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# MECHANISM OF MOLECULAR HYDROGEN EMISSION FROM COAL DURING THE SELF-HEATING PROCESS: A TGA/DSC STUDY

Aviv Hassid<sup>1</sup>, Steffen Krzack<sup>2</sup> and Haim Cohen<sup>\*1</sup>

<sup>1</sup>Department of Chemical Sciences, Ariel University, Ramat HaGolan St 65, Ariel, Israel.

<sup>2</sup>Institute of Energy Process Engineering and Chemical Engineering, TU Bergakademie

Freiberg, Akademiestraße 6, 09599 Freiberg, Germany.

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\*Corresponding Author Haim Cohen Department of Chemical Sciences, Ariel University, Ramat HaGolan St 65, Ariel, Israel.

# ABSTRACT

Coals (Lignite and Bituminous), are a major source of energy worldwide and also its utilization is a source of environmental hazards. Upon exposure to the atmosphere post mining or during storage, these coals undergo exothermic LTO (Low Temperature Oxidation) process by atmospheric oxygen, that diminishes their calorific value and involves emission of toxic and flammable gases, endangering people and environment. It may lead to self-heating and potentially to fire eruptions if the temperature exceeds 300°C. One of the most hazardous

released gases is  $H_2$ , released in Bituminous coals but not in Lignite. Thus, unexplained explosions in underground coal mines where no accumulation of coal dust, methane, or carbon monoxide was reported (the common source of explosions), could stem from hydrogen accumulation. It was suggested that  $H_2$  release from coal hydroperoxides oxidation of formaldehyde produce unstable dioxirane which decomposes to hydrogen and carbon dioxide. The combined TGA (Thermal Gravimetric Analysis) /DSC (Differential Scanning Calorimetry) unit is a new and unique technique to follow the LTO process, it corroborated the suggested mechanism and provided critical insights into the thermal processes and mechanisms involved in the  $H_2$  generation via the LTO process. This emphasizes the importance of the TGA/DSC in studying complex chemical and thermal reactions.

**KEYWORDS:** Bituminous coal, Lignite coal, Low Temperature Oxidation, combined TGA/DSC, H<sub>2</sub> emission from coal, Dioxirane from Formaldehyde.

# 1. INTRODUCTION

Lignite and Bituminous coals are the 2 main solid fossil fuels used for power production and the steel industry<sup>[1]-[3]</sup> and probably will stay as an important source<sup>[4]</sup> in the next decades until green energy sources that can compete economically with them will be developed. From the moment that the mined coal is exposed to the atmosphere, low temperature oxidation processes (LTO) begin to occur, in a temperature range between room temperature and approximately 150°C, which reduce the quality of the coals to be used as energy source.<sup>[5]-[9]</sup> The rate of these processes is dependent on the chemical nature of the coal macromolecule. The coal macromolecule main constituent is carbon C, but it contains also hydrogen H, oxygen O, nitrogen N, sulfur S and some moisture and inorganic matter.<sup>[10]</sup> The organic structure is composed of aromatic rings (which is the source of the black color of the coal) but also several organic functional groups<sup>[10]-[16]</sup> such as aliphatic -C-H bonds, aldehydes - CH=O, amines -NH, thiols -SH, alcohols -OH groups, carbonyls C=O and this is just a short list. The LTO process is the result of the gas/solid reactions of atmospheric oxygen O<sub>2</sub>, with the coal macromolecule.

The lignite coal is much more reactive than the bituminous coal and thus can't be stored and has to be used immediately post the mining process.<sup>[17]-[20]</sup> This is the reason that the utilities have to be in the vicinity of the mine. The source of the LTO higher reactivity of the lignite is the much higher content of the more reactive aliphatic -C-H groups compared to the more stable aromatic -CH groups.

In contrast, the lower LTO reactivity of bituminous coals enables long storage periods and thus it can be transported over large distances by trains or ships and stored in the yards of the utilities for months or even years.<sup>[21]</sup> Thus, for example Israel which has no coal resources is using coal as an important source for electricity supply.<sup>[22]</sup> In order to obtain safe supply, the 2 large utilities in Israel have several months coal supply which is stored in the yards of the utilities under open air in large piles.

The overall LTO process is an exothermic process and if the heat dissipation from the coal pile where the coal is stored, is lower than the heat release via the LTO process, self-heating of the pile and formation of hot spots can occur. In extreme cases if the temperature of the hot spot in the pile exceeds 300°C, self-ignition and fire eruption will rise.<sup>[23]-[26]</sup> Indeed, in the 2 coal storage yards of Israel Electric Corp., in Hadera and Ashkelon several small fires erupted in the past.<sup>[8],[27]</sup> and it continues to be a safety treat, Fig 1.



Fig 1: Fire at Rutenberg Coal Fired Power Station, Ashkelon, Israel (November, 2008).

The self-heating process and fires cause maintenance problems which result in higher operational costs to the utility.

