Extraction of aliphatic hydrocarbons and formation of new ones at superheated steam temperatures from demineralized anthracite from Vrška Čuka (Serbia)

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Abstract

Extraction of aliphatic hydrocarbons from demineralized coal using superheated steam is a promising method for reducing the industrial production costs. In the present study, extractions were performed at superheated steam temperatures without a catalyst (373 to 473 K; 2-20 h). The greatest yield of extracted organic matter was obtained during the first 2 h (4.0 to 6.1 % of the initial sample mass). At longer times, solubility values varied, suggesting that the release of aliphatic hydrocarbons depends on their location within different structural domains of the organic matrix. The high maturity of the organic matter indicates that the anthracite sample is in the metagenesis phase. Gas chromatography with flame ionization detection showed that extraction yielded n-paraffins, primarily the energetically significant C12 to C19 homologues, comprising 50 to 61 % of extracted compounds after 20 h. Comparison with less mature coals (lignite and brown coal) from the same area revealed a similar trend, though, with increasing coalification, the proportion of n-paraffins decreased and terpenes increased. Fourier transform infrared spectroscopy of the dry residue after extraction showed that methyl groups (2972 cm^{-1}) were lost after 2 hours at all temperatures, while complete removal of aliphatic structures, including ethyl groups (2924, 2852 and 1377 cm^{-1}), occurred after 20 h. The detected paraffins and terpenes originated from methyl and ethyl groups extracted from the organic matrix. Additionally, while lignite and brown coal gave nearly identical results, lignite lacked independently bound methyl groups.

Keywords: coal, solubility, maturation, paraffins, methyl groups.

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1. INTRODUCTION

The Triassic period brought significant changes to the planet's flora and fauna. For unknown reasons, at the end of this period (around 205 million years ago), a major biological crisis occurred, resulting in mass extinction (>70 %) of plant and animal species [1]. Geological records of this crisis on the Balkan peninsula are primarily found in Eastern Serbia (Carpatho-Balkan region). The extinction of flora led to the accumulation of dead plant material along the shores of the Carpathian Sea, as fluctuations in sea level (first retreating and then advancing) resulted in repeated deposition and coverage of organic matter in this area [2-5]. From the deposited material, anthracite deposits were formed in Vrška Čuka, Dobra and Jerma.

The Vrška Čuka mine is in eastern Serbia (the northernmost part of the Stara Planina mountain). The geology of this area, as well as the full succession of Jurassic rock layers, has been well studied [6-9]. The coal itself is of a black-grey colour, has a metallic-glass sheen, and, depending on its metamorphic state, can appear in graphite form. In recent years, there has been increasing discussion about the economic feasibility of exploiting this mine and the possibility of

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its closure. Certainly, the economic development of this region is partially tied to this mine. The main issue is that this type of coal is not widely used but is rather employed for specific industrial needs. In this regard, it is necessary to find a new role for it in potential industrial production. This work provides a partial contribution to that effort.

The removal of aliphatic hydrocarbons from aromatic ones in geochemical studies using water extraction under supercritical conditions is relatively well-known (many authors). To date, this technique has primarily been used for the determination of aliphatic hydrocarbons in petroleum source rocks [10]. Besides water vapor, carbon dioxide with or without additives is also frequently used [11-12]. Additionally, there are reverse cases of extracting aromatic hydrocarbons from aliphatic chains [13]. Both extraction processes are part of modern industrial needs, particularly in the industries of plastics, rubber, adhesives, etc. Beyond the classic separation of aliphatic from aromatic compounds for industrial purposes, their separation can also be utilized for environmental purposes, where these compounds are present as pollutants in various types of soil [14]. Previous studies on anthracite from Vrška Čuka have shown a high presence of aromatic hydrocarbons [15,16] that are associated with aliphatic hydrocarbons in short chains. In the development and practical application of this technique, industrially and economically developed countries have played a significant role, particularly in advancing the technology of coal-to-liquid (CTL) conversion. The profitability of synthesizing new hydrocarbons from coal depends on the type of coal (its maturation), the quantity and quality of the fuel produced, as well as the environmental consequences of the technological process itself. The primary focus has been taken on using low-quality coal with a lower degree of maturation. In contrast, data published on the kinetics of CTL formation from anthracite, as well as its synthesis at lower temperatures without the use of catalysts, remain very scarce. Accordingly, this analysis focuses on the extraction of aliphatic hydrocarbon chains at superheated water vapor (SHWV) temperatures of 373-473 K.

There are several methods for extracting aliphatic compounds. The development of methods for recovering these compounds from natural resources such as oil and coal is of growing interest due to their increasing industrial applications [17]. Inexpensive methods are particularly important, as they reduce the costs of industrial production [18]. This focus on innovative extraction approaches has become especially relevant considering the continuously rising costs of industrial manufacturing [19]. Accordingly, in the present study, emphasis was placed on the recovery of aliphatic hydrocarbons from high calorific hard coals, such as anthracite, at different temperatures using SHWV.

2. EXPERIMENTAL

2. 1. Thermal solubility experiments

Coal samples of anthracite, brown coal and lignite were obtained from the surface coal dump. The samples were ground in a vibratory mill with a ceramic ball, at a vibration intensity of 8 on the instrument scale 018, for 30 min (VEB MLW Medizintechnik Leipzig, German Democratic Republic, GDR). Subsequently, the samples were dried for 12 h in a laboratory oven at 355 K and transferred to a desiccator, where they were kept until a constant mass was achieved. The procedure for separating inorganic fractions from kerogen in geological samples is well-established [20-22]. Coal samples were demineralized for 72 h using an HF (22 M)-HCl (12 M) mixture at 353 K, followed by treatment with boiling HCl (12 M) for 12 h. The obtained organic residue was thoroughly rinsed with deionized water (Fisher, HPLC grade; <0.1 μS), ensuring that that all residual acid was removed. Removal of bitumen was performed in a Soxhlet apparatus for 72 h at 355 K using a benzene/methanol azeotropic mixture (6:1, v/v; J.T. Baker, HPLC grade), until the solvent in the extraction flask became clear. After that, the demineralized coal sample was dried again to remove residual solvent (355 K, 8 h).

