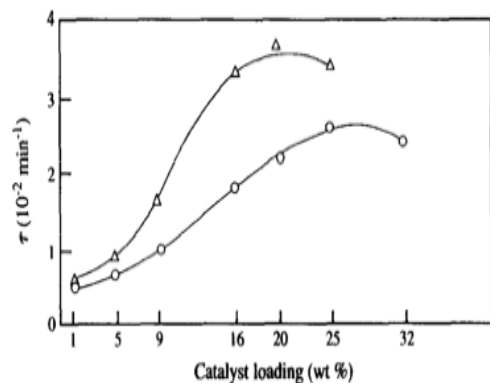

Figure 8. Effect of catalyst loading on reaction rate at 880°C for K_2CO_3 (Δ) Na_2CO_3 (*o*) [13].

2.1.2.3. IRON OXIDES

Dispersed iron catalysts were also considered as promising material for promoting coal char CO_2 gasification. Japanese scientists K.Asami, P.Sears, E.Eurimsky, Y.Ohtsuka [14] investigated gasification of brown coal and char with carbon dioxide using iron catalysts precipitated from an aqueous solution of $FeCl_3$. They concluded that the presence of iron catalyst can decrease the temperature, at which maximum rate of CO formation is achieved by *130-160 °C* lower temperatures or even a more significant lowering could be observed with higher loading in the range of ≤ *3%_{wt}* Fe.

Iron increased char conversion, specific rates in isothermal gasification. It resulted in complete gasification within a short reaction time. Precipitated iron occurs as fine oxide-hydroxide (FeOOH) particles, which are mainly reduced to the form of Fe_3C and then transformed in the initial phase of gasification reaction into α-Fe and γ-Fe and finally oxidized into iron oxides FeO and Fe_3O_4. Iron cations reactions during gasification are discussed in terms of solid-gas and solid-solid reactions. British Marco A. Saucedo's [15] research group investigated influence of iron-based oxygen carrier for CO_2 gasification of lignite coal. As presented in Table 1, at *1073 K*, time needed to exceed *50,80,95%_{wt}* of conversion are just slightly lower for the usage iron oxide bed instead of bed of

silica sand. However, at both *1123* and *1173 K*, time needed to exceed *80%_{wt}* of coal conversion was *45%_{wt}* lower in a bed of Fe_2O_3. For experiments performed at the same temperature, the time to reach equal conversion of coal was evidently shorter when iron oxide was used as a bed material instead of sand. This dependence increased with raising gasification temperature. Coal char conversion dependence on iron oxide addition is also presented in Figure 9a.
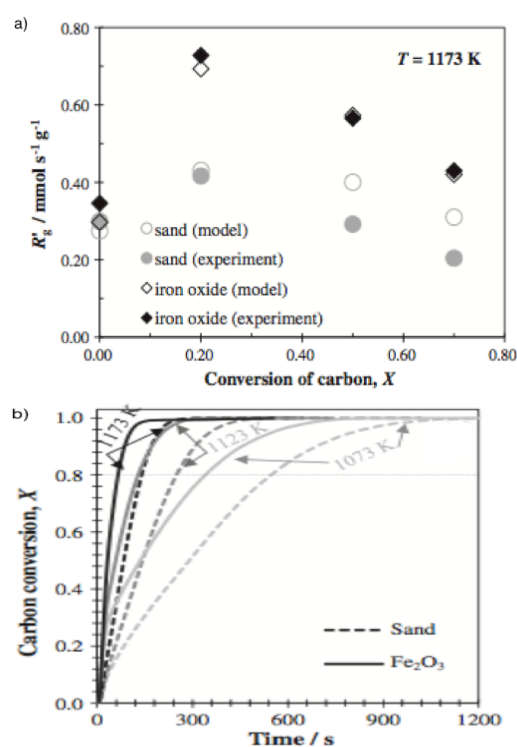

Figure 9. Effect of Fe_2O_3 addition on two factors: a) gasification rate and b) carbon conversion [14].

