Mechanism Underlying the Emission of Gases during the Low-Temperature Oxidation of Bituminous and Lignite Coal Piles: The Involvement of Radicals

Tze'ela Taub, Aviv Hassid, Sharon Ruthstein, and Haim Cohen*

ABSTRACT: Coal is one of the major fuels for power generation, and it will continue in this capacity for the next several decades. Two types of coal are mainly used: lignite and bituminous coals. When exposed to air, post-mining, the coal surface undergoes LTO (low-temperature oxidation) at RT-150 °C according to the atmospheric oxygen level. The LTO process decreases the caloric value of the coal, and consequently, different gases are released [mainly carbon oxides (CO, CO₂), water vapor, hydrogen (H₂), and also some low molecular-weight organic gases (C₁−₅)]. Some of these gases are toxic and flammable. In extreme cases, fires erupt. The mechanism by which the molecular oxygen oxidizes the coal macromolecule at the temperature range of 30−150 °C (LTO process) is complex and also involves a chain of radical reactions; however, the exact underlying mechanism is not yet clear. The LTO process was studied in detail by simulating the processes occurring in the coal piles by using two coal types: an American Bailey coal, used in Israeli coal-fired utilities and a German Hambach lignite, used in German utilities. The mechanism underlying the LTO process and the radical reactions that are involved are discussed in detail.

INTRODUCTION

Coal is a very complex material comprising several organic macromolecules that also contain some inorganic components; the calorific value of coal largely depends on its rank (which is determined by the carbon content and the calorific value). Two main types of coal serve as fossil fuels: lignite and bituminous coals. Coal piles stored in open air are exposed to atmospheric oxygen and consequently undergo a low-temperature oxidation (LTO) process. This process (in the temperature range of RT-150 °C) consists of different types of chemical chain reactions that eventually emit gaseous products, mainly CO₂/H₂O but also smaller amounts of CO, C₁−₅ hydrocarbons, and H₂. An additional phenomenon that occurs during the LTO process is the self-heating of the coal piles (due to the exothermic reactions of the LTO process). In extreme cases, fires erupt in the coal piles.

As a result of the LTO process, the calorific value of the coal decreases, and the combustion profile of the coal to be used as fuel also changes; this often causes problems when operating power plants.

The exact mechanism underlying the LTO process has not yet been fully determined because it consists of many complex reactions; however, it definitely occurs at the surface of the porous coal particles, mainly inside the macropores, which are wide enough to allow the atmospheric oxygen (the oxidation reagent) to diffuse inside and the product gasses to be released from inside the pores.

The suggested mechanism of the LTO process consists of several stages, as described in Scheme 1:

1. Adsorption of atmospheric oxygen onto the coal surface (Stage A).
2. Conversion of physically adsorbed oxygen into chemically adsorbed oxygen (Stage B).
3. Decomposition of chemisorbed oxygen into surface oxides and hydroperoxide groups (Stage C).
4. Partial decomposition of surface oxides and hydroperoxide groups (Stage D).
5. Decomposition of carbon oxides and water vapor (Stage E).

The activation energy of the physically adsorbed and chemisorbed oxygen molecule is reduced appreciatively by the weakening of the double bond of the O=O molecule. Consequently, in the next stage, B, the decomposition process of the chemisorbed molecular oxygen results in the formation of surface oxides and hydroperoxide groups. These products continue to partially decompose until stage C, affording as major products low molecular-weight inorganic gases, such as carbon oxides (CO and CO₂), water vapor, and minor amounts of molecular...
intermediates, although there was no direct proof of this (usually, the radicals appeared as very short-lived, unstable intermediates).

Electron paramagnetic resonance (EPR) spectroscopic studies have shown that during the LTO process, stable carbon-based radicals in the oxidized coal in bituminous and lignite coals are formed. This proves that radicals exist as intermediates during the LTO process.

Liotta et al. have suggested that the radicals are formed when atmospheric oxygen attacks the coal; the oxidized coal is formed via radical reactions, as presented in Scheme 2.

The suggested mechanism, presented in Scheme 2, does not accurately describe the LTO process. For example, according to the above mechanism, the oxygen-centered radicals only result from the oxidation reaction of atmospheric O₂. Importantly, this does not take into account the formation of oxygen-centered radical sites that stem from the inherent oxygen content of the coal macromolecule structure (see Figure 2 below). Furthermore, the mechanism does not describe in detail the nature of the precursor functional groups that form the carbon- and oxygen-centered radicals. Moreover, according to this mechanism, the initiation stage results from C–H bond cleavage; this affords a carbon-centered radical C* and molecular hydrogen. Although it is produced by the secondary reactions, reaction (5b), H₂ is considered to be a reduction product that is formed from carbonaceous materials even at low temperatures, >308 K. In addition, the first initiation reaction (6), shown in Scheme 2, is not thermodynamically possible: the bond strength of the aliphatic C–H is ~1,882,800 J/kg and bonds will not break up in the low-temperature range of 303–423 K (the temperature range of the LTO process). Moreover, the products of reaction (10) (as CO* + OH and not CO₂* + C*) due to the cleavage of the peroxide group in the O–O–H bond).

