DOCTORAL THESIS

Wet Air Oxidation of Oil Shale

Kristiina Kaldas

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KRISTIINA KALDAS

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Department of Chemistry and Biotechnology
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Supervisor:	Prof. Margus Lopp Department of Chemistry and Biotechnology Tallinn University of Technology Tallinn, Estonia
Co-supervisor:	Dr. Gert Preegel Lignin and MCC sales engineer Graanul Biotech OÜ Tallinn, Estonia
Opponents:	Prof. Tapio Salmi Industrial Chemistry and Reaction Engineering Åbo Akademi University Turku, Finland
	Dr. Indrek Aarna Development Manager Viru Keemia Grupp Kohtla-Järve, Estonia

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Declaration:
Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Kristiina Kaldas

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KRISTIINA KALDAS

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Contents

List of Publications

The list of author’s publications, on the basis of which the thesis has been prepared:

I K. Kaldas, G. Preegel, K. Muldma and M. Lopp, “Reactivity of Aliphatic Dicarboxylic Acids in Wet Air Oxidation Conditions,” *Industrial & Engineering Chemistry Research*, vol. 58, no. 25, pp. 10855−10863, 2019.

II K. Kaldas, G. Preegel, K. Muldma and M. Lopp, “Wet Air Oxidation of Oil Shales: Kerogen Dissolution and Dicarboxylic Acid Formation,” *ACS Omega*, vol. 5, no. 35, pp. 22021−22030, 2020.

III K. Kaldas, A. Niidu, G. Preegel, J. M. Uustalu, K. Muldma and M. Lopp, “Aspects of kerogen oxidative dissolution in subcritical water using oxygen from air,” *Oil Shale*, vol. 38, no. 3, pp. 199−214, 2021.

Author’s Contribution to the Publications

Contribution to the papers in this thesis are:

I The author planned and conducted a major part of the experiments. The author wrote the manuscript, with contributions from the co-authors and complied the supporting information.

II The author planned and conducted a great part of the experiments. The author wrote the manuscript, with contributions from the co-authors and complied the supporting information.

III The author contributed actively to the planning and conducting the experimental and analytical part. The author wrote the manuscript, with contributions from the co-authors.

Introduction

In 2016, Estonia celebrated 100 years of oil shale mining. Estonia has always been a country of oil shale energy, but as traditional values change due to ambitious climate targets, alternatives in oil shale processing are being sought. One option is shale oil production, but are there any others?

The aim of this work is to contribute to our knowledge of the conversion process of complex organic matrices of unconventional fossil fuels, such as oil shale. It is a real challenge for chemists because the substrate, e.g. oil shale kerogen, does not follow a regular polymer pattern, making high selectivity difficult to achieve along with high yields of the desired products. This work is limited to the partial oxidative degradation of kerogen using the wet air oxidation (WAO) process. The idea is to depolymerise the organic material by disrupting the most oxidation-sensitive bonds/functionalities, making the solid and insoluble kerogen water soluble (Figure 1). It is important that the decomposition of the kerogen is only partial, with minimal CO_2 emissions and maximum yield of soluble organic material. As a method, WAO has the advantage of exploiting technical solutions that already exist and inexpensive reagents (water and oxygen). Depending on the conditions applied, WAO is considered sufficient to decompose both higher and lower molecular weight compounds, with both unsaturated and saturated chains. The main disadvantage of WAO implementation is its low selectivity.

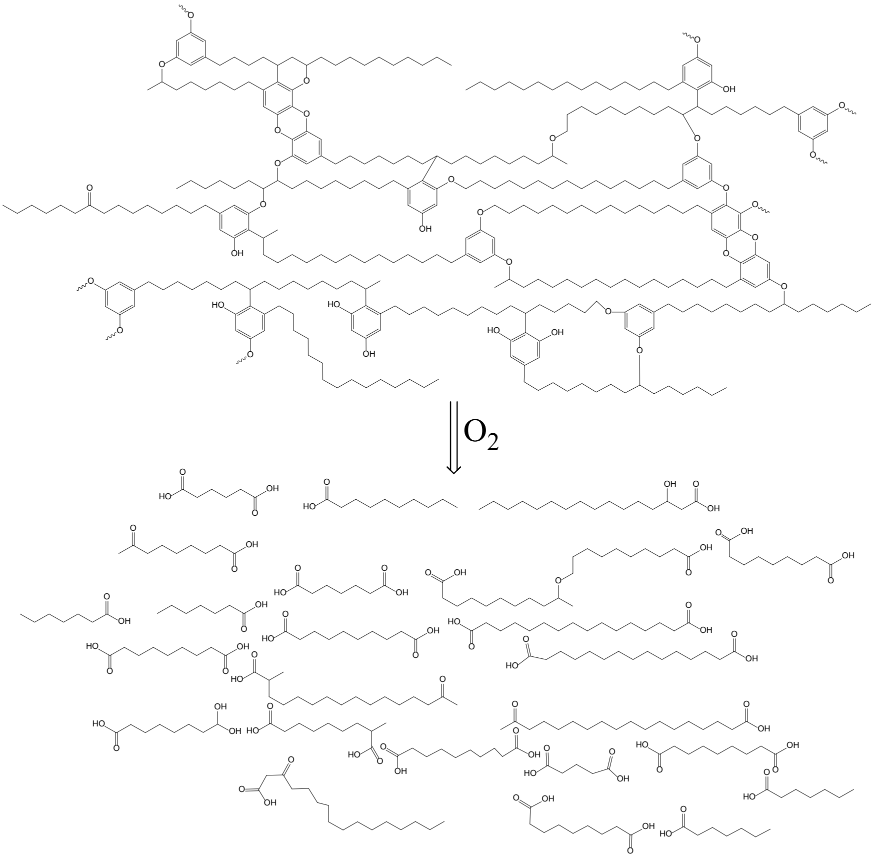


Figure 1. A possible transformation of kerogen into valuable carboxylic acids with WAO.

This thesis first gives a brief overview of the nature of oil shale and its constituents. It also presents a comprehensive overview of the oxidation methods that have been applied to oil shale to date. The second part of the literature chapter focuses on the WAO method. The behaviour of carboxylic acids, phenolic compounds and other known polymers under WAO conditions is discussed in more detail to draw parallels with the degradation of kerogen or its products. The literature section is followed by an overview of the methods used, a description of the reactor system and experimental design, and the analytical procedure. The third part of the thesis discusses the results obtained in the oxidation of oil shale in a batch reactor under subcritical conditions (10-60 bar and 150-200°C), accompanied by the reactivity tests of pure dicarboxylic acids (DCAs) under the same conditions (**Publications I-III**). The extent of kerogen oxidation was elucidated mainly in terms of conversion, yield of dissolved organic matter and the amount of DCAs in it, and CO_2 emission from oxidation. Based on the carbon distribution between solid, aqueous and gaseous phases, a possible pathway of kerogen oxidation is discussed. This is supported by an analysis of the product mixture obtained by using different techniques to identify the main oxidation intermediates formed. The effects of pH, various metal salts and radicals generating organic compounds are presented. In addition, the oxidation results of oil shale types different from kukersite, and further oxidation of water-soluble products obtained from kerogen are provided. The overall objective of the work was to evaluate the conditions affording the highest number of oxygenated products with minimal CO_2 emission. The results provide a basis for deciding whether oil shale valorisation by WAO could be an alternative process for oil shale utilisation.

Abbreviations

AA	Acetic acid
CA	Carboxylic acids
CE	Capillary electrophoresis
$C_{diss.}$	Carbon in dissolved phase
C_4	Succinic acid, butanedioic acid
C_5	Glutaric acid, pentanedioic acid
C_6	Adipic acid, hexanedioic acid
C_7	Pimelic acid, heptanedioic acid
C_8	Suberic acid, octanedioic acid
C_9	Azelaic acid, nonanedioic acid
C_{10}	Sebacic acid, decanedioic acid
C to CO_2	Organic carbon emitted as carbon dioxide
DCA	Dicarboxylic acid
DME	Dimethyl ester of dicarboxylic acid
Eq.	equivalent
ESP ash	Oil shale ash from an electrostatic precipitator
FA	Formic acid
GC-FID	Gas chromatography with flame ionization detector
GC-MS	Gas chromatography–mass spectrometry
Ker	Kerogen content
LC-MS	Liquid chromatography–mass spectrometry
n.d.	Not determined
OM	Organic matter
Ox. ash	Mineral residues from previous oxidations
SO	Solubilized organics, collected after derivatization
WAO	Wet air oxidation
WSA	Water soluble carboxylic acids
wt%	Weight percentage

1 Literature Overview

This literature survey covers the general properties of oil shale in order to clarify its complex nature and the possible techniques that can be used for its transformation into chemicals and other valuable products. The main focus of the overview is on previous results of kerogen oxidation and the WAO process. Examples of the applicability of WAO are given from the perspective of kerogen structural units and possible oxidation products. In addition, a brief overview of the properties, usages and existing methods of obtaining DCAs is provided.

1.1 Oil Shale

1.1.1 General characteristics of different oil shales

Oil shale is a sedimentary rock rich in organic matter (OM) called kerogen, the content of which may have a lower limit of 10% and an upper limit of 60% [1]. A shale kerogen is a solid and insoluble matter, tightly bound within the inorganic minerals. It can be used as a source for oil production or burned for energy. Oil shale is one of the most abundant fossil fuel reserves on Earth, occurring in more than 40 countries [2]–[4]. The largest oil shale deposits are in the United States, Russia and Brazil, but there are also notable deposits in Jordan, Morocco, Australia, China and Estonia [5]. Before oil shale can be converted into energy, oil or other valuable products, it must first be mined. Oil shale deposits near the surface are mined using open-pit methods, while deeper deposits are mined using conventional underground mining methods, or are processed in situ. Globally, oil shale utilization has been in the background for many decades as crude oil and coal resources have been cheaper to extract. In recent years, global forecasts for oil shale mining show a rapid increase due to rising energy demand. This is mainly driven by developments in China and Jordan, but there is also an increasing trend in the processing of tar sands (especially in Canada) [6]. Tar sands from one of the unconventional fuels and organic-rich sedimentary rocks that contain most of OM as bitumen soluble in organic solvents, and are therefore not discussed in detail in this review.

Table 1. Main characteristics of different oil shales and their kerogens [3]–[5], [7]–[9].

Country	Deposit	Age	Origin	van Krev. type	OM, wt%	C in ker, wt%	H/C in ker	O/C in ker	Oil yield %
USA	Green River	Eocene	lacustrine	I	16-21	80-81	1.5-1.6	0.05-0.07	10-11
Jordan	Lajjun	Cretaceous	marine	I/II	20-28	68-69	1.3-1.4	0.06-0.1	8-12
Estonia	Estonia	Ordovician	marine	I/II	30-45	76-77	1.4-1.5	0.13-0.16	20-22
China	Fushun	Tertiary	terrestrial	I	19-21	79.7	1.5	0.07	7-8
Australia	Stuart	Tertiary	lacustrine	I	27	83.6	1.6	0.03	9-14
Brazil	Irati	Premian	marine	II	16-30	68.1	1.8	0.18	7-8

The classification of oil shale is often based on two main characteristics: age and the nature of the depositional environment of the shale. The age of the oil shale determines the extent of its maturation, i.e. how long the ancient biota and mineral residues have decayed in the subsurface [1]. On the geological time scale, "the oldest" oil shales originate from the Cambrian period, 600 million years ago [4], [10]. The depositional environment describes the composition of the biota from which the organic matter of the oil shale is derived. On this basis, kerogens are classified as marine, lacustrine or terrestrial (Table 1). The lipid-rich organic matter of marine oil shales originates mainly from marine algae and dinoflagellates, lacustrine oil shales from algae of fresh water or salt water, and terrestrial oil shales from terrestrial plants, spores and pollen [11]. Organic matter can thus be considered as a highly polymerised substance formed from algae, bacteria or plant material after a series of physicochemical reactions, dispersed in sediments. The main elements present in kerogen are carbon, hydrogen, oxygen, nitrogen and sulphur.

For a consistent description of the different kerogens, the van Krevelen diagram (Figure 2) is used, which was originally created for coals [1], [3], [11]. The method is based on the H/C and O/C ratios determined in kerogens by elemental analysis, which makes it possible to estimate the degree of thermal maturity and the relative amount of oil that can be produced by pyrolysis [12], [13]. During thermal maturation, kerogen becomes depleted in hydrogen and approaches nearly pure carbon; the oil-producing potential is decreased. Type I kerogens are oil prone with a high H/C (≥ 1.5), low O/C (< 0.1) and low sulphur content. Type II kerogens are also oil prone, having an H/C value of 1.2-1.5 and a slightly higher O/C value, in the range of 0.05-0.15. Type II kerogens are also considered the most heterogeneous, with a higher sulphur content than other kerogens. Kerogens of type III are gas prone and are characterised as having low H/C values (< 1.0) and high O/C values (0.1-0.3). Type IV is the least aliphatic kerogen, with very low H/C (0.5-0.6) and moderate O/C (> 0.1), and it is not considered an energy or oil source. In general, the H/C ratio also characterises the ratio between aromatic and aliphatic carbon in organic matter and O/C the content of oxygen-containing functionalities.

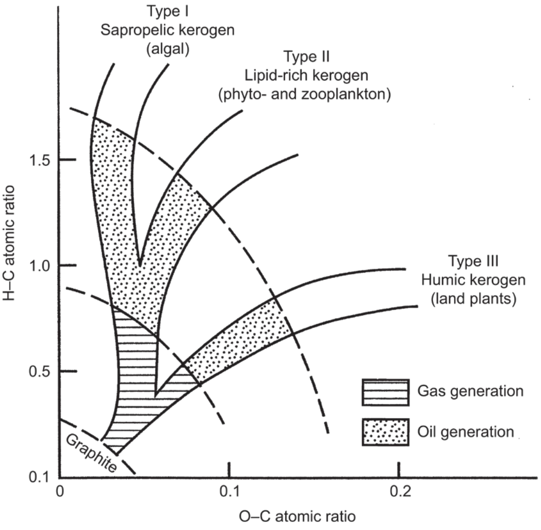


Figure 2. The van Krevelen diagram [14]*. Reprinted with permission of Elsevier.*

Regardless of the type of kerogen, most kerogens are insoluble in common organic solvents [1], [10]. Some oil shales do contain soluble matter − bitumen − but its share rarely exceeds 3% [4], [10], [14]. The insolubility of kerogen is explained by the assumption that kerogens have not received sufficiently high temperatures (i.e. thermal stress at depth) during the maturation period to release the hydrocarbons and gases from the organic polymeric network, as is the case with petroleum [10].

Additional classification can be made on the basis of mineral composition, which also varies from deposit to deposit. Table 2 shows the mineral compositions of inorganic fraction of the shale rock from the USA, China, Estonia and Jordan, analysed as mineral oxides [4], [9], [15]. It is clear that both Ca and Si contents vary greatly depending on the deposit. Some oil shales are described as carbonaceous, with large quantities of various carbonates, of which calcite, dolomite and siderite are the most common [14]. Carbonate-rich shales are often deposited so that kerogen-rich layers are compressed between calcite layers, making the mining and processing of organic matter difficult. Siliceous shales contain large amounts of mineral silica (quartz, feldspar and clay).

Table 2. Mineral matter composition (wt%) of different oil shales [4], [9], [15].

	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	TiO_2	SO_3
Green River	43.8	12.2	4.6	2.4	3.3	22.1	9.4	-	2.2
Kukersite	30.0	9.8	4.3	3.6	0.3	40.4	7.2	0.6	3.8
Jordan	28.3	6.7	2.8	0	0.2	53.3	-	0.4	8.4
Fushun	58.0	28.0	6.2	1.4	1.2	1.4	0.9	1.2	1.8

Some oil shales also contain sulphide minerals, such as pyrite and marcasite [3], [4]. For example, the sulphur content in Jordan shales is more than twice that of other known shales [4], [8], [16].

1.1.2 Properties of Estonian oil shale

Estonian oil shales are among the most studied oil shales in the world. The founder of modern oil shale research in Estonia, Paul Kogerman, contributed a great deal to the understanding of the structure of Estonian oil shales as early as the 1920s [17]–[19]. He defined the organic matter of kukersite as a highly polymerised "resinic substance" mixed with calcium salts of fatty acids [20]. Based on an analysis of the shale oil, phenolic compounds, such as *o*-, *m*-, *p*-cresols and saturated hydrocarbons, were identified as the major components of the kerogen. According to his studies, kerogen decomposes only when heated, or in a solution of concentrated nitric acid [20]. Moreover, Kogerman placed great emphasis on the practical use of oil shale: the production of shale oil. Thus, he studied the organic composition of the oil extracted in different retorts and at different temperatures [19], [21]. The majority of the compounds found in kukersite oil are similar to those present in petroleum. A substantial difference is the presence of phenolic ethers, polyphenols and fatty acids in shale oil. Hydrogenation was proposed as a suitable technique to obtain lighter fractions of the oil and to achieve desulphurisation of the oil [22]. Kogerman concluded that shale oil could be considered a source of raw materials for the chemical industry [21].

Beside kukersite, there is another type of oil shale in Estonia, graptolite argillite (Dictyonema shale) [23], [24]. So far, only kukersite shale has been widely used for oil and energy production. The reason for neglecting Dictyonema shale is its low organic matter content (15-20%) and low calorific value (4.2-6.7 MJ/kg) [2]. The dark grey Dictyonema was mined for a short time in the 1950s for the extraction of uranium.

The formation of kukersite dates back to the Ordovician age (400 million years ago) and it covers a large area in north-east and north Estonia, in the Baltic Oil Shale Basin. Organic-rich kukersite is widely distributed in sediments where mineable layers (1.5-3.2 m) alternate with interbeds of limestone [24]. In the Estonian deposits, kukersite is found at a depth of 0-100 m. Estonia has about 4.8 billion tonnes of kukersite reserves, of which one billion tonnes have already been extracted and another one billion tonnes of oil shale is similarly extractable and processable [2], [25]. Kukersite is a carbonaceous shale, i.e. the content of carbonate minerals in kukersite is between 20 and 70% by weight, but often more than 50% is found (mainly Ca and Mg carbonates: calcite and dolomite). The rest of the minerals are of terrigenous origin (sediments carried from the land to the sea) [26] and include quartz and other silicates (illite and feldspar), as well as pyrite and chlorite [2], [24]. Various noble metals, such as Ni, Co and Cr, are also present in the mineral part of the oil shale, although in minor amounts (less than 0.1 wt%) [4].

The average kerogen content in kukersite is estimated to be about 35% by weight, but varies considerably within the deposit: in some places the OM content is exceptionally high, reaching 50-60% by weight [2], [24], [27]. The calorific value of kukersite is highly dependent on the mineral content and usually ranges from 8.5 to 13.5 MJ/kg. The kerogen of kukersite has a specific gravity of 0.99-1.01 and is insoluble in most organic solvents. The calorific value of pure kerogen is on average 37.2 MJ/kg. Kukersite usually has a light-brown colour and it's believed to be entirely of marine origin [14]. Kukersite is distinguished among other shales by two features: a high content of long-chain hydrocarbons and a high content of oxygen. The oxygen is mainly incorporated in different phenol and resorcinol molecules [28], [29], which are not commonly present in abundance in crude oil [30], [31]. The amount of sulphur (1.5 wt%) present in the form of sulphides, sulphates and organic sulphur compounds is considered to be low compared with other exploited oil shales (Table 2).

Studies have shown that the main components of kukersite kerogen are derived from the accumulation of a particular colonial microorganism called *Gleocapsomorpha Prisca* [32]–[34]. A high proportion of both linear aliphatic chains and phenols originate from the cell walls of *G.prisca* [32]. The best known descriptions of kerogen structure come from Lille´s [29] solid-state NMR studies and Blokker's [35] quantification of individual hydrocarbons and functional groups from RuO_4 oxidation studies, together with biological considerations. The model designed by Lille (Figure 3) states that most of the methylene groups (80%) occur in aliphatic chains, with an average length of 7.5 methylene units [34]. About 40% of the oxygen is located in hydroxyl groups, and another 30% in ether linkages, which are assumed to be cross-linking units. The aromatic carbon content of kukersite kerogen has been estimated to be 21.7% [29]. In Lille´s model, however, the alkyl chains longer than 15 carbon atoms were ignored. It was acknowledged that, as the ^{13}C MAS NMR method did not make it possible to determine the abundance of methylene groups in alkyl chains, flash pyrolysis results were fitted to the model in agreement with the elemental composition of kerogen.

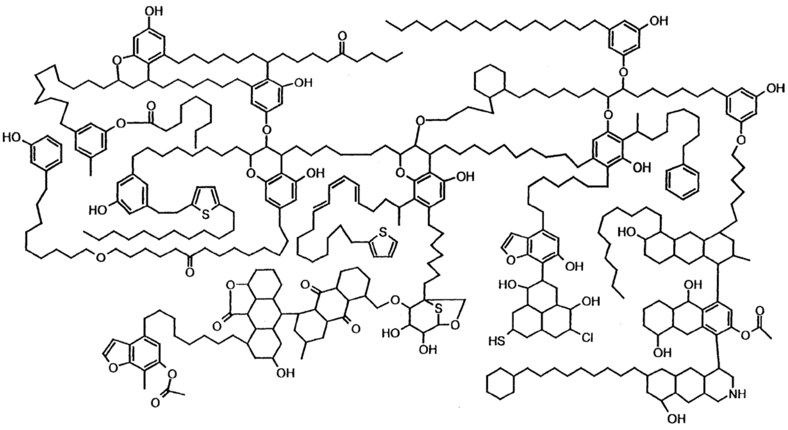


Figure 3. Designed model of kukersite kerogen by Lille et al. [29] *Reprinted with permission of Elsevier.*

Blokker et al. [35] proposed a simplified model of kukersite kerogen (Figure 4), consisting solely of n-alkenyl resorcinol units. The presence of n-alkenyl resorcinol polymer was covered by kerogen oxidation results in which carboxylic acids or compounds containing carbonyl groups were formed as the main products. Blokker used ruthenium tetroxide (RuO_4), a highly reactive yet selective oxidising agent which decomposes aromatic rings with electron-donating substituents to CO_2 [36], [37]. For example, when a phenol with a long alkyl substitution is oxidised, the oxidation starts at the aromatic ring and results in a carboxylic acid with the length of the alkyl. Once formed, aliphatic structures are inert to further oxidation with RuO_4 [37]. In general, the amount of CO_2 released should correspond to the number of phenolic groups. Therefore, Blokker determined that the average length of carbon skeleton chains is in the range of C_5 to C_{20} (with an average value around C_{15} - C_{17}) which is significantly higher than that proposed by Lille.

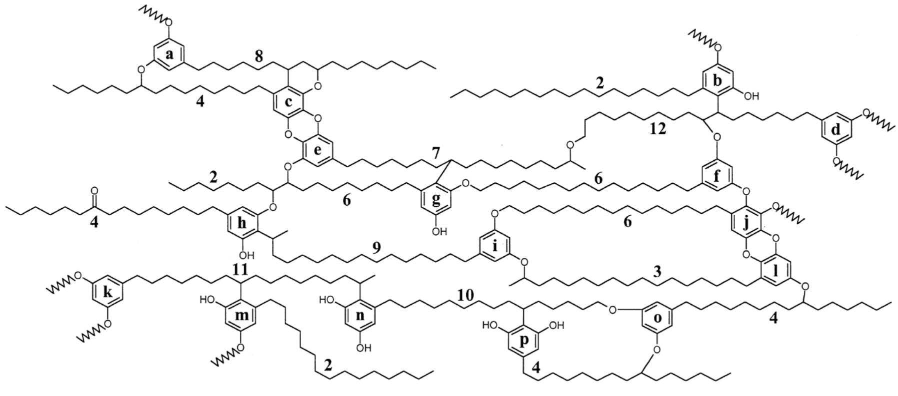


Figure 4. Designed model of kukersite kerogen by Blokker et al. [35] *Reprinted with permission of Elsevier. The numbers refer to different compounds obtained from RuO_4 oxidation.*

1.1.3 Current use of oil shales

Similar to other fossil fuels, such as coal and oil, oil shale can be burned without pre-treatment to produce energy and heat. However, since the use of oil shale for energy production is associated with significant environmental impacts, such as high CO_2 emissions and NO_x and SO_2 releases (currently these gases are mostly absorbed), the focus is now on shale oil extraction by pyrolysis [2], [6], [38]. Shale oil belongs to the group of unconventional oils and its resources are estimated to be four times the conventional crude oil resources, i.e. 411 (in some papers even 690) and 160 billion tonnes, respectively [3], [4], [38].

In the pyrolysis of oil shale, the macromolecular network of the organic matrix is degraded by heat at 400-500 °C without access to oxygen to a mixture of liquid and gaseous products. In fact, the depolymerisation of kerogen occurs as low as 320-350 °C, leading to the formation of an asphalt-like substance called thermobitumen [4], [39]. By further increases in temperature, thermobitumen is cracked into various compounds with different molecular weights and volatilities. Similar to natural crude oil, shale oil is mainly composed of aliphatic and cyclic aliphatics, aromatics and olefins [30], [40], although the amount of unsaturated compounds is higher. Compared to petroleum, shale oil also has a higher content of nitrogen, sulphur and oxygen compounds [40]. Therefore, further processing, such as hydrotreating, is recommended.

Shale oil can be pyrolysed either by in situ retorting at the depth of the deposit, or by processing at the surface. In Estonia, only above-ground pyrolytic extraction is used. The main part produced from oil shale retorting is classified as a heavy oil and is commonly used as a marine fuel additive, as well as a component of wood impregnation oil and asphalt [5], [24]. At present, China and Estonia are the top shale oil producers, with production in China expected to expand rapidly [6], [41]. In Estonia, the new generation retort Enefit280 was launched, which stated to have the lowest environmental impact of all retorting methods: it produces electricity from waste heat, in addition to shale oil and retorting gas [42]. Recently, it has been shown that processing oil shale along with organic waste – shredded tyres and plastic waste – can increase the amount of oil output [25], [43]. To date, alkyl resorcinols are extracted from the wastewater stream of the retorting process [44] and are used as moulding or epoxy adhesives, or as ingredients for hair dyes and cosmetics [25].

1.1.4 Kukersite oxidation

The oxidation of oil shale was first introduced as a method for the investigation of kerogen structure [1]. Attempts to break down the organic skeleton of kukersite using potassium permanganate in an alkaline solution began in the 1920s, with Paul Kogerman leading the way [45]. The method of choice comes from coal studies in which benzene polycarboxylic acids were formed by oxidation along with short-chain carboxylic acids and CO_2 [18], [46]. $KMnO_4$ as a strong oxidising agent is capable of oxidising aldehydes and alcohols to carboxylic acids, but also disrupts the carbon double bonds or phenols by the formation of corresponding diacids or ketones. The kerogen of kukersite was found to be mainly aliphatic in nature, as no aromatic acids were identified in the oxidised product [1], [45]. The work of Kogerman was intensively continued in the 1950s-1980s in the Institute of Chemistry of the Estonian SSR Academy of Sciences [47]. There, a new generation of researchers – Olaf Eisen, Mark Gubrgrits, Ülo Lille, Ilmar Klesment, Aleksandra Fomina, Kaarli Urov and many others – contributed to the investigation of oil shale chemistry [48].

It was demonstrated that the oxidation of kukersite can produce aliphatic dicarboxylic acids (C_4 - C_{10}) as the main oxidation products [49]. The yield of DCAs was reported to reach 60 wt% per kerogen when a combined stepwise oxidation method was used. Later studies by Bajc et al. showed that the 33-step alkaline permanganate degradation of kukersite can lead to 40 wt% oxidation products, but only half of these (20% per kerogen) were identified as DCAs [50]. Abundant amounts of other acids, such as tricarboxylic acids (C_6 – C_{18}) and alkylsuccinic acids (C_{11} – C_{20}), were also formed.

In addition to alkali permanganate oxidation, the treatment of kukersite with nitric acid was introduced as a method for DCA production by Fomina and co-workers [1], [47], [51]. With the use of highly concentrated HNO_3, a mixture of organic acids was obtained with a yield of 50-55% at 130 °C within 2.5 h. It was estimated that the product contained 85-90% DCAs of C_4 - C_{10}. At that time (in the 1950s and 60s), Estonia was part of the Soviet Union, where there was a growing demand for nylon products, and thus a pilot plant for the production of DCAs from kukersite was built. From a periodic reactor system consisting of four stainless steel reactors for the oxidation of kerogen concentrate 90% (ker-90) at 140°C with 30% HNO_3, DCAs were obtained with a yield of 26.3% [47]. In addition, the production of polyurethanes and plant growth promoters from the oxidation by-products was investigated as part of product development [47]. The results of the work were disclosed in several dissertations and patents [52], [53]. In the late 1980s, there were plans to increase the production capacity up to 25000 tonnes of DCAs per year by building a larger scale plant, but this never happened due to political changes. The HNO_3-based technology had several drawbacks, including the release of toxic N_2O and NO_x gases, the use of flammable kerogen concentrate and the presence of nitrated compounds in the product. The HNO_3-based oxidation method is being re-examined in the Industrial Chemistry laboratory in the Tallinn University of Technology (including by the author of this dissertation) [54].

Shortly after the first publications of Fomina et al. [49], [51], [55], a group of scientists from the former Lensoviet Institute of Technology (Leningrad, Russia) started investigations on the air oxidation of kukersite (from the Gdov deposit). In 1961-1962, three publications [56]–[58] appeared describing the use of a continuous air flow passed through an aqueous solution of 85% kerogen concentrate (K-85). The experiments were carried out at temperatures of 100-220 °C and pressures of 1-10 MPa in water, in aqueous alkali solution (NaOH or Na_2CO_3) or in acetic acid. Several other publications also appeared discussing possible technological schemes for the oxidation of oil shale. The main steps of the procedure applied are presented in Figure 5 [53]. The oxidation results of 100 g of kerogen were reported as weight percents of all separate fractions A-D. Fraction D (ether extract) was defined as the DCA fraction. The results obtained in a strongly basic solution (2.4 g NaOH was added per g kerogen) are shown in Table 3. It is noteworthy that the yield of fraction D was high even at the lowest applied temperature. Unfortunately, the actual composition of fraction D was not determined and the actual yields from the initial kerogen content (not from “oxidised kerogen”) were not presented.

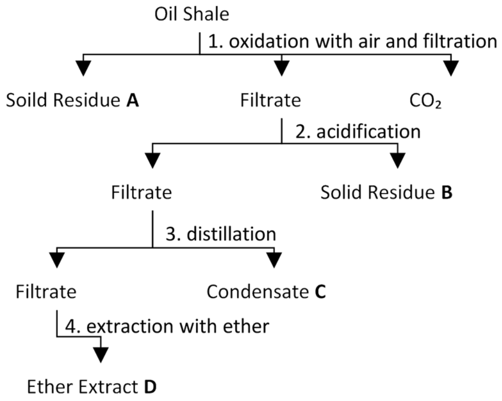


Figure 5. Scheme for oil shale oxidation with air and work-up by Proskurjakov et al. [56], where A corresponds to unreacted oil shale, B to insoluble acids with high molecular weight, C to monocarboxylic acids and D to the main fraction of DCAs.

Table 3. Results by Proskurjakov et al. [56] of oxidising 50 g/L of K-85 at 100 atm of air for 5 h with NaOH 2.4 g/g per kerogen.

	Fractions per 100 g of oxidised kerogen, g			
T, °C	CO_2	B	C	D
170	91.7	21.5	7.1	25.4
150	70.6	26.8	7.0	26.6
130	54.8	43.6	5.9	22.6
120	44.7	56.8	4.6	19.5

In the following papers, an air pressure of 40 atm was used instead of 100 atm. Some of the published results [57] are presented in Table 4, where the DCAs yield is given by the amount of product obtained after the purification of fraction D by column chromatography. They found that air pressure of 40 atm was sufficient to achieve complete conversion of kerogen in 3 h. It is noteworthy that the amount of the purified DCA fraction (in Table 3) was less than half that of the crude ether fraction D (Table 4). This indicates that the actual concentration of DCAs was lower than that reported as fraction D. Calculating the yield of pure DCAs per initial kerogen content, it can be seen that the yield of DCA was not higher than 12%. Proskurjakov et al. [57] also showed that the content of insoluble acids decreased (fraction B) and the concentration of low molecular acids among the individual DCAs increased when temperature, pressure or reaction time was increased. The addition of NaOH affected the amount of insoluble acids, which doubled in alkali. One of the best results was obtained with a 30% NaOH addition in a 3 h reaction, where the yield of purified DCAs per starting kerogen was 18.5% and the C_7-C_{10} content was 51.7% [57]. Although the result stood out from the others, no explanation was given as to why these conditions proved to be the best. Oxidation in the presence of acetic acid resulted in a yield of up to 50% per reaction depth when water was completely replaced by acetic acid. In the absence of the original materials, it is not known to the author of this thesis at what pressures these experiments were carried out and how the products were subsequently separated.

Table 4. Results by Proskurjakov et al. [57] *of oxidising 50 g/L of K-85 in water at 40 atm of air.*

			Fractions from 100 g of oxidised kerogen, g		DCA yield from the initial kerogen
T, °C	Time, h	Conversion, %	B	DCA ($C_4 – C_{10}$)	DCA ($C_4 – C_{10}$), %^{b}
150	5	34.9	32.8	12.2	4.3
160	5	53.7	32.1	18.9	10.2
175	5	100	10.8	3.9	3.9
175^a	3	100	29.2	11.2	11.2
150^a	3	89.6	59.0	13.4	12.0
175	3	83.9	14.6	10.7	8.9

^{a}with 60% of NaOH from kerogen content; ^{b}calculated by the author of this dissertation according to the results of Proskurjakov et al. [57].

Both the Fomina and the Proskurjakov groups used kerogen concentrate as a substrate, in order to develop a DCA technology. In the oil shale industry, the oil shale is enriched in heavy magnetite suspensions or by wet settling of the mineral part of the oil shale, which makes it possible to achieve oil shale concentrate with an OM content of 40% [24]. At laboratory scale, flotation with heavy saturated liquids, such as $CaCl_2$, can be used to obtain oil shale concentrates up to 70% of OM content. This method is based solely on the difference in specific gravity of the OM (0.9-1.3 g/cm^3) and the mineral part of oil shale (carbonates 2.4 g/cm^3) [10]. When a higher OM content was required, as in Fomina´s work, an acid treatment with concentrated acids, such as an HCl/HF mixture (HCl to remove carbonates and HF for mineral oxides and silicates) or HNO_3 to separate the kerogen from the oil shale organic/mineral matrix is used [1], [10]. It should be noted that the chemical treatment of kerogen may change the properties of the used kerogen.

1.1.5 Oxidation of other shales

In addition to the Estonian and Russian studies, there are also descriptions of the oxidation of oil shale from other deposits (Green River, USA; Fushun, Maoming and Longkou, China). For example, it has been shown that of the Fushun, Longkou and Maoming oil shales, the Longkou shale was the easiest to oxidise with air in an alkaline medium [4]. A mixture of organic acids can be obtained from Longkou oil shale with a yield of 50% per organic carbon content. Unlike kukersite, the oxidation products from Chinese shale yielded a high proportion of water-insoluble acids, which mainly contained aromatic acids. It was shown that these types of acids can be effectively used as an additive in crude oil to reduce its viscosity. Another example is the oxidation of Maoming shale by ruthenium tetroxide, which afforded aliphatic DCA over a broad spectrum (C_6 – C_{29}) [37]. Saturated CAs were also present in a wide range, from short to long chains (C_{32}).

For Green River shale, it has been shown that long boiling in potassium permanganate solution results in full conversion of the kerogen to volatile acids and CO_2, indicating the absence of resistant structures, such as paraffins [1], [59]. The stepwise oxidation of Green River shale with alkali potassium permanganate resulted in 77% of the kerogen carbon being converted to medium molecular weight products and the rest to CO_2 [59]. Of these medium molecular weight products, cycloalkanes were identified in 34%, aromatic compounds in 10-15%, and heterocyclic compounds in 45-60% amounts. Depending on the used oxidation conditions, isoprenoid acids (C_{14} – C_{17}), saturated straight chain DCA (C_2 – C_{15}) and CA (C_7 – C_{25}) were found among the degradation products. The structure of the Green River kerogen is therefore associated with saturated cyclic substances containing a high proportion of heteroatoms [1], [60], [61]. It has been proposed that the system is held together by short hydrocarbon chains and ether bridges. The oxidative cleavage is assumed to be initiated adjacent to these oxygen bridges and heteroatoms in the cycle. By increasing the oxidation efficiency or reaction time, the decomposition of the cyclic structures increases the proportion of short-chain DCAs in the oxidation product [61], [62]. The results obtained with the ruthenium tetroxide oxidation were similar and indicated low aromaticity (6-11% [4]) and high amounts of CA and DCA with a carbon number $<C_{12}$ [37]. The oxygenated sample contained a significant amount of cyclic material, confirming earlier results.