Moreover, as it may be seen in Figure 9b Fe_2O_3 addition caused increase of gasification rate, at higher temperatures, (*1173 K*), its value, during first *60-120 s*, when devolatization takes place, could be even 2 times higher in experiments with Fe_2O_3 than in a bed of sand.

Table 1. Holding time vs carbon corversion, for the gasification of Hambach lignite char, in the bed of (I) silica sand and (II) Fe_2O_3 [15].

x	Silica sand			Fe₂O₃		
	1073K	1123K	1173K	1073K	1123K	1173K
50%	995	480	240	915	300	150
80%	2520	980	420	2080	550	230
95%	>3710	1525	585	3180	910	355

3. EXPERIMENT

3.1. SAMPLE PREPARATION

Brown coal from the *Turów* minefield, located in Lower Silesia coalfield (Poland), was used for experiments. Parent coal and prepared coal char proximate and ultimate characterizations are presented in Table 2. This specific type of coal was chosen due to the outstanding high ash content in the coal matrix.

Table 2. Parent coal "Turów" and coal char properties.

Indicated parameter	Symbol	Unit	Parent coal "Turów"		Coal char "Turów"	
			Value	+/-	Value	+/-
Moisture (tot.) content	W_t^r	%	36.9	0.7	-	-
Moisture content	W^a	%	6.4	0.1	2.0	-
Ash content	A^a	%	27.7	0.2	51.1	-
Volatile content	V^a	%	38.06	0.17	0.61	-
High Heating Value	Q_s^a	kJ/mol	17842	83	15719	-
Low Heating Value	Q_i^a	kJ/mol	16860	101	15607	-
Sulfur content	S_t^a	%	1.52	0.04	1.16	-
Sulfur content	S_A^a	%	0.07	0.06	0.10	-
Sulfur content	S_c^a	%	1.45	0.05	1.06	-
Carbon content	C_t^a	%	44.2	0.6	45.8	-
Hydrogen content	H_t^a	%	3.78	0.27	0.29	-
Nitrogen content	N^a	%	0.44	0.15	0.46	-
Oxygen content (cal.)	O_d^a	%	16.03	0.69	-	-
Phosphorus content	P^a	%	0.027	0.002	0.039	-
Chlorine content	Cl^a	%	0.013	0.017	0.009	-
Fluorine content	F^a	%	0.036	0.017	0.055	-

For further research investigating mineral matter influence on the kinetics of coal chars gasification 6 mixtures of specified coal chars with 1,3 and 5%$_{wt}$ additions of iron oxide and limestone were prepared. To provide conditions simulating distribution of mineral matter a small as possible of compound powders were needed. For this purpose Sigma Aldrich's iron oxide (Fe_2O_3) was used. It was characterized by *99%* purity and particles were sized *<5* micrometres. As the second type of catalyst representing mineral matter, compound limestone was used. Limestone catalyst was mainly (>90%) composed from calcium carbonate ($CaCO_3$), however it contained some contaminants (SiO_2 + NR, Fe_2O_3, $MgCO_3$, Al_2O_3). It was milled to the size of particles *<200* micrometres. This guaranteed the accomplishment of particle's distribution goals. The coal char mixtures with artificial catalysts, and obtained after gasification residues samples were tested by Scanning Electron Microscopes (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) analysis. Pictures of mineral oxides distribution on coal char are presented in Figure 10.
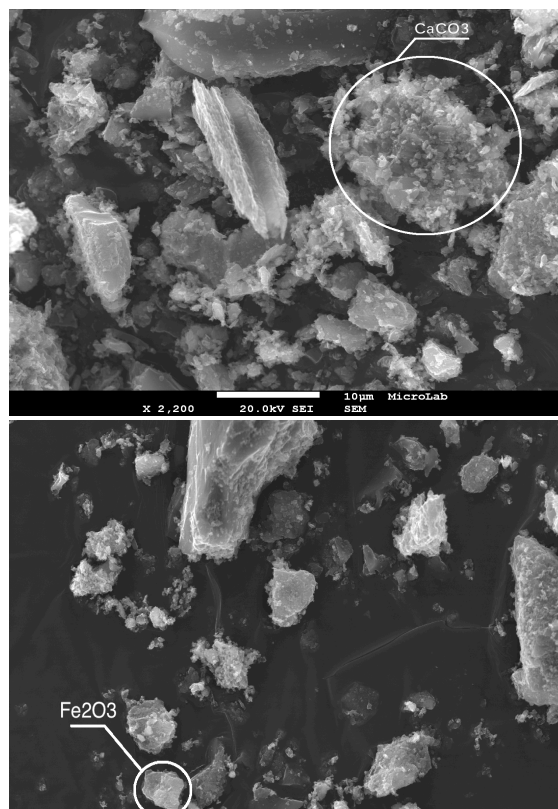

