Proceedings of the Estonian Academy of Sciences,
2014, **63**, 1, 75–85
doi: 10.3176/proc.2014.1.10
Available online at www.eap.ee/proceedings

ENVIRONMENTAL CHEMISTRY

Coupling of resorcinols in retorted kukersite semi-coke

Jaan Habicht* and Uno Mäeorg

Institute of Chemistry, University of Tartu, Ravila 14a, 50141 Tartu, Estonia

Received 15 February 2013, revised 2 August 2013, accepted 6 August 2013, available online 14 March 2014

Abstract. Coupling products of three major phenols appearing in the waste streams of shale oil production from kukersite oil shale were isolated and analysed using high-resolution mass spectrometry (HRMS). The pattern of water-soluble phenols in retorted kukersite semi-coke leachate changes quickly during weathering. The amount of phenols decreases, but the rate of disappearance is dissimilar for different constituents. Oxidation experiments with three major phenols (resorcinol, 5-methyl resorcinol, and 2,5-dimethylresorcinol) and their mixtures in pairs were performed in a reaction medium similar to semi-coke leachate. Reaction products were detected using silica gel thin layer chromatography (TLC) and isolated for further analysis by silica gel dry-column chromatography. The composition of primary reaction products was confirmed by nuclear magnetic resonance (NMR) spectroscopy. The primary coupling products of the studied resorcinols included the corresponding dimeric mono- and diquinones. Further coupling brought about the formation of water-insoluble products, which is the reason for the disappearance of resorcinols from the leachate.

Key words: waste chemistry, retorted kukersite, semi-coke leachate, resorcinol, 5-methylresorcinol, 2,5-dimethylresorcinol, coupling.

INTRODUCTION

The shale oil production process is a resource of many phenols, especially alkyl-resorcinols. The total amount of water-soluble phenols from high unit capacity generators for shale oil production from kukersite (Kiviter process) is over 5.5 kg per tonne of processed shale; for 5-methyl resorcinol it is more than 1.5 kg and for 2,5-dimethyl resorcinol more than 0.4 kg per tonne [1]. These two resorcinols make up more than one third of the total amount of the phenols generated in the process. The phenol patterns of retort water and heavy oil washing water are rather similar. The phenol pattern of the medium-light shale oil fraction differs considerably. The amount of monoatomic phenols makes up less than 3% of the total water-soluble phenols formed during the shale oil production process. The patterns of phenols from different shale oil production processes are also different, but the major compounds are the same.

Oil shale phenols are useful building blocks in polymer chemistry, particularly in the preparation of phenol formaldehyde resins [2]. On the other hand, these phenols appear in production waste, which can result in severe environmental pollution. The solid waste of shale oil production from lumpy kukersite oil shale – semi-coke – has been deposited in embankments neighbouring production facilities. The environmental hazardousness of retorted oil shale has been largely attributed to phenols found in semi-coke, particularly the water-soluble fraction of these compounds [3].

Co-disposal of semi-coke with process water (wet deposition) was legally used in Estonia until the end of the 20th century. For a long time phenols originating from the process water caused significant pollution in the whole shale oil production region. The management scheme of retorted kukersite semi-coke was changed at the beginning of the new millennium. Process water was not allowed to be added to semi-coke, and semi-wet retort residue was transported to a deposition area. As semi-coke had been associated with phenols for ages, no special attention was paid to the continuous appearance

* Corresponding author, jaan.habicht@ut.ee

of phenols in the leachate. Our earlier study of the origin of these phenols showed that most of them still originate from the process water added to the waste residue and even from the groundwater that had been contaminated with phenols before it was used for cooling the semi-coke [4].

The existing literature describes oxidation of phenols in different conditions [5]. The first experiments on the oxidizability of oil shale phenols were carried out 50 years ago. The practical effort already then focused on the treatment of shale oil industry wastewater. In their early studies Kirso and her colleagues studied the oxidation kinetics of alkyl-substituted phenols with molecular oxygen in an alkaline and neutral aqueous environment [6–8]. Experiments were performed with phenol, cresols, 2,4,6-trichlorophenol, *o*- and *p*-benzylphenols, and 1-naphtol in the temperature range 30–80 °C and the pH range 9.5–13. A rise in the temperature accelerated the oxidation of all the phenols studied. Functional group analysis of the products showed that the formation of the carbonyl group and aliphatic carboxylic acid is predominant at lower temperatures and higher pH. In most of the studied phenols the polymer formation rate, which was counted from the rise in the optical density of the samples, was higher at higher temperatures and the medium pH range. The oxidation rate of substituted phenols is higher, but it also depends on the molecular structure of the particular phenol [8]. Experiments were also performed with real retort water from tunnel ovens and from an experimental plant of solid head carrier (SHC) technology. According to the data of functional group analysis of reaction products, phenols with initial concentrations 0.2–0.3 g-eq/L were oxidized to the corresponding quinones and carboxylic acids in 4-hour experiments at 40 °C and pH 12.8. The share of polymers amongst the reaction products was found to be rather low, and the decomposition rate of phenols exceeded 40% in both experiments [6].

As oxidation is widely used in the dephenolization of retort water, wastewater of the process contains oxidation products of phenols. Oxidation of oil shale phenols in close to natural conditions has also been studied. Trapido and Gubergrits studied the kinetics of oxidation and photooxidation of resorcinol and 5-methylresorcinol in distilled water and in model Baltic Sea water [9]. They found no difference in the oxidation kinetics of the process in different water media. In the photooxidation experiments the oxidation rate was much higher in both types of water (up to 3 magnitudes), but four times lower in the seawater. The initial concentration of resorcinol and 5-methylresorcinol in the experiments was 0.18 mmol/L. The concentration of the remaining resorcinols was determined spectrophotometrically, and the samples were analysed by thin layer chromatography (TLC). Formation of polymeric products was expected, as some material was also detected at the start line of TLC plates.

Mamedov and co-workers studied the oxidation of resorcinol in an alkaline medium [10]. They found that 1.33 mol/L of resorcinol in an equimolar sodium hydroxide water solution that was purged with oxygen reveals oligomeric products that can be characterized as dark brown or black tar-like compounds, soluble in polar organic solvents.

Oxidation of phenolic compounds in ozonation and photo-catalytic oxidation processes of wastewaters from shale oil production was studied by Preis et al. [11]. The photo-oxidative treatment of phenolic solutions was found to be more effective in acidic and strongly alkaline media. Methylated phenolic compounds yield better to photo-oxidation than non-methylated compounds. The authors also measured the decrease in phenol concentration in their experiments; however, no additional information is available about the oxidation products.