The LTO process is consisted of the following steps<sup>[12]-[14], [20], [28], [29]</sup>, Scheme 1:

1. Physical absorption of  $O_2$  inside the pores of the coal:

 $\text{Coal} + \text{O}_2 \xrightarrow{\phantom{a}} \text{O}_{2(\text{ads})}$ 

2. Chemisorption of the adsorbed oxygen:

 $O_{2(adsorbed)} \rightarrow O_{2(chemisorbed)}$ 



3. Chemisorbed oxygen decomposition to surface oxides

 $O_{2(chemisorbed)} \rightarrow Surface oxides$ 



4. Surface Oxides  $\rightarrow$  Oxidation products (mainly CO<sub>2</sub>)

Scheme 1: Mechanism of LTO process in coal.

The main product of decomposition of the surface oxides is carbon dioxide but also some secondary reactions result in release of much smaller amounts of toxic and fire hazardous gaseous product such as carbon monoxide, CO and low molecular weight hydrocarbons<sup>[12]-[14]</sup>  $C_nH_m$  (mainly methane, CH<sub>4</sub>) and ethylene. Also, the emission of these gases is temperature dependent and increases appreciably when the temperature is higher than 80°C.

Steps 3 and 4 are composed of course of several complex reactions which result in the final different products.

If the coal storage post mining is in confined storage facilities (such as bunkers or ship holds during the marine transport of the coal), risks of explosions because of accumulation of explosive gases such as methane or carbon monoxide above the LEL (Lower Explosion Limit) or coal dust in air might occur. Indeed, the main concern is in the operation in underground mines and thus, methane and carbon monoxide monitors are posted in the mines to give alarm if the concentrations are increased and also appropriate ventilation is carried out including filtering of the dust formed during the mining processes. Sampling inside self-heated coal piles indicated indeed the presence of carbon monoxide and low molecular weight hydrocarbons.<sup>[5]</sup>

In 1991 the first report<sup>[30]</sup> appeared to suggest that emission of molecular hydrogen  $H_2$ , as a result of secondary reaction, accompanies also the LTO process in bituminous coals and that in simulation reactors it is observed that the amount of the hydrogen produced is relative to the amount of molecular oxygen O<sub>2</sub>, consumed by the LTO process. This is quite a surprising finding, because molecular hydrogen is a reduction process product, whereas the LTO is an oxidation process. The laboratory studies<sup>[31]-[33]</sup> have shown that the hydrogen gas released during self-heating of coal occurs only in bituminous coals but not in lignite coals.

The fact that no former report was published earlier was probably, because no effort was done to analyze molecular hydrogen while sampling gases in self-heated coal piles in storage. In order to have the answer to this question we have sampled the gasses inside hot spots occurring in coal piles in Orot Rabin coal utility and found that indeed molecular hydrogen is also produced in the samples using mass spectrometry to analyze it.<sup>[8]</sup>

This observation indicates that hydrogen gas accumulation in mines or confined spaces containing coal could be another cause of explosion. Indeed, some unexplained explosions did occur in well ventilated (no dust accumulation) coal mines in which installed methane and carbon monoxide detectors didn't show any increase in the concentrations of these gases prior to the explosion.<sup>[34],[35]</sup> If the hydrogen content accumulated to >4.1% (LEL in air) this might have been the source of these unexpected explosions.

In order to determine the source of the  $H_2$  release and the chemistry involved, a research effort has been carried out to determine the mechanism by which it is produced in conjunction with the LTO process. Namely, to understand why the amounts of hydrogen gas released (reduction product) is correlated to the amounts of oxygen consumed (oxidation reaction).

A possible source for the hydrogen gas formed during the LTO process is the unstable cyclic dioxirane intermediate,  $H_2CO_2$ , which has been reported<sup>[36]-[38]</sup> to be formed via ozonolysis of carbon double bonds (e.g. from ethylene) and decomposes to carbon dioxide and molecular hydrogen<sup>[39]</sup> (reaction (4), see below) and has been determined using infrared spectroscopy. It has been suggested that oxidation of formaldehyde via strong oxidizing reagents like hydroperoxide occurs via the formation of dioxirane<sup>[31], [40]</sup> as an intermediate.

The following suggestion for the mechanism was given:

During steps 1-3: Scheme, one of the surface oxides produced is the hydroperoxide - OOH at the surface of the coal macromolecule.

Also, during the heating of the coal some formaldehyde (which is known to be found adsorbed in the coal<sup>[5]</sup>), is released.

It was reported<sup>[20], [31]</sup> that during the oxidation of formaldehyde by strong oxidation reagent (hydroperoxides) the dioxirane ring,  $H_2CO_2$  is formed and it can decompose either to carbon dioxide and molecular hydrogen (and this is the source of the molecular hydrogen accompanying the LTO process in coal) or serve as a hydrogenation reagent of organic double bonds to yield hydrocarbon and carbon dioxide.

Namely, the mechanism by which  $H_2$  is produced via the LTO process is dependent on the amount of dioxirane formed. The dioxirane is formed by oxidation of formaldehyde by hydroperoxide groups which are formed by the LTO process and thus the amount of

dioxirane is linear to the amount of -O-O-H groups formed. And the amount of the hydroperoxide groups is linear to the amount of consumed molecular atmospheric oxygen which reacts with the coal via the LTO process inside the pores.<sup>[41]</sup> The larger the pores, the higher the amount of oxygen absorbed and contribute to the LTO process. Thus, the amount of hydrogen produced (a reduction product) will be linearly dependent on the amount of the consumed oxygen (an oxidation reagent).