Figure 10. Left) SEM picture of limestone (*3%$_{wt}$*) particles distribution on the coal char surface. Right) SEM picture of Fe_2O_3 (*3%$_{wt}$*) particles distribution on the coal char surface.

$$g(x) = 3\left[1 - (1-x)^{\frac{1}{3}}\right] \qquad (6)$$

$$I(E_a, T) = \int_{T_0}^{T} exp\left(\frac{-E_a}{R*T}\right) dT \qquad (7)$$

Each model is based on assuming contracting volume (*R3*) fitting model [7].

4.2.1. LIMESTONE CATALYST

As presented in Figure 11, the activation energy calculated using all models was in similar range. It is approximately *230-250 kJ/mol* for conversion values greater than *0.2* and pre-exponential factor *logA* are approximately *7-8s^{-1}* for FWO and KAS models and *10-12 s^{-1}* for the Friedman method. Those results are comparable to the one obtained by other research group investigating coal char gasification [61], who calculated the activation energy *(245 kJ/mol)* and pre-exponential factor (7.41 s^{-1}) using the F1 method. Comparing to the parent coal gasification tests performed by [66], char gasification reveals a significantly higher value. It can be justified by the passivation of the char surface. The activation

energy and pre-exponential factor increase significantly for all samples in the conversion range from the beginning of the gasification to the conversion *0.4*. Then, it stabilizes and obtains above-mentioned value for the rest course of the reaction. The catalyst effect of limestone addition was observed only for *3%wt* limestone loading, but only in the first stage of the gasification up to *0.4* conversions. The activation energy in this range of conversion is approximately *10 kJ/mol* lower with the limestone catalyst. *1%wt* and *5%wt* $CaCO_3$ loading do not only showed lack of catalytic effect but as well inhibited coal char gasification. Thus the small or even lack of catalytic effect of limestone addition was probably due to a relatively large limestone sample size, which resulted in transport limitations. R.C. Rimpe and R.E. Sears concluded in their paper [16] that calcium inherent to the coal does not necessary provokes any additives.
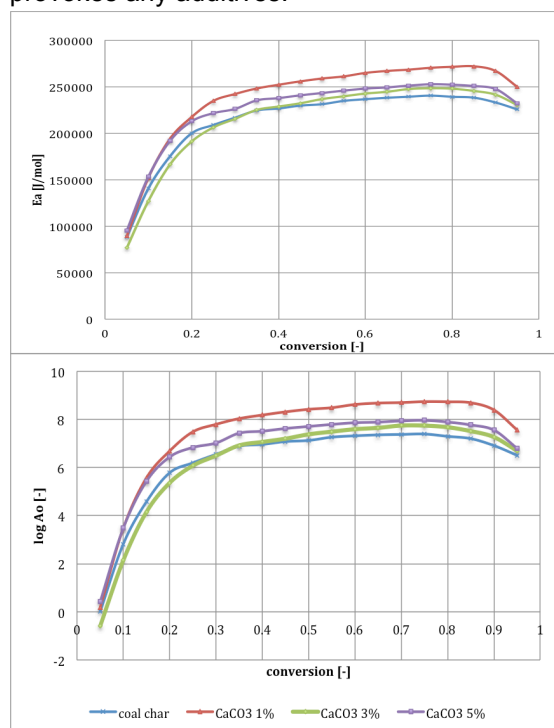

Figure 11. Coal char with limestone catalyst gasification Flynn Wall Ozawa modelling results: activation energy and pre-exponential factor.