Thus, in our opinion, the experimental results indicate that the chain reaction, in Scheme 2, should be modified.

On the other hand, as a result of the LTO process, studies using EPR spectroscopy have characterized different types of stable carbon-centered radicals. Figure 1 shows the EPR spectra of a stable carbon-centered radical (in bituminous coal), a carbon-centered radical adjacent to an oxygen atom (in lignite coal), and an aliphatic carbon-centered radical (found in both coals) formed via the LTO process.

A primary mechanism was suggested based on these findings; it is shown in Scheme 3.

This mechanism describes in detail the adsorption of the molecular oxygen in the porous coal macromolecule by reactions (15), (16), the formation of carbon-centered radicals via the cleavage of the hydroperoxide group, forming two types of “O” radicals, and reaction (17); this finally reacts with aliphatic hydrogen to yield a carbon-centered radical, reactions (18) and (19).

The chemical composition of the coal influences the type of radicals being formed during the oxidation process. When EPR spectroscopy is used, it is possible to differentiate between radicals with different chemical environments due to the change in the g-value, which depends on it. Atoms, such as an adjacent heteroatom, are located near a polyaromatic system. This may create different resonance structures with this polyaromatic system or with radicals if such atoms are available nearby or if an oxygen atom is adjacent to an aromatic system. Here, the delocalization resonance structures may include an oxygen atom to create an oxygen-centered radical; this can be deduced through the g-value of the radical. This is because the radicals are not directly affected by the coal’s rank, that is, the percentage of carbon in the coal. Each type of coal contains a different chemical environment; thus, it emphasizes a different g-value, so it is possible to distinguish between the different types of radicals. An example is given in Figure 2a.
macromolecule of bituminous coal, with a high coal rank and Figure 2b: a macromolecule of lignite coal, with a low coal rank. When the coal rank is lower, the hydrogen content and the oxygen content are appreciably higher. This fact affects the reactivity of the coal via the LTO process.1,10 The aliphatic C−H group of the coal is much more reactive compared with the aromatic C−H group; thus, it is the main active ingredient involved in the LTO. Thus, lignite coals are much more reactive than bituminous coals via the LTO process.16

The structural variability that exists between the two coal grades causes differences in two aspects: changes in the structure of the coal and the content as well as the amounts of the released gasses. We decided to investigate the LTO process occurring in (1) German lignite coal, which is an important source of electrical power in Germany and (2) American bituminous coal, which is used in utilities in Israel. The results could shed more light on the very complex mechanism underlying these gas/solid reactions.

**RESULTS AND DISCUSSION**

Two types of coals: high-rank bituminous and low-rank lignite were studied. Bituminous coal from the USA (Bailey Co.) was denoted as BA and lignite coal from Germany (Hambach coal)
was denoted as HA. As previously mentioned, the BA coal serves as fuel in pulverized coal-fired power plants in Israel, and the lignite is used in German utilities.17,18 In addition, active carbon was used as a reference (denoted as AC) due to its high carbon content (98%) and almost no hydrogen (<2%). The properties of the three types of coals (qualitative data) are listed in Table 1.

| coal type | hydrogen content | water content | carbon content |
|-----------|------------------|---------------|----------------|
| HA        | high content of aliphatic hydrogen (~50%) | high | mainly aliphatic |
| BA        | high content of aromatic hydrogen (~8%) | low | mainly aromatic |
| AC        | no hydrogen | None | only aromatic (graphite rings, no hydrogen) |

BA has the highest carbon content19 (the higher grade anthracite coal is not economically feasible as fossil fuel in power plants), and it has a high calorific value (~33,472,000 J/kg). HA has a high aliphatic content19 (a lower coal rank) and thus undergoes a much faster LTO process than BA. Its calorific value is appreciably lower (~23,012,000 J/kg). As for AC, it contains no hydrogen at all (the carbon has an aromatic/graphitic structure),17,20 and thus, it does not undergo the LTO process.