Each of the five demineralized coal samples (2.9990, 3.0015, 3.0020, 2.9900 and 3.0005 g) was accurately weighed and combined with 15 cm^3 of deionized water in a Teflon capsule (total volume 42.4 cm^3; free volume 24.4 cm^3). The capsules were sealed with Teflon lids and then placed into steel reactors (Figure 1), which ensured hermetic sealing. The lids and capsules were secured with steel screws. The reactors were placed in a muffle furnace and heated to 373, 398, 423, 448 and 473 K (Figure 2). The corresponding saturated pressure values of water at each temperature were taken from thermo-dynamic tables based on the liquid-vapor phase equilibrium as follows: 373 K - 100 kPa, 398 K - 230 kPa, 423 K - 480 kPa,

448 K - 890·kPa and 473 K - 1550·kPa. These values are determined solely by temperature and represent the equilibrium vapor pressure; they do not depend on the free volume in the reactor.

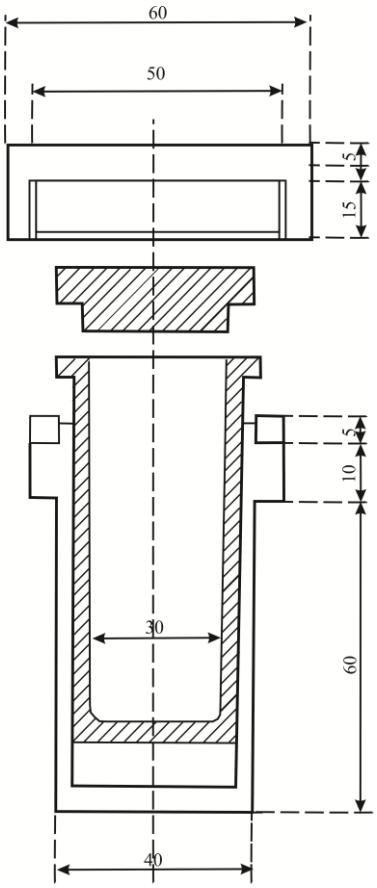

Figure 1. *Schematic representation of the reactor*

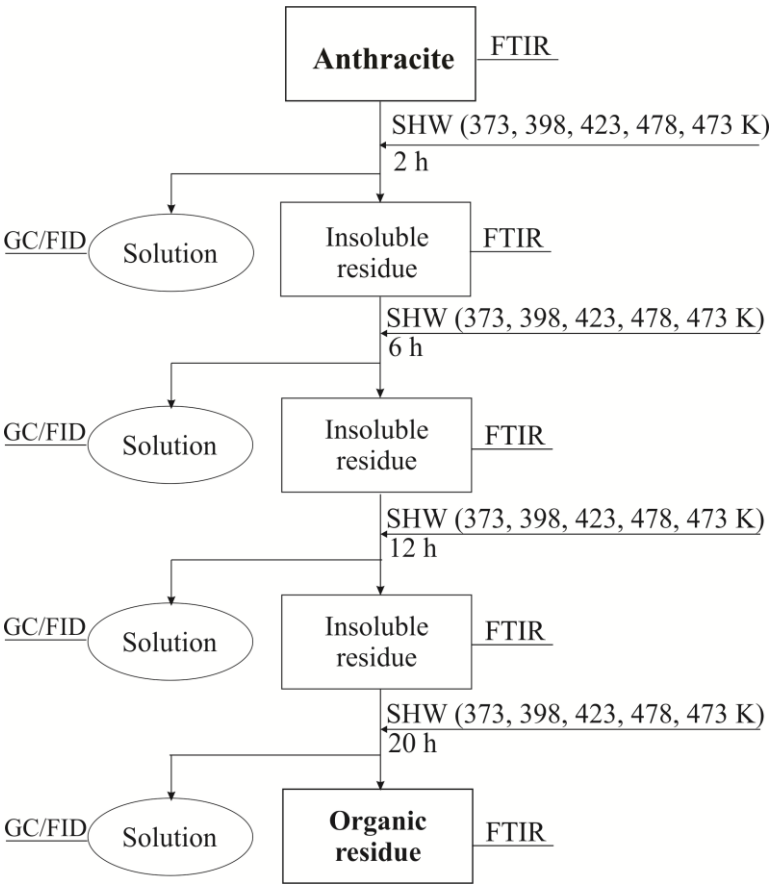

Figure 2. *Flow chart of extraction procedure*

After each extraction phase, the samples were filtered, dried, and the residue mass was measured. Portions of the solution and coal residue were preserved for chromatographic analysis and Fourier transform infrared (FTIR) spectroscopy, respectively. For each extraction, the mass of solution and coal residue recovered was calculated as a fraction of the initial sample mass. This procedure was repeated by heating the extraction residues for additional periods of 4, 6 and 8 hours after the initial 2-hour heating; at the start of each extraction, a fresh equal amount of deionized water was added. The total mass fraction recovered was obtained by summing the individual fractions from each extraction step.

The heating was conducted in a muffle furnace (Carbolite, Germany), with the temperature determined with an accuracy of ±2 K. This method is similar to the process of semicoke obtaining at low temperatures, with the research emphasis placed on the content and composition of the soluble phase. The research was carried out with 3 samples with 20 experiments each (5 different temperatures in four different intervals).

2. 2. Analytical methods

2. 2. 1. Ultimate analysis

Ultimate analysis was performed using a Vario EL III C, H, N, S/O Elemental Analyzer (ElementarAnalysensysteme GmbH, Hanau-Germany). This analysis was performed at the Faculty of Chemistry (University of Belgrade, Serbia) under the following conditions: the combustion temperature of 1150 °C, helium as the carrier gas and a thermal conductivity detector (TCD). The dynamic working range of the apparatus is as follows: C: 0.03 to 20.00 mg; H: 0.03 to 3.00 mg; N: 0.03 to 2.00 mg; S: 0.03 to 6.00 mg.