4.2.2. IRON (III) OXIDE CATALYST

As it may be seen in Figure 12, the activation energy calculated using all models were in a similar range, as comparable to the limestone catalyst tests. It is approximately 240-250

kJ/mol for conversion values greater than 0.2 and pre-exponential factor logA are approximately 7-8 s-1 for FWO and 6-8 s-1 KAS models and 10-12 s-1 for the Friedman method.
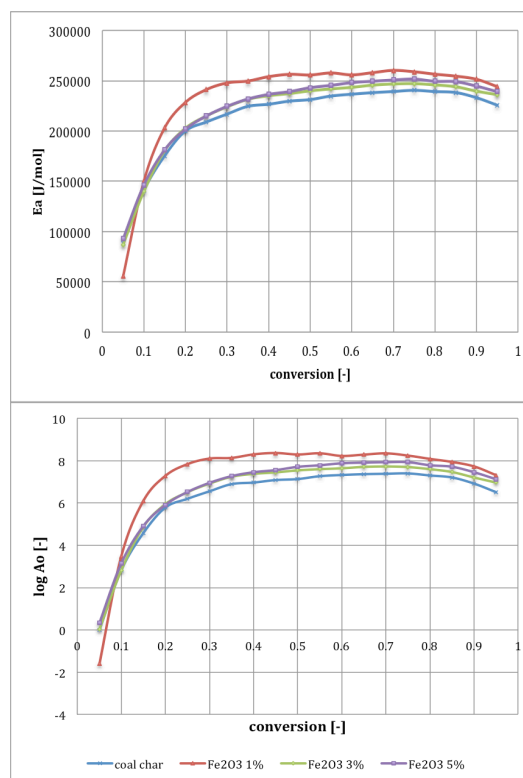

Figure 12. Coal char with Fe_2O_3 catalyst gasification Flynn Wall Ozawa modelling results: activation energy and pre-exponential factor.

Those results are comparable with one obtained by other research group investigating coal char gasification [17], who calculated the activation energy (*245 kJ/mol*) and pre-exponential factor (*7.41 s^{-1}*) using F1 method. Comparing to the parent coal gasification tests performed by [18], char gasification reveals a significantly higher value. It can be justified by the passivation of the char surface. The activation energy and pre-exponential factor increase significantly for all samples in the conversion range from the beginning of the gasification to the conversion *0.3*. Then, it stabilizes and obtains above-mentioned value for the rest of course of reaction. Catalyst effect of iron (III) oxide addition was observed only in the first stage of the gasification up to *0.1* conversions for *1%wt* of addition, *0.2* for *3%wt* and *5%wt* addition. In the rest of conversion range Fe_2O_3 loading do not only showed lack of catalytic effect but as well inhibited coal char

gasification. Thus the small or even lack of catalytic effect of iron (oxide) addition was probably due to a relatively large iron (oxide) particle size, which resulted as well as in limestone case in transport limitations [19]. Japan scientist [19] reached conclusion that catalysts particle size is very important factor. Finely dispersed catalyst shows the highest activities. Moreover, they concluded that due to high catalytic effect of iron dependence on the coal type. They found that iron drastically promotes brown coal, the effect is much smaller for bituminous coal. As coal char is characterized by high coal rank it may not influence its gasification.

3.2. ISOCONVERSIONAL THERMOGRAVIMETRY

For thermogravimetric research under isoconversional conditions produced by Netzsch TG 209 *F1 Libra* was used. It is designed for heating the sample up to *1100 ^oC* with specified heating and cooling rates (*0.001 K/min* to *200 K/min*). *5 mg* samples of the coal char and the coal char's mixtures were tested. They were gasified with CO_2 flow (supplied by gas supply unit at the level of *50 ml/min*). For each type of sample tests were performed with three different heating rates: *1 K/min, 3 K/min* and *5 K/min*.

