



# Examination of molecular weight distributions of primary pyrolysis oils from three different oil shales via direct pyrolysis Field Ionization Spectrometry



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## HIGHLIGHTS

- Py-FIMS of oil shales indicates 3 distinct pyrolysis regions below 710 °C.
- Py-FIMS of oil shales containing thermally softening and non-softening kerogens.
- FIMS based molecular weight distributions of total oils and oils from distinct regions.
- Py-FIMS oils from a non-softening kerogen exhibit lowest molecular weights parameters.

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## ABSTRACT

The present study was focused on molecular weight and molecular weight distribution values of pyrolysis oils that could be useful in modeling oil shale thermochemical conversion processes, consistent with principles adopted in advanced coal pyrolysis modeling. Direct pyrolysis Field Ionization Spectrometry (py-FIMS) was applied to evaluate these parameters for volatilizing pyrolysis products with molecular weights greater than 50 daltons. Stepwise heating, with an overall rate of 10 °C min<sup>-1</sup> up to 710 °C, was used. The oil shales studied were Kukersite and Dictyonema oil shales from Estonia and Green River formation oil shale from the United States. Comparison of molecular distributions indicated a decreasing trend in molecular weight parameters (average molecular weight and width of the molecular weight distribution) of oils from higher oil yield oil shales to lower oil yield oil shales. In addition, the molecular weight trends seen among pyrolyzates from this study, under py-FIMS conditions, were compared to published values for pyrolyzates under other pyrolysis conditions and also to published values of the average molecular weight between cross-links for these three oil shales.

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## 1. Introduction

Recently, due to the increasing search for alternative energy resources, utilization of oil shale reserves has received renewed interest. It is estimated that world oil shale resources are equivalent to more than 2.9 trillion barrels of recoverable oil [1], which exceeds estimated conventional oil reserves by about two to three times. Although oil shale utilization has a long history [2] and resources are abundant and widespread, currently only a few countries exploit oil shale at the commercial scale. The main reason for this is that oil shale is a low grade solid fossil fuel with organic matter ranging typically from only 10% to 40%. The main component of the organic matter in oil shale, kerogen, has a

macromolecular network structure and is swellable in organic solvents [3]. The macromolecular network structure must be broken down by pyrolytic thermochemical conversion processes to release oil from the parent oil shale matrix. The overall pyrolysis process is extremely complex and is composed of a variety of chemical and physical sub-processes. This includes phenomena that are generally overlooked (at least quantitatively) in oil shale pyrolysis modeling science, such as whether or not the kerogen softens in the pre-pyrolysis region [4,5], thermal swelling of the kerogen in the case of higher grade oil shales that contain softening kerogen [6] or vaporization of primary tar [7,8].

The oil yield per organic matter content of different oil shales varies widely [9,10] – typically it is higher for oil shales containing kerogen that softens during pyrolysis and lower for oil shales containing kerogen that does not soften. In Estonia there are two kinds of oil shale: Kukersite, which contains softening kerogen (Type I/II

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kerogen; classified according to H/C and O/C ratios on the Van Krevelen diagram) and gives a higher oil yield, and Dictyonema, which contains non-softening kerogen (Type II kerogen) and gives a lower oil yield. This is somewhat similar to the oil shale resources in the United States, where western oil shales could be characterized as containing high oil yield, softening, Type I kerogen and eastern oil shales as containing low oil yield, non-softening, Type II kerogen.

Generally, the pyrolytic thermochemical conversion of oil shale organic matter is described by principles similar to those used for coals [11,12]. Although oil shales, like coals, are solid fossil fuels, they have a significantly higher mineral content (seen as a disadvantage) and organic matter richer in hydrogen (seen as an advantage). Therefore, oil shale conversion to oil (or tar, used as synonyms in this study) via a low-temperature pyrolysis process (also called retorting) has historically been the most favored oil shale thermochemical conversion process [2,13]. Recovery of oil from oil shales is based on thermal decomposition of the kerogen, the cross-linked macromolecular organic matter of oil shale. Thermal degradation of kerogen releases fragments with a range of molecular weights because kerogens are composed of a large variety of structures with a variety of bond strengths. Given that the organic matter of both coal and oil shale is mostly a cross-linked macromolecular structure, it is worth noting that a coal pyrolysis FG-DVC model (Functional Group-Dopolymerization Vaporization Crosslinking Model) uses the number average and standard deviation of the molecular weight distribution of the monomers as input parameters [14]. For the model, the molecular weight distribution of the monomers was assumed to follow a Gaussian distribution and was described with a mean and a standard deviation. These parameters were estimated from direct pyrolysis Field Ionization Mass spectrometry (or py-FIMS) measurements (i.e. from pyrolysis measurements of coal samples within direct inlet to the field ionization mass spectrometer). Field ionization is a soft ionization that results in molecular ions with no significant fragmentation [13]. On the basis of the rapid evaporation and detection of the tarry material formed during pyrolysis under deep vacuum conditions in FIMS (soft ionization), one can assume that there are structural similarities between tar constituents and the parent macromolecular network. The tarry material could represent a size distribution of structural units (so called monomers) that form larger structures (so called oligomers) between the cross-links of the parent macromolecular network.

