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Physical and Chemical Aspects of Oil Agglomeration as a Method for Preparing Salty Coal for Thermal Processing

Tetiana Shendrik[1], *Volodymyr Biletskyi*[2], *Natalia Desna*[3*]

[1] *M. Lytvynenko Institute of Physical-Organic and Coal Chemistry (IPOCC) National Academy of Sciences of Ukraine, 02160, Kyiv*
[2] *National Technical University "Kharkiv Polytechnic Institute" (NTU HPI), 61002, Kharkiv, 21 Kyrpychova Str., Ukraine*
[3] *State University of Economics and Technology, 50005, Kryvyi Rih, 16 Medychna Str., Ukraine*

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Abstract

The article presents the results of coal-oil agglomeration of salty coal (SC) and examines how the properties of its components – coal and M100 mazut – impact the process. The research employed methods such as X-ray phase analysis (XPA), electron paramagnetic resonance (EPR), infrared (IR) spectroscopy, and functional chemical analysis. The study was found that oil agglomeration of salty coal not only changes technical characteristics (reducing ash content, salinity, and moisture) but also involves several physical and chemical interactions between the active centres of coal organic matter (COM) and the oil agent. EPR analysis revealed that the paramagnetic centre content (PMC) in the agglomerate was significantly lower than in its precursor components. This indicates a sharp shift in the intermolecular interactions within the system. X-ray diffraction results showed structural changes in the coal, noticeable even with just 5% mazut content in the raw material. The coal agglomerate, with around 30% mazut, displayed an increase in the proportion of non-aromatic (polynaphthenic) fragments in the overall agglomerate structure (~70% compared to ~48% in the raw coal) and greater structural ordering (the h/l ratio doubled). IR spectroscopy and functional analysis showed that the concentration of quinone structures on the surface of the coal grains in the agglomerated products was lower than in the original samples, suggesting the direct reactivity of quinones in the process. Additionally, the active involvement of product's organic matter thio- or ether bonds in the formation of coal-oil aggregates is also possible. Comparative studies of changes in band intensity and position in the IR spectra confirmed this conclusion. EPR data further suggest that RO2· or RS2· radicals are likely involved in the recombination reactions of coal and oil agent PMCs. Pyrolysis tests of salty coal, its mixture with mazut, and the coal-oil agglomerate showed that oil agglomeration significantly influences the thermolysis results. Pyrolysis of agglomerated coal demonstrated an additive increase in the organic matter conversion rate, as clearly seen from the yields of gaseous products and tar. These findings suggest that oil agglomeration is a promising method for preparing salty coal for thermal processing.

Keywords: *Salty coal; Oil agglomeration; XPA; EPR; IR spectroscopy; Pyrolysis.*

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1. Introduction

The relevance and significance of the proposed research, presented to the scientific community, is primarily due to the unusual raw material, the coal with a high content of alkali metal salts, particularly sodium. This is referred to as "salty" or "salted" coal (SC), which serves as a backup fuel resource for several countries, including Ukraine, China, Poland, Russia, and others [1]. Another key aspect is the originality of the proposed primary processing method for such coal through a special enrichment and dewatering process – oil agglomeration. Its contemporary presentation and challenges are discussed in more detail in the review [2].

The agglomeration of this type of fuel can not only reduce its excessive ash content and moisture but also lower the levels of soluble salts, while improving its reactivity and transportability. At the same time, oil agglomeration plays an important role in reducing environmental pollution caused by coal usage, by minimising the formation of coal waste. The process's effectiveness is assessed in terms of increasing the organic matter content (OMC) and reducing the ash in the agglomerated product [3].

Moreover, oil agglomeration is a versatile technique for enriching fine coal, making optimal use of the difference in hydrophobicity between the coal particle and mineral matter surfaces. The growth of agglomerates to the required size is mainly determined by the acceleration and speed at which water and oil molecules move [4].

Returning to the salty coal agglomeration as a raw material, it is worth noting (reminding) that, historically, during the 1950s and 1960s, a number of thermal power plants (TPPs) in the UK, USA and Germany operated using salted coal [5-7]. However, the significant difficulties caused by slagging and corrosion of boiler heating surfaces led to a shift in the raw material base at these plants. The mines extracting salty coal were closed, and researchers were tasked with finding new, viable technologies for its use.

In Ukraine, salty coal is currently seen as a resource with deferred demand, considering its substantial reserves and acceptable fuel properties [1,8], with potential for inclusion in the country's energy raw material base. Research into various approaches for determining optimal ways to use SC is ongoing at academic and educational institutions [8-9].

In this aspect, the SC oil agglomeration appears to be one of the optimal methods for preparing salty coal for integrated (or fuel) conversion, as it combines ash and salt removal with the gradual improvement of the raw material's quality. This is achieved through the structuring (agglomeration) of fine polydisperse coal phase in an aqueous medium using oil reagents. However, the details and mechanisms of oil agglomeration of salty coal are still not fully understood, despite a number of more recent publications on this topic [2-4,9-10].

A schematic representation of the general stages of the oil agglomeration process is provided in [10].

