Asphaltenes from Ethylene Tar as a Potential Raw Material to Obtain High Value-Added Products

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Abstract: Ethylene tar is the main byproduct of ethylene synthesis obtained via pyrolysis of hydrocarbon feedstock. With the growing demand for ethylene, the efficient use of ethylene tar is of great importance from both an economic and an ecological point of view. It contains significant amounts of polycyclic aromatic hydrocarbons, which can be designated as technogenic asphaltenes. Such polyaromatic structures can be isolated and used as a synthetic platform for modification and molecular engineering, similar to petroleum asphaltenes. In this study, the possibility of modifying technogenic asphaltenes by oxidizing reagents used previously for petroleum asphaltenes was shown for the first time. Technogenic asphaltenes contain significantly fewer heteroatomic structures and have a lower molecular weight compared to petroleum asphaltenes. The compositional features of technogenic asphaltenes ensure deeper oxidation with the formation of various O-containing products, whose properties can vary significantly depending on the reaction conditions. At the same time, the general patterns of oxidative modification of technogenic asphaltenes correspond to the oxidation processes of petroleum asphaltenes. The modification products obtained in this way can be used as sorbents, catalysts, fillers for polymers, adhesive additives for road bitumens, etc.

Keywords: ethylene tar; asphaltenes; chemical modification; oxidizing agent; carbon material

1. Introduction

Ethylene tar (ET) is a major by-product in the process of hydrocarbon feedstock pyrolysis. Most pyrolysis plants use naphtha and gasoline as raw materials, but at the transition from light raw materials to heavier ones (gas oils, fuel oils, tars), the yield of ET and the fraction of polycyclic aromatic compounds in its composition significantly increases [1–3].

Currently, ET is mainly used as a raw material for the production of technical and pitch coke or as a component of boiler fuel. Given the growing demand for ethylene [4], expanding the efficient use of ET is of great importance from both economic and environmental aspects. It is known that ET contains a significant amount of various aromatic compounds and can be used as a raw material for the production of bi- and polycyclic hydrocarbons, as well as for the production of high added-value products [5–7]. The complexity of the hydrocarbon composition and the high content of technogenic asphaltenes and olefins restricts the production of new materials from ET [1–3,8–12]. The asphaltenes content in ET can reach 22 wt. % and they are highly prone to carbonization, which hampers the production of high-quality carbon materials through traditional thermal processes. Thus, the authors of [8,10,12] showed that the presence of asphaltenes in ET leads to the formation of an irregular mosaic texture of needle coke, and their removal promotes the de-
development of the mesophase and improves the quality of the product. In the above-mentioned works, asphaltenes are considered only as an undesirable component of ET, and there is no information in the literature on the study of ET asphaltenes as raw materials for the production of valuable products. From a structural viewpoint, technogenic asphaltenes are characterized as polycyclic aromatic compounds with short pendant alkyl substituents. As for the elemental composition, they contain small amounts of oxygen and sulfur along with carbon and hydrogen. ET asphaltenes, in analogy to petroleum asphaltenes, can be used as a synthetic platform for modification and molecular engineering with the aim of the preparation of various materials.

Many works are devoted to the modification of petroleum asphaltenes. Modified asphaltenes can be used in the production of sorbents and catalysts [13–19], precursors of carbon materials [20–25], components for energy storage and conversion in alternative energetics [26–29], and for other purposes [30]. Production of such materials is possible due to the high reactivity of asphaltenes molecules, which easily undergo sulfonation [30–32], nitration, and other reactions [13–16,33], as a result of which various functional groups are added to the polycondensed aromatic core. Oxidative modification of asphaltenes could afford various products depending on reaction conditions and oxidant type [31–40]. It has been shown that treatment of asphaltenes with concentrated sulfuric and nitric acids leads to the cleavage of peripheral aliphatic chains and partial destruction of the carbon backbone [31–33]. Oxidation with potassium permanganate produces hydroxyl, carboxyl, and carboxylic acid groups [34–36], whereas the Hummers oxidation also produces epoxy groups [18]. Low-temperature catalytic oxidation of asphaltenes with the mixture of hydrogen peroxide and propionic aldehyde results in the condensation of molecules, cleavage of side alkyl chains, and addition of oxygen [39]. When asphaltenes are treated with peroxyacetic acid under mild conditions, occluded saturated hydrocarbons are released, which can be used for the obtaining of geochemical information and carboxyl derivatives of asphaltenes [34,38,39]. Exposure to aqueous solution of sodium percarbonate at high temperature and pressure could give various oxidative condensation products, such as aromatic and aliphatic carboxylic acids, which can be used as adhesive additives to road bitumens and sorbents for purifying water from phenol [40].

In this work, the possibility of chemical modification of technogenic asphaltenes isolated from ET will be investigated using inexpensive and available persulfate and peroxide oxidants in order to obtain various oxidates. The compositional features of technogenic asphaltenes will obviously influence the composition of the products of their oxidative modification. The use of various oxidants, as well as varying the reaction conditions for the oxidative modification of technogenic asphaltenes, will make it possible to evaluate the possibility of preparation of sorbents, catalysts, carbon materials, and other value-added products based on them.

2. Materials and Methods

2.1. Materials

ET (IBP 80 °C, FBP 371.5 °C, residue 10 wt. %, Conradson carbon residue 13.0 wt. %) was obtained from PJSC Nizhnekamskneftekhim (Russia). Asphaltenes of ET-A and OIL-A were isolated using the IP 143 method from ET and crude oil from the Ashalchinskoye field (Russia) (Figure 1).
2.2. Oxidative Modifications of Asphaltenes

2.2.1. Oxidation of Asphaltenes with (NH₄)₂S₂O₈/H₂SO₄

Modification of ET-A asphaltenes was performed according to the procedure described in [32] with ammonium persulfate (AP) in sulfuric acid (SA). The yield of the product (black powder, insoluble in aromatic and chloro-organic solvents) further denoted as AP/SA was 0.89 g.

2.2.2. Oxidation of Asphaltenes with (NH₄)₂S₂O₈/CH₃COOH

ET-A were modified according to the modification procedure from [32], and SA was replaced by 100 wt. % acetic acid (AA). In addition, asphaltenes were previously dissolved in CH₂Cl₂ and a catalytic amount of mineral acid (SA, 100 wt. %) was added during the process. The resulting reaction mixture was washed with water, after which the organic layer was separated, dried over CaCl₂, and the CH₂Cl₂ was removed under vacuum. The yