**Wet Air Oxidation of Oil Shales: Kerogen Dissolution and Dicarboxylic Acid Formation**

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**ABSTRACT:** Until now, the oil shale kukersite has been used mainly for energy and oil production. To broaden the possible applications of oil shales, the wet air oxidation of kukersite (an organic-rich sedimentary rock from Estonia) was studied. Kukersite was oxidized with an oxygen-rich gas in water at temperatures up to 200 °C and pressures up to 60 bar. The efficiency of this batch process was evaluated from organic matter conversion, from the amount of solubilized organics obtained, and from the rate of dicarboxylic acid (DCA) formation. The effect of several reaction parameters—pressure, temperature, time, acid/base additives, substrate concentration, the origin of a substrate and its organic matter content, and so forth—was measured. A conversion of 91% in total organic carbon was achieved at 175 °C with 40 bar of the 1:1 oxygen/nitrogen mixture in 3 h without the presence of any additives. Under basic conditions, high yields (up to 50%) of dissolved organic matter were obtained with 8% of DCA; the best results are obtained with K₂CO₃ and KOH. The highest DCA outcome (12%) within the 3 h reaction time was obtained in the presence of acetic acid. It was found that temperatures higher than 185 °C, pressures over 30 bar of PO₂, and long reaction times in the acidic media caused a considerable decrease in the DCA outcome. It was also found that the same process can be applied to shales of different origins, although with lower DCA yields.

1. INTRODUCTION

An oil shale is a sedimentary rock consisting of organic matter—kerogen—and inorganic matter. The compositions of a kerogen from different shales vary substantially. The structure of the kerogen is mainly represented as an aliphatic branched macromolecule cross-linked with aromatic, usually phenolic, units and differently bonded oxygen atoms in various ratios. The Estonian oil shale kukersite is from the Ordovician period and has an exceptionally high organic matter content, reaching 30–50%. The most common technologies for oil shale processing are pyrolysis for a laboratory-scale synthesis. They obtained 40% of di-alkenyl resorcinol building blocks. The modeling of the kerogen structure with ¹³C MAS NMR by Lille et al. mainly confirmed this assumption. In the 1930–1940s, it was shown that the oxidation of the kukersite kerogen with potassium permanganate resulted in the formation of dicarboxylic acid (DCA). Investigations to break down the kerogen with nitric acid in order to get DCAs were conducted by a work group led by Fomina. They obtained aliphatic DCAs up to 40% from the kerogen. The developed process, however, was never industrially implemented. In 2001, Bajc et al. investigated DCA formation with an alkaline permanganate oxidation method using a 33-step process on a laboratory-scale synthesis. They obtained 40% of different oxidation products (w/w on kerogen), of which 52% were aliphatic DCAs.

Wet air oxidation (WAO) is considered an environmentally friendly process with water as a solvent and air as an oxidant. Catalytic WAO has been successfully used for the valorization of lignin and its model substrates into valuable chemicals suggested that the organic matter is mainly composed of n-alkenyl resorcinol building blocks. The modeling of the kerogen structure with ¹³C MAS NMR by Lille et al. mainly confirmed this assumption. In the 1930–1940s, it was shown that the oxidation of the kukersite kerogen with potassium permanganate resulted in the formation of dicarboxylic acid (DCA). Investigations to break down the kerogen with nitric acid in order to get DCAs were conducted by a work group led by Fomina. They obtained aliphatic DCAs up to 40% from the kerogen. The developed process, however, was never industrially implemented. In 2001, Bajc et al. investigated DCA formation with an alkaline permanganate oxidation method using a 33-step process on a laboratory-scale synthesis. They obtained 40% of different oxidation products (w/w on kerogen), of which 52% were aliphatic DCAs.

Wet air oxidation (WAO) is considered an environmentally friendly process with water as a solvent and air as an oxidant. Catalytic WAO has been successfully used for the valorization of lignin and its model substrates into valuable chemicals.

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and can be further applied for the transformation of partly oxidized compounds (e.g., keto acids) to the DCA. Recently, it has been demonstrated that an analogous method called “oxy-cracking” can be effectively used for the enhancement of petroleum coke, asphaltene, and even oil sand tailings, thus indicating that the chemolytic oil shale degradation with the WAO process may be an option to get valuable products, for example, DCA, from oil shales.