Consumption of O2 and the Emission of Carbon Oxides (CO2, CO). The glass vials with the coal samples were heated in the oven at 95 °C, and the atmospheric oxygen in the gas phase in the vials was consumed via the LTO process; it released gaseous products (mainly carbon oxides) via the LTO process. Coal that was oxidized at 95 °C in the air for long periods (2–5 weeks) was also used in order to check changes in its reactivity toward the LTO process. The LTO process occurring in large coal piles stored in open air was simulated by using small 25 mL glass sealed vials containing 2 g of coal heated in the oven at 95 °C as batch reactors. The gas content in the vial was analyzed after several LTO experiments with t as the oxygen period (in the time range of 0–48 h). The GC analysis of the gaseous atmosphere in the vials revealed that it is mainly composed of nitrogen (N2), oxygen (O2), carbon dioxide (CO2), and some carbon monoxide (CO) as well as minor concentrations of methane (CH4), ethylene (C2H4), and ethane (C2H6). The oxygen concentration is dependent on t and is reduced upon its increase. This process occurs for the two coals studied. For each coal, two types of LTO experiments were carried out: with fresh coal and with aged coal (LTO simulation in air atmosphere at 95 °C in the oven for 5 weeks, denoted as Coal 5w). The oxygen and nitrogen concentrations in the gas phase (in the vials) as a function of the oxidation period t are presented in Table 2 and those of the carbon oxides are presented in Table 3.

Table 1. Qualitative data: Coal Content of H/Water/C.

| coal type | hydrogen content | water content | carbon content |
|-----------|------------------|---------------|----------------|
| BA        | high content of aliphatic hydrogen (~50%) | high | mainly aliphatic |
| HA        | high content of aromatic hydrogen (~8%) | low | mainly aromatic |
| AC        | no hydrogen | None | only aromatic (graphite rings, no hydrogen) |

Table 2. Dependence of the O2 and N2 Concentrations in the Gas Phase of the BA and HA Coals on the LTO Period, t.*

| t (h) | BA fresh | BA 5w | HA fresh | HA 5w |
|-------|----------|-------|----------|-------|
| 0     | 20.9     | 77.4  | 20.9     | 78.0  |
| 0.5   | 20.6     | 77.4  | 20.9     | 78.0  |
| 3     | 19.0     | 78.4  | 19.4     | 79.2  |
| 6     | 14.6     | 81.8  | 17.5     | 80.8  |
| 12    | 13.8     | 82.7  | 15.6     | 82.2  |
| 24    | 13.5     | 83.0  | 14.0     | 83.3  |
| 48    | 4.0      | 87.0  | 8.3      | 88.1  |

*2 g of coal in a closed 25 mL vial heated at 95 °C in an oven for different periods, t.
The Results of the AC Analysis are Presented in Table 4 and Figure 3.

The results, presented in Table 4 and Figure 3, show that the AC and the aged AC (AC 2w aged at 95 °C in the air) do not react with the atmospheric oxygen (the O2 concentration was reduced only slightly >3 and >1.5%, respectively, compared with ∼90% reduction with the two coals, Figure 4) and probably, the carbon dioxide observed results from the release of the adsorbed gas inside the porous structure of the activated carbon with a high surface area. The CO2 observed is definitely not by the LTO process.

Thus, the experiments with the activated carbon validate the conclusion that oxygen consumption and the changes in the chemical composition of the coals are due to the LTO process.

As shown in Table 3 and Figure 4, the low-rank HA (much younger in age compared with BA) is appreciably more reactive toward atmospheric oxygen via the LTO process, compared with the higher rank BA. This probably confirms the conclusion that the active sites that are involved in the LTO process are associated with the aliphatic coal C−H content, which is much higher (Table 2) in the HA than in the BA.2,21

The Results of the AC Analysis are Presented in Table 4 and Figure 3.

Table 3. Dependence of the CO2 and CO Concentrations in the Gas Phase of the BA and HA Coals on the LTO Period, t

| t (h) | BA fresh | | BA 5w | | HA fresh | | HA 5w |
|-------|----------|----------|--------|----------|--------|----------|--------|
|       | % CO2    | % CO     | % CO2  | % CO     | % CO2  | % CO     |
| 0     | 0.04     | 0.00     | 0.04   | 0.00     | 0.04   | 0.00     |
| 0.5   | 1.2      | 0.00     | 2.0    | 0.00     | 1.47   | 0.00     |
| 3     | 1.4      | 0.00     | 2.5    | 0.00     | 1.60   | 0.00     |
| 6     | 1.5      | 0.2      | 2.7    | 0.9      | 2.81   | 0.00     |
| 12    | 1.7      | 0.5      | 2.6    | 0.9      | 8.56   | 0.53     |
| 24    | 1.9      | 0.7      | 2.7    | 0.8      | 12.2   | 0.86     |
| 48    | 2.5      | 1.1      | 6.7    | 2.3      | 12.4   | 0.95     |

% 2 g of coal in a closed 25 mL vial heated at 95 °C in the oven for different periods, t.

