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TGA/DSC ANALYSIS AS A TOOL FOR EVALUATING THE LOW TEMPERATURE OXIDATION OF COALS

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ABSTRACT

Coal represents the predominant energy resource globally for electricity generation and the steel industry, a role it is expected to maintain in the foreseeable future. The two primary types of coal that were utilized are Lignite Hambach (HA), also known as brown coal, and Bituminous Bailey (BA), also known as Steam Coal. Lignites necessitate immediate utilization post-mining due to their chemical reactivity, whereas Bituminous coals can be stored and transported prior to use. During storage, Bituminous coals are susceptible to self-heating, leading to the emission of toxic and fire-hazardous gases. In extreme cases, this self-heating can escalate to spontaneous combustion fires, primarily driven by Low Temperature Oxidation (LTO) processes occurring between room temperature and approximately 150°C. This study employs thermal analysis (specifically combined TGA/DSC) and Gas Chromatography to evaluate the LTO process. This study also found a stronger interaction between the moisture in the BA coal and the coal macromolecule surface. Additionally, this study found an exothermic process occurring during the endothermic evaporation of moisture and is related to molecular hydrogen accompanying the LTO process via formaldehyde oxidation to yield dioxirane which decomposes to produce molecular hydrogen and carbon dioxide.

KEYWORDS: Lignite coal, Bituminous coal, Low Temperature Oxidation, TGA/DSC, Dioxirane.

1. INTRODUCTION

Coal has been, and still is, one of the largest energy resources in the world and definitely will stay as such in the forthcoming decades until renewable energies take the major role and will be pricewise, competing with fossil fuels.

Coal is not a single material and the coalification processes of vegetation produce several types of coals dependent mainly on the duration of the process. The different coal types are characterized by several properties like carbon content, moisture, volatile matter, ash content etc. and produce different calorific values upon combustion. The combination of all those properties determines the coal type: lignite, sub-bituminous, bituminous or anthracites.

Lignite (Sometimes defined as brown coal) -10 to 20 million years coalification. Carbon content (dfw- dry water free basis) in the range of 60%-70%, high moisture content (up to 50%) and high volatile matter content (in the range of 50.5-52.4% dfw), low ash content (in the range of 4.0-5.1% dfw) and calorific value of 6.7-25.3 kJ/g.

Sub-Bituminous and Bituminous coal -20 to 50 million years coalification. Carbon content in the range of 69%-82% dfw, medium moisture content (up to 50%) and medium volatile matter content (in the range of 14-37.2% dfw), medium ash content (in the range of 7.7-13.8% dfw) and calorific value of 19-33 kJ/g.

Anthracite – 100+ million years coalification. Very high carbon content in the range of 80%-98% dfw, very low moisture content (<1%) and very low volatile matter content, in the range of 8-10% dfw, low ash content, in the range of 3-10% dfw and high calorific value of 30-35 kJ/g.[1]-[13]

The Anthracite, which is the highest-grade coal is much more expensive than the lignite and the bituminous coals and also accounts for small percentage of the coals available and thus it is not used as fuel for power production[2],[3],[14],[15],[16] Therefore, the lignite and the bituminous coals which are the main coals used for power generation[1], [6] are the subject of this study.

1.1 Low Temperature Oxidation (LTO) of Coal[17]-[19]

The coals post the mining process are in contact with atmospheric oxygen and are exposed to chemical transformation via low temperature processes and the reactivity is dependent on the coal type. Lignite coals are very reactive and thus can't be stored and have to be used immediately, post the mining process. For this reason, the utilities have to be near to the mine and the mined coal is grinded and injected into the utility's boiler. On the other hand, bituminous and sub-bituminous coals are less reactive and thus can be stored for long periods (months or even years) in large piles prior to its combustion at the yards of the utilities and of course, can be transported over large distances via trains or ships. Therefore, even countries that do not have coal as a natural resource (like Israel), can import it by sea or land transportation, and store it in large stockpiles prior to the combustion in the utility. The lignite is a low to medium calorific value coal (6.7-25.3 kJ/Kg) whereas the bituminous coal has a higher energy content (19-33 kJ/Kg).

As discussed, when coal is exposed to air, post the mining process (either in storage piles or even during transportation), a process of low temperature (RT-150°C) atmospheric exothermic oxidation occurs which results in reduction of the calorific value. In extreme cases if the heat dissipation from the coal pile is lower than the heat evolved by the oxidation reactions, self-heating of the coal piles (formation of hot spots in the pile) and release of toxic and flammable gasses will occur. If the temperature of the hot spots exceeds 300°C, self-ignition and fire eruption might start.

Thus, the atmospheric storage of coal in large piles, might result in maintenance problems and increase costs of power production using coal as the energy source.

The LTO (Low Temperature Oxidation) of coal is a very complex process of several steps and consists of physical adsorption of atmospheric oxygen, chemisorption and chemical reactions, Figure 1 and Scheme 1.

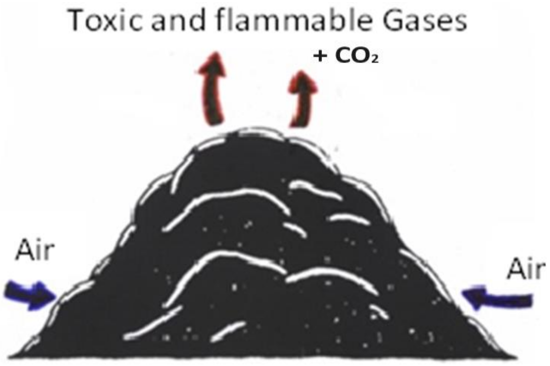


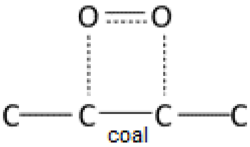
Figure 1: Atmospheric oxidation processes in a coal pile.[16]

Step 1: Physical adsorption

Physical adsorption of atmospheric oxygen inside the coal pores. Slightly exothermic.

Step 2: Chemisorption

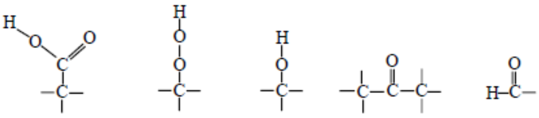
Partial cleavage of the O=O double bond of the physically adsorbed oxygen to yield chemisorbed O_2. Endothermic process.