Kamenev and co-workers investigated changes in the phenol content of biologically and chemically treated wastewater of the vertical retort and SHC process [12]. These authors propose biological oxidation in combination with ozonation as a prospective method for an efficient phenolic effluent treatment. Since phenols are relatively reactive compounds, they can participate in many sequential reactions, where the end products are highly condensed and oxidized. The condensation reactions of oil shale phenols have been studied far more in connection with synthesis than with environmental chemistry.

Christjanson and co-workers studied the condensation reactions of *o*- and *p*-cresols [13]. They found that the coupling of resorcinols is very complicated and produces a complex mixture of compounds. The same authors studied also self-condensation of *o*- and *p*-methylolphenols and their co-condensation with phenol [14]. A mechanism for alkali-catalysed condensation was ascertained, and the structure of the polycondensate from hydroxymethylphenols was studied in [15]. The mechanism of the reaction and the structure of resol resin in alkaline conditions are dependent on phenoxide ions.

Musso and co-workers carried out basic and experimental studies on phenol oxidation reactions, including autoxidation of 5-methylresorcinol and 2,5-dimethylresorcinol in ammonia and potassium hydroxide [16,17]. According to their results, the autoxidation products of 2,5-dimetylresorcinol in ammonia are dyes analogous to those forming from 5-methylresorcinol (orcinol). Autoxidation of 2,5-dimethylresorcinol is faster and yields oxidized products, which are more stable than those of 5-methylresorcinol oxidation. Autoxidation of both resorcinols in potassium hydroxide solution reveals dimeric mono- and diquinone (Fig. 1) and additionally a trimeric diquinone, which was not detected in a 5-methylresorcinol autoxidation mixture. The oxidation

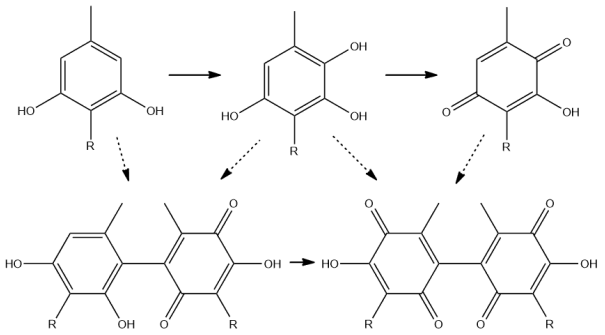

Fig. 1. Oxidation and coupling of 5-methylresorcinol (R═H) and 2,5-dimethylresorcinol (R═CH_3) in potassium hydroxide solution as described by Musso [18].

of orcinol with potassium ferricyanide in alkaline solution produces a mixture of polymers [18]. Coupling, which leads to corresponding biphenyl formation, occurs when orcinol anion is added to hydroxylquinone.

Dimeric diquinone is formed both as a result of further oxidation of the dimeric monoquinone and when hydroxylated resorcinol reacts with quinone.

Although oxidation of oil shale phenols has been studied from different aspects, little is still known about processes occurring in the waste residue. The aim of this study was to investigate the chemistry behind the disappearance of water-soluble phenols and particularly resorcinols from retorted kukersite semi-coke. Our field experiments showed quick disappearance of particular resorcinols from the semi-coke leachate. In our laboratory experiments, we first studied changes in the phenol composition of semi-coke leachate, then performed experiments where phenols were added to the leachate, and finally made experiments in a medium consisting of the main inorganic constituents of semi-coke leachate and the particular resorcinols. Oxidation products of resorcinols were detected directly from samples extracted from reaction mixtures or those fractioned by silica gel chromatography. At first we only wanted to identify the primary coupling products of resorcinol, 5-methylresorcinol, and 2,5-methylresorcinol, which we had detected in the retorted kukersite semi-coke leachate. However, in fact, we succeeded in hitting more than 50 new compounds when analysing the reaction mixtures of the laboratory oxidation and coupling experiments.

MATERIALS AND METHODS

The semi-coke samples used in the study originated from the shale oil production company Kiviõli Keemiatööstus, Estonia. The samples were collected from the water-sealed discharge system of the gaseous heat carrier retort as sub-samples of about 1 kg and mixed into one composite sample (12–13 kg). Since the Kiviõli plant utilizes only partly enriched lumpy oil shale for shale oil production, the waste contains a considerable amount of limestone. Larger limestone particles (>5 cm in diameter) were not incorporated in the composite sample. The samples were kept in closed polyethylene buckets. After the storage buckets were closed, the air was blown out using argon to prevent oxidation and carbonatization processes. The samples used for water content and dry weight estimations were dried for 24 h at a temperature of 105 °C. In the laboratory weathering experiments the semi-coke portions (500 g as dry weight) were placed in polyethylene boxes. The samples were kept uncovered at room temperature (20 ± 1 °C) and irrigated daily with distilled water to retain the initial moisture content (30 ± 2%). For leachate collection, distilled water was added to semi-coke in a ratio 1 L/kg, the boxes were closed with a cover, and stored for additional 24 hours. Leachate was collected and filtered through a glass-fibre filter S 200 (Sartorius).

The batch leaching tests were carried out by means of the compliance test for the leaching of granular waste materials according to the Estonian standard EVS-EN 12457 [19]. Distilled water was added to the 500 g (as dry weight) semi-coke samples in a ratio 2 L/kg (liquid : solid ratio L/S 2 : 1). Mixing was performed by rolling the samples in closed plastic bottles for 24 hours in a laboratory roller mixer. After solid phase sedimentation the leachate was collected, filtered, and stored in closed laboratory bottles. In multiple-stage leaching tests the sample was weighed for true dilution calculation, distilled water was added in a ratio of L/S 2 : 1, and the procedure was performed repeatedly.

In the experiments where resorcinols were added to semi-coke, the leachate of an 8-week-aged semi-coke sample was collected. Resorcinols were added as water solution to adjust the final concentration to 10 mmol/L, and the leachate was poured back on the semi-coke sample. In 1 hour the excess liquid was poured off the semi-coke, the samples were stored in open boxes, and the leachate was collected as in the other weathering experiments.

In the model experiments for the detection and analysis of primary coupling products, saturated calcium hydroxide solution was prepared as the reaction medium at room temperature, filtered, and 1 M potassium hydroxide solution was added to reach pH 12.6. Resorcinols were added to 250 or 500 mL of the reaction medium in glass flasks to a final concentration of 4 mmol/L. Air was purged through the solution (approximately 1 volume per minute) at room temperature. As the pH of the reaction medium drops due to carbonatization, KOH solution was added to the reaction mixture to retain the initial pH.

Before extraction, the pH of the samples was lowered to 4 with HCl. Phenols were extracted with 0.3

volume ethyl acetate. For preparative extraction of samples containing resorcinol, the pH was lowered to 1.5. The extraction samples were dried with sodium sulphate and concentrated at room temperature if necessary by purging argon through the samples.