The research has shown<sup>[20],[31]</sup> that indeed formaldehyde in the presence of bituminous coal is oxidized by hydrogen peroxide to yield carbon dioxide and molecular hydrogen. The kinetics of the reaction has been studied and indeed the reaction is pseudo 1<sup>st</sup> order in formaldehyde concentration and also in molecular oxygen partial pressure. The activation energy was also determined in the temperature range 55-115°C.<sup>[28],[42]</sup>

The dioxirane decomposition is exothermic, and thus heat release will occur during the process. However, no information on the rates and the temperature effects has been obtained on the hydrogen production reaction during the self-heating of bituminous coals. Also, no estimates of the amounts of formaldehyde release from the bituminous coal could be obtained.

However, no direct evidence for the exact parameters affecting the suggested reaction (e.g. temperature effects, dioxirane concentration, the amounts of emitted formaldehyde from the self-heated coal via the LTO process etc.) was reported so far.

Recently, the combined TGA (Thermal Gravimetric Analysis) /DSC (Differential Scanning Calorimetry) unit has been utilized<sup>[6]</sup> as an efficient tool to analyze coal properties and also to determine mass changes and energetic processes which accompanies the LTO process of Lignite<sup>[43]</sup> and bituminous coals. This technique might shed light on the suggested mechanism to produce  $H_2$  via the LTO process. Getting a better insight into the mechanism of hydrogen emission from coal, might lead into finding ways to reduce and inhibit the release of these toxic and flammable gases, and reduce the hazards of self-ignition of coal and the occurrence of explosions in coal mines.

During this study an exothermic process which has been observed, is probably another experimental evidence, that corroborates the mechanism suggested to explain the reaction pattern that is the source of molecular hydrogen emission from bituminous coals upon the exposure of coal to air atmosphere.

We have decided to check in detail the process that leads to the formation of the molecular hydrogen during the LTO process and to verify the energetics and quantitative amounts of formaldehyde and dioxirane formed in this process. As no hydrogen emission is observed in lignite coals the study is focused of a typical bituminous coal Bailey American coal used in Israeli utilities.

The results of the thermal methods adopted to study the LTO process of coal also give quantitative measures to the amounts of formaldehyde released from bituminous coal during the process of self-heating of the coal during storage and the temperature effect as well as to the rates of the reaction.

## 2. EXPERIMENTAL

## Materials

Coals- The coal used for this study is a bituminous American coal (Pittsburgh No. 6) produced by Bailey Co. (denoted as BA) and it is used in coal utilities for power production. Its elemental analysis is: Carbon content 75.11%, Hydrogen content 3.23%, Oxygen content 10.92%, Nitrogen content 1.68% (based on DFW dry ash free coal) and calorific value of 26 kJ/Kg.<sup>[6]</sup> In order to compare the bituminous coal to lignite coal, a German lignite coal from Hambach (denoted as HA) and is used in German utilities. It's elemental analysis is: Carbon content 64.64%, Hydrogen content 4.55%, Oxygen content 24.14%, Nitrogen content 0.79% on DFW dry ash free coal) and calorific value (based of 16 kJ/Kg. The coal types chosen for the study are typical to lignite coals used (in Germany) and worldwide for power production.

The coals were stored in sealed containers under nitrogen atmosphere and have been used as is, fresh without any treatment.

In a recent publication<sup>[6]</sup>, the properties of the different coals were determined using the combined TGA/DSC technique. The properties of the different coal samples are given in Table 1.

| Ash DF [%] | Volatile gases DF [%] | Moisture [%] | Coal type |
|------------|-----------------------|--------------|-----------|
| 8.09       | 21.14                 | 3.13         | BA fresh  |
| 7.46       | 50.79                 | 43.6         | HA fresh  |

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).

# Methods

The coals have been analyzed with the Netzsch combined TGA/DSC model STA 449C unit in air atmosphere.

The combined TGA/DSC device is a tool for diagnosing and analyzing processes that occur in a material under different temperature conditions.

The direct measurement in TGA is the measurement of the mass of the sample as a function of time/temperature: when the sample is exposed to a variable/constant temperature under a certain gas environment, it undergoes chemical/physical processes (such as oxidation, adsorption, drying, decomposition) responsible for mass increase/decrease.

The DSC device works in parallel with the TGA. Using this device, one can measure the heat emission/absorption at any temperature occurring in the sample during the process in question and can check whether the process is endothermic (such as moisture) or exothermic (such as the oxidation process).

As discussed in an earlier publication<sup>[6]</sup>, the TGA/DSC enables experiments with relatively small samples (in this case 38.82-50.64 mg).

In a typical LTO (Low Temperature Oxidation) experiment in the thermal analyzer, the coal sample is heated from 30°C to an isothermal temperature of 115 °C/ 95 °C/ 65 °C (the latter 2 target temperatures, as stated in the article, were performed in order to compare it to the measurements of the LTO at 115 °C), the heating rate was 10 °C/min, (8.5 minutes duration) and then, kept isothermally for 24 hours. Each analysis was performed 3 times to validate our result.

The temperatures ranges for the experiments were chosen because as mentioned in the introduction, the LTO occurs in the temperature between room temperature up to 150°C (at a higher temperature the rate increases very fast approaching self ignition of the coal.