Table 4. Dependence of the O2 and CO2 Concentrations in the Gas Phase of the AC Coal on the LTO Period, t

| t (h) | AC fresh | | AC 2w |
|-------|----------|--------|
|       | % O2     | % CO2  |
| 0.5   | 20.98    | 0.08   |
| 3     | 20.24    | 0.16   |
| 6     | 19.50    | 0.40   |
| 12    | 18.13    | 1.65   |
| 24    | 17.84    | 2.63   |
| 48    | 17.41    | 3.04   |

% 2 g of coal in a closed 25 mL vial heated at 95 °C in the oven for different periods, t.

Figure 3. % O2 and (b) % CO2 of coal samples after different oxidation time periods for AC: fresh (no aging) or 5w (aged).

Figure 4. Dependence of % O2 in the gas phase on the oxidation time period t at 95 °C for the BA and HA coal ranks: fresh (no aging) or 5w (aged).

As shown in Table 3 and Figure 4, the low-rank HA (much younger in age compared with BA) is appreciably more reactive toward atmospheric oxygen via the LTO process, compared with the higher rank BA. This probably confirms the conclusion that the active sites that are involved in the LTO process are associated with the aliphatic coal C−H content, which is much higher (Table 2) in the HA than in the BA.2,21
The BA coal contains many more aromatic C–H groups, which are more stable and of course less reactive. However, for both coals, those that were aged for 5 weeks were less active. This is seen graphically in Figure 5. It is clear that the source of experiment upon the addition of the atmospheric oxygen, which reacted with the aged coal BA 5w; therefore, the surface oxides contribute to the release of the CO2 formed. In contrast, almost no surface oxides (the precursors to CO formation) that formed during the aging process decomposed and yielded CO.

Probably, some surface oxides that decompose and yield carbon dioxide could be carboxylic surface oxides via the reaction

\[
\text{coal-COOH} \rightarrow \text{coal-H} + \text{CO}_2
\]  

(20)

whereas the aldehyde surface groups will yield carbon monoxide

\[
\text{coal-CHO} \rightarrow \text{coal-H} + \text{CO}
\]  

(21)

The reactivity of the HA coal during the LTO process is much higher than that of the BA coal (see Figure 5). This means that only 2.25% of the reacting atmospheric oxygen was released as carbon dioxide; whereas with fresh HA coal, it reached 6.45%. Indeed, this is why lignite coals cannot be stored in piles but instead have to be used immediately after the mining process.

The same discussion concerning the LTO process and specifically the production of carbon oxides could not be taken into account for the HA coal, since an appreciable amount of the oxygen in the carbon oxides released in this case is formed from the inherent oxygen content of the HA coal (which is part of the coal macromolecule backbone) and not from atmospheric oxygen (see below).

In order to have a good estimate of the carbon oxides that result from the LTO process, experiments were carried with fresh coal; however, the air atmosphere in the small glass reactors was replaced by an inert argon atmosphere. It was found that with the lignite HA coal, appreciable amounts of carbon dioxide (7.1% of the atmosphere in the vial) were released but no carbon monoxide emission was observed (<0.1% of the atmosphere in the vial). The experiment with the fresh BA coal was repeated; the amount of CO2 was <0.2% and the amount of CO was <0.05% of the atmosphere in the vial.

This observation shows that the carbon oxides released result from the LTO process in BA but that with the HA coal, an appreciable amount of carbon dioxide is produced by decomposition of the inherent oxygen that is part of the coal macromolecule backbone. This is probably produced by decomposition of all surface carboxylic groups (–COOH) via reaction 20; these –COOH groups already exist in the HA coal as inherent oxygen prior to the LTO process. When the HA coal is heated in the oven at 95 °C, these –COOH groups decompose and also produce carbon dioxide in addition to that which is formed via the LTO process from atmospheric oxygen.

The amount of CO produced via the LTO process is much smaller than the amount of CO2. This means that the main surface oxides produced via the LTO process are surface carboxylic groups (–COOH) and not aldehyde groups (–CHO). The data for the CO release is presented in Table 3 and Figure 6.

As shown in Figure 6, the emission of CO with the aged (5w) coals is greater than that observed with the fresh ones. This indicates that some –CHO surface groups formed during the 5 week aging process decomposed when heated in the oven at 95 °C, in addition to the CO produced via the LTO process.

---

**Figure 5.** Dependence of % CO2 in the gas phase on the oxidation time periods t at 95 °C for the BA and HA coal ranks: fresh (no aging) or 5w (aged).

This is seen graphically in Figure 5. It is clear that the source of the lower activity of the aged coal toward O2 stems from the fact that the number of available active sites at the surface of the aged coal is lower than that of the fresh coal.

The results of the CO2 released are presented in Figure 5 and Table 3.

Another interesting observation is that most of the reacting oxygen is not released as carbon dioxide or carbon monoxide but instead forms oxo functional groups (surface oxides) at the surface of the coal macromolecule. Thus, in the BA coal (Tables 3 and 4) after 24 h of the LTO process, 16.9% of the O2 (of the initial 20.4% concentration) reacted, but only 1.9% of CO2 and 0.7% of CO were released. The percentage of atmospheric O2 that reacted with the coal via the LTO process and is released as carbon oxides was calculated

\[
\% \text{O}_2 \text{ in the carbon oxides released} = \% \text{CO}_2 + 0.5 \times \% \text{CO}
\]

This means that only 2.25% of the reacting atmospheric oxygen was released as carbon dioxide 1.9 (\% CO2) + 0.5 × 0.7 (\% CO). Thus, it indicates that only about one O2 molecule out of seven that reacted with the coal via the LTO process to produce surface oxides have decomposed to yield gaseous carbon oxides (CO2 and CO), whereas with the reference AC, all O2 molecules that have reacted produced CO2!!! This conclusion is further corroborated by the fact that the amount of CO2 released with the aged BA coal (BA 5w) in the same experiment (at t = 24 h of the LTO process) have increased appreciably to 2.7% (from 1.9% in the fresh BA coal), whereas the amount of CO almost did not change (0.7% in the fresh BA coal to 0.8% in the aged BA 5w coal). This observation indicates that some surface oxides (the precursors to CO formation) formed at the surface of the aged BA 5w coal during the 5 weeks of aging in the vials at 95 °C and that they also decomposed in the vials during the 0–48 h kinetic
The mechanism by which the −COOH and −CHO surface oxides are formed is probably by attacking the hydroperoxide groups (which were formed by reaction (3), Scheme 1) adjacent to active aliphatic −CH groups of the coal macromolecule backbone; this mechanism is presented in Scheme 4:

Scheme 4, in our opinion, presents a more reasonable mechanism for the formation of stable radicals in the coals that underwent the LTO process (as detected by the EPR spectroscopy,8,10,19 see Figure 1). It also shows a thermodynamically favored path for the release of carbon oxides via the coals’ LTO process.

**Release of Low Molecular-Weight Organic Products (Methane, Ethane, and Ethylene) via the LTO Process.** During the LTO process, small amounts of low molecular-weight organic gases are released, mainly methane CH₄, Ethane C₂H₆, and ethylene C₂H₄. The results, summing up the emission of methane, are presented in Table 5 and Figure 7.

When comparing bituminous and lignite coal, it was noted that fresh BA emits much more CH₄ than does fresh HA. However, the aged BA coal releases almost no methane. It is well known17 that bituminous coal contains coal bed methane (CBM), which is adsorbed inside the pores of the coal. Thus, when considering the difference between the aged BA coal and the fresh BA coal, it can be concluded that most of the methane released from the fresh BA coal is not a LTO product but instead is probably adsorbed coal bed methane that exists in the pores, which is desorbed and diffused to the gaseous atmosphere due to heating at 95 °C. Interestingly, in the aged

### Table 5. Dependence of the CH₄ Concentration in the Gas Phase of the BA and HA Coals on the LTO Period, t

| t (h) | BA fresh | BA 5w | HA fresh | HA 5w |
|------|----------|-------|----------|-------|
| 0.5  | 10       | 0     | 1        | 0     |
| 3    | 20       | 0     | 1        | 0     |
| 6    | 30       | 10    | 10       | 10    |
| 12   | 40       | 10    | 2        | 20    |
| 24   | 60       | 20    | 2        | 30    |
| 48   | 430      | 10    | 3        | 50    |

*2 g of coal in a closed 25 mL vial heated at 95 °C in an oven for different periods, t.*

---

*Figure 6. Dependence of the % CO in the gas phase on the oxidation time periods t at 95 °C for the BA and HA coal ranks: fresh (no aging) or 5w (aged).*

*Figure 7. Emission of CH₄ in the BA and HA coals during the LTO process as a function of the LTO period, t.*

---

Scheme 4. Possible Mechanism for the Formation of Carbon Oxides and Stable Radicals as the Final Products of the LTO of Coal

### Figure 6.

**Figure 6.** Dependence of the % CO in the gas phase on the oxidation time periods t at 95 °C for the BA and HA coal ranks: fresh (no aging) or 5w (aged).