In the 1960s, Proskuryakov and his group introduced a method of oil shale (Gdov shale, Russia) oxidation with continuous flow of air in neutral or basic aqueous solutions. Gdov shale has the same geological formation as that of kukersite but different deposits. This approach was presented as an alternative to nitric acid oxidation and is similar to the WAO process used in the present investigation. The presence of a DCA in air-oxidized kerogen was stated, including insoluble high-molecular-weight acids (the latter were not analyzed in detail). However, their investigation suffers from analytical weakness of sixties last century. The reported yields of DCAs (up to 25–30%) obtained from the crude ether extract were based on the amount of the oxidized kerogen of the shale and not on the amount of the initial kerogen in the experiment. Because of that all presented values seem higher and are incomparable with each other. So, the real DCA yields remains unclear and the conclusions drawn by Proskuryakov et al. are partly misleading. Because of that, all presented values were seemingly high and incomparable. It is not explained how the oxidation depth was calculated, so the obtained DCA yield remains unclear. Moreover, the yields of DCAs were considered equal to the presented amount of the crude ether extract (according to our estimations, this fraction contains less than 50% of individual DCAs). Because of these indistinct analytical data, it is impossible to follow up the real amount of DCAs formed, and the conclusions drawn by Proskuryakov et al. are partly misleading. Thus, it was necessary to ascertain the effectiveness of WAO for oil shale degradation and provide evidence-based quantitative results. According to our knowledge, there are no other publications on oxidative hydrothermal conversion of oil shales with gaseous oxygen under subcritical conditions aiming for production of DCAs.

In the present work, we performed the WAO of kukersite and characterized the main products formed under different reaction conditions and in the presence of various additives. The effectiveness of the WAO process was evaluated by comparing the conversion of organic carbon, the amount of dissolved kerogen, the DCA formation, and CO₂ emissions. In this respect, other sedimentary rocks such as Green River and Jordanian shales were also compared.

### 2. EXPERIMENTAL WORK

#### 2.1. Materials

Oil shales and their organic content concentrates were obtained from the Oil Shale Competence Center Estonia in Kohtla-Järve. The results of additional analysis and the details of the used materials are presented in the Supporting Information (Sections S1 and S2). The used samples had a particle size <45 μm. The native oil shale K-45 and the oil shale concentrates K-70 and K-90 have kerogen contents close to 45, 70, and 90%, respectively. For the used samples, the elemental (C, H, N, and S) and metal contents were determined, and the oxygen contents were calculated according to GOST 2408.3−95. The chemical compositions of the used oil shale samples are listed in Tables 1 and 2.

### 2.2. Experimental Procedures and Setup

The experiments were carried out in a 100 mL stainless steel pressure reactor (4566C, Parr Instrument Company, Moline, IL, USA) with a heating oven, a mechanical gas entrainment impeller, a pressure gauge, and a reactor controller. A stirring speed of 1000 rpm was set to achieve an effective gas—solid transfer. In a typical experiment, 1 g of the oil shale or its concentrate was weighed into a reactor containing 50 mL of distilled water and a specified amount of additive (base, acid, etc.). The reactor was pressurized with gas and heated to a specified temperature. The WAO experiments were carried out at temperatures ranging from 125 to 200 °C and pressures ranging from 20 to 60 bar. The beginning of the reaction was counted as the point when the reaction temperature was 5 °C lower from the set point. At the end of the reaction, the mixing speed was reduced to the minimum, and the reactor was cooled to room temperature. After depressurization, the evolved gas was collected and analyzed using a gas chromatography (GC) thermal conductivity detector. The sample for capillary electrophoresis (CE) was taken straight from the reaction mixture, and the pH was measured using a pH meter inoLab pH7310. The reaction mixture was transferred into weighed centrifuge tubes, and the solid residue was separated via centrifugation. The residue was rinsed with distilled water and then with a 0.1 M KOH solution to dissolve all carboxylic acids. The supernatant was acidified with HCl if needed, and water was evaporated. The dry sample was either sent for elemental analysis or esterified using a 2:1 methanol—chloroform mixture (with a catalytic amount of concentrated H₂SO₄) in a Dean–Stark apparatus. The esterified product was analyzed with GC—flame ionization detection (FID) as DCA dimethyl esters (DMEs), and GC—mass spectrometry (MS) and liquid chromatography (LC)—MS were used if needed. The precipitate from the centrifuge tubes (unreacted substrate) was dried (105 °C, 24 h) and weighed for the elemental analysis.