2. 2. 2. Gas chromatography-mass spectrometry and gas chromatography-flame ionization detection analysis

The same volume of each sample (1 cm^3) was transferred into test tubes, mixed with 1 cm^3 of *n*-hexane (LC-MS grade, Fisher Scientific, Germany) and vigorously shaken for 5 minutes. After shaking, the samples were allowed to stand for approximately 1 minute until clear phase separation occurred. The upper hexane layer was transferred by glass Pasteur pipettes directly into syringes fitted with 33 mm diameter PTFE sterile syringe filters (hexane-compatible, 0.45 µm pore size). A single extraction step by n-hexane was used. Filtered hexane extracts were subjected to GC/MS analysis performed using an Agilent Technologies 7890B gas chromatograph, equipped with a weakly polar silica capillary column, HP-5MS (5 % diphenyl- and 95 % dimethyl-polysiloxane, 30 m × 0.25 mm, 0.25 µm film thickness; Agilent Technologies, St. Louis, MO, USA), and coupled with an inert, selective 5977A mass detector of the same company. The samples (5 µl) were injected in spitless mode. Helium was used as the carrier gas at a constant flow rate of 1 ml min^{-1}. The oven temperature was programmed to rise from 353 to 583 K at a rate of 10 K min^{-1} and then held at 583 K for 10 min. The temperatures of the MSD transfer line, ion source, and quadruple mass analyser were set at 573, 500 and 423 K, respectively. The ionization voltage was 70 eV and the mass range *m*/*z* 35 to 650. The flows of the carrier gas (He), make up gas (N_2), fuel gas (H_2) and oxidizing gas (air) were 1, 25, 30 and 400 ml min^{-1}, respectively. The gas chromatography-mass spectrometry (GC/MS) and gas chromatography with flame ionization detection (GC/FID) analyses were performed at the Faculty of Technology, University of Niš, Serbia.

GC/FID analysis was carried out under identical experimental conditions as GC/MS. The temperature of the flame-ionization detector (FID) was set at 573 K. Data processing was performed using MSD Chem-Station (version F.01.00.1903), MassHunter Qualitative Analysis (version B.06.00) and AMDIS (version 2.70) software [23] (Agilent Technologies, USA). Baseline correction was carried out automatically by the software, while peak deconvolution and identification were performed using AMDIS with default settings. Manual reintegration was applied only when required in cases of overlapping peaks to ensure accurate peak area determination. Identification of extract constituents was based on comparison of the compounds' retention indices with those reported in the literature and comparison of their mass spectra with reference spectra from the Wiley 6 [24], NIST2011 [25] and RTLPEST3 [26] libraries. Retention indices of the components from the analysed samples were experimentally determined using a homologous series of *n*-alkanes from C_8-C_{20} and C_{21}-C_{40} as standards. The semi-quantitative composition (content, %) of the samples was determined by the area normalization method, based on the automatically integrated peak areas of the GC/FID signal, without any corrections.

2. 2. 3. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectroscopy analysis was performed on the initial samples and on the dry residues after individual extraction stages. Anthracite, demineralized coal and demineralized coal residue were finely powdered and dispersed evenly in anhydrous potassium bromide (KBr) pellets (1 mg *per* 150 mg KBr). The mixture was then subjected to vacuuming and pressing under a pressure of 200 MPa to obtain the appropriate lozenges. FTIR spectra were obtained using a Bomem MB-100 spectrometer (Hartmann and Braun, Canada) set to generate uniform spectra (Faculty of Technology, University of Niš, Serbia). The acquisition parameters were as follows: spectral range 4000 to 400 cm^{-1}, 10 scans, and baseline treatment using interactive polynomial ($\underline{C}X^2$ and $\underline{D}X^3$). Background scanning was performed with a pellet made of anhydrous KBr.

3. RESULTS AND DISCUSSION

3. 1. Elemental analysis

Based on elemental analysis, the H/C and O/C ratios were calculated for all three coal samples analyzed (*i.e.* anthracite, brown coal, and lignite) and plotted on a van-Krevelen diagram. This diagram illustrates the maturation pathway of organic matter, distinguishing the diagenesis, catagenesis and metagenesis regions (Figure 3). Unlike anthracite from Vrška Čuka (metagenesis), brown coal from Sokobanja and lignite from Kostolac are characterized by a low degree of coalification and are still in the diagenesis stage. Based on these results and previous observations, it can be concluded that with increasing coalification, the proportion of n-paraffins decreases, while the proportion of terpenes increases.