Chemisorbed O_2

Step 3: Formation of surface oxides

Decomposition of chemisorbed O_2 to yield different surface oxides. Exothermic process



Step 4: Decomposition of surface oxides

Primary process, Exothermic process

$$surface\ oxides^{i} \rightarrow CO_{2\,(g)} + H2O_{2\,(g)}$$

Secondary processes. Slightly exothermic processes

$$surface\ oxides^{ii} \rightarrow CO_{(g)}$$

$$surface\ oxides^{iii} \rightarrow CnH_{m}\ (low\ molecular\ mass\ hydrocarbons)$$

$$surface\ oxides^{iv} \rightarrow H_{2\,(g)}$$

$$surface\ oxides^{v} \rightarrow CH_{2}O\ (formaldehyde)$$

Scheme 1: The LTO process of coal

The coal has a pore structure which consists of micro-, meso- and macropores.[4], [15] The atmospheric oxygen, which is in contact with the coal undergoes physical adsorption of the oxygen in the pores of the coal and the adsorbed O_2 undergoes chemisorption which is the formation of activated oxygen with partial bonds with the carbon atoms of the coal macromolecule. The activated oxygen undergoes surface reaction with the coal to form surface oxides which decompose mainly to CO_2 and H_2O as the primary products. But some surface oxides can decompose and yield carbon monoxide, CO, low molecular mass hydrocarbons C_nH_m and molecular hydrogen H_2 or CH_2O. The decomposition mechanisms consist of several complex reactions[4] and is the source of the emission of toxic and flammable gasses. The secondary processes (Step 4, Scheme 1) are temperature dependent and thus the amount of these flammable and explosive gasses increase appreciably with temperature rise.

The entire process is thermodynamically identical to the process of burning coal, meaning it emits a considerable amount of heat.

As the overall LTO process is exothermic (steps 1,3,4 in Scheme 1 are exothermic), self-heating of the pile might occur, if the heat dissipation from the coal pile is not efficient enough. If the temperature increases to >300^0C than self-ignition of the flammable gasses will start a fire in the coal pile (Figure 2). Fire eruptions or hot spots occurrence in large coal piles increase the maintenance and operational costs in the storage yards appreciable.

Figure 2: Fire in a coal pile at Rutenburg Coal Fired Power Station, Ashkelon, Israel (March, 2003)

In rare cases, if the LTO occurs in a confined space explosion might occur due to the accumulated hydrogen, H_2, or carbon monoxide CO or methane, CH_4, gasses which might reach the LEL (Lower Explosion Limit) in air.

These events of explosions due to accumulation of flammable and explosive gasses emissions which result from the LTO process in the confined space, occur especially in underground coal mines[14] but also in coal bunkers.[14]

Usually, the study of the chemical processes occurring during the LTO process are carried out in simulation batch reactors using gas chromatography, infra-red spectroscopy or mass spectrometry for the analysis of the gasses produced in this process.[14] The combined TGA/DSC thermal analyzer can help appreciably in shedding more light on this complex LTO process.

What is TGA/DSC[1]

The combined TGA/DSC is an instrument that measures on-line, mass changes of solids in conjunction with the energy absorbed/released (exothermic or endothermic processes) due to physical or chemical processes occurring to the solid sample studied. The system can be connected to a mass spectrometer which can measure on-line, the gasses produced during the experiment.

According to the specific gas and temperature that the sample is exposed to, the change in the sample mass and the heat (that is being produced or consumed) is measured. This information can help in a better understanding of the LTO process and the mechanism involved in the complex reactions occurring.

2. Experimental

2.1 Materials

Coals- Two types of coal have been studied[1]

- Bituminous Bailey (BA) coal from USA.

Elemental analysis: C 75.11%, H 3.23%, O 10.92%, N 1.68% (DF="dry free"/after drying). The calorific value of the fresh coal is ~26 kJ/Kg.

- Lignite Hambach (HA) coal from Germany.

Elemental analysis: C 64.64%, H 4.55%, O 24.14%, N 0.79% (DF="dry free"/after drying). The calorific value of the fresh coal is ~16 kJ/Kg.

Unless using fresh coals, the coals have been treated as follows

Grinding of the coal, sieving to several batches according to particle size and heating in a vacuum oven (1milibar pressure) at 60^{o}C for 24 hours.

The coals were kept in sealed glass vials under nitrogen atmosphere at room temperature, prior to using it for the experiments.

The different BA coals samples studied were: Fresh coal; grinded and treated (see above) particle size 74-250 µm; grinded and treated (see above) particle size 250-350µm; grinded and treated (see above) particle size >350 µm.

The different HA coals samples studied were: Fresh coal; grinded and treated (see above) particle size 200-500 µm; grinded and treated (see above) particle size >200 µm; grinded and treated (see above) particle size >500 µm.

In a recent publication,[1] the properties of the different coals studied in this work were determined using the combined TGA/DSC technique[1]. The properties of the different coal samples are given, Table 1.

Table 1: Calculated values of moisture, ash and volatile content obtained from the TG experiments with treated and fresh coals (DF="dry free"/after drying).[1]

Ash DF [%]	Volatile gases DF [%]	Moisture [%]	Coal type
4.08	34.15	2.86	**BA 350X**
5.83	33.72	1.86	**BA 250X350**
6.48	33.42	2.23	**BA 74X250**
5.63	48.74	11.27	**HA 500X**
5.51	49.32	10.94	**HA 200X500**
5.94	48.75	9.74	**HA X200**
8.09	21.14	3.13	**BA fresh**
7.46	50.79	43.6	**HA fresh**

2.2 Methods

In order to analyze the LTO process, each coal sample has been studied in the combined TGA/DSC unit under air environment.

The LTO (Low Temperature Oxidation) experiments in the combined TG/DSC unit started at 30°C and the sample is heated up to 115 °C at a heating rate of 5-10 °C/min, (20-30 minutes duration) and then, kept isothermally for 24/72h.

All the methods include few duplicated for each measurement to insure its validity.

Combined TGA/DSC LTO Experiments: For the TGA/DSC experiments, each coal was studied in 3 different samples of each coal: fresh (as received) and 2 grain sizes. All these measurements were carried under air atmosphere.

The experiments for 72 hours period was carried out using a different Netzsch TGA/DSC unit, model STA 409C/CD.

Also, another TGA/DSC unit has been used Netzsch TGA/DSC, model STA 449C "Jupiter". These TGA/DSC has the sensitivity of 0.01mg.

Gas Chromatography LTO Experiments: In order to study the LTO of the coals with the coals, batch reactor studies in 25 ml glass vials (sealed by 20mm rubber stoppers) were carried out.

Each reactor contained different mass of coal (particle size>500 □m) for the HA coal and (particle size > 350 □m) for the BA coal.

The reactors were heated to 115^{o}C in a FISHER ISOTEMP^{R} VACUUM OVEN (model 281) and BIFA oven (model PA 36B). Gas samples of 0.5ml volume were taken from the reactor by VICI PRECISION SAMPELING glass syringe and injected to the GC.

The GC used for the gas analysis was Agilent GC model 7890B with a TCD detector and the separation of the gasses was carried out in a 60mx0.32mm capillary column (Agilent model 113-4362 GS-GASPRO).

The initial atmosphere in the reactors was air and gas in the GC was air and the carrier gas in the gas chromatograph was He.