### 2.3. Analytical Methods

The esterified sample was qualitatively and quantitatively analyzed with a Shimadzu GC-2010 FID gas chromatograph using a 30 m polyimide-coated fused silica Zebron ZB-SHT Inferno (0.25 μm) capillary column programmed at 10 °C/min from 50 °C (a 4 min hold isothermally) to 300 °C (a 3 min hold isothermally).

A GC—MS analysis was carried out with a Shimadzu GC—MS QP2010 gas chromatograph mass spectrometer using a 30 m polyimide-coated fused silica Zebron ZB-5 (0.50 μm) capillary column and 70 eV EI. The oven temperature was programmed from 60 to 300 °C at 10 °C/min with He as the carrier gas.

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#### Table 1. Chemical Compositions of the Organic Matter (wt %) of the Oil Shale Samples Used[^a]

| Sample | C [%] | H [%] | N [%] | S [%] | O [%] | TIC [%] | TOC [%] | OM [%] |
|--------|-------|-------|-------|-------|-------|---------|---------|-------|
| K-45   | 38.4  | 4.4   | 0.12  | 1.7   | 17.7  | 3.2     | 35.1    | 47.1  |
| K-70   | 38.4  | 7.3   | 0.14  | 1.6   | 15.8  | 1.4     | 57.0    | 75.6  |
| K-90   | 68.0  | 8.0   | 0.2   | 1.3   | 14.5  | 0.2     | 67.8    | 90    |

[^a]: TIC—total inorganic carbon; TOC—total organic carbon; and OM—total organic matter.
In the case of high-performance liquid chromatography—Fourier transform infrared (HPLC—FTIR) or subjected to high-resolution mass spectrometry (HRMS) and CE, the sample was taken immediately after opening the reaction vessel; for elemental analysis, the sample was analyzed after water removal. Elemental analysis was performed on a Vario MACRO CHNS Cube analyzer and a rapid OXY Cube for O. The description of the CE and HPLC procedures is given in the Supporting Information, together with the analysis results.

Gas analysis was carried out with a Shimadzu GC-2014 gas chromatograph with a valve system, which made it possible to determine all of the gases of interest in a single run. To analyze O₂, N₂, and CO₂, a 3 m molecular sieve 5 Å packed column (OD 1/8”, ID 2 mm, 80/100 mesh) was used, and for CO₂ analysis, a 9 m 25% DC-200/Shimalite packed column (60/80 mesh, OD 1/8”, ID 2 mm) was used. The oven temperature was programmed from 60 °C (a 2 min hold isothermally) to 120 °C (a 4 min hold isothermally) to 10 °C/min.

### 2.4. Determination of Products

The conversion of organic carbon was calculated from the elemental analysis of the solid residue (eq 1). The information about the extent of organic carbon was calculated from the elemental analysis of the gas phase. The percent value of C CO₂ shows the percent amount of organic carbon converted to CO₂ during the reaction (eq 2).

\[
\text{Conversion} = 1 - \frac{\text{TOC in the solid residue [mg]}}{\text{TOC in the initial oil shale [mg]}} \times 100
\]  

\[
\text{C in } \text{CO}_2 = \frac{\text{C in the form of CO}_2 \text{ [mg]}}{\text{TOC in the initial oil shale [mg]}} \times 100
\]

A typical sample of the water-soluble part of the reaction mixture contained around 80% of the organic material, with the remaining 20% being inorganic. After drying the solubilized part from the water phase (a sticky yellowish-brown viscous mass), it was either analyzed directly (by elemental analysis or Fourier transform infrared) or subjected to high-resolution liquid chromatography—MS and GC–MS analysis after the derivatization step (Supporting Information, Section S3). The yield of water-solubilized oxygenated products (SO) was calculated with respect to the kerogen content, which indicates the extent of kerogen solubilization. For the presentation of organic C distribution, the elemental analysis was always carried out before the esterification step.

The amount of the formed DCAs was determined from the esterified samples as DMEs in a mixture with SO by GC. Calibrations for the DME homologs succinic (C₄), glutaric (C₅), adipic (C₆), pimelic (C₇), suberic (C₈), azelaic (C₉), and sebacic (C₁₀) acid were made. The DCA values were calculated from the measured DME values, taking into account the DCA distribution and the molecular mass change in esterification. The percent yield of DCAs (C₄–C₁₀) was calculated with respect to the organic matter content (eq 4). If needed, the DCA distribution is presented as the percentage of a long-chain DCA to the overall amount of DCAs measured (abbreviated as (C₆–C₁₀)/(C₄–C₁₀)).

\[
Yield \text{ of DCA(C₄–C₁₀)} = \frac{\text{mass of DCA [mg]}}{\text{mass of organic matter in the oil shale [mg]}} \times 100
\]  

\[
Yield \text{ of SO} = \frac{\text{mass of SO [mg]}}{\text{mass of organic matter in the oil shale [mg]}} \times 100
\]  

### 3. RESULTS AND DISCUSSION

#### 3.1. Kerogen Solubilization and DCA Formation: The Effect of Reaction Time

From the early work of Proskurjakov, the initial reaction conditions were selected as follows: temperature 175 °C, 40 bar of an oxygen-containing gas, and water with no additives for the reaction medium. To increase the oxygen fugacity, mainly a SO/50 O₂/N₂ mixture was used. An enriched oil shale (K-70) with a kerogen content of ~70% was used as a substrate in most of the experiments done. The yields of DCA and SO (mean value) at different reaction times are given in Table 3.

### Table 2. Metal Contents (wt %) of the Used Oil Shale Samples

|     | Ca [%] | Mg [%] | Al [%] | Fe [%] | K [%] | Zn [mg/kg] | Cu [mg/kg] | Mn [mg/kg] | Ni [mg/kg] | Co [mg/kg] | Cr [mg/kg] |
|-----|--------|--------|--------|--------|-------|------------|------------|------------|------------|------------|------------|
| K-45| 9.6    | 1.6    | 1.9    | 1.5    | 1.4   | 166        | 4.2        | 107        | <4         | <4         | <1         |
| K-70| 4.7    | 0.7    | 1.4    | 0.9    | 1.0   | 4.8        | 1.1        | 95.4       | 18.4       | 1.1        | 22.2       |
| K-90| 0.6    | 0.3    | 0.9    | 0.3    | 0.6   | 2.4        | 0.6        | 15.8       | 12.5       | 0.6        | 16.1       |

*Measured with the microwave plasma atomic emission spectrometry method by an Agilent 4200 system at the Oil Shale Competence Center, Kohila-Järve.

During the process, organic carbon was converted to water-soluble compounds (including DCA), other organic substances, and carbon dioxide. Figure 1 illustrates the material balance of organic carbon during the reaction. Oxidation of 1 g of K-70 under selected conditions over 90% conversion of organic carbon was observed within 3 h. However, 44% of the initial carbon was released as CO₂, and only 18% of it was converted to SO. This means that from the 1 g of K-70, 920 mg of CO₂ was formed and 254 mg of SO was collected (see the Supporting Information, Section S4). The SO contained a large number of different organic compounds, including 59 mg of DCA (estimated from 70 mg of the measured DME (C₄–C₁₀)). In addition to DCAs, the presence of monocarboxylic...
acids, their branched and keto-substituted isomers, tricarboxylic acids, and alcohols was evidenced by LC–MS and GC–MS (see the Supporting Information, Section S3), similarly to previous studies.\textsuperscript{12,20} As the reaction progressed, we also observed a continuous loss of carbon in the form of acetic acid and formic acid (Supporting Information, Figure S14), carbon monoxide, and other lighter carbon-containing substances that were not captured by the methods mentioned above.

Under a prolonged reaction time (e.g., after 3 h), the destructive oxidation of the acids and SO was higher than their formation (Table 3). The changes in DCA distribution were observed in the course of the process so that the amount of long-chain DCAs diminished over time and the amount of short-chain DCAs increased. As shown in a previous paper,\textsuperscript{13} higher-molecular-weight DCAs are exposed to further oxidation and are thus gradually transformed to lower-molecular-weight DCAs. The maximum concentration of organic C in the solution (SO) was observed after a 2 h reaction (Figure 1) and it decreased from there onward. This means that SO was also susceptible to further oxidation, and its decomposition was simultaneous with kerogen dissolution (oxidative degradation of kerogen). The yield of derivatized SO (measured in an esterified form), however, was almost constant during the first 3 h (Table 3). The measured SO may have appeared as a constant because of the constantly increasing amount of bounded oxygen and the additional methyl groups added in the esterification step. Only at extended reaction times (6 h), the decrease in the total amount of SO was observed.

As expected, the elemental analysis of SO before the esterification confirmed that the O/C ratio increased during the oxidation (Table 4). After 1 h, the O/C ratio had quadrupled compared to the initial kerogen, indicating the effective insertion of oxygen into the kerogen polymeric molecules. Also, the amount of organic C in solid kerogen was directly connected to the amount of the excreted CO\textsubscript{2}. Moreover, the pH of the reaction mixture decreased from 7 to 2.8, indicating the acidic nature of the oxidation products. It was also confirmed that the oil shale was insoluble in water under selected reaction conditions in the absence of an oxygen-containing gas (experiments were performed under atmospheric pressure or when using 40 bar of CO\textsubscript{2}; data not shown).

### 3.2. Effect of Pressure

The effect of oxidant pressure on K-70 (20 g/L) oxidation and DCA formation was studied with a 50/50 O\textsubscript{2}/N\textsubscript{2} mixture in the overall pressure range of 20–60 bar at a constant temperature (175 °C). As expected, lower pressure resulted in the lower conversion of kerogen and also a lower DCA yield (Figure 2A1,A2). The pressure at 40 bar and higher resulted in over 90% conversion and up to 10% yield of DCAs. Furthermore, only a slight increase in CO\textsubscript{2} was observed when changing the pressure from 40 to 60 bar (corresponding to the 20–30 bar of pO\textsubscript{2}), indicating the possibility of usage of even higher pressures. However, at a higher pressure, the DCA distribution shifted toward the short-chain DCAs, indicating that at pressures over 40 bar, secondary reactions would start to prevail where the SO and DCA are further degraded.

Different gas mixtures (21, 50, and 100% of O\textsubscript{2} in a mixture with N\textsubscript{2}) at a constant pressure of 40 bar were also tested. The highest partial pressure used (40 bar of pO\textsubscript{2} with pure O\textsubscript{2} gas) resulted not only in a deeper conversion of kerogen but also in the loss of DCAs (Figure 2B1,B2). Moreover, a considerable increase in CO\textsubscript{2} and a decrease in SO were observed when compared to the 20 or 30 bar of pO\textsubscript{2}. This indicates that by controlling the amount of oxygen, the selectivity to valuable products can be increased. It was observed that the highest yields of DCAs were obtained when applying around 40 bar of the O\textsubscript{2}/N\textsubscript{2} mixture (pO\textsubscript{2} = 20 bar) for K-70 under selected conditions, for example, an amount of oxygen that was sufficient for kerogen solubilization and insufficient for overoxidation and degradation of the DCA or SO. It is important to note that if the oil shale concentration in the reactor is raised, the amount of the oxidant required increases (Supporting Information, Section S5).

### 3.3. Effect of Temperature

Temperature is another key parameter affecting the WAO process. The conversion of the oil shale concentrate K-70 was investigated in a range of 150–200 °C. It was evident that the temperature rise enhanced both the kerogen conversion and the CO\textsubscript{2} formation (Figure 3). At higher temperatures (>175 °C), more than 50% of the initial organic carbon was converted to CO\textsubscript{2} within 3 h. The rise in the CO\textsubscript{2} amount was accompanied by a loss in the amount of SO. This indicates that the temperature rise caused faster degradation of the primary oxygenated intermediates. A similar phenomenon was described in our previous work for DCA stability, where we found that at 200 °C, a considerable degradation of DCAs (C4–C10) occurred.\textsuperscript{14} When the WAO of the oil shale was carried out at lower temperatures, ranging from 150 to 165 °C, the yield of the formed DCAs was less than 6%. In this respect, the temperature range for the acceptable conversion of the oil shale to SO and the formation of DCAs is around 175 °C.

