

## The Lille-Blokker model – an excellent tool to describe the structure of kukersite

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**Abstract.** *The structure of kukersite organic matter has been a matter of scientific investigation and disputes over a hundred years. When considering the publications on the subject the authors of the current article concluded that the structure of kukersite is well described by a model proposed independently by Ülo Lille and Peter Blokker at the beginning of this millennium. This model characterizes the behaviour of kukersite in thermal processing and predicts the behaviour of oil shale kerogen in oxidation and other chemical transformations. The structural model may serve as a basis for new technologies for oil shale processing in order to get valuable chemicals directly from it.*

**Keywords:** *kukersite, structural model, thermal processing, chemical transformation.*

### 1. Introduction

Estonian oil shale, kukersite, is a sedimentary rock that contains up to 70% of organic matter which is named kerogen. It has been used on a large scale for production of energy and oil throughout all of the 20th century (see an overview and references in [1]). Kukersite was formed in Ordovician period 450 million years ago and, based on kerogen nature, it is categorized into shales of type I (sapropelic) and type II (lipid-rich) kerogens, according to Vandenbroucke and Largeau [2]. The origin and structure of kukersite have been the subject of research and discussions already for a long time. Already in the early 20th century it was suggested by Zalesky [3, 4] and Fokin [5] that the kerogen of kukersite was formed mainly from microorganisms *Gloeocapsomorpha prisca*. This assumption was confirmed to be basically true more than 70 years later [6].

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## 2. Overview of the early structural studies

The chemical structure of kukersite kerogen has been a subject of investigations and discussions for more than a hundred years. A milestone in the structural studies was laid by Paul Kogerman [7] by the following statement: “Probably the organic matter of kukersite consists of a mixture of unsaturated open chain and cyclic hydrocarbons with a small amount of unsaturated acids and traces of paraffins.” Kogerman also introduced the oxidation method to investigate the structure of kukersite. He found that in the oxidation of kukersite with potassium permanganate benzoic acids were not formed and proposed that the aromatic hydrocarbons are not present in kukersite kerogen [7, 8]. In addition, Kogerman [9] also discovered the formation of fatty acids in the oxidation product. Shortly after that Fomina and Pobul [10–12] established that kerogen oxidation with potassium permanganate afforded dicarboxylic acids. They suggested that kukersite represents a polycondensation product of non-aromatic fatty and naphthenic acids. This suggestion neglects the fact that the kukersite pyrolysis oil contains ~20% of alkyl resorcinols. The analytical abilities of those days were weak, and Fomina [13], Pobul et al. [14] and Fomina [15] were unable to find phenolic subunits in kukersite kerogen. So, they suggested that kerogen contains levoglycosane-like structures (“watery humus”) and the resorcinols found in the shale oil form in the retorting process. They stated that differently from humites kukersite consists of polymeric fatty acids [13–15].

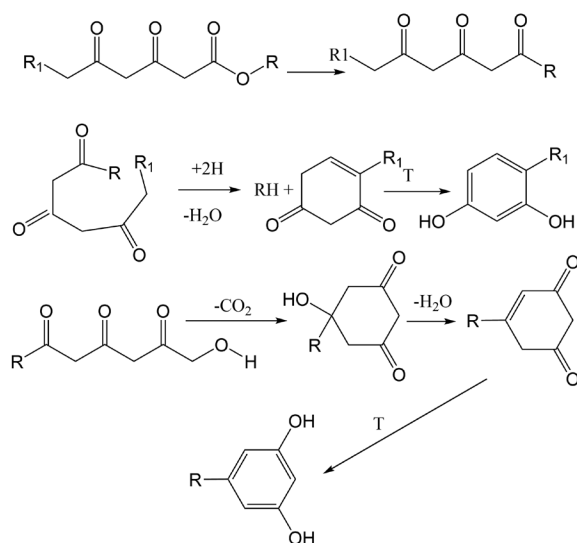


Fig. 1. Formation of resorcinols during the pyrolysis of kerogen from lipid-like fragments according to a hypothesis by Arro and Klesment [21].