### Figure 7.

**Figure 7.** Emission of CH₄ in the BA and HA coals during the LTO process as a function of the LTO period, t.
coal, all coal bed methane has already been released, and thus, the aged coal releases hardly any methane upon reheating it to 95 °C in the LTO experiment. In the HA fresh coal, almost no methane was released.

**Emission of C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6}**. During the LTO experiments, it was also observed that much smaller concentrations of Ethylene (C\textsubscript{2}H\textsubscript{4}) and Ethane (C\textsubscript{2}H\textsubscript{6}) were released, as shown in Table 6.

| t   | BA fresh | BA 5w | HA fresh | HA 5w |
|-----|----------|-------|----------|-------|
| 0.5h| 0/0      | 0/0   | 0/0      | 0/0   |
| 3h  | 0/0      | 20/0  | 0/0      | 10/0  |
| 6h  | 10/0     | 20/0  | 10/0     | 20/0  |
| 12h | 20/10    | 30/10 | 10/0     | 40/0  |
| 24h | 50/10    | 50/20 | 20/0     | 60/0  |
| 48h | 110/20   | 90/30 | 20/0     | 70/0  |

*2 g of coal in a closed 25 mL vial heated at 95 °C in an oven for different periods, t.*

The trends for C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} formation are shown in Figures 8 and 9.

![Figure 8. % C\textsubscript{2}H\textsubscript{4} from coal samples after oxidation time periods for high (BA) and low (HA) coal ranks: fresh (no aging) or 5w (aged).](image)

![Figure 9. % C\textsubscript{2}H\textsubscript{6} of coal samples after oxidation time periods for high (BA) and low (HA) coal ranks: fresh (no aging) or 5w (aged).](image)

As obtained from Table 6 and Figure 8, the amount of ethylene (C\textsubscript{2}H\textsubscript{4}) is greater in aged (5w) coal than in fresh coal. This indicates that ethylene is being formed during the LTO process: more ethylene occurs where there are more surface oxides. Another interesting finding is that the BA coal produces more ethylene than the HA coal (Table 6). This finding appears to be in agreement with the fact that BA coal contains a higher percentage of carbon in its macromolecule than HA does.

As for the formation of ethane (Table 6 and Figure 9), it is clear that it is formed in very small amounts, and when BA coal is compared to HA coal; apparently, BA forms ethane during the LTO process, whereas HA does not form it at all. This is probably because of differences in the carbon to hydrogen ratio between the BA coal and the HA coal.

### CONCLUSIONS

1. The low-temperature atmospheric oxidation reaction in bituminous coal is the source of CO\textsubscript{2} emission, upon storage under atmospheric conditions for long periods.
2. The emission of CO\textsubscript{2} from lignite coals partly stems from the oxygen content in the coal itself and only partly via the LTO process with atmospheric oxygen.
3. The precursor species to carbon dioxide are carboxylic $-\text{COOH}$ in the coal and the aldehyde $-\text{CHO}$ to carbon monoxide emission. In lignite coal, most of the emitted CO\textsubscript{2} is from a structural source, whose chemical composition has high lignite content.
4. Carbon monoxide emission from heated coals in the RT-150 °C range is produced from the LTO process from atmospheric oxygen.
5. Emission of methane from bituminous coal upon heating is by desorption of the existing coalbed methane from the coal pores and not via the LTO process.

### EXPERIMENTAL SECTION

**Coals Used.** The coal samples used in the studies were prepared by grinding and sieving coal to a particle size of 74 μm ≤ X ≤ 250 μm. The coal samples were then dried under vacuum in a Heraeus vacuum oven (model VT6060) for 24 h at 60 °C. Two types of coals were studied: bituminous and lignite. In order to obtain a better understanding of how the oxygen and hydrogen content as well as the mineral matter in the coal affects the LTO process, active carbon was used as a reference.

The bituminous coal was from the USA (denoted as BA, for Bailey); it is a Pittsburgh no. 6 bituminous coal. The lignite coal was from Germany (denoted as HA, for Hambach); it is...
Lignite coal. The AC was produced via pyrolysis of peat as a biological source at a high temperature; it is very porous and has a high surface area (300–500 m²). The AC is commonly used as an effective trap for cleaning pollutants in water or as an adsorbent in the filters of gas masks (resulting in relatively high moisture content (Table 7) in the AC). Moreover, this AC is highly purified (steam activated and acid washed) in a powder form. The AC is suitable to serve as a reference due to its very high carbon content (Table 7). The Bailey bituminous coal was supplied by the Israel Electricity Co., where it is used as fossil fuel. The lignite coal was supplied by the Institute of Energy Process Engineering and Chemical Engineering IEC of Freiberg, Germany and is used in German utilities. The selected properties of all coals used in this study are presented in Table 7.