### 3.4. Effect of Kerogen Content

Three different concentrates of kuskerite were tested, keeping the remaining operating parameters constant. The obtained results are presented in Figure 4. By using the concentrate K-90, a significant decrease in SO was observed compared to the

**Table 4. Changes in the Organic Carbon and Oxygen Distribution after the WAO Process**

| time h  | TOC [%] | O [%] | O/C |
|---------|---------|-------|-----|
| initial K-70 | 0 | 57.0 | 15.8 | 0.21 |
| SO\textsuperscript{a} | 1 | 38.0 | 42.7 | 0.84 |
| SO\textsuperscript{b} | 3 | 25.9 | 46.0 | 1.3 |

\textsuperscript{a} Analyzed before the esterification step; T = 175 °C; P\text{total} = 40 bar of 50% O\textsubscript{2}; and 20 g/L of K-70 in distilled water.
experiments with K-40 and K-70, whereas the yield of DCAs calculated from the kerogen content was nearly constant in all cases. The experiments with K-45 resulted in 43% of SO even though the excess of the oxidant per organic carbon content was nearly doubled. In Figure 4, the notation “DME + other” represents the estimated amounts of SO that were observable in the GC–FID chromatogram (volatile oxygenated products; Supporting Information, Section S5). As is shown, the proportion of volatile organics to whole SO increased when more concentrated kerogen was used. All this indicate that the oil shale matrix had a substantial role in its transformation: the mineral part supported the kerogen dissolution and DCA formation by preventing its fast decomposition. It can be suggested that after careful optimization, the use of a native oil shale (K-45) as the substrate will result in even higher DCA yields than with K-70.

3.5. Effect of Base Additives on the Oxidative Destruction of Kerogen. A basic medium might support the solubility of a heavy polyfunctional hydrocarbon material, allowing a better contact with dissolved oxygen. This phenomenon has been observed with lignin34,35 and petcoke processing.26 Furthermore, in a basic solution, free CO₂ could be bounded in the form of carbonates, minimizing the CO₂ emission during the process. The effects of several bases as oxidation additives were compared at the same concentration level (60 wt % per kerogen). As presented in Table 5, the conversion of kerogen was high (>90%) with all alkalis despite their different buffering abilities. However, the DCA values obtained were close to or lower than the values measured in experiments

Figure 2. Effect of pressure when using a SO/50 O₂/N₂ mixture at pressures of 20−60 bar (A1 and A2) and when using 40 bar of different gas mixtures (B1 and B2). Reaction conditions: T = 175 °C, t = 3 h, and 20 g/L of K-70 in distilled water.

Figure 3. Effect of temperature. Reaction conditions: T = 3 h; Pₜₜₒₜₜ = 40 bar of 50% O₂; and 20 g/L of K-70 in distilled water.

Figure 4. Effect of the organic matter content in the substrate. Reaction conditions: T = 175 °C; Pₜₜₒₜₜ = 40 bar of 50% O₂; t = 3 h, and 20 g/L of the oil shale.
Table 5. Kerogen Dissolution with the Addition of Various Bases

| base              | conversion [%] | yield of DCA [%] (C6–C10/C4–C10) | pH (after reaction) |
|------------------|--------------|-------------------------------|-------------------|
| Na₂CO₃           | 98           | 4.4 (37%)                     | 7, 5              |
| Ca(OH)₂          | 93           | 5.8 (36%)                     | 6, 5              |
| Na₂SiO₃          | 95           | 6.7 (26%)                     | 5, 5              |
| NaOH             | 99           | 5.4 (38%)                     | 8, 5              |
| KOH              | 99           | 8.2 (32%)                     | 9                 |
| K₂CO₃            | 98           | 7.6 (28%)                     | 6, 5              |

*Reaction conditions: T = 175 °C; Ptotal = 40 bar of 50% O₂; 20 g/L of K-70; t = 3 h; 60 wt % of base; and before the reaction pH > 9 in all cases.

Without any alkali, indicating that no particular gain in DCAs was achieved. From the selected alkalis, the addition of KOH was most efficacious (corresponding to 8.2% of DCAs). KOH, Ca(OH)₂, and K₂CO₃ were also compared by changing the alkali concentrations from 20 to 80 wt % under constant conditions (Supporting Information, Section S6). The decrease in DCA yields was observed with 80 wt % of each base. The usage of a strong base (KOH) resulted in a curve-shaped trend from which the experiment with 60 wt % of alkali continued to have the best yield. Slight variations of DCA (C₄–C₁₀) yields were also observed with K₂CO₃ or Ca(OH)₂; however, no improvement in the amount of DCA was detected. It can be suggested that destruction of kerogen at low K₂CO₃ or Ca(OH)₂ concentrations is similar to the process when no additives were used.