3. RESULTS AND DISCUSSION

In order to determine the reaction rates of the atmospheric oxygen, O_2, with the coals, batch reactor studies have been carried out under air atmosphere. Atmospheric oxygen, O_2, is the reacting gas with the coal in the simulation of the LTO process and carbon dioxide, CO_2, is one of the main products (see **Scheme 1**) and thus, it is essential to determine the rate of oxygen consumption compared to that of the amount of the emitted carbon dioxide as a product. Also the nitrogen, N2, concentration was determined. Determination of the rates was calculated using the gas chromatograph for the analysis of the gasses in the gas phase of the batch reactors. As the concentrations of the residual gases (CO, H_2 and low molecular weight hydrocarbons) is small, their concentrations were not determined.

3.1 Oxygen reactivity and Carbon Dioxide production via the LTO Process

Small (25ml) glass vials were used as batch reactors. In order to determine the rate of atmospheric oxygen consumption, 0.5 grams of BA coal (particle size > 350 µm) or 0.5 grams of HA coal (particle size>500 µm) in air were heated in the batch reactors in the oven isothermally at 115°C for different periods of time (0-20 hrs.). Gas samples from the vials were taken and injected to the GC and the concentrations of nitrogen, N_2, oxygen, O_2, and carbon dioxide, CO_2, were determined. The results are given, Table 2.

The calculation of the rates was carried out using the equations:

$Rate_{O2\ consumed}$=(25/22,400)*(1/t*coal mass)*(%O_2 consumed/100) [moles O_2/hour*gms coal]

$Rate_{CO2\ formed}$=(25/22,400)*(1/t*coal mass)*(%CO_2 formed/100) [moles CO_2/hour*gms coal]

Table 2: Analysis of the concentrations of the oxygen, nitrogen and carbon dioxide gasses during the LTO process of HA and BA coals at 115°C.

BA Coal				
Oxidation Time [hrs]	**$[O_2]$ [%]**	**$[O_2]_{consumed}$ [%]**	**$[N_2]$ [%]**	**$[CO_2]$ [%]**
0	21	0	78	0.04
0.5	19.5	1.49	80.39	0.1
1	16.7	2.22	80.01	1.21
2	14.7	5.29	82.3	2
20	0	21	94.1	5.9

HA Coal				
Oxidation Time [hrs]	**$[O_2]$ [%]**	**$[O_2]_{consumed}$ [%]**	**$[N_2]$ [%]**	**$[CO_2]$ [%]**
0	21	0	78	0.04
0.33	19.7	1.34	78.9	0.94
0.67	11.4	8.56	79.5	8.7
2	0	21	78.5	21.5

In order to determine the rates, the results of the O_2 consumption and CO_2 emission via the LTO reaction at 115°C in the reactors were calculated, in which the percent of the consumption of the initial atmospheric oxygen was <20%, thus the expected error in the rates will be <20%.

The calculation of the rate is according to the following equation:

Rate={% of O_2 consumed x reactor volume}/{100 x 22,400 x reaction time x coal mass}

Where: % of oxygen consumed is taken from Table 2

Reactor volume is 25 cc

Volume of 1 mole gas 22,400 cc

Reaction time is taken from Table 2

Coal mass is 0.5 grams

And the units of the rate are: **moles gas produced/hour x gm coal**

The results of the reactivity pattern of the LTO process for the two coals at 115°C have indicated that indeed the lignite HA coal is much more reactive than the BA bituminous coal. The source of this higher reactivity of the LTO process of the HA lignite coal compared to the BA bituminous coal is the much higher content of active aliphatic C-H groups in the HA coal compared to that in the BA coal in which the more stable aromatic group C-H groups content is appreciably higher.[15]

LTO in Bituminous BA Coal- The calculated rates of molecular oxygen consumption by the BA coal were: $6.65x10^{-5}$; $4.95x10^{-5}$; $5.90x10^{-5}$ moles O_2/hour x gm coal and the emission rates of carbon dioxide produced by the LTO at 115°C were $4.47x10^{-6}$; $2.70x10^{-5}$; $2.23x10^{-5}$ moles CO_2/hour x gm BA coal for 0.50, 1.0 and 2.0 hours of reaction.

The results indicate that the rate of oxygen consumption by the LTO process is constant in the initial stages, average of $5.84x10^{-5}$ moles O_2/hour x gm BA coal or $1.87x10^{-3}$ grams O_2/hour x gm BA coal. The average value for a long LTO process (24 or 72 hours) carbon dioxide production is $2.46x10^{-5}$ moles CO_2/hour x gm coal or $1.08x10^{-3}$ grams CO_2/hour x gm coal

However, the process of carbon dioxide emission occurs at a much slower rate compared to the molecular oxygen consumption (steps 1-3, Scheme 1) of the LTO process. The reaction with the oxygen occurs immediately upon heating to the 115°C but only after half an hour of LTO it reaches the stage where the surface oxides formed can decompose to produce the final product of carbon dioxide.

Furthermore, when all oxygen in the reactor has reacted (post 24 hours of the LTO process), the amount of carbon dioxide produced is much smaller than the amount of the molecular oxygen consumed. This means that only a fraction of the surface oxides produced by the LTO process decompose to yield carbon dioxide and most of them stay as stable oxides at the surface of the coal macromolecule. If one uses the ratio of final CO_2 content produced vs. amount of reacting O_2 in the reactors as the criteria, then the conclusion is that less than 50% of the reacting oxygen is decomposed to yield carbon dioxide and the rest of the reacting oxygen produces stable surface oxides. Using the initial rates method calculated above (average of $5.84x10^{-5}$ moles O_2/hour x gm BA coal and $2.46x10^{-5}$ moles CO_2/hour x gm coal) than the conclusion is that only 42% of the reacting atmospheric oxygen via the LTO process of BA bituminous coal at 115^oC yields the gaseous product of CO_2. And the remaining amount of the reacting oxygen via the LTO process, produce stable surface-oxides (Scheme 1) that don't decompose to yield carbon dioxide, namely it is expected that the mass of the BA coal undergoing the LTO process will increase!!. Indeed, this is what is observed experimentally with the TGA unit (see below).

In order to have a better estimate and compare the expected change in mass of the coal (as measured by the TGA) and the calculation based on the oxygen consumption by the coal (mass increase) via the LTO process versus the carbon dioxide emissions (mass decrease) a calculation based on the oxygen consumption and carbon dioxide emission (the kinetic study of the LTO process using the GC analysis of the gaseous different content in the reactors), have been carried out.

The calculated reaction rates (see above based on Table 2 results) can be used (It has been reported that the rate of the LTO process is not affected by the particle size of the coal[14] as the reaction occurs at the inner surface of the pore structure which is much higher than the outer surface of the coal particles).
The value of O_2 consumption is: $5.84x10^{-5}$ moles O_2/hour x gm BA coal
The value of CO_2 produced is: $2.46x10^{-5}$ moles CO_2/hour x gm BA coal
Namely, the conclusion is that less than half of the atmospheric oxygen which reacts via the LTO process is released as CO_2.