Silica gel TLC was used for the detection and silica gel column chromatography for the preparative separation of resorcinols and their oxidation and coupling products. A simple semi-quantitative TLC separation protocol was worked out for the detection and separation of the studied phenolic compounds. The TLC analyses were carried out on 0.5 mm silica plates (Kieselgel 60 F254, Merck) and 0.2 mm improved resolution silica sheets (Alugram®Sil G/UV$_{254}$, Macherey-Nagel). The plates and sheets were cut into 10-cm tall pieces of desired width. Samples of 2–5 μL were applied to the plate and eluted with hexane/ethyl acetate (7 : 3 vol/vol). The plates were dipped in potassium permanganate solution (0.1–0.2%) to visualize the uncoloured spots and photographed after drying in air. Preparative dry-column chromatography was carried out on silica gel (Merck Kieselgel, 70–320 mesh). Silica gel columns of 10 cm height were prepared in dialysis membrane tubing (diameter 15 or 28 mm). The samples were mixed with silica gel, dried in air, transferred to the top of the column, and covered with a thin silica gel layer. The columns were eluted with hexane/ethyl acetate (7 : 3 vol/vol) till the eluent reached the bottom of the column and then cut into 1-cm segments for the separation of different chromatography fractions. Coupling products were eluted from silica gel with ethyl acetate and analysed by TLC.

The composition of primary reaction products was confirmed by nuclear magnetic resonance (NMR) spectroscopy. The ^{1}H NMR spectra were recorded at 200 MHz and the ^{13}C NMR spectra at 50 MHz on a Bruker AC 200P spectrometer in DMSO-D$_6$. High-resolution mass spectrometry (HRMS) of the samples was carried out on an LTQ Orbitrap mass spectrometer. Samples diluted 1 : 1 with acetonitrile were injected.

RESULTS AND DISCUSSION

The results of the laboratory leaching test of semi-coke samples are presented in a TLC chromatogram (Fig. 2). There are drastic differences in the phenol patterns of the semi-coke leachate collected 24 hours, 1 week, and 8 weeks from the beginning of the weathering experiment (lanes 1, 2, and 3, respectively). Three resorcinols – 5-methylresorcinol, 2,5-dimethylresorcinol, and resorcinol – were the major phenols in the leachate of the fresh semi-coke sample collected after 24 hours (lane 1). The composition of a 1-week-old leachate was different from that of the fresh semi-coke and contained some new components (lane 2). The 8-week sample

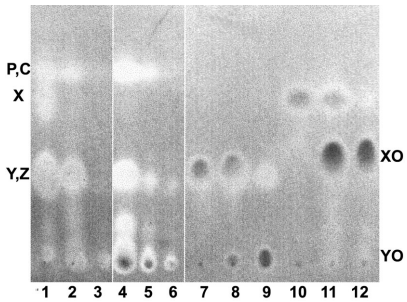

Fig. 2. TLC chromatogram of extracts of semi-coke leachates on silica plates. The mobility of the following constituents is marked: P – phenol; C – cresols; X – 2,5-dimethylresorcinol; Y – 5-methylresorcinol; Z – resorcinol; XO and YO are X and Y coupling products, respectively.

leachate contained only traces of the initial phenols (lane 3). The phenol pattern of fresh 24-hour semi-coke leachate was very close to that of oil wash water, which we had previously analysed, where 5-methylresorcinol was the major water-soluble organic constituent. Control experiments with semi-coke samples where distilled water was added in a ratio of 1 L/kg and the samples were stored in closed polyethylene boxes for the same time periods as in the weathering experiments showed no change in the phenol pattern of the leachate. Oxidation and coupling do not occur when air, and particularly oxygen, has no access to semi-coke.

Semi-coke batch leaching tests were performed to see if there was any sign of sorption of phenols to semi-coke. The result of the laboratory batch leaching test is shown in Fig. 2, lanes 4–6. A triple leaching test (L/S 2 : 1) was performed with the 1-week-old semi-coke sample. The three consecutive leachates show a comparable decrease in the concentration of phenols. Our tests clearly showed that the phenols were predominantly in the water phase, and no considerable accrual of phenols from the semi-coke residue could be detected. Dilution of phenols in the batch leaching test was proportional to the eluent volume or even higher due to the ongoing oxidation of phenols, which we could not completely avoid. Lanes 7–12 of Fig. 2 present the results of the experiments where 5-methylresorcinol or 2,5-dimethylresorcinol was added to the semi-coke leachate, applied to semi-coke and the eluates were collected daily during one week. The initial, day 2, and day 7 chromatograms of the eluate samples with 5-methylresorcinol are on lanes 7, 8, and 9, respectively. A decrease in the concentration of 5-methylresorcinol and the appearance of a product marked YO can be followed. 2,5-Dimethylresorcinol (initial sample, lane 10) reacted much more quickly (day 1 sample, lane 11) and practically disappeared in 2 days (lane 12). It also yielded one product on the used TLC plates, which is marked XO. TLC sheets with improved resolution were used for a more detailed analysis of conversion products of resorcinols.

Table 1. Preparation of samples for NMR spectroscopy and HRMS

Sample	Initial composition	Reaction time, h	Separation procedure
X	2,5-Dimethylresorcinol	24	Extraction, concentration
X1	2,5-Dimethylresorcinol	20	Extraction, concentration, silica gel chromatography
X2	Product isolated from sample X1	20	Extraction, concentration, silica gel chromatography
Y	5-Methylresorcinol	96	Extraction, concentration, silica gel chromatography
Z	Resorcinol	72	Extraction, concentration
XY	2,5-Dimethylresorcinol, 5-Methylresorcinol	24	Extraction, concentration, silica gel chromatography
XZ	2,5-Dimethylresorcinol, Resorcinol	24	Extraction, concentration, silica gel chromatography
YZ	5-Methylresorcinol, Resorcinol	72	Extraction, concentration

Table 1 provides information on the preparation of samples for NMR spectroscopy and HRMS analyses. Reaction time was chosen according to the results of analytical experiments in order to obtain a maximum amount of reaction products for further analysis. Samples X1, X2, and XY were analysed using NMR spectroscopy, and samples X, Y, Z, XY, XZ, and YZ were analysed using HRMS.

The concentration of the resorcinols in the model experiments was chosen in the range of the highest total phenol concentration that we had previously detected in the fresh semi-coke leachate. It differs significantly from the phenol concentrations used for kinetic studies and oxidation experiments in the cited literature. The reason for this is understandable: to study the chemical processes in retorted kukersite we followed the concentration of the major phenolic constituents in the waste.

The reaction medium consisted of two major inorganic components in the semi-coke leachate. For a better comparison of the experimental data, the initial concentration of every single resorcinol in the oxidation experiments was 4 mmol/L. The initial concentration of the primary reaction product in sample X1, which was further oxidized, was 500 mg/L. The purity and identity of the extracted products were first determined using TLC.