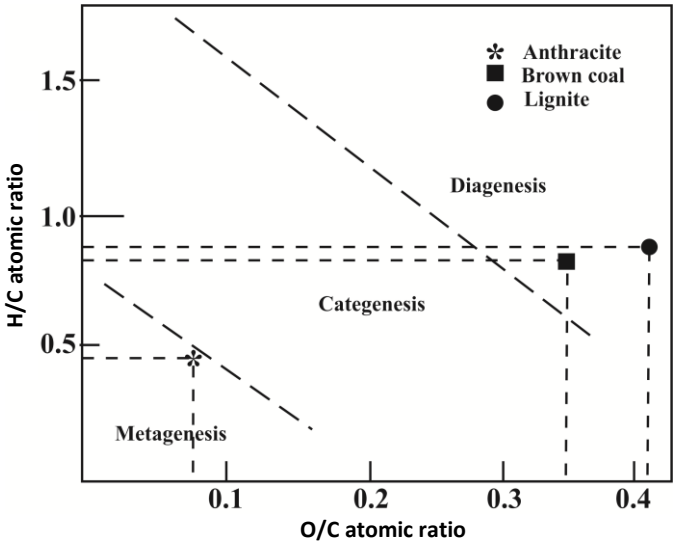

***Figure 3**. Van-Krevelen diagram for Vrška Čuka (anthracite), Sokobanja (brown coal) and Kostolac (lignite) coals*

3. 2. Thermal solubility experiments

As pointed out in the Experimental section, thermal solubility analyses of Vrška Čuka demineralized anthracite were performed at 373, 398, 423, 448 and 473 K (Table 1). At all temperatures, the greatest extraction of organic matter occurred within the first 2 h. After that, the extraction rate decreased over time, except in the case of the sample at 473 K, where solubility after 12 h was greater than after 6 h. This result may be due to further decomposition or transformation of organic molecules at higher temperatures, leading to the formation of additional soluble groups. This assumption is supported by the fact that after 12 h of extraction, there was no further decrease in the residue mass. Therefore, in addition to the diminishing amount of material available for extraction, the results of the thermal dissolution experiments do not show a linear trend, likely due to the dissolution and release of structurally diverse aliphatic chains at different temperatures and time intervals.

***Table 1**. Thermal solubility experiments of the Vrška Čuka demineralized anthracite*

Time, h	Content of dissolved organic matter (relative to initial demineralized sample mass) ± standard deviation, %				
	373 K	398 K	423 K	448 K	473 K
2	6.1±0.2	4.0±0.2	4.7±0.2	5.5±0.3	5.0±0.3
6	5.5±0.2	3.8±0.2	1.5±0.1	1.1±0.1	1.0±0.1
12	3.0±0.1	0.0±0.0	1.0±0.1	1.1±0.1	2.2±0.1
20	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0	0.0±0.0
Total	14.6±0.5	7.8±0.4	6.3±0.4	7.7±0.5	8.2±0.5

The extraction results of this demineralized coal were compared with the extraction results of neighbouring coals of other types under the same conditions (Kostolac lignite and Sokobanja brown coal). The comparison results are presented in Table 2, showing that coal at a lower maturation stage exhibits better solubility.

***Table 2**. Comparison of thermal solubility results of the investigated demineralized coals after 2 h at different temperatures*

Sample	Contentof dissolved organic matter (relative to initial demineralized sample mass)) ± standard deviation, %				
	373 K	398 K	423 K	448 K	473 K
VČ	6.1±0.2	4.0±0.2	4.7±0.2	5.5±0.3	5.0±0.3
KL	15.3±0.7	13.2±0.6	13.8±0.6	14.4±0.6	14.9±0.6
SB	9.8±0.5	9.1±0.5	9.1±0.5	9.5±0.5	9.7±0.5

VČ- Vrška Čuka anthracite, KL - Kostolac lignite, SB - Sokobanja brown coal

3. 3. Gas chromatography with flame ionization detection analyses

Certainly, the extraction/dissolution process leads to changes in the composition of organic matter, as new compounds (paraffins and olefins) are formed, as shown in Reactions (1) and (2).

$nCO + (2n+1)\ H_2 = nH_2O + C_nH_{2n+2}$ (paraffins) (1)

$nCO + 2nH_2 = nH_2O + C_nH_{2n}$ (olefins) (2)

Figure 4 and Table 3 show the formed compounds and their contents at the initial temperature in the study (373 K) as well as at the initial, middle and final time intervals [(a) 2 h, (b) 12 and (c) 20 h, Figure 4].

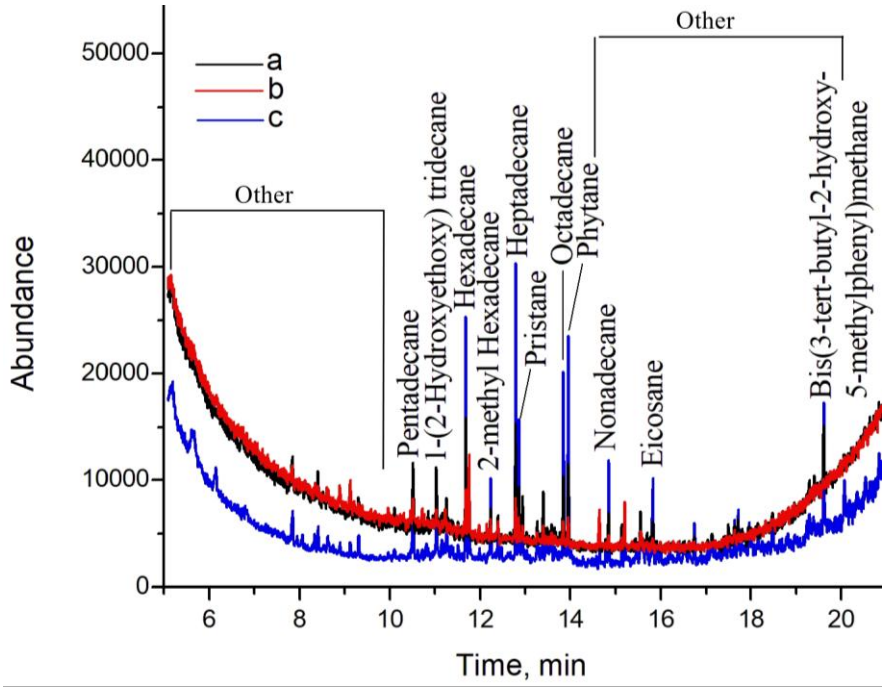

Figure 4. *GC/FID chromatograms of dissolved components obtained by heating the demineralized Vrška Čuka anthracite at 373 K (a-2 h, b-12 h and c-20 h)*

Table 3*. Mass percentage of extracted components in the solution phase from demineralized Vrška Čuka anthracite at 373 K at different extraction times*