This result corroborates the former conclusion that most of the oxygen molecules reacting with the coal via the LTO process upon storage of bituminous coal piles under open air will produce stable surface oxides which do not decompose and that the calorific value of the coal will be somewhat reduced.

Mass Changes in the Coal via the LTO Process- The change in the mass of the coal post the evaporation process is the result of mass increase due to molecular oxygen uptake vs mass decrease via emission of carbon dioxide (the residual gasses emission is much smaller than that of CO_2 and thus is negligible).

Assuming average of $5.84x10^{-5}$ moles O_2/hour x gm BA coal or $1.87x10^{-3}$ grams O_2/hour x gm BA coal and $2.46x10^{-5}$ moles CO_2/hour x gm coal or $1.08x10^{-3}$ grams CO_2/hour x gm coal it is possible to estimate the expected changes in the mass of a coal sample which is examined experimentally in the combined TGA/DSC unit (see section 3.2 and 3.3).

LTO in Lignite HA Coal- The rates of molecular oxygen consumption by the HA coal were: $9.06x10^{-5}$ and $2.85x10^{-4}$ moles O_2/hour x gm coal and $6.30x10^{-5}$; $2.92x10^{-4}$ moles CO_2/hour x gm coal for 0.33, 0.67 hours of reaction. As the LTO process is much faster compared to the BA bituminous coal, the actual value is $2.85x10^{-4}$ moles O_2/hour x gm HA coal and $2.92x10^{-4}$ moles CO_2/hour x gm HA coal or $9.12x10^{-3}$ gm O_2/hour x gm HA coal and $1.28x10^{-2}$ gm CO_2/hour x gm HA coal. Namely, the amount of carbon dioxide emitted is somewhat larger than the amount of atmospheric oxygen which reacts with the HA lignite coal via the LTO process!!. As it is reasonable to assume that also in the HA coal some stable surface oxides are formed (like in the case of the bituminous BA coal) it indicates that during the self-heating of the lignite HA coal some intrinsic oxygen (oxygen which is part of the building components- elements of the HA coal) of the coal decompose also to yield carbon dioxide.

This corroborates the fact that the HA coal (young lignite coal) is much more reactive than the BA coal (medium age bituminous coal) towards the LTO process. This result stems from the fact that the lignite coal contains much higher percent of aliphatic -C-H groups which are more reactive than the corresponding aromatic -C-H occurring in the bituminous coals. Also, the rate of oxygen consumption post 40 minutes of heating the reactor at 115^oC, $2.92x10^{-4}$ moles CO_2/hour x gm, is much higher than after 20 minutes, $6.30x10^{-5}$ moles CO_2/hour x gm.

The final conclusion concerning the behavior of the HA lignite coal towards the LTO process indicates that appreciable amount of the carbon dioxide formed in the LTO process of the HA lignite coal is a product of oxygen groups occurring in the coal which decompose upon heating to produce carbon dioxide.

3.2 Combined TGA/DSC Experiments

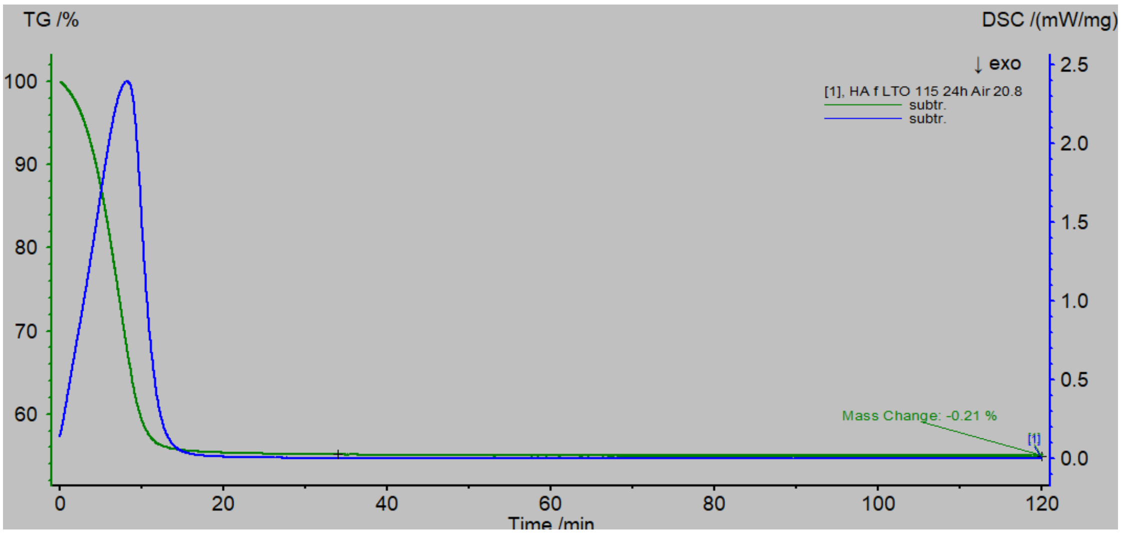
The combined TGA/DSC experiments have been carried out with 3 units: 2 units

(Netzsch TGA/DSC unit, model STA 409C/CD and Netzsch TGA/DSC, model STA 449C “Jupiter”) that for analysis of the content of the released gasses due to the temperature (115^{o}C) and the LTO process.

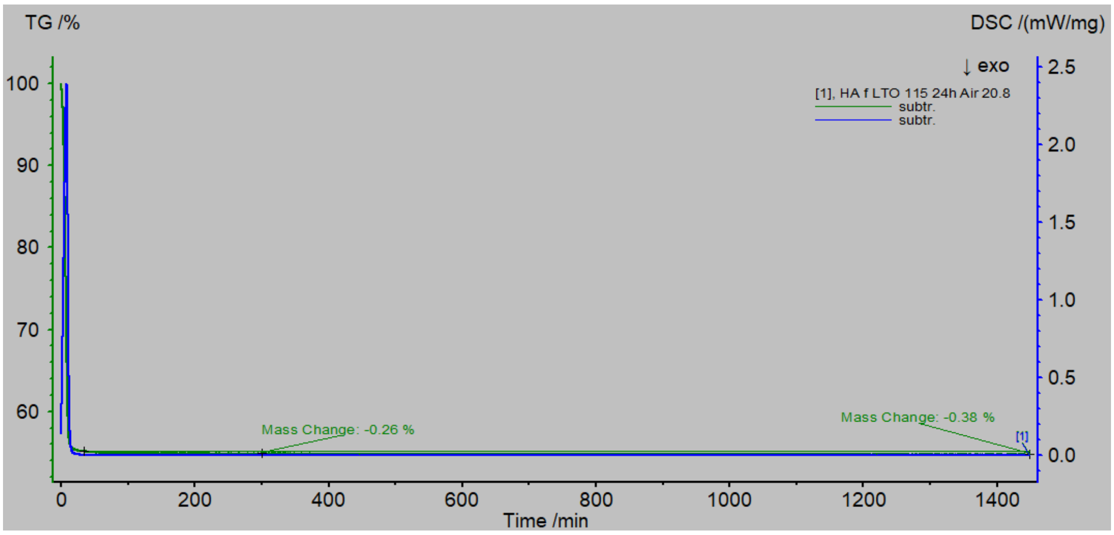
In the combined TGA/DSC experiments the mass of the coal sample which is heated isothermally at 115^{o}C is measured and can be reduced due to moisture evaporation or emission of gases as a result of the LTO process, or increased as a result of formation of physically or chemically adsorbed atmospheric molecular oxygen or formation of surface oxides.