In addition a second thermal unit (Mettler Toledo, model STARe TGA/DSC 1, GC100) was also used in order to validate the results.

Every experiment was carried 3 times in order to have good reproducibility and validity of of the results. The accuracy of the TGA/DSC unit in determination of the mass is 0.1  $\mu$ g and the DSC accuracy is <1  $\mu$ W.

NETZSCH SOFTWARE Proteus<sup>®</sup> 6.1.0 was used to analyze the TGA/DSC graphs. The units of the mass axis of the TGA graph were mass % and the units of the heat emission/absorption axis of the DSC graph were mW/mg.

In the 115 °C graphs the mass loss between 30°C and until stable mass was reached (12 min in the BA and 18min in the HA) was calculated, in addition to the mass loss after 5 hours and 24 hours.

In the 115  $^{\circ}$ C and the 95  $^{\circ}$ C graphs, were it was found an exothermic process during the final stages of the moisture evaporation, the area of the exothermic process was calculated in order to calculate the value of the exothermic process.

# 3. RESULTS AND DISCUSSION

The simulation experiments of the LTO process in the BA bituminous coal have been carried out during 24 hours. A 41.01 mg BA coal has been heated in air atmosphere (air flow rate of 25ml/minute) from 30 to 115°C at 10°C/minute heating rate and after reaching the desired 115°C kept isothermally for 24 hours measuring the mass changes and heat emission/absorption events during the LTO period, Fig 2a.



Fig 2: The thermal/mass changes (the combined TGA/DSC) occurring during the LTO of 41.01mg BA bituminous coal sample at 115°C\* for a. LTO duration 24 hours b. The first 40mins LTO\*

\*During the first 8.5 minutes the sample is heated from 30 to 115°C and then kept isothermally----- TGA curve ------ DSC curve

The results indicate that during the whole process there is a slight increase of the sample mass, 0.11% due to the LTO process (which stems from formation of stable surface oxides in the coal via the LTO process). However, during the initial stages (first 23 minutes) there is an appreciable reduction in mass and also a simultaneous endothermic process. This is expected as the moisture content of the coal undergoes evaporation during the heating process of the coal from room temperature to 115°C. In order to follow accurately these processes, the first 40 minutes of the experiment are shown, Fig 2b.

As can be clearly seen, the initial mass reduction (moisture evaporation) occurs during the heating process of the coal from 30 to 115°C (the first 8.5 minutes) and the moisture content evaporated is 2.32% (in good accordance with the coal moisture content, Table 1 in the experimental section). The evaporation process is endothermic as expected. However, the DSC curve indicates that in addition to the endothermic event there is an exothermic process which occurs also at the final stages of the moisture evaporation. Whereas the endothermic process is due to the moisture's evaporation (mass reduction), the exothermic process is not accompanied by any observed appreciable mass changes.

In order to determine if a parallel situation occurs also in a lignite coal, we have repeated the experiment with HA German lignite coal, Fig 3.



Fig 3: The thermal/mass changes (the combined TGA/DSC) occurring during the LTO of 40.76mg HA Lignite coal sample at 115°C\* for a. LTO duration 24 hours b. The first 40mins LTO\*

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\*During the first 8.5 minutes the sample is heated from 30 to 115°C and then kept isothermally ------TGA curve -----DSC curve

In the lignite coal, no exothermic event is observed, only the evaporation of the moisture, Fig 3b, and the evaporation process is terminated at ~12 minutes in which the moisture content, 44.6%, is evaporated (also, in good accordance with the coal moisture content, Table 1 in the experimental section).

Namely, there is a basic difference between the lignite HA coal and the bituminous BA coal.

In several studies reported<sup>[20], [26], [30]</sup> in our group, the basic differences in the LTO process in bituminous compared to lignite coal are:

- 1. In bituminous coals the LTO process results in mass increase due to the fact that only partial percentage of the surface oxides formed (Scheme 1, step 3) decompose and thus there is some increase in weight. Whereas, in the lignite coals, which are much more reactive, appreciable amounts of the oxygen content in the carbon dioxide released via the LTO process is that of intrinsic oxygen which is an inherent part of the coal macromolecule structure.
- 2. In the lignite coals there is no release of molecular hydrogen which accompanies the LTO process (Scheme 1, step 4: see above and reactions 1-4: see below).

Thus, we have decided to explore further and check if the exothermic event could be due to the process of molecular hydrogen release from bituminous coals.

The first evaluation that should be carried out is to separate between the exothermic and endothermic processes and determine the amount of heat (exothermic or endothermic release) of these two processes. In order to differentiate between the endothermic and the exothermic process it is assumed that the endothermic event should have an unsymmetrical bell-shaped curve (like that found in the case of the HA lignite coal) and have drowned a hypothetical curve, Fig 4.



Fig 4: Hypothetic endothermic curve of the evaporation process of a 41.01mg BA coal at 115°C.

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

The value of the extra exothermic process according to Fig 4, is equal to the area which is marked in the blue lined area and is calculated to be 50.14 J/gram coal.

The molecular hydrogen produced is of course a reduction product. However, the LTO process is an oxidation process and thus this is an unusual situation that should have a reasonable explanation. Furthermore, it is reported<sup>[6], [19]</sup> that the amount of H<sub>2</sub> produced (reduction process) is relative to the amount of O<sub>2</sub> consumed (oxidation process) by the LTO process!.