1.2 Wet Air Oxidation

The term *wet air oxidation* (WAO) can be defined as the oxidative degradation of organic compounds in water with oxygen gas. So far, this process has mainly been used for treating wastewater streams from pulp mills, dyeing plants and oil refineries, as well as waste from the food industry and municipal streams [63]–[66]. This means that such organic pollutants as phenols, chloro- or thio-compounds, aromatic acids etc. are removed by degradation to CO_2, low-molecular weight carboxylic acids and other end products like inorganic halides or sulfates. The first commercial WAO application dates back to the 1950s, when F. J. Zimmermann patented a process using a 10 MPa air supply at 270 °C to treat sulfite waste liquor [67]. Nowadays, the main industrial non-catalytic wet oxidation processes operate at temperature ranges of 150-325 °C and pressures of 2-12 MPa [65]. These conditions correspond to the subcritical range in which the applied pressure maintains water in the liquid phase even though the temperature is above its boiling point [66], [68]. Industrial WAO treatments are often run in continuous mode [69], while for laboratory experiments batch-type closed reactor systems are often used (Figure 6**)**.

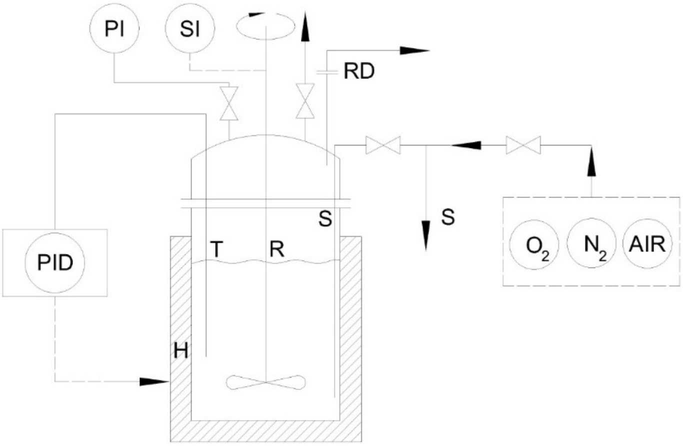


Figure 6. Typical experimental setup for small-scale WAO experiments. Modified from [70]. H – heater; R – reaction vessel; T – thermometer; S – sample; SI – speed indicator; PI – pressure indicator; RD – rupture disk; PID – controller.

The chemical reactions that occur during the WAO process are categorised as non-selective free radical reactions. High temperatures induce homolytic bonds to break, and thus radical reactions are evidenced in subcritical regions [65], [71], [72]. The oxidation of organic wastes occurs in the liquid phase, where the reactive oxygen species or induced alkyl radicals attack the substrate molecules. The initiation of radical chains is often represented as an oxygen-substrate or an oxygen-water interaction (Eqs. 1-3) [65], [70], [73]–[75]. However, it is still questionable whether oxygen in pressurised water is reactive enough to abstract the hydrogen or if the initiation is actually triggered by the interaction of some metal elements, such as the material of the reactor wall [76]. The propagation step is covered by reactions with formed peroxide and hydroxyl radicals (Eqs. 4-8) and thus the transformation of the substrate is observed. In addition to radical reactions, reactions involving water as a reactant or acid/base-catalysed reactions are enhanced [77] because the ionic strength of the water increases with increasing temperature ($K_w = 10^{-11}$ at 250 °C and 10^{-14} at 25°C) [71]. With increasing temperature, the dielectric constant of water also decreases (D = 78.5 at 25 °C and 34.8 at 200 °C), meaning that the solubility of hydrophobic molecules increases, thereby favouring reactions with complex matrices [71], [78]. It is also important to note that under subcritical conditions the solubility of oxygen in water is significantly higher than under normal conditions (e.g. 0.04 mol/kg at 50 bar and 162 °C; 0.0012 mol/kg at 1 bar and 25 °C) [79], [80]. In a real reaction mixture, the gas-to-liquid transfer and thus the mixing efficiency must also be considered [64], [69]. As a result of these several factors, a mixture of products is often formed, even with a single substrate, making it difficult to distinguish the reaction mechanism. Therefore, the transformation of OM or other substrates is often described with chemical oxygen demand and/or quantification of the products. The rate of oxidation of organic compounds is mainly discussed in terms of the nature or resistance of the specific substrate to oxidation.

$H_2O + O_2 \rightarrow HO_2^{\cdot} + HO^{\cdot}$ [Eq. 1]
$RH + O_2 \rightarrow R^{\cdot} + HO_2^{\cdot}$ [Eq. 2]
$R^{\cdot} + O_2 \rightarrow ROO^{\cdot}$ [Eq. 3]
$RH + HO^{\cdot} \rightarrow R^{\cdot} + H_2O$ [Eq. 4]
$RH + HO_2^{\cdot} \rightarrow R^{\cdot} + H_2O_2$ [Eq. 5]
$ROO^{\cdot} + RH \rightarrow R^{\cdot} + ROOH$ [Eq. 6]
$ROOH \rightarrow RO^{\cdot} + HO^{\cdot}$ [Eq. 7]
$RO^{\cdot} + RH \rightarrow ROH + R^{\cdot}$ [Eq. 8]

In 1991 Li et al. [68] proposed a generalised kinetic model for the wet oxidation of organic compounds according to which initial organics **A** are either oxidised directly to end products **C** (CO_2 and H_2O) or through intermediates **B** (Figure 7). The strength of the parent material is characterised by the relationship between two competing pathways. High conversion of the substrate depends not only on the properties of the substrate, O_2 concentration and temperature, but also on residence time, concentration of the feed material, speed of agitation, pH, reactor material and geometry [65], [81], [82]. When a sufficient temperature or other conditions are not met, a partial oxidation occurs. Partial oxidation can be a valid method for obtaining oxidation intermediates, which in turn can be valuable starting materials for the chemical industry. Since kerogen is composed of various structural units, each with different characteristics, the oxidation of kerogen is challenging. Examples of the behaviour of the most abundant structural moieties in kerogen, such as phenolic groups or aliphatic acids, during the WAO process are given below.

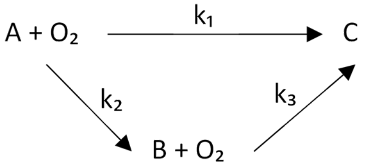


Figure 7. Generalised kinetic model for WAO [68]

1.2.1 Catalytic WAO

In order to lower the working temperature and pressure, and increase the selectivity towards desired products, different catalysts have been tested for WAO systems. Both homogeneous and heterogeneous catalysts have been examined. One of the main advantages of using a homogeneous catalysis is that a smaller and simpler reactor system can be used. The benefit of using a heterogeneous catalyst is the ease of its further isolation from products. In the present study, only the possible catalytic effects of the metallic elements present in the inorganic matrix of the oil shale are discussed. Since kerogen is embedded with inorganic matter, the catalytic behaviour of these inorganic elements may have an effect on the oxidation reaction.

$$Co^{2+} + ROOH \longrightarrow Co^{3+} + RO^{\cdot} + {}^{-}OH$$

$$Co^{3+} + ROOH \longrightarrow Co^{2+} + ROO^{\cdot} + H^{+}$$

Figure 8. Hydroperoxide decomposition catalysed by cobalt [72], [75], [83]

Among the metals from the oil shale mineral part, Co, Cu, Cr and Fe are known to have catalytic activity in WAO processes [64], [65], [72], [84]. Cu, Fe, Co and Mn nitrates in amounts of 20 mmol were shown to increase the oxidation (5 bar of O_2; 200 °C) efficiency of oil shale refining effluents containing phenols, organic acids, amines, residual hydrocarbons etc. at a TOC concentration of 9 g/L [84]. Cu and Fe also had slight synergistic effects when added together to the same solution. The same phenomenon was observed with Cu and Fe sulphates in the oxidation of sewage sludge under 56 bar of air [85]. Cu salts (especially nitrates) have also exhibited strong catalytic activity towards acetic acid, which is usually considered a refractory intermediate, by doubling its oxidation rate when compared to uncatalysed reactions [86]. In homogeneous form (as nitrate, sulphate or acetate salts), these first row transition metals are believed to act via a radical chain, i.e. an electron transfer from the metal to the organic substrate initiates alkyl hydroperoxides to decompose, and thus active (alkyl-)peroxide or hydroxyl radicals are formed in solution (Figure 8) [72], [75], [83]. The catalytic ability of these metals is associated with their redox properties. Arena et al. [87] showed that Cu^{2+}, which promoted the fastest phenol conversion, also has the most favourable redox potential ($E_{Cu^{2+}/Cu^{+}}$ = 0.171 eV) compared to Fe^{3+} ($E_{Fe^{3+}/Fe^{2+}}$ = 0.771 eV) and Mn^{2+}($E_{MnO_2/Mn^{2+}}$ = 1.229 eV). Imamura [72], however, strongly disagrees that the main function of these metal elements is to decompose the hydroperoxides formed. He points out that hydroperoxides decompose easily under WAO conditions due to the high temperatures or contact with the reactor wall [65], [71], [88]. Therefore, the high catalytic performance of metal catalysts is also attributable to the physical properties (solubility at a given pH) and to the ability to form coordination complexes even in the homogeneous form [84], [85], [89]. Many of the listed catalysts have shown increased performance in the lower pH range [84] or if inserted as solids (e.g. as oxides or with supporting material like alumina or ceria) [65], [90], [91]. It is not known how these metals participate in oxidation when occurring in the mineral formations that are characteristic of oil shale: dolomite, illite, feldspar, kaolinite, etc. No obvious effects of these metals have been demonstrated during pyrolysis [15].

In addition to metallic elements, organic co-oxidants can also exert a catalytic effect by increasing the oxidation rate of the substrate [92], [93]. Co-oxidants can be defined as more readily oxidising compounds that generate active organic radicals, which subsequently attack other organic compounds in solution. Phenol has been shown to increase the oxidation rate of nitrobenzene [92], 1,3-dimethylbenzene [94], thiocyanate [95] and even low molecular weight dicarboxylic acids: succinic and maleic acid [63]. Therefore, oxidisable materials, such as lignin and polysaccharide fragments, can act as co-oxidants towards oxidation-resistant intermediates formed from the same material [63], [96]. In other words, recirculation of the effluent in a process where new batches of unreacted material are continuously added promotes the further oxidation of recalcitrant products. A synergistic effect on oxidation has also been noted between morpholine and diethanolamine [97], formic and acetic acid [98], and sodium salts of malonate and succinate (Table 5) [93]. In all of these examples, a radical chain network is induced by highly reactive compounds formed during the rapid decomposition of the co-oxidant. Recently, it was demonstrated that the effect of co-oxidation can be further enhanced in the presence of homogeneous metal catalysts, such as Cu(II) [99].

Table 5. Sodium malonate induced co-oxidation^{a} [93]

	% compound removal	
Compound	Without sodium malonate	With sodium malonate
Sodium acetate	<2	9.1
Sodium propionate	<2	24.6
Sodium succinate	<2	19.5
Sodium glutarate	<2	16.4

^{a}Conditions: T = 165 °C; P_{O_2} = 5 bar; 4.4 M NaOH synthetic Bayer liquor, 2 h

1.2.2 WAO of (substituted) phenols

A lot of information can be found on the WAO of phenol as it is a frequently occurring compound in wastewater streams and is therefore used as a model pollutant in studies. According to a recent review on the removal of phenolic compounds [81], the uncatalysed phenol oxidation under WAO conditions requires remarkably high temperatures (above 175 °C). The temperature can be reduced to 120-140 °C by adding catalytic species, such as Cu(II) [82], [100]. In addition, it has been shown that the oxidation of phenolic compounds is pH sensitive: a rapid phenol oxidation occurs in strongly alkaline (pH >10) and in slightly acidic (pH 2-7) conditions, while almost no oxidation occurs in the pH region 7-10 [81], [82], [101]. The phenol/oxygen ratio (e.g. oxygen pressure) affects the rate of oxidation and determines the extent of oxidation, as well as the spectrum of the formed intermediates. The oxidative degradation of phenol is thought to be initiated by the formation of 1,2- or 1,4-dihydroxybenzene and its rapid oxidation to *orto-* or *para*-benzoquinone (Figure 9) [102], [103]. This is followed by the formation of unsaturated diacids (such as muconic acid and maleic acid). Since these are subjected to further oxidation, the accumulation of low molecular weight acids, mainly propionic acid, oxalic acid, formic acid and acetic acid, is often detected [64], [101], [102], [104].

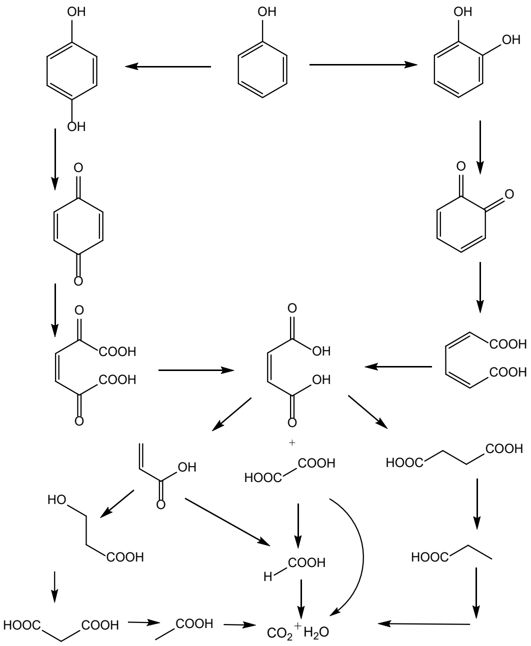


Figure 9. Proposed reaction path for phenol oxidation [81], [102], [103]

It is believed that 3-hydroxyphenol or resorcinol follows a reaction pathway similar to phenol [81], [103], [105]. Degradation of resorcinol has been shown to occur at temperatures as low as 150 °C under non-catalytic WAO conditions and moderate oxygen regimes [105]. Considering phenol oxidation as a radical substitution reaction, electron donating groups, such as hydroxy and methoxy, offer stabilisation to radical intermediates, increase the electron density on the aromatic ring and thus the oxidation rate (Figure 10) [103]. For that reason resorcinol is expected to alter oxidation even faster than phenol.

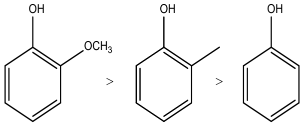


Figure 10. The order of oxidation for substituted phenols [103]

1.2.3 WAO of carboxylic acids

One of the major limitations in using the WAO process as a final purification process for waste streams is the slow oxidation rate of carboxylic acids. Particular attention has been paid to acetic acid, which is often a refractory intermediate and provides a barrier before the complete removal of organic compounds with WAO. It has been shown that the removal of acetic acid below 200 °C is negligible with or without an external catalyst in WAO [66], [90], [106], [107]. Acetic acid is also much more stable than acids with the same or shorter carbon chain lengths, such as oxalic acid and formic acid [64], [66], [106]. In many other cases, reactivity increases as the molecular weight of the organic compound increases. For example, both mono- and dicarboxylic acids with six carbons have been shown to be more reactive than corresponding compounds with five carbons

[66], [72]. Imamura [72] related the reactivity of organic substances in WAO directly to the ratio of oxygen to molecular weight, and showed through a number of examples that the longer the hydrocarbon chain per oxygen, the faster the decomposition of a given compound. Due to the polarisation of the carbonyl group, either the α- or the β-carbons of carboxylic acids are considered the most reactive sites [108]–[110]. Unsaturated carboxylic acids have been shown to be more reactive than the corresponding saturated acids due to the ease of radical addition to the carbon-carbon double bond [109]. The higher the molecular weight of the substrate and the more functional groups it contains, the more difficult it is to distinguish a specific reaction mechanism.

To the best of our knowledge, the oxidation of long-chain DCAs (C_9 and C_{10}), which is the focus of this dissertation, has only been studied by Jin and his co-workers [111], [112], who showed that under sub- and supercritical conditions DCA oxidation can proceed in parallel at different oxidation sites: α-carbon, β-carbon and γ-carbon, all leading to different oxidation products. The oxidation of C_9 and C_{10} was studied in a pressure reactor with the oxidant H_2O_2 in water at temperatures from 300 °C to 400 °C. To avoid complete oxidation, an insufficient amount of oxidant was intentionally applied, so that oxidation pathways could be formulated based on the intermediate products. In the oxidation of C_{10}, the main intermediates were DCAs with carbon numbers 2-9. Experiments with greater oxidant supplies indicated that short-chain acids formed at the expense of the long-chain acids, as a gradual increase in their concentration was observed. Considering that the α-hydrogen next to the carboxyl-group is the most acidic proton in the compound, the formation of C_4-C_9 DCAs was attributed to the α-oxidation pathway. As shown in Figure 11, after the removal of α-hydrogen by an active radical (e.g. a hydroxyl radical), the formed alkyl radical is assumed to react with oxygen to produce a peroxy radical. Upon the addition of hydrogen, the hydroperoxide decomposes to DCAs with one less carbon atom. Jin et al. [111], [112] also demonstrated the presence of aldehyde acids as dimethyl acetals. The formation of (ω-1)-keto monocarboxylic acids was suggested to follow the β-oxidation pathway initiated by β-hydrogen abstraction and ensued by the decarboxylation of β-keto dicarboxylic acid. The γ-oxidation pathway was proposed to explain the formation of γ-lactones containing a carboxyl group in the side chain. When hydrogen is abstracted from the γ-position, hydroxy acid is produced, which subsequently loses a water molecule and forms a cyclic ester.

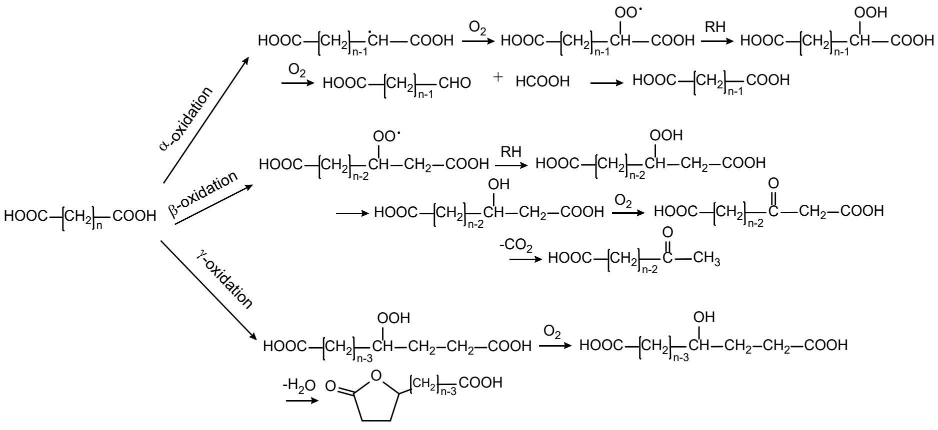


Figure 11. Reaction pathways proposed for the oxidation of DCA at α-, β- and γ-carbons. Modified from Jin et al. [111], [112].

A number of reaction pathways were also proposed for the further oxidation of (ω-1)-keto monocarboxylic acids (Figure 12) [111], since these compounds have reactive sites on carbons near the carboxyl and also the keto groups. It was suggested that when oxidation occurs at the α- or β-position of the keto group, a shorter DCA is formed, along with acetic acid release. When further oxidation is initiated adjacent to the carboxyl group, a similar oxidation mechanism occurs as described in Figure 11, except that diketone is formed from the β-route.

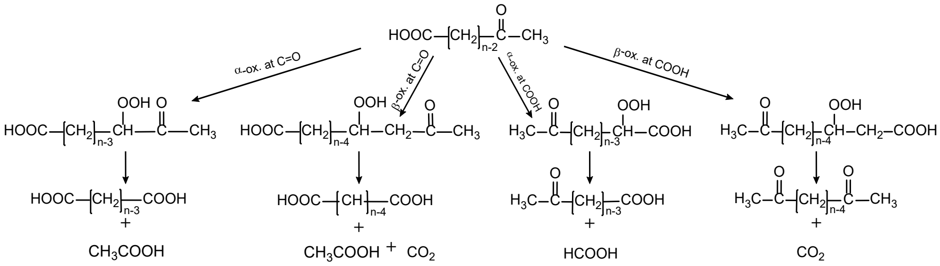


Figure 12. Further oxidation pathways of (ω-1)-keto monocarboxylic acids. Adapted from Jin et al. [111] with permission from Elsevier.

In addition, the presence of simple monocarboxylic acids (CA) was identified, although in much lower concentrations (except for acetic and formic acid) than that for DCAs or keto acids. CAs with carbon numbers 8 and 9 were detected only at very low oxygen levels. It was suggested that the formation of CAs might be the result of the oxidative decarboxylation of DCA occurring as a minor pathway.

1.2.4 Partial WAO of lignin, asphaltene or other complicated matrices as a possible model for kerogen oxidation

As mentioned above, the oxidation of rich mixtures of organic compounds can be challenging because each compound reacts differently to oxidation under WAO conditions. If the goal is the complete decomposition of organics, the use of harsh oxidative conditions - high temperature and high pressure along with various catalysts or catalyst systems - solves the problem. The situation is completely different if the aim is to obtain value-added chemicals by means of partial oxidation. Although oxidation under WAO conditions is often very unselective, it is still a method of choice for converting polymer matrices with irregular structures into valuable products. In addition to being environmentally friendly, the WAO method is often less time consuming than enzymatic or other low temperature processes. The oxidation results of other polymeric materials may serve as good bases to find a solution for the oxidation of kerogen.

The partial oxidation of lignin from pulping process at temperatures of 175-225 °C and with oxygen pressure at 5-15 bar is an example of the transformation of complex matrices [113]. The main products obtained were short-chain CAs and DCAs, such as formic acid, acetic acid, succinic acid, oxalic acid and glutaconic acid. Unlike kukersite kerogen, lignin is short on long aliphatic structures but rich in phenolic monomers and aryl ether linkages that are susceptible to oxidation [113]–[115]. In strongly alkaline conditions, complete conversion of lignin was achieved at 190°C with 1 MPa of oxygen in 1 h [116], [117]. Vanillin, *p*-hydroxybenzaldehyde and other valuable aromatic compounds can be produced but require significantly milder conditions (e.g. 80 °C at 3-12 bar of O_2 [115]). Selectivity towards these products can be increased with the addition of a catalyst, as with copper and cobalt complexes [115], [118] or alumina supported Pd catalysts [119]. Nevertheless, the process optimisation is crucial as subsequent oxidation of the desired products to CO_2 follows [115], [119]. In addition, repolymerisation and condensation have been detected as competing reactions which reduced the overall yield [113], [118], [120]. A repolymerisation has been associated with highly reactive phenolic monomers that are likely to yield condensation products [100], [113].

Since 2016, a group of scientists from the University of Calgary have published a series of articles on oxy-cracking asphaltenes [121], [122], oil sands tailings [123] and petroleum coke [124], [125]. The method was introduced as a combination of oxidation and cracking, with the applied conditions (temperature 170-230 °C, pure oxygen 3.5-5.2 MPa in alkaline solution (pH 8-10)) perfectly fitting the WAO ranges. The aim was to convert solid residues from heavy oil and bitumen distillation into water-soluble products, with a minimum amount of CO_2. Both asphaltenes and petroleum coke were described as polycyclic aromatic structures containing S, N, and various metals in significant amounts. For example, 97% of the original asphaltenes were converted with a selectivity of 60% to a mixture of water-soluble carboxylic acids (WSAs) that contained methyl ethers, naphthenic acids, phenols and other water-soluble organics. The addition of alkali was required to keep the formed organics in solution and to capture the released CO_2 as Na_2CO_3. The high molecular weight compounds were gradually oxidised to lower molecular weight compounds via effective oxygen incorporation. The effect of stirring rate was studied for various substrates, all showing that a mixing speed above a 500 rpm, mass transfer effect becomes negligible as a turbulent regime is reached [121], [125]. Oxy-cracking was also addressed as a suitable method for demineralisation as the residual matter contained more metals than the WSA fraction (Table 6). These results were consistent with the work of the Polish group from the late 1970s [126], [127], where the oxidation of asphaltenes with similar molecular weights and elemental compositions was investigated. Similar operating conditions, such as temperatures of 225-230 °C, atmospheric pressures of 6.4-6.8 MPa, and the use of intensive stirring under alkaline conditions were considered to be optimal. The maximum yield of WSA obtained was 56%, which contained mainly low molecular weight DCAs (C_2-C_4) and benzene polycarboxylic acids. The described method may be called partial WAO or oxy-cracking, depending on the author´s choice: both are informative. The conclusions from these studies can be used for kerogen oxidation.

Table 6. Elemental distribution between WSA and solid residue (mg) after petcoke oxidation at 230°C, 5.2 MPa for 2 h [125]

	C	H	N	S	Ni	Fe	Co
Petcoke	845	38	16	45	0.3	0.57	0.15
WSA	747	34	7	27	0.2	0.02	0.02
Solid residue	41	3	3	12	0.1	1.09	0.04

1.3 The value of dicarboxylic acids

DCAs are white crystalline solids that have various applications, including the preparation of polymer fibres (polyamides, polyesters), plastics, elastomers and lubricants [128]. Long chain DCAs, such as azelaic and sebacic acid, are valued ingredients for cosmetics and pharmaceutical preparations [129], [130]. In recent decades, aliphatic polyesters have gained increasing attention because they are susceptible to biological attack and can therefore be considered biodegradable. For example, polyesters from 1,4-butanediol and azelaic or succinic acid are fully biodegradable and compostable [131], [132]. The mechanical properties are close to those of polypropylene, which currently accounts for nearly 20% of global plastic production [133].

Of the group of DCAs studied in this dissertation, adipic acid has the widest commercial use as a nylon-6,6 monomer [134], [135]. The petroleum-derived method for adipic acid production is well-known, based on cyclohexane oxidation in a two-step process [136]. In the second step, HNO_3 is used as an oxidant, producing the undesirable by-product N_2O. Although an effective thermal destruction strategy for N_2O removal exists [137], most adipic acid is produced in countries where no emission abatement is applied, posing a risk to the environment [138]. This is one of the reasons why alternative ways of obtaining DCAs are important. Progress has been made in the use of oxygen alone throughout the process of adipic acid production [135], [139]. Among the methods currently being actively developed [134], [138], [140]–[142], the implementation of genetically engineered yeasts for producing succinic or adipic acid from monosaccharides of lignocellulosic biomass is a promising alternative to the existing methods. It is expected that in the near future most of the succinic acid production plants using petrochemical feedstocks will be replaced by those using bio-based monomers e.g. from the fermentation of sugars [133].

The main characteristics of the investigated DCAs, which are essential for the analysis and separation of acid mixtures from kerogen oxidation, are presented in Table 7. The physical and chemical properties of aliphatic DCAs differ remarkably from those of monocarboxylic acids, being greatly affected by the second carboxyl group in the molecule, and by a number of methylene groups between the carboxyl groups. The length of the aliphatic chain leads to an odd-even effect, which means that the solubility in water is lower for DCAs with even numbers of carbons than for DCAs containing odd numbers of carbons [143], [144]. The melting point and also the decarboxylation temperature alternates along the acid series [128]. This effect, however, diminishes with an increase in the chain length, so that from the C_8 diacid onwards all of the following acids may be regarded as insoluble in water, as the hydrophobic properties predominate.

Table 7. Main characteristics of DCA C_4 - C_{10}

Name	Abr.	M, g/mol	Solubility in water at 20°C, g/L	T_m, °C	T_b, °C	pKa_1	pKa_2
Succinic acid	C_4	118.09	54.7-64	185	235	4.2	5.6
Glutaric acid	C_5	132.12	390-565	96.5	303	4.3	5.3
Adipic acid	C_6	146.14	13.1-18.6	152	337.5	4.4	5.3
Pimelic acid	C_7	160.17	47.3-50	106	342	4.6	5.6
Suberic acid	C_8	174.20	1.5-1.6	142	345.5	4.5	5.5
Azelaic acid	C_9	188.22	2.4	106.5	357	4.5	5.3
Sebacic acid	C_{10}	202.25	1	134.5	354	4.6	5.6

Data obtained from the referred publication: melting point T_m[145], [146]; boiling point T_b[147]; solubility [147], [148] and pKa values [149], [150]

2 Motivation and Aims of the Work

There exists an urgent need to expand the understanding of the transformation processes of complex organic matrices of unconventional fossil fuels, such as oil shale. The general aim of the present work is to investigate whether WAO is a suitable transformation method for converting kukersite kerogen into valuable feedstock chemicals. The word “valuable” indicates chemicals of which prices and ranges of application are a lot wider than shale oil has.

The specific aims of the study were:

(1) to elucidate the possibility of the oxidation of kerogen in order to obtain DCAs in the highest possible yield,
(2) to evaluate the reactivity of main oxidation products (DCAs) under WAO conditions,
(3) to examine the influence of temperature, oxidant pressure, reaction time, different basic and acidic additives towards DCA and oil shale oxidation,
(4) to investigate the process of kerogen oxidation in respect to carbon distribution between three phases,
(5) to identify the main drivers for kerogen and DCA oxidative decomposition.

3 Details of Used Methods

3.1 Equipment and procedures

In this work, pressure reactor systems (4566C or 4575A) from Parr Instrument Company (Moline, Il, USA) were used. The reactor vessels were available in two sizes: 100 ml and 500 ml. The 100 ml vessels were also available in two construction materials: stainless steel (SS -316) and Hastelloy (alloy C-276 of Fe, Cr, Ni, Mo and Mn). Depending on the specific accessories attached, both reactors could have a maximum operating temperature of 350 °C and a pressure of 200 bar. Continuous and uniform stirring was ensured by a four-bladed turbine impeller moved by a magnetic drive. In a typical experiment, the reactor was charged with a specified amount of substrate material and distilled water, pressurised with an oxygen-containing gas and heated to the desired temperature. In every case, the volume above the solution was kept constant, meaning that the reactor vessels were always filled to the same capacity, either with a water-oil shale slurry or water-DCA mixture. The zero-reaction time was always considered to be 5 °C from the actual temperature, since the final temperature rise was set low to avoid overheating. The average warm-up period from room temperature to the selected temperature was 10 minutes. At the end of the reaction, the mixing rate was reduced to a minimum, and the reactor was cooled to room temperature and depressurised. To analyse the emitted gas, a gas sample was taken during depressurisation and analysed by GC-TCD (Shimadzu GC-2014). The aqueous reaction mixture was analysed for pH (with a pH metre inoLab pH7310), weighed and transferred to centrifuge tubes (in the case of oil shale) or flasks (in the case of DCA reactivity tests). Additional rinsing was performed with a 0.1 M KOH solution to dissolve any remaining solids or DCAs. In the WAO of oil shale, the solid was separated from the liquid phase and dried for elemental analysis. The aqueous phase was either concentrated and derivatised in a methanol solution for the measurement of dimethyl esters of DCAs with GC-FID (Shimadzu GC-2010) or analysed directly using capillary electrophoresis (CE, Agilent 7100). To estimate the dissolved carbon concentration, the liquid phase was concentrated to dryness and measured by elemental analysis (Vario MACRO CHNS analyser). Details of the named and additional analytical methods used, GC-MS, LC-MS etc., can be found in the experimental sections of **Publications I-III**.

3.2 Characterisation of the materials used

Before the oxidation experiments, oil shale samples were analysed for their elemental compositions and metal contents (Table 8). Depending on the heterogeneity of the oil shale and the analysis method chosen (EAS, EDS, AAS etc.), the results varied slightly, but not to an extent that would prevent general conclusions. Most commonly, unreacted and reacted oil shale samples were compared by the content of total organic carbon (TOC) and total inorganic carbon (TIC). On average, the native oil shale used in this work had an OM content of 45%. The relatively high OM value was attributed to the fact that the oil shale was ground and sieved before use, which raised the concentration of fine particles high in kerogen in the sample. Unless otherwise stated, the used samples had particle sizes <45 µm. To obtain kerogen concentrates, either flotation in saturated $CaCl_2$ or treatment with strong acids (HCl/HF) was applied. The latter were carried out by the Oil Shale Competence Centre in Kohtla-Järve.

Table 8. Elemental composition of oil shale samples used in ***Publication II****, wt%*

	C	H	N	S	TIC	TOC	OM	Ca	Mg	Al	Fe
K-45	38.4	4.4	0.12	1.7	3.2	35.1	47	9.6	1.6	1.9	1.5
K-70	58.4	7.3	0.14	1.6	1.4	57.0	75	4.7	0.7	1.4	0.9
K-90	68.0	8.0	0.20	1.3	0.2	67.8	90	0.6	0.3	0.9	0.3

3.3 Calculations

The reactivity of DCAs was mainly estimated via the quantified recovery (Eq. 9):

$$DCA\ recovery = \frac{amount\ of\ DCA\ measured\ after\ WAO}{amount\ of\ DCA\ initially\ inserted} \cdot 100 \qquad \text{[Eq. 9]}$$

The distribution of DCAs was given as a mass ratio of each DCA to the cumulative weight of seven DCAs (C_4 - C_{10}). If needed, the percentage of long-chain DCAs (C_7-C_{10}) to the total weight of DCAs (C_4 - C_{10}) is presented to emphasise the changes in the composition of the product.

The oil shale oxidation was described by various parameters, such as organic carbon distribution between the solid, liquid and gas phases, and with the yield of DCAs or water-soluble products. The amount of organic carbon reacted and the amount of dissolved carbon were both based on elemental analysis and presented as the weight % from the initial value (Eq. 10).

$$C,\% = \frac{post\text{−}oxidation\ TOC,\%\times weighed\ residue,g}{initial\ TOC,\%\times initial\ oil\ shale,g} \qquad \text{[Eq. 10]}$$

The amount of CO_2 was determined from the gas phase analysis and also presented as a ratio of the initial carbon. The yield of DCAs, and in some cases the yield of dissolved products (SO – solubilised organics), were expressed as a weight % of the initial OM content (Eq. 11). The use of OM in the calculations assumed that, in addition to organic C, H and O entered into the composition of the water-soluble products. It should also be noted that a significant amount of the oxygen in the final product was added during oxidation. A clear distinction needs to be made between the yield of SO and dissolved C. The amount of SO was measured after the methanol derivatisation of the concentrated liquid phase, which allowed for the removal of water-soluble inorganics (roughly 20-25% of the sample), but included additional methyl groups. The amount of dissolved C was measured directly from the separated liquid phase after water evaporation and thus provides a more accurate value for organic carbon content. Both approaches suffered from losses during water evaporation, especially for the volatile carboxylic acids.

$$Yield\ of\ DCA\ or\ SO,\% = \frac{DCA\ or\ SO,g}{OM,\%\times initial\ oil\ shale,g} \qquad \text{[Eq. 11]}$$

4 Results and Discussion

The results of this dissertation are based on three publications. The work can be formally divided into two main parts: the reactivity of DCAs (the valuable oxidation products) in selected WAO conditions (**Publication I**), and oil shale oxidation in various condition ranges by focusing on product yields, conversion and carbon distribution (**Publications II and III**). In addition, a discussion of possible reaction pathways and further valorisation of the oxidation product is given.

4.1 DCA reactivity

The aim of studying the reactivity of DCAs under subcritical oxidative conditions was to provide a basis for the possible production of DCAs from highly polymerised organic material (e.g. the kerogen of the oil shale) prior to conversion to final oxidation products (CO_2 and water). In the present work, most of the research has been carried out with a model mixture of seven DCAs (C_4-C_{10}), which, to the best of the author's knowledge, has not been studied before. For that, DCAs (C_4-C_{10}) were added in concentrations of 1 g/L (50 mg of each DCA per 50 ml of water) to a stainless-steel reactor. The purpose of oxidising seven DCAs in a mixture is that the oxidation of oil shale kerogen or other polymeric materials never produces a single compound, but rather a mixture of several compounds. Therefore, observation of the extent of the oxidisability of the expected products in a solution gives the best indication of their endurance at real oxidation conditions. To simplify the presentation of the results, several graphs were constructed based on the most reacted acid, which in most cases was the DCA with the longest hydrocarbon chain (C_{10}). The ranges of the tested experimental conditions correspond to the oil shale oxidation conditions.