No	Paraffins C_{12}-C_{19}	Formula	RI^{exp}	RI^{lit}	Method	Content, %		
						2 h	12 h	20 h
1.	Tridecane	$C_{13}H_{28}$	1298	1300	RI, MS	<1	<1	<1
2.	Tetradecane	$C_{14}H_{30}$	1398	1400	RI, MS	<1	<1	<1
3.	Pentadecane	$C_{15}H_{32}$	1498	1500	RI, MS	5	3	<1
4.	Hexadecane	$C_{16}H_{34}$	1599	1600	RI, MS	7	8	10
5.	2-Metyl-hexadecane	$C_{17}H_{36}$	1656	1666	RI, MS	5	5	6
6.	Heptadecane	$C_{17}H_{36}$	1698	1700	RI, MS	11	7	11
7.	Pristane	$C_{19}H_{40}$	1713	1704	RI, MS	6	11	7
8.	Octadecane	$C_{18}H_{38}$	1798	1800	RI, MS	8	8	9
9.	Nonadecane	$C_{19}H_{40}$	1898	1900	RI, MS	5	5	4
	Total paraffins C_{12}-C_{19}					48	48	50
	n-Paraffins	No.: 1-4,6,8, 9				39	38	37
	Terpenoid alkane	No.: 5, 7				12	13	13
	Other					1	1	<1
	Total identified					100	100	100

RI^{lit}-Retention indices from literature [27]; RI^{exp}: Experimentally determined retention indices using a homologous series of *n*-alkanes (C_8-C_{20} and C_{21}-C_{40}) on the HP-5MS column. MS: constituent identified by mass-spectra comparison; RI: constituent identified by retention index matching.

The total mass fraction of components after complete dissolution was determined by summing their individual mass fractions, which were calculated as the percentage of the soluble phase shown in Table 2. At this temperature, the proportion of newly formed paraffins (C_{12} to C_{19}), *n*-paraffins ($C_{1\text{-}4,\ 6,\ 8,\ 9}$) and terpenoid alkane remains relatively constant (Table 3). Olefins were not detected in any sample. Similar but not identical trends are observed in the contents of these compounds after 20 h of dissolution across all five temperatures (Table 4). Based on the presented results, the mass fraction of all formed paraffins remains relatively constant up to 423 K. At temperatures between 423 and 473 K, the

proportion of C_{12}-C_{19} paraffins increases, while that of *n*-paraffins ($C_{1\text{-}4,\ 6,\ 8,\ 9}$) decreases. The content of terpenoid alkane decreases slightly with increasing temperature. Also, olefins were not detected. These increases and decreases are within a range of ≤20 %.

***Table 4**. Mass percentage of extracted components in the solution phase from demineralized Vrška Čuka anthracite after 20 hours of dissolution at different temperatures*

No	Paraffins C_{12}-C_{19}	Formula	RI^{exp}	RI^{lit}	Method	Content, %				
						373 K	398 K	423 K	448 K	473 K
1.	Tridecane	$C_{13}H_{28}$	1298	1300	RI, MS	<1	<1	<1	1	2
2.	Tetradecane	$C_{14}H_{30}$	1398	1400	RI, MS	<1	<1	1	1	2
3.	Pentadecane	$C_{15}H_{32}$	1498	1500	RI, MS	<1	3	3	4	4
4.	Hexadecane	$C_{16}H_{34}$	1599	1600	RI, MS	10	9	9	10	10
5.	2-Metyl-hexadecane	$C_{17}H_{36}$	1656	1666	RI, MS	11	10	10	11	13
6.	Heptadecane	$C_{17}H_{36}$	1698	1700	RI, MS	6	8	8	8	9
7.	Pristane	$C_{19}H_{40}$	1713	1704	RI, MS	9	8	8	9	9
8.	Octadecane	$C_{18}H_{38}$	1798	1800	RI, MS	7	7	7	7	7
9.	Nonadecane	$C_{19}H_{40}$	1898	1900	RI, MS	4	5	5	5	5
Total paraffins C_{12}-C_{19}						50	51	51	56	61
n-Paraffins		No.: 1-4,6,8, 9				37	36	36	31	27
Terpenoid alkane		No.: 5, 7				13	12	12	12	11
Other						<1	1	1	1	1
Total identified						100	100	100	100	100

The composition of the soluble phase obtained during the extraction of Vrška Čuka anthracite was qualitatively and quantitatively compared with those obtained from demineralized lignite from Kostolac (57 % organic matter in coal) and brown coal from Sokobanja (64 % organic matter in coal), which are coals of lower maturity (Figure 5).

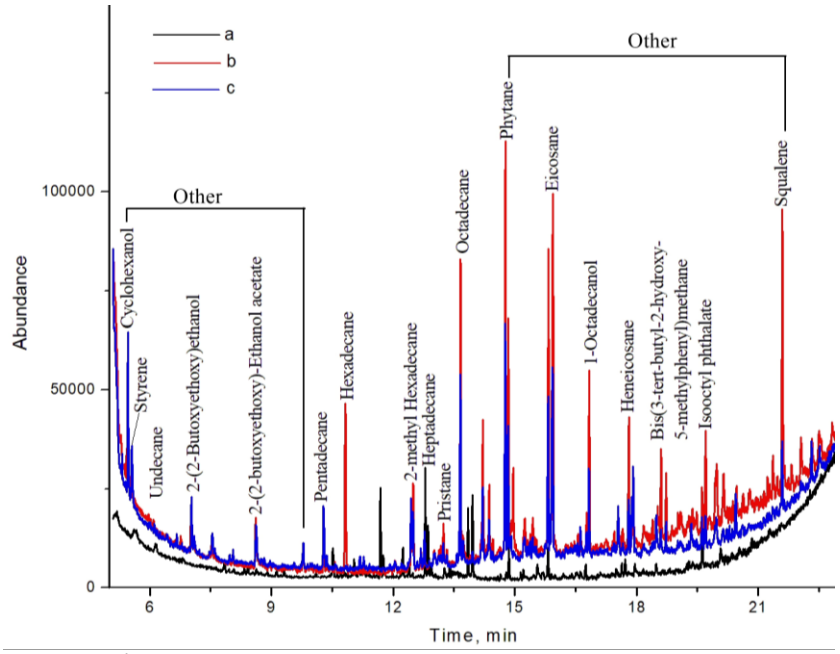

***Figure 5.** GC/FID chromatograms of soluble phases after 2 h of dissolution of demineralized (a) lignite, (b) brown coal and (c) anthracite*

The quantitative comparative results are presented in Table 5, where the soluble phases obtained after the first 20 h of dissolution at 373 K were selected, as they exhibited the highest mass percentages of the formed aliphatic compounds. It can be observed that with increasing coalification, the proportion of *n*-paraffins decreases, while the proportion of terpenes increases.