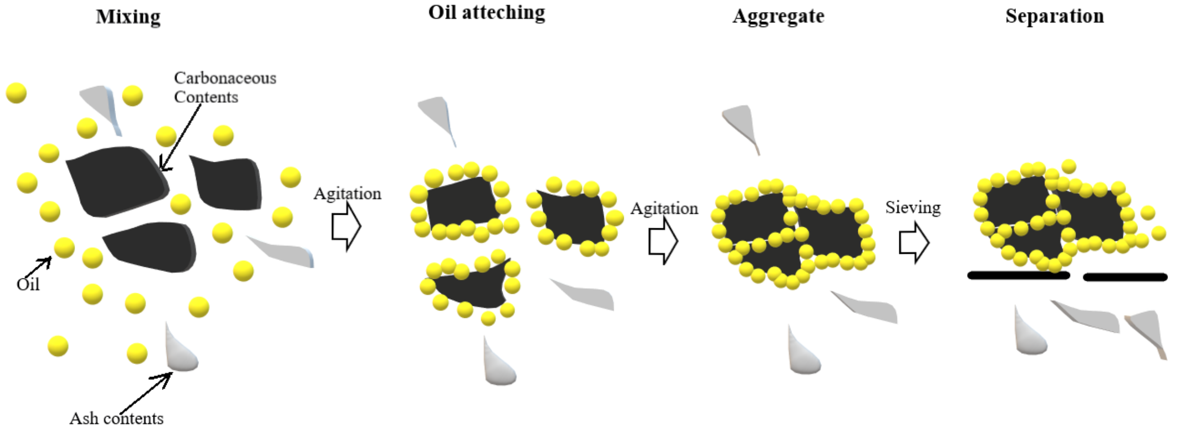

Figure 1. Principle and concept of oil agglomeration for coal cleaning.

While investigating the oil agglomeration of different types of coal with varying quality and metamorphism, the authors of [10] have identified several factors that influence the characteristics of the agglomerate and the efficiency of incorporating purified coal into the agglomerate. These factors include not only the type of oil and the ash content of the raw material but also the oxygen content and the ratio of aromatic to aliphatic fragments in the coal structure.

According to the authors of [11], the primary sub-process of oil agglomeration, the contact between the reagent and the coal grain (shown as the Mixing sub-process in Figure 1), is crucial. They provide a detailed analysis of the factors that determine the outcomes of each phase of this sub-process. For the interaction phase (the interaction of coal grains and oil droplets), important factors include the size of the interacting objects, the Reynolds number (Re), the density of the coal and the liquid; the kinematic viscosity, and the energy dissipation of the turbulent flow. In the approach phase (between coal grains and oil droplets), their surface properties play a key role, determining the direction and magnitude of wedging pressure, the pH value, the presence of surfactants, the temperature of the aqueous environment; and the shape of the coal grains. In the water film breakage phase (on the coal surface), the same factors as in the approach phase are important, along with the relative speed of the objects, their mass, and the viscosity of the water.

For the sub-process of oil attachment to the coal surface (shown as the Oil attachment sub-process in Figure 1), the main factors include the viscosity of the binding oil, the presence of accompanying chemical interactions between the oil and coal, the surface tension of the oil, the volume of the oil droplet, and the kinetic energy of the aggregate-shaping objects [11].

In [12], the authors observed how factors like the coal's ash content, agitation time (turbulent mixing) of the water-coal-oil pulp, its loss and density, as well as the type of oil reagent influence the oil agglomeration process. They showed that it is possible to effectively enrich coal with a particle size of 0–0.1 (2) mm and an ash content of 10–70%, while also self-regulating the oil agglomeration process as the ash content increases (i.e., the characteristics of the coal-oil agglomerate and agglomeration remain stable even as the ash content of the raw coal rises).

However, these studies focus mainly on the technological and operational aspects of aggregating conventional power plant coal, addressing factors like metamorphism, oxidation, petrographic composition, surfactants, substrate mixing time and intensity. [2-4,10,12]. They do not, however, consider the physical and chemical aspects of the process, nor do they explore the impact of salinity on the efficiency and outcomes of agglomerating coal with a high salt content.

The coal aggregate-shaping process is based on the mechanism of adhesive interaction between the oleophilic parts of the coal surface and oils, resulting in selective (partial) wetting and gradual agglomeration of the coal-oil phase in a turbulent water flow. Hydrophilic coal particles and mineral compounds that do not absorb oil are not included in the aggregates, which allows them to be removed as gangue suspension [12]. During oil agglomeration, coal soaking and swelling are generally reduced, and losses of ultrafine coal fractions are minimised.

Given the specific nature of coal with a high salt content, and in order to improve the efficiency of the process, the authors have developed a conceptual process for producing a new quality of agglomerates from Ukrainian salty coal.

The proposed two-stage oiling of salty coal grains allows to create a mosaic of hydrophilic-hydrophobic surface during the first stage of the process (Figure 2). The hydrophilic areas act as "windows" through which dissolved salts are removed into the aqueous phase, while the hydrophobic areas become the centres for further agglomeration of the coal grains.