Additionally, the oil shale ash from an electrostatic precipitator (ESP ash; details given in the Supporting Information, Section S7) from the Estonian thermal power plant was tested as a solid base. As the ESP ash contains a wide variety of metal oxides and is mainly classified as a waste product of the oil shale industry, it could be one of the most cost-effective catalysts for WAO processes. A similar type of oil shale ash used in this work showed good performance for lignin removal under catalytic WAO conditions, 86% at 150 °C with 10 bar of O₂. It was found that 100 mg of ash per 1 g of K-70 was not sufficient to keep the solution alkaline: after 1 h, the initial pH of the reaction mixture (11–12) decreased to pH 5 (Figure 5). Using 500 mg of ash per 1 g of K-70, however, afforded up to 32% of solubilized organics and minor differences in the yields of DCAs (C₄–C₁₀) when comparing the ESP ash to KOH and NaOH. This indicates that if the quantities are large enough, the ESP ash may be used instead of hydroxides for inducing kerogen solubilization.

3.6. Effect of Acid Additives on the Oxidative Destruction of Kerogen. The effect of the acidic medium was mainly studied in the presence of acetic acid; mineral acids were avoided because of their corrosive effect on the reactors. Acidic conditions may be essential for promoting the catalytic effects of metals found in the inorganic part of the oil shale (Fe, Cu, Mn, etc; Table 2) and thus increasing the oxidizing ability of oxygen. Preliminary tests with a native oil shale (K-45) showed that the addition of acetic acid (5 mL in 50 mL of water) afforded a 12.1% yield of DCAs. In addition, it was confirmed that the acetic acid itself was stable under the selected conditions (Supporting Information, Section S8).

The effect of acetic acid on K-70 dissolution and DCA formation was studied by varying acetic acid concentrations from 1 to 100% (Figure 6). As shown, acetic acid in concentrations up to 20 vol % also resulted in a high yield of DCAs (12.3%) for K-70. However, at these acetic acid concentrations, the amount of solubilized organics stayed relatively low (25–30%). By increasing the acetic acid concentration, the amount of solubilized organics slightly increased, whereas the amount of DCAs started to decrease, indicating the rise of other side reactions (e.g., polymerization), which may inhibit the formation of DCAs at the same period of time. In all cases, the complete conversion of kerogen was achieved within 3 h, regardless of the acetic acid concentration and type of kerogen (results for K-45 given in the Supporting Information, Section S8).

3.7. Comparison of Acidic and Basic Media. The effect of the reaction time on conversion, SO, DCA, and CO₂ formation was compared under constant conditions in alkaline (60 wt % of KOH) and in acidic (20 vol % of acetic acid) media (Figure 7). Within the average, the kerogen conversion in acetic acid and in KOH solution after 1 h was similarly high (85–90%), while under neutral conditions, it was lower (60%; Figure 7A). This points to a significantly shorter induction period in acidic and alkaline media than in water at 175 °C despite the possible differences in the oxidation pathways. As expected, the oil shale dissolution in acetic acid was...
accompanied by formation of a high amount of CO₂ for 1−3 h, while in water, the amount of CO₂ increased consistently (Figure 7B). The alkali solution is advantageous for keeping CO₂ emissions low during the whole WAO process. In addition to CO₂ reduction, a substantial benefit of base contribution to kerogen degradation is the formation of SO in constantly higher amounts (Figure 7C). It was found that the maximum amount of solubilized organics (38−49%) was obtained after 2−3 h of the reaction, depending on the alkali used (see the values for Ca(OH)₂ and K₂CO₃ in the Supporting Information, Section S6). As discussed above, the ongoing oxidation of SO becomes predominant after the first 2−3 h and DCAs begin to form at the expense of the dissolved part. The decrease in SO amount was the fastest in the presence of acetic acid, indicating that the oxygenated intermediates may have higher reactivity at acidic pH. Further destruction of the formed intermediates can be suppressed by adding a base. The comparison of GC−FID chromatograms (Figure 8) and GC−MS analysis (Supporting Information, Table S3) of derivatized SO obtained from K-70 oxidation in different reaction media supports this suggestion.