| sample | moisture | Ash | VM | wt % | analytical data | wt %, db |
|--------|----------|-----|----|------|-----------------|---------|
|        |          |     |    |      | C    | H   | O  | S  | N  | CV (J g⁻¹) |
| HA     | 34.53    | 5.09| 52.39|      | 66.12| 4.32| 23.65| 0.16| 1.64| 25,323     |
| BA     | 5.87     | 7.78| 37.20|      | 78.07| 5.18| 5.84 | 1.50| 1.50| 29,258     |
| AC     | 11.5     | 0.1%| 88.5 |      | >98  | <2  | <2  |     |     |            |

Table 7. Properties of Coals

The main contaminants in coal are hydrogen and oxygen. In the case of lignite, the H content is mainly in the functional groups, such as −C−OH, −CHO, −COOH, and as aliphatic hydrogen. For bituminous coal, the H content is mainly of aromatic C−H bonds; the main ingredient in the BA coal is aromatic C, whereas in the HA coal the aliphatic component dominates. In order to have a blank reference, AC was chosen because it contains no C−H bonds (all hydrogen is from adsorbed water) and it contains no C−O bonds.

Simulations of the LTO (weathering or aging) process of the coals used for the experiments were carried out at 95 °C in an oven in air atmosphere. The aging of the coal samples was carried out in an open glass beaker, charged with 100 g of coal (particle size 74 μm ≤ X ≤ 250 μm) and exposed to air, at 95 °C. The aging was carried out for periods of 2 or 5 weeks in a MRC oven (model MF3000). The oxygen concentration in the oven was maintained at 21% throughout the oxidation periods to simulate the LTO process. After the aging process was finished, the beaker was removed from the oven, 2 g samples of fresh (non-aged coal) and of the aged coals were inserted into vials (25 mL volume), and then sealed using a rubber septum and an aluminum cap, as presented in Figure 10. These vials were used as batch reactors in air atmosphere and heated at 95 °C in an LLG LABWARE oven, model uniOVEN 42, for different time periods (in hours): 0.5, 3, 6, 12, 24, and 48 in order to carry out the time-dependent LTO process. Next, the gas composition of the gas phase of each vial was analyzed by gas chromatography (GC), as detailed below.

Gas samples from the vials were taken with 0.5 mL gas-tight syringes (A2 PS) and 0.2 mL of the samples were injected and analyzed by GC.

**Chemicals.** The gasses used were He, Air, and H₂. All gasses were of CP grade, and the water used throughout this study was ultrapure water with a resistance of 18 mΩ/CM.

**Gas Chromatography.** The gases (N₂, O₂, CO₂, CO, CH₄, C₂H₄, C₃H₆, and hydrocarbons) in the reactor atmosphere were analyzed using GC (Agilent Technologies model 7890B) equipped with a thermal conductivity detector and a flame ionization detector connected in series. The gases were separated on a column (carbosieve B 1/8 in, 9 ft stainless steel) using a temperature-programmed mode. The accuracy of the determination of the gases was ± 2%. Argon gas cannot be separated from oxygen in the GC column; thus, the value determined for oxygen includes ~0.93% argon gas.

Since the reactions studied are gas/solid surface reactions, the reproducibility of the results is not very accurate. Therefore, each experiment was carried out in triplicate to reduce the experimental error. However, it is estimated that the experimental error in the analysis is ± 15% mainly due to the nature of the heterogeneous reactions studied in the experiments.

**Author Information**

**Corresponding Author**

Haim Cohen — Department of Chemical Sciences, Ariel University, Ariel 40700, Israel; Chemistry Department, Ben-Gurion University of the Negev, Beer Sheva 84105, Israel; orcid.org/0000-0003-4098-8765; Email: hcohen@ariel.ac.il
**Acknowledgments**

S.R. acknowledges the support of the Israel Ministry of Science grant (#3-14330).

**References**

1. Taub, T.; Ruthstein, S.; Cohen, H. Involvement of carbon-centered radicals in the aging process of coals under atmospheric conditions: an EPR study. *Phys. Chem. 2018*, 20, 27025–27035.

2. Aizenstát, Z.; Green, U.; Starck, S.; Weidner, C.; Cohen, H. Modes of formation of carbon oxides (COx (x = 1,2)) from coals during atmospheric storage: Part 1 effect of coal rank. *Energy Fuels 2010*, 24, 6366–6374.

3. Green, U.; Aizenstát, Z.; Gieldmeister, F.; Cohen, H. CO 2 Adsorption Inside the Pore Structure of Different Rank Coals during Low Temperature Oxidation of Open Air Coal Stockpiles. *Energy Fuels 2011*, 25, 4211–4215.