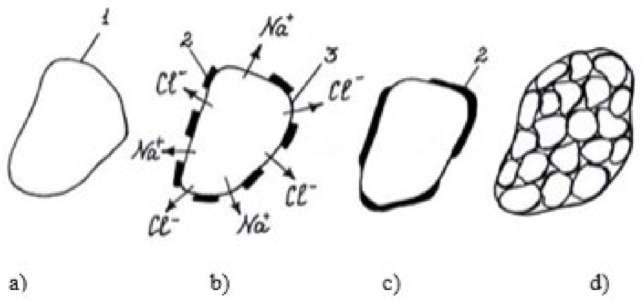

Figure 2. Transformation of the Dispersed Mass of Salty Coal During the Combined "Desalination – Agglomeration" Process: a – original coal grain; b – coal grain after treatment with the first dose of reagent; c - coal grain after treatment with the second dose of reagent; d – coal-oil agglomerate: 1 – outer surface of the salty coal particles; 2 – oil film on the surface of the salty coal; 3 - hydrophilic "windows" in the coal grains through which salts are removed.

The handling properties of coal-oil agglomerates, in terms of dewatering, hydraulic transport, combustion, and coking, are significantly better than those of naturally crushed coal [2,11-12].

Considering the key structural characteristics of the studied Chinese coal types, the authors [10] found, among others, that oxygenic functional groups (which are hydrophilic by nature) prevented the oil binder from adhering to the coal surface and forming a sizeable aggregate. Additionally, aromatic functional groups in the coal had poor interactions with the aliphatic functional groups in the oil binder [10], likely due to steric obstructivity. These effects highlight the need for further research into the physical and chemical phenomena occurring at the coal-binder interface. These aspects of the process (the chemical structure of both the coal material and the oil binder), along with their main interactions, which impart new qualities to the product, have not been fully explored.

The main goal of this study is to examine the key physical and chemical phenomena occurring at the coal-oil interaction, which are essential for understanding the mechanism and outcomes of the oil agglomeration process for "salty" coal, as well as to assess its impact on the handling properties of the agglomerated coal.

To obtain data for predicting the properties of the agglomeration product and selecting the most effective oil reagents.

The objectives of the study are to investigate the physical and chemical interactions between coal and oil during the oil agglomeration process of "salty" coal using X-ray structural (phase) analysis, EPR, IR spectroscopy, and functional chemical analysis and to evaluate the handling properties of the oil agglomeration product of the studied coal.

2. Experimental -methods and materials

The study was conducted on core samples of coal from the Novomoskovsk deposit in Western Donbas (Dnipropetrovsk region, Ukraine). The raw material used was Grade D salty coal from seam $c4_1$ (borehole 2-2) with the following properties: W^a=21.4%; A_B^d=9.9% ; C^{daf}=72.8%; H^{daf}=5.0; V^{daf}=42.8, and a Na_2O content in ash of 9.3%.

Mazut M100 was used as the oil binder. At 20°C, the maximum density of M100 mazut is 1015 kg/m^3, with a viscosity of 50 mm^2/s. it has a low ash content (≤ 0.15%) and a sulphur content ranging from 0.5% to 3.5%. Its combustion heat is between 39.4–40.7 MJ/kg.

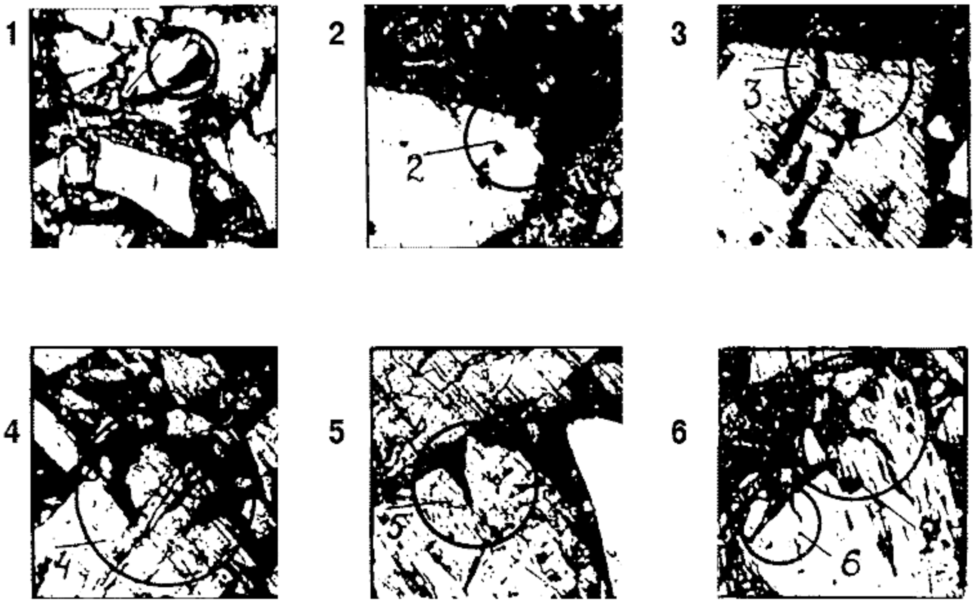

Figure 3. Fragments of polished sections of coal-mazut agglomerates. The circles highlight areas with protrusions, indentions, cavities, cracks and pores in the coal grains where the oil binder has penetrated, x200.