The suggested mechanism<sup>[20],[26],[31]</sup> for the molecular hydrogen production which accompanied the LTO process which explains the results is as follows:

- i. One of the emitted compounds which occurs during the self-heating process of the coal (because of the LTO process) is formaldehyde H<sub>2</sub>CO.<sup>[5]</sup>
- ii. During the LTO process formation of several surface oxides does occur. One of the surface oxides produced during the process is the hydroperoxide groups -C-O-O-H<sup>[31]</sup> and the amount produced is relative to the amount of O<sub>2</sub> consumed.
- iii. The emitted formaldehyde reacts with the hydroperoxide groups to produce the dioxirane ring (a well-known compound, formed during the decomposition of formaldehyde contaminated atmosphere.
- iv. The dioxirane is an unstable compound which decomposes via a strong exothermic reaction to molecular hydrogen and carbon dioxide.

Namely, the following mechanism is responsible for the  $H_2$  produced during the LTO process:

(1) 
$$O_2 + Coal - H \longrightarrow_{Coal} O_{OH}$$
  
(2)  $Coal - A \longrightarrow_{Coal} Coal + H_2CO$   
(3)  $H_2CO +_{Coal} O_{OH} \longrightarrow_{Coal} O_{OH} + H_2C O_{OH}$   
(4)  $H_2C O_{O} \longrightarrow_{CO_2 + H_2} O_{OH}$ 

Thus, the source of the exothermic event observed is probably the exothermic decomposition of the dioxirane and the enthalpy of decomposition is reported<sup>[44]</sup> to be  $\Box$ H=-415.9 kJ/mol.

As the value of the exothermic event observed was calculated to be 50.14 J/gr coal, the amount of molecular hydrogen released will be  $50.14/415,900 = 1.21*10^{-4}$  mole/gram BA coal.

In order to check if the same type of exothermic process occurs also at lower temperatures, we have carried out the LTO experiments at lower temperatures, 95°C, Fig 5a, and 65°C, Fig 5c.





Fig 5: LTO (using TGA/DSC) of BA coal at lower temperatures. a. 50.64 mg fresh BA coal sample at 95°C in air atmosphere. b. Hypothetic endothermic curve of the evaporation process of the BA coal sample at 95°C. c. 38.82 mg fresh BA coal sample at 65°C in air atmosphere.

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

As can be clearly seen, Fig 5a, the exothermic process occurs also at  $95^{\circ}$ C but there is no trace of this event at  $65^{\circ}$ C, Fig 5c. Namely at this temperature, there is no release of formaldehyde and no formation of dioxirane.

This is also supported by recent publication<sup>[13], [43], [45]</sup> where it was found that at 60-70°C and below, the oxidation process is slower and the higher the temperature, the amounts of the  $H_2$  produced is increased due to a faster LTO process.

This finding is also supported by other publications<sup>[46],[47]</sup>, where it was stated that the formaldehyde presence is correlated to the release of molecular hydrogen, a process which occurs mainly via the LTO process, and at T>100°C there is a significant increase in its formation.

In order to determine the size of the exothermic process at 95°C the same evaluation carried out for the 115°C temperature, was done and the value of the extra exothermic process, Fig 5b, was calculated to be 44.09 J/gram coal compared to the 50.14J/gram coal at 115°C.

Namely the amount of dioxirane formed at  $95^{\circ}$ C is:  $44.09/415,900 = 1.06*10^{-4}$  mole/gram BA coal.

This result is reasonable as it is expected that at a lower temperature the amount of released formaldehyde from the heated coal is temperature dependent and it will be smaller.

It is also interesting to compare the reported values of released molecular hydrogen in batch reactor studies to the amounts of dioxirane produced in the combined TGA/DSC unit as calculated from the experiments carried out in the present thermal instrumentation of the combined TGA/DSC unit. The amount of H<sub>2</sub> produced in 120ml reactors in air with 0.500 grams of BA coal containing  $9.0*10^{-3}$  moles of O<sub>2</sub> at  $95^{\circ}$ C with BA coal is 646ppmv.<sup>[20]</sup> Converting the amount from the ppmv value to moles per gram coals, a value of  $6.9*10^{-6}$  moles H<sub>2</sub>/gram BA coal is calculated.

The dioxirane formed can decompose to carbon dioxide and molecular hydrogen via:

$$H_2C \swarrow 0 \longrightarrow CO_2 + H_2$$

But it can also serve as an efficient hydrogenation reagent to the double bonds occurring in the coal macromolecule via



The amount of molecular hydrogen produced via the dioxirane decomposition,  $6.9*10^{-6}$  moles H<sub>2</sub>/gram BA coal, is much smaller compared to the calculated amount of dioxirane formed,  $1.06*10^{-4}$  moles/gram BA coal. This result indicates that most of the dioxirane (formed via the oxidation of coal released formaldehyde by hydroperoxide groups) serves as a hydrogenation reagent with the coal macromolecule. This is reasonable, as the dioxirane molecule is formed at the surface of the coal macromolecule and in order to decompose to molecular hydrogen it has to diffuse outside from the surface of the coal macromolecule prior to decomposition to hydrogen and carbon dioxide. Furthermore, the double bond content in bituminous coals is quite high, Fig 6.