The first process which occurs in the coals is evaporation of the moisture (as the temperature 115^{o}C is above the boiling point of water). Thus, the moisture content can be determined. When all the moisture has evaporated (the process occurs in the first 20 minutes) the slower process of the LTO dominates the mass changes.

HA Lignite Coal- A typical TGA/DSC graph is given for fresh HA coal, Figure 3, and for fresh BA coal, Figure 4.



a



b

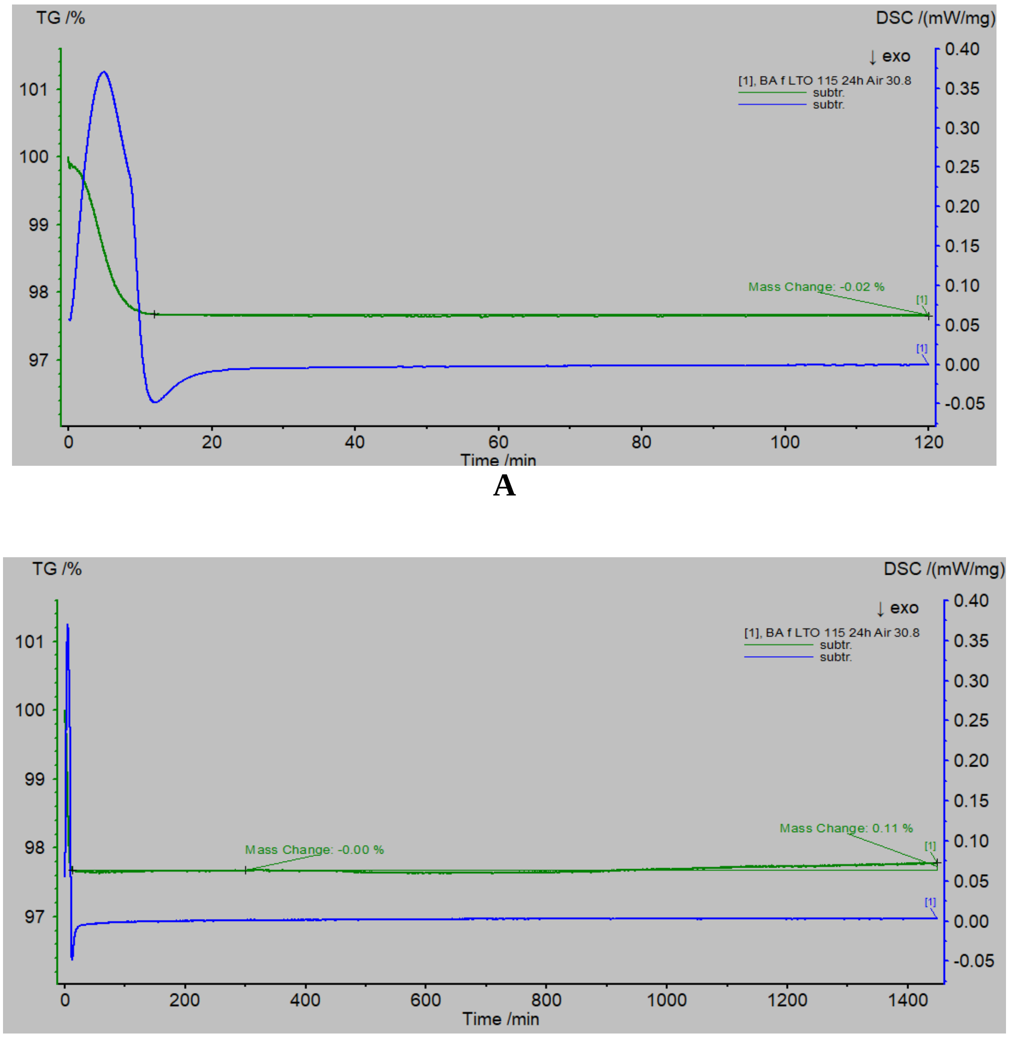
Figure 3: A TGA/DSC of 40.86 mg fresh HA coal sample at 115°C. a Measurement time 120 minutes. b Measurement time 1400 minutes.

----- TGA curve ------ DSC curve

As can be clearly seen, Figure 3a, the process of moisture evaporation from the fresh untreated HA lignite coal is an endothermic process in which 44.86% of the mass is composed of moisture that is evaporated during the first 17 minutes of the heating process at 115°C. During the 24 hours period of heating at 115°C of the coal which accounts to the LTO process, Figure 3b, a further small decrease of mass, 0.38% of the initial mass is observed. This observation shows that the LTO process of the HA lignite coal results in actual reaction of active groups of the coal with the adsorbed/chemisorbed atmospheric oxygen resulting in a mass reduction process.

The endothermic process of the water evaporation (the DSC results) lasted for ~18 minutes and gave a value of 1,027.6 J/gram coal, namely ΔH_{evap}=1027.6J/gram coal. As the moisture content of the coal determined in the experiment is 44.86% the actual enthalpy of moisture evaporation value is: ΔH_{evap}=41.2 kJ/mole water. As the enthalpy of pure water evaporation at 100°C is 40.6 kJ/mole water, it indicates that the moisture evaporation is equal or a little bit larger than the evaporation enthalpy of liquid water. Namely, the evaporation process of the water content in the HA lignite coal is the result of decomposition of the hydrogen bonds in the moisture content of ~40% occurring in the coal. Thus, it indicates that there is almost no appreciable electrostatic interaction between the water molecules in the HA lignite coal and the coal surface

BA Bituminous Coal- When the fresh bituminous BA coal is heated at 115°C, Figure 4, a different behavior is observed. In the initial process of moisture evaporation.



A

b

Figure 4: A TGA/DSC of 40.96 mg fresh BA coal sample at 115°C. a Measurement time 120 minutes. b Measurement time 1400 minutes.