A TLC chromatogram of 2,5-dimethylresorcinol oxidation and coupling is presented in Fig. 3. Lanes 1–5 are 16-, 24-, 48-, 72-, and 120-hour samples of the reaction mixture extract, respectively. Oxidation of 2,5-dimethylresorcinol revealed two major products in our experimental conditions. Analysis of the samples showed that the reaction product marked later X dimeric rq was accumulated first and converted to another product marked X dimeric qq. These two alkaline coupling products of 2,5-dimethylresorcinol were first described by Musso and co-workers, who performed oxidation experiments with 2,5-dimethylresorcinol (400 mmol/L) in potassium hydroxide (800 mmol/L) water solution [17]. They suggested that dimeric diquinone (X dimeric qq)

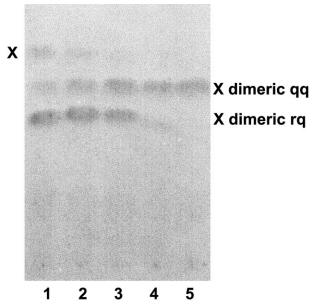

Fig. 3. TLC chromatogram of 2,5-dimethylresorcinol (X) oxidation and coupling products on silica sheets. The analysed products are marked on the right.

can form in the oxidation of dimeric monoquinone and in the reaction of hydroxylated resorcinol with quinone. In our experiment we could follow the oxidation of the dimeric monoquinone; this is supposedly the main reaction in our conditions.

Figure 4 shows a TLC chromatogram of the primary coupling products extracted from the reaction mixtures. The reaction mixtures initially contained 4 mM/L of 2,5-dimethylresorcinol or 5-methylresorcinol and the mixtures with two resorcinols 4 mM/L of 2,5-dimethyl-

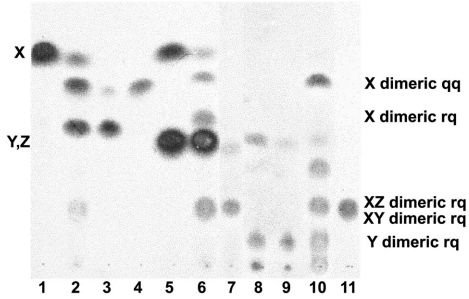

Fig. 4. TLC chromatogram of 2,5-dimethylresorcinol (X), 5-methylresorcinol (Y), and resorcinol (Z) primary coupling products on silica sheets. The analysed products are marked on the right.

resorcinol and resorcinol or 2,5-dimethylresorcinol and 5-methylresorcinol.

As the number of the identified reaction products increased quickly, and the IUPAC nomenclature was of no help for describing the structural similarities of the found compounds, we introduced a labelling code system for the description of the studied products and product families. In this labelling system, X corresponds to 2,5-dimethylresorcinol and its oxidation products, which form the coupled molecules; Y corresponds to 5-methylresorcinol; Z to resorcinol; and XY, XZ, and YZ to the coupling products of the corresponding resorcinols and their primary oxidation products – hydroxyquinones and quinones in pairs; r, h, and q in a name correspond to resorcinol, hydroxylated resorcinol, and quinone in the coupled molecule, respectively.

2,5-Dimethylresorcinol (lane 1) yielded two major oxidation products in a 20-hour reaction mixture extract (lane 2). We used sample X (Table 1) for the isolation of the primary reaction product marked X dimeric rq, lane 3. In the subsequent reaction the primary coupling product X dimeric rq revealed the product marked X dimeric qq (lane 4). 2,5-Dimethylresorcinol together with resorcinol, lane 5, gave two coupling products of 2,5-dimethylresorcinol in a 24-hour reaction mixture, the same as on lane 2, and a product that was separated by silica gel chromatography (lane 7) and identified as XZ dimeric rq. Lanes 8 and 9 show the chromatogram of a 96-hour oxidation and coupling reaction product of 5-methylresorcinol and the main product isolated by silica gel chromatography marked Y dimeric rq. The product marked as XY dimeric rq (lane 11) was one of the primary reaction products isolated in the preparative scale from the reaction mixture of 2,5-dimethylresorcinol together with 5-methylresorcinol (lane 10).

All TLC experiments were performed in similar elution conditions using hexane and ethyl acetate mixture (70 : 30 vol/vol) as the eluent. TLC has been used for chemical class separation of shale oil components, including phenols [20], for quantitative analysis of substituted phenols [21], and also for the detection of oil shale resorcinol derivatives [9]. The eluent composition varies depending on the objective. Our simple protocol with hexane/ethyl acetate as the eluent was developed to be used for TLC separation and detection of coupling products of resorcinols, as well as for silica gel column chromatography. Resorcinol, 5-methylresorcinol, and 2,5-dimethylresorcinol are colourless; the primary coupling products are coloured. We still used potassium permanganate solution for more consistent visualization of the spots in the TLC separation, which allowed semi-quantitative estimation of the proportions of particular constituents. As all the studied primary oxidation products were separable in the elution conditions used, very close mobility of 5-methylresorcinol and resorcinol in TLC was not a problem.

Table 2 presents ^{13}C NMR spectra of three coupling products. The results of NMR analysis confirmed the earlier data of Musso and Rathjen [16]. The identified products of the coupling reaction are quinones. The two major oxidation products of 2,5-dimethylresorcinol are dimeric monoquinone (X dimeric rq) and dimeric diquinone (X dimeric qq). The present study showed that both quinones were stable and could be isolated from the reaction mixture.

We also analysed the NMR spectrum of one of the major primary coupling products in the reaction mixture, i.e. 2,5-dimethylresorcinol together with 5-methylresorcinol (Fig. 4, lane 11), and can confirm that we isolated a dimeric monoquinone consisting of 2,5-dimethylresorcinol and 5-methylresorcinol moieties. Another coupling product, which had a higher mobility in our TLC eluent, can also be detected in the chromatogram (Fig. 4, lane 10). Following the evolution scheme of the same product as in 2,5-dimethylresorcinol coupling, we may suggest that this product is an oxidation product of the dimeric monoquinone XY dimeric rq, the corresponding dimeric diquinone.