4.1.1 Effects of pressure and temperature

The initial series of experiments revealed that all of the DCAs investigated exhibited good resistance to oxidation at 175 °C in the oxygen partial pressure range of 8.4-40 bar during 3-hour reactions (Table 9). A slight decrease, around 10%, was observed only for the DCAs with the longest aliphatic chains (C_9 and C_{10}). This degradation was avoided when acetic acid was added to the reaction medium. Temperature, on the other hand, had a strong effect on the decomposition of DCAs, so that at 200 °C the conversion of C_{10} was up to 90% (Figure 13). In the final reaction mixture, short-chain DCAs (C_4 and C_5) accounted for 60% of the total acids. This indicated that long-chain DCAs are more susceptible to oxidation and that short-chain DCAs form at the expense of the long-chain DCAs.

Table 9. Recovery of DCAs (%) at different oxygen concentrations.[a]

O_2, [%]	pH	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}
21	5	100	103	103	102	100	99	101
50	4	99	103	102	98	96	92	89
100	4	86*	99	102	101	101	99	101
50	2[b]	85*	96	99	98	98	96	98

[a]Reaction conditions: 175 °C; 40 bar of oxygen containing gas; 3 h; [DCA] = 1 g/L. [b]10 vol% solution of acetic acid. *A decrease in C_4 and C_5 concentration was due to the high volatility of the corresponding diesters in the analytical sample preparation. Adapted from **Publication I**.

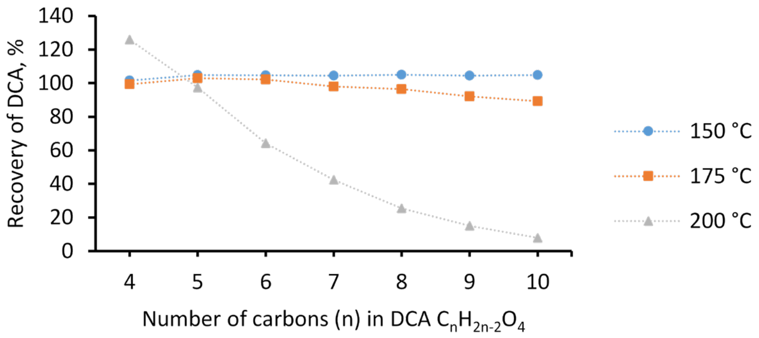


Figure 13. Recovery of DCAs at different temperatures. Reaction conditions: 40 bar of 50% O_2*; 3 h; [DCA] = 1 g/L. Adapted from* ***Publication I****.*

According to previous studies [111], [112], the degradation of DCAs proceeds in a gradual manner, initiated by the oxidation at the α-carbon of the carboxyl group, resulting in lower weight DCAs (Table 10). In order to better analyse the intermediates of the oxidation, the oxidation of C_{10} (sebacic acid) was studied separately. From the resulting mixture, (ω-1)-oxoacids were the second most abundant group of compounds, indicating the occurrence of β-oxidation. The formation of mono-carboxylic acids, namely acetic and formic acids, was also observed. The other products identified included hydroxy-substituted CA and aldehyde acids, which can be classified as intermediates in the α- and β-oxidation pathways. All of this suggests that, despite the different temperatures (175 vs 300 °C) and oxidants (air vs H_2O_2) applied in this work and in the work by Jin et al. [111], [112], the decomposition of long-chain DCAs is similar under a wide range of subcritical conditions. The presence of parallel oxidation pathways implies that the desired DCA are reactive and the oxidation of the polymerised matter may lead to the formation of a very complex mixture of acids.

Table 10. The main intermediates in sebacic acid oxidation

Compounds	Structure/Name	Mol. weight	Comments
Dicarboxylic acids	$HOOC\text{-}(CH_2)_n\text{-}COOH^{a,b}$	118 up to 202	n = 2 - 8
(ω-1)-oxo acids	$CH_3CO(CH_2)\text{-}COOH^{b}$ $CH_3CO(CH_2)_n\text{-}COOH^{a,b}$	102 up to 144; 172	n = 2 - 4; 6
Carboxylic acids	$HOOCH^{c}$; $HOOCCH_3^{c}$ $HOOC\text{-}(CH_2)_nCH_3^{a,b}$	46; 60; 88; 102	n = 2-3
Aldehyde acids	5-oxopentanoic acid[a] 9-oxononanoic acid[a]	116; 172	
Hydroxy-substituted carboxylic acids	3-hydroxyhexanoic acid[a]	132	
Dihydroxy-substituted carboxylic acids	2,2-dihydroxyacetic acid[b] 2,3-dihydroxypropanoic acid[b] 2,3-dihydroxyheptanoic acid[b]	92; 106; 162	

Detected from a [a]derivatised sample with GC-MS; [b]aqueous reaction mixture with LC-MS; [c]aqueous reaction mixture with CE. Reaction conditions: 40 bar of 50% O_2; 3 h; 175 °C; $[C_{10}]$ = 2 g/L. Adapted from **Publication I** supporting information.

Later, in Mesi's bachelor's thesis (supervised by the author of present dissertation), the reactivities of C_4, C_6, C_8 and C_{10} were investigated separately in a Hastelloy reactor [151]. Interestingly, the recovery of C_{10} was only 20% after a 3h reaction at 175 °C with 40 bar of 50% O_2. Increased recovery was also evidenced for C_8 yielding 80% of the original value. C_4 and C_6 remained unreacted regardless of the reactor material and the reaction time. The inconsistency between the results obtained in the stainless steel and the Hastelloy reactors was attributed to the strong effect of the reactors construction materials, as described in Section 1.2.1. Such metallic surfaces as stainless steel may either initiate (see section 1.2.1) or terminate free radical reactions that induce organic material oxidation [65]. There are also examples in the literature of WAO efficiency being higher in glass-lined reactors or Hastelloy reactors than in stainless steel reactors [88], [101], [152]. Thus, it is imperative to assess the influence of the reactor parameters (incl. material) on reactions when optimising WAO process conditions.

4.1.2 Effect of alkali additives

The effect of alkali and alkaline earth metals on the reactivity of DCAs is of particular interest because these elements are part of the inorganic fraction of oil shale. Depending on the substrate and the exact WAO procedure used, alkaline conditions or an alkali salt addition can either scavenge the radical reactions, preventing the oxidation of organics, or accelerate their decomposition by incorporating ionic mechanisms [65]. Therefore, it was important to determine the effects of different bases on DCAs and their mixtures.

An increase in long-chain DCA decomposition was observed by the addition of NaOH, KOH and $Ca(OH)_2$ (Figure 14**A**). The extent to which DCAs were oxidised depended on the amount of hydroxide added: the higher the excess over the acids, the more the DCA (C_{10}) was converted (20 eq. was only tested with KOH). On the other hand, the addition of ammonia maintained the stability of DCAs at pH above 9. Indicating that the effect of pH, e.g. concentration of OH and H ions (experiments with acetic acid addition in Table 9), was not decisive on DCAs reactivity when the reaction medium was lacking of metal ions. The effect of a base appeared to depend on the content of the alkali cation. Interestingly, the amount of C_{10} recovered was less with $Ca(OH)_2$, which is very slightly soluble even in boiling water, than with the same amount of NaOH or KOH. The use of equimolar amount of alkali hydroxide retained the stability of DCAs, indicating the formation of stable DCA salts. However, since the valence of these metal atoms is different, the number of metal ions required for the formation of DCA-salts also differs. Therefore, it can be assumed that at same concentration level (e.g. 2.2 eq. of alkali hydroxide) the amount of free Ca ions is higher than for monovalent Na and K, which explains the results with $Ca(OH)_2$.

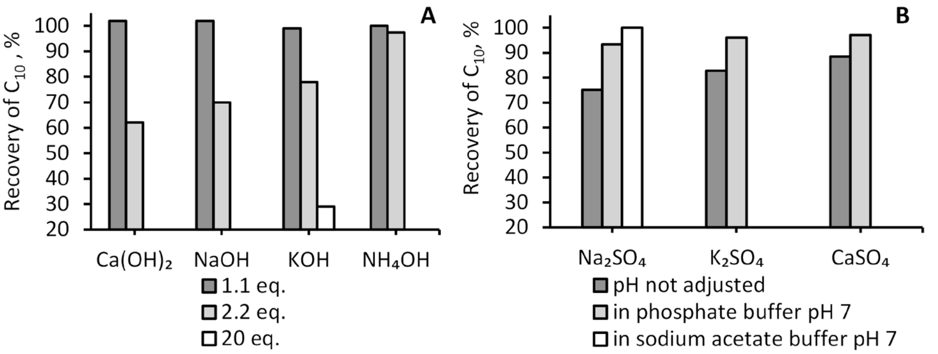


*Figure 14. Reactivity of C_{10} in alkali solutions with different concentrations (**A**) and in sulphate solutions (**B**). Reaction conditions: 40 bar of 50% O_2; 175 °C; 3 h; [DCA] = 1 g/L; 1.1 eq. of salt per mol of DCA. Modified from **Publication I**.*

The effect of the selected metal cations was also tested in the form of their neutral salts, e.g. sulphates (Figure 14**B**) and nitrates (Figure 15). In these experiments, the pH decreased to around 3 during the reaction. A similar degradation of long-chain acids was observed as with the presence of hydroxides, but the degree of catalytic effect among sulphates and nitrates appeared to depend on the water solubility of the added salts. For better comparison, the solubility data of the compounds studied (according to Lide [150]) at 25 °C in 100 g of water is presented in Figure 15 (in brackets). It is assumed that at the reaction conditions used, these solubilities are further increased, however in the same order. Interestingly, the oxidation of DCAs in the presence of these same metal salts was completely suppressed in the buffer solutions where pH was kept neutral throughout the oxidation process (Figure 14**B**; acetate buffer was only tested with Na_2SO_4). High recovery of DCA was also observed in the presence of Ca, Na and K carbonates which kept the pH in the weakly alkaline range (7-8) (Figure 15). The following conclusions were drawn: Na, K and Ca (in concentrations above the DCA) promote the oxidation of dicarboxylic acids, especially long-chain dicarboxylic acids during WAO in both basic and acidic media, but not in neutral media. Therefore, DCAs can be recovered in high yields from neutral solutions. The extent of oxidation is related to the concentration of the alkali cation in the solution, which in turn, is determined by the nature of the counter anion. The latter also influences the pH of reaction medium. When the alkalis were compared at concentrations where the cations M^{2+} were added at 1.1 equiv. and M^{1+} at 2.2 eq., NaOH had the greatest effect on the reactivity of DCAs.

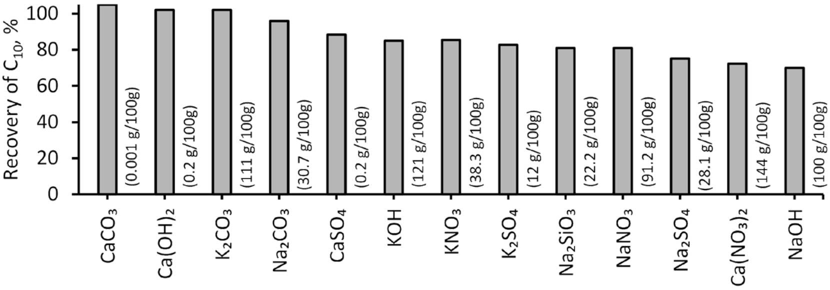


*Figure 15. Recovery of sebacic acid in oxidation. Reaction conditions: 40 bar of 50% O_2; 175 °C; 3 h; [DCA] = 1 g/L; 2,2 eq. of additive with general formula of M^+X^- or 1,1 eq. of additive with general formula of $M^{2+}X^{2-}$, $M^{2+}(X^-)_2$ or $(M^+)_2X^{2-}$ per mol of DCA. The solubility data (at 25 °C per 100 g of water) of each compound is given in brackets [150]. Modified from **Publication I**.*

Publication I also examined the catalytic effects of Fe, Mn, Cu, and Co sulphates. The same trends applied to these transition metals as to alkalis: oxidation was dependent on the concentration of the metal cation and the pH of the reaction medium. The addition of iron salts led to extensive oxidation of the C_{10}, so that only 5% of the initial value was recovered. Decomposition of DCAs was completely avoided at controlled pH in the presence of all metal salts.

4.1.3 Effects of co-oxidation

In the preliminary experiments on the oxidation of oil shale at 175°C, the DCA distribution in the mixture obtained was nearly always shifted towards the short-chain DCAs. It was realised that the oxidation of DCAs, in addition to inorganic components, can be affected by other organic compounds in the same solution. Supposing that the kukersite kerogen contains about 20% resorcinol units (according to Lille [29]), methyl resorcinols were tested as co-oxidants. Additionally, the effect of malonic acid, as a possible degradation product of substituted phenols and DCAs, on the oxidation of long-chain DCA (C_{10}) was investigated.

Both, 5-methylresorcinol and 2-methylresorcinol induced the oxidation of C_{10} to a great extent, leaving less than 10% of the acid unreacted after 3 h of oxidation at 175 °C with 40 bar of 50% O_2 (Figure 16; results for the 2-methylresorcinol in **Publication I**). Based on molar yield (moles of formed DCAs per moles of initial C_{10}), 23% of the initial C_{10} was converted to C_4, 12% to C_5 and 4% to C_6-C_9. This indicates that roughly 25-30% of the carbon in the initial C_{10} now appeared in the composition of shorter chain DCAs. The longer the reaction time, the higher the yield of short-chain DCAs and vice versa. In addition to the short-chain DCAs, acetic acid, formic acid and (ω-1)-oxoacids of various lengths were detected. The effects of co-oxidation on DCAs with shorter hydrocarbon chains were not studied in this work. However, the results demonstrate that the reactivity of higher DCAs towards oxidation strongly increased in the presence of resorcinolic compounds.

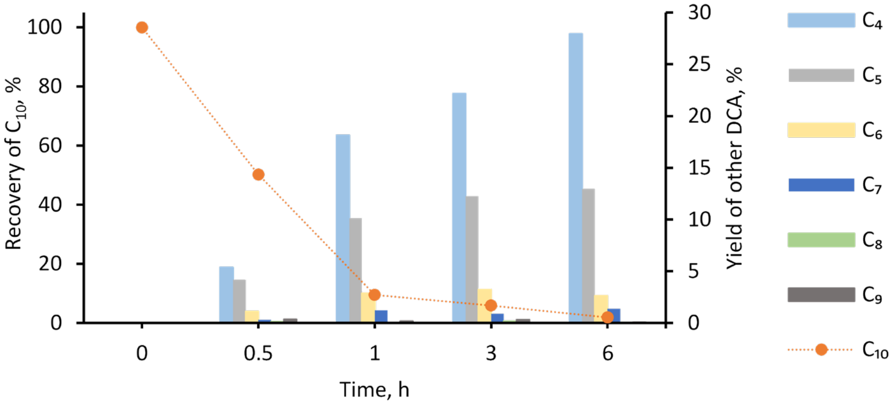


*Figure 16. Co-oxidation of C_{10} with methylresorcinol. Reaction conditions: $[C_{10}]$ = 2 g/L; [resorcinol] = 1.24 g/L (1 eq.); 40 bar of 50% O_2; 175 °C; 3 h. Adapted from **Publication I**.*

It is important to note that no resorcinol was left after a 1 h reaction. The gas phase analysis confirmed that the CO_2 release in the first hour was several times higher than in all subsequent hours, indicating the effective decomposition of resorcinolic units under selected conditions. In **Publication I**, the reactivity of 5-methylresorcinol was studied separately under the same conditions that were applied for co-oxidation studies (175 °C with 40 bars of 50% O_2). A GC-MS and LC -MS analysis of the reaction mixture revealed the presence of succinic acid, 2-methylsuccinic acid, 3-hydroxypropanoic acid, 3-hydroxybutanoic acid, fumaric acid, 3-methylpent-2-endioic acid, 2,3,5-trihydroxytoluene, 3-methyl-2,5-dioxohex-3-enedioic acid and some other intermediates, including acetic and formic acids. These results suggest a degradation mechanism similar to that described for phenols (Figure 9). Figure 17 shows that the decomposition of 2-methylresorcinol took 1 hour at 175°C and only 20 minutes at 185°C (unpublished results). It was determined that 30 mg of acetic acid, about 15 mg of formic acid and 2-3 mg of succinic acid were formed during the oxidation of 100 mg of methylresorcinol.

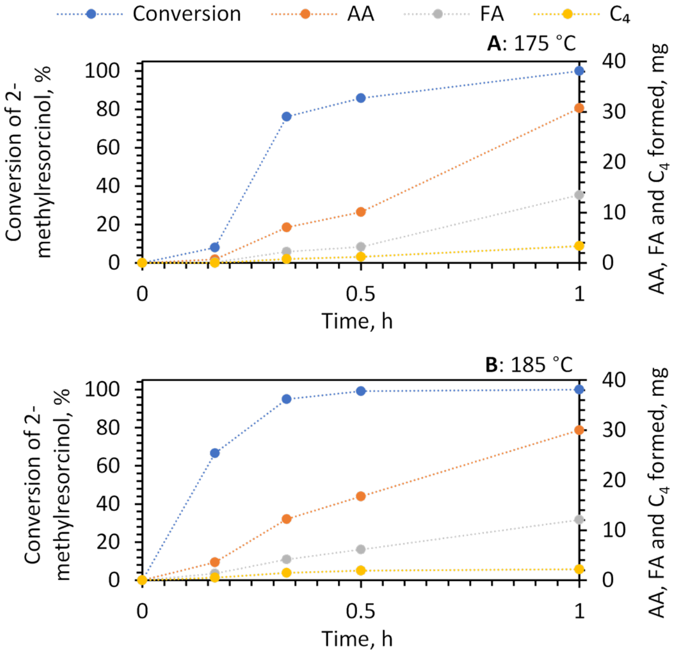
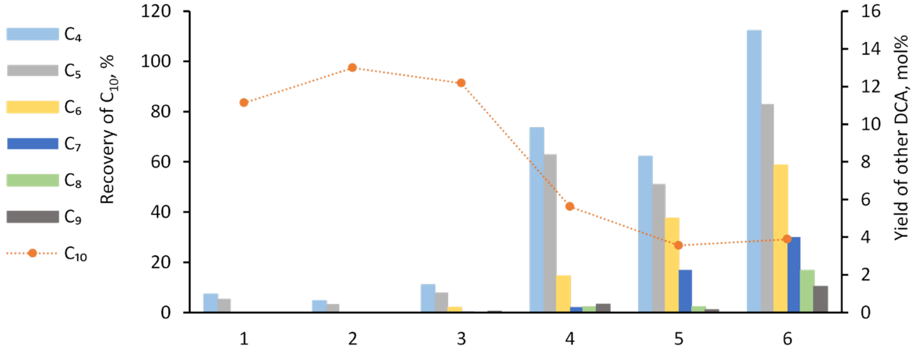


*Figure 17. Oxidation of 2-methylresorcinol with 40 bar of 50% O_2 at temperatures of 175 °C (**A**) and 185 °C (**B**).*

In the presence of malonic acid as a co-oxidant, a similar oxidation pattern was seen as with resorcinols (Figure 18). The recovery of C_{10}, however, was higher (42%) than that with resorcinol: even with 2 eq. of malonic acid the decomposition was less than with 1 eq. of resorcinol. In addition, the effect of malonic acid as a co-oxidant was studied together with acidic and alkaline additives. When the reaction was carried out in a 10% acetic acid solution, the effect of a malonic acid addition was negligible and a recovery of 91% of C_{10} was observed, suggesting that acidic conditions have an inhibitory effect on the co-oxidation of long-chain DCAs. When a 0.1 M KOH solution was used as a solvent, the rate of C_{10} oxidation was increased to the point where only 27% of the initial C_{10} remained. Under basic conditions, the differences in the conversion of C_{10} with and without malonic acid were small. However, both the percentage of carbon recovered and the molar yield of the short-chain DCAs formed indicated that with malonic acid the transformation of organic matter to CO_2 was higher. Therefore, it can be said that the co-oxidative effect of malonic acid is further enhanced under basic conditions.



Co-oxidant			Malonic acid	Malonic acid	Malonic acid	
Additive		10% AA	10% AA		0.1 M KOH	0.1 M KOH
Recovery of C_{10}, %	83	97	91	42	27	29
Yield of other DCA, mol%	1	<1	2	21	22	41
Recovery of org. C as DCA, %	84	98	93	52	38	51

Figure 18. Co-oxidation of C_{10} by malonic acid. Reaction conditions: $[C_{10}]$ = 2 g/L; [malonic acid] = 2 g/L (2 eq.); 40 bar of 50% O_2; 175 °C; 3 h. Adapted from ***Publication I****.*

4.1.4 Effect of oil shale

For further work with oil shale, it was important to evaluate in more detail the effects of the total oil shale matrix on DCA destruction (Table 11). This effect was investigated by the oxidation of DCAs (C_6-C_{10}) in a pot together with oil shale concentrates. The same oxidation conditions were used as in the DCA reactivity test: 175°C at 40 bar 50% O_2 for 3 h. After oxidation, the content of DCAs in the solution was measured and corrected with the average value of DCA formed from oil shale oxidation. It was found that the higher the kerogen concentration in the shale, the less long-chain DCAs were recovered. When oil shale with an organic matter content of 90% was used, no traces of C_9 or C_{10} were detected after the reaction. On the other hand, experiments with mineral residues from previous oxidations (ox. ash) had no effect on the reactivity of DCAs. Similarly, DCAs were fully recovered when oxidised with fly ash from the forth field of an Estonian oil shale power plant (ESP ash; elemental composition in **Publication II**), which was alkaline in nature. It was concluded that the oxidation of DCAs is mainly accelerated by the presence of kerogen and most likely by the resorcinol units in kerogen.

Proceeding from the results with ash, carbonates and $Ca(OH)_2$ were also tested as oxidation additives. Only a partial improvement in the yield was observed, possibly due to an excess of the added base over DCA. It was not possible to determine a minimum (equivalent) amount of base needed, because the decomposition of the oil shale itself leads to a constant increase in acidity.

In addition, it was tested whether acetic acid in solution with oil shale had a similar reactivity-reducing effect as found with pure DCAs. Under the reaction conditions used, the expected effect did not occur as the long-chain DCAs decomposed during the reaction. When an additional amount of 5-methylresorcinol was added, the oxidation rate increased for all DCAs, resulting in a significantly lower recovery for C_6 and C_7. This implicitly suggests again that the decomposition of resorcinol-like functionalities of oil shale promotes DCA oxidation. It was concluded that there is no simple solution to prevent further oxidation of DCAs during WAO.

Table 11. The effects of oil shale constituents on DCA (C_6-C_{10}) destruction[a]

No	Additive	Overall recovery	C_6	C_7	C_8	C_9	C_{10}
1	-	95%	100	98	96	92	89
2	ESP ash	97%	96	96	95	97	100
3	ox. ash	98%	99	99	99	98	97
4	K-45	40%	70	54	35	23	16
5	K-70	30%	74	50	18	6	2
6	K-90	**22%**	76	31	4	0	0
7	K-70 + $Ca(OH)_2$	47%	73	60	43	31	27
8	K-70 + K_2CO_3	35%	72	44	29	18	11
9	K-70 + $CaCO_3$	34%	64	46	28	18	13
10	K-70 + CH_3COOH	21%	58	27	15	2	0
11	K-70 + 5-Me-resorcinol	**13%**	43	17	3	2	1
12	K-45 + K_2CO_3	45%	75	55	41	30	23
13	K-45 + $CaCO_3$	36%	62	46	31	22	16
14	K-45 + CH_3COOH	33%	77	49	25	11	3
15	K-45 + KOH	32%	62	41	27	18	12

[a] Reaction conditions: T = 175 °C; P = 4 bar of 50% O_2; 3 h; [DCA] = 1 g/L; 20 g/L of oil shale, its concentrate or ash in water with 60 wt% of $Ca(OH)_2$, K_2CO_3, $CaCO_3$ or KOH; or in 10 vol% acetic acid solution. Adapted from **Publication III**.

4.2 Oil shale oxidation in WAO conditions

4.2.1 Effect of reaction time

A temperature of 175 °C and a pressure of 40 bar of the oxygen-containing gas were chosen for model conditions from the data of the early work of the Proskuryakov group [56]–[58]. First, it was confirmed that no thermal destruction of the oil shale matrix occurred at 175°C in water when the gas phase did not contain oxygen (40 bar CO_2). Next, the preliminary experiments showed that an oil shale concentration of 20 g/L afforded organic carbon conversion of over 90% (Table 12) after a reasonable reaction time (3 h). Therefore, 20 g/L was considered a suitable oil shale concentration for the existing reactor capacity and for further experiments. Despite efforts to achieve repeatable results, high variability in both conversion and yield was frequently observed to a 3-5% extent. This variability was mainly attributed to the heterogeneity of the oil shale samples, which led to variations in the composition of the resulting product. Therefore, the following data are often given as averages of the several parallel experiments.

The first series of experiments for dependence on the reaction time were carried out in a 100 ml reactor at 175 °C with 40 bar of 50% O_2. It was observed that the kerogen was oxidised relatively fast under the selected reaction conditions, with a carbon conversion of 57% within the first hour (Table 12). After 6 h there was only 2% of organic carbon left in the solid residue, indicating full conversion of organic matter. The amount of water-soluble products (SO) peaked after 1 h and then slowly began to decrease.

The amount of DCAs, however, increased much more slowly than expected, reaching 12% only after 6 h of the reaction. The DCA mixture obtained after 6 h of oxidation consisted mostly of C_4 and C_5 with only 9% of C_6 – C_{10} DCAs compared with 35% of C_6 – C_{10} after 1 h of reaction. Thus, the changes in the DCA distribution in the course of the process revealed, that long-chain DCAs are not stable during the oil shale oxidation process and decompose to short-chain DCAs. In addition, the highest yield of DCAs was accompanied by high CO_2 release (55% of the initial organic carbon). All of this led to the conclusion that despite the 12% DCA yield, a long reaction time does not afford optimal results.

Table 11. Products of K-70 oxidation without any additives[a]

Time, h	Conversion, %	SO, %	DCA, %	DME in SO, %	C to CO_2, %	DCA distribution (C_6-C_{10}/C_4-C_{10}), %
1	57	36	3.2	11	20	35
2	85	33	7.4	25	36	21
3	91	33	8.3	28	44	18
6	98	26	12.2	53	57	9

[a]Reaction conditions: T= 175 °C; P = 40 bar of 50 % O_2; 20 g/L of K-70 in 100 ml vessel. Adapted from **Publication II**.

In **Publication III**, time-dependent experiments using different gas mixtures (air, 50/50 and pure oxygen) were investigated with regard to the carbon distribution in the products and in the unreacted substance (Figure 19). Experiments were conducted in a 500 ml reactor to collect higher amounts of dissolved organics for more accurate dissolved carbon determination. All trends that were observed at lower concentrations were also present at higher concentrations. About 30% of the original carbon was dissolved after the first hour, after which the percentage steadily declined. Although, half of the oxygen originally added was still present after 3 h (more than 20% by volume), further transformation of the already dissolved material was slower.

The use of air at 40 bar corresponds to oxygen in the gas phase nearly equimolar to carbon in the solid kerogen. Under these conditions, a continuous decrease in solid carbon and the emission of CO_2 were observed throughout the 5-hour reaction time until there was no oxygen left in the gas phase. The dissolution of the kerogen carbon was in parallel with the CO_2 emission until the oxygen concentration in the gas phase dropped below 5 vol%.

At 40 bar of pure oxygen, the maximum dissolution was reached even before the first hour. Two distinct stages may be distinguished: the first fast stage, in which the initial carbon in the kerogen was intensively oxidised, and a second, slower stage, in which further oxidation of the already dissolved material took place. The limiting factor for the first stage was the depletion of the un-dissolved carbon. Interestingly, at the point where the highest amount of dissolved carbon was observed, the amount of the formed CO_2 was more than 10% higher than that with 40 bar of 50% O_2. The data on DCA formation (unpublished results) also showed that short-chain DCAs dominated over long-chain DCAs even at the beginning of the reaction. The amount of C_4 increased continuously after the complete dissolution of the solid kerogen carbon. It can be assumed that under 40 bar of pure oxygen the further oxidation of the already dissolved substances is substantially faster and more dominant.

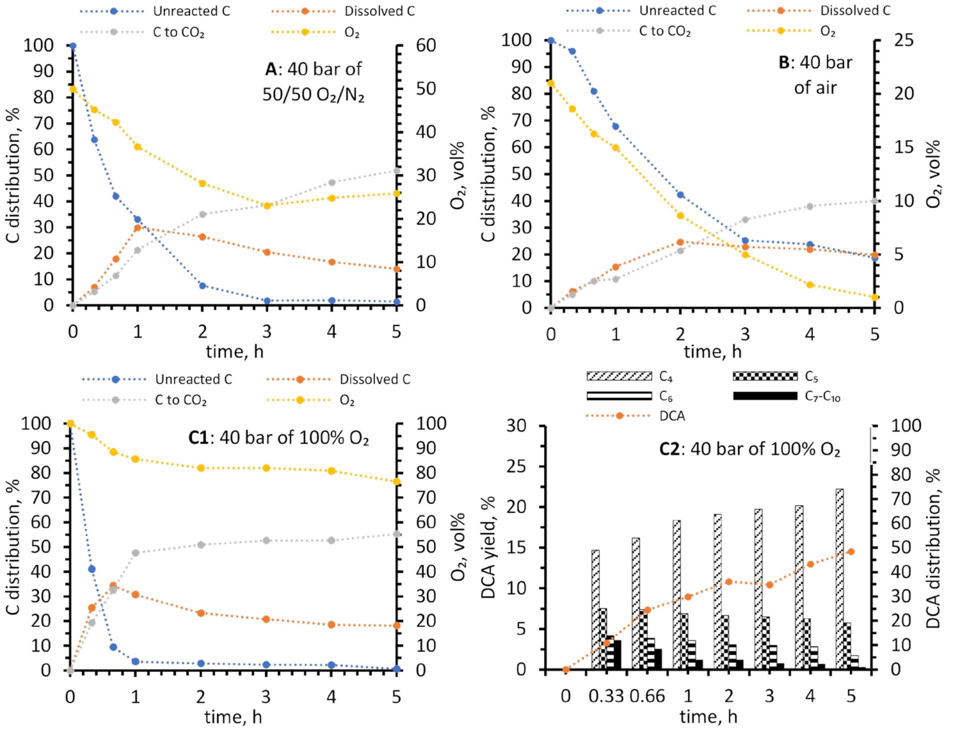


Figure 19. Distribution of organic carbon between solid (unreacted C), liquid (dissolved C) and gaseous (C to CO_2) phases in time dependent experiments with different gas mixtures. Reaction conditions: T= 175 °C; P = 40 bar; 20 g/L of K-70 in 500 ml vessel. Modified from ***Publication III****.*

Time-dependent experiments were also performed with different gas mixtures at oil shale concentrations of 30 g/L and 40 g/L by increasing the amount of K-70 added to the reactor (the corresponding Figures are in **Publication III**). Other parameters, such as temperature and volume of the solution, were kept constant. As expected, changing the ratio of oxygen and organic carbon shifted the optimum of the reaction. A higher amount of substrate requires a higher amount of oxidant and thus similar trends were observed as with 40 bar of air at an oil shale concentration of 20 g/L, where the oxidation process slowed down rapidly due to the depletion of oxygen.

4.2.2 Composition of the reaction mixture

When oil shale was oxidised in water without additional additives, the pH of the reaction mixture decreased from 7 to 2.8 during the oxidation process, indicating the formation of acidic products. An elemental analysis of the dissolved products showed that the O/C molar ratio had quadrupled compared to the initial kerogen after the first hour of oxidation (Table 13). The extensive changes in elemental composition indicate that the decomposition of the kerogen structure is a consequence of the rapid insertion of oxygen. In addition to DCAs, which were analysed qualitatively and quantitatively, GC-MS and LC-MS analyses indicated the presence of monocarboxylic acids, their branched and oxo- or hydroxy-substituted isomers, tricarboxylic acids, other alcohols etc. Similar to other common WAO processes, the accumulation of acetic acid was detected up to a concentration of 2.5 g/L, along with the formation of formic acid at slightly lower concentrations. An example of the distribution of organic substances according to the functional groups and their relative content in the solution (measured by GCxGC-MS) is shown in Figure 20. The analytical results presented were obtained in the K-70 oxidation with the addition of a base (K_2CO_3), i.e. the content of intermediates was significantly higher than in the experiments without a base, as will be discussed in the next sections.

Table 12. The content of organic carbon and oxygen after the WAO process.[a]

	Time, h	TOC, %	O, %	O/C
Initial K-70	0	57.0	15.8	0.21
Dissolved organics	1	38.0	42.7	0.84
Dissolved organics	3	25.9	46.0	1.3

[a]Reaction conditions: T= 175 °C; P = 40 bar of 50 % O_2; 20 g/L of K-70. Adapted from **Publication II**.

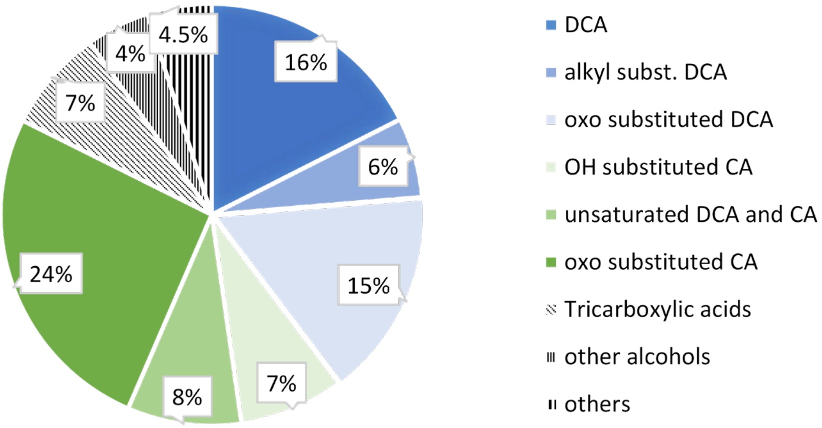


*Figure 20. Relative content of derivatised solubilised organics based on the main functional groups. Reaction conditions: T = 175 °C; P = 40 bar of 50% O_2; 3 h; 60 wt% of K_2CO_3; 20 g/L of K-70. Modified from **Publication II** supporting information.*

4.2.3 Effect of temperature and pressure

Since temperature and oxygen pressure are the key parameters affecting the oxidation of oil shale in WAO conditions, these parameters were examined in several series.

As shown in Figure 21, a temperature of 150 °C was not sufficient to achieve the conversion of organic carbon of more than 50% within a reasonable time frame (3 h) at an initial pressure of 40 bar of 50% O_2. As this temperature was also associated with low DCA and SO yields, it was considered unsuitable for further investigation.

At 165 °C, 80% of C conversion and 40% of SO yield were obtained with only 22% of the carbon transformed to CO_2 during a 3 h reaction. This suggests that an increase in temperature significantly promotes the decomposition of the kerogen matrix into water-soluble compounds. At this temperature, the overall yield of DCAs remained low (6%), of which the content of long-chain DCAs was above 25%, indicating little over-oxidation compared with higher temperatures. The high amount of SO and low DCAs also suggested that under WAO conditions DCAs were not the primary oxidation products of the kerogen, but formed by further oxidation of dissolved material: further oxidation is required to form DCAs. A temperature increase of 10 degrees increased the carbon conversion together with the overall yield of DCAs and CO_2 emissions and decreased the amount of dissolved compounds.

At 200 °C, the yield of DCAs ceased to increase, indicating their fast formation and simultaneous extensive degradation. Focusing on the highest possible DCA yield, a temperature of 175-185 °C can be considered the optimal temperature range for the oxidation of oil shale in WAO.

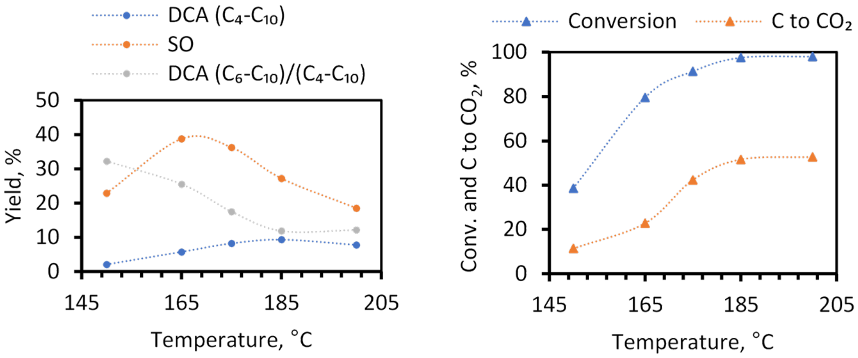


*Figure 21. The effect of temperature on K-70 oxidation. Reaction conditions: T = 3 h; P = 40 bar of 50 % O_2; 20 g/L of K-70. Modified from **Publication II.***

The effect of oxidant pressure was first studied at a constant temperature (175 °C) during the 3 h oxidation of K-70 (Figure 22). As expected, low oxygen partial pressure, either with 20 bar of O_2 50% (pO_2 10 bar) or 40 bar of air (pO_2 8.4 bar), lowered both conversion and DCA yield. However, with pO_2 8-10 bar the concentration of long-chain DCAs among other DCAs was higher than with other gas mixtures. On the other hand, when 40 bar of pure oxygen was used, further oxidation of the already dissolved material was pronounced, leading to a decrease in SO and an increase in CO_2. The use of a 50/50 mixture of O_2/N_2 as an oxidant at 40-60 bar appeared to be the most suitable for obtaining high conversion and DCA yields over 10% with lower CO_2 emissions. Since further degradation of the desired product is a problem, obtaining high yields requires precise control of the oxygen content. At this point, it must be emphasised that the results presented are valid only at the selected oil shale concentration (20 g/L) and the used reactor capacity.