Figure 6 shows the mass spectra of the most abundant components after dissolution (20 h) at 373 K in the Vrška Čuka demineralized anthracite samples.

***Table 5**. Mass percentage of extracted components in the solution phase from demineralized anthracite, lignite, and brown coal after 20 h at 373 K*

No	Paraffins C_{12}-C_{19}	Formula	RI^{exp}	RI^{lit}	Method	Content (%)		
						KL	SB	VČ
1.	Tridecane	$C_{13}H_{28}$	1298	1300	RI, MS	<1	<1	<1
2.	Tetradecane	$C_{14}H_{30}$	1398	1400	RI, MS	<1	<1	<1
3.	Pentadecane	$C_{15}H_{32}$	1498	1500	RI, MS	<1	2	<1
4.	Hexadecane	$C_{16}H_{34}$	1599	1600	RI, MS	25	22	10
5.	2-Metyl-hexadecane	$C_{17}H_{36}$	1656	1666	RI, MS	27	19	11
6.	Heptadecane	$C_{17}H_{36}$	1698	1700	RI, MS	6	8	8
7.	Pristane	$C_{19}H_{40}$	1713	1704	RI, MS	<1	2	9
8.	Octadecane	$C_{18}H_{38}$	1798	1800	RI, MS	<1	3	7
9.	Nonadecane	$C_{19}H_{40}$	1898	1900	RI, MS	<1	2	4
	Total paraffins C_{12}-C_{19}					54	53	49
	n-Paraffins	No.: 1-4,6,8, 9				45	43	47
	Terpenoid alkane	No.: 5, 7				1	4	13
	Other					<1	<1	<1
	Total identified					100	100	100

KL - Kostolac lignite, SB - Sokobanja brown coal, VČ - Vrška Čuka anthracite

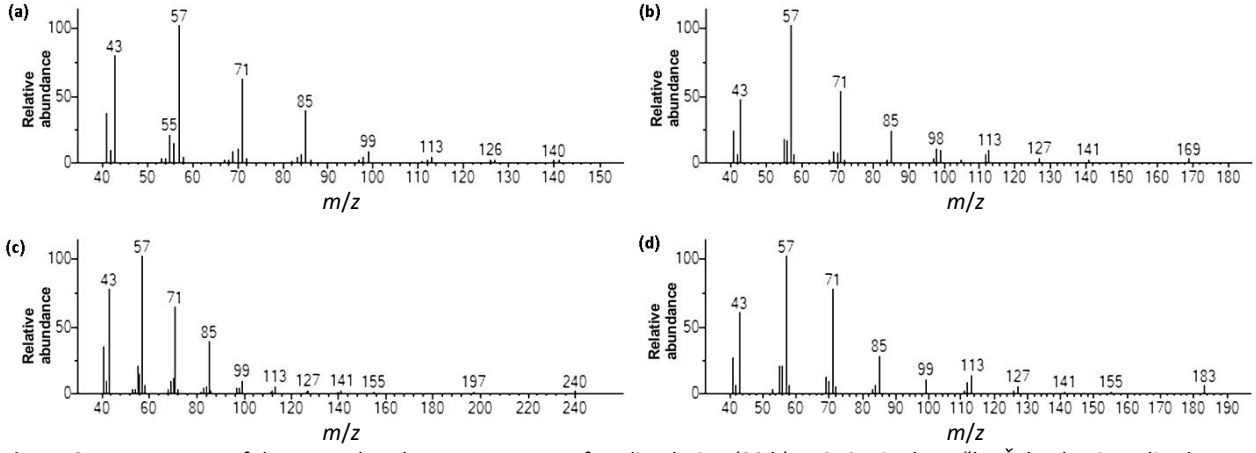

***Figure 6.** Mass spectra of the most abundant components after dissolution (20 h) at 373 K in the Vrška Čuka demineralized anthracite samples: (a) hexadecane, (b) 2-methyl hexadecane, (c) heptadecane and (d) pristane*

3. 4. Fourier transform infrared spectroscopy analysis

The present study of organic matter from Vrška Čuka anthracite confirms a high concentration of aromatic hydrocarbons and a minor amount of aliphatic hydrocarbons [15,16]. After 2 hours of extraction at 473 K, methyl groups (CH_3) with an absorption peak at 2972 cm^{-1} were extracted/removed from the organic residue (Figure 7). These methyl groups are likely those independently bound within the macromolecular structure of the coal-derived organic matter. In contrast, ethyl groups (CH_2) in the chain (absorption peaks at 2924, 2852, and 1377 cm^{-1}) remained unchanged. Further extraction revealed that after 20 hours, the complete removal of aliphatic compounds occurred (*i.e.* in addition to CH_3 groups, CH_2 groups also disappeared, as indicated by the absence of aliphatic structures in the 2960 to 2860 cm^{-1} region). The peak at ~1692 cm^{-1} is characteristic of the carbonyl (C=O) stretching vibration. This peak, along with the peak at 1635 cm^{-1} (attributed to conjugated C=C bonds), remained unchanged. Peaks at approximately 1585 and 1455 cm^{-1} originate from carboxylic group -COO- [28]. Similarly, changes were not observed in these peaks or in the peaks of aromatic structures in the 880 to 770 cm^{-1} region.