The main advantage from acetic acid contribution is fast formation of DCA, especially at the beginning of the process. For instance, after 1 h, 7% of the DCA was formed in an acetic acid solution, whereas in the KOH solution, less than 3% of the DCA was measured after the same time period (Figure 7D). However, further oxidation results in loss of DCA under acidic conditions, so after 6 h, only 8% of the DCA was left in the reaction product. In the alkali, the DCA yields were more consistent at prolonged reaction times. It can be proposed that...
Nevertheless, the yield of SO in an alkali solution reached more than 95% at 150 °C. Therefore, the acetic acid solution is a preferred environment for the WAO of oil shales when aiming at the highest yields of DCAs in a fast manner.

The effect of oxygen partial pressure and temperature in acidic and basic media followed similar trends to those observed without additives (Figure 9, details given in the Supporting Information, Section S9). In all solutions, the selectivity to DCA formation and separated SO was the highest at 40 bar of 50% O2. The amount of both products were decreased at lowered (pO2 21%) and elevated (pO2 100%) oxygen pressures, regardless of pH. This highlights the conclusion that the amount of oxygen applied must be controlled carefully to obtain the highest yields of valuable oxidation products. By increasing the temperature, the yield of SO is decreased, regardless of the reaction medium. Nevertheless, the yield of SO in an alkali solution reached more than 45% already at 150 °C and remained above 35% even at 200 °C. This provides evidence that the basic media supports the dissolution of the kerogen matrix better than the acidic media.

### 3.8. Applications of Oil Shales with Different Origins

Two other shales, from the Green River (USA; type I40) and Jordan (type II40), were subjected to the same WAO process to establish the feasibility of the oxidation data obtained from kukersite (between types I and II40,41). The Green River shale has the greatest potential to lend DCAs in the highest yields [in Table 6, the yield of DCAs is calculated from the total organic carbon (TOC) value]. Although the process is not optimized for other shales, the use of Green River shale is promising as it afforded 4.8% of DCAs.

![Graph](https://pubs.acs.org/doi/10.1021/acsomega.0c01466)

**Figure 9.** Effect of oxygen partial pressure and temperature on K-70 oxidation in acidic and basic solutions (A at T = 175 °C and B at P = 40 bar of 50% O2). Reaction conditions: t = 3 h; P_total = 40 bar; and 20 g/L of K-70 in distilled water, with 60 wt % of K2CO3 or in 20 vol % of acetic acid solution.

4. CONCLUSIONS

The WAO partial degradation of the oil shale organic matrix enables to dissolve a remarkable amount of its organic mass. From the reaction without any catalyst or external additive, 33% of kerogen was converted to a mixture of semipolymeric dissolved organic material and ~10% of aliphatic DCA. This process can be enhanced with KOH, K2CO3, and especially with the ESP ash, affording dissolved organics up to 52% from kerogen after only 1 h.

The results showed that the kerogen structure is changed during the WAO process via the effective insertion of oxygen, causing its dissolution and DCA formation. The simultaneous oxidation of dissolved organics, however, did not substantially increase the yield of the DCA but considerably increased the CO2 emission. This process was found to be the fastest in an acidic medium. The optimum conditions of the WAO process for these products from an oil shale in a concentration of 20 g/L were at a temperature of 175 °C and a pressure of 40 bar when using a 50/50 mixture of O2 and N2 as the oxidizer. We propose that only by controlling the amount of the oxidant (oxygen) and avoiding overoxidation, high yields of DCAs and dissolved organics can be obtained.

It was shown that the basic and acidic additives have significant effects on reaction rate and product formation: under basic conditions, higher yields of dissolved organics were observed together with lower CO2 levels; in an acidic medium (acetic acid solution), the highest yields of DCAs (around 12% of DCAs from kerogen) were obtained. The use of a native oil shale in WAO gave us good results as the oil shale concentrates.

The WAO process to dissolve kerogen and obtain DCAs can be applied to the Green River and Jordan shales.

### Table 6. DCAs from Different Shales Using the WAO Process

| Shale       | TOC [%] | Conversion [%] | Yield of DCA [%] |
|-------------|---------|----------------|-----------------|
| Kukersite   | 35.1    | 95             | 10.8            |
| Green River | 13.0    | 93             | 4.8             |
| Jordan      | 12.7    | 82             | 2.8             |

*Reaction conditions: T = 175 °C; P_total = 40 bar of 50% O2; t = 3 h; and 20 g/L of oil shale in distilled water. Yield of DCAs (C4–C10) is calculated from the TOC value.*

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01466.

Description of products, specification of the used analytical method, and additional experiments (PDF)
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Notes

The authors declare no competing financial interest.

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