

CHARACTERIZATION OF THE PYROLYTIC WATER FROM SHALE OIL INDUSTRY

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***Abstract.** Currently there are two different industrial shale oil production processes utilized in Estonia called Galoter and Kiviter. It is known that the composition of pyrolytic water from these processes is different. The most emphasized difference lies in the concentration of phenols. However, the general composition of the water has not been very deeply investigated. Therefore, the purpose of this paper was to study the pyrolytic water from solid heat carrier technology (SHC). The pyrolytic water from the SHC process was subjected to headspace gas chromatography-mass spectrometry (GC-MS) analysis for the identification of organic compounds and to inductively coupled plasma mass spectrometry (ICP-MS) analysis for the identification of trace elements. The parameters generally used to describe wastewater – biochemical oxygen demand (BOD_7), chemical oxygen demand (COD_C), suspended solids, dry residue, total organic carbon (TOC), pH, oil products, conductivity, amounts of phosphorus, nitrogen and sulphur –, were also measured. The analysed water contained surprisingly high amounts of sulphur and nitrogen, 0.03% and 0.24%, respectively. It was found that the water did not contain any significant amounts of toxic metals and it exhibited good biodegradability.*

***Keywords:** pyrolytic water, shale oil industry, oil shale pyrolysis, solid heat carrier technology.*

1. Introduction

Shale oil is produced from oil shale by using thermal treatment – pyrolysis. During the retorting process of oil shale, its organic part is decomposed into four main components: shale oil, retort gas, semi-coke and pyrolytic water [1–4]. It is expected that the US will reach a shale oil production amount of 1.4 million barrels per day by 2020, thereby causing the generation of a large

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amount of wastewater [5]. In order to find ways to utilize pyrolytic water it needs to be thoroughly analysed.

The properties of spent shale are highly dependent on the retorting process, wherein generally significant amounts of total dissolved solids, sulfate, carbonate and other ions are found [6]. It is also known that the above-mentioned pyrolytic water generally contains a large amount of volatile and recalcitrant organic compounds like phenols and also inorganic compounds such as ammonium and sulphates [1]. Among pyrolytic waters from retorting of different oil shales, the environmental issues related to the utilization of pyrolytic water for pyrolysis of Estonian oil shale are perhaps the most studied. Therefore it is also known that the composition of pyrolytic water from the Kiviter and Galoter processes is different. The compounds that have historically attracted researchers' attention in relation to the environmental issues are water-soluble dibasic phenols – alkylresorcinols. Among different phenols resorcinol, 2-methyl-, 4-methyl-, 5-methyl-, 2,5-dimethyl-, 4,5-dimethyl- and 5-ethylresorcinol are identified as the main phenolic compounds [7]. As the concentration of these phenols in pyrolytic water is relatively high, the water from the Kiviter process (gas generator) is used as a raw material for the production of these valuable resorcinols. As a further development, these resorcinols could be used for the production of anti-oxidant, biocidal and other agents [8].

However, these phenols form only part of the organic compounds in the pyrolytic water. Therefore, possible pollutants and potentially useful separable substances still need to be identified. As this type of water is rich in composition, it is worth investigating whether it is possible and economically beneficial to separate and manufacture chemicals from it. If the quantities of chemicals are too small, the water is directed to purification. For that it is also necessary to know the quantities and types of different compounds in order to find the best purification method. Trace metals need to be analysed since they are partially mobilized during retorting and may cause environmental pollution during processing and waste disposal [9].

The goal of this paper was to investigate the composition of the pyrolytic water and to compare the obtained results with data found in the literature. The types of volatile organic compounds (phenols, alcohols, etc.) were determined. For the identification headspace gas chromatography-mass spectrometry (GC-MS) was used. The amounts of C, H, N and S were determined via elemental analysis. Additionally, the amount of trace metals was determined using inductively coupled plasma mass spectrometry (ICP-MS). All of these results can be used for determining the possible toxicity of the wastewater.

2. Experimental

The organic compounds were identified using an Agilent 7890A gas chromatograph and an Agilent 5975C Inert MSD mass spectrometer. The column used was an Agilent HP-5MS with a constant helium (He, purity 6.0) flow rate of 1 mL/min. The samples were injected using an Agilent GC Sampler 80 autosampler. 7 g of Na₂SO₄ was added to a 3 mL raw water sample in a 20 mL vial. The mixture was subjected to thermostatic treatment at 60 °C for 10 min. Afterwards, a gas phase sample was taken which was then subjected to GC analysis. The temperature program used was as follows: 40 °C (held for 5 min), heating at 8 °C/min to 180 °C, followed by heating to 250 °C with a heating rate of 30 °C/min. The total run time was 24.8 min. The injector temperature was 250 °C and the split ratio was 10:1.