Recently, Zheng *et al.* [29] investigated the low-temperature oxidation of anthracite, as well as the stability of its aliphatic structures. The temperatures applied in their experiments (253 to 423 K), correspond to the temperatures of SHWV used in our study over similar time intervals.

Their results demonstrated that aliphatic moieties located within the interlayer space of the organic matrix are more stable than those situated at its periphery. In contrast to their approach, our method showed that the application of SHWV

leads to the complete detachment of aliphatic structures from the organic residue already at 373 K. A common feature of both approaches is the discontinuous behaviour observed in the stability of aliphatic structures within the samples.

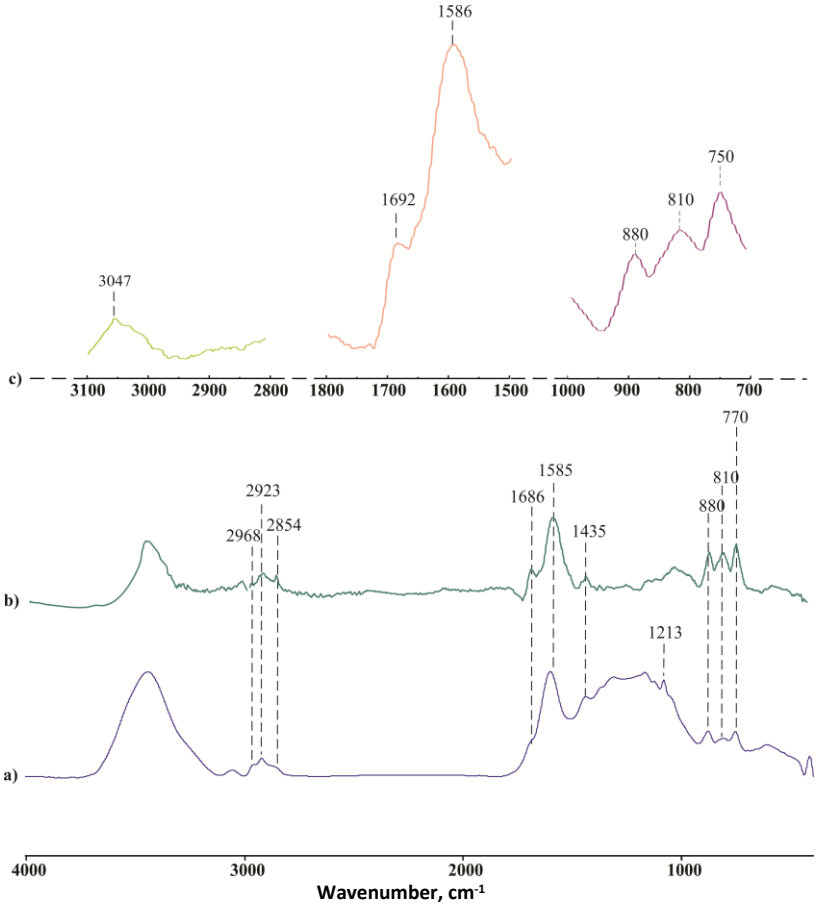

Figure 7. *FTIR spectra of anthracite from Vrška Čuka: a) initial demineralized sample, b) residue after 2 hours of extraction and c) residue after 20 hours of extraction at 473 K*

To compare different coals, FTIR spectra of the organic matter and the organic residue remaining after 2 hours of extraction from Sokobanja brown coal and Kostolac lignite are also presented (Figures 8 and 9, respectively).

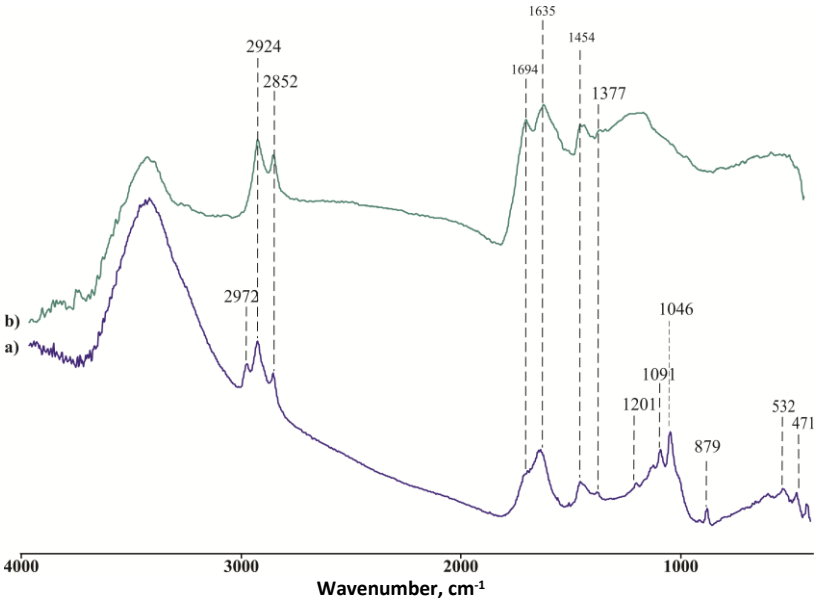

Figure 8. *FTIR spectra of brown coal from Sokobanja: a) initial demineralized sample and b) residue after 2 hours of extraction at 473 K*