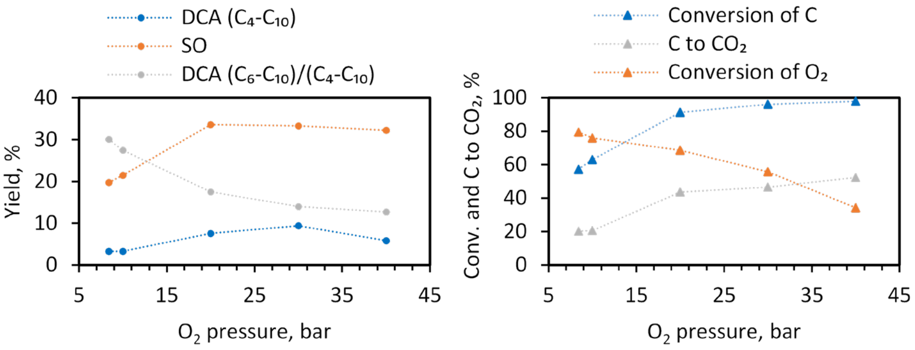


*Figure 22. The effect of pressure when using different gas mixtures (21%, 50% and 100% of O_2) and pressures (20-60 bar of 50% O_2). Reaction conditions: T = 175 °C, t = 3 h, 20 g/L of K-70. Modified from **Publication II**.*

In **Publication III,** the effects of pressure and temperature were investigated in parallel by focusing only on the C distribution between the gas, liquid and solid phases with 1-hour experiments (Figure 23). For these experiments 2.5 g/L of K-70 was used instead of 20 g/L, to ensure a sufficient amount of oxidant throughout the reaction. In principal, carbon distribution coincides well with previous findings, with some additional observations:

- At 165°C the conversion of organic carbon in kerogen and the evolution of CO_2 are nearly linearly dependent on pressure: the higher the pressure, the higher the conversion.
- The higher the temperature, the lower the amount of O_2 required for intensive oxidation, e.g. at 185°C a more than 60% conversion of oil shale kerogen was observed at a pressure of 10 bar O_2.
- The amount of dissolved carbon was also almost in equilibrium with the CO_2 emitted, e.g. after 1 h at 185 °C with 30 bar of O_2, 34.2 % of the carbon had been dissolved and 34.6 % of the carbon had been emitted as CO_2, indicating that the formation of CO_2 is unavoidable when oxidising kerogen with oxygen.
- In the pressure range of 20-40 bar, there were no differences between the temperatures 175 and 185 °C in terms of dissolved carbon, suggesting that the limit of maximum dissolution had been reached.
- As the temperature increased, the loss in carbon balance increased due to a higher number of low-molecular weight compounds. The increasing amount of formed acetic and formic acids measured before the evaporation step serves as evidence (data not shown).

It should be mentioned, that since a three times shorter reaction period was used, the measured values were correspondingly lower than previously described (Figure 21 and 22).

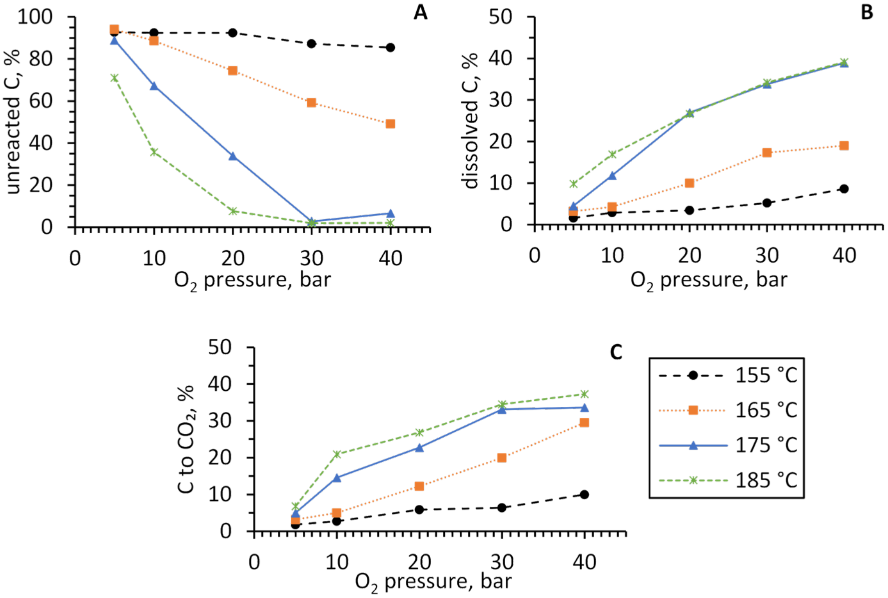


*Figure 23. Time- and pressure-dependent experiments with 2.5 g/L K-70 and 100% of O_2 for 1 h. Adapted from **Publication III.***

4.2.4 Effect of kerogen content

As described above, oil shale samples containing 70% organic matter (K-70) were used in most experiments. K-70 enabled to assess the carbon concentration in the oxidation products better, because the amount of product per gram of oil shale was higher. In addition, enrichment up to 70% can be achieved by flotation, i.e. physical separation, avoiding chemical changes in the kerogen. To investigate how the kerogen content affects the oxidation process, K-45 (native oil shale) and oil shale concentrate K-90 (chemically enriched) were tested as substrates for oxidation (Figure 24). To our surprise, the experiments with K-45 yielded 43% of SO and with K-90 only 16% of SO from the organic matter content. Since the degree of organic carbon conversion was the same, oxygen deficiency could be excluded. In the case of K-90, no C_8-C_{10} were detected in the mixture of DCAs obtained after 3 hours of reaction, but with K-45 they accounted for 16% of the total DCAs. Since both SO and the amount of long-chain DCA were higher in the case of K-45, it was proposed that the presence of the inorganic matrix of the oil shale might have a protective effect (e.g. termination of the radical chain or by DCA-salt formation) against further oxidation of the solutes. The phenomenon observed could also be related to the co-oxidation effect described in section 4.1.3, which is associated with a high concentration of resorcinols in K-90.

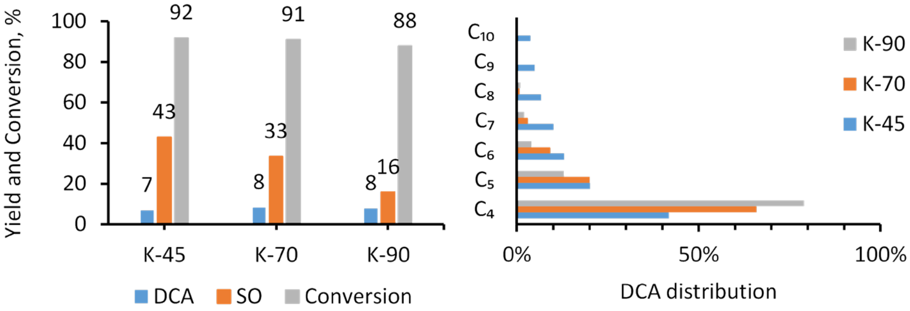


*Figure 24. Effect of the kerogen concentration in the initial oil shale. Reaction conditions: 175 °C, 40 bar of 50% O_2, 3 h, 20 g/L of oil shale. Modified from **Publication II**.*

4.2.5 Acidic and alkali additives in oil shale oxidation

Various alkalis as oxidation additives were tested mainly for three reasons:

- to assist the solubility of the newly formed oxygenated compounds,
- to reduce their further oxidation rate,
- to sequester released CO_2.

The bases selected for the WAO of K-70 (Table 13) were the same as those used in the DCA reactivity tests. All bases were compared at a concentration of 60 wt% per kerogen content. Other concentration levels of KOH, $Ca(OH)_2$ and K_2CO_3 were also tested, but 60% proved to be optimal (details in **Publication II**). The use of alkalis resulted in over 90% conversion of organic carbon within 3 hours. The DCA yield, on the other hand, did not increase (a maximum of 8.2%) or rather decreased compared to the results obtained without any additive. Nevertheless, the percentage of long-chain DCAs in the total DCA mixture obtained after 3 hours of reaction always remained above 25%.

Table 13. K-70 oxidation with the addition of various alkalis[a]

Base	Conversion, %	Yield of DCA, % (C_6-C_{10}/C_4-C_{10})	C in CO_2 %	SO %	pH (after reaction)
Na_2CO_3	98	4.4 (37 %)	n.d	39	7.5
$Ca(OH)_2$	93	5.8 (36 %)	32	38	6.5
Na_2SiO_3	95	6.7 (26 %)	n.d	44	5.5
NaOH	99	5.4 (38 %)	34	47	8.5
KOH	99	8.2 (32 %)	33	49	9
K_2CO_3	98	7.6 (28 %)	35	46	6.5
ESP ash[b]	96	7.2 (31%)	36	50	9

[a]Reaction conditions: T = 175 °C; P = 40 bar of 50% O_2; 20 g/L of K-70; t = 3 h; 60 wt% of base; before the reaction pH > 9 in all cases; [b]500 mg of ESP ash per 1 g of K-70. Adapted from **Publication II**.

In addition, oil shale ash from an electrostatic precipitator was tested as a solid base. ESP ash has basic properties as it contains a variety of metal oxides, CaO and SiO_2 being the most common constituents (details in **Publication II**). It was found that the use of 500 mg of ash per 1 g of K-70 resulted in as high a SO yield (50%) as the use of KOH (49%). The yield of DCA also remained similar (7%) to that obtained when alkali hydroxides were used (5-8%). Even though the amount of ash required was quite high, the use of ESP ash instead of alkali hydroxides could be an option as it is mainly classified as a waste product of the oil shale industry with a negative selling price and is therefore very cost effective.

Time-dependent experiments showed that the induction time in alkali (KOH) was significantly shorter than in water, and nearly complete conversion of carbon was observed after 2h at 175°C (Figure 25). Alkali hydroxides decreased the amount of CO_2 released by up to 30% in the 3-h reaction at 175°C with 20 g/L K-70. In addition, alkali hydroxides increased the yield of SO up to 49% compared to 33% SO in a reaction without additives. At longer reaction times (6 h), a decrease in SO was also observed in basic media, but the overall amount remained consistently higher than in media without an addition.

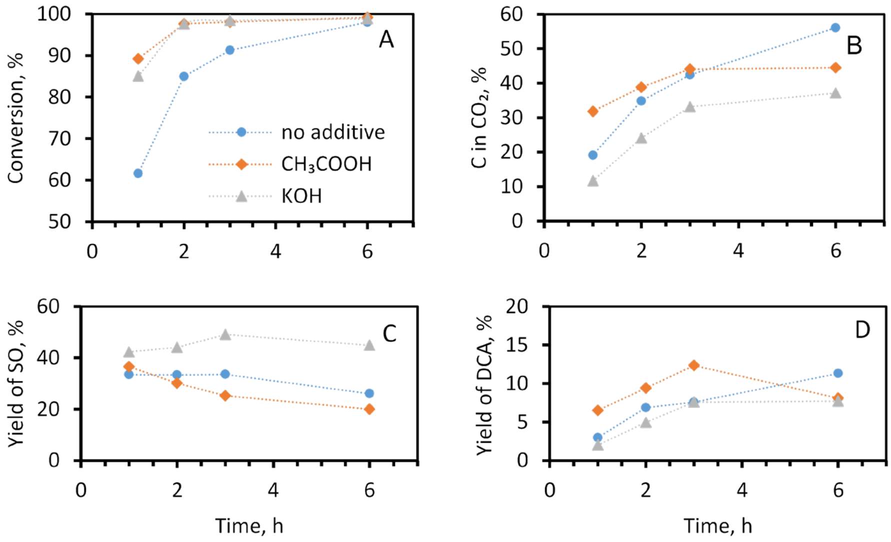


Figure 25. Time-dependent kerogen oxidation at different pH levels (A: the conversion of organic carbon; B: the amount of organic carbon converted to CO_2; C: the yield of water-soluble products; D: the yield of DCA). Reaction conditions: T= 175 °C; P = 40 bar of 50 % O_2; 20 g/L of K-70 in dist. water, with 60 wt% of KOH or in 20 vol% acetic acid solution. Adapted from ***Publication II****.*

The effect of the alkalis was compared with the oxidation in acetic acid solution. Acidic conditions were expected to either promote oxidation via the metal elements present in the inorganic matrix of oil shale (e.g. Fe and Cu), or reduce the effect of co-oxidation.

Acetic acid was a suitable additive as it is non-corrosive (unlike mineral acids) and non-reactive under selected conditions (tested in separate experiments in **Publication II**). Acetic acid was used as a 10-20% solution, as this gave the highest DCA yield compared to more concentrated solutions (details in **Publication II**). As with the use of alkali hydroxides, oxidation of K-70 in acetic acid solution showed a short induction time, resulting in complete carbon conversion within 2 hours. In acidic media, however, the yield of dissolved organic matter was consistently lower and the amount of CO_2 released was consistently higher than in water without additives or with base additives, suggesting that the intermediates formed have higher reactivity in the low pH range. Acetic acid solution was the only medium where a decrease in the total DCA yield was observed after a 6 h reaction. This is consistent with the results described in section 4.1.4., that acetic acid does not decrease the rate of DCA destruction in the presence of oil shale. The main advantage of adding acetic acid was that DCAs were formed rapidly (a 1 h experiment gave a 7% yield of DCA), which favours the use of short reaction times.

In Figure 26, the acidic and basic media are compared at three different oxygen pressures and at four different temperatures. The highest DCA yield (12.3%) was obtained in the acetic acid solution and the highest SO yield (46%) in a K_2CO_3 solution at 40 bar with a 50/50 mixture of O_2/N_2. The use of 100% oxygen led to over-oxidation of the solute during the 3-hour reaction time, so a shorter reaction time would be beneficial. A comparison of different temperatures for the 3-hour reaction indicated that 175 °C was preferable for the acetic acid solution and 185 °C for the basic solution. It was suggested that in alkali the water-soluble secondary intermediates require higher temperatures for further transformation to DCAs.

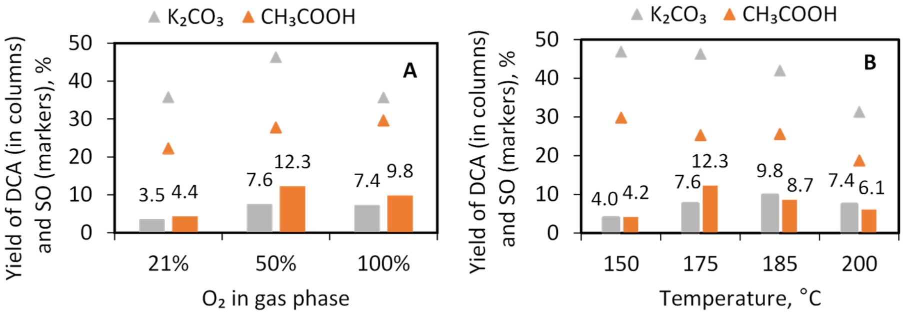


*Figure 26. The effect of oxygen partial pressure and temperature on K-70 oxidation in acidic and basic solutions (**A** at T = 175 °C and **B** at P = 40 bar of 50 % O_2). Reaction conditions: t = 3 h; P = 40 bar; 20 g/L of K-70 in dist. water, with 60 wt% of K_2CO_3 or in 20 vol% acetic acid solution. Adapted from **Publication II**.*

4.2.6 Insights into the kerogen oxidation pathway

The following observations emerged from the results of the oxidation of oil shale:

- Oxidation of oil shale kerogen is controlled by the ratio of oxygen to organic carbon in the reaction media.
- The formation of CO_2 during kerogen dissolution is inevitable: as soon as some of the kerogen reacts with oxygen and becomes soluble in water, CO_2 is released. This means that for kerogen to dissolve, part of the kerogen structure must be completely decomposed.
- Alkyl-substituted resorcinols are very sensitive to oxidation under WAO conditions.
- Relying on the kerogen structure models in Section 1.1.2, it may be assumed that kerogen oxidation starts with the oxidation of resorcinol units. Therefore, oxidation at the level of a single kerogen unit can be considered to consist of two distinct steps:
    - The resorcinol units are decomposed, whereupon the remainder of the organic matter (aliphatic linkages between resorcinols) becomes water soluble.
    - Already dissolved substances are further oxidised.

Since the solute concentration is low at the beginning of the reaction, most of the CO_2 produced can be attributed to resorcinol degradation. This is shown in Figure 27, which compares the conversion of organic carbon with the amount of CO_2 produced under different oxygen regimes. To achieve 90% conversion, the same amount of CO_2 was produced at both 50% and 100% oxygen. When air was used as the oxidant, more CO_2 was produced per organic carbon. This suggests that the longer it takes to achieve the desired conversion, the greater the contribution of the parallel oxidation processes to the total amount of CO_2. Therefore, the oxidation of kerogen should be carried out quickly with a sufficient amount of oxygen so that the further oxidation of solutes makes a minimal contribution to the amount of CO_2 produced. The higher the excess of oxygen with respect to kerogen C (the experiment with 100% O_2), the more crucial the choice of reaction time, since the oxidation rate is significantly increased.

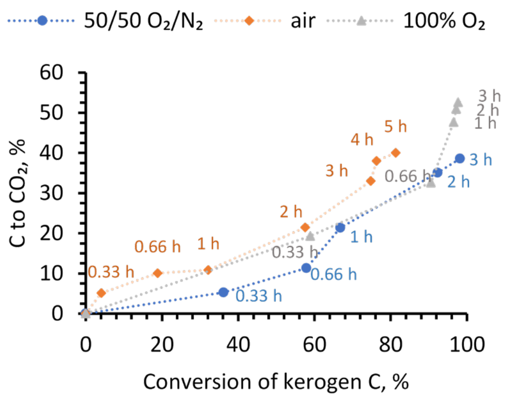


Figure 27. CO_2 formation per organic carbon conversion at 175 °C and 40 bar of different oxygen mixtures with 20 g/L of K-70. Modified from ***Publication III****.*

4.2.7 Other oil shales in WAO

To investigate whether the applied WAO procedure is a feasible technology for other oil shales, Green River and Jordan shales were also tested. The chemical compositions of the oil shale samples used are described in Table 14. The kerogens of both shales are believed to contain considerable amounts of saturated aliphatic chains that could be precursors of DCAs [4]. However, these shales have a lower content of oxy-aromatic carbon, so that the structural units are not predominantly of the resorcinol type [60], [153], [154]. Applying exactly the same conditions used for the oxidation of kukersite, 93% conversion was obtained for Green River and 85% for Jordan (Table 14). The soluble fraction contained aliphatic DCAs, but the yields were modest: 5% for Green River and 3% for Jordan oil shales. The mixture of DCAs from the Green River and from the Jordan shale oxidation, contained short-chain DCAs in higher amounts than from the K-45 (native kukersite) oxidation. Nevertheless, the fact that DCAs were formed in measurable amounts from a non-optimised oxidation process of these shales emphasises that a similar oxidation process could be used to dissolve other oil shales and also to obtain DCAs.

Table 14. The chemical composition of oil shale samples used (wt%) and the results of oxidation[a]

	Green River	Jordan	Kukersite
C	17.3	18.6	38.4
H	1.9	1.6	4.4
N	0.2	0.3	0.1
S	0.7	2.8	1.7
TIC	4.3	5.9	3.3
TOC	13	12.7	35.1
DCA, %[b]	4.8	2.8	10.8
(C_6-C_{10}/C_4-C_{10}), %	23	28	43
Conversion, %	93	82	95

[a]Reaction conditions: T = 175 °C; P = 40 bar of 50% O_2; t = 3 h; 20 g/L of oil shale in water. [b]Yield of DCAs is calculated from the TOC value. Modified from **Publication II**.

4.2.8 Further valorisation of dissolved matter

When oxidising kukersite K-70 at 175 °C with 40 bar of 50% O_2 roughly 25% of SO may be characterised as aliphatic DCAs. The remainder can be described as a complicated mixture of various carboxylic acids and alcohols with different molecular weights (see Section 4.2.2). The DCAs content in SO decreased to 15% when basic conditions were applied. As mentioned above, a large part of the DCAs is the result of further oxidation of the primarily dissolved material. Therefore, it was investigated whether the content of DCAs could be increased by a separate oxidation of SO.

Thus, the SO obtained from the oxidation of K-70 in alkali was oxidised for a second time at 175 °C with 40 bar 50% O_2 together with 40 wt% KOH or K_2CO_3. The addition of a base was necessary to increase the solubility of the isolated SO in the reaction medium. The total amount of DCAs increased by 30-37% from the original value. However, the distribution of DCAs was still shifted towards C_4. The reactions were also accompanied by a substantial amount of CO_2 formation (1.1-1.5 g CO_2 per 1 g reacted SO).

The valorisation of SO was also tested by another oxidation method. SO was subjected to oxidation with nitric acid: 5 ml of conc. HNO_3 was applied to 1 g of SO at 80°C and stirred for 3 hours. The total amount of DCA in the obtained product increased by 125%. Also, a significant increase in oxidation selectivity was observed: the content of medium chain acids (C_6 and C_7) increased and the number of intermediates decreased (Figure 28). These individual experiments demonstrated that the solutes separated during the oxidation of oil shale can be further converted to DCAs by other oxidation methods, increasing the value of the product.

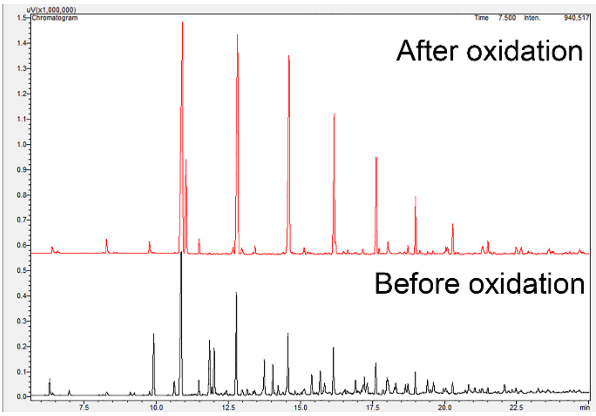


*Figure 28. GC-FID chromatogram of solubilised organics before and after the HNO_3 oxidation. Adapted from **Publication III**.*

5 Conclusions

As the environmental aspect of technological output is of high interest nowadays, there is an urgent need for processes that make it possible to convert rigid polymeric matrices, such as kerogen, into chemicals via methods that do not include the use of toxic organic solvents or reagents. The oxidation of kukersite kerogen with air in water under moderate temperatures is a possible alternative to existing methods for transforming oil shale.

The results of the thesis can be outlined as follows:

- Efficient kerogen degradation can be achieved from a temperature of 165°C under 40 bar of oxygen-containing gas. The method allows to capture more than 30% of the original organic carbon in the kerogen as water-soluble acids and alcohols.
- The highest yield of DCAs observed was 15% when oxidising oil shale concentrate at 175 °C with pure oxygen for 5 hours. The yield and composition of DCAs was strongly influenced by the combination of applied temperature, pressure and reaction time.
- Pure DCAs (C_4-C_{10}) do not react significantly in mixture or individually at temperatures below 200 °C under 40 bar O_2 in a stainless-steel reactor. The stability of pure acids can be further enhanced by adding acetic acid.
- In the presence of alkali metals and co-oxidants, such as methylresorcinols and malonic acid, the decomposition of long-chain DCAs was observed. The reactivity of long-chain DCAs was also affected by the presence of oil shale kerogen.
- DCAs were shown to degrade sequentially, from higher acids towards C_4 and acetic acid, both of which proved to be recalcitrant under the conditions applied. An analysis of the product mixture obtained indicated α- and β-oxidation.
- The formation of undesirable products was most dependent on the oxidant pressure, temperature, residence time and the concentration of kerogen. The reactivity of the formed intermediates to further oxidation was also dependent on the concentration of acidic or basic additives in the reaction medium.
- It was found that kerogen cannot be oxidatively dissolved in a way that no CO_2 is released. The initial formation of CO_2 was attributed to the degradation of resorcinols.
- A technologically viable option for achieving the highest kerogen dissolution in water is to apply slight oxygen excess at a temperature of 175°C or higher with minimum residence time. The addition of a base promotes higher solubility of oxygenated products and decreases the amount of CO_2 released.

This study revealed that kerogen is an attractive natural polymer from which useful and valuable chemicals (e.g. DCAs) can be produced. However, it remains a challenge to utilise the resulting CO_2 and achieve a higher yield of DCAs.

References

[1] B. Durand, *Sedimentary organic matter and kerogen. Definition and quantitative importance of kerogen.* Paris: Edistions Technip., 1980.

[2] A. Raukas and J. M. Punning, *Energy Environ. Sci.*, vol. 2, no. 7, pp. 723–728, 2009,

[3] J. R. Dyni, *Oil Shale*, vol. 20, no. 3, pp. 193–252, 2003.

[4] J. Qian and L. Yin, *Oil Shale - Petroleum Alternative*. Bejing: China Petrochemical Press, 2010.

[5] J. G. Speight, “Oil Shale Resources,” *Shale Oil Production Processes*, NY: Gulf Professional Publishing, 2012, pp. 35–73.

[6] World Energy Council, “World Energy Resources,” 2016. [Online]. Available: https://www.worldenergy.org/assets/images/imported/2016/10/World-Energy-Resources-Full-report-2016.10.03.pdf

[7] N. E. Altun, C. Hiçyilmaz, J. Y. Hwang, A. S. Bağci, and M. V. Kök, *Oil Shale*, vol. 23, no. 3, pp. 211–227, 2006.

[8] Z. Abu-Hamatteh and A. Al-Shawabkeh, *Cent. Eur. Geol.*, vol. 51, no. 4, pp. 379–395, 2008.

[9] E. S. Hrayshat, *Energy Sources, Part A Recover. Util. Environ. Eff.*, vol. 30, no. 20, pp. 1915–1920, 2008.

[10] M. Vandenbroucke and C. Largeau, *Org. Geochem.*, vol. 38, no. 5, pp. 719–833, 2007.

[11] A. Hutton, S. Bharati, and T. Robl, *Energy and Fuels*, vol. 8, no. 6, pp. 1478–1488, 1994.

[12] K. E. Peters, X. Xia, A. E. Pomerantz, and O. C. Mullins, “Geochemistry Applied to Evaluation of Unconventional Resources,” *Unconventional Oil and Gas Resources Handbook: Evaluation and Development*, no. 1, NY: Gulf Professional Publishing, 2016, pp. 71–126.

[13] K. E. Peters and M. R. Cassa, “Applied source rock geochemistry,” *The petroleum system - from source to trap: AAPG Memoir 60*, no. 60, NY: American Association of Petroleum Geologists, 1994, pp. 93–120.

[14] J. G. Speight, “Origin and Properties of Oil Shale,” *Shale Oil Production Processes*, NY: Gulf Professional Publishing, 2012, pp. 1–33.

[15] B. Maaten, L. Loo, A. Konist, and A. Siirde, *J. Therm. Anal. Calorim.*, vol. 131, no. 3, pp. 2087–2091, 2018.

[16] I. Johannes, L. Tiikma, H. Luik, and G. Š. Arajeva, *Int. J. Eng. Appl. Sci.*, vol. 6, no. 5, pp. 23–35, 2015.

[17] P. N. Kogerman, *J. Inst. Pet. Technol.*, vol. 11, no. 50, pp. 210–224, 1925.

[18] P. N. Kogerman, *Acta Comment. Univ. Dorpat. A Math. Phys. Medica*, vol. 3, no. 6, pp. 1–25, 1922.

[19] P. N. Kogerman, *J. Inst. Pet. Technol. Abstr.*, vol. 13, pp. 346–347, 1927.

[20] P. N. Kogerman, *J. Inst. Pet. Technol. Abstr.*, vol. 17, pp. 569–570, 1931.

[21] P. N. Kogerman, “Estonian Shale Oils,” *The Science of Petroleum IV*, vol. 4, London: Oxford University Press, 1938, pp. 3107–3112.

[22] P. N. Kogerman and J. Kopwillem, *J. Inst. Pet. Technol.*, vol. 18, pp. 833–845, 1932.

[23] A. Aaloe, H. Bauert, and A. Soesoo, *Kukersite oil shale*, no. March 2007. Tallinn: MTÜ GEOGuide Baltoscandia, 1997.

[24] V. Kattai, T. Saadre, and L. Savitski, *Estonian Oil Shale: geology, resource, mining (in Estonian)*. Tallinn: Eesti Geoloogiakeskus, 2000.

[25] Eesti Energia, Viru Keemia Grupp, Kiviõli Keemiatööstus, and Oil Shale Competence Centre, *Estonian Oil Shale Industry Yearbook*. 2018.

[26] A. Aaloe, H. Bauert, and A. Soesoo, *Kukersite oil shale*. Tallinn: MTÜ GEOGuide Baltoscandia, 2007.

[27] M. Veiderma, *Oil Shale*, vol. 20, no. 3, pp. 295–303, 2003.

[28] J. Shi, Y. Ma, S. Li, J. Wu, Y. Zhu, and J. Teng, *Energy and Fuels*, vol. 31, no. 5, pp. 4808–4816, 2017.

[29] Ü. Lille, I. Heinmaa, and T. Pehk, *Fuel*, vol. 82, no. 7, pp. 799–804, 2003.

[30] J. G. Speight, “Refining Shale Oil,” *Shale Oil Production Processes*, NY: Gulf Professional Publishing, 2012, pp. 139–163.

[31] C. Barker, “Origin, Composition and Properties of Petroleum,” *Enhanced oil recovery,* NY: Elsevier, 1985, pp. 11–45.

[32] S. Derenne, C. LArgeau, P. Landais, and A. Rochdi, *Fuel*, vol. 73, no. 4, pp. 626–628, 1994.

[33] S. Derenne, C. Largeau, E. Casadevall, J. S. Sinninghe Damsté, E. W. Tegelaar, and J. W. de Leeuw, *Org. Geochem.*, vol. 16, no. 4–6, pp. 873–888, 1990.

[34] Ü. Lille, *Oil Shale*, vol. 20, no. 3, pp. 253–263, 2003.

[35] P. Blokker, P. Van Bergen, R. Pancost, M. E. Collinson, J. W. De Leeuw, and J. S. Sinninghe Damste, *Geochim. Cosmochim. Acta*, vol. 65, no. 6, pp. 885–900, 2001.

[36] W. H. Ilsley, R. A. Zingaro, and J. H. Zoeller, *Fuel*, vol. 65, pp. 1216–1220, 1986.

[37] R. J. Boucher, G. Standen, and G. Eglinton, *Fuel*, vol. 70, pp. 695–702, 1991.

[38] Easac, “A study on the EU oil shale industry – viewed in the light of the Estonian experience,” 2007. [Online]. Available: https://easac.eu/fileadmin/PDF_s/reports_statements/Study.pdf

[39] E. Jürs and E. Reinsalu, *Eesti põlevkivi töötlemine (in Estonian)*. Kiviõli, Tallinn: Tallinn University of Technology, 2015.

[40] Z. S. Baird, O. Järvik, R. Rannaveski, and V. Oja, *OSF Prepr.*, pp. 1–27, 2020.

[41] J. Qian, S. Li, and J. Wang, *Oil Shale. A Sci. J.*, vol. 20, no. 3, pp. 356–359, 2003.

[42] J. G. Speight, “Mining and Retorting,” *Shale Oil Production Processes*, no. 1, NY: Gulf Professional Publishing, 2012, pp. 93–122.

[43] O. Pihl, A. Niidu, N. Merkulova, M. Fomitsov, A. Siirde, and M. Tshepelevitsh, *Oil Shale*, vol. 36, no. 2S, pp. 188–196, 2019.

[44] I. Kamenev, R. Munter, L. Pikkov, and L. Kekisheva, *Oil Shale*, vol. 20, no. 4, pp. 443–457, 2003.

[45] P. N. Kogerman, “Hundred years of the chemical investigation of an oil shale: the chemical constitution of the Estonian oil shale ‘kukersite’ – Oil Shale and Cannel Coal.,” *Inst. Petroleum Conf.*, 1938, pp. 115–123.

[46] A. W. Bone and R. Quarendon, *Proc. R. Soc. A*, vol. 110, no. 775, pp. 537–542, 1926.

[47] R. Veski and S. Veski, *Oil Shale*, vol. 36, no. 1, pp. 76–95, 2019.

[48] H. Martinson, *Bibliography of research papers by staff of the Institute of Chemistry 1947-1972*. Tallinn: Institute of Chemistry, Academy of Sciences of Estonia, 1973.

[49] A. S. Fomina and L. Pobul, *Acad. Sci. Est. SSR*, vol. 6, no. 2, pp. 190–198, 1957.

[50] S. Bajc, A. Amblès, C. Largeau, S. Derenne, and D. Vitorović, *Org. Geochem.*, vol. 32, no. 6, pp. 773–784, 2001.

[51] Z. Degtereva and A. Fomina, *Acad. Sci. Est. SSR*, vol. 8, no. 2, pp. 122–136, 1959.

[52] A. Fomina, L. Pobul, Z. Degtereva, R. Veski, O. Kirret, I. Nikopensius *et al.*, “Method for processing causticobiolites of the sapropelite type with an oxidizing agent,” German Patent 2259502, Dec. 5, 1972.
[53] A. Fomina, L. Pobul, Z. Degtereva, R. Veski, O. Kirret, I. Nikopensius *et al.*, “Method for processing caustobilites of sapropelite type with oxidizer,” Australian Patent 1973052367, Feb. 20, 1974.
[54] M. Lopp, K. Kaldas, G. Preegel, K. Muldma, and A. Niidu, “Põlevkivi kerogeeni oksüdeeriva lahustamise meetod,” EE 201900020 A, 2019.
[55] L. Pobul and A. Fomina, *Acad. Sci. Est. SSR*, vol. 11, no. 3, 1962.
[56] V. A. Proskurjakov and Z. V. Soloveichik, *Tr. Vsesoj. N.I.Instituta po Pererab. i Issl. Topl.*, vol. 10, pp. 64–80, 1961.
[57] V. A. Proskurjakov and Z. V. Soloveichik, *Tr. Vsesoj. N.I.Instituta po Pererab. i Issl. Topl.*, vol. 10, pp. 81–90, 1961.
[58] V. A. Proskurjakov, V. I. Yakovlev, and O. I. Kudrjukov, *Tr. Vsesoj. N.I.Instituta po Pererab. i Issl. Topl.*, vol. 11, pp. 20–27, 1962.
[59] W. E. Robinson, “Origin and Characteristics of Green River Oil Shale,” *Oil Shale*, vol. 3, no. Chapter 4, NY: Elsevier, 1976, pp. 61–79.
[60] M. J. Trewhella, I. J. F. Poplett, and A. Grint, *Fuel*, vol. 65, no. 4, pp. 541–546, 1986.
[61] A. O. Barakat and T. F. Yen, *Energy and Fuels*, vol. 2, no. 2, pp. 181–185, 1988.
[62] A. O. Barakat and T. F. Yen, *Fuel*, vol. 66, pp. 587–593, 1987.
[63] M. J. Birchmeier, J. G. Hill, C. J. Houtman, R. H. Atalla, and I. A. Weinstock, *Ind. Eng. Chem. Res.*, vol. 39, no. 1, pp. 55–64, 2000.
[64] H. Debellefontaine, M. Chakchouk, J. N. Foussard, D. Tissot, and P. Striolo, *Environ. Pollut.*, vol. 92, no. 2, pp. 155–164, 1996.
[65] S. K. Bhargava, J. Tardio, J. Prasad, K. Föger, D. B. Akolekar, and S. C. Grocott, *Ind. Eng. Chem. Res.*, vol. 45, no. 4, pp. 1221–1258, 2006.
[66] V. S. Mishra, V. V. Mahajani, and J. B. Joshi, *Ind. Eng. Chem. Res.*, vol. 34, no. 1, pp. 2–48, 1995.
[67] F. J. Zimmermann, "Waste disposal," US Patent 2665249, Mar. 27, 1954.
[68] L. Li, P. Chen, and E. F. Gloyna, *AIChE J.*, vol. 37, no. 11, pp. 1687–1697, 1991.
[69] H. Debellefontaine and J. N. Foussard, *Waste Manag.*, vol. 20, no. 1, pp. 15–25, 2000.
[70] M. N. Ingale, J. B. Joshi, V. V. Mahajani, and M. K. Gada, *Process Saf. Environ. Prot.*, vol. 74, no. 4, pp. 265–272, 1996.
[71] M. Möller, P. Nilges, F. Harnisch, and U. Schröder, *ChemSusChem*, vol. 4, no. 5, pp. 566–579, 2011.
[72] S. Imamura, *Ind. Eng. Chem. Res.*, vol. 38, no. 5, pp. 1743–1753, 1999.
[73] V. Tufano, *Chem. Eng. Technol.*, vol. 16, no. 3, pp. 186–190, 1993.
[74] R. V. Shende and V. V. Mahajani, *Ind. Eng. Chem. Res.*, vol. 33, no. 12, pp. 3125–3130, 1994.
[75] D. Mantzavinos, E. Lauer, R. Hellenbrand, A. G. Livingston, and I. S. Metcalfe, *Water Sci. Technol.*, vol. 36, no. 2–3, pp. 109–116, 1997.
[76] A. B. Thomsen, *Water Res.*, vol. 32, no. 1, pp. 136–146, 1998.
[77] A. Kruse and E. Dinjus, *J. Supercrit. Fluids*, vol. 39, no. 3, pp. 362–380, 2007.
[78] M. Plaza and C. Turner, *TrAC - Trends Anal. Chem.*, vol. 71, pp. 39–54, 2015.
[79] H. A. Pray, C. E. Schweickert, and B. H. Minnich, *Ind. Eng. Chem.*, vol. 44, no. 5, pp. 1146–1151, 1952.