The elemental analysis was done using a Vario MACRO CHNS Cube system. Trace elements were quantified using Thermo iCAP Qc Quadrupole ICP-MS.

The general parameters of the samples were measured using the following methods. The seven-day biochemical oxygen demand (BOD₇) was measured according to ISO 5815-1 [10]. For the conductivity measurement EVS-EN 27888 [11] was used. The suspended solids (SS) were measured according to EVS-EN 872 [12]. The chemical oxygen demand (COD_{Cr}) was measured according to ISO 6060 [13]. The total dissolved solids (TDS) were analysed according to SFS 3008 [14]. For the pH measurement, ISO 10523 [15] was followed. The total phosphorus amount was analysed according to EVS-EN ISO 6878 Sec. 7 [16]. The total nitrogen amount was measured using the Kjeldahl method as described in SFS 5505 [17]. The total organic carbon (TOC) content was measured according to EVS-EN 1484 [18]. The sulphur amount was measured using EVS-EN ISO 11885 [19]. The amount of oil products (C10–C40) was measured using EVS-EN ISO 9377-2 [20]. The phenol index (PI) was determined following the ISO 6439 method [21].

3. Results and discussion

3.1. Description of general parameters

It is known that chemical oxygen demand (COD), biochemical oxygen demand (BOD), total nitrogen content and total phosphorus content are the significant parameters that characterize the ecological danger of wastewater [22]. Therefore they need to be measured with extreme precision. All the measured parameters and the respective results are presented in Tables 1–3.

When comparing the obtained results with literature data, it can be seen that the studied water from the solid heat carrier (SHC) process exhibits higher

Table 1. Parameters of the analysed wastewater sample

Parameter	Value	Unit	Literature value*
BOD ₇	14	gO ₂ /L	5.5, 34.9 [1]
Conductivity	12	mS/cm	10.4 [1]
SS	105 ± 77.1	mg/L	–
COD _{Cr}	26	gO ₂ /L	39.7 [1]
TDS	1.85 ± 0.49	g/L	1.8 [7]
pH	9	–	8.88 [1], 9 [23]
P _{total}	< 0.2	mg/L	–
N _{total}	1.9	g/L	0.6 [7]**
TOC	8.6 ± 0.7	gC/L	7.1, 9 [1], 7 [23]
S _{total}	3.05 ± 0.5	g/L	0.19 [7]
C ₁₀ –C ₄₀	0.056 ± 0.01	g/L	–
PI	0.73 ± 0.03	g/L	0.73–1.05 [1]

* Values found for pyrolytic water from solid heat carrier technology;

** average annual concentration; “–” represents no data.

Table 2. Elemental composition of the analysed wastewater, wt%

C	H	N	S
0.95	10.09	0.24	0.03

conductivity, smaller COD_{Cr} and slightly higher pH values. The phenol index is similar to that reported in the literature, although total phenol amount is usually shown. There are a number of similarities between the results obtained in this work and the data found in the literature. For example, the TOC value and dry matter content are almost similar. The BOD₇ value nicely falls into the range reported in the literature. Contrary to the similarities, it is remarkable that the total sulphur content was in our case about 3 g/L, whereas the literature values were several magnitudes lower. The results of elemental analysis given in Table 2 are in good correlation with the data in Table 1. The starting material, kukersite, is known to contain up to 3% sulphur, whereas about 3.3% of the mineral matter is pyrite [24]. The higher sulphur content in the pyrolytic water is favourable since as a consequence there is less sulphur in the produced oil. The relatively large content of sulphur and nitrogen (Table 2) might be one of the reasons of the fairly repugnant smell of the sample.

As can be seen from Table 1, the phenol content is similar to the data found in the literature. It is known that the concentration of phenolic substances depends on the used oil shale treatment process and the conditions of the contact between oil and water in condensers and decanters [22]. Although the works reported in the literature might have utilized the same technological process, the results may differ greatly due to several reasons. For example, the differences might lie in raw oil shale and the retorting conditions might also differ. The content of phenols is of high importance due to their effect on the toxicity of the water – it has been

shown that about 75% of the toxicity of semi-coke heap water is caused by phenolic compounds, whereas the pH and heavy metal content do not have a noticeable effect [25].

According to the regulations in order to discharge industrial wastewater, the COD value of biologically treated water should not exceed 250 mg/L (degree of purification at least 75%). The concentration of phenols is also limited – the monobasic phenols in the effluent should not exceed 0.1 mg/L [26]. BOD_7/COD_{Cr} is about 0.54, indicating that the water has good biodegradability, the COD_{Cr} value still needs to be reduced before the water can be subjected to biochemical purification.

3.2. Trace elements analysis

As mentioned above, the trace element amounts were analysed using ICP-MS. The results are presented in Table 3.