We used NMR also to analyse a few other reaction products from other reaction mixtures, but faced difficulties dissolving the samples in d_6-dimethyl sulphoxide. This was one reason why we found it rational to study the composition of the reaction mixtures by HRMS. The results show the capability of the particular HRMS procedure to detect coupled resorcinols. We will try to refrain from any quantitative comments on the HRMS results. Apparently, the major coupling products detected by TLC correspond to HRMS mass peaks with

Table 2. ^{13}C NMR spectra of oxidation and coupling products of 2,5-dimethylresorcinol and 2,5-dimethylresorcinol together with 5-methylresorcinol

Sample	C_{methyl}		$=C_{arH}$	$=C_{ar}–$					$C_{carbonyl}$		Composition
X1	8.16	8.71	107.90	108.02	112.76	116.59	132.99	139.64	183.60	186.60	Dimeric monoquinone
	12.60	19.30		141.86	152.46	152.85	155.62				(X dimeric rq)
X2	7.81	12.58	–	116.35	138.11	138.93	153.39		182.47	185.47	Dimeric diquinone
											(X dimeric qq)
XY	8.02	12.40	100.27	112.47	116.70	137.20	138.95	142.41	183.72	186.55	Dimeric monoquinone
	19.40		107.93	152.76	155.00	157.84					(XY dimeric rq)

the highest intensity. Three major initial coupling products of 2,5-dimethylresorcinol are dimeric monoquinone, dimeric diquinone, and trimeric diquinone. The 5-methylresorcinol coupling revealed only one major product that we could detect by TLC, identified as dimeric monoquinone (Y dimeric rq) and not a dimeric diquinone (Y dimeric qq), which however was detected by HRMS. Musso and Rathjen [16] described five autoxidation products of 2,5-dimethylresorcinol and 5-methylresorcinol corresponding to dimeric monoquinones marked X and Y dimeric rq, dimeric diquinones marked X and Y dimeric qq, and the trimeric diquinone X trimeric rq. However, we identified additionally many more new oligomeric structures. Reaction products with similar molecular structures were found in the reaction mixtures of different resorcinols and their mixtures. Table 3 presents the molecular formulas and the proposed molecular structures of the coupling products detected by HRMS. We looked for molecular ions $[M+H]^+$ as well as $[M+Na]^+$. For some molecular structures we did not detect $[M+H]^+$ molecular ions, or the intensity of the particular $[M+Na]^+$ molecular ion was much higher. Therefore Table 3 shows the masses corresponding to $[M+Na]^+$. The HRMS results confirmed our hypothesis that similar molecular structures were formed in the coupling of all the studied resorcinols and their mixtures. However, the exact molecular structure behind the molecular formula and the mass detected can not always be determined.

The HRMS data need not provide information about the sequence of different resorcinol moieties in the detected oligomeric molecules. The reaction products form product families in paired mixtures. The mass peak remains the same while the composite molecules and their sequence in the oligomeric structure can be different. One can only suggest the structures that are formed preferentially because of the different reaction capability of the constituent molecules.

The mass peaks corresponding to dimeric molecules consisting of resorcinol and quinone (dimeric rq) and hydroxylated resorcinol and quinone (dimeric hq) were detected in the reaction mixtures of all three resorcinols. While dimeric diquinone (dimeric qq) was detected in 2,5-dimethylresorcinol and 5-methylresorcinol oxidation mixtures, dimeric hydroxylated resorcinol (dimeric hh) occurred only in the reaction mixture of 2,5-dimethylresorcinol. In paired mixtures dimeric rq and dimeric hq were found again in all three samples. Trimeric and tetrameric structures were found in the reaction mixtures of 2,5-dimethylresorcinol and 5-methylresorcinol. We could not detect any trimeric structures in the reaction mixture of 2,5-dimethylresorcinol together with 5-methylresorcinol.

Tetrameric structures were found; they consist of two or three 2,5-dimethylresorcinol and two or one 5-methylresorcinol moieties, respectively. Besides C–C coupled oligomeric structures we also found high-intensity mass spectra peaks corresponding to tetrameric, pentameric, and hexameric molecules, which formed in the C–O coupling reaction or even two or three C–O coupling reactions. We describe hexameric structures in the paired reaction mixtures of 2,5-dimethylresorcinol together with 5-methylresorcinol and resorcinol, which contain three or four 2,5-dimethylresorcinol moieties and three or two 5-methylresorcinol or resorcinol moieties, where C–O coupling has occurred, listed as 3X3Y, 3X3Z, 4X2Y, and 4X2Z hexameric hq O. Such molecular structures are grouped separately from C–C coupled molecules in Table 3. The C–O coupling of resorcinols was also suggested by Musso and co-workers [17,18], but no particular structures were described. We detected coupling products of one of the resorcinols also in the reaction mixtures of resorcinols in pairs. We also found mass peaks of molecular structures that should have a third quinone in the molecule (marked qqq). We presented masses to molecular formulas of some proposed molecular structures characteristic of different product families if one of the identification criteria, mass accuracy or peak intensity, was not completely fulfilled. These molecular formulas and the measured molecular ion masses are shown by regular font in Table 3. In an alkaline medium, resorcinols are oxidized in the presence of oxygen. The primary products of oxidation are the corresponding hydroquinones and quinones. In order to detect the initial oxidation products of resorcinols, which provide a poor molecular ion signal in the positive ionization mode, ionization was made in the negative mode. We detected the respective trihydroxybenzenes in all the mixtures and the corresponding quinones in samples containing 2,5-dimethylresorcinol and 5-methylresorcinol. The present study confirmed the reaction mechanism proposed by Musso where oxidized resorcinol reacts with resorcinol in the C–C coupling reaction [18]. However, the emerging molecular structures can be far more complex because of C–O coupling reactions.

The following paragraphs and Fig. 5 present some structures of coupled resorcinols that were detected in the present study. The molecular structures of these coupled molecules are marked in the register as Y tetrameric hq, 2XZ trimeric qq, and X tetrameric hq O. The systematic names of the three molecules are given in the legend to the figure.

These examples represent the molecular ions that gave very intensive mass peaks in the HRMS analysis of particular reaction mixtures. As we promised not to give any quantitative estimation based on molecular ion mass peak intensity, we can only comment that these structures could be molecules that are preferably formed as (a) and (c), or are presumably stable diquinones like (b), which gave the third intensive mass peak (the

Table 3. Molecular mass detection from molecular ion spectra of coupling products