4. Grossman, S.; Davidi, S.; Cohen, H. Emission of toxic and fire hazardous gases from open air coal stockpiles. *Fuel 1994*, 73, 1184–1188.

5. Kolker, A.; Engle, M.; Stracher, G.; Hower, J.; Prakash, A.; Lawrence, L.; Schure, T.; Heffern, E. Emissions from Coal Fires and Their Impact on the Environment; USGS Publications, 2009; p 3084.

6. Grossman, S. L.; Davidi, S.; Cohen, H. Evolution of molecular hydrogen during the atmospheric oxidation of coal. *Fuel 1991*, 70, 897–898.

7. Wang, H.; Dlugogorski, B. Z.; Kennedy, E. M. Coal oxidation at low temperatures: oxygen consumption, oxidation products, reaction mechanism and kinetic modelling. *Prog. Energy Combust. Sci. 2003*, 29, 487–513.

8. Green, U.; Keinan-Adamsky, K.; Attia, S.; Aizenstát, Z.; Goobes, G.; Ruthstein, S.; Cohen, H. 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. 2014*, 16, 9364–9370.

9. Davidi, S.; Grossman, S. L.; Cohen, H. Organic volatiles emissions accompanying the low-temperature atmospheric storage of bituminous coals. *Fuel 1995*, 74, 1357–1362.

10. Green, U.; Aizenstát, Z.; Ruthstein, S.; Cohen, H. Stable radicals formation in coals undergoing weathering: effect of coal rank. *Phys. Chem. 2012*, 14, 13046.

11. Liotta, R.; Brons, G.; Isaacs, J. Oxidative weathering of Illinois No.6 coal. *Fuel 1983*, 62, 781–791.

12. Grossman, S.; Wegener, I.; Wanzl, W.; Davidi, S.; Cohen, H. Molecular hydrogen evolution as a consequence of atmospheric oxidation of coal: 3. Thermogravimetric flow reactor studies. *Fuel 1994*, 73, 762–767.

13. Khvoryuchenko, O. V.; Frank, B. Theoretical Investigation of Anion-Radical States of Edge-Oxidized Carbon Model Clusters. *J. Phys. Chem. A 2017*, 121, 3167–3173.

14. Solomon, P. R. *New Approaches in Coal Chemistry*, ACS Symposium Series; American Chemical Society: DC, 1981; Vol. 169.

15. Cheng, W.; Xue, J.; Xie, J.; Zhou, G.; Nie, W. A Model of Lignite Macromolecular Structures and Its Effect on the Wettability of Coal: A Case Study. *Energy Fuels 2017*, 31, 13834–13841.

16. Nagroho, Y. S.; McIntosh, A. C.; Gibbs, B. M. Low-temperature oxidation of single and blended coals. *Fuel 2000*, 79, 1951–1961.

17. Speight, J. G. *The Chemistry and Technology of Coal*, 3rd ed.; CRC Press, 2012.

18. Cohen, H.; Green, U. Reducing Coal Storage Costs and Gas Emissions Monitoring in Coal Reserves; Internal Report to the Israeli Electricity Corporation, 2012.

19. Green, U.; Aizenstát, Z.; Ruthstein, S.; Cohen, H. Reducing the spin-spin interaction of stable carbon radicals. *Phys. Chem. 2013*, 15, 6182–6184.

20. Razzighorova, M.; Budinova, T.; Petrov, N.; Minkova, V. Purification of water by activated carbons from apricot stones, lignites and anthracite. *Water Res. 1998*, 32, 2135–2139.

21. Cohen, H.; Green, U.; Aizenstát, Z.; Hower, J. C.; Hatch, R. 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, 5626–5631.

22. “Activated Charcoal Norit,” Sigma-Aldrich. https://www.sigmaaldrich.com/catalog/product/sigal/53663?lang=en&region=IL, 2019 (accessed 2019-08-29).

23. Ogawa, M.; Yoshida, N. Intramolecular distribution of stable nitrogen and oxygen isotopes of nitrous oxide emitted during coal combustion. *Chemosphere 2005*, 61, 877–887.

24. Molina, A.; Murphy, J. J.; Winter, F.; Haynes, B. S.; Blevins, L. G.; Shadid, C. R. Pathways for conversion of char nitrogen to nitric oxide during pulverized coal combustion. *Combust. Flame 2009*, 156, 574–587.

25. Chauffoureaux, J. C. Separation And Preconcentration Of Trace Substances. I —Preconcentration For Inorganic Trace Analysis. *Pure Appl. Chem. 1979*, 51, 1195–1212.