4. RESULTS AND DISCUSSION

4.2. KINETIC MODELS RESULTS

In order to calculate the kinetic parameters of coal char gasification, three previously described models were applied, namely: Integral Flynn-Wall-Ozawa model, maximum rate Kissinger-Akahira-Sunose model and differential Friedman model. Isoconversional models consider the activation energy to be constant, therefore discretization of fixed values of conversion for which the calculation are made. For each curve for plot of conversion dependence on the temperature, *5%* steps of conversion were calculated. Research group supervised by Xuejun Qi [20] investigated the effect of iron on Shenfu coal char gasification reactivity. They observed that carbon conversion rate increased with the rise of iron loading within *0-2 %$_{wt}$*.
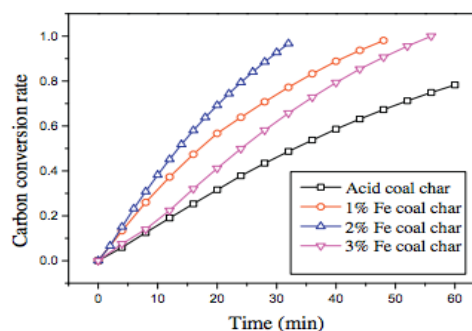

Figure 13. Carbon conversion rate during CO_2 char gasification [70,71].

However, as it may be seen in Figure 13 further increase of iron loading had no obvious catalytic effect. It may be result, as in this case, of a suppressing effect, related to the aggregation of iron catalyst [21], leading to the loose of the catalyst surface area.

The fine iron particles have high mobility and high activity, which can promote the gasification of char. Unfortunately, size of iron particle rises with the increase of catalyst loading, which leads to the reduction of catalytic effect on char.
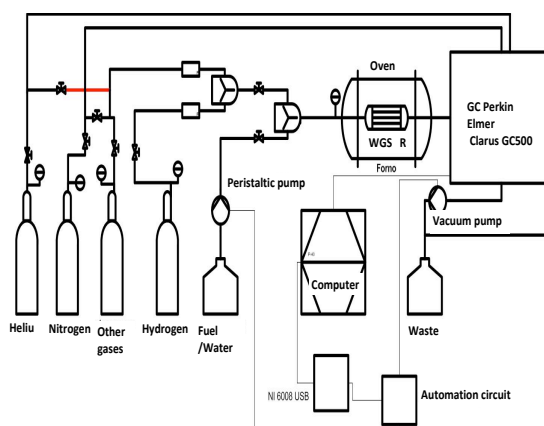
4.3. COAL CHARS GASIFICATION RESEARCH

Figure 14. Laboratory reactor scale process arrangement.

To investigate deeply the mechanism of coal char gasification and mineral matter's influence on it, research in laboratory scale chemical reactor was performed as well. This part of the dissertation investigation took place in Instituto Superior Tecnico in Lisbon at the Department of Mechanical Engineering under the supervision of Doctor Rui Costa Neto. There occurred

certain challenges of process design and its implementation into reality. The main goal of this part of research was to scale up the process from the thermogravimetric weight to the laboratory installation with a chemical reactor. For this purpose, an installation's arrangement, presented in Figure 14, was necessary for tests undergoing with carbon dioxide gas flow in a ceramic reactor placed in the oven enabling heating up the sampled fixed into it up to $1100^{o}C$.
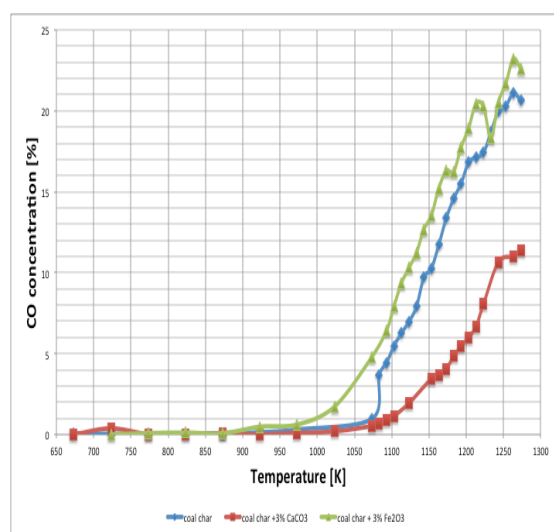
4.3.1. COAL CHAR GASIFICATION RESULTS

Figure 15. Concentration of CO in syngas produced vs. process temperature.