----- TGA curve ------ DSC curve

From the coal, Figure 4a, the process is terminated at ~12 minutes in which the moisture content evaporated is much smaller than that of the HA lignite coal, 2.8-3.3% of the mass. However, the DSC curve shows that during the 12 minutes in which the endothermic evaporation process takes place (mass reduction due to the endothermic process of moisture evaporation) an additional second exothermic process occurs which starts at ~8.5 minutes from the beginning of the experiment.

In order to differentiate between the endothermic and the exothermic process we have assumed that the endothermic process should have a bell shaped curve (like in the case of the HA lignite coal) and have drowned a hypothetical curve, Figure 5.

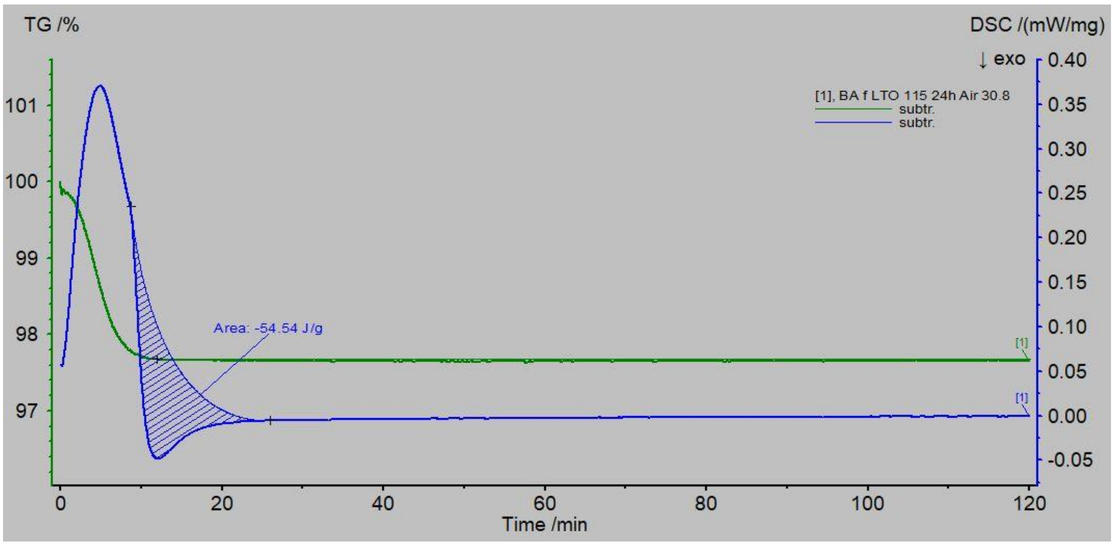


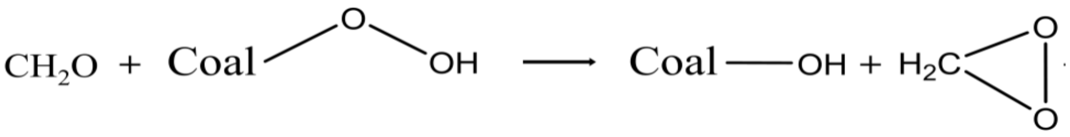
Figure 5: Hypothetic endothermic curve of the evaporation process in BA coal. Blue The real DSC curve, Black The hypothetical curve.

The value of the extra exothermic process according to Figure 5, is equal to the area which is marked by blue lines and is calculated to be 54.5 J/gram coal.

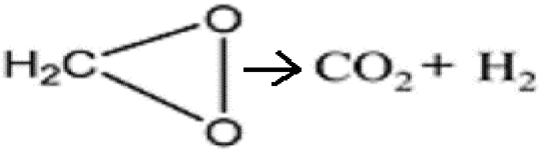
The value of the theoretical endothermic process which is the moisture evaporation gave a calculated value of 1027.6 J/gram coal, namely ΔH_{evap}=1027.6J/gram coal.

A possible potential process that can explain this exotherm is the emission process of molecular hydrogen that have been reported in our laboratory in 2009[20] during studies of the LTO process including sampling of gasses in hot points occurring in storage yards of utilities.[21]

The explanation to this process was the suggestion that traces of absorbed formaldehyde are oxidized by hydroperoxide groups which were formed by the LTO process via the consecutive reactions[14] 1,2:



1.

2. 

The decomposition reaction of the unstable intermediate dioxirane is very exothermic and have been reported[20] to be very exothermic ΔH=-415.9 kJ/mol. If this fast reaction is the source of the exothermic process observed than the amount of formaldehyde produced upon the heating of the coal is ~1x10^{-4} moles/gr.

During the 24 hours period of heating at 115°C of the coal which accounts to the LTO process, Figure 4b, a further small increase of mass, 0.11% of the initial mass is observed. The overall mass increase indicates that only partial percentage of the reacting atmospheric oxygen via the LTO process decomposed to yield the final products of carbon dioxide, CO_2, and water, H_2O and that appreciable amount of the initial reacting oxygen remains at the surface of the BA bituminous coal as stable surface oxides and thus the calorific value of stored coal piles is reduced and the overall weight is increased. This observation is in accord with the conclusion of the reactivity studies of the LTO using the GC analysis (see above) for the O_2 consumption compared to CO_2 emission of the BA bituminous coal.

The endothermic process of the water evaporation (the DSC results) lasted for ~12 minutes and gave a calculated value of 1027.6 J/gram coal (see above), namely ΔH_{evap}=1027.6J/gram coal. From the hypothetic, Figure 5, As the moisture content determined in the experiment in the BA coal is 2.32%, the enthalpy of evaporation of the water could be calculated to be: ΔH_{evap}=141.4 kJ/mole water. This is a very large value, much larger than the value for the HA lignite coal ΔH_{evap}=41.2 kJ/mole water or $\square H_{evap}$=40.6 kJ/mole water for pure water.

The results of the mass changes during the LTO process for 24 hours in the 2 coals for the various coal samples are summed up in Table 3.

Table 3: The change in mass in HA and BA coals after 72 hours of the LTO process at 115^{o}C measured by the TGA/DSC combined unit.

	Initial mass	**Water content**	**Δmass***
BA fresh	40.96mg	0.95mg (2.32%)	0.04mg (0.1%)**
HA fresh	40.86mg	18.33mg (44.86%)	-0.15mg (-0.67%)**
BA fresh	47.1mg	1.6mg (3.39%)	0.02mg (0.04%)
BA 74x250	42.36mg	1.02mg (2.41%)	0.69mg (1.67%)
BA 350x	54.0mg	1.5mg (2.78%)	0.34mg (0.65%)
HA fresh	49.5mg	20.58mg (41.58%)	-0.2mg (-0.69%)
HA x200	46.5mg	5.48mg (11.78%)	-0.4mg (-0.98%)
HA 500x	45.4mg	4.96mg (10.93%)	-0.47mg (-1.16%)

Water content- Taken as the mass percent reduction compared to the initial mass.