The coal samples were ground in a ball mill, homogenized through quartering, and stored in airtight containers. The ground coal measuring 0–3 mm was treated with M100 oil agent to enhance its surface hydrophobicity under specific conditions [9]. The adduct was then mixed with water in a certain ratio and processed with a second (main) dose of oil agent, heated to 90°C. the required amount of reagent was determined experimentally to ensure granule formation, depending on the particle size of the coal phase and the thickness of the oil binder's contact films. Further studies showed that the amount of mazut depends on the coal particle size and the number of hydrophilic centres on the surface of the organic matter [9,11]. The more hydrophilic the coal surface, the greater the amount of oil needed to form coal-oil aggregates. The mixture was stirred in an aqueous suspension (coal : water = 1:1) using a paddle mixer under turbulent conditions for 10–15 minutes. As a result, salty coal agglomerates were obtained, containing 23% (A-23) and 29% (A-29%) M100 mazut.

A visual study of oil penetration into the porous structure of the coal constituent was conducted at the coal-oil boundary using a NEOPHOT-21microscope [30]. Figure 3 demonstrates how the oil binder infiltrates coal grain pores and cracks, as well as the intergranular spaces within the coal-oil aggregate.

The source materials and agglomeration products were analysed using a range of physical and chemical methods.

2.1. Electron paramagnetic resonance (EPR)

EPR spectroscopy is a well-established method for studying the structure and properties of organic matter. It is widely used to analyse both synthetic and natural high-molecular compounds [13-15]. However, there are still discrepancies in the interpretation of paramagnetic centres in complex mineral materials like coal [14]. EPR spectra at the very least provide several insights on the studied material [13,15]:

- concentration (N_x, spins/g) of paramagnetic centres (PMC). The integral intensity of the energy absorption line is used to estimate the number of PMCs in the system.
- ΔH line width indicates how PMCs interact with their surroundings, including spin centres and carbon framework nuclei (as it is in our case); $\Delta H = 1/T_1 + 1/T_2$

where T_1 is the spin-spin relaxation time; T_2 is the spin-lattice relaxation time, in seconds [14].

Spectroscopic splitting factor (g-factor) determines the position of the absorption line in the EPR spectra in unpaired electron systems and helps identify the type of PMCs present. To determine N_x, sample spectra were compared to a reference material with a known number of unpaired electrons. MgO powder with a Mn^{+2} microaddition served as the internal reference.

The sample ΔH_x EPR signal width was measured as the distance between the peak and trough of the PMC absorption derivative. This was calculated using the reference value ΔH_p= 86.76 G, which represents the distance between the third and fourth components of the Mn^{+2} fine structure signal of paramagnetic ions.

EPR spectra were recorded using a RE-1306 radio-spectrometer, operating in the 3-centimetre range (X-band). The sample EPR measurements were taken in air at room temperature. The accuracy of PMC concentration measurements was 10%, with ΔH accuracy at 0.5 G (Gauss), and g-factor at ± 0.0002. Table 1 represents the paramagnetic characteristics of the studied samples.

2.2. X-ray phase analysis (XPA)

The structural changes in coal organisation during the oil agglomeration process were examined using X-ray structure (phase) analysis (XSA, XPA). The X-ray structure analysis relies on the theory of X-ray diffraction, as outlined in [17–19], among others.

Diffraction patterns of powdered samples were recorded using a "DRON UM-1" diffractometer with CuK_α radiation. For this purpose, Soller slits and a nickel filter were used. The resulting diffractograms are shown below (Figure 4).

Peak deconvolution on the diffraction patterns was performed using the Erdmann-Polak approach [18], and the data were interpreted based on experimental and theoretical findings [19].

The following X-ray structural parameters were calculated: interplanar spacing for various types of carbon structures (d_{002}, $d_{\gamma 1-3}$), minimal repeat period d_{10}; interlayer ordering values *h/l* for each structure type; integral intensities for peaks 002 and γ-components of organic matter structures; structural element sizes of supramolecular organisation parameters (SMO): L_a and L_c parameters for longitudinal size and thickness of the structural fragment stack, respectively; the number of layers in an "m" stack [17]. Measurement accuracy was $\pm 1\ A^0$ for L_a, $\pm 0.5\ A^0$ for L_c, and $\pm 0.03A^0$ for d.