Fig 6: A scheme suggested to represent the bituminous coal macromolecule structure.<sup>[6],[26]</sup>

The double bonds are marked with orange.

The above scheme also get validation from previous measurements other groups done to determine the functional groups and aliphatic/aromatic bonds in coal.<sup>[48], [49]</sup>

The fact that no molecular hydrogen is formed during the LTO of the lignite HA coal could stem from 2 possible reasons:

- i. During the self-heating of the lignite coal there is no emission of formaldehyde which is the precursor to the dioxirane intermediate which decomposes to carbon dioxide and hydrogen.
- ii. Dioxirane is formed via the same mechanism which occurs with the BA bituminous coal but as the active double bond content available for hydrogenation in the lignite coal macromolecule is much higher, all the dioxirane reacts via the hydrogenation path, reaction (5) and thus no molecular hydrogen is formed.

The second reason is more reasonable in our opinion as the LTO reactivity of lignite coal is much higher than that of the bituminous coal.

## 4. CONCLUSIONS

The results of this study show definitely the importance of the combined TGA/DSC instrument as an additional very valuable tool that can help appreciably in determination of complex mechanisms and help in appropriate operational conditions in order to prevent environmental hazards such as explosions in underground coal mines or confined coal storage facilities.

Not only that it corroborated the suggested mechanism which explained the formation of molecular hydrogen,  $H_2$  (a reduction product) via the Low Temperature Oxidation of coals (oxidation reaction) but moreover, it added very important information concerning the hydrogen evolution reaction mechanism, which can explain explosions in underground coal mines where no methane, carbon monoxide or dust accumulation has been reported prior to the explosion:

- 1. It showed that the formation and decomposition reactions of the dioxirane occurred at relatively low temperatures (at 95 and 115°C), but it is inhibited if the temperature is kept at 65°C or lower.
- It gave information on the amounts of formaldehyde that is released from the BA bituminous coal during the self-heating of the BA bituminous coal via the Low Temperature Oxidation of the coal during storage.
- 3. It showed that most of the dioxirane formed serves as a hydrogenation reagent of the coal macromolecule and didn't decompose to yield hydrogen and carbon dioxide.
- 4. It gives good estimates to the rate of the oxidation of the formaldehyde which is relatively fast and occurs in few minutes at 95-115°C.
- 5. The utilization of the combined TGA/DSC unit enabled for the first time to estimate the amount of formaldehyde absorbed inside the coal pores and of course the amount of dioxirane produced.
- 6. It is recommended that in confined spaces containing bituminous coals (including underground coal mines, bunkers or coal ships holds) hydrogen detectors should be installed in order to determine and alarm if hydrogen accumulation is occurring in these installations in order to avoid potential explosion risk stemming from this process.

## **Declaration of competing interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

All data is presented in the article. Any further data will be made available upon request to the corresponding author.

#### **CRediT** authorship contribution statement

Aviv Hassid: Writing – original draft, Writing - review & editing, Investigation, Formal analysis.

Haim Cohen. Corresponding author: Writing - review & editing, Supervision.

Steffen Krzack: Supervision.

## 5. REFERENCES

- Shah A. K. a, Combustion Engineering and Fuel Technology, Oxford & IBH Publishing Company, New Delhi, 1974.
- Unsworth J. F. Barratt D and R. T. Roberts. Coal Quality and Combsution Performance, An International Perspective, Elsevier, Amsterdam, 1991.
- Kural O., Coal Resources, Propertieas, Utilization, Pollution, Library of Congress, Washington, 1994.
- 4. IEA International Energy Agency, Coal 2023 Analysis and forecast to 2026, IEA publication, 2023; 1-130.
- Nelson, C. R., Chemistry of Coal Weathering; Ed.; Elsevier: Amsterdam, The Netherlands, 1989.
- Hassid, A., Klinger, M., Krzack, S., & Cohen, H. TGA-DSC combined coal analysis as a tool for QC (quality control) and reactivity patterns of coals. *ACS Omega*, 2022; 7(2): 1893-1907. » http://dx.doi.org/10.1021/acsomega.1c05296
- Wu, M. M.; Robbins, G. A.; Winschel, R. A. Burke, F. P. Low-temperature coal weathering: its chemical nature and effects on coal properties. *Energy & Fuels*, 1988; 2: 150–157. https://doi.org/10.1021/ef00008a009
- Green U., Aizenshtat Z., Metzger L. and Cohen H. Field and Laboratory Simulation Study of Hot Spots in Stockpiled Bituminous Coal. *Energy & Fuels*, 2012; 26(12): 7230-7235. https://doi.org/10.1021/ef301474t
- Liotta, R.; Brons, G.; Isaacs, J. Oxidative weathering of Illinois No.6 coal. *Fuel*, 1983;
   62: 781. https://doi.org/10.1016/0016-2361(83)90028-5