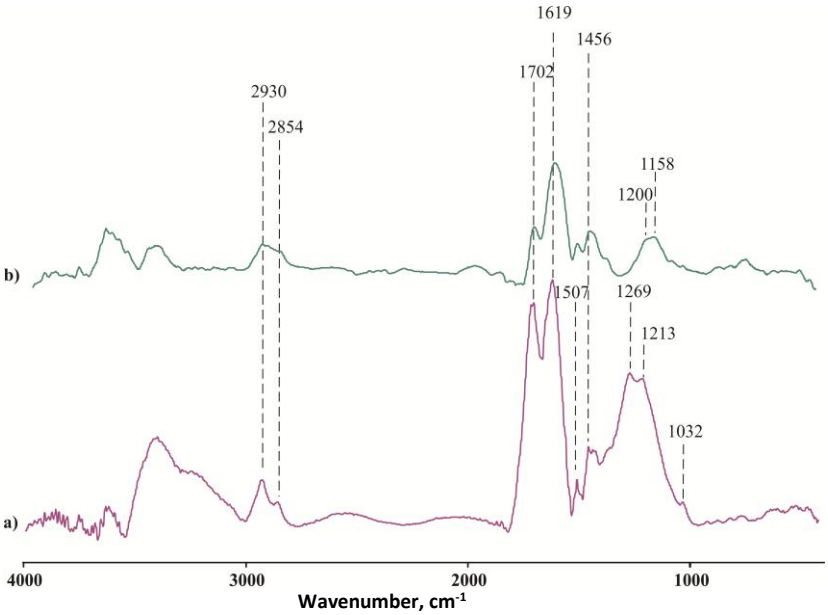

Figure 9. *FTIR spectra of lignite from Kostolac: a) initial demineralized sample and b) residue after 2 hours of extraction at 473 K*

In the case of the organic matter in Sokobanja brown coal, a broad band around 3400 cm^{-1} represents physically adsorbed water. Here, the loss of CH_3 groups, indicated by the disappearance of the absorption peak at 2972 cm^{-1}, likely corresponds to methyl groups that were present as side chains or isolated substituents on the macromolecular structure. In contrast, CH_2 groups in the chain (absorption peaks at 2924, 2852 and 1377 cm^{-1}) remained unchanged. Small peaks at 1201, 1091 and 1046 cm^{-1} originate from C-O and C-O-C bonds of alcohols, hydrogen peroxide and ethers. These peaks disappeared after extraction, along with peaks below 1000 cm^{-1}, attributed to C=C-H. Peaks at 1694 cm^{-1}, 1585 cm^{-1} and 1456 cm^{-1} remained unchanged. These two coals are compared because they are from the same area, but of different maturities.

4. CONCLUSION

Thermal solubility experiments performed in the present study show that the solubility rate of organic matter from demineralized anthracite from Vrška Čuka (Serbia) is highest during the first two hours of extraction. FTIR analysis reveals that during these initial 2 hours at all investigated temperatures, there is a loss of methyl groups, likely present as side chains attached to aromatic rings in the organic matrix. In the subsequent hours of dissolution, gradual degradation of ethyl groups occurred, leading to their complete removal after 20 hours. In lignite and brown coal samples, ethyl groups are also gradually removed during extraction, while methyl groups are either absent or present only in minor amounts.

The extracted solutions from demineralized anthracite from Vrška Čuka, obtained at extraction temperatures up to 423 K, show almost constant stable mass fractions of all paraffins. With further increases in the extraction temperature up to 473 K, the proportion of C_{12}-C_{19} paraffins increases, while the proportion of *n*-paraffins ($C_{1\text{-}4,\ 6,\ 8,\ 9}$) decreases reciprocally. In all analyses, the extracted solutions from anthracite showed stable terpene content, whereas the compared lignite and brown coal samples exhibited an increase in terpene levels. This difference can be attributed to their respective stages of coalification: anthracite is highly mature (metagenesis), while brown coal and lignite are less mature and remain in the diagenesis stage.

The results of this study demonstrate that the extraction method employed is effective for the quantitative extraction and separation of both short- and long-chain aliphatic hydrocarbons from the coal organic matter. Analysis of the extraction yield of aliphatic hydrocarbons enables the selection of the most suitable SHWV temperature for quantitative extraction, depending on the intended application, and provides insight into the method's potential uses.

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Ekstrakcija alifatičnih ugljovodonika iz demineralizovanog antracita sa lokaliteta Vrška Čuka (Srbija) pregrejanom vodenom parom na različitim temperaturama

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(Naučni rad)

Izvod

Ekstrakcija alifatičnih ugljovodonika pregrejanom vodenom parom iz organskih ostataka uglja predstavlja perspektivnu metodu zbog smanjenja industrijskih troškova potrebnih za njihovo dobijanje. U ovom radu ekstrakcija je izvedena u opsegu temperatura bez prisustva katalizatora (373 do 473 K; 2-20 h). Najveći prinos izdvojene organske materije ostvaren je tokom prva 2 h (4,0 do 6,1 % početne mase uzorka). Pri dužim vremenima, vrednosti rastvorljivosti su varirale, što ukazuje da oslobađanje alifatičnih ugljovodonika zavisi od njihovog položaja u različitim strukturnim domenima organske matrice. Visok stepen zrelosti organske materije ukazuje da je uzorak antracita u fazi metageneze. Gasna hromatografija sa plameno-jonizacionom detekcijom pokazala jeda ekstrakcija do stvaranja n-parafina, prvenstveno energetski značajnih homologa C12 do C19, koji čine 50 do 61 % izdvojenih jedinjenja nakon 20 sati. Poređenje sa manje zrelim ugljevima (lignit i mrki ugalj) iz istog područja je pokazalo sličnu tendenciju, ali sa povećanjem ugljenifikacije/sazrevanja, udeo n-parafina se smanjuje, dok se udeo terpena povećava. Infracrvena spektroskopija sa Furijeovom transformacijom suvog ostatka nakon ekstrakcije pokazala je da su metil-grupe (2972 cm^{-1}) nestale nakon 2 sata na svim temperaturama, dok je potpuna eliminacija alifatičnih struktura, uključujući etil-grupe (2924, 2852 i 1377 cm^{-1}), zabeležena nakon 20 sati. Detektovani parafini i terpeni potiču od metil- i etil-grupa ekstrahovanih iz organskog ostatka uglja. Dodatno, iako su lignit i mrki ugalj dali gotovo identične rezultate, u lignitu nisu detektovane nezavisno vezane metil-grupe.

Ključne reči: ugalj, rastvorljivost, sazrevanje, parafini, metil grupe