Molecular structure	Mol. formula (X family)	Calculated $[M+H(Na)]^+$	Measured $[M+H(Na)]^+$	Mol. formula (Y family)	Calculated $[M+H(Na)]^+$	Measured $[M+H(Na)]^+$
Dimeric rq	**C16H16O5**	289.10705	**289.10621**	**C14H12O5**	261.07575	**261.07523**
Dimeric qq	**C16H14O6**	303.08631	**303.08502**	**C14H10O6**	275.05501	**275.05407**
Dimeric hq	**C16H16O6**	305.10196	**305.10078**	**C14H12O6**	277.07066	**277.06937**
Dimeric hh	**C16H18O6**	307.11761	**307.11667**	C14H14O6		nd
Trimeric rq	**C24H24O7**	425.15948	**425.15767**	**C21H18O7**	383.11253	**383.11143**
Trimeric qq	**C24H22O8**	439.13874	**439.13785**	**C21H16O8**	397.09179	**397.09091**
Trimeric hq	C24H24O8	463.13634*	463.13376*	**C21H18O8**	399.10744	**399.10615**
Tetrameric rq	C32H32O9	561.21191	561.20748	**C28H24O9**	505.14931	**505.14683**
Tetrameric qq	**C32H30O10**	575.19117*	**575.18922***	C28H22O10		nd
Tetrameric hq	**C32H32O10**	577.20682	**577.20421**	**C28H24O10**	521.14422	**521.14294**
Hexameric qq	C48H46O14		nd	**C42H34O14**	763.20213	**763.19987**
Hexameric hq	C48H48O14	849.31168	849.30708	C42H36O14		nd
Tetrameric qqq O	**C32H28O11**	611.15238*	**611.14948***	C28H20O11		nd
Tetrameric qq O	**C32H30O11**	613.16803*	**613.16580***	**C28H22O11**	557.10543*	**557.10379***
Tetrameric hq O	**C32H32O11**	593.20174	**593.19935**	C28H24O11		nd
Tetrameric qq q 2O	**C32H28O12**	627.14730*	**627.14487***	C28H20O12		dna
Tetrameric qq 2O	**C32H30O12**	629.16295*	**629.16055***	C28H22O12		dna
Tetrameric hq O	**C32H32O12**	609.19665	**609.19414**	C28H24O12		dna
Pentameric qq q O	C40H36O13	725.22287	725.21795	C35H26O13		dna
Pentameric qq O	**C40H38O13**	749.22046*	**749.21829***	C35H28O13		nd
Pentameric qq q 2O	**C40H36O14**	763.19973*	**763.19737***	C35H26O14		dna
Pentameric qq 2O	**C40H38O14**	743.23343	**743.23098**	C35H28O14		dna
Pentameric qqq 3O	**C40H36O15**	779.19464*	**779.19181***	C35H26O15		dna
Pentameric qq 2O	**C40H38O15**	759.22835	**759.22501**	C35H28O15		dna
Hexameric qqq O	C48H44O15	861.27530	861.27088	**C42H32O15**	777.18140	**777.17859**
Hexameric qq O	**C48H46O15**	885.27289*	**885.27109***	**C42H34O15**	779.19705	**779.19320**
Hexameric hq O	C48H48O15	865.30660	865.30359	**C42H36O15**	781.21270	**781.21216**
Hexameric qqq 2O	**C48H44O16**	899.25216*	**899.25049***	C42H32O16		dna
Molecular structure	(XY family)	$[M+H(Na)]^+$	$[M+H(Na)]^+$	(XZ family)	$[M+H(Na)]^+$	$[M+H(Na)]^+$
Dimeric rq	**C15H14O5**	275.09140	**275.09034**	**C14H12O5**	261.07575	**261.07514**
Dimeric qq	C15H12O6	289.07121	289.07009	**C14H10O6**	297.03696*	**297.03642***
Dimeric hq	**C15H14O6**	291.08631	**291.08500**	**C14H12O6**	277.07066	**277.06974**
Dimeric hh	C15H16O6		nd	**C14H14O6**	279.08631	**279.08519**
2X(Y/Z) trimeric rq	C23H22O7		nd	**C22H20O7**	397.12818	**397.12642**
2X(Y/Z) trimeric qq	C23H20O8		nd	**C22H18O8**	411.10744	**411.10582**
2X(Y/Z) trimeric hq	C23H22O8		nd	**C22H20O8**	413.12309	**413.12226**
2X(2Y/2Z) tetrameric rq	C30H28O9		nd	**C28H24O9**	527.13125*	**527.12898***
2X(2Y/2Z) tetrameric qq	C30H26O10		nd	**C28H22O10**	541.11052*	**541.10817***
2X(2Y/2Z) tetrameric hq	**C30H28O10**	549.17552	**549.17318**	**C28H24O10**	543.12617*	**543.12480***
3X(Y/Z) tetrameric hq	**C31H30O10**	585.17312*	**585.17051***	**C30H28O10**	571.15747*	**571.15528***
3X(3Y/3Z) hexameric hq O	**C45H42O15**	823.25965	**823.25703**	**C42H36O15**	803.19464*	**803.19233***
4X(2Y/2Z) hexameric hq O	**C46H44O15**	837.27530	**837.27257**	**C44H40O15**	831.22594*	**831.22530***
Molecular structure	(YZ family)	$[M+H]^+$	$[M+H]^+$	(Z family)**	$[M+H]^+$	$[M+H]^+$
Dimeric rq	**C13H10O5**	247.06010	**247.05953**	**C12H8O5**	233.04445	**233.04379**
Dimeric qq	**C13H8O6**	261.03936	**261.03934**	C12H6O6		nd
Dimeric hq	**C13H10O6**	263.05501	**263.05378**	**C12H8O6**	249.03936	**249.03802**
Dimeric hh	C13H12O6	265.07066	265.06925	C12H10O6	251.05501	251.05357
2YZ trimeric rq	**C20H16O7**	391.07882	**391.07719**			
2YZ trimeric qq	C20H14O8	383.07614	383.07418			
2Y2Z tetrameric hq	**C26H20O10**	493.11292	**493.11088**			
3YZ tetrameric hq	**C27H22O10**	507.12857	**507.12626**			

* Identified as $[M+Na]^+$.

** Measured in sampleYZ.

The number before the resorcinol symbols in the description of the molecular structure indicates the number of the corresponding resorcinol moieties or oxidation products in the molecule; O indicates C–O coupling (grey background); qqq marks the third quinoid structure in the molecule; confirmed molecular formulas with mass accuracy <5 ppm are in bold; nd – not detected; dna – data not analysed.