Klesment et al. [16] studied kukersite pyrolysis oil and on the basis of that made the suggestions on kukersite structure. The researchers asserted that the oil reflects the native structure of kukersite and proposed, similarly to Pobul et al. [14], that C12 fragments in the oil are formed from the fatty acid fragments in kerogen. Klesment et al. [17] and Klesment [18] also proposed that resorcinols present in the oil are formed from ketones and aldehydes derived from the native kerogen polyesters during the thermal cyclization and aromatization. This hypothesis of resorcinol formation from lipid-like hydroxy carboxylic acid polymer (oxy fatty acid fragments) during pyrolysis over 400 °C was stated by Klesment [19] and Klesment and Nappa [20] repeatedly later as well, and they outlined the scheme for the formation of resorcinols during pyrolysis.

Already in the mid-fifties, on the basis of data on hydrogenation with hydrogen iodide and AlBr<sub>3</sub>, Raudsepp [22, 23] found that phenolic ether-like structures are present in kukersite kerogen, approximately one aromatic ring in respect to 13–17 carbon atoms.

A comprehensive investigation of the kukersite structure was carried out by Lippmaa, under the supervision of Professor Aarna [24]. They obtained a similar result to that afforded by Raudsepp, confirming that the content of aromatic phenols in kukersite kerogen remains in the range of 15–22% and that the content of naphthenic rings is in the range of 50–75%. In the late 1970s Lippmaa et al. [25] reinvestigated the kukersite structure by solid-state <sup>13</sup>C NMR spectra and confirmed that the content of aromatic carbons with oxy-substituents in kerogen is about 18–20%.

### 3. Advances towards the structural model for kukersite

A new era began with the stepwise oxidation of kukersite kerogen with KMnO<sub>4</sub> followed by analysis of the esters by modern gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) carried out by Bajc et al. [26]. They noticed the presence of alkyl mono-, di-, tri- and tetracarboxylic acids in the oxidation product and stated that if resorcinol moieties exist in kukersite, these are lost in the course of oxidation. In addition, the existence of abundant amounts of C–O fragments in the solid nondegraded residue was also observed [26].

Having started to investigate the kukersite retort oil, Lille et al. [27] and Lille [28] separated and identified five different alkylresorcinols. Unlike Klesment et al. [17] and Klesment [18, 19], Lille [29] considered the formation of phenolic hydroxyls during the thermal treatment from alcoholic hydroxyl groups of hydroxy fatty acids or keto acids unrealistic, because in pyrolytic conditions these groups transform completely to pyrolytic water. Lille et al. [30] put forward that the 1,3-benzenediol nucleus present in oil was preserved from original poly-β-keto structural elements of several species of extant algae.

The investigators had noticed that these structural units serve as “markers” of biological origin in the fossil organic matter [31–35]. On the basis of all these data Lille [36] proposed in 1999 that the main structural elements of native kerogen are the derivatives of 1,3-benzenetriols connected with each other by aliphatic carbon chains. Indeed, the biological nature and origin of resorcinols have later been referred to by several researchers [37–39]. On the basis of the  $^{13}\text{C}$  NMR spectra of kerogen Lille et al. [40] and Lille [41] confirmed the above suggestion in 2003 and proposed a kukersite kerogen model as presented in Figure 2. These results are in good accordance with those of the earlier NMR studies carried out by Lippmaa et al. [24, 25].