As Table 3 reveals, there are no significant amounts of heavy metals in the water. To the best of our knowledge, there is no data in the literature about the concentrations of metals in such wastewater samples. In our work, the highest values are for Mg and Fe, 0.465 and 0.273 ppm, respectively. The concentrations of toxic elements are fairly low (the highest concentration is that of As, 0.102 ppm), thereby showing no significant toxicity. When comparing these results with the concentrations found in raw oil shale, the concentrations in the pyrolytic water are marginal. For example, Reinik et al. [27] showed the concentration of As to be in the range of 7 to 21 ppm in Estonian oil shale. This is to be expected as Patterson et al. [9] found that most elements were mobilized mainly to the oil and to a lesser extent to the retort water. For comparison, the retort water obtained when treating Condor oil shale contained as much as 1 ppm of As and 0.6 ppm of Se [9]. In contrast, the results obtained in the current work showed much lower values for trace elements in the pyrolytic water.

Table 3. The identified metals in the wastewater, ppm

Element	Content
Li	0.001
Mg	0.465
Ti	0.091
Cr	0.016
Mn	0.018
Fe	0.273
Ni	0.011
Zn	0.065
As	0.102
Se	0.002
Sr	0.001
Pb	0.002

3.3. Headspace GC-MS analysis

As mentioned above, the composition of the pyrolytic water has not been well studied. The present study aimed to fulfil the gap by analysing the compounds with significant volatility. For the analysis the headspace GC-MS technique was used. From the obtained chromatograms a large number of different organic compounds were identified. Only compounds exhibiting significant signal intensities were identified with the aid of Agilent MSD ChemStation with built-in NIST library. For all the identified compounds the probability of compound identification was over 70%. For detailed compositional analysis, the results of the chromatograms obtained are shown in Figures 1–4.

During the first few minutes of the analysis (visualized in Fig. 1) the main peaks are attributed to acetone (A, r_t 2.2 min), 2-butanone (B, r_t 2.7 min) and 2-pentanone (C, r_t 3.75 min). Additionally, volatile chlorine-containing organic compounds, as well as benzene (D, r_t 3.5 min), thiophene (E, r_t 3.6 min) and 3-pentanone (F, r_t 4.05 min) were identified.

In the second part of the chromatogram (Fig. 2) mainly oxygen-containing compounds can be seen. The main peaks are attributed to various ketones (unmarked, r_t 5.5, 5.6, 6.1, 6.55, 8.05, 8.2, 9.1, 9.5 and 9.9 min). Additionally, pyridine (G, r_t 5.1 min), toluene (H, r_t 5.9 min), tetrahydrothiophene (I, r_t 7.0 min), 2-methylpyridine (J, r_t 7.3 min) and 2,6-dimethylpyridine (K, r_t 9.4 min) were detected. In addition to the relatively high sulphur content, the existence of pyridine might be another reason for the unpleasant odour of the sample.

In Figure 3 the peaks are attributed to cycloalkenes (L, r_t 10.3 min), cyclopentyl-ethanone (M, r_t 10.6 min), oxygen-containing compounds (unmarked, r_t 10.7–11.8 min), for example, cyclohexanone and alcohols. The most intense peak is due to the existence of phenol (N, r_t 11.85 min).

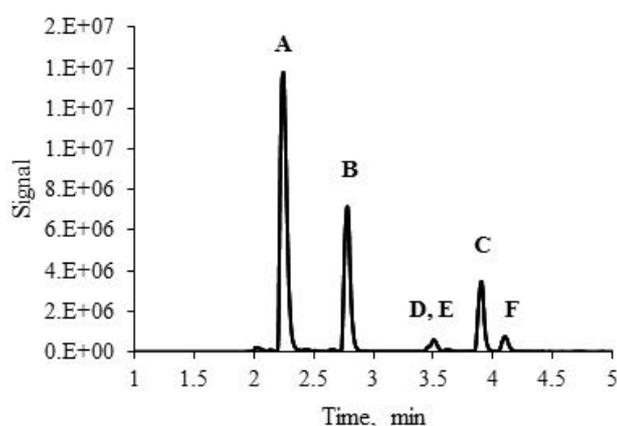


Fig. 1. Chromatogram of compounds eluting between 1 and 5 minutes.

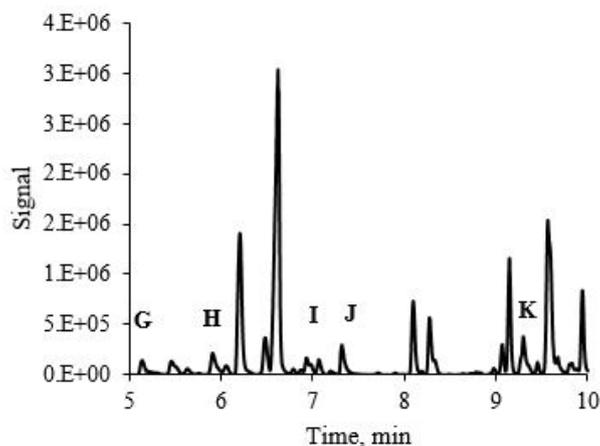


Fig. 2. Chromatogram of compounds eluting between 5 and 10 minutes.