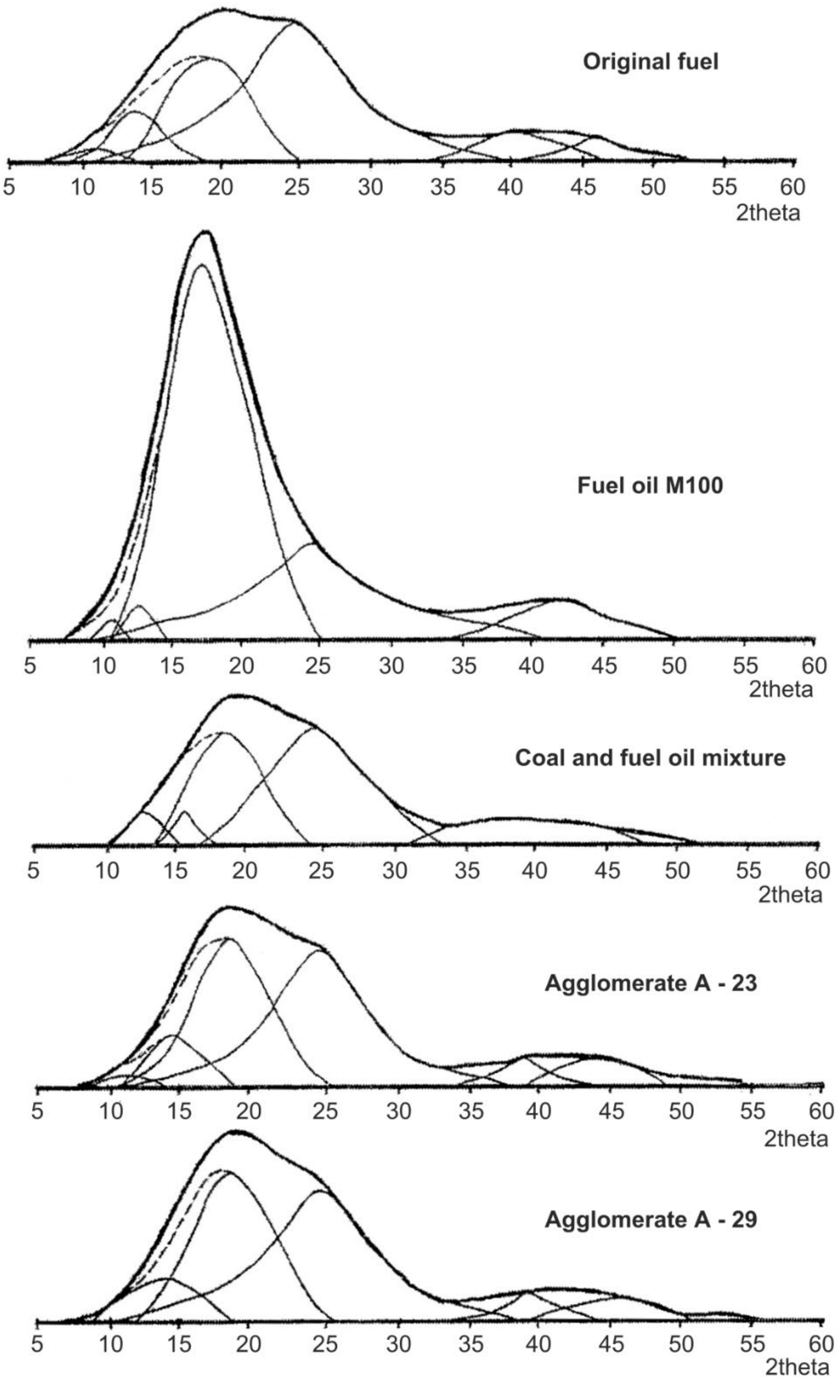

Figure 4. Diffraction patterns of the studied products.

2.3. Determining the oxygen-containing groups in the studied samples

Up to now, several methods are available for determining the content of oxygenic functional groups (OFG) in coal, each drawing their own reasons for criticism [20-22]. In this sturdy, we used modified acetate and barium methods to measure the concentration of carboxylic and phenolic hydroxylic groups, respectively [20]. These methods allowed us to track changes in OFG content across different processes and COM conversion products, ensuring reproductible results. The relative parallel data error for COOH groups was 1.8%, with a root-mean-square deviation of S_0 ± 0.03 mg-eq/g. For the total content of COOH and OH_{phen} groups, as well as quinones, the relative error was ≤1.5%, with S_0 of ±0.04 [23].

2.4. Infrared spectroscopy

Infrared spectroscopy is one of the most effective methods for analysing the organic and inorganic components of coal and other solid fossil fuels (SFF) [24-26]. Structural group analysis using IR spectra involves identifying characteristic absorption bands and linking them to the corresponding functional groups, taking into account the frequency values of absorption peaks, band shape and intensity [24]. The IR spectra of coal and coal-based products were recorded using a Specord 75-IR spectrometer, with spectral processing performed based on separate studies [25]. Analysed samples were prepared as KBr pellets with a 0.5% concentration, ground in a laboratory mill for 60 minutes.

2.5. Pyrolysis methods for the studied coal and its agglomerates

To determine the quantitative yield of thermal destruction products for the SC and its agglomerates, we used a quartz reactor assembly, allowing us to study raw pyrolysis conditions and raw material properties affect key process parameters. The heating rate was 5°/min, with pyrolysis performed at 500°C, and an isothermal holding time of 15 minutes in a nitrogen atmosphere. The procedure sequence and the corresponding calculations are detailed in [27].

3. Results and discussion

To better understand the processes and results of oil agglomeration in salted coal, we have obtained X-ray structural (phase), IR spectroscopic, paramagnetic, and other physical and chemical properties for the raw coal, the intermediate product (coal + 5% mazut), and the coal-oil agglomerates.

The data obtained (Table 1) show that the initial dose of (5% by mass) oil component does not have a significant effect on the paramagnetism of the coal. The M100 mazut itself contained three types of paramagnetic centres, which differed sharply in their nature and relaxation properties.