***Δmass- Taken as the mass percent reduction compared to the dried mass.**

The results are in mg and in the brackets in mass percent.

**** Measured after 24 hours of LTO at 115^{o}C.**

In the fresh HA samples the moisture content was 43.22%, whereas in the treated sieved samples (sieved and kept in vacuum-1 millibar at 60^{o}C for 24 hours- section 2.1) the average moisture content was ~11.3% for the >200µm or the >500µm fractions. The reason for this difference is that probably, 2 types of water occur in the coal: regular moisture which is evacuate during the treatment 924 hours in a vacuum oven at 60^{o}C) and intrinsic water which was not evacuated. The intrinsic water are the water molecules that are somehow bound (probably via hydrogen bonds) or via electrostatic interactions to the coal surface. Upon the treatment at 60^{o}C, only the non-bonded water is evaporated and the intrinsic water is not evacuated. Only at 115^{o}C the intrinsic water does evaporate. Namely, the combined TGA/DSC analysis shows that the water content in the HA coal consists of 2 types of water molecules!!!.

In the BA coal samples there is, essentially, no difference in the moisture content determination between the fresh coal sample and the sieved treated coal. The average moisture percent in the fresh or sieved fractions is much smaller compared to the HA lignite coal and is equal to 2.50±0.30%. This indicates that the water content in the BA bituminous coal is composed of intrinsic water which is trapped inside the coals pore structure. Namely, the water molecules in the bituminous coal has a strong interaction with the coal macromolecule and are bound probably, via dipole interactions to the coal. Indeed, the DSC results (see below) corroborates this conclusion.

3.3 Comparison between mass changes via the LTO process between the GC experiments and the combined TGA/DSC results) - expected mass changes (calculated GC) vs Experimental results (combined TGA/DSC)

The results of the weight measurements via the combined TGA/DSC experiments show definitely that there is a basic difference in long term reaction times (up to 72 hours duration) of the LTO process at 115°C between the low-grade HA lignite coal and the higher-grade BA bituminous coal. In the experiments with the HA different coal samples, there is always a decrease in mass, whereas in the BA coal there is an increase in mass.

As the HA lignite coal is much more reactive and also certain percentage of the oxygen content in the carbon dioxide released stems from the inherent coal oxygen content, it is reasonable that the final result of the LTO process will be a decrease in the mass of the reacting lignite coal. Whereas, the BA bituminous coal is much more stable towards the LTO process. Furthermore, the source for this behavior is the formation of stable surface oxides (see Scheme 1) from the LTO process at the bituminous BA coal surface. From the reaction rates of the LTO process for the atmospheric oxygen consumption and the emission of the carbon dioxide measured in the vials via gas chromatography the theoretical value of mass changes to the coals via the LTO process at 115°C can be calculated and compared to the actual values obtained in the TGA experiments. The calculation, is based on the assumption that in the combined TGA/DSC experiments there is a constant flow of heated air at 115°C through the coals and thus there is a constant concentration of 21% oxygen which is the fuel of the LTO process.

The equation for the theoretical calculation is

$(O_2 \text{ rate } \mathbf{X} - CO_2 \text{ rate } \mathbf{X}\ 32/44)_{\textbf{in mass units}}$ **X** LTO heating time **X** Coal Mass

Where: O_2 rate units **grams O_2 / grams Coal X hour**

And: CO_2 rate **X** 32/44 units **grams of O_2 in CO_2 grams/ grams Coal X hour**

Assuming that all the oxygen content in the carbon dioxide produced by the LTO process, emerges from atmospheric oxygen.

The actual mass changes in the coals were measured in the combined TGA/DSC experiments (Table 3).

Example 1

BA fresh coal sample

Sample: BA fresh

Initial Mass: 40.96 mg

Mass post Water Evaporation: 40.01 mg

Mass post 72 hours LTA at 115°C: 40.05 mg

□Mass post 72 hours LTA at 115°C: 0.04 mg

Rate of O_2 consumed via the LTO process at 115°C: $1.87x10^{-3}$ grams O_2/hour x gm BA coal, or if all the reacting oxygen via the LTO process at 115°C (assuming a constant LTO rate), is released as carbon dioxide, the amount of O_2 consumed by the BA coal undergoing the LTO process after 24 hours of reaction will be:

$1.87x10^{-3}$ x 1000 x 0.04096 x 24 = 1.84mg

However, the amount of CO_2 produced via the LTO process at 115°C (when the rate is $1.08x10^{-3}$ grams of CO_2/hour x gm coal) is calculated to be:

$1.08x10^{-3}$ x 1000 x 0.04096 x 24 =1.06 mg

The amount of carbon reacting via the LTO process and released from the BA coal (mass reduction of the coal) as carbon dioxide is:

1.06 x 12/44 = 0.289 mg

The amount of reacting oxygen in the LTO process in the released carbon dioxide is:

1.06 - 0.289 = 0.771 mg

Thus, the amount of stable oxides formed at the surface of the BA coal via the LTO process at 115°C for 24 hours is:

1.84 - 0.771 = 1.07 mg

And the mass change of the coal sample will be

Amount of surface oxides – Amount of carbon released as carbon dioxide

Or:

1.07 – 0.289 = 0.781 mg

Namely, according to the results of the gas chromatographic determination of the atmospheric oxygen and carbon content in the reactors and the rates of reacting oxygen which forms stable surface oxides and the released carbon dioxide there should be an increase in the mass of the BA coal sample after 24 hours of the LTO process at 115^{o}C of 0.781 milligrams. The measured value in the combined TGA/DSC experiment was of mass increase in the BA coal mass of 0.04 milligrams or ~5% of the theoretical value.

Example 2

HA fresh coal sample

Sample: HA fresh
Initial Mass: 40.86 mg
Mass post Water Evaporation: 22,53 mg
Mass post 72 hours LTA at 115^{o}C: 22.38 mg
□Mass post 72 hours LTA at 115^{o}C: 0.15 mg

Rate of O_2 consumed via the LTO process at 115^{o}C: $9.12x10^{-3}$ grams O_2/hour x gm BA coal, or if all the reacting oxygen via the LTO process at 115^{o}C (assuming a constant LTO rate), is released as carbon dioxide, the amount of O_2 consumed by the BA coal undergoing the LTO process after 24 hours of reaction will be:

$9.12x10^{-3}$ x 1000 x 0.02253 x 24 = 4.93mg

However, the amount of CO_2 produced via the LTO process at 115^{o}C (when the rate is $1.28x10^{-2}$ grams of CO_2/hour x gm coal) is calculated to be

$1.28x10^{-2}$ x 1000 x 0.02253 x 24 =6.92 mg

The mass decrease in the HA coal after 24 hours of LTO at 115^{o}C is

6.92 - 4.93 = 1.99 mg

Namely, according to the results of the gas chromatographic determination of the atmospheric oxygen and carbon dioxide content in the reactors and the rates reacting oxygen which forms stable surface oxides and the released carbon dioxide there should be an increase in the mass of the BA coal sample after 24 hours of the LTO process at 115^{o}C of 0.781 milligrams. The measured value in the combined TGA/DSC experiment was of mass increase in the BA coal mass of 0.04 milligrams or ~5% of the theoretical value.