[80] M. Geng and Z. Duan, *Geochim. Cosmochim. Acta*, vol. 74, no. 19, pp. 5631–5640, 2010.

[81] L. Zhou, H. Cao, C. Descorme, and Y. Xie, *Front. Environ. Sci. Eng.*, vol. 12, no. 1, pp. 1–20, 2018.

[82] R. R. Zapico, P. Marín, F. V. Díez, and S. Ordóñez, *Chem. Eng. J.*, vol. 270, pp. 122–132, 2015.

[83] M. G. Clerici and O. A. Kholdeeva, Eds., *Liquid Phase Oxidation via Heterogeneous Catalysis*. New Jersey: John Wiley & Sons, Inc., 2013.

[84] J. Prasad, J. Tardio, D. B. Akolekar, S. K. Bhargava, and S. C. Grocott, *Ind. Eng. Chem. Res.*, vol. 43, no. 20, pp. 6363–6368, 2004.

[85] M. Bernardi, D. Cretenot, S. Deleris, C. Descorme, J. Chauzy, and M. Besson, *Catal. Today*, vol. 157, no. 1–4, pp. 420–424, 2010.

[86] S. Imamura, T. Sakai, and T. Ikuyama, *J. Japan Pet. Inst.*, vol. 25, no. 2, pp. 74–80, 1982.

[87] F. Arena, C. Italiano, A. Raneri, and C. Saja, *Appl. Catal. B Environ.*, vol. 99, no. 1–2, pp. 321–328, 2010.

[88] S. T. Kolaczkowski, P. Plucinski, F. J. Beltran, F. J. Rivas, and D. B. McLurgh, *Chem. Eng. J.*, vol. 73, no. 2, pp. 143–160, 1999.

[89] S. Collado, D. Quero, A. Laca, and M. Diaz, *Ind. Eng. Chem. Res.*, vol. 49, no. 24, pp. 12405–12413, 2010.

[90] S. Imamura, H. Kinunaka, and N. Kawabata, *Bull. Chem. Soc. Jpn.*, vol. 55, no. 11, pp. 3679–3680, 1982.

[91] D. Mantzavinos, R. Hellenbrand, A. G. Livingston, and I. S. Metcalfe, *Appl. Catal. B Environ.*, vol. 7, no. 3–4, pp. 379–396, 1996.

[92] D. Fu, J. Chen, and X. Liang, *Chemosphere*, vol. 59, no. 6, pp. 905–908, 2005.

[93] J. Tardio, S. K. Bhargava, S. Eyer, and D. B. Akolekar, *Ind. Eng. Chem. Res.*, vol. 43, no. 3, pp. 669–674, 2004.

[94] R. S. Willms, D. D. Reible, D. M. Wetzel, and D. P. Harrison, *Ind. Eng. Chem. Res.*, vol. 26, no. 3, pp. 606–612, 1987.

[95] J. Vicenete and M. Diaz, *Environ. Sci. Technol.*, vol. 37, no. 7, pp. 1457–1462, 2003.

[96] D. M. Sonnen, R. S. Reiner, R. H. Atalla, and I. A. Weinstock, *Ind. Eng. Chem. Res.*, vol. 36, no. 10, pp. 4134–4142, 1997.

[97] V. S. Mishra, J. B. Joshi, and V. V. Mahajani, *Water Res.*, vol. 28, no. 7, pp. 1601–1608, 1994.

[98] R. V. Shende and J. Levee, *Ind. Eng. Chem. Res.*, vol. 38, no. 10, pp. 3830–3837, 1999.

[99] D. Fu, F. Zhang, L. Wang, F. Yang, and X. Liang, *Chinese J. Catal.*, vol. 36, no. 7, pp. 952–956, 2015.

[100] A. Garg and A. Mishra, *J. Hazardous, Toxic, Radioact. Waste*, vol. 17, no. 2, pp. 89–96, 2013.

[101] S. T. Kolaczkowski, F. J. Beltran, D. B. McLurgh, and F. J. Rivas, *Process Saf. Environ. Prot.*, vol. 75, no. 4, pp. 257–265, 1997.

[102] H. R. Devlin and I. J. Harris, *Ind. Eng. Chem. Fundam.*, vol. 23, no. 4, pp. 387–392, 1984.

[103] H. S. Joglekar, S. D. Samant, and J. B. Joshi, *Water Res.*, vol. 25, no. 2, pp. 135–145, 1991.

[104] S. Lefèvre, O. Boutin, J. H. Ferrasse, L. Malleret, R. Faucherand, and A. Viand, *Chemosphere*, vol. 84, no. 9, pp. 1208–1215, 2011.

[105] B. Weber, A. Chavez, J. Morales-Mejia, S. Eichenauer, E. A. Stadlbauer, and R. Almanza, *J. Environ. Manage.*, vol. 161, pp. 137–143, 2015.

[106] R. V. Shende and V. V. Mahajani, *Ind. Eng. Chem. Res.*, vol. 36, no. 11, pp. 4809–4814, 1997.

[107] S. I. Imamura, A. Hirano, and N. Kawabata, *Ind. Eng. Chem. Prod. Res. Dev.*, vol. 21, no. 4, pp. 570–575, 1982.

[108] R. V. Shende and J. Levee, *Ind. Eng. Chem. Res.*, vol. 38, no. 7, pp. 2557–2563, 1999.

[109] R. V. Shende and J. Levec, *Ind. Eng. Chem. Res.*, vol. 39, no. 1, pp. 40–47, 2000.

[110] E. T. Denisov, N. I. Mitskevich, and V. E. Agabekov, *Liquid-Phase Oxidation of Oxygen-Containing Compounds*. New York: Consultants Bureau, 1977.

[111] F. Jin, J. Cao, A. Kishita, H. Enomoto, and T. Moriya, *J. Supercrit. Fluids*, vol. 44, no. 3, pp. 331–340, 2008.

[112] F. Jin, J. Cao, H. Enomoto, and T. Moriya, *J. Supercrit. Fluids*, vol. 39, pp. 80–88, 2006.

[113] A. G. Demesa, A. Laari, I. Turunen, and M. Sillanpa, *Chem. Eng. Technol.*, vol. 38, no. 12, pp. 2270–2278, 2015.

[114] S. Irmak, J. Kang, and M. Wilkins, *Bioresour. Technol. Reports*, vol. 9, no. 12, pp. 100377, 2020.

[115] A. Azarpira, J. Ralph, and F. Lu, *Bioenergy Res.*, vol. 7, no. 1, pp. 78–86, 2014.

[116] M. Kindsigo and J. Kallas, *Proc. Est. Acad. Sci. Chem*, vol. 55, no. 3, pp. 132–144, 2006.

[117] M. Kindsigo, M. Hautaniemi, and J. Kallas, *Environ. Chem. Lett.*, vol. 7, no. 2, pp. 155–160, 2009.

[118] R. Behling, S. Valange, and G. Chatel, *Green Chem.*, vol. 18, no. 7, pp. 1839–1854, 2016.

[119] F. G. Sales, L. C. A. Maranhão, N. M. Lima Filho, and C. A. M. Abreu, *Ind. Eng. Chem. Res.*, vol. 45, no. 20, pp. 6627–6631, 2006.

[120] C. Cheng, J. Wang, D. Shen, J. Xue, S. Guan, S. Gu *et al.*, *Polymers*, vol. 9, no. 240, pp. 1-25, 2017.

[121] M. Ashtari, L. Carbognani, and P. Pereira-Almao, *Energy and Fuels*, vol. 30, no. 7, pp. 5470–5482, 2016.

[122] M. Ashtari, L. Carbognani Ortega, F. Lopez-Linares, A. Eldood, and P. Pereira-Almao, *Energy and Fuels*, vol. 30, no. 6, pp. 4596–4608, 2016.

[123] G. Nafie, A. D. Manasrah, B. Mackay, I. Badran, and N. N. Nassar, *Ind. Eng. Chem. Res.*, vol. 58, no. 12, pp. 4988–4996, 2019.

[124] A. D. Manasrah, A. Hassan, and N. N. Nassar, *Can. J. Chem. Eng.*, vol. 97, no. 11, pp. 2794–2803, 2019.

[125] A. D. Manasrah, N. N. Nassar, and L. C. Ortega, *Fuel*, vol. 215, no. November 2017, pp. 865–878, 2018.

[126] V. I. Antonishin, V. V. Gumenetskii, and B. S. Grinenko, *Pet. Chem. U.S.S.R*, vol. 17, no. 4, pp. 244–256, 1977.

[127] V. I. Antonishin and V. V. Gumenetskii, *Pet. Chem. U.S.S.R*, vol. 19, pp. 16–25, 1980.

[128] B. Cornils and P. Lappe, “Dicarboxylic Acids, Aliphatic,” *Ullmann’s Encyclopedia of Industrial Chemistry*, 2000.

[129] A. Fitton and K. L. Goa, *Drugs*, vol. 41, pp. 780–798, 1991.

[130] G. Mingrone, L. Castagneto-Gissey, and K. Macé, *Br. J. Clin. Pharmacol.*, vol. 75, no. 3, pp. 671–676, 2013.

[131] A. Celli, M. Colonna, A. Gandini, C. Gioia, T. M. Lacerda, and M. Vannini, "Polymers from Monomers Derived from Biomass," *Chemicals and Fuels from Bio-Based Building Blocks*, Wiley-VCH, 2016, pp. 315–350.

[132] A. Díaz, R. Katsarava, and J. Puiggalí, *Int. J. Mol. Sci.*, vol. 15, no. 5, pp. 7064–7123, 2014.

[133] P. F. H. Harmsen, M. M. Hackmann, and H. L. Bos, *Biofuels, Bioprod. Biorefining*, vol. 8, pp. 306–324, 2014.

[134] W. Yan, G. Zhang, J. Wang, M. Liu, Y. Sun, Z. Zhou *et al.*, *Front. Chem.*, vol. 8, no. March, pp. 1–12, 2020.

[135] S. Van De Vyver and Y. Román-Leshkov, *Catal. Sci. Technol.*, vol. 3, no. 6, pp. 1465–1479, 2013.

[136] Goodyear Tire & Rubber Company, "Process for the Manufacture of Adipic Acid," US patent 1844626, Jul. 20, 1958.

[137] L. Schneider, M. Lazarus, and A. Kollmuss, "Industrial N2O Projects Under the CDM: Adipic Acid - A Case of Carbon Leakage?," WP-US-1006, 2010.

[138] A. Corona, M. J. Biddy, D. R. Vardon, M. Birkved, M. Z. Hauschild, and G. T. Beckham, *Green Chem.*, vol. 20, no. 16, pp. 3857–3866, 2018.

[139] D. Bonnet, T. Ireland, E. Fache, and J. P. Simonato, *Green Chem.*, vol. 8, no. 6, pp. 556–559, 2006.

[140] E. Skoog, J. H. Shin, V. Saez-Jimenez, V. Mapelli, and L. Olsson, *Biotechnol. Adv.*, vol. 36, no. 8, pp. 2248–2263, 2018.

[141] S. Li, W. Deng, S. Wang, P. Wang, D. An, Y. Li *et al.*, *ChemSusChem*, vol. 11, no. 13, pp. 1995–2028, 2018.

[142] K. Raj, S. Partow, K. Correia, A. N. Khusnutdinova, A. F. Yakunin, and R. Mahadevan, *Metab. Eng. Commun.*, vol. 6, no. November 2017, pp. 28–32, 2018.

[143] H. Zhang, C. Xie, Z. Liu, J. Gong, Y. Bao, M. Zhang *et al.*, *Ind. Eng. Chem. Res.*, vol. 52, no. 51, pp. 18458–18465, 2013.

[144] H. Zhang, Q. Yin, Z. Liu, J. Gong, Y. Bao, M. Zhang *et al.*, *J. Chem. Thermodyn.*, vol. 77, pp. 91–97, 2014.

[145] M. Bilde, B. Svenningsson, J. Mønster, and T. Rosenørn, *Environ. Sci. Technol.*, vol. 37, no. 7, pp. 1371–1378, 2003.

[146] K. Muraishi and Y. Suzuki, *Thermochim. Acta*, vol. 232, no. 2, pp. 195–203, 1994,

[147] S. H. Yalkowsky and Y. He, *Handbook of Aqueous Solubility Data (1st ed.)*. Boca Raton: CRC Press, 2003.

[148] S. D. Brooks, M. E. Wise, M. Cushing, and M. A. Tolbert, *Geophys. Res. Lett.*, vol. 29, no. 19, 2002.

[149] M. Dlugosz and J. M. Antosiewicz, *Z.Naturforsch*, vol. 59a, pp. 873–874, 2004.

[150] D. R. Lide, *CRC Handbook of Chemistry and Physics, Internet Version 2005*. [Online]. Available: http://www.hbcpnetbase.com.

[151] J.-R. Mesi, "Wet Oxidation of Aliphatic Dicarboxylic Acids: Reactivity and Kinetic Aspects," B.S thesis, School of Engineering, Taltech, Tallinn 2020.

[152] R. L. Holliday, B. Y. M. Jong, and J. W. Kolis, *J. Supercrit. Fluids*, vol. 12, no. 3, pp. 255–260, 1998.

[153] W. Chu, X. Cao, K. Schmidt-Rohr, J. E. Birdwell, and J. Mao, *Energy and Fuels*, vol. 33, no. 2, pp. 645–653, 2019.

[154] S. R. Kelemen *et al.*, *Energy and Fuels*, vol. 21, no. 3, pp. 1548–1561, 2007.

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My biggest and most important thanks go to my family. To my husband Henry, who has encouraged me, applauded me, cared for the children, and comforted me when needed. With love, I cherish my two children, Kaia and Joosep, who did not judge me when my hours at the university got too long and accepted my good-night kiss.

Abstract
Wet air oxidation of oil shale

In a rapidly growing society, the demand for energy, as well as for all kinds of products and materials, is constantly increasing. On the other hand, both consumption and production need to change in order to meet the climate targets set. Solutions are being sought in the use of renewable resources and in the recycling of wastes, but a more efficient use of non-renewable minerals would also make an important contribution.

Oil shale is one of the most abundant fossil fuels in the world, but its use has been limited to direct combustion or oil and gas extraction. Depending on where the oil shale is deposited, the organic matter (kerogen) can be a feedstock for the production of a number of chemicals. Previous studies have shown that both aromatic compounds and carboxylic acids with different chain lengths can be extracted from the kerogen of the kukersite found in Estonia. Consequently, innovative and clean technologies should be researched and developed to enable the production of chemicals of commercial interest from oil shale kerogen.

In this thesis, the oxidative degradation of Estonian shale to dicarboxylic acids in heated water under oxygen pressure (WAO) was studied. The results and discussion section is divided into two main chapters, the first focusing on the reactivity of the products obtainable from the kerogen (dicarboxylic acids) and the second on the oxidation of the oil shale. In both chapters, the extent of oxidation is studied in terms of oxygen pressure, temperature, reaction time and the addition of various additives, with an emphasis on product selectivity and conversion. The results are derived from a series of experiments, from which the factors most affecting the oxidation of the kerogen and products have been identified. Advantages and challenges of oil shale oxidation with WAO are addressed and discussed.

The reactivity of seven dicarboxylic acids was studied in batch under subcritical conditions which had not been studied before. The results revealed that DCAs with long aliphatic chains were subject to further oxidation if the pH was not controlled. The novelty of this work is the use of abundant metal elements and organic co-oxidants to study the oxidative decomposition of longer DCAs in WAO at temperatures of 150-200 °C.

The study on the oxidation of kukersite kerogen sought to find all possible factors influencing it because there have been no recent studies in this field. The results demonstrated that in the temperature range 165-185 °C and at an oxygen pressure of 20-40 bar, a large part of the organic matter in the shale can be converted into water-soluble compounds in a short period of time. A large fraction of the compounds obtained were identified as aliphatic dicarboxylic acids and their further oxidation products. It was shown how various basic or acidic additives promote the oxidation of kerogen and alter the composition of the resulting product mixtures. Based on the product analysis and the distribution of organic carbon between the formed phases, the basic mechanism of the oxidative degradation of kerogen was evaluated and the origins of the released CO_2 were explained. The same method proved to be efficient with kerogens of different origins.

In conclusion, this work contributes to the existing knowledge of kerogen conversion processes and kerogen's potential use as fine chemical substrates. It also extends the applicability of wet oxidation for the degradation of complex polymeric materials. The production of DCAs from polymerised materials, such as kerogen, could contribute to further diversification of the DCA market.

Lühikokkuvõte
Põlevkivi oksüdeerimine vees hapniku mõjul

Aina kasvava rahvaarvuga ühiskonnas suureneb pidevalt nõudlus energiale kui ka kõikvõimalike toodete ja materjalide järele. Teisalt tuleb omaks võtta ühiskonnas seatud kliimaeesmärgid, nii et muutuma peavad nii tarbimine kui tootmine. Kuigi lahendusi otsitakse nii taastuvate ressursside kasutuselevõtust kui ka jääkmaterjalide ümbertöötlemisest, annaks ka taastumatute maavarade senisest parem väärindamine eesmärgi saavutamiseks olulise panuse.

Põlevkivi on üks maailmas enimlevinud fossiilseid kütuseid, kuid selles peituv rikkus on senini leidnud kasutust vaid otsepõletamisel või õli ja gaasi tootmisel. Sõltuvalt põlevkivi leiukohast võib põlevkivis leiduv orgaaniline aine (kerogeen) olla lähtematerjaliks aga ka mitmete kemikaalide tootmisele. Varasemad uuringud on näidanud, et Eestis leiduvast kukersiidi kerogeenist on võimalik eraldada nii aromaatseid ühendeid kui ka erineva ahela pikkusega karboksüülhappeid. Sellest tulenevalt tuleb senisest enam uurida ja arendada uuenduslikke ja puhtaid tehnoloogiaid, mis võimaldaks toota keemiatööstusele olulisi lähetaineid kasutades maksimaalselt ära kerogeeni struktuuri iseärasusi.

Käesolevas doktoritöös uuriti Eesti põlevkivi oksüdeerivat lagundamist dikarboksüülhapeteks vees hapniku rõhul. Doktoritöö tulemuste ja arutelu osa on jagatud kahte suuremasse peatükki, millest esimene keskendub kerogeenist saadavate produktide (dikarboksüülhapete) reaktiivsusele reaktsioonikeskkonnas, ning teine põlevkivi oksüdatsiooni uurimisele. Mõlemas alapeatükis on uuritud oksüdatsiooni ulatuse sõltuvust hapniku rõhust, temperatuurist, reaktsiooniajast ja erinevatest lisanditest. Tulemused on esitatud mitmete sõltuvusgraafikutena, mille põhjal on toodud välja nii kerogeeni enda kui ka produktide oksüdatsiooni enim mõjutavad tegurid.

Uuriti seitsme dikarboksüülhappe reaktiivsust subkriitilistes tingimustes ühes segus, mille kohta puuduvad varasemad näited. Leiti, et muutuva pH-ga reaktsioonikeskkonnas on pikema ahelaga dikarboksüülhapped märkimisväärselt tundlikumad oksüdatsioonile kui lühema ahelaga happed. Käesoleva töö uudsuseks on asjaolu, et pikemate dikarboksüülhapete oksüdatiivset lagunemist uuriti ka sõltuvalt mitmetest levinud metallilistest elementidest ning orgaanilistest kaas-oksüdeerijatest.

Näidati, et temperatuurivahemikus 165-185 °C ja hapniku rõhul 20-40 bar on lühikese aja jooksul võimalik muundada suur osa põlevkivi orgaanilisest ainest vees lahustuvateks ühenditeks lühikese aja jooksul. Tõestati, et suure osa saadavatest ühenditest moodustavad alifaatse ahelaga dikarboksüülhapped ja nende edasise oksüdatsiooni produktid. Näidati, kuidas erinevad aluselised või happelised lisandid soodustavad kerogeeni oksüdatsiooni ja muudavad saadud produkti segude koostist. Produkti segude järjepideva kirjeldamise ning orgaanilise süsiniku jaotuse alusel hinnati kerogeeni oksüdatiivse lagunemise põhilist mehhanismi ja seletati emiteeruva CO_2 päritolu. Täiendavalt näidati, et sama meetodiga on võimalik lisaks Eestis leiduvale kukersiidile lagundada ka teisi maailmas leiduvate põlevkivide kerogeene.

Kokkuvõtteks võib väita, et käesolev töö avardab olemasolevaid teadmisi kerogeeni muundamisprotsessidest ja selle võimalikust kasutusest peenkeemia toorainena. Ühtlasi näitab töö seda, kuidas märgoksüdatsiooni protsessi on võimalik rakendada keeruliste polümeersete materjalide lagundamiseks ning dikarboksüülhapete tootmiseks.

Appendix 1

Publication I

K. Kaldas, G. Preegel, K. Muldma and M. Lopp, “Reactivity of Aliphatic Dicarboxylic Acids in Wet Air Oxidation Conditions,” *Industrial & Engineering Chemistry Research*, vol. 58, no. 25, pp. 10855−10863, 2019

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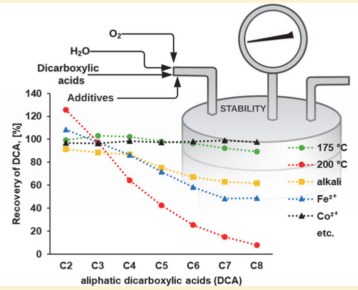
Reactivity of Aliphatic Dicarboxylic Acids in Wet Air Oxidation Conditions

Kristiina Kaldas,[†] Gert Preegel,[†] Kati Muldma,[†] and Margus Lopp*[,†]

[†]Department of Chemistry and Biotechnology, Faculty of Science, Tallinn University of Technology, Ehitajate tee 5, Tallinn, 19086, Estonia

Supporting Information

ABSTRACT: The reactivity of the aliphatic dicarboxylic acids (DCAs) mixtures in conditions similar to industrial wet air oxidation (WAO) process conditions has been investigated. DCAs have potential to be separated during WAO of highly polymerized organic matter (e.g., organic waste, biomass, kerogen in oil shale) before transforming to final oxidation products (CO_2 and water). However, a shortage of information about the DCAs stability in such processes restricts this application. The influence of oxygen pressure, temperature, pH, various metal salts, and radical generating organic compounds on DCAs possible transformation was established. High stability of DCAs (C4−C10) was shown at 175 °C with 40 bar of oxygen mixture in wide pH range. The increase in the DCA decomposition with the formation of lower chain DCAs was found to be inevitable in the presence of alkali and homogeneous iron or copper salts in nonbuffered solutions. The relationship between organic co-oxidants, such as malonic acid and resorcinols, and the stability of DCAs was studied. Of them, 5-methylresorcinol was the most efficacious in increasing oxidation of DCAs, and retention values of less than 10% were observed.



1. INTRODUCTION

Aliphatic dicarboxylic acids (DCAs) with the general formula HOOC-$(CH)_n$-COOH have a broad range of industrial applications, such as use in plasticizers,[1] lubricating oils,[2] different types of polymers,[3] and pharmaceuticals,[4] etc. The most common methods for DCAs production are the oxidative cleavage of cyclic compounds[5] or unsaturated monocarboxylic acids, the oxidation of ω,ω'-diols, and the hydrogenation of unsaturated DCAs.[6,7] Short-chain DCAs ($n < 4$) can be obtained also by bioprocesses from lignin, glycose, and other biomass resources.[5,8,9] In addition to the above-mentioned methods, partial wet air oxidation (WAO) has great potential to be a valuable and environmentally friendly platform for carboxylic acids production if organic wastes and abundant highly polymerized organic matter are used as feedstock.[10−14]

The WAO process has received considerable attention over the last three decades in relation to recycling industrial wastes.[15] In these processes, the waste molecules are oxidized in water at elevated temperature and pressure using oxygen as an oxidant.[16] Both subcritical (at 125−320 °C and at 0.5−20 MPa) and supercritical (>374 °C and >22 MPa) conditions have been applied.[17] Superheated water is a nontoxic, nonexplosive, and environmentally friendly reaction medium for dissolving organic molecules and gases.[15] Moreover, water itself may act not only as a solvent, but also as a reagent or a catalyst, mainly because of its increased acidity (at 250 °C $pK_a = \sim 11$ and at 25 °C $pK_a = 14$).[18,19]

The use of WAO in wastewater treatment has been investigated thoroughly. Therefore, a great part of research has been focused on the total destruction of organics, and the amount of retained total organic carbon (TOC) is often considered as a prime indicator of process efficiency.[20] However, the stability of individual intermediates formed during the oxidation has received relatively little attention, and this limits the use of partial WAO in order to obtain fine chemicals. There is considerable data concerning acetic and formic acid, which are frequently formed in the process and have high resistance to oxidation; they are classified as major byproducts.[20−22] Previous investigations have shown that DCAs can be attainable via different types of oxidative conversion of organic wastes and biomass.[23−25] Moreover, there are reports on WAO processes where DCAs were obtained, but these were primarily focused only on short-chain DCA.[26−29] Some researchers have demonstrated the complete removal of these short-chain DCAs under specific conditions,[30−32] although the wider spectrum of their reactivity has not been studied. Accordingly, there is still a deficiency of information on how environmentally friendly routes such as WAO can be used for the production of DCAs, especially for DCAs with longer aliphatic chains ($n > 4$). We believe that partial WAO of organic wastes and highly polymerized organic matter is a promising option for producing DCAs.

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Most researchers rationalize the chemistry of the WAO of organic compounds as proceeding via a free radical chain mechanism. Owing to the presence of free-radical intermediates (e.g., hydroxyl radicals[33]) it is evident that the whole process is sensitive to physical (temperature, pressure, stirring speed, and reactor material) and chemical (pH, additives, co-oxidizers, and intermediates) parameters.[18,34] Beside the free radical oxidation reactions, other chemical transformations such as hydrolysis, decarboxylation, and (oxidative) thermal degradation of organic molecules, may occur.[15] This again causes a nonselective process for which the exact sequence of the reaction steps, especially in the case of a complex organic mixture, is difficult to establish and control. The addition of catalysts to a WAO system supports the main reactions and enhances the conversion to the target compounds.[15,16,34]

The aim of this work is to expand the information available about WAO of organic material and to create a foundation for the production of DCAs by establishing their reactivity in subcritical oxidative conditions. Specifically, the effects of temperature, pH, alkalis, transition metals, and co-oxidants on the reactivity of DCA at subcritical WAO conditions were investigated. In our opinion, knowledge of the DCA oxidative decomposition and its limits helps to modify WAO processes to produce valuable DCAs instead of producing greenhouse gas CO_2.

2. EXPERIMENTAL APPARATUS AND PROCEDURE

2.1. Materials. Butanedioic acid (succinic acid) (>99,5%) was purchased from Fisher Chemicals. Pentanedioic acid (glutaric acid) (99%), heptanedioic acid (pimelic acid) (98%), octanedioic acid (suberic acid) (99%), nonanedioic acid (azelaic acid) (98%), and decanedioic acid (sebacic acid) (98%) were obtained from Acros Organics. Propanedioic acid (malonic acid) (99%) was obtained from Alfa Aesar, and hexanedioic acid (adipic acid) (99%) was obtained from Sigma-Aldrich. Dimethylesters used as standard compounds, such as dimethyl nonanedioate (>98%) and dimethyl decanedioate (>98%), were purchased from Tokyo Chemical Industry Co. Ltd. Dimethyl propanedioate (>98%) and dimethyl octanedioate (99%) were purchased from Alfa Aesar, dimethyl butanedioate (98%) and dimethyl heptanedioate (99%) were obtained from Sigma-Aldrich, and dimethyl pentanedioate (98%) and dimethyl hexanedioate (>98%) were obtained from Acros Organics. 5-Methylresorcinol (99%) and 2-methylresorcinol (99%) were obtained from Viru Keemia Grupp AS. Phosphate buffer solution pH 7 was purchased from Acros Organics, and sodium acetate 3 M buffer solution pH 7.0 was purchased from Alfa Aesar. All other substrates and reagents were purchased in highest analytical purity from commercial suppliers and used as received.

2.2. Equipment and Procedure. In this study most experiments were carried out at subcritical conditions at a temperature of 175 °C and pressure of 40 bar (4 MPa). A temperature of 175 °C was chosen considering two main factors: the thermal stability of most DCAs and the effective temperature of the WAO process for organic destruction.[29,34,35] A 100 mL stainless steel pressure reactor (4566C, Parr Instrument Company, Moline, Il, USA) supplied with a heating oven, mechanical gas entrainment impeller, pressure gauge, and a reactor controller, was used. The stirring speed was 1000 rpm to achieve effective gas transfer to the solution (it is known that a stirring speed slower than 500 rpm may decrease the performance of the same type reactor[35]). Dicarboxylic acids (50 mg of each) were weighed into a reactor containing 50 mL of distilled water. The reactor was pressurized with gas and heated to 175 °C. The zero-reaction time was counted from the point when the temperature had reached 170 °C. At the end of the reaction, the mixing speed was reduced to the minimum and the reactor was cooled down to room temperature. Then the reactor was depressurized, and gas was collected and analyzed with GC-TCD. The pH value of the reaction mixture was measured (pH-meter inoLab pH7310), the reaction mixture was transferred into a round-bottomed flask, and extra rinsing was done with distilled water and with 0.1 M KOH solution to solubilize the solid residue (in the case of metal-salts, 0.1 M HCl solution was also used for rinsing). The mixture was acidified with concentrated HCl, and the water was evaporated. The remaining solid was esterified with a methanol to chloroform 2:1 mixture and concentrated H_2SO_4 using a Dean–Stark apparatus.

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-5HT Inferno (0.25 μm) capillary column, programmed 10 °C/min from 50 °C (5 min hold isothermally) to 320 °C (3 min hold isothermally). Gas chromatography–mass spectroscopy (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. NMR spectroscopy was performed when necessary with a Bruker Avance III 400 MHz spectrometer. In the case of high performance liquid chromatography–high resolution MS (HPLC–HRMS) and capillary electrophoresis (CE), the sample was taken right after opening the reaction vessel. High resolution mass spectra were obtained on an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS spectrometer by using ESI ionization. An Agilent 3D CE-DAD instrument (Agilent Technologies, Waldbronn, Germany) with a Tracedec CCD was used for the separation of acetate and formate. The conductivity detector cell was incorporated into the 3D CE capillary cassette. Analyses were carried out using a 50 μm i.d., 375 μm o.d., 50 cm total length (Polymicro Technologies, Phoenix, AZ, USA) capillary with a slight modification of a previously described BGE which consisted of 20 mM MES, 20 mM HIS, and 30 μM CTAB at pH 6.[36] The modification consisted of excluding 18-crown-6 as NH_4^+ and K^+ were not analyzed. Samples were injected hydrodynamically by applying a pressure of 50 mbar. The applied voltage was −18 kV. The gas analysis was performed with a Shimadzu GC-2014 gas chromatograph with a valve system which allowed the determination all the gases of interest in a single run. To analyze O_2, N_2, and CO, a 3 m molecular sieve Molsieve 5 Å packed column (80/100 mesh, i.d. 2 mm) was used, and to analyze CO_2 a 9 m Shimalite packed column was used. The oven temperature was programmed from 40 °C (3 min hold isothermally) to 100 °C 20 °C/min (3 min hold isothermally) at 20 °C/min to 140 °C (2 min hold isothermally) at 10 °C/min.

3. RESULTS AND DISCUSSION

3.1. DCA Stability at Different Temperatures and Oxygen Pressures. At room temperature aliphatic DCAs (n = 0–8) are colorless, odorless, and crystalline substances.[7]

Table 1. Recovery (%) of DCAs after Oxidation in Subcritical Conditions[a]

O_2, [%]	pH	succinic acid, [%]	glutaric acid, [%]	adipic acid, [%]	pimelic acid, [%]	suberic acid, [%]	azelaic acid, [%]	sebacic acid, [%]	sum, [%]
21	5	100	103	103	102	100	99	101	100
50	4	99	103	102	98	96	92	89	97
100	4	86	99	102	101	101	99	101	98
50	2[b]	85	96	99	98	98	96	98	96

[a]Reaction conditions: 40 bar of O_2/N_2 mixture; 175 °C; 3 h; [DCA] = 1g/L. [b]10 vol % solution of acetic acid.

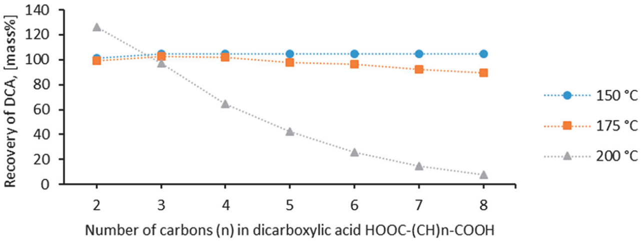


Figure 1. Recovery of DCAs at various temperatures. (Conditions: 40 bar of 50/50 O_2/N_2 mixture; 3 h; [DCA] = 1g/L.)

Under normal conditions, most DCAs are resistant to oxidation (the exceptions are oxalic and malonic acid).[37,38] However, this does not necessarily apply to superheated water. Imamura et al. have described the oxidation of succinic acid with 58% conversion at 248 °C at 1.0 MPa of O_2 (4 MPa of overall pressure). However, at the same conditions, the conversion of adipic acid was only 27%. When Co/Bi oxide was applied as a catalyst, the conversion of both these DCAs was almost 100%.[30] To the best of our knowledge, the only references on the mechanism of long-chain DCA (azelaic and sebacic acid) oxidation has been reported by Jin et al. for sub- and supercritical water oxidation (from 300 to 400 °C) using H_2O_2 as an oxidant. They showed that the oxidation of selected DCAs follows a free-radical mechanism pathway and the DCAs are gradually converted to lower molecular weight DCAs and carboxylic acids. They proposed that the main oxidation sites (α-, β-, and γ-carbon from the carbonyl group) and major intermediates are short-chain DCAs, $(\omega - 1)$-oxo acids, and γ-lactones.[39,40] Still, there is no sufficient quantitative information about the effect of pH and other additives on the oxidation.

First we studied the stability of a DCA artificial mixture in water at different O_2 concentrations (21% O_2 (air), a 50% O_2 (with N_2), and 100% O_2) and determined the quantity of each DCA after oxidation. Table 1 shows that the oxygen rate did not influence noticeably the stability of the DCAs in a 3 h period. Only traces of other formed compounds were detected, mainly $(\omega - 1)$-oxo acids. No formation of CO_2 in the gas mixture was observed. A decreased amount of succinic acid is most likely a result of the high volatility of dimethyl succinate, causing losses during the preparation of the analytical sample.

The same trend was observed when the reaction was carried out in an acetic acid solution (10 vol %). Lower pH values (pH 2) did not affect the stability of DCAs appreciably, suggesting that these DCAs ($n = 2-8$) are highly resistant to oxidation in water under selected conditions and also in the presence of acetic acid.