This work sought to determine molecular weight parameters of primary pyrolysis oils (or tars, the term preferred in coal science) from Kukersite (Estonia), Green River formation (USA) and Dictyonema (Estonia) oil shales by using direct pyrolysis FIMS. No similar investigation was found for oil shales. For oil shale oils/tars there are some molecular weight distribution data that were measured by FIMS, but in these studies the oils/tars prepared in pyrolytic reactors were analyzed by FIMS. For example, for Green River formation oil shale (from USA) see [16–18], for Kukersite oil shale (from Estonia) see [7], for Israeli oil shale see [16] and for Sunbury oil shale (from Kentucky, USA) see [17]. However, there have been several similar direct pyrolysis FIMS studies on coals [19–22] because from the 1970s to 1990s extensive coal pyrolysis studies were performed, with an emphasis on simultaneously occurring physical and chemical processes [11,12]. The present study is carried out with the view that oil shale and coal have fundamental similarities in their pyrolytic behavior, and thus, the parameters sought mirror those used in one of the advanced coal pyrolysis models, the Functional Group-Dopolymerization Vaporization Crosslinking Model [14]. Moreover, there is relatively little information available about molecular weight parameters for oil shale pyrolysis oils (or tars). The data available are mostly for

the average molecular weight of the whole crude oil or low boiling fractions [23–25].

## 2. Experimental

### 2.1. Materials

Oil shales used in this study were Estonian Kukersite oil shale (as concentrated Kukersite kerogen containing 91% organic matter), Estonian Dictyonema oil shale (as concentrated Dictyonema kerogen containing 60% organic matter) and Green River formation oil shale (containing 14% organic matter) from Utah, USA. Elemental compositions (C, H, N) of these samples were determined using an Exeter Analytical model CE440 elemental analyzer. The elemental composition of organic matter was calculated, taking into account carbonaceous CO<sub>2</sub> and the ash content.

The concentrated Kukersite oil shale kerogen used had an organic content of about 91% and was obtained from an original commercial grade oil shale with an organic matter content of about 35%. The concentrated oil shale organic matter, or kerogen, was produced using the flotation technique [26]. Ultimate analysis, on a dry basis, gave 8.8 wt.% ash, 67.85 wt.% C, 8.12 wt.% H, 0.36 wt.% N. As carbonaceous CO<sub>2</sub> content was negligible, then the elemental composition of the organic matter was estimated to be 74.4 wt.% C, 8.9 wt.% H, 0.4 wt.% N, 16.3 wt.% O + S (by difference).

The concentrated Dictyonema oil shale kerogen was concentrated to about 60% organic matter from the original shale, which had about 19% organic matter content. The kerogen was concentrated via the flotation technique [26]. Ultimate analysis, on a dry basis, gave 40.3 wt.% ash, 49.3 wt.% C, 5.67 wt.% H, 0.54 wt.% N. As carbonaceous CO<sub>2</sub> content was negligible, then the elemental composition of the organic matter was estimated to be 83.1 wt.% C, 9.5 wt.% H, 0.9 wt.% N, 6.5 wt.% O + S (by difference).

Green River formation oil shale had an organic matter content of 14% and was used as received. Ultimate analysis, on a dry basis, gave 67.8 wt.% ash, 16.81 wt.% C, 1.66 wt.% H, 0.22 wt.% N. As carbonaceous CO<sub>2</sub> content was 18.2 wt.%, then the elemental composition of the organic matter was estimated to be 84.7 wt.% C, 11.9 wt.% H, 2.2 wt.% N, 1.2 wt.% O + S (by difference).

For a comparative experiment, the Kukersite concentrated kerogen sample was heated for 2 h at 400 °C in a closed vessel to turn part of the kerogen into a thermobitumen/oil mixture. By definition, the thermobitumen is the pyrolysis intermediate which is soluble in organic solvents and non-volatile at its formation temperatures. Oil, by contrast, is defined as volatile at its formation temperatures. As a result, about 30% of the kerogen was turned into a thermobitumen/oil mixture. Evolution of the thermobitumen/oil mixture in py-FIMS below 300 °C should be driven by vapor pressure, and could therefore roughly indicate an average molecular weight value of compounds able to vaporize at given temperature under experimental conditions. The thermobitumen/oil mixture formed had species with molecular weights from about 150 to 700 daltons (estimated from FIMS spectra in the temperature range from 50 to 300 °C).

### 2.2. Direct pyrolysis in Field Ionization Mass Spectrometer (FIMS)

A direct pyrolysis into the inlet of the Field Ionization Mass Spectrometer (FIMS) was carried out on roughly 0.5–1 mg of air-dry oil shale samples (the exact size depended on the mineral matter content). The FIMS experiments were conducted at Rostock University by a laboratory led by Professor Peter

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