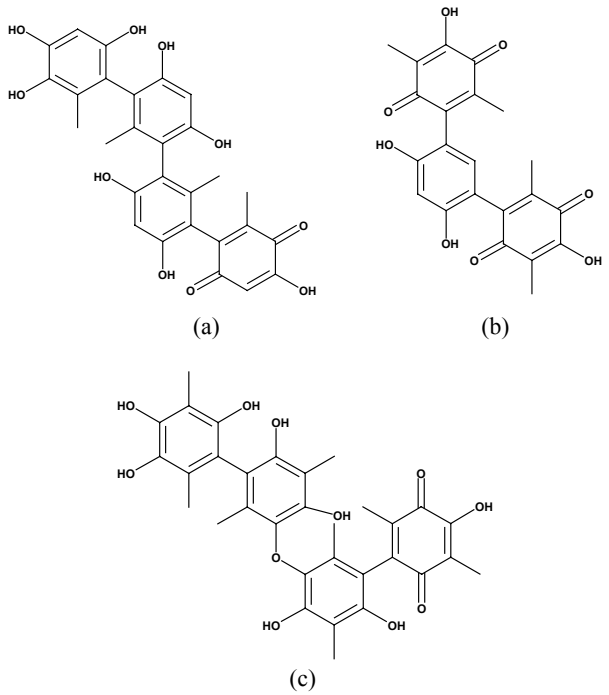

Fig. 5. Suggested structures of coupled resorcinols.
(a) Tetrameric monoquinone: 2-{2,4-dihydroxy-3,6-dimethyl-5-[(2′,4,4′,5′,6-pentahydroxy-2,3′,5,6′-tetramethyl[1,1′-biphenyl]-3-yl)oxy]phenyl}-5-hydroxy-3,6-dimethylbenzo-1,4-quinone;
(b) trimeric diquinone: 2-[2,4-dihydroxy-5-(4-hydroxy-2,5-dimethyl-3,6-dioxo-1,4-cyclohexadienyl)phenyl]-5-hydroxy-3,6-dimethyl-2,5-cyclohexadiene-1,4-dione;
(c) tetrameric monoquinone: 2-{2,4-dihydroxy-3,6-dimethyl-5-[(2′,4,4′,5′,6-pentahydroxy-2,3′,5,6′-tetramethylbiphenyl-3-yl)oxy]phenyl}-5-hydroxy-3,6-dimethylbenzo-1,4-quinone.

structure marked as 2XZ trimeric qq) in the reaction mixture of 2,5-dimethylresorcinol together with resorcinol after the dimeric monoquinone marked as XZ dimeric rq and tetrameric monoquinone marked as 2X2Z tetrameric hq.

In real waste streams one does not deal with a single resorcinol, which means that a huge variety of different reaction products may emerge. The quantities of reaction products will depend on the initial concentration of particular phenols and their reactivity. 5-Methylresorcinol and 2,5-dimethylresorcinol are the predominant phenols in retort water and oil wash water. These are the major phenols that were also found in retorted kukersite fresh semi-coke leachate. Consequently, one should initially see dimeric structures arising from the reaction of 5-methyl resorcinol with 2,5-dimethylresorcinol oxidation products and 5-methylresorcinol coupling products in the leachate, as in the particular reaction mixtures. Such molecules as dimeric monoquinones, marked XY dimeric rq and Y dimeric rq, can be clearly detected in the 1-week semi-coke leachate chromatogram in Fig. 2, lane 4. The analysis of the phenol pattern of the leachates in field experiments showed that 2,5-dimethylresorcinol disappeared from the leachate very quickly, in a few days after landfilling. This is in good accordance with laboratory experiments, which show the highest reaction rate of 2,5-dimethylresorcinol in oxidation and coupling reactions compared with 5-methylresorcinol and resorcinol.

CONCLUSIONS

Phenols constitute a considerable part of the overall contamination of the hydrosphere. Both physico-chemical and biological oxidative reactions play a significant role in the process of self-cleaning. Phenol oxidation has been studied mainly in concentrated solutions, often in alcohol solutions, and under special conditions (increased temperature and pressure). There is a study on the kinetics of resorcinol oxidation in distilled water and sea water [9]. The authors of all these studies pay attention to primary oxidation products that can be identified by methods of simple functional group analysis. Investigation of multiple coupling products used to be difficult because of the absence of easy and relevant analysis techniques.

Phenols have been considered also as primary pollutants produced by the shale oil industry. Although their appearance in semi-coke could be substantially diminished, they will continuously appear in the waste streams of shale oil production. Our study is the first attempt to follow chemical reactions with major oil shale phenols occurring in the waste of shale oil production, i.e. in retorted kukersite semi-coke. The waste is continually deposited in former embankments, which have been transformed into applicable landfills.

Our laboratory investigation confirmed the data of semi-coke leachate analysis in the field experiments, which also showed that the concentration of phenols decreases rapidly when semi-coke is in contact with the air. According to our experimental data, phenols are associated with semi-coke in the water. Resorcinols in retorted kukersite semi-coke oxidize and undergo coupling reactions. The rates of these reactions are different for different resorcinols. Primary coupling products of 5-methylresorcinol and 2,5-dimethylresorcinol were first detected in the experiments where resorcinols were added to semi-coke and then in kukersite semi-coke leachate.

In the model experiments, primary coupling products of resorcinol, 5-methylresorcinol, and 2,5-dimethylresorcinol and their mixtures in pairs were detected by TLC, separated by silica gel column chromatography if necessary, and analysed by NMR spectroscopy and HRMS. The primary coupling products identified in oxidation experiments as well as in the leachate included dimeric hydroxyl resorcinols, monoquinones, and

diquinones emerging in the C–C coupling reaction. The found more complex oligomeric structures represent combinations of different quinoids, formed both in C–C and C–O coupling reactions. The same coupling products were detected in semi-coke leachate and laboratory oxidation experiments. Coupling products of different resorcinols form similar product families, which refers to uniform coupling mechanisms. A strongly alkaline medium of retorted kukersite and that of the leachate enhance oxidation and coupling reactions.

In the conditions enabling oxidation, major oil shale phenols in the retorted oil shale undergo coupling, which can be regarded as a natural self-cleaning process. This process can be easily enhanced by applying appropriate waste management procedures. The results of the study will be useful both for waste chemists and microbiologists, who make proposals for chemical treatment of shale oil industry wastewater or try to get rid of the residual phenols utilizing microbial capabilities.