Table 1. EPR spectrum characteristics of the samples.

Indication	ΔH, G	g-factor	N, spins/g
	Original Coal		
Signal	4.6	2.0035	$8.9\cdot10^{17}$
Mazut			
Signal 1	4.6	2.0031	$9.7\cdot10^{16}$
Signal 2	12.4	2.0169	not defined
Signal 3	320	≈ 4	not defined
Coal+5% mazut			
Signal	4.9	2.0036	$8.9\cdot10^{17}$
	Agglomerate		
Signal A-23	4.8	2.0035	$1.4\cdot10^{16}$
Signal A-29	5.1	2.0035	$4.8\cdot10^{16}$

Analysing the literature sources allowed us to identify signal 1 as corresponding to π-conjugated systems [13–15], signal 3 as related to iron-containing paramagnetic (or ferromagnetic) structures [14], and signal 2, with a g-factor of 2.017 and ΔH = 12 G, as likely associated with peroxidic R-O-O• or sulphide R-S-S• radicals [15].

The paramagnetic properties of the agglomerates are quite similar to those of the raw coal, except for a noticeable reduction in PMC content.

It is clear that mazut, when added in certain proportions (20-30%) and under the conditions described, significantly reduces (by 20-70 times) the concentration of unpaired electrons. This indicates the recombination of aryl (and/or aroxyl) radicals, as reflected by the g-factor value of 2.0035. At the same time, there is an increase in L_a and L_c values, which reflect the supramolecular structure of the organic matter of the samples (see Table 3). It is likely that new simple ether bonds are formed in the organic matter of the agglomeration products, as confirmed below by IR spectroscopy data.

Since type 2 signals from the mazut were not observed in the agglomerates, we can assume that the active radicals reacted with the COM, resulting in the formation of non-paramagnetic oxygen- (sulphur-) containing groups and the recombination of aryl (aroxyl) radical components. The disappearance of type 3 centres can be explained by the transfer of iron-containing compounds into the aqueous phase during active slurry mixing.

The observed changes strongly suggest chemical interactions between the coal and the mazut, or at least a significant alteration in the intermolecular interactions within the system, the formation of H-bonds in the coal-mazut interphase zone. Water, as a strong hydrolysing agent, likely plays an important role in this process [11]. If this is the case, changes in the supramolecular organisation of the coal matrix and in the composition of active oxygen-containing groups are inevitable. Indeed (as shown in Table 2), during the agglomeration of salty coal, the concentration of carboxyl and quinone groups decreased, while the concentration of phenolic hydroxyls increased. This increase in phenolic groups may be related to the partial restoration of quinones by proton-donor fragments in the mazut structure, as well as to the hydrolysis of phenolates during the agglomeration process, which includes an aqueous treatment stage. The decrease in carboxyl group content could be due to their partial binding in complexes, ether forms, or decarboxylation.

Importantly, the agglomeration process resulted in a significant reduction in the sodium content, with coal desalting approaching 56%. At the same time, the expected increase in the calorific value of the adduct was observed (Table 2).

Table 2. Certain characteristics of coal and agglomerates.

Sample	Oxygen-containing groups, mg-eq/g			Sodium content, mg-eq/g		Heat of combustion, MJ/kg
	OH_{phen}	COOH	quinones	in coal	in ash	
Original coal	1.60	0.20	9.3	0.30	4.08	24.3
A-23	2.44	0.11	7.1	0.10	1.77	28.2
A-29	2.40	0.10	6.5	0.10	1.88	28.6

Let us take a closer look at how the diffraction profile of the source components changes at different stages of agglomerate formation (Figure 5).

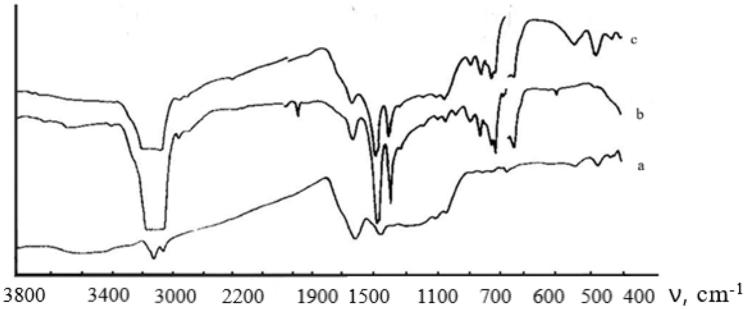

Figure 5. Reviewed IR spectra of A-23 agglomerate and its components: a – coal under study; b – M100 mazut; c – mazut-coal aggregate.

Figure 4 demonstrates that the main X-ray diffraction peak for the raw coal and mazut consists of at least two prominent halos: 1 – the peak 002 (at the angles of $2\theta \approx 25^\circ$), which is caused by the reflection of the X-ray beam from graphitoid networks, polyarenic in nature and arranged into relatively orderly stacks of several layers; 2 – peak (or γ-band at $2\theta \approx 18\text{-}20^\circ$), which is attributed to the ordering of non-aromatic (polynaphthenic, boghead-like) structures [19]. In the mazut, unlike the coal, the majority of the structures are non-aromatic polynaphthenic fragments (with the primary γ-band at $2\theta \approx 18\text{-}20^\circ$). These structures are arranged into stacks (with the average number of layers n ~ 3.6). they are highly ordered (the h/l parameter reaches a maximum value of 3.8), and the interlayer distance is ~ 0.49 nm.