To investigate the effect of temperature, experiments were carried out at 150, 175, and 200 °C with a 50/50 mixture of O_2/N_2 at 40 bar. Distinct from the oxygen pressure, higher temperature had a strong effect on the stability of DCAs. Figure 1 and Figure 2C present significant decomposition of long-chain DCAs to short-chain DCAs at 200 °C. It is noteworthy that the amount of the succinic acid ($n = 2$) was ~30% higher than in the initial mixture, although only 60% of initial DCAs were recovered in total. Additionally ~10% (by mass) of other oxidation products, such as $(\omega - 1)$-oxo acids were detected (Figure 2C), together with a rise in CO_2 in the gas phase. On the basis of these data we propose that at 200 °C the oxidation of DCAs occurs mainly at the α-carbon, leading to short-chain DCAs. Oxidation at the β-position, resulting in $(\omega - 1)$-oxo acids proceeds in a smaller extent.

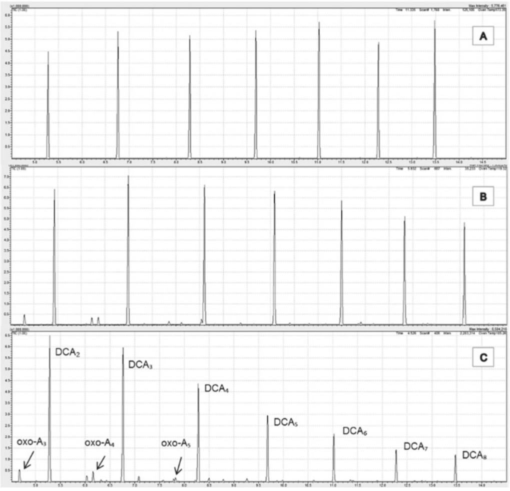


Figure 2. Corresponding GC−MS spectra of DCA recovery at various temperatures in 3 h reactions at (A) 150 °C; (B) 175 °C; (C) 200 °C. DCA_n refers to dicarboxylic acid and oxo-A_n to $(\omega - 1)$-oxo acids, subscripts refer to $(CH_2)_n$ number, $n = 2-8$.

3.2. Stability of DCAs in Alkaline Solutions.

Although almost no decomposition of DCAs at 175 °C in water and in the presence of acetic acid was observed, the effects of the

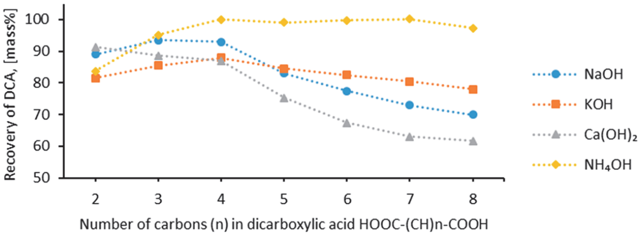


Figure 3. Stability of DCAs in alkali. (Conditions: [DCA] = 1 g/L; 2.2 equiv of alkali per mol of DCA; 40 bar of 50/50 O_2/N_2 mixture; 175 °C; 3 h.)

different alkalis to the DCAs stability were tested next. According to literature, alkalis can prevent the oxidation of organic compounds even at excessive concentrations.[31,32,25] Alkaline conditions may decrease the oxidizing strength of free-radical intermediates that form during wet oxidation,[15] because of the scavenging properties of hydroxide and carbonate ions to hydroxyl radicals.[41] However, there are also examples where alkalis, especially basic oxides, accelerate the decomposition of organic compounds (phenols).[42−44]

To establish the stability of DCAs in alkalis, experiments with a mixture of DCAs with 50/50 O_2/N_2 at 40 bar and at 175 °C for 3 h were carried out. Figure 3 shows the obtained results of the addition of 2.2 equiv of base where pH values were maintained above 9.

The reactivity of the DCAs is strongly increased in an alkali solution, whereas in the presence of ammonia, the stability of DCAs was retained indicating that the effect of alkali cations on stability is more prominent than the effect of pH. It is noteworthy that no significant accumulation of succinic or glutaric acid within the 3 h reaction was observed, as it was seen at 200 °C in water (see Figure 2). In an alkali solution the oxidation proceeds slowly toward low molecular weight carboxylic acids, such as acetic acid and formic acid, and finally toward the complete destruction of DCAs to CO_2 and H_2O (e.g., in the presence of KOH 4 mg of formic acid and 13 mg of CO_2 were detected, acetic acid was present but not quantified). These results slightly differ from those obtained by Tardio et al., which showed the high stability of succinic and glutaric acids toward oxidation in 7 M NaOH solution.[31,32] Compared with other hydroxides, $Ca(OH)_2$ had the greatest effect on oxidation, although the solubility of $Ca(OH)_2$ in the reaction medium is much lower than that for NaOH and KOH. A possible explanation has been proposed by Jin and Enomoto[21] who have suggested that Ca^{2+} is more capable of forming complexes with oxygen atoms than Na^+ or K^+, which supports oxidation. It must be considered that the amount of each DCA at the end of the reaction does not reflect the exact stability of that DCA but rather a dynamic conversion of a long-chain DCA to a short-chain DCA. The exception is sebacic acid (the DCA with the highest carbon number in the mixture) whose observed amount in the end at the reaction corresponds to its stability.

To have better understanding of the impact of alkalis, experiments at different alkali ratios were carried out. The results plotted in Figure 4 show that almost no oxidation occurred while using 1 equiv of $Ca(OH)_2$ (all calcium is bound to a DCA salt). Therefore, the initial idea that DCAs (n = 2−8) in the form of insoluble calcium salts in a reaction mixture are more stable toward oxidation is true. The stability was retained also with lower amounts of NaOH. In a separate experiment with sebacic acid we found that 20 equiv of KOH caused extensive decomposition, and only 30% of sebacic acid was recovered (a single point in Figure 4). These numbers show clearly that the content of the alkali cation affects the reactivity of DCAs.

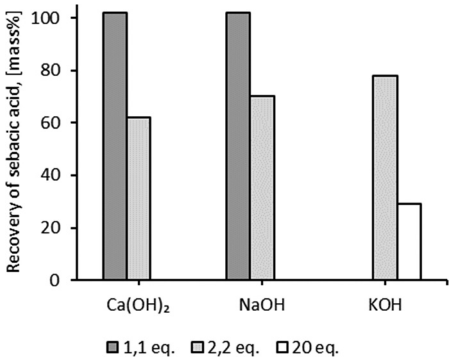


Figure 4. Stability of dicarboxylic acids in various alkali solutions with different concentrations. (Conditions: 40 bar of 50/50 O_2/N_2 mixture; 175 °C; 3 h; [DCA] = 1g/L.)

The effects of sodium, potassium, and calcium content on DCA stability was further investigated by adding these cations in the form of neutral salts (nitrates, sulfates). Figure 5, panels A and B show that the DCA stability was affected by these salts and a similar behavior pattern was seen in terms of DCA recovery. The pH decreased to a value of ca. 3 during 3 h, due to the decomposition of long-chain DCA and the formation of short-chain DCAs. The order of activity in terms of overall oxidation coincide with the solubility of selected salts—the salt with the highest solubility had the greatest effect on DCAs oxidation. Additional experiments were done at controlled pH by using phosphate or acetate buffer solutions as a reaction medium (Figure 5C). At neutral pH range the catalytic effect of all alkali cations was negligible despite the high solubility of Na and K sulfates in used mediums. These results indicate that Na, K, and Ca cations do not induce the decomposition of DCAs (n = 2−8) at pH 7 and DCAs can be recovered with high yields from neutral waters.

Figure 6 illustrates the dependence of the DCA reactivity on the presence of various bases and salts at oxidative conditions when pH is not adjusted. For better comparison the recovery yields of sebacic acid were chosen to represent long-chain DCA. Figure 6 also shows the observed stability of DCA in the

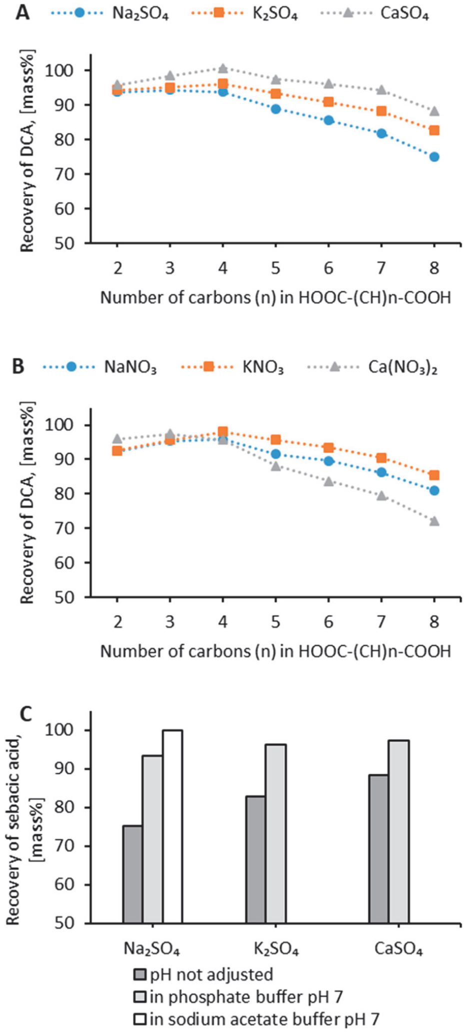


Figure 5. Recovery of DCA in sulfate and nitrate solutions. (A) Sulfates, pH not adjusted; (B) nitrates, pH not adjusted; (C) sulfates, pH adjusted with buffer. (Conditions: 40 bar of 50/50 O2/N2 mixture; 175 °C; 3 h; [DCA] = 1g/L; the amount of salt was calculated, taking into account its oxidation state, so 2.2 equiv for additive (salt) with general formula of $M^{+}X^{-}$ and 1.1 equiv for salts with general formula of $M^{2+}X^{2-}$, $M^{2+}(X^{-})_2$ or $(M^{+})_2X^{2-}$ per mol of DCA.)

presence of Na, K, and Ca carbonates and sodium metasilicate (Na_2SiO_3). In the presence of carbonates the reaction mixture stayed weakly alkaline (pH 7−8) and DCAs were recovered almost quantitatively. However, Na_2SiO_3 acted similarly to alkalis, with a moderate effect on oxidation. The best recovery of sebacic acid was achieved in the presence of $CaCO_3$ and the lowest in the NaOH solution. These results indicate that the oxidation process is very dependent on the nature and on the concentration of the alkali cation. As demonstrated above Ca^{2+} has a protective effect not higher than at 1 equiv level (see Figure 4). However, the relationship between an anion and DCA reactivity also holds great importance because the nature of an anion determines the solubility properties and induced pH. For this reason the comparison of selected bases is never entirely straightforward (e.g., $CaCO_3$ is almost insoluble in water,[45] liberating very few Ca^{2+} ions to the solution). In neutral conditions the salts additives have little effect on stability, while in slightly acidic and in strongly basic media the oxidation of DCA increased significantly.

3.3. Effect of Homogeneous Metal-Based Catalysts.

We also studied the catalytic effects of Fe^{3+}, Fe^{2+}, Mn^{2+}, Cu^{2+}, and Co^{2+} cations on DCA oxidation. The catalytic potential of metal cations has received considerable attention in literature in regard to the complete mineralization of organic matter.[20,34,44,46,47] These metal ions interact with dissolved molecular oxygen and produce free radicals by being able to shift between different oxidation states.[18,46] Selected cations have shown high efficiency on TOC removal from wastewaters, especially in cases of low molecular weight carboxylic acids or phenolic wastes.[20,48] To the best of our knowledge, there is no information about the effect of these ions on the stability of long-chain DCAs under subcritical conditions. The obtained results are presented in Figure 7.

These figures show clearly that iron salts have the highest catalytic activity on sebacic acid stability when pH is not adjusted. Less than 5% of initial sebacic acid was recovered after a 3 h reaction with $Fe_2(SO_4)_3$. The effect of iron salts depends on the concentration of the metal cation and on its oxidation state (Fe^{2+} or Fe^{3+}). Surprisingly, the double amount of $FeSO_4$ (40 mol %) showed lower activity than the 20 mol % of $Fe_2(SO_4)_3$. When buffer solution was added to stabilize the pH, none of the salts catalyzed the DCA oxidation (Figure 7B). Similarly to that of the alkalis the decomposition process is not favored at neutral pH range. This may be attributed to the deficiency of H ions or OH ions that are required for the initiation reaction of DCA in WAO, which is also in agreement with results reported in literature.[15]

Cu^{2+} had a moderate catalytic effect on sebacic acid oxidation (30% of the initial acid was oxidized). At the same time, Mn^{2+} and Co^{2+} were almost inactive under selected conditions. This result is in good agreement with observations by Arena et al.[46] about Mn^{2+} poor oxidation strength toward phenols. They suggested that metal ions with higher redox potential (such as Mn^{2+}) are less active catalytic species than metal ions with lower redox potential (such as Cu^{2+}). It can be concluded that dissolved metal cations, especially iron, must be considered as a reason for the oxidative decomposition of long-chain DCAs in water.

3.4. Effect of Co-oxidation.

In the co-oxidation process, the organic molecule is oxidized by additional radicals generated from other organic compounds also oxidizing in the same reaction medium.[15] Tardio et al. have described the decomposition of sodium succinate and sodium glutarate in the presence of sodium malonate in an alkali solution.[31,32,49] They proposed that the oxidation is initiated by the reaction between hydroxyl ions and malonic acid α-hydrogen, forming malonate alkyl radicals which act as active co-oxidizers.

We studied the effect of malonic acid by adding it to a sebacic acid solution at various pH values (Figure 8). As demonstrated above, the stability of long-chain DCA such as sebacic acid is high in a neutral and acidic media if no co-oxidants are present. We have found that in a 10% acetic acid solution the recovery of sebacic acid was even higher than in a

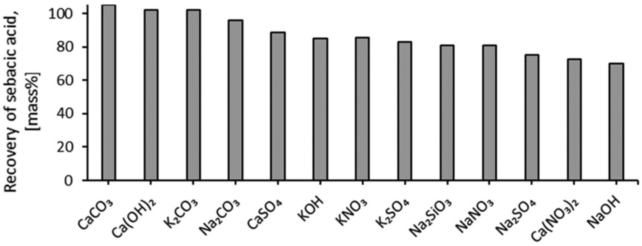


Figure 6. Recovery of sebacic acid in oxidation. (Conditions: 40 bar of 50/50 O_2/N_2 mixture; 175 °C; 3 h; [DCA] = 1g/L; 2.2 equiv of additive with general formula of M^+X^- or 1.1 equiv of additive with general formula of $M^{2+}X^{2-}$, $M^{2+}(X^-)_2$ or $(M^+)_2X^{2-}$ per mol of DCA.)

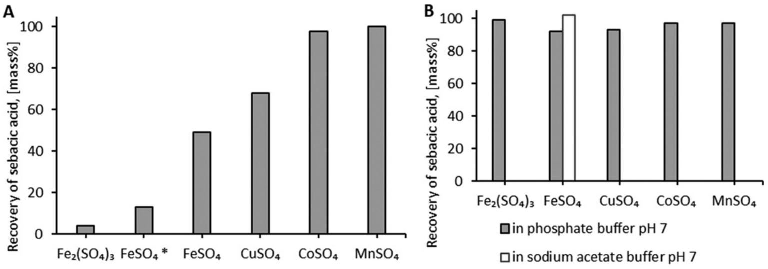
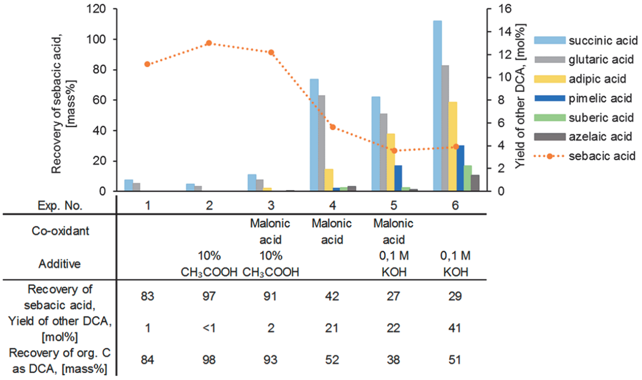


Figure 7. Stability of sebacic acid with different metal-salts. (A) pH not adjusted; (B) pH adjusted with buffer. (Conditions: 40 bar of 50/50 O_2/N_2 mixture; 175 °C; 3 h; [DCA] = 1g/L; metal salts 20 mol %; *40 mol %.)



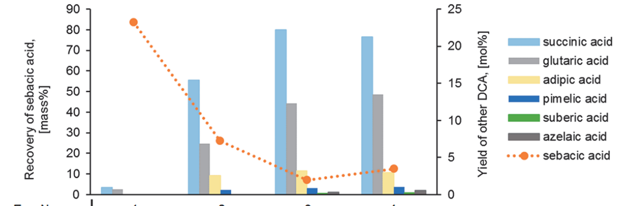
Exp. No.	1	2	3	4	5	6
Co-oxidant			Malonic acid	Malonic acid	Malonic acid	
Additive		10% CH_3COOH	10% CH_3COOH		0,1 M KOH	0,1 M KOH
Recovery of sebacic acid,	83	97	91	42	27	29
Yield of other DCA, [mol%]	1	<1	2	21	22	41
Recovery of org. C as DCA, [mass%]	84	98	93	52	38	51

Figure 8. Co-oxidation of sebacic acid and malonic acid. (Conditions: [sebacic acid] = 2 g/L; [malonic acid] = 2 g/L (2 equiv); 40 bar of 50/50 O_2/N_2 mixture; 175 °C; 3 h.)

neutral solution (Figure 8, exp. 1 and 2). This result indicates that acidic conditions have an inhibiting effect on the oxidation of long-chain DCA.

In the presence of malonic acid as a co-oxidizer, the stability of sebacic acid was slightly decreased in an acidic medium (Figure 8, exp. 3). However, in a neutral solution the effect of an malonic acid on sebacic acid oxidation was notable, and less than 50% of sebacic acid was recovered (Figure 8, exp. 4). Even more extreme was the effect of malonic acid in basic conditions—up to 70% of sebacic acid was converted into various oxidation products (Figure 8, exp. 5). The percentage of recovered carbon (the estimated amount of carbon that appeared in sebacic acid and in formed products after the reaction, Figure 8) indicated that the transformation of carbon to CO_2 was also greater when malonic acid was added. A detailed analysis of the reaction mixture (without workup) using HPLC−HRMS revealed the presence of nearly all smaller DCAs, glycolic acid, and other (hydroxy-substituted) carboxylic acids; however, no traces of malonic acid were found (presented in Supporting Information, Table S2). We can conclude that malonic acid plays an important role as a co-oxidizer in the oxidative destruction of sebacic acid with oxygen.

Lastly, the co-oxidation effect of resorcinols on sebacic acid oxidation was studied. 5-Methyl- and 2-methylresorcinols were selected for models of phenolic structures.[10,18] Phenols follow a free radical mechanism under WAO conditions and produce intermediates (e.g., succinic acid, fumaric acid, malonic acid,



Exp. No	1	2	3	4
Co-oxidant		5-Me-resorcinol	5-Me-resorcinol	2-Me-resorcinol
Additive		10% CH_3COOH		
Recovery of sebacic acid,	83	26	7	13
Yield of other DCA, [mol%]	1	25	39	40
Recovery of org. C as DCA, [mass%]	84	37	25	31

Figure 9. Co-oxidation of sebacic acid by methylresorcinols. (Conditions: [sebacic acid] = 2 g/L; [resorcinol] = 1.24 g/L (1 equiv); 40 bar of 50/50 O_2/N_2 mixture; 175 °C; 3 h.)

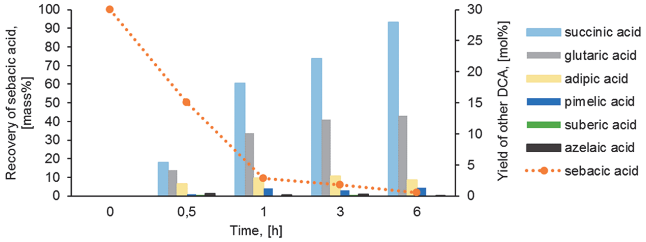


Figure 10. Time-dependence of co-oxidation reaction by 5-methylresorcinol. (Conditions: [sebacic acid] = 2 g/L; [resorcinol] = 1.24 g/L (1 equiv); 40 bar of 50/50 O_2/N_2 mixture; 175 °C.)

acetic acid, and oxalic acid) promoting the oxidation of other organic compounds.[43,50] Our results are presented in Figure 9.

The oxidation of sebacic acid together with 2-methylresorcinol or 5-methylresorcinol under neutral conditions was fast. After a 3 h reaction less than 10% of the sebacic acid was recovered (Figure 9, exp. 3), while most of the other DCAs (n = 2−7) and the corresponding (ω − 1)-keto acids were formed and detected. No co-oxidant (resorcinol) was left in the reaction mixture. The oxidation efficiency with methylresorcinols was significantly higher than with malonic acid even though a smaller amount of co-oxidant (1 equiv of methylresorcinol) was used (Figure 9, exp. 3, and Figure 8, exp. 4, respectively). In 10% acetic acid ~30% of sebacic acid was retained, consistently indicating the inhibitive effect of an acidic medium on DCA oxidation. This result agrees with the observations of Kolaczkowski et al.[43] on efficient phenol removal from water mixtures at neutral conditions and which was strongly suppressed in an acidic medium (at pH lower than 2).

We also compared the oxidation of sebacic acid in the presence of 5-methylresorcinols at different reaction times (0.5, 1, 3, and 6 h; Figure 10). The oxidation of long-chain DCA in the presence 5-methylresorcinols occurred very fast, with less than 10% sebacic acid left after 1 h. It is evident that the amount of the short-chain DCAs grows over time. After 1 h, the oxidation rate decreased, possibly due to a lack of co-oxidant radicals after the total decomposition of resorcinol. In addition, the liquid phase of the reactions was analyzed and a slight accumulation of acetic acid and formic acid was observed (as described by many authors[18,43,44]). It was also found that ~$^2/_3$ of the whole CO_2 had formed during the first hour (Table 2). Only a slight increase in the total quantity of CO_2 within the next 5 h was detected. These results demonstrate the strong influence of phenolic compounds on oxidation and, therefore, on the stability of higher DCAs in oxidative conditions.

Table 2. Products in Sebacic Acid Co-Oxidation Reaction by Resorcinol

reaction time, h	acetic acid, mg	formic acid, mg	CO_2, mg
1	8.2	11.6	89
3	24	15	121
6	27	11	126

4. CONCLUSIONS

The aim of the present paper was to identify the reactivity of aliphatic DCAs (n = 2−8) in conditions similar to the industrial WAO process. Selected DCAs showed high stability in oxidation with a 50/50 O_2/N_2 mixture at 40 bar up to 175 °C in wide pH range (pH values from 2 to 9). However, at 200 °C considerable oxidation was observed and long-chain DCAs were transformed to short-chain DCAs. The presence of alkali metals accelerated the decomposition of DCA in nonbuffered solutions. Higher alkali concentrations were found to result in enhanced oxidation. The order of reactivity correlated well with the solubility of added salt—the stability decreased as the solubility increased. DCA destruction was also supported by the addition of transition-metals, and Fe cations showed the highest performance. We were able to diminish the decomposition of DCA in the presence of all metal salts used at controlled pH (pH 7). Due to the radical nature of the WAO process, DCAs were also affected strongly by various organic compounds which are able to form radicals under the conditions used. The lowest DCA stability was observed for experiments with 5-methyl resorcinol; however, acidic conditions were found to suppress this oxidation rate. In our opinion, the obtained results about DCA reactivity in WAO conditions is a good foundation for expanding the WAO of organic material toward the formation of DCAs. We believe that the use of the WAO system in order to obtain DCA may be possible when the presence of co-oxidizers (mainly phenolic compounds) is carefully eliminated and the pH can be adjusted.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.iecr.9b01643.

> Detailed description of products and intermediates, specification of the analytical method used, additional experiments to ascertain the origin of intermediate products (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: margus.lopp@taltech.ee.

ORCID

Margus Lopp: 0000-0002-8041-2595

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Godwin, A. D. Plasticizers. In *Applied Plastic Engineering Handbook*; Kutz, M., Ed.; Elsevier Inc: New York, 2011; pp 487−502.

(2) Gryglewicz, S.; Stankiewicz, M.; Oko, F. A.; Surawska, I. Esters of Dicarboxylic Acids as Additives for Lubricating Oils. *Tribol. Int.* **2006**, *39*, 560−564.

(3) Diaz, A.; Katsarava, R.; Puiggali, J. Synthesis, Properties and Applications of Biodegradable Polymers Derived From Diols and Dicarboxylic Acids: From Polyesters to Poly(ester amide)s. *Int. J. Mol. Sci.* **2014**, *15*, 7064−7123.

(4) Mingrone, G.; Castagneto-Gissey, L.; Macé, K. Use of Dicarboxylic Acids in Type 2 Diabetes. *J. Clin. Pharmacol.* **2013**, *75*, 671−676.

(5) Corona, A.; Biddy, M. J.; Vardon, D. R.; Birkved, M.; Hauschild, M. Z.; Beckham, G. T. Life Cycle Assessment for Adipic Acid Production from Lignin. *Green Chem.* **2018**, *20*, 3857.

(6) Van de Vyver, S.; Román-Leshkov, Y. Emerging Catalytic Processes for the Production of Adipic Acid. *Catal. Sci. Technol.* **2013**, *3*, 1465−1479.

(7) Cornils, B.; Lappe, P. Dicarboxylic Acids, Aliphatic. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim., 2011; pp 1−19.

(8) Clomburg, J. M.; Blankschien, M. D.; Vick, J. E.; Chou, A.; Kim, S.; Gonzalez, R. Integrated Engineering of β-oxidation Reversal and ω-oxidation Pathways for the Synthesis of Medium Chain ω-functionalized Carboxylic Acids. *Metab. Eng.* **2015**, *28*, 202−212.

(9) Raj, K.; Partow, S.; Correia, K.; Khusnutdinova, A. N.; Yakunin, A. F.; Mahadevan, R. Biocatalytic Production of Adipic Acid from Glucose Using Engineered *Saccharomyces cerevisiae*. *Metabolic Engineering Communications.* **2018**, *6*, 28−32.

(10) Ma, R.; Xu, Y.; Zhang, X. Catalytic Oxidation of Biorefinery Lignin to Value-added Chemicals to Support Sustainable Biofuel Production. *ChemSusChem* **2015**, *8*, 24−51.

(11) Cherubini, F.; Stromman, A. H. Chemicals from Lignocellulosic Biomass: Opportunities, Perspectives, and Potential of Biorefinery Systems. *Biofuels, Bioprod. Biorefin.* **2001**, *5*, 548−561.

(12) Zhou, Z.; Jin, F.; Enomoto, H.; Moriya, T.; Higashigima, H. A Continuous Flow Reaction System for Producing Acetic Acid by Wet Oxidation of Biomass Waste. *J. Mater. Sci.* **2006**, *41*, 1501−1507.

(13) Jin, F.; Yun, J.; Li, G.; Kishita, A.; Tohji, K.; Enomoto, H. Hydrothermal Conversion of Carbohydrate Biomass into Formic Acid at Mild Temperatures. *Green Chem.* **2008**, *10*, 612−615.

(14) Haghighat, P.; Ortega, L.; Pereira-Almao, P. Experimental Study on Catalytic Hydroprocessing of Solubilized Asphaltene in Water: A Proof of Concept to Upgrade Asphaltene in the Aqueous Phase. *Energy Fuels* **2016**, *30*, 2904−2918.

(15) Bhargava, S. K.; Tardio, J.; Prasad, J.; Foger, K.; Akolekar, D. B.; Grocott, S. C. Wet Oxidation and Catalytic Wet Oxidation. *Ind. Eng. Chem. Res.* **2006**, *45*, 1221−1258.

(16) Mishra, V. S.; Mahajani, V. V.; Joshi, J. B. Wet Air Oxidation. *Ind. Eng. Chem. Res.* **1995**, *34*, 2−48.

(17) Jin, F.-M.; Kishita, A.; Moriya, T.; Enomoto, H. Kinetics of food wastes with H_2O_2 in supercritical water. *J. Supercrit. Fluids* **2001**, *19*, 251−262.

(18) Zhou, L.; Cao, H.; Descorme, C.; Xie, Y. Phenolic Compounds Removal by Wet Air Oxidation Based Processes. *Front. Environ. Sci. Eng.* **2018**, *12*, 1−20.

(19) Silverstein, T. P.; Heller, S. T. pK_a values in the undergraduate curriculum: what is the real pK_a of water? *J. Chem. Educ.* **2017**, *94*, 690−695.

(20) Debellefontaine, H.; Chakchouk, M.; Foussard, J. N.; Tissot, D.; Striolo, P. Treatment of Organic Aqueous Wastes: Wet Air Oxidation and Wet Peroxide Oxidation. *Environ. Pollut.* **1996**, *92*, 155−164.

(21) Jin, F.; Enomoto, H. Rapid and Highly Selective Conversion of Biomass into Value-added Products in Hydrothermal Conditions: Chemistry of Acid/Base-catalysed and Oxidation Reactions. *Energy Environ. Sci.* **2011**, *4*, 382−397.

(22) Suzuki, H.; Cao, J.; Jin, F.; Kishita, A.; Enomoto, H.; Moriya, T. Wet Oxidation of Lignin Model Compounds and Acetic Acid Production. *J. Mater. Sci.* **2006**, *41*, 1591−1597.

(23) Cronin, D. J.; Zhang, X.; Bartley, J.; Doherty, W. O. S. Lignin Depolymerization to Carboxylic Acid with Sodium Percarbonate. *ACS Sustainable Chem. Eng.* **2017**, *5*, 6253−6260.

(24) Kang, J.; Irmak, S.; Wilkins, M. Conversion of Lignin into Renewable Carboxylic Acid Compounds by Advanced Oxidation Process. *Renewable Energy* **2019**, *135*, 951−962.

(25) Yin, G.; Jin, F.; Yao, G.; Jing, Z. Hydrothermal Conversion of Catechol into Four-Carbon Dicarboxylic Acids. *Ind. Eng. Chem. Res.* **2015**, *54*, 68−75.

(26) Reza, M. T.; Freitas, A.; Yang, X.; Coronella, C. J. Wet Air Oxidation of Hydrothermal Carbonization (HTC) Process Liquid. *ACS Sustainable Chem. Eng.* **2016**, *4*, 3250−3254.

(27) Antonyraj, C. A.; Huynh, N. T. T.; Lee, K. W.; Kim, Y. J.; Shin, S.; Shin, J. S.; Cho, J. K. Base-free Oxidation of 5-hydroxymethyl-2-

furfural to 2,5-furan dicarboxylic acid over basic metal oxide-supported ruthenium catalysts under aqueous conditions. *J. Chem. Sci.* **2018**, *130*, 156.

(28) Martin-Hernandez, M.; Carrera, J.; Suarez-Ojeda, M. E.; Besson, M.; Descorme, C. Catalytic wet air oxidation of high strength *p*-nitrophenol wastewater over Ru and Pt catalysts: Influence of the reaction conditions on biodegradability enhancement. *Appl. Catal., B* **2012**, *123-124*, 141−150.

(29) Demesa, A. G.; Laari, A.; Turunen, I.; Sillanpää, M. Alkaline Partial Wet Oxidation of Lignin for the Production of Carboxylic Acids. *Chem. Eng. Technol.* **2015**, *38*, 2770−2278.

(30) Imamura, S.; Kinunaka, H.; Kawabata, N. The Wet Oxidation of Organic Compounds Catalyzed by Co-Bi Complex Oxide. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3679−3680.

(31) Tardio, J.; Bhargava, S.; Prasad, J.; Akolekar, D. B. Catalytic Wet Oxidation of Sodium Salts of Citric, Lactic, Malic and Tartaric Acids in Highly Alkaline, High Ionic Strength Solution. *Top. Catal.* **2005**, *33*, 193−199.

(32) Tardio, J.; Bhargava, S. K.; Eyer, S.; Akolekar, D. B. Low-Temperature Wet Oxidation of Sodium Salts of Low Molecular Weight Mono- and Dicarboxylic Acids in Synthetic Bayer Liquor. *Ind. Eng. Chem. Res.* **2004**, *43*, 669−674.

(33) Robert, R.; Barbati, S.; Ricq, N.; Ambrosio, M. Intermediates in Wet Oxidation of Cellulose: Identification of Hydroxyl Radical and Characterization of Hydrogen Peroxide. *Water Res.* **2002**, *36*, 4821−4829.

(34) Sushma; Kumari, M.; Saroha, A. K. Performance of Various Catalysts on Treatment of Refractory Pollutants in Industrial Wastewater by Catalytic Wet Air Oxidation: A review. *J. Environ. Manage.* **2018**, *228*, 169−188.

(35) Manasrah, A. D.; Nassar, N. N.; Ortega, L. C. Conversion of Petroleum Coke into Valuable Products Using Oxy-Cracking Technique. *Fuel* **2018**, *215*, 865−878.

(36) Kobrin, E.-G.; Lees, H.; Fomitšenko, M.; Kaljurand, M.; Kuban, P. Fingerprinting Postblast Explosive Residues by Portable Capillary Electrophoresis with Contactless Conductivity Detection. *Electrophoresis* **2014**, *35*, 1165−1172.

(37) Li, L.; Chen, P.; Gloyna, E. F. Generalized Kinetic Model for Wet Oxidation of Organic Compounds. *AIChE J.* **1991**, *37*, 1687−1697.

(38) Strittmatter, H.; Hildbrand, S.; Pollak, P. Malonic Acid and Derivates. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2012; pp 157−174.

(39) Jin, F.; Cao, J.; Enomoto, H.; Moriya, T. Identification of Oxidation Products and Oxidation Pathways of High Molecular Weight Dicarboxylic Acids under Hydrothermal Conditions. *J. Supercrit. Fluids* **2006**, *39*, 80−88.

(40) Jin, F.; Cao, J.; Kishita, A.; Enomoto, H.; Moriya, T. Oxidation Reactions of High Molecular Weight Dicarboxylic Acids in Sub- and Supercritical Water. *J. Supercrit. Fluids* **2008**, *44*, 331−340.

(41) Thomsen, A. B. Degradation of Quinoline by Wet Oxidation − Kinetic Aspects and Reaction Mechanisms. *Water Res.* **1998**, *32*, 136−146.

(42) Kojima, Y.; Fukuta, T.; Yamada, T.; Onyango, M. S.; Bernardo, E. C.; Matsuda, H.; Yagishita, K. Catalytic Wet Oxidation of *o*-chlorophenol at Mild Temperatures under Alkaline Conditions. *Water Res.* **2005**, *39*, 29−36.

(43) Kolaczkowski, S. T.; Beltran, F.; McLurgh, D. B.; Rivas, F. J. Wet Air Oxidation of Phenol: Factors That May Influence Global Kinetics. *Process Saf. Environ. Prot.* **1997**, *75*, 257−265.

(44) Mantzavinos, D.; Hellenbrand, R.; Livingston, A. G.; Metcalfe, I. S. Catalytic Wet Oxidation of *p*-coumaric Acid: Partial Oxidation Intermediates, Reaction Pathways and Catalyst Leaching. *Appl. Catal., B* **1996**, *7*, 379−396.

(45) Lide, D. R., Ed. *CRC Handbook of Chemistry and Physics*, Internet Vesrion 2005; CRC Press: Boca Raton, FL, 2005.

(46) Arena, F.; Italiano, C.; Raneri, A.; Saja, C. Mechanistic and Kinetic Insights into the Wet Air Oxidation of Phenol with Oxygen (CWAO) by Homogeneous and Heterogeneous Transition-metal Catalysts. *Appl. Catal., B* **2010**, *99*, 321−328.

(47) Tomas, R. A. F.; Bordado, J. C. M.; Gomes, J. F. P. p-Xylene Oxidation to Terephthalic Acid: A Literature Review Oriented toward Process Optimization and Development. *Chem. Rev.* **2013**, *113*, 7421−7469.

(48) Prasad, J.; Tardio, J.; Akolekar, D. B.; Bhargava, S. K.; Grocott, S. C. Catalytic Wet Oxidation of Stripped Sour Water from an Oil-Shale Refining Process. *Ind. Eng. Chem. Res.* **2004**, *43*, 6363−6368.

(49) Tardio, J.; Bhargava, S.; Eyer, S.; Sumich, M.; Akolekar, D. B. *Ind. Eng. Chem. Res.* **2004**, *43*, 847−851.