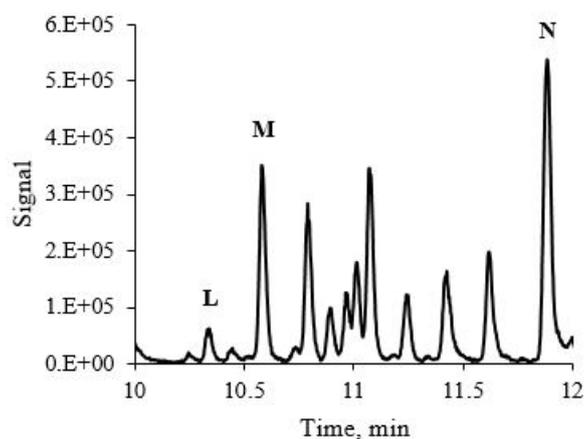


Fig. 3. Chromatogram of compounds eluting between 10 and 12 minutes.

The end of the chromatogram (Fig. 4) shows oxygen-containing compounds (unmarked, r_t 12.1-14.0 min) like mono-substituted phenols (O, r_t 13.5, 13.9 min). Additionally, some oxygen- or nitrogen-containing compounds exhibit an intensive peak (P, r_t 14.4 min). The small peaks near the end of the chromatogram are attributed to cyclic sulphur-containing substances (Q, r_t 15.2, 15.3 min).

As described above, the most abundant organic components exhibited ketone functionalities. For comparison, the major organic components of the pyrolytic water from the hydrothermal liquefaction of biomass include acetic acid and glycolic acid, whereas ketones are found in much smaller quantities [28]. The abundance of ketones in the pyrolytic water of shale oil industry is

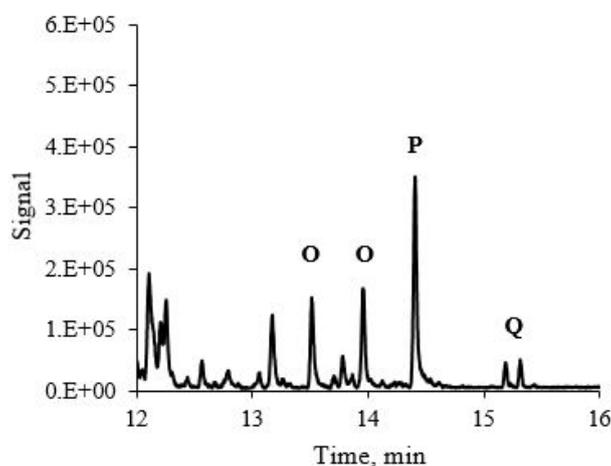


Fig. 4. Chromatogram of compounds eluting between 12 and 16 minutes.

caused by the contact between water and the lighter fractions of oil, which contain substances with ketone functionalities. Some researchers have reported carboxylic acids (up to the length of C_{12}), which are the dominant class of compounds present in the pyrolytic water of Rundle deposit in Australia [23, 20].

All these results lead to a conclusion that the composition of the pyrolytic water from the SHC process is very complex. It was reported already in the 1980s that oil shale retort water (pyrolytic water) contains a wide range of compounds – from compounds being highly biodegradable to those that are highly inhibitory and resistant to biological oxidation [29]. One should keep in mind that the utilized oil shales are of different origin and composition and the used technological processes are different. The water analysed in this paper contained relatively large amounts of different organic substances, but separation of beneficial compounds is unlikely due to the too low concentrations of these compounds in the studied water. A lot of the identified compounds are ketones and alcohols. These will be degraded during the biochemical purification process, as also indicated by the high BOD_7 value, thereby showing no possible inhibiting effect in the purification process. This conclusion is purely hypothetical as it is based on the identified compounds. In order to provide more conclusive results, a quantitative analysis will be required.

4. Conclusions

In this study, the main parameters of the pyrolytic water from shale oil industry utilizing solid heat carrier technology were analysed. The water exhibited good biodegradability (BOD_7/COD_{Cr} was about 0.54). Addi-

tionally it was found that the water contained a number of different ketones and had a relatively high concentration of nitrogen and sulphur, 0.24% and 0.03%, respectively. It was also concluded that most of the identified organic substances would degrade during the biochemical treatment. The results were in very good accordance with literature data. The trace metals present in the water were also quantified. It was found that the water did not contain significant amounts of toxic metals. As was the most abundant element with a concentration of 0.102 ppm, however, this value was still some magnitudes smaller than the respective concentration in raw oil shale. Other trace elements had even lower concentrations.

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