After coal agglomeration, the structure of the agglomerate (Figure 4) is much closer to the raw coal structure than the mazut. However, semi-quantitative analysis of the diffraction patterns (Table 3) reveals some clear differences. For instance, when mazut content reaches around 30%, the agglomerate, as expected, shows a significantly higher proportion of non-aromatic structures (~50%) in the overall structural unit of the agglomerate compared to ~30% in the coal. Additionally, there is an increase in the orderliness of non-aromatic part of the agglomerate (h/l increases from 1.06 to 1.56). The 002 peak, however, remains relatively unchanged.

This suggests that the agglomeration process of salty coal leads to a substantial increase in the proportion of ordered polynaphthenic links in the final product's overall structure.

The data in Table 3 also show that small changes in the structural organisation of the coal begin as soon as the first dose of mazut (5%) is added. However, the refinement of the supramolecular structure of the organic material is completed during the agglomeration stage itself.

Table 3. X-ray structural characteristics of objects (nm).

Sample	d_{002}	$d_{\gamma1}$	$d_{\gamma2}$	L_a	L_a	L_c		h/l		Relative Sin., x10		n
				(Al)	(Ar)	002	γ_1	002	γ_1	S_{002}	S_γ	
Coal	0.356	0.467	0.632	2.1	2.8	1.00	1.20	1.23	1.06	5.9	3.0	3.9
Mazut	0.356	0.487	0.684	4.0	-	0.93	1.15	0.77	3.79	2.8	6.8	3.6
Coal + 5% M100 Mazut	0.356	0.467	0.553	1.3	-	0.97	1.26	1.04	1.25	5.0	3.8	3.7
A-23	0.356	0.467	0.590	4.8	2.4	1.13	1.28	1.24	1.56	4.9	4.0	4.2
A-29	0.356	0.467	0.632	3.6	2.2	0.97	1.15	1.25	1.40	5.0	4.0	3.7

The reviewed IR spectra of the samples (Figure 5) and a detailed analysis of the characteristic bands provide further insights into the transformations occurring during the oiling process of salty coal (Table 4).

Spectral processing was performed using the baseline method. The spectra were analysed and the bands assigned based on [24-26]. The results show that M100 mazut differs significantly from the other samples due to its higher content of non-aromatic structures (CH_2 groups with 3 ν = 2920 cm^{-1}), thio- or ether bonds (ν = 1060 cm^{-1}), and the presence and high concentration of structures with two adjacent H-atoms in the aromatic ring (ν = 820 cm^{-1}). The proportion of methyl groups (bands with ν = 2860 and 1460 cm^{-1}) remains relatively constant across samples. The carboxyl group content in the mazut is almost zero. Compared to the coal, carboxyl groups are significantly reduced in the agglomerates, more so than would be expected from mechanical (additive) mixing of mazut with the coal. These data align well with the functional analysis.

The composition of the oil agent is also notably different in terms of C=O quinone structures linked by hydrogen bonds [24]. In the agglomeration products, the concentration of quinones is lower than in the raw samples. This is consistent with data in Table 2, suggesting that quinones are directly reactive during the oil agglomeration process of salty coal. The IR spectroscopy results also suggest that thio- or ether bonds (ν = 1060 cm^1) in the mazut play an active role in forming the coal-mazut aggregates, further supporting the idea that $RO_2\cdot$ or $RS_2\cdot$ radicals are involved in reactions between the coal and the oil agent.

Table 4. Parameters of IR spectra for the studied samples. relative intensity (Ix/I3400) of characteristic vibration bands.

Sample	I_{2920}/I_{3400}	I_{2860}/I_{3400}	I_{1700}/I_{3400}	I_{1620}/I_{3400}	I_{1460}/I_{3400}	I_{1370}/I_{3400}	I_{1120}/I_{3400}	I_{1060}/I_{3400}	I_{820}/I_{3400}
Coal	0.57	0.67	1.52	1.68	0.59	0.93	0.57	0.77	0.15
Mazut	6.20	0.61	0.09	5.33	0.47	0.74	0.33	5.19	1.00
A-23	2.41	0.63	0.99	1.31	0.75	1.22	0.39	0.73	0.17
A-29	1.94	0.59	0.63	1.56	0.74	0.90	0.42	0.91	0.23

A detailed analysis of the change in the relative intensities of characteristic bands in the IR spectra shows that the intensities of the bands with ν = 2920 and 2860 cm^{-1}, corresponding to the valence vibrations of CH2 and CH3 groups, are almost additively proportional to the mazut content in the system. There is a noticeable, but minor, antagonism (negative additivity) for the bands with ν=1700 cm^{-1} (valence vibrations of C=O in carboxyl groups) and with ν=1120 cm^{-1} (planar vibrations of alcohol groups). A more significant deviation from additivity towards intensity reduction is observed for the bands with ν=1060 cm^{-1} (valence vibrations of secondary alcohol groups) and with ν=1620 cm^{-1} (valence vibrations of C=O in ketones, diketones, or quinones), which aligns with the functional analysis results. At the same time, expected synergistic effects are observed. These are related to non-additive increases in intensity for the bands with ν = 1370 cm^{-1} (valence vibrations of etheric groups – ethers) and with ν = 1460 cm^{-1} (deformation vibrations in aldehyde groups).