(50) Devlin, H. R.; Harris, I. J. Mechanism of the Oxidation of Aqueous Phenol with Dissolved Oxygen. *Ind. Eng. Chem. Fundam.* **1984**, *23*, 387−392.

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Appendix 2

Publication II
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Article

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

Kristiina Kaldas, Gert Preegel, Kati Muldma, and Margus Lopp*

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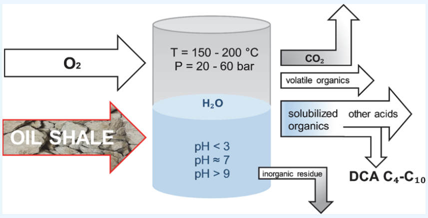
ABSTRACT: Until now, the oil shale kukersite has been used mainly for energy and oil production. To broaden the possible applications of oil shales, the wet air oxidation of kukersite (an organic-rich sedimentary rock from Estonia) was studied. Kukersite was oxidized with an oxygen-rich gas in water 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 K_2CO_3 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 pO_2, 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.[1] 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.[1,2] The Estonian oil shale kukersite is from the Ordovician period and has an exceptionally high organic matter content, reaching 30−50%.[3,4] The most common technologies for oil shale processing are pyrolysis for affording shale oil and direct burning for energy production. Because of the large and high-quality oil shale deposits in Estonia, the oil shale industry is one of the most developed in the world.[5] Besides power and shale oil, phenolic-based products are also produced from oil shales.[6,7] The present deployment of oil shales (especially direct burning) causes large CO_2 emissions,[8] and therefore, the need for alternative oil shale converting processes is essential.

The structure and potential usage of kukersite has been studied and evaluated through different techniques. Studies based on the analysis of pyrolysis products[9,10] confirmed its lipidic nature. However, the presence of relatively high proportions of reactive oxygen-containing moieties (resorcinols) creates a precondition for the low-temperature degradation of kukersite to value-added chemicals.[1,11] Blokker et al. used a RuO_4 degradation for kukersite and found a wide range of carboxyl groups in the degraded product. They suggested that the organic matter is mainly composed of n-alkenyl resorcinol building blocks.[12] The modeling of the kerogen structure with ^{13}C MAS NMR by Lille et al. mainly confirmed this assumption.[13] In the 1930−1940s,[1,14,15] it was shown that the oxidation of the kukersite kerogen with potassium permanganate resulted in the formation of dicarboxylic acid (DCA).[16] 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.[17−19] The developed process, however, was never industrially implemented.[15] In 2001, Bajc et al.[20] 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.[21] Catalytic WAO has been successfully used for the valorization of lignin[22,23] and its model substrates into valuable chemicals[24]

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and can be further applied for the transformation of partly oxidized compounds (e.g., keto acids) to the DCA.[25] Recently, it has been demonstrated that an analogous method called "oxy-cracking" can be effectively used for the enhancement of petroleum coke,[26,27] asphaltenes,[28] and even oil sand tailings,[29] 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, Proskurjakov and his group introduced a method of oil shale (Gdov shale, Russia) oxidation with continuous flow of air in neutral or basic aqueous solutions.[30−32] 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 Proskurjakov 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 CO_2 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.

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

	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	58.4	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.

All the other reagents were of highest analytical purity and purchased from commercial suppliers and used as received.

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.[26] 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° 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 collected separately, 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 H_2SO_4) in a Dean−Stark apparatus. The esterified product was analyzed with GC−flame ionization detection (FID) as DCA dimethyl esters (DMEs, C4−C10), 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-5HT 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.

Table 2. Metal Contents (wt %) of the Used Oil Shale Samples[a]

	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

[a] Measured with the microwave plasma atomic emission spectrometry method by an Agilent 4200 system at the Oil Shale Competence Center, Kohtla-Järve.

In the case of high-performance liquid chromatography−high-resolution MS (HPLC−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−HRMS analysis procedure 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 O_2, N_2, and CO, a 3 m molecular sieve 5 Å packed column (OD 1/8″, ID 2 mm, 80/100 mesh) was used, and for CO_2 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) at 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 the overall oxidation was supported by analyzing the CO_2 levels in the gas phase. The percent value of C_{CO_2} shows the amount of organic carbon converted to CO_2 during the oxidation compared to that of the initial organic carbon content in kerogen (eq 2).

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

$$\text{C in CO}_2 = \frac{\text{C in the form of CO}_2\text{ [mg]}}{\text{TOC in the initial oil shale [mg]}} \cdot 100\% \tag{2}$$

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)].

$$\text{Yield of SO} = \frac{\text{mass of SO [mg]}}{\text{mass of organic matter in the oil shale [mg]}} \cdot 100\% \tag{3}$$

$$\text{Yield of DCA(C4−C10)} = \frac{\text{mass of DCA[mg]}}{\text{mass of organic matter in the oil shale [mg]}} \cdot 100\% \tag{4}$$

3. RESULTS AND DISCUSSION

3.1. Kerogen Solubilization and DCA Formation: The Effect of Reaction Time. From the early work of Proskurjakov,[30−32] 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 50/50 O_2/N_2 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 3. Products of K-70 Dissolution without Any Additives[a]

time [h]	conversion [%]	SO [%]	DCA [%]	DME in SO, [%]	C_{CO_2} [%]	DCA distribution (C6−C10/C4−C10)
1	57	36	3.2	11	20	35
2	85	33	7.4	25	36	21
3	91	33	8.3	28	44	18
6	98	26	12.2	53	57	9

[a] Reaction conditions: T = 175 °C; P_{total} = 40 bar of 50% O_2; and 20 g/L of K-70.

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 CO_2, and only 18% of it was converted to SO. This means that from the 1 g of K-70, 920 mg of CO_2 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

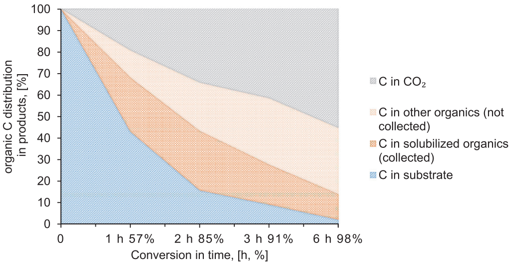

Figure 1. Organic C distribution in products over the time range. “C in other organics” represents the amount of carbon found in the forms of CO_2, acetic acid, formic acid, and other (volatile) undefined compounds that were not collected as SO; reaction conditions: T = 175 °C; P_{total} = 40 bar of 50% O_2; and 20 g/L of K-70 in distilled water.

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.[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,[33] 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 hour, 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_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_2; data not shown).

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[a]	1	38.0	42.7	0.84
SO[a]	3	25.9	46.0	1.3

[a] Analyzed before the esterification step; T = 175 °C; P_{total} = 40 bar of 50% O_2; and 20 g/L of K-70 in distilled water.

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_2/N_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_2 was observed when changing the pressure from 40 to 60 bar (corresponding to the 20–30 bar of pO_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_2 in a mixture with N_2) at a constant pressure of 40 bar were also tested. The highest partial pressure used (40 bar of pO_2 with pure O_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_2 and a decrease in SO were observed when compared to the 20 or 30 bar of pO_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_2/N_2 mixture (pO_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_2 formation (Figure 3). At higher temperatures (>175 °C), more than 50% of the initial organic carbon was converted to CO_2 within 3 h. The rise in the CO_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) occured.[33] 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 kukersite 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

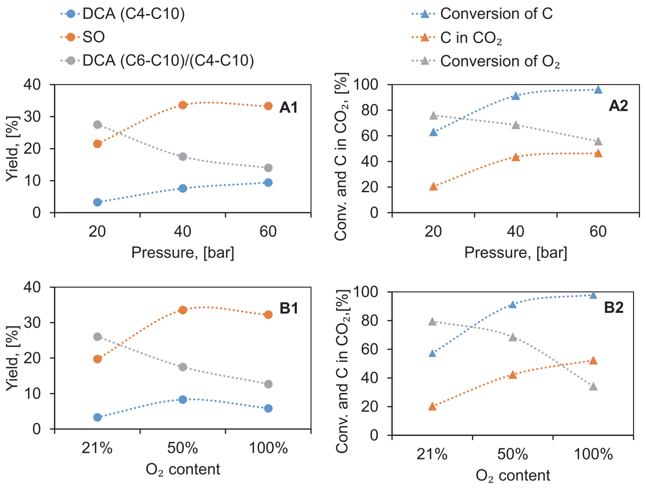

Figure 2. Effect of pressure when using a 50/50 O_2/N_2 mixture at pressures of 20−60 bar (A1 and A2) and when using 40 bar of different gas mixtures (B1 and B2). Reaction conditions: T = 175 °C, t = 3 h, and 20 g/L of K-70 in distilled water.

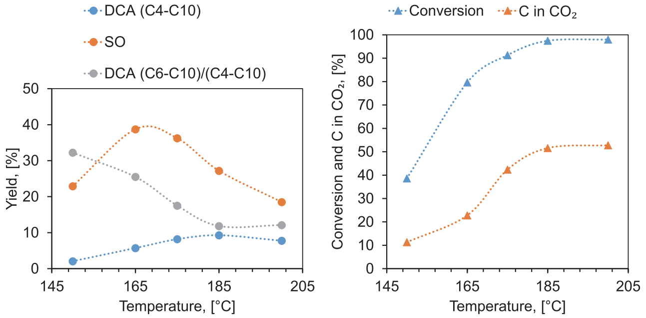

Figure 3. Effect of temperature. Reaction conditions: T = 3 h; P_{total} = 40 bar of 50% O_2; and 20 g/L of K-70 in distilled water.

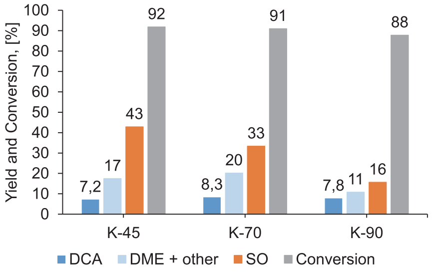

Figure 4. Effect of the organic matter content in the substrate. Reaction conditions: T = 175 °C; P_{total} = 40 bar of 50% O_2; t = 3 h, and 20 g/L of the oil shale.

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 lignin[34,35] and petcoke processing.[26] Furthermore, in a basic solution, free CO_2 could be bounded in the form of carbonates, minimizing the CO_2 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

Table 5. Kerogen Dissolution with the Addition of Various Bases[a]

base	conversion [%]	yield of DCA [%] (C6–C10/C4–C10)	pH (after reaction)
Na_2CO_3	98	4.4 (37%)	7, 5
$Ca(OH)_2$	93	5.8 (36%)	6, 5
Na_2SiO_3	95	6.7 (26%)	5, 5
NaOH	99	5.4 (38%)	8, 5
KOH	99	8.2 (32%)	9
K_2CO_3	98	7.6 (28%)	6, 5

[a] Reaction conditions: T = 175 °C; P_{total} = 40 bar of 50% O_2; 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 K_2CO_3 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 K_2CO_3 or $Ca(OH)_2$; however, no improvement in the amount of DCA was detected. It can be suggested that destruction of kerogen at low K_2CO_3 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 O_2.[36] 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 52% 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.

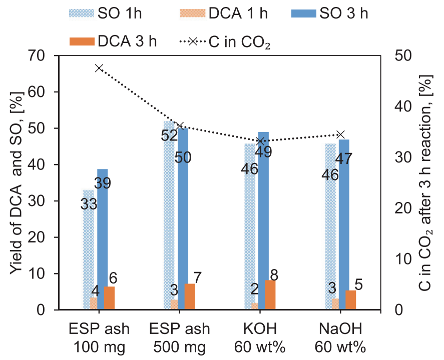

Figure 5. Effect of oil shale ash as a catalyst. Reaction conditions: T = 175 °C; P_{total} = 40 bar of 50% O_2; 20 g/L of K-70; t = 3 h; and 60 wt % of base or ESP ash at presented amount.

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.[21,37,38] 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).

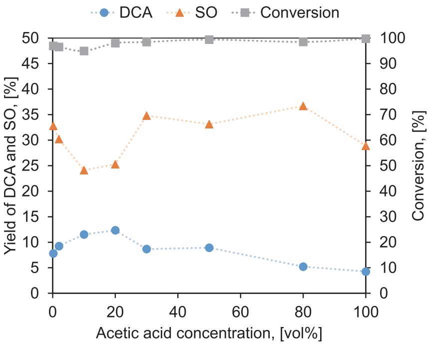

Figure 6. Effect of acetic acid concentration on K-70 oxidation. Reaction conditions: T = 175 °C; P_{total} = 40 bar of 50% O_2; 20 g/L of K-70; t = 3 h; and acetic acid solution at presented vol %.

3.7. Comparison of Acidic and Basic Media. The effect of the reaction time on conversion, SO, DCA, and CO_2 formation was compared under constant conditions in alkali (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 alkali media than in water at 175 °C despite the possible differences in the oxidation pathways.[21] As expected, the oil shale dissolution in acetic acid was

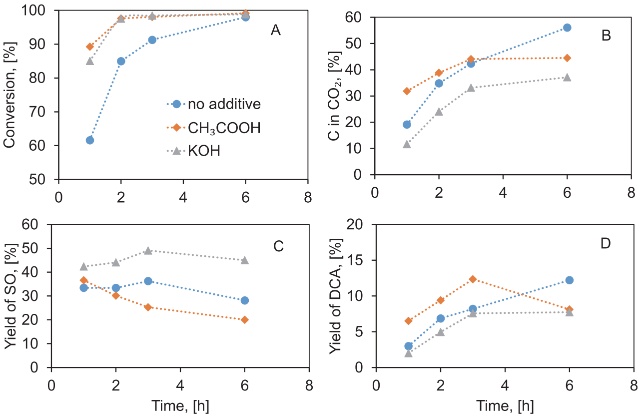

Figure 7. Effect of reaction times on kerogen solubilization at different pH levels (A: the conversion of organic carbon; B: the amount of organic carbon converted to CO_2; C: the yield of water−SO products; and D: the yield of DCA). Reaction conditions: T = 175 °C; P_{total} = 40 bar of 50% O_2; and 20 g/L of K-70 in distilled water, with 60 wt % of K_2CO_3 or in 20 vol % of acetic acid solution.

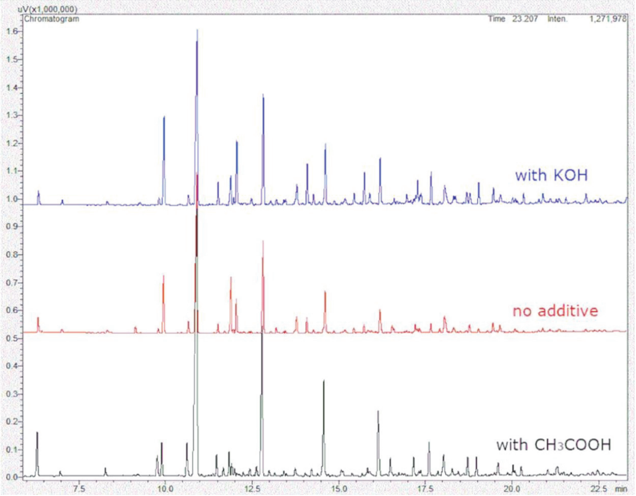

Figure 8. Comparison of derivatized SO (GC-FID chromatograms) obtained from the WAO of K-70 in different reaction media. Reaction conditions: T = 175 °C; P_{total} = 40 bar of 50% O_2; t = 3 h; and 20 g/L of K-70 in distilled water, with 60 wt % of K_2CO_3 or in 20 vol % of acetic acid solution.

accompanied by formation of a high amount of CO_2 for 1−3 h, while in water, the amount of CO_2 increased consistently (Figure 7B). The alkali solution is advantageous for keeping CO_2 emissions low during the whole WAO process.

In addition to CO_2 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 K_2CO_3 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

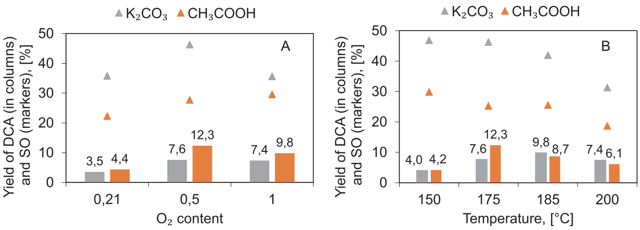

Figure 9. Effect of oxygen partial pressure and temperature on K-70 oxidation in acidic and basic solutions (A at T = 175 °C and B at P = 40 bar of 50% O_2). Reaction conditions: t = 3 h; P_{total} = 40 bar; and 20 g/L of K-70 in distilled water, with 60 wt % of K_2CO_3 or in 20 vol % of acetic acid solution.

the increased stability of intermediates formed in the alkali also inhibits the formation of DCAs, and thus, the DCA yields never reached as high as in the acetic acid solution at a temperature of 175 °C. Therefore, the acetic acid solution is a preferred environment for the WAO of oil shales when aiming 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% O_2. The amount of both products were decreased at lowered (pO_2 21%) and elevated (pO_2 100%) 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 I[39]) and Jordan (type II[39]), were subjected to the same WAO process to establish the feasibility of the oxidation data obtained from kukersite (between types I and II[40,41]). The Green River shale used had an organic C content of 13.0% and a sulfur content of 0.7%, while the Jordan shale had an organic C content of 12.7% and a sulfur content of 2.8%. The Green River shale and kukersite are the two most extensively studied kerogens, and, according to the literature, similar oxidation products can be expected.[1,42,43] The Jordan shale also has an aliphatic nature, but the mineral composition is different.[44,45]

Table 6 shows that despite the different origins and compositions of the shales, they behave similarly in the WAO process. Of them, kukersite has the greatest potential to afford 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.

Table 6. DCAs from Different Shales Using the WAO Process[a]

	TOC [%]	conversion [%]	yield of DCA[b] [%]
kukersite	35.1	95	10.8
Green River	13.0	93	4.8
Jordan	12.7	82	2.8

[a] Reaction conditions: T = 175 °C; P_{total} = 40 bar of 50% O_2; t = 3 h; and 20 g/L of oil shale in distilled water. [b] Yield of DCAs (C4−C10) is calculated from the TOC value.

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, K_2CO_3, 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 CO_2 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 O_2 and N_2 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 CO_2 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.

■ 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)

AUTHOR INFORMATION

Corresponding Author

Margus Lopp − *Department of Chemistry and Biotechnology, Faculty of Science, Tallinn University of Technology, 19086 Tallinn, Estonia;* orcid.org/0000-0002-8041-2595; Email: margus.lopp@taltech.ee

Authors

Kristiina Kaldas − *Department of Chemistry and Biotechnology, Faculty of Science, Tallinn University of Technology, 19086 Tallinn, Estonia*

Gert Preegel − *Department of Chemistry and Biotechnology, Faculty of Science, Tallinn University of Technology, 19086 Tallinn, Estonia*

Kati Muldma − *Department of Chemistry and Biotechnology, Faculty of Science, Tallinn University of Technology, 19086 Tallinn, Estonia*

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c01466

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Durand, B. *Sedimentary Organic Matter and Kerogen. Definition and Quantitative Importance of Kerogen*; Edistions Technip.: Paris, 1980.

(2) Vandenbroucke, M.; Largeau, C. Kerogen Origin, Evolution and Structure. *Org. Geochem.* **2007**, *38*, 719−833.

(3) Lille, Ü. Current Views on the Origin of Estonian Kukersite Kerogen. *Oil Shale* **2002**, *19*, 3−18.

(4) Veiderma, M. Estonian Oil Shale-Resources and Usage. *Oil Shale* **2003**, *20*, 295−303.

(5) Easac, A. *A study on the EU oil shale industry--viewed in the light of the Estonian experience. A report by EASAC to the Committee on Industry, Research and Energy of the European Parliament*, 2007.

(6) Baird, Z. S.; Oja, V.; Järvik, O. Distribution of Hydroxyl Groups in Kukersite Shale Oil: Quantitative Determination Using Fourier Transform Infrared (FT-IR) Spectroscopy. *Appl. Spectrosc.* **2015**, *69*, 555−562.

(7) Kann, J.; Raukas, A.; Siirde, A. About the Gasification of Kukersite Oil Shale. *Oil Shale* **2013**, *30*, 283−293.

(8) Kallemets, K. Economic Sustainability of Estonian Shale Oil Industry until 2030. *Oil Shale* **2016**, *33*, 272−289.

(9) Derenne, S.; Largeau, C.; Casadevall, E.; Sinninghe Damsté, J. S.; Tegelaar, E. W.; de Leeuw, J. W. Characterization of Estonian Kukersite by Spectroscopy and Pyrolysis: Evidence for Abundant Alkyl Phenolic Moieties in an Ordovician, Marine, Type II/I Kerogen. *Org. Geochem.* **1990**, *16*, 873−888.

(10) Klesment, I. Application of chromatographic methods in biogeochemical investigations. *J. Chromatogr.* **1974**, *91*, 705−713.

(11) Shi, J.; Ma, Y.; Li, S.; Wu, J.; Zhu, Y.; Teng, J. Characteristics of Estonian Oil Shale Kerogen and Its Pyrolysates with Thermal Bitumen as a Pyrolytic Intermediate. *Energy Fuel.* **2017**, *31*, 4808−4816.

(12) Blokker, P.; Van Bergen, P.; Pancost, R.; Collinson, M. E.; De Leeuw, J. W.; Sinninghe Damste, J. S. The Chemical Structure of Gloeocapsomorpha Prisca Microfossils: Implications for Their Origin. *Geochim. Cosmochim. Acta* **2001**, *65*, 885−900.

(13) Lille, Ü.; Heinmaa, I.; Pehk, T. Molecular model of Estonian kukersite kerogen evaluated by 13C MAS NMR spectra. *Fuel* **2003**, *82*, 799−804.

(14) Kogerman, P. N. Hundred Years of the Chemical Investigation of an Oil Shale: The Chemical Constitution of the Estonian Oil Shale "Kukersite" − Oil Shale and Cannel Coal. *International Petroleum Conference*; The Institute of Petroleum: glasgow, 1938; pp 115−123.

(15) Veski, R.; Veski, S. Aliphatic Dicarboxylic Acids from Oil Shale Organic Matter − Historic Review. *Oil Shale* **2019**, *36*, 76−95.

(16) Fomina, A. S.; Pobul, L. The Deriving of Dibasic Aliphatic Acids from a New Raw Material. *Acad. Sci. Est. SSR* **1957**, *6*, 190−198.

(17) Degtereva, Z.; Fomina, A. Production of Dibasic Acids C4-C10 from Oil Shale Kukersite. *Acad. Sci. Est. SSR* **1959**, *8*, 122−136.

(18) Männik, E.; Fomina, A.; Kann, J.; Ikonopistseva, O. Analysis of Mixtures of Dicarboxylic Acids Obtained at the Oxidation of Kukersite Kerogen by the Method of Gas-Liquid Chromatography. *Acad. Sci. Est. SSR* **1968**, *17*.

(19) Pobul, L.; Fomina, A. Purification and Fractioning of Mixtures of Saturated Dicarbonic Acids Obtained at the Oxidation of Kukersite Kerogen. *Acad. Sci. Est. SSR* **1962**, *11* ().

(20) Bajc, S.; Amblès, A.; Largeau, C.; Derenne, S.; Vitorović, D. Precursor Biostructures in Kerogen Matrix Revealed by Oxidative Degradation: Oxidation of Kerogen from Estonian Kukersite. *Org. Geochem.* **2001**, *32*, 773−784.

(21) Bhargava, S. K.; Tardio, J.; Prasad, J.; Föger, K.; Akolekar, D. B.; Grocott, S. C. Wet Oxidation and Catalytic Wet Oxidation. *Ind. Eng. Chem. Res.* **2006**, *45*, 1221−1258.

(22) Sales, F. G.; Maranhão, L. C. A.; Lima Filho, N. M.; Abreu, C. A. M. Kinetic Evaluation and Modeling of Lignin Catalytic Wet Oxidation to Selective Production of Aromatic Aldehydes. *Ind. Eng. Chem. Res.* **2006**, *45*, 6627−6631.

(23) Niu, M.; Hou, Y.; Wu, W.; Yang, R. Degradation of Lignin in NaVO3-H2SO4 Aqueous Solution with Oxygen. *Fuel Process. Technol.* **2017**, *161*, 295−303.

(24) Behling, R.; Valange, S.; Chatel, G. Heterogeneous Catalytic Oxidation for Lignin Valorization into Valuable Chemicals: What Results? What Limitations? What Trends? *Green Chem.* **2016**, *18*, 1839−1854.

(25) Liu, J.; Du, Z.; Lu, T.; Xu, J. Conversion of Levulinate into Succinate through Catalytic Oxidative Carbon-Carbon Bond Cleavage with Dioxygen. *ChemSusChem* **2013**, *6*, 2255−2258.

(26) Manasrah, A. D.; Nassar, N. N.; Ortega, L. C. Conversion of Petroleum Coke into Valuable Products Using Oxy-Cracking Technique. *Fuel* **2018**, *215*, 865−878.

(27) Manasrah, A. D.; Hassan, A.; Nassar, N. N. Enhancement of petroleum coke thermal reactivity using Oxy-cracking technique. *Can. J. Chem. Eng.* **2019**, *97*, 2794−2803.

(28) Ashtari, M.; Carbognani, L.; Pereira-Almao, P. Asphaltenes Aqueous Conversion to Humic and Fulvic Analogs via Oxy-Cracking. *Energy Fuel.* **2016**, *30*, 5470−5482.

(29) Nafie, G.; Manasrah, A. D.; Mackay, B.; Badran, I.; Nassar, N. N. Oxy-Cracking Reaction for Enhanced Settling and Dewaterability of Oil Sands Tailings. *Ind. Eng. Chem. Res.* **2019**, *58*, 4988−4996.

(30) Proskurjakov, V. A.; Soloveichik, Z. V. Oxidation of Oil Shale by Atmospheric Oxygen. Oxidation of an Aqueous-Alkaline

Suspension of Gdowski Shale in an Autoclave. *Tr. Vsesoj. N.I.Instituta po Pererab. i Issl. Topl.* **1961**, *10*, 64−80.

(31) Proskurjakov, V. A.; Soloveichik, Z. V. Oxidation of Oil Shale by Atmospheric Oxygen. Oxidation of Gdov Shales with Continuous Air Supply. *Tr. Vsesoj. N. I.Instituta po Pererab. i Issl. Topl.* **1961**, *10*, 81−90.

(32) Proskurjakov, V. A.; Yakovlev, V. I.; Kudrjukov, O. I. Oxidation of Oil Shale by Atmospheric Oxygen. Oxidation of Common Syrtian Shales. *Tr. Vsesoj. N.I.Instituta po Pererab. i Issl. Topl.* **1962**, *11*, 20−27.

(33) Kaldas, K.; Preegel, G.; Muldma, K.; Lopp, M. Reactivity of Aliphatic Dicarboxylic Acids in Wet Air Oxidation Conditions. *Ind. Eng. Chem. Res.* **2019**, *58*, 10855−10863.

(34) Kindsigo, M.; Kallas, J. Degradation of Lignins by Wet Oxidation: Model Water Solutions. *Proc. Est. Acad. Sci. Chem.* **2006**, *55*, 132−144.

(35) Irmak, S.; Kang, J.; Wilkins, M. Depolymerization of Lignin by Wet Air Oxidation. *Bioresour. Technol.* **2020**, *9*, 100377.

(36) Kindsigo, M.; Kuusik, R.; Kallas, J. Oil Shale Ash as a Catalyst in Wastewater Treatment in the Pulp and Paper Industry. *WIT Trans. Ecol. Environ.* **2010**, *140*, 403−414.

(37) Prasad, J.; Tardio, J.; Akolekar, D. B.; Bhargava, S. K.; Grocott, S. C. Catalytic Wet Oxidation of Stripped Sour Water from an Oil-Shale Refining Process. *Ind. Eng. Chem. Res.* **2004**, *43*, 6363−6368.

(38) Velegraki, T.; Nouli, E.; Katsoni, A.; Yentekakis, I. V.; Mantzavinos, D. Wet Oxidation of Benzoic Acid Catalyzed by Cupric Ions: Key Parameters Affecting Induction Period and Conversion. *Appl. Catal. B Environ.* **2011**, *101*, 479−485.

(39) Peters, K. E.; Cassa, M. R. Applied Source Rock Geochemistry. *The Petroleum System—From Source to Trap*; AAPG Mem. 60, 1994; pp 93−120.

(40) Hutton, A.; Bharati, S.; Robl, T. Chemical and Petrographic Classification of Kerogen/Macerals. *Energy Fuel.* **1994**, *8*, 1478−1488.

(41) Altun, N. E.; Hiçyilmaz, C.; Hwang, J. Y.; Bağci, A. S.; Kök, M. V. Oil Shales in the World and Turkey; Reserves, Current Situation and Future Prospects: A Review. *Oil Shale* **2006**, *23*, 211−227.

(42) Barakat, A.; Yen, T. Kerogen structure by stepwise oxidationUse of sodium dichromate in glacial acetic acid. *Fuel* **1987**, *66*, 587−593.

(43) Barakat, A. O.; Yen, T. F. Size Distribution of the Straight-Chain Structures in Type I and II Kerogens. *Energy Fuel.* **1988**, *2*, 181−185.

(44) Tiikma, L.; Johannes, I.; Luik, H.; Lepp, A.; Sharayeva, G. Extraction of Oil from Jordanian Attarat Oil Shale. *Oil Shale* **2015**, *32*, 218−239.

(45) El-Rub, Z. A.; Kujawa, J.; Albarahmieh, E.; Al-Rifai, N.; Qaimari, F.; Al-Gharabli, S. High Throughput Screening and Characterization Methods of Jordanian Oil Shale as a Case Study. *Energies* **2019**, *12* (). https://doi.org/ DOI: 10.3390/en12163148.

Appendix 3

Publication III

K. Kaldas, A. Niidu, G. Preegel, J. M. Uustalu, K. Muldma and M. Lopp, “Aspects of kerogen oxidative dissolution in subcritical water using oxygen from air,” *Oil Shale*, vol. 38, no. 3, pp. 199−214, 2021

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Aspects of kerogen oxidative dissolution in subcritical water using oxygen from air

Kristiina Kaldas, Allan Niidu, Gert Preegel, Jaan Mihkel Uustalu, Kati Muldma, Margus Lopp*

Laboratory of Industrial Chemistry, Department of Chemistry and Biotechnology, Tallinn University of Technology, Ehitajate tee 5, 19086 Tallinn, Estonia

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Abstract. *Society's growing demands on everyday products and materials are increasingly difficult to meet in an environment that seeks to avoid petroleum-based processes. Instead of abandoning fossil materials altogether, more research should be done on their efficient and clean conversion. One option for this is the oxidative dissolution of kerogen in water under conditions that satisfy the subcritical range (T = 150–200 °C, pO_2 = 0.5–4 MPa). The resulting mixture contains a substantial amount of various aliphatic carboxylic and dicarboxylic acids. Both batch and semi-continuous processes were set up to find the main factors and optimal conditions for the kerogen dissolution process. The rate of transformation of organic carbon to dissolved organic compounds was mainly influenced by elevated temperature and oxygen partial pressure. To obtain high yields of organic carbon dissolution and to avoid the formation of excess CO_2, the oxidation of kerogen should be carried out fast (< 1 h) and under high oxygen pressure. By employing a temperature of 175 °C and O_2 pressure of 2 MPa, over 65% of the initial organic carbon dissolves in about one hour. Prolonged reaction times or harsher oxidation conditions resulted in a rapid degradation of dissolved matter and also of the valuable products formed. The organic matter content of the initial oil shale had a direct effect on the further degradation of dicarboxylic acid and consequently on the overall yield. The suitability of using a trickle-bed reactor for kerogen dissolution is discussed in detail on the basis of experimental results.*

Keywords: *kerogen dissolution, wet air oxidation, dicarboxylic acids.*

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* Corresponding author: e-mail *margus.lopp@taltech.ee*

1. Introduction

Development of sustainable processes to valorize the existing raw organic materials, including organic wastes, has become an essential target for the chemical industry. Estonian oil shale, a sedimentary rock from the Ordovician era, called Kukersite [1], is used for production of electricity and crude oil. The commercial value of organic compounds from oil shale organic matter (kerogen) may be several times higher than that from the current use of oil shale (e.g. shale oil and phenols). The search for alternative approaches to a more efficient utilization of kerogen should be based on knowledge of its structure. According to Blokker et al. [2], Lille et al. [3] and Lille [4] the heterogeneous kerogen matrix consists of building blocks composed of large alkyl and alkenyl fragments joined by resorcinol units. In the selection of a suitable process for dissolving the organic matter of Kukersite, parallels with lignin-carbohydrate complexes can be drawn, among which oxidative depolymerization methods have been reported [5–7]. The main monomeric products separable from these complex organic structures are carboxylic acids and their analogs. These compounds can serve as starting materials for both the chemical and materials industries [8–11]. The commercial value of organic compounds from oil shale organic matter (kerogen) may be several times higher than that from the current use of oil shale (e.g. shale oil and phenols) [12, 13].

It has been shown previously that up to 40% of the kerogen in Kukersite is convertible to a mixture of aliphatic dicarboxylic acids (DCAs) by using oxidative conditions [13, 14]. Various processes, such as oxidation with nitric acid [13, 15–17] or potassium permanganate [18–20], as well as use of a continuous flow of air fed through basic aqueous solutions [21–23] have been examined. Unfortunately, most of the cited works date back more than 50 years, and thus there is a lack of information on whether these applications are feasible in a modern industrial environment.

Kaldas et al. [24] have reported that oil shale could be dissolved via oxidative degradation using a wet air oxidation (WAO) process. The main advantage of the WAO method compared to conventional petrochemical processes is a shorter route from organic sediments to chemicals, lower temperatures, use of water as a solvent and air as an oxidant. As the WAO process is widely used in wastewater treatment, technical solutions are readily available [25–27]. It has been demonstrated that by use of the WAO process at 175 °C for 3 h the yield of water soluble chemical compounds can be up to 50% of the initial kerogen content [24]. Moreover, 20–30% of these soluble compounds represent aliphatic dicarboxylic acids. Beside Estonian Kukersite, Jordanian and Green River (USA) shales behave similarly.

In the present work, the main focus was on determining the distribution of organic carbon between solid, liquid and gaseous phases throughout the reaction period rather than on the yield of DCA. Kukersite was subjected to the WAO process in wider pressure and substrate concentration ranges than in the work by Kaldas et al. [24], namely 0.5–4 MPa and 2.5–40 g/L, and at temperatures of 155–185 °C in 500 ml batch reactors. The aim was to establish the optimal conditions for obtaining a maximum yield of organic carbon in liquid phase by avoiding its over-oxidation to CO_2. Examples and a discussion of scalability and use of semi-continuous processes are presented. In the final part of the work the formation of DCAs is discussed with respect to their secondary destruction in the course of oxidation.

2. Experimental

Oil shale (kerogen content ~45%; K-45) and its concentrate (kerogen content ~70%; K-70) were obtained from the Oil Shale Competence Centre Estonia in Kohtla-Järve. The studied samples, K-70 and K-45, had particle sizes < 45 µm and < 90 µm, respectively. The elemental analysis results for these oil shale samples are given in Table 1 and additional information on their mineral contents can be found in the research by Kaldas et al. [24].

Table 1. The chemical composition of oil shale samples, wt%[a]

Sample	C	H	N	S	O	TIC	TOC
K-70	57.8	6.7	0.16	0.7	19.1	1.3	56.5
K-45	38.4	4.4	0.12	1.7	17.7	3.2	35.1

[a] TIC – total inorganic carbon; TOC – total organic carbon

For WAO experiments the same protocol was followed as previously [24]. Large scale experiments were carried out in a 500 mL stainless steel pressure reactor (4575A, Parr Instrument Company, Moline, Il, USA) having similar properties as the 100 ml reactor used earlier. Briefly, a specified amount of oil shale concentrate K-70 was weighed into the reactor together with distilled water. The reactor was pressurized up to a selected level with oxygen-containing gas, heated to the desired temperature and stirred at a speed of 1000 rpm. Three different gas mixtures were used: synthetic air (21% O_2 and 79% N_2), pure oxygen (100% O_2) and a 50/50 mixture of O_2 and N_2. The time zero (t_0) of the reaction was taken as the point when the reaction temperature reached 5 °C below the set point. At the end of the reaction, the reactor was cooled and depressurized, the evolved gas was collected, and analyzed using gas chromatography with a thermal conductivity detector (GC-TCD). The unreacted solid residue was separated by centrifugation, dried at 105 °C for 24 h and weighed. These samples were then subjected to elemental analysis. The supernatant was collected separately, water was evaporated and the resulting sample (dissolved matter) was sent for elemental analysis. For determining the content of DCAs, a portion of the sample was esterified and analyzed as

DCA dimethyl esters (DME, C4–C10) by using gas chromatography with a flame ionization detector (GC-FID).