The sum-up of the values for the different coal sample obtained by the TGA experiments and the calculated values based on the GC results are given in Table 4.

Table 4: The experimental (TGA) and calculated (GC) values of mass changes in HA and BA coals via the LTO process at 115°C*.

	Dried mass	Δmass (TGA)* experimental	Δmass (GC) calculated
BA fresh	40.01mg	0.04mg (0.1%)**	0.781 (1.95%)
HA fresh	22.53mg	-0.15mg (-0.67%)**	1,99 (8.83%)
BA fresh	45.5mg	0.02mg (0.04%)	0.898 (1.97%)
BA 74x250	41.34mg	0.69mg (1.67%)	0.808 (1.95%)
BA 350x	52.5mg	0.34mg (0.65%)	1.06 (1.98%)
HA fresh	28.92mg	-0.2mg (-0.69%)	2.55 (8,82%)
HA x200	41.02mg	-0.4mg (-0.98%)	4.11 (10.0%)
HA 500x	40.44mg	-0.47mg (-1.16%)	4.01 (9.68%)

***Δmass- Taken as the mass percent reduction compared to the dried mass.**
The results are in mg and in the brackets in mass percent

As can be clearly seen, the young lignite HA coal is a much more reactive coal towards the LTO process and the result of the process is mass reduction via the carbon dioxide emission which is appreciably larger than the mass increase due to the oxygen chemisorption of the reacting atmospheric oxygen. In the BA bituminous coal there is an increase of the mass via the LTO process because of the formation of stable surface oxides which do no decompose to yield carbon dioxide.

In both coals, the amount or mass change observed experimentally via the TGA unit is only 5-10% compared to the calculated values based on the GC analysis of the consumed oxygen and released carbon dioxide. The reason for this discrepancy stems probably from the fact that the reaction rate (which has been determined by the initial rates method) is decreased appreciably upon the continuation of the oxidation process due to blocking of the pores of the coal and inactivation of the coal macromolecule surface towards further oxidation.

3.4 Interaction of water with the coals

The water adsorbed in the coals can be inside the pores of the coal or trapped between the coal particles. Two major types of pores occur, the macropores (0.96 m^2/gram for the BA coal and 1,41 m^2/gram for the HA coal) and micropores (39.5 m^2/gram for the BA coal and 110 m^2/gram for the HA coal).[15],[24] In the BA bituminous coal the moisture content is only 2.83% and thus it is possible that all the water is locked inside the pores. In the HA lignite coal, the water content is very large (>40w%) and this means that most of the water occurs as moisture trapped between the coal particles. Thus, most of the water molecules interact via hydrogen bonds with the adjacent water molecules and only small fraction is locked inside the pores, probably ~5% at most. Thus, the calculated evaporation enthalpy ΔH=41.2 kJ/mole is just a little bit higher than that of pure water ΔH=40.6 kJ/mole.[22-29] It is reasonable that the interaction of the locked water inside the pores is much higher than the moisture trapped between the coal particles. Indeed, in the BA bituminous coal where the moisture content is much smaller (~2-3w%) all the water is contained inside the pores. And in this case, the evaporation enthalpy is much higher, ΔH=141.4 kJ/mole indicating a very strong interaction between the water molecules locked inside the pores. When a coal sample at room temperature (22°C) is inserted inside the combined TGA/DSC unit at 115°C the coal is heated to the operating temperature and the adsorbed water is evaporated. The enthalpy of evaporation (DSC results) of the adsorbed water (moisture) in the coals studied in conjunction with the water content (TGA results) has been determined to be 41.2 kJ/mole for the fresh lignite coal and 141.4 kJ/mole for the fresh bituminous BA coal.

The results indicate that there is a very difference the enthalpy of the evaporation process of the adsorbed water/moisture in the lignite coal compared to the bituminous coal. Also, the results of the water content of the lignite HA coal point out that the it contains 2 types of water: regular water which is the dominant part of the moisture contained in the coal (~32%) and a second type of water- intrinsic water which is water molecules (~10%) attached via electrostatic interaction to the surface of the coal macromolecule. In the sieved coal, which was also treated for 24 hours under vacuum at 60°C (section 2.1) the regular moisture has been evaporated and the water content has been reduced from ~43% in the fresh coal to ~11% and only the intrinsic water was not evaporated by the process.

The total enthalpy of evaporation of the water in the HA lignite coal is ΔH=41.2 kJ/mole water which is very similar to the heat of evaporation of liquid water:
□H 40.25 kJ/mole water found in the literature[22-29] and this result indicates that the interaction of the moisture content in the HA coal with the coal macromolecule is the same as that of liquid water, namely that of the hydrogen bonds.

The value is much larger than the hydrogen bonds occurring in liquid water and may point out that partial chemical bonds are formed between the water molecules and the coal macromolecule inside the pores.

The source of this strong interaction stems probably from the much larger aromatic nature of the bituminous coal compared to the lignite coal. The water molecules have a very strong interaction with the coal surface in the pores which is much larger than the hydrogen bonds occurring in pure water. The enthalpy of evaporation is 3 times higher than that of liquid water.

4. CONCLUSIONS

Definitely, the study reported here has shown that the combined TGA/DSC is a very powerful analytical system that can be used in addition to other commonly used techniques in order to evaluate the chemical stability of different coals towards its' reactivity with atmospheric oxygen via the LTO (Low Temperature Oxidation) process and might help in elucidating better improved storage maintenance of coals in the yards of utilities.

Furthermore, it supplies an accurate determination of the moisture content in the coal to be used in a combustion process including the energy needed for the evaporation process. This property is important for the actual efficient operation of coal combustion in utilities.

Surprisingly, the TGA/DSC analysis has proved that there is a very strong interaction between the water adsorbed in the bituminous BA coal whereas the evaporation process in the lignite coal is the same as that of pure water. This result stems probably from the much larger interaction of the adsorbed water in the pores of the bituminous coal with the much higher aromatic nature compared to the lignite coal where most of the water occurs outside the pores and thus the main interaction is due to hydrogen bonds between the water molecules.

Also, there is good correlation between the gas chromatographic results, determined in the gas phase and the thermogravimetric results concerning mass changes occurring in the coal as a result of the LTO processes.

The combined TGA/DSC experiments have revealed an exothermic process which occurs during the evaporation process of moisture in the BA bituminous coal and this finding has corroborated the suggestion that the molecular hydrogen emission as part of the LTO process is the source of hydroperoxide coal surface groups with formaldehyde to yield dioxirane which decomposes to yield molecular hydrogen.

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