Results of performed "in-situ" fixed bed coal char gasification tests are presented in Figure 15, left. They confirmed those obtained during TG tests. It shows constant influence of mineral oxides addition while up scaling. Gasification reaction as it was concluded before, started at temperature about *1000 K*, from there CO concentration started to be larger than *1%* in process gas. Addition of $3\%_{wt}$ of limestone inhibited coal char gasification, obtained in same temperatures CO concentrations were lower then one obtained in pure coal char gasification. As depicted, addition of $3\%_{wt}$ of iron (III) oxide promoted CO production, its concentrations obtained in same temperatures were slightly higher then one obtained in pure coal char gasification.

5. SUMMARY

Literature reports that several factors have a great impact on coal char gasification in a CO_2 atmosphere. Among them could be considered: coal rank, process temperature, process and gas pressure, gas composition (CO_2 concentration), coal and ash chemical composition, additional mineral catalyst, pore structure, and particle size. Their impacts were briefly presented in the *Literature part* of this paper. Influence of mineral matter presence and its composition, due to its possible catalytic effect is today under great interest of research groups. In this paper impact of artificial addition of limestone and iron (III) oxide were investigated. Presented in *Experimental part* results of performed thermogravimetric, SEM, EDS, "in-situ" fixed-bed reactor tests led to several conclusions.

Firstly, prepared coal chars were stabilized and chemically deactivated. It was hard to gasify them, and conversions were achieved at the high temperatures. This was caused by the fact that they were characterized by relatively high ash content. Obtained reaction rates, conversions and activation energies were comparable to the ones presented by other research groups [22] investigation kinetics of coal char gasification in carbon dioxide.

Secondly, investigated mineral oxides additions were in most ranges inhibiting coal char gasification. In principle, two effects are expected, i.e. higher coal char conversion and shift of reaction equilibrium to carbon monoxide direction. As it may be concluded from Thermogravimetric results, there was no positive effect on gasification progress. Limestone addition only in $3\%_{wt}$ loading and up to *0.4* conversion rate showed catalysis effect. Iron (III) oxide was catalysing coal char gasification only up to *0.1* conversion rate. Those results correlates with one obtained by Tanaka S, Uemura T, Ishizaki [10]. It may by stated that mineral matter in coal needs time to be activated as catalyst and this results in increasing of rate. In a later stage catalytic effect becomes weaker because reaction surface is blocked by ash layer. However, gasification tests in the fixed bed reactor,

addition of iron oxide (III) showed desired shift of the reaction equilibrium to the carbon monoxide production direction.

Thirdly, dispersion of catalyst over the organic matrix is a major consideration when studying gasification and catalyst effects. Prepared samples were milled and sieved under *100 µm* particle-size. It was believed that it would guarantee mapping of mineral matter distribution in coal matrix. Instead small particles were deprived of macro-pores and contact area between carbon and artificial catalyst loading was hindered. Moreover, at high conversions, exposure of included minerals on the char surface was mostly caused by fragmentation. In the later stage of gasification, the char particle fragmented into a few particles of *20–30 µm* as indicated by SEM pictures [23]. Addition of limestone or iron (III) oxide catalyst did not promote coal char gasification: its particles conglomerated and blocked active sites.

Fourthly, chosen due to its simplicity and low costs, physical mixing of coal char sample with artificial mineral oxide catalyst method [24] was not the proper way to map mineral matter distribution in coal matrix. For future research, the "wet-method" of loading catalyst particles on coal char surface from its solution should be taken under investigation [25].

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