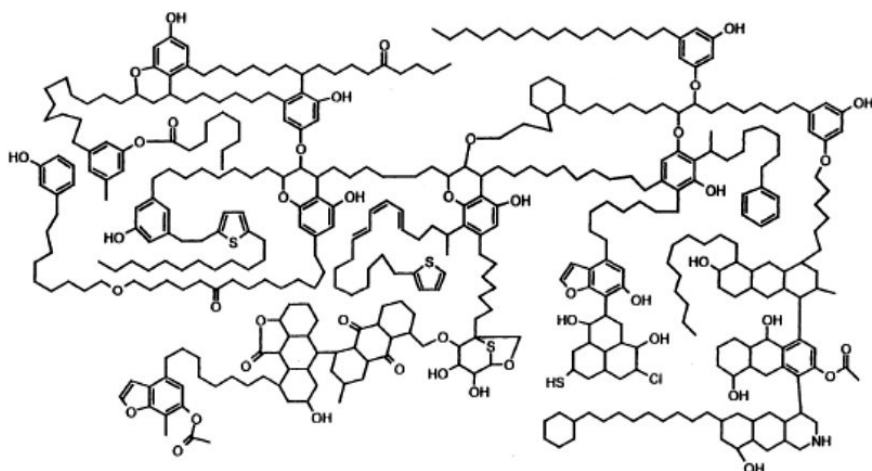


Fig. 2. The kerogen structure proposed by Lille et al. [40] and Lille [41].

Independently of the investigators mentioned above, Blokker et al. [42] conducted in 2001 a comprehensive study on the oxidation of Estonian kukersite kerogen with  $\text{RuO}_4$  and analysed the formed products by GC, GC-MS and pyrolysis-gas chromatography-mass spectrometry (py-GC-MS). The research team compared the results with those obtained by oxidation of North-American Guttenberg oil shale. Similarly to Lille [41], it was found that kukersite kerogen consists of 1,3-benzenetriol rings connected with each other mainly by aliphatic carbon chains [42]. In addition, the chemism of the formation of dicarboxylic acids from kukersite during oxidation, with one carbon of resorcinol transforming into the carboxylic acid moiety, was clearly demonstrated. The simplified proposed chemism of the process is presented in Figure 3.

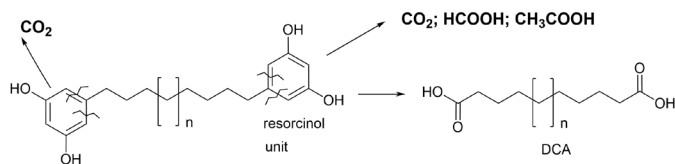


Fig. 3. Proposed reaction mechanism of the formation of dicarboxylic acids from kerogen.

Blokker et al. [42] also proposed a structural model of kukersite kerogen, the simplified version of which is presented in Figure 4.

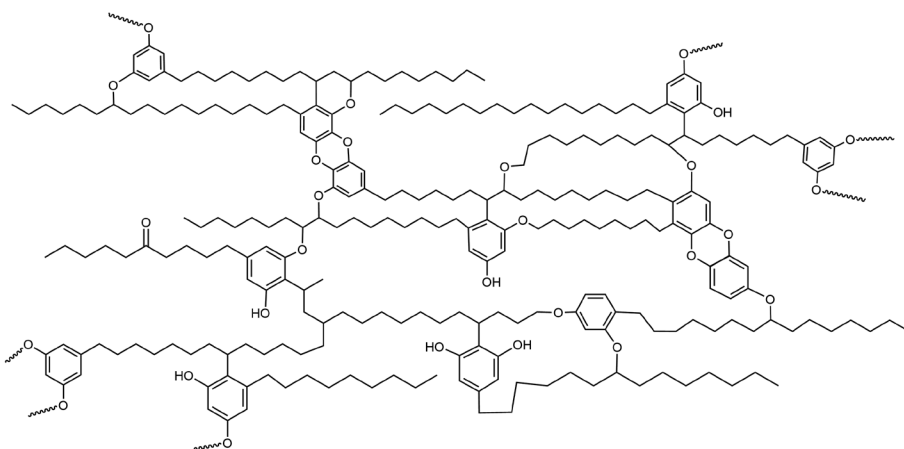


Fig. 4. The kukersite kerogen structure, according to Blokker et al. [42].