REFERENCES

1. Tiikma, L., Mölder, L., and Tamvelius, H. Resources of water-soluble alkylresorcinols in the oil fractions and retort water formed by processing oil shale in generators of high unit capacity. *Oil Shale*, 1991, **8**, 350–354.
2. Koel, M. and Bunger, J. Overview of program on US–Estonian science and technology cooperation on oil shale research and utilization (strategic importance of oil shale studies for Estonia and USA). *Oil Shale*, 2005, **22**, 65–79.
3. Kahru, A., Maloverjan, A., Sillak, H., and Põllumaa, L. The toxicity and fate of phenolic pollutants in the contaminated soils associated with the oil shale industry. *Environ. Sci. Pollut. Res.*, 2002, **9**, 27–33.
4. Habicht, J. and Mäeorg, U. Retorted oil shale – a true synthesis laboratory. In *30th Estonian Chemistry Days, Abstracts of Scientific Conference*. Tartu, 2007, 29.
5. Yamamura, S. Oxidation of phenols. In *The Chemistry of Phenols* (Rappoport, Z., ed.). John Wiley & Sons Ltd., 2003, 1153–1346.
6. Kirso, U., Gubergrits, M., and Kuiv, K. Oxidizability of phenols contained in tar waters from tunnel kilns and a unit with a solid heat carrier. *Slantsevaya Khimiya*, 1966, **4**, 19–22 (in Russian).
7. Kirso, U., Kuiv, K., and Gubergrits, M. Kinetics of phenol and m-cresol oxidation by molecular oxygen in an aqueous medium. *Zhurnal Prikladnoj Khimii*, 1967, **40**, 1583–1589 (in Russian).
8. Kirso, U., Gubergrits, M., and Kuiv, K. Kinetics of the oxidation of substituted monohydric phenols by molecular oxygen in an aqueous medium. *Zhurnal Prikladnoj Khimii*, 1968, **41**, 1257–1261 (in Russian).
9. Trapido, M. and Gubergrits, M. Oxidation of resorcinols in water. *ENSV TA Toim. Keemia*, 1980, **29**, 103–108.
10. Mamedov, A., Aslanova, T., Alekperov, A., and Alieva, N. Features and products of oxidation of 1,3-benzendiol by oxygen in an alkaline medium. *Azerbajdzhanskii Khimicheskii Zhurnal*, 2004, 59–63 (in Russian).
11. Preis, S., Terentyeva, Y., and Rozkov, A. Photocatalytic oxidation of phenolic compounds in wastewater from oil shale treatment. *Water Sci. Technol.*, 1997, **35**, 165–174.
12. Kamenev, I., Munter, R., Pikkov, L., and Kekisheva, L. Wastewater treatment in oil shale chemical industry. *Oil Shale*, 2003, **20**, 443–457.
13. Christjanson, P., Kööosel, A., and Suurpere, A. Evaluation of condensation rate of methylolphenols. *Oil Shale*, 1998, **15**, 374–383.
14. Christjanson, P., Kööosel, A., and Suurpere, A. Condensation of methylolphenols. *Oil Shale*, 1999, **16**, 369–376.
15. Chrisjanson, P., Pehk, T., Siimer, K., and Paju, J. Structure of polycondensates from hydroxymethylphenols. *J. Appl. Polymer Sci.*, 2008, **107**, 1226–1234.
16. Musso, H. and Rathjen, C. Die Autoxydationsprodukte des 2.5-Dimethyl-resorcins in Ammoniak und Kalilauge. *Chem. Ber.*, 1963, **96**, 1593–1609.
17. Musso, H., Gizycki, U., Krämer, H., and Döpp, H. Über den Autoxydations-mechanismus bei Resorcinderivaten. *Chem. Ber.*, 1965, **98**, 3952–3963.
18. Musso, H. Über Phenol-Oxidationen. *Angew. Chem.*, 1963, **75**, 965–977.
19. Eesti Standard EVS-EN 12457-1:2002. Characterisation of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 1: One stage batch test at a liquid to solid ratio of 2 l/kg for materials with particle size below 4 mm (without or with size reduction). Eesti Standardikeskus, 2002.
20. Harvey, T., Matheson, T., and Pratt, C. Chemical class separation of organics in shale oil by thin-layer chromatography. *Anal. Chem.*, 1984, **56**, 1277–1281.
21. Fisher, W., Bund, O., and Hauck, H. Thin-layer chromatographic analysis of phenols on TLC aluminium sheets RP-18 F_{254s}. *Frensius J. Anal. Chem.*, 1996, **354**, 889–891.

Resortsinoolide kondensatsioon kukersiidi poolkoksis

Jaan Habicht ja Uno Mäeorg

Põlevkiviõli tootmise jäätmeid puudutav temaatika tundus vanade ladestusalade prügilateks kohendamise ja osalise sulgemise projekti käivitudes oma aktuaalsust kaotavat. Pärast tunamullust suletava ladestusala põlengut Kohtla-Järvel ja poolkoksi nõrgvete puhastamiseks algselt planeeritud tehnoloogia ilmselget mitterakendatavust on aga nii ladestatavate jäätmete koostise kui ka nõrgvete teema taas päevakorral. Retordijäätmete käitlemise probleemide

sisuline lahendamine ladestamisel toimuvate keemiliste protsesside mõistmisel nõuab aga paradigmaatilist muutmist. Alles seejärel saame rääkida nimetatud jäätmete tegelikust keskkonnaohtlikkusest, efektiivsete käitlustehnoloogiate rakendamisest ja isegi retordijäätmete looduslikust isepuhastusvõimest.

Käesolevas töös uuriti põlevkivi poolkoksi ladestamisel fenoolsete ühenditega toimuvaid muutusi. Selgus, et nõrgvees leitavate mono- ja difenoolide kogus väheneb väga kiiresti. Resortsinoolid, mis moodustavad lahustunud orgaanilistest ühenditest olulise osa, kaovad ladestamisel nõrgveest väga lühikese aja jooksul, erinevate fenoolide kontsentratsioonide vähenemise kiirus on aga erinev. Resortsinoolide koguste vähenemisega kaasneb algul uute leostuvate ühendite teke, seejärel aga nimetatud reaktsiooniproduktide kiire kadumine edasise kondensatsiooni tõttu. Resortsinoolide oksüdatsioonil tekkinud esmaste kondensatsiooniproduktide analüüsiks kasutasime planaarkromatograafiat. Seejärel eraldasime üksikud ühendid silikageelkuivkolonnikromatograafia abil. Tuuma magnetresonantsspektroskoopia ja kõrglahutusmassispektromeetria abil identifitseerisime rohkem kui 50 seni kirjeldamata keemilist ühendit. Uuritud kolme fenooli, 2,5-dimetüülresortsinooli, 5-metüülresortsinooli ja resortsinooli oksüdatsioonil ning kondensatsioonil tekivad süsinik-süsinik-sidemega esmalt dimeersed mono- ja dikinoonid. Jätkureaktsioonide oligomeersed produktid võivad moodustuda ka süsinik-hapnik-sidemete tekke kaudu.

Nimetatud sünteesiprotsessid toimuvad arvestatava kiirusega tugevalt leeliselises keskkonnas. Poolkoksi mineraalne maatriks on oma koostise tõttu selle reaktsioonikeskkonna leelisdepooks ja värskete retordijäätmete keemilise reaktiivsuse üheks oluliseks põhjuseks. Et oksüdatsiooniprotsessideks on vajalik hapnik, kirjeldavad meie katsed protsesse, mis toimuvad looduses eeskätt jäätmeladestu pinnal, kuhu värsked retordijäätmed esmalt ka satuvad. Fenoolide oksüdatsiooni ja kondensatsiooni poolkoksis saab käsitleda loodusliku isepuhastusena. Fenoolide kondensatsiooniproduktid on vees halvasti lahustuvad, ei leostu ja väljuvad seega olulisel määral keskkonda ohustavast aineringest. See, millises ulatuses isepuhastusvõime realiseerub, sõltub olulisel määral fenoolsete ühendite kogustest jäätmetes. Meie uuringud kinnitavad, et põlevkiviõli tootmise retordijäätmetes ladestamisel toimuvate keemiliste protsesside tulemusena muutub oluliselt nii leostuvate orgaaniliste ainete nimistu kui ka kogus. Seda on nii füüsikaliste, keemiliste kui ka bioloogiliste heit- ja nõrgvee puhastustehnoloogiate rakendamiseks mõistlik teada ja arvestada.