The performance of the band with ν = 820 cm^{-1}, which is characteristic of out-of-plane vibrations of C-H groups in different types of substitution, shows a negative deviation from additivity in intensity depending on the M100 content in the samples. This can be explained by the increased ordering of the non-aromatic portion of the organic matter as the mazut content rises (see Table 3).

Clearly, the agglomeration of salty coal leads to a significant increase in the proportion of ordered polynaphthenic chains in the overall structure of the final product. Based on the IR spectra, we can conclude that intermolecular hydrogen bonding (band with 3400 cm^{-1}) plays a stronger role during the agglomeration of the studied coal.

The absorption bands in the 400–500 cm^{-1} range are likely associated with the mineral (ash) content in the raw coal, and the increased intensity in the agglomerate can be explained by the insolubility of minerals (such as quartz and pyrite) during the agglomeration process in the water-oil suspension, which then concentrates in the product.

The data obtained through several methods on the diverse new properties of the target products (salty coal agglomerates) suggest that changes in the conversion rate of the SC prepared for thermal processing are likely.

For example, comparative studies were conducted on the pyrolysis process for salty coal, its mixture with mazut and the A-23 agglomerate in quartz reactor at 500°C, with a hearting rate of 5°/min and an isothermal holding time of 15 minutes in a nitrogen atmosphere [27]. The results are shown in Table 5.

The results indicate that pure oil agglomeration (as a process of aggregating fine particles and desalinating the SC) has a significantly positive impact on the pyrolysis process, unlike the weaker effect of mechanically added and mixed oil. At the same time, the conversion rate of the organic matter increases considerably, which is evident from the yield of gaseous products and tar. A notable non-additive increase occurs for the yield of gaseous products during the pyrolysis of the agglomerated coal.

Table 5. Pyrolysis outcomes for salty coal, mechanical coal-mazut mixture and coal-oil agglomerate.

Sample	Pyrolysis product yield, mass. %.			
	Solid residue	Tar	Pyrogenic moisture	Gas
Coal	68.9	1.5	13.6	16.0
Coal + 5% M100 Mazut	65.3	4.5	6.2	24.0
A-23 Agglomerate	56.4	5.9	0.2	37.5

The results of thermolysis (Table 5) suggest that the solid residue (carbonisate) from the agglomerate could serve as a valuable precursor for carbon sorbents. This is supported by the conversion rate of the raw material OM (43.6% of the mass) and high yield of gaseous products.

Having regard to several studies on the co-conversion of coal and coke by-products [28-29], the thermolysis of SC agglomerates with M100 (and other oils with similar properties, such as coke by-products) could enhance the mechanical strength (MS) of carbonisate-based sorbents of the studied raw material. Further, MS is one of the main quality indicators that determines the potential applications of carbon sorbents.

The data presented in this study suggest that processing salty coal through oil agglomeration may be not only promising but also environmentally viable.

4. Conclusions

Comparative studies of salty coal agglomerates and their components (raw coal and M100 mazut), based on the XPA, EPR, IR spectroscopy, and functional chemical analysis, reveal structural changes at all hierarchy levels due to physical and chemical interactions between the active centres of the coal’s organic matter and the oil agent. Specifically:

- EPR analysis showed that the paramagnetic properties of the agglomerates are similar to those of raw coal, except for a significant reduction of PMC content following oil agglomeration. This suggests a major shift in the intermolecular interactions within the system.
- IR spectroscopy noted a molecular-level transformation in the coal’s organic mass during its oil agglomeration, including a decrease in carboxyl and quinone groups, alongside an increase in phenolic hydroxyl and ether compounds.
- X-ray structural analysis provided evidence of changes in the supramolecular structure of the COM due to its oil agglomeration. When mazut content is around 20-30%, the agglomerate contains a higher proportion of non-aromatic structures (~65–70%) in the overall structural unit of the agglomerate (compared to ~48% in coal). Additionally, the polynaphthenic part of the agglomerate becomes more ordered (h/l increases from 1.06 to 1.56). The 002 peak (graphitoid structures) remains largely unchanged.

Oil agglomeration significantly enhances pyrolysis compared to mechanically added and mixed oil. It leads to a greater conversion of organic matter, evident in the increased production of gaseous products and tar. Additionally, oil agglomeration of salty coal results in a product with a higher calorific value (28 MJ/kg), an ash content of 10 ± 2%, and a significantly reduced salt content (Na_2O < 2%) [9], making it a valuable energy resource with broader range of applications.

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To whom correspondence should be addressed: Dr. Natalia Desna, State University of Economics and Technology, 50005, Kryvyi Rih, 16 Medychna Str., Ukraine, E-mail: desnana@ukr.net