- Van Krevelen, D. W. Coal: Typology, Chemistry, Physics, Constitution, 5<sup>th</sup> ed.; Elsevier: Amsterdam, The Netherlands, 2005.
- Smith K. L., Smoot L. D., Fletcher T. H. and Pugmire R. J. The Structure and Reaction Process of Coal. Plenum Press, 1994.
- Jiawen Cai, Shengqiang Yang, Wancheng Zheng, Wanxin Song, Rajender Gupta. Dissect the capacity of low-temperature oxidation of coal with different metamorphic degrees. *Fuel*, 2021; 292: 120256. https://doi.org/10.1016/j.fuel.2021.120256.
- Xin-xiao Lu et al. An novel experimental study on the thermorunaway behavior and kinetic characteristics of oxidation coal in a low temperature reoxidation process, *Fuel*, 2022; 310: Part B, 122162, https://doi.org/10.1016/j.fuel.2021.122162.
- Chengyong Wang et al. Chemical Structure Characteristics and Model Construction of Coal with Three Kinds of Coalification Degrees, ACS Omega, 2024; 9(1): 1881-1893. DOI: 10.1021/acsomega.3c08574.
- Schobert H. H., Bartle K. D. Lynch L. J. Coal Science. ACS Symposium Series, 1991;
   461.
- H. Wang, B. Z. Dulgogorski and E. M. Kennedy. Thermal decomposition of solid oxygenated complexes formed by coal oxidation at low temperatures. *Fuel*, 2002; 81(15): 1913-1923. https://doi.org/10.1016/S0016-2361(02)00122-9
- 17. Taub, T., Hassid A., Ruthstein S., and Cohen H.. Mechanism underlying the emission of gases during the low-temperature oxidation of bituminous and lignite coal piles: The involvement of radicals. *ACS Omega*, 2020; 5(44): 28500. doi:10.1021/acsomega.0c02841
- Green U. et al. Elucidating the role of stable carbon radicals in the low temperature oxidation of coals by coupled {EPR-NMR} spectroscopy - a method to characterize surfaces of porous carbon materials.. *Phys. Chem. Chem. Phys.*, 2014; 16: 9364–9370.
- Solomon, P. R. In New Approaches in Coal Chemistry; ACS Symposium Series, Vol. 169, American Chemical Society: Washington, DC, 1981.
- 20. Hassid, A, Krzack, S., Cohen, H.. TGA-DSC Analysis As a Tool for Evaluating the Low Temperature Oxidation of Coals. *WJERT*, 2024; 10(9): 64-90.
- 21. S. Davidi, S. L. Grossman and H. Cohen. Organic volatiles emissions accompanying the low-temperature atmospheric storage of bituminous coals, *Fuel*, 1995; 74(9): 1357–1362.
- 22. IEA. IEC Report on the State of the Electricity Sector. (2023). https://www.gov.il/BlobFolder/generalpage/dochmeshek/he/Files\_doch\_meshek\_hashmal \_IEC\_AnnualReport\_2022\_nnn.pdf accessed: September 2024.

- 23. O'Keefe J.M.K. et al. Old Smokey coal fire, Floyd County, Kentucky: Estimates of gaseous emission rates. *Int. J. Coal Geology*, 2011; 87: 150-156. https://doi.org/10.1016/j.coal.2011.06.005
- 24. Engle M.A et al. Gas emissions, minerals, and tars associated with three coal fires, Powder River basin, USA. *Science of the Total Environment*, 2012; 420: 146–159. 10.1016/j.scitotenv.2012.01.037.
- Grossman, S. L., Davidi, S., & Cohen, H.. Molecular hydrogen evolution as a consequence of atmospheric oxidation of coal: 1. Batch reactor simulations. *Fuel*, 1993; 72(2): 193-197.
- 26. Z. Aizenstat, U. Green, S. Stark, C. Weidner, and H. Cohen. Modes of formation of carbon oxides (COx (x = 1,2)) from coals during atmospheric storage: Part i effect of coal rank. *Energy & Fuels*, 2010; 24(12): 6366–6374.
- 27. IEC. The Israel Electric Corporation Ltd. Financial Reports for 2023. IEC. https://ieccontent.iec.co.il/media/eiyjpekg/the\_israel\_electric\_cofinancial\_reports\_december\_31\_2023.pdf. Accessed September 2024.
- 28. Uri Green, Zeev Aizenshtat, James C. Hower, Rachel Hatch, and Haim Cohen. Modes of Formation of Carbon Oxides [COx (x = 1 or 2)] from Coals during Atmospheric Storage. Part 2: Effect of Coal Rank on the Kinetics. *Energy & Fuels*, 2011; 25(12): 5626–5631. https://doi.org/10.1021/ef2012479
- 29. Grossman S.L, Davidi S., Sokolov K. and Cohen H. Proc, 8<sup>th</sup> Int. Conf. Coal Science, 1995; 1: 473.
- 30. Grossman, S.L., Davidi, S. and Cohen, H. Evolution of molecular hydrogen during the atmospheric oxidation of coal. *Fuel*, 1991; 70(7): 897-897. *https://doi.org/10.1016/0016-2361(91)90202-L*
- Grossman S.L., Wegener I., Wanzl W., Davidi S. and Cohen H. Molecular hydrogen evolution as a consequence of atmospheric oxidation of coal: 3. Thermogravimetric flow reactor studies. *Fuels*, 1994; 73(5): 762-767. https://doi.org/10.1016/0016-2361(94)90021-3
- 32. Nehemia, V., Davidi, S., & Cohen, H. Emission of hydrogen gas from weathered steam coal piles via formaldehyde as a precursor: I. Oxidative decomposition of formaldehyde catalyzed by coal – batch reactor studies. *Fuel*, 1999; 78(7): 775-780.
- 33. Cohen, H., Green, U.. Oxidative Decomposition of Formaldehyde Catalyzed by a Bituminous Coal. *Energy & Fuels*, 2009; 23(6): 3078–3082. https://doi.org/10.1021/ef9001583