The similarity between these two models is evident, however, the models were built by using data from different analysis methods and different research approaches.

The characteristic features of these two structural models are the following:

- The backbone of kukersite kerogen is built on the basis of resorcinol units.
- The resorcinol units are connected to each other with aliphatic carbon chains.
- The ratio of free phenolic hydroxyl groups to the phenolic ether groups is not exactly defined.

When taking into account the molecular formula of kukersite kerogen  $\text{C}_{10}\text{H}_{15.2}\text{O}_{0.93}\text{S}_{0.08}\text{N}_{0.037}$ , these two models can be generalized as a basic Lille-Blokker structural model for kukersite kerogen structure by adding sulphur and nitrogen elements and some alicyclic rings. The generalized Lille-Blokker model is illustrated in Figure 5.

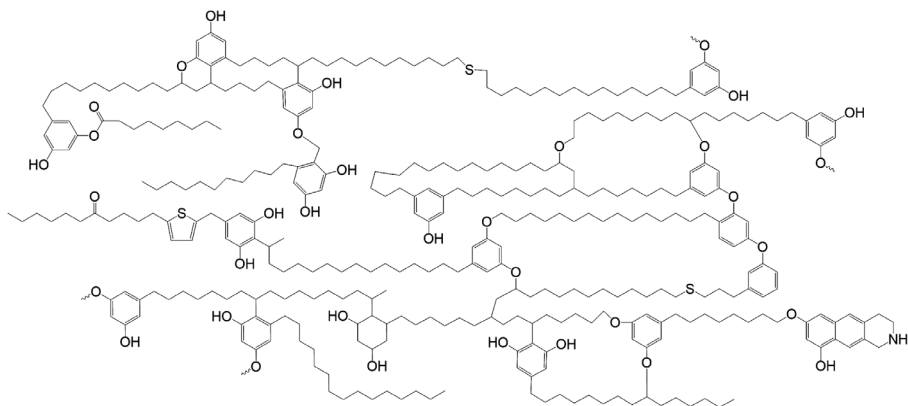


Fig. 5. The Lille-Blokker structural model of kukersite kerogen with a molecular formula  $C_{10}H_{15.2}O_{0.93}S_{0.08}N_{0.03}$ .

This model explains well the results of the oxidation of kerogen: the alkyl interlinked resorcinol units are oxidized and form dicarboxylic acids.  $CO_2$ , formic acid and acetic acid are formed from alkylresorcinol subunit destruction.

On the basis of the Lille-Blokker kerogen model one may suppose that the oxidation of kerogen occurs roughly in a two-step process: the first step is the oxidation of oxidation-labile resorcinol subunits leading to the depolymerization of the cross-linked native structure of kerogen, and the second step is the oxidation of the primary oxidized material into smaller molecules (carboxylic acids, etc., and  $CO_2/H_2O$ ). Indeed, we have previously observed that 2- and 5-methylresorcinols are very unstable towards air oxidation and decompose quickly. Even more, resorcinol additives promote the air oxidation of kerogen [43]. We recently studied the oxidation of kukersite with air oxygen and the obtained results also support the Lille-Blokker model [44, 45].

On the other hand, the content of oil from the thermal retorting process without access of air supports also the model: pyrogenic decomposition of the kerogen native structure, liberating the alkyl resorcinol subunits to the oil (approximately 20%), is expected from the model. The Lille-Blokker model is valid only for the kukersite-type kerogens.

#### 4. Conclusions

The fruitful study of the Estonian oil shale structure over more than the last hundred years has led to a general understanding of its structure which is well generalized independently by Lille and Blokker in their proposed models. The similarity of these structures provides a basis to name these proposals as a Lille-Blokker model of kukersite. When developing the oil shale conversion

processes the Lille-Blokker structural model may serve as a basis for selecting new structure-based conversion methods and promote technological alternatives to the present oil production, in order to get valuable chemicals directly from oil shale.

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