The distribution of carbon between the unreacted kerogen and dissolved organics phase was calculated using the carbon concentrations from elemental analysis times the weight of the materials in these phases, divided by the initial carbon content in oil shale (Eq.). Elemental analysis was performed on a Vario MACRO CHNS Cube analyzer and a rapid OXY Cube for O. The measured CO_2 and O_2 levels in the gas phase provided a measure of the total extent of oxidation. Gas analysis was carried out with a Shimadzu GC-2014 gas chromatograph with a sample valve system, which made it possible to determine all of the gases of interest in a single run. From the measured CO_2 values, the content of gasified carbon was determined. However, depending on the operating conditions, complete carbon mass balance was not always achieved. The imbalance was mainly caused by the fraction of dissolved low-molecular-weight organic carbon-containing compounds that was lost during the evaporation step, as also reported earlier [24]:

$$C, \% = \frac{\text{post- oxidation TOC, \% × weighed residue, mg}}{\text{initial TOC, \% × initial oil shale, mg}}$$

For DCA determination, the esterified sample of the dissolved organics was qualitatively and quantitatively analyzed with a Shimadzu GC-2010 FID gas chromatograph using a 30 m polyimide-coated fused silica Zebron ZB-5HT Inferno (0.25 μm) capillary column programmed at 10 °C/min from 50 °C (with a 4 min isothermal hold) to 300 °C (with a 3 min isothermal hold). For further details of the analysis method used, please refer to the earlier publication [24].

3. Results and discussion

3.1. Time-dependent dissolution of Kukersite kerogen

The distribution of organic carbon between kerogen, dissolved product in the water phase and CO_2 in the gas phase as a function of reaction time is shown in Figure 1 along with the decrease in O_2. Oil shale at concentrations of 20–40 g/L in water was treated at an initial pressure of synthetic air of 4 MPa (pO_2 0.84 MPa), or a 50/50 mixture of O_2/N_2 (pO_2 2 MPa) at 175 °C. The results obtained confirmed the conclusion of the previous research [24] that the kerogen dissolution reaction is completed within 3 h (Figs. 1a, 1c). At low kerogen concentrations relative to oxygen, the dissolution process stopped due to depletion of kerogen. The oxidation process, however, continued with oxidation of the dissolved organics to CO_2 at a different reaction rate. When the oxidant was added to a nearly equimolar amount of

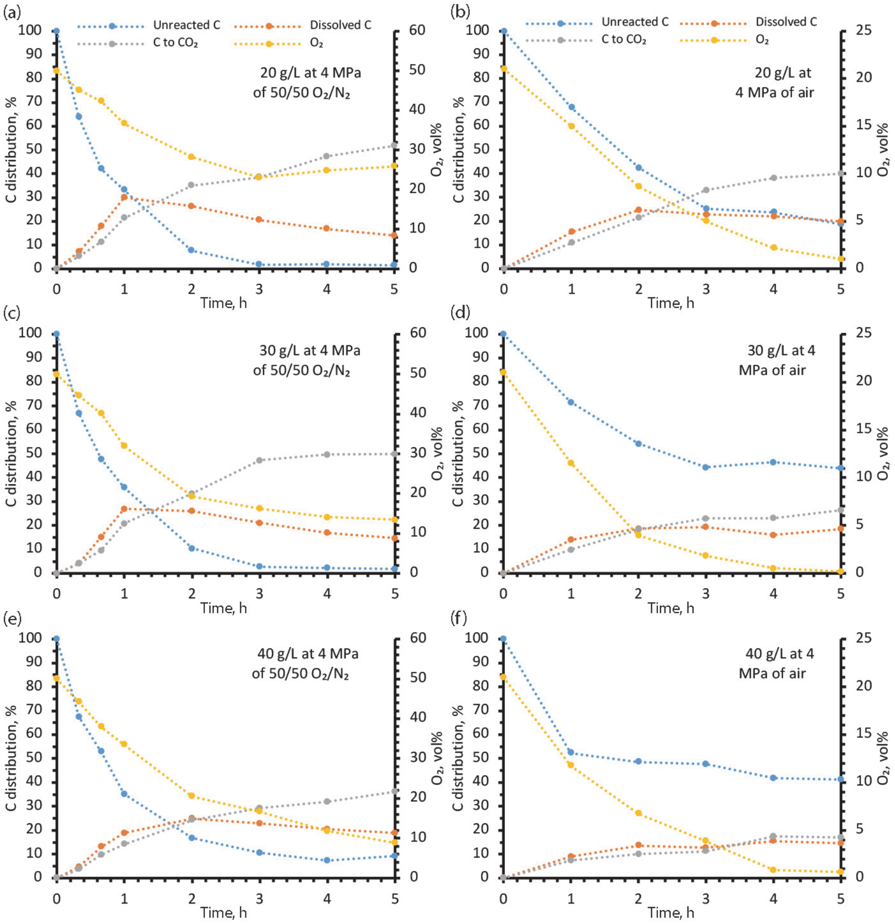

Fig. 1. The effect of oil shale concentration in time dependent experiments at 175 °C on the distribution of organic carbon between solid (unreacted C), dissolved (dissolved C) and gaseous (C to CO_2) forms.

organic carbon (Figs. 1b, 1e), a continuous decrease in the organic carbon content of the solid kerogen and an increase in the carbon content of the gas phase were observed throughout the entire reaction period. At high kerogen concentrations compared to oxygen, the oxidation process stopped because of depletion of oxygen (Figs. 1d, 1f). When synthetic air was used as an oxidant, the oxygen deficiency occurred already at an early stage of oxidation.

Carbon distribution data show that the dissolution of kerogen carbon paralleled the formation of CO_2. Even after a complete conversion of the initial organic carbon of kerogen, a considerable CO_2 formation occurred. As long as oxygen was still present in the medium, further oxidative reactions

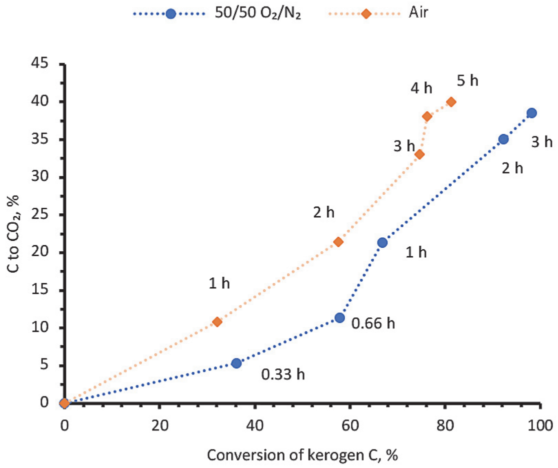

Fig. 2. CO_2 evolution per organic carbon conversion at 175 °C and 4 MPa with 20 g/L of K-70.

took place, as evidenced by the increase in CO_2 during the 4th and 5th hours of the reaction (Fig. 1a). The experimental data strongly suggest that in the long run and in the excess of oxygen the oxidation will continue until all organic carbon is converted to CO_2.

Comparing the conversion of kerogen carbon with the formation of CO_2 at different oxygen concentrations, it can be seen that at higher oxygen concentration less CO_2 and more dissolved organic compounds were generated (Fig. 2). At short reaction times, the oxidation of dissolved organics had a smaller contribution to the amount of evolved CO_2. This suggests that the production of dissolved organic compounds should be conducted in a short period of time.

The experimental data show that the mechanism of kerogen disintegration is similar to a common WAO mechanism, in which the oxidation of organic compounds proceeds in two steps [28–30]. With oil shale kerogen, the first reaction step is the oxidation of the resorcinol entities of kerogen [2]. Within that time, the carbon linkages between resorcinol units become water-soluble, while the rest of the resorcinol is rapidly oxidized to CO_2. It can be assumed that this step is predominant during the first hour of kerogen oxidation. The second reaction step represents a further oxidation of the dissolved material, with additional CO_2 release. Further discussion, additional experiments and calculations are required to prove this suggestion.

3.2. The effect of temperature and pressure on Kukersite kerogen dissolution

To investigate the influence of pressure and temperature on the distribution of organic carbon, oil shale K-70 at a low concentration (2.5 g/L, to ensure a sufficient oxygen concentration throughout the experiment) was treated with pure oxygen. The results obtained in the "one-hour" experiments are shown in Figure 3. It can be seen that the effect of pressure was minimal at the lowest temperature (150 °C). The conversion of kerogen followed a nearly linear dependence on the pressure of the oxidant at temperatures of 165–175 °C, showing an increase in the effective amount of oxidant relative to kerogen. At the highest temperature, the linearity from the oxidant pressure abated as the amount of organic carbon in the reaction mixture decreased rapidly: at 185 °C and 0.5 MPa, a quarter of the initial organic carbon had already been converted. At pressures below the saturated vapor pressure (0.9 MPa at 175 °C [31]), the conditions fall out of the subcritical region, leading to other degradation pathways that were not studied in this work.

It is notable that increasing the temperatures above 175 °C did not increase the amount of carbon in the dissolved organic compounds. Figure 3 shows that the formation of dissolved organic carbon was in equilibrium with their oxidation to CO_2. Thus, it is evident that during kerogen dissolution at subcritical conditions, the formation of CO_2 was unavoidable.

The data also showed that the loss in the carbon material balance increased with temperature. This could be explained by the increasing number of low-

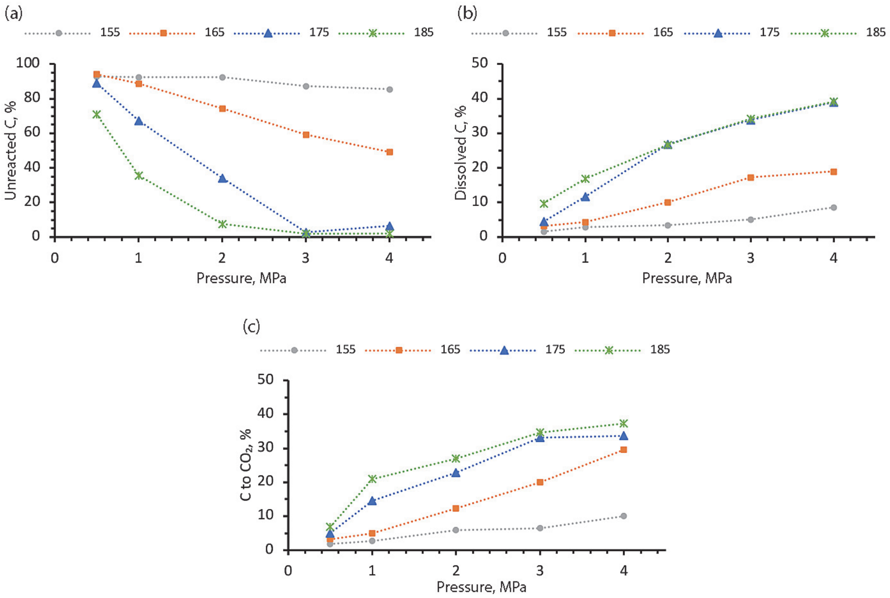

Fig. 3. Time- and pressure-dependent experiments with 2.5 g/L K-70 and 100% O_2 for 1 h.

molecular-weight compounds (volatile intermediates) formed in parallel, i.e. the number of compounds lost during the evaporation process increased with temperature, indicating that temperatures higher than 185 °C should be avoided since over-oxidation processes of already dissolved organics prevailed. It can be concluded that the optimum operating conditions for an efficient dissolution of kerogen were the following: temperature 175–185 °C and O_2 partial pressure 2–3 MPa.

By considering the results of all oxidation experiments conducted at 175 °C and pO_2 of 2 MPa with different kerogen concentrations, the oxygen consumption during the first hour was calculated. At an initial O/C ratio from 20:1 to 1.5:1, the consumption was approximately 0.8 mol of O_2 per reacted carbon, suggesting that the oxidation process was independent of oxygen concentration within these limits and the composition of the dissolved organics from this step was similar.

3.3. Semi-continuous process for dissolving Kukersite

Experiments on dissolving kerogen in a semi-continuous mode were performed in a trickle-bed reactor (made of stainless steel, d_{inner} = 15.6 mm, length = 600 mm). Thus, 10 g of oil shale (K-70) was packed in layers with quartz wool and sand (40 g, d ≥ 90 μm). The upper part of the reactor was filled with glass beads (d = 3 mm, 70 g) to ensure a uniform distribution of the liquid in the reactor (Fig. 4).

The continuous removal of dissolved kerogen from the reaction medium was expected to minimize the contact time of the dissolved kerogen with oxygen in the reactor and prevent over-oxidation. Various temperatures (150–200 °C), air flow rates (20–400 ml/ min) and water flow rates (0.3–0.9 ml/min) were tested. Liquid and gas samples were collected at 15 min intervals.

As seen from Table 2, an increase in temperature and the ratio of oxygen to oil shale afforded a higher conversion of organic carbon. This means that the same trends observed above for a batch process also applied to a semi-continuous process. The overall conversion rate of kerogen, however, was significantly lower than that in batch reactors. Moreover, the amount of CO_2 emitted per organic carbon consumed in the reaction did not decrease compared to the experiments above. The amount of dissolved organics obtained (measured as esterified product) was also considerably lower than expected. The distribution of DCAs in the dissolved product showed a preference for short-chain DCAs (represented as the ratio of high-molecular-weight DCA to total DCA, C7–C10/DCA, Table 2), similarly to that observed in batch reactors [24]. A significant drawback that arose during the operation of the trickle-bed reactor was the local overheating of the oil shale bed. This led to local thermal decomposition processes and a sudden rise in the observed CO_2

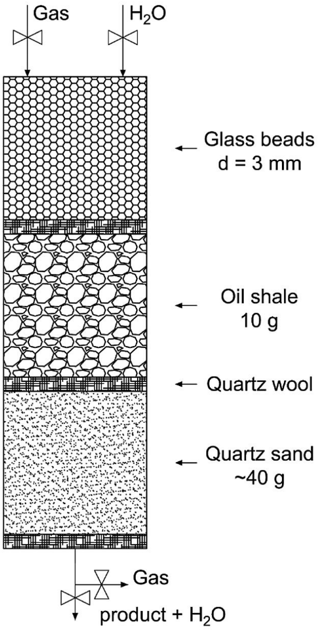

Fig. 4. The scheme of the trickle-bed reactor used.

values, as can be seen from the experiments carried out at a water flow rate of 0.3 ml/min (Table 2, exp 4 and exp 7). Therefore, the water flow rate through the reactor was kept high, which resulted in an overdiluted product and made the subsequent product isolation time and energy consuming.

In an experiment where a 10% acetic acid solution was used instead of distilled water for faster kerogen conversion [24], the product formation profile (Fig. 5) was not substantially different from that of the other experiments (see

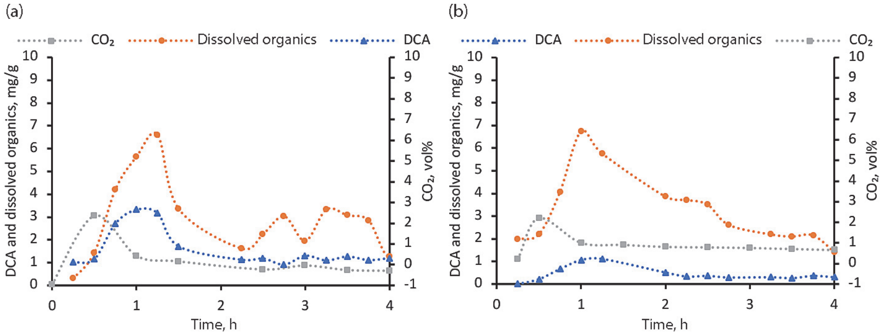

Fig. 5. K-70 dissolution in the trickle-bed reactor: (a) corresponds to exp 2 and (b) to exp 6 in Table 2.

Table 2. Results of K-70 oxidation in the trickle-bed reactor

Exp	T, °C	H_2O, ml/min	Air, ml/min	Time, h	C spent, g	Unreacted C, %	C to CO_2, %[a]	Dissolved organics, mg/g[b]	(C7–C10)/DCA, %
1	150	0.6	400	4	1.08	82	17	37.0	24
2[c]	175	0.6	400	5	3.18	50	19	58.5	8
3	175	0.6	100	4	1.43	78	24	16.2	12
4	175	0.3	100	4	1.31	78	38	23.6	n.d
5	175	0.9	20	8	0.79	87	33	31.6	n.d
6[c]	200	0.6	400	4	2.88	52	22	45.7	n.d
7	200	0.3	100	4	1.24	79	57	18.6	13

[a] on the basis of spent carbon; [b] on the basis of initial oil shale (10 g); [c] 10% acetic acid solution was used instead of pure water. Abbreviation: Exp – experiment.

Table 2, exp 2 and exp 6). The process proceeded with two different reaction rates – the fast initial step and the subsequent slow period. Based on the structure of kerogen [2, 3], it may be suggested that the active groups on the surface of kerogen react first and then mass transfer becomes a limiting factor driving the reaction rate down. It was concluded that the used trickle-bed set-up was not applicable as a base of this process.

3.4. Further valorization of dissolved organics

The dissolved kerogen organics sample contained ~20–30% of DCAs on average. The rest was a mixture of monocarboxylic acids, branched and polycarboxylic acids, alcohols and ethers with various carbon skeletons (for more details, see [24]). Fractional distillation under the reduced pressure of nonderivatized DCAs directly from this mixture was unsuccessful due to the relatively high boiling points of carboxylic acids. Only the DCAs with the lowest boiling points (C4 and C5) were separable by distillation.

In order to evaluate whether the amount of DCAs would increase with additional oxidation, the mixture from the WAO process (free of inorganic salts) was further oxidized with a 4 MPa O_2/N_2 mixture at 175 °C for 3 hours in the presence of 40 wt% KOH or K_2CO_3 to increase the solubility of the isolated organics in the reaction medium. We found that the amount of DCAs increased by 30% of their initial value, while the total amount of dissolved organics decreased by more than 50% due to the additional CO_2 formation. The decomposition of dissolved organics to CO_2 was too extensive to consider the uncatalyzed WAO process in an alkaline medium as a feasible route to increase the DCA yield. To prove that the dissolved organics have the potential to yield additional DCA, the isolated dissolved organics were subjected to oxidation using nitric acid as an oxidant [17]. Applying 5 ml of 65% HNO_3 per 1 g of dissolved organics at 80 °C for 3 hours, the amount of DCAs in the product increased by 125%. As shown in Figure 6, the product contained less isomeric DCAs after nitric acid oxidation. The result proves that a substantial part of the dissolved organics can be converted into DCAs, which increases the value of the product.

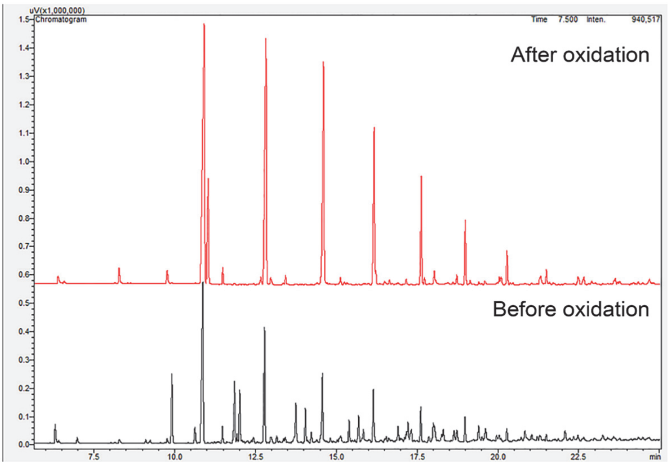

Fig. 6. GC-FID chromatogram of solubilized organics before and after the HNO_3 oxidation.

3.5. DCA destruction in the presence of oil shale

It has been previously shown that the distribution of DCAs in the product is affected by the initial kerogen concentration of oil shale. Thus, when a native oil shale with a kerogen concentration of 45% (K-45) was oxidized, the total DCA fraction contained up to 40% of long-chain DCAs (C6–C10). For K-70 and K-90, the amount of C6–C10 DCAs was 14% and 7%, respectively [24]. It has also been demonstrated that pure DCAs are relatively stable in water up to 175 °C or higher, but the presence of bases or organic co-oxidants induces their decomposition [32]. Therefore, the decomposition of the formed products is an essential factor when adapting the WAO process to oil shale to obtain DCA.

To understand the catalytic effect of oil shale and its components on DCA decomposition, we conducted experiments in which the stability of long-chain DCAs was monitored at WAO conditions. Thus, each dicarboxylic acid in the C6–C10 range was weighed into a reactor together with oil shale and water, and its recovered amount was measured after stirring at 175 °C, with 4 MPa of O_2/N_2 (50/50) for 3 h. The obtained value of each DCA was corrected with an average value of DCA obtained from oil shale in these conditions. The data in Table 3 reveal that all oil shale concentrates affected DCA decomposition. The oil shale concentrate with the highest organic matter content (K-90) affected the decomposition of DCA the most, and no long-chain DCAs (C9–C10) were left after a 3 h time (Table 3, exps 4–6). It is noticeable that the mineral part of oil shale (mineral ash from previous oxidation – "ox. ash" and ash from electrostatic filters of oil shale power station – "ESP ash") hindered DCA decomposition in comparison with "no additive" cases (Table 3, exps 1–3). On the other hand, in the presence of oil shale, selected inorganic salts or bases did not reduce DCA decomposition significantly (2–7% increase in recovery;

Table 3. The effect of additives on DCA (C6-C10) decomposition in the WAO process[a]

Exp	Additive	Overall recovery, %	C6	C7	C8	C9	C10
1	–	95	100	98	96	92	89
2	ESP ash	97	96	96	95	97	100
3	Ox. ash	98	99	99	99	98	97
4	K-45	40	70	54	35	23	16
5	K-70	30	74	50	18	6	2
6	K-90	22	76	31	4	0	0
7	K-70 + $Ca(OH)_2$	47	73	60	43	31	27
8	K-70 + K_2CO_3	35	72	44	29	18	11
9	K-70 + $CaCO_3$	34	64	46	28	18	13
10	K-70 + CH_3COOH	21	58	27	15	2	0
11	K-70 + 5-Me-resorcinol	13	43	17	3	2	1
12	K-45 + K_2CO_3	45	75	55	41	30	23
13	K-45 + $CaCO_3$	36	62	46	31	22	16
14	K-45 + CH_3COOH	33	77	49	25	11	3
15	K-45 + KOH	32	62	41	27	18	12

[a] Reaction conditions: T = 175 °C, P = 4 MPa of the 50/50 O_2/N_2 mixture, time = 3 h, oil shale or its concentrate in c = 20 g/L. * Ox. ash – ash separated after WAO experiment; ESP ash – fly ash from electrostatic precipitator filters of oil shale power station.

Table 3, exps 7–9, 12–15). We suggest that the high reactivity of DCA in the WAO process is due to the co-oxidation by some kerogen components. As mentioned before, the oxidative decomposition of kerogen is initiated by phenol-type resorcinol moieties [2]. Indeed, the addition of radical generating compounds such as 5-Me-resorcinol substantially increased the decomposition of DCAs (Table 3, exp 11), meaning that this process could have been caused by the presence of resorcinol units in kerogen. Accordingly, the decomposition rate of DCAs is accelerated when oil shale with high organic content and thereby with high resorcinol content is used. This also explains why the final distribution of chain lengths of DCAs observed after the WAO process does not reflect the actual lengths of the aliphatic subunits in the kerogen.

All this makes the choice of optimal conditions for an effective WAO process very important in order to minimize the degradation of the product during the dissolution of kerogen.

4. Conclusions

The oxidation of kerogen to water-soluble organic compounds that can be directly used or upgraded to value-added products should be considered as an alternative direction for improving the oil shale industry. The experimental results of kerogen dissolution under oxidative conditions in subcritical water showed that over 65% of the organic carbon dissolved in about 1 hour at a temperature of 175 °C and a pressure of O_2 of 2 MPa.

A direct dependence of kerogen transformation on the oxidant amount at different oil shale concentrations was observed. To avoid excessive oxidation of dissolved organics and high CO_2 formation, the kerogen oxidation process should be conducted with the shortest possible reaction times with excess oxygen. It was demonstrated that the minimum working temperature of the process is 165 °C.

The decomposition of dicarboxylic acids, the most valuable products of dissolved organics, strongly depends on the oil shale organic matter content. Oil shale with the highest degree of kerogen induced the decomposition of DCAs the most. It was also shown that the amount of DCAs in the mixture of dissolved organics can be doubled by additional oxidation with nitric acid.

The application of a semi-continuous process using a trickle-bed reactor did not improve the yield of dissolved organics and the method was considered unsuitable for kerogen dissolution.

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REFERENCES

1. Derenne, S., Largeau, C., Casadevall, E., Sinninghe Damsté, J. S., Tegelaar, E. W., de Leeuw, J. W. Characterization of Estonian Kukersite by spectroscopy and pyrolysis: Evidence for abundant alkyl phenolic moieties in an Ordovician, marine, type II/I kerogen. *Org. Geochem.*, 1990, **16**(4–6), 873–888.
2. Blokker, P., Van Bergen, P., Pancost, R., Collinson, M. E., De Leeuw, J. W., Sinninghe Damste, J. S. The chemical structure of Gloeocapsomorpha prisca microfossils: implications for their origin. *Geochim. Cosmochim. Acta*, 2001, **65**(6), 885–900.
3. Lille, Ü., Heinmaa, I., Pehk, T. Molecular model of Estonian kukersite kerogen evaluated by ^{13}C MAS NMR spectra. *Fuel*, 2003, **82**(7), 799–804.
4. Lille, Ü. Current knowledge on the origin and structure of Estonian kukersite kerogen. *Oil Shale*, 2003, **20**(3), 253–263.
5. Behling, R., Valange, S., Chatel, G. Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: What results? What limitations? What trends? *Green Chem.*, 2016, **18**(7), 1839–1854.
6. Demesa, A. G., Laari, A., Turunen, I., Sillanpa, M. Alkaline partial wet oxidation of lignin for the production of carboxylic acids. *Chem. Eng. Technol.*, 2015, **38**(12), 2270–2278.
7. Kindsigo, M., Kallas, J. Degradation of lignins by wet oxidation: model water solutions. *Proc. Est. Acad. Sci. Chem*., 2006, **55**(3), 132–144.
8. Cherubini, F., Stromman, A. H. Chemicals from lignocellulosic biomass: opportunities, perspectives, and potential of biorefinery systems. *Biofuel. Bioprod. Bior.*, 2011, **5**(5), 548–561.
9. Wang, Z., Yan, J., Wang, T., Zai, Y., Qiu, L., Wang, Q. Fabrication and properties of a bio-based biodegradable thermoplastic polyurethane elastomer. *Polymers*, 2019, **11**(7), 1–13.
10. Cornils, B., Lappe, P. Dicarboxylic acids, aliphatic. In: *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2000.
11. Yuan, W.-G., Liu, G.-L., Huang, C., Li, Y.-D., Zeng, J.-B. Highly stretchable, recyclable, and fast room temperature self-healable biobased elastomers using polycondensation. *Macromolecules*, 2020, **53**(22), 9847–9858.
12. Kallemets, K. Economic sustainability of Estonian shale oil industry until 2030. *Oil Shale*, 2016, **33**(3), 272–289.
13. Veski, R., Veski, S. Aliphatic dicarboxylic acids from oil shale organic matter –

historic review. *Oil Shale*, 2019, **36**(1), 76–95.

14. Durand, B. *Sedimentary Organic Matter and Kerogen: Definition and Quantitative Importance of Kerogen.* Editions Technip., Paris, 1980.
15. Degtereva, Z., Fomina, A. Production of dibasic acids C4-C10 from oil shale kukersite. *Acad. Sci. Est. SSR*, 1959, **8**(2), 122–136 (in Russian).
16. Pobul, L., Fomina, A. Purification and fractionation of mixtures of saturated dicarbonic acids obtained by the oxidation of kukersite kerogen. *Acad. Sci. Est. SSR*, 1962, **11**(3), 203–211 (in Russian).
17. Fomina, A., Pobul, L., Degterjowa, S., Veski, R., Kirret, O., Nikopensius, I., Männik, A., Pärn, A., Poom, A., Murumets, K., Ulanen, J., Tänav, I., Kotov, A. *Method for Processing Causticobiolites of the Sapropelite Type with an Oxidizing Agent*. German Patent No. 2259502, 1974.
18. Fomina, A. S., Pobul, L. The deriving of dibasic aliphatic acids from a new raw material. *Acad. Sci. Est. SSR*, 1957, **6**(2), 190–198.
19. Kogerman, P. N. Hundred years of the chemical investigation of an oil shale: the chemical constitution of the Estonian oil shale "Kukersite". In: *Oil Shale and Cannel Coal*. International Petroleum Conference. The Institute of Petroleum, Glasgow, 1938, 115–123.
20. Bajc, S., Amblès, A., Largeau, C., Derenne, S., Vitorović, D. Precursor biostructures in kerogen matrix revealed by oxidative degradation: oxidation of kerogen from Estonian kukersite. *Org. Geochem.*, 2001, **32**(6), 773–784.
21. Proskuryakov, V. A., Soloveichik, Z. V. Oxidation of oil shale by atmospheric oxygen. 1. Oxidation of an aqueous alkaline suspension of Gdov shales in an autoclave. *Tr. Vsesoj. N. I. Instituta po Pererab. i Issl. Topl.*, 1961, **10**, 64–80 (in Russian).
22. Proskuryakov, V. A., Soloveichik, Z. V. Oxidation of oil shale by atmospheric oxygen. 2. Oxidation of Gdov shales with continuous air supply. *Tr. Vsesoj. N. I. Instituta po Pererab. i Issl. Topl.*, 1961, **10**, 81–90 (in Russian).
23. Proskuryakov, V. A., Yakovlev, V. I., Kudrjukov, O. I. Oxidation of oil shale by atmospheric oxygen. 3. Oxidation of common Syrtian shales. *Tr. Vsesoj. N. I. Instituta po Pererab. i Issl. Topl.*, 1962, **11**, 20–27 (in Russian).
24. Kaldas, K., Preegel, G., Muldma, K., Lopp, M. Wet air oxidation of oil shales: Kerogen dissolution and dicarboxylic acid formation. *ACS Omega*, 2020, **5**(35), 22021–22030.
25. Kolaczkowski, S. T., Plucinski, P., Beltran, F. J., Rivas, F. J., McLurgh, D. B. Wet air oxidation: a review of process technologies and aspects in reactor design. *Chem. Eng. J.*, 1999, **73**(2), 143–160.
26. Luck, F. A review of industrial catalytic wet air oxidation processes. *Catal. Today*, 1996, **27**(1–2), 195–202.
27. Bhargava, S. K., Tardio, J., Prasad, J., Föger, K., Akolekar, D. B., Grocott, S. C. Wet oxidation and catalytic wet oxidation. *Ind. Eng. Chem. Res.*, 2006, **45**(4), 1221–1258.
28. Li, L., Chen, P., Gloyna, E. F. Generalized kinetic model for wet oxidation of organic compounds. *AIChE J.*, 1991, **37**(11), 1687–1697.

29. Lin, S. H., Ho, S. J., Wu, C. L. Kinetic and performance characteristics of wet air oxidation of high-concentration wastewater. *Ind. Eng. Chem. Res.*, 1996, **35**(1), 307–314.
30. Sánchez-Oneto, J., Portela, J. R., Nebot, E., Martínez-de-la-Ossa, E. J. Wet air oxidation of long-chain carboxylic acids. *Chem. Eng. J.*, 2004, **100**(1–3), 43–50.
31. *CRC Handbook of Chemistry and Physics, Internet Version 2005* (Lide, D. R., ed.), 2005. http://www.hbcpnctbasc.com
32. Kaldas, K., Preegel, G., Muldma, K., Lopp, M. Reactivity of aliphatic dicarboxylic acids in wet air oxidation conditions. *Ind. Eng. Chem. Res.*, 2019, **58**(25), 10855–10863.

Author’s other publications and conference presentations

Other publications

1. K. Kriis, T. Melnik, K. Lips, I. Juhanson, S. Kaabel, I. Järving and T. Kanger, “Asymmetric synthesis of 2,3,4-trisubstituted piperidines,” *Synthesis*, vol. 46, no. 3, pp. 604−614, 2017.
2. M. Lopp, K. Kaldas, G. Preegel, K. Muldma and A. Niidu, “Oxidative leaching method of oil shale kerogen,” Estonian Patent EE201900020, 2021.

Conference presentations

1. K. Kaldas, J. M. Uustalu, A. Niidu, K. Muldma, G. Preegel, and M. Lopp, Structural consideration of kukersite from air oxidation,” GSFMT Scientific Conference, Tartu, Estonia, 2021. (Oral)
2. K. Kaldas, G. Preegel, K. Muldma, A. Niidu and M. Lopp, “Wet air oxidation of oil shales - factors affecting dicarboxylic acids production,” XI Oil Shale Conference, Jõhvi, Estonia, 2019. (Poster)
3. K. Kaldas, G. Preegel, K. Muldma, A. Niidu and M. Lopp, “Wet air oxidation of oil shales - reactive species affecting dicarboxylic acids production,“ 5th International Congress on Catalysis for Biorefineries (CatBior V), Turku/Åbo, Finland, 2019. (Poster)

Curriculum vitae

Personal data

Name: Kristiina Kaldas
Date of birth: 09.04.1991
Place of birth: Rapla, Estonia
Citizenship: Estonian

Contact data

E-mail: kristiina.lips@taltech.ee

Education

2017–…	Tallinn University of Technology, Chemistry and Biotechnology, Ph.D.
2012–2013	exchange student in the University of Masaryk, field of chemistry
2012–2016	Tallinn University of Technology, Applied Chemistry and Biotechnology (*cum laude*), M.Sc.
2009–2012	Tallinn University of Technology, Applied Chemistry and Biotechnology (*cum laude*), B.Sc.
2006–2009	Rapla Vesiroosi High School (gold medal)

Language competence

Estonian	native
English	fluent
Russian	beginner

Professional employment

2017–…	Tallinn University of Technology, Department of Chemistry and Biotechnology, junior researcher
2016–2017	Tallinn University of Technology, Department of Chemistry and Biotechnology, engineer

Honors and awards

2019	Dora Plus Ph.D student mobility (1.1) Scholarship (The Archimedes Foundation)
2016	Estonian National Contest for University Students, 2nd prize on a field of natural science and technology among master`s students.
2012	Scholarship from Cambrex Tallinn AS

Teaching experience and supervision

2020	supervision of the Bachelor thesis by Jennie-Ry Mesi (School of Engineering, Tallinn University of Technology)
Fall 2019	Organic Chemistry I, exercise tutorials (undergraduate course)

Elulookirjeldus

Isikuandmed

Nimi:	Kristiina Kaldas (end. Lips)
Sünniaeg:	09.04.1991
Sünnikoht:	Rapla, Eesti
Kodakondsus:	eesti

Kontaktandmed

E-post:	kristiina.lips@taltech.ee

Hariduskäik

2017–…	Tallinna Tehnikaülikool, Keemia ja biotehnoloogia, Ph.D.
2012–2013	vahetusõpingud ülikoolis Masaryk, keemia eriala
2012–2016	Tallinna Tehnikaülikool, Rakenduskeemia ja biotehnoloogia (*cum laude*), M.Sc.
2009–2012	Tallinn Tehnikaülikool, Rakenduskeemia ja biotehnoloogia (*cum laude*), B.Sc.
2006–2009	Rapla Vesiroosi Gümnaasium (kuldmedal)

Keelteoskus

eesti keel	emakeel
inglise keel	kõrgtase
vene keel	algtase

Teenistuskäik

2017–…	Tallinna Tehnikaülikool, Keemia ja biotehnoloogia instituut, nooremteadur
2016–2017	Tallinna Tehnikaülikool, Keemia ja biotehnoloogia instituut, insener

Teaduspreemiad ja tunnustused

2019	Doktorantide õpirände stipendium (1.1) (SA Archimedes)
2016	Üliõpilaste teadustööde riiklik konkurss, II preemia magistritööde seas loodusteaduste ja tehnika valdkonnas
2012	AS Cambrex Tallinn stipendium

Õpetamiskogemus ja juhendamine

2020	Jennie-Ry Mesi bakalaureusetöö juhendamine (Energiatehnoloogia instituut, Tallinna Tehnikaülikool)
Sügis 2019	Orgaaniline keemia I, harjutustunnid (bakalaureuseõpe)

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