- 34. Grossman S. L., Davidi S. and Cohen H. Emission of toxic and fire hazardous gases from open air coal stockpiles," *Fuel*, 1994; 73(7): 1184–1188.
- 35. Grossman S. L., Davidi S., Wegener I., Wanzl W. and Cohen H.. Explosion risks of bituminous coals in contact with air. Due to molecular hydrogen accumulation in confined spaces (underground mines and ship holds) - A hypothesis study. *Erdol Erdgas Kohle*, 1996; 122(7/8): 322-324.
- Lovas F.J., Suenram R. D. Identification of dioxirane (H<sub>2</sub>COO) in ozone-olefin reactions via microwave spectroscopy. *Chemical Physics Letters*, 1977; 51: 453-456.
- 37. Suenram R.D., Lovas F.J. Dioxirane. Its synthesis, microwave spectrum, structure, and dipole moment. Journal of The American Chemical Society, 1978; 100(68): 5117-5122. https://doi.org/10.1021/ja00484a034
- 38. Martinez R. I., Huie R. E. and Herron J. T. Mass spectrometric detection of dioxirane, H<sub>2</sub>COO, and its decomposition products, H2 and CO, from the reaction of ozone with ethylene. *Chemical Physics Letters*, 1977; 511977(3): 457-459. DOI: 10.1016/0009-2614(77)85399-2
- Cremer D., Kraka E., Szalay P.G. Decomposition modes of dioxirane, methyldioxirane and dimethyldioxirane—A CCSD (T), MR-AQCC and DFT investigation. *Chemical Physics* Letters, 1998; 292: 97-109)
- 40. Haiwie Li, Enhanced Degradation of Indoor Formaldehyde by Room Temperature Catalytic Reaction, PhD Thesis, 2019.
- 41. Aitao Zhou, Jingyu An, Kai Wang, Yiqiao Wang, Zhiyuan Xu, Yuexin Yang, Yida Wang, Characteristics of low-temperature oxidative heating and gas production in coal storage under forced convection: Influencing factors and mechanisms, Science of The Total Environment, 2025; 959: 178014, ISSN 0048-9697, https://doi.org/10.1016/j.scitotenv.2024.178014.
- 42. Fujitsuka, H., Ashida, R., Kawase, M., & Miura, K. Examination of Low-Temperature Oxidation of Low-Rank Coals, Aiming at Understanding Their Self-Ignition Tendency. Energy & Fuels, 2014; 28(4): 2402–2407. doi:10.1021/ef402484u ???
- 43. Zhang, X.et al. Influence of mudstone on coal spontaneous combustion characteristics and oxidation kinetics analysis. *Sci Rep.*, 2024; 14: 974. https://doi.org/10.1038/s41598-024-59797-8
- 44. Josep M, Anglada, Josep M. Bofill, Santiago Olivella, Albert Solé. Theoretical Investigation of the Low-Lying Electronic States of Dioxirane: Ring Opening to

Dioxymethylene and Dissociation into CO<sub>2</sub> and H<sub>2</sub>, *The Journal of Physical Chemistry A*, 2024; 102(19): 3398-3406. (1998) DOI: 10.1021/jp980501

- 45. Hao Liu, Zenghua Li, Yongliang Yang, Guodong Miao, Purui Li, Guoqin Wang, Effect of low-temperature pre-oxidation on the self-heating of coal, Fuel, 2024; 356; 129550. ISSN 0016-2361, https://doi.org/10.1016/j.fuel.2023.129550.
- 46. Wang, Y., Wu, J., Xue, S., Wang, J., & Zhang, Y. Experimental Study on the Molecular Hydrogen Release Mechanism during Low-Temperature Oxidation of Coal. Energy & Fuels, 2017; 31(5): 5498–5506. doi:10.1021/acs.energyfuels.6b024
- 47. Wang, Y., Wu, J., Xue, S., Wang, J., Zhang, Y., & Tang, Y. Hydrogen production by low-temperature oxidation of coal: Exploration of the relationship between aliphatic C H conversion and molecular hydrogen release. International Journal of Hydrogen Energy, 2017; 42(39): 25063–25073. doi:10.1016/j.ijhydene.2017.08.04
- 48. Qingmin Shi, Xinyue Zhao, Shuangming Wang, Hongchao Zhao, Ruijun Ji, Chunhao Li, Bingyang Kou, Jun Zhao, Differences in pyrolysis behavior and volatiles of tar-rich coal with various origins, Fuel Processing Technology, 2025; 268: 108181, ISSN 0378-3820, https://doi.org/10.1016/j.fuproc.2025.108181.
- 49. Zhou, C., Zhang, Y., Wang, J., Xue, S., Wu, J., & Chang, L. Study on the relationship between microscopic functional group and coal mass changes during low-temperature oxidation of coal. International Journal of Coal Geology, 171: 212–222. doi:10.1016/j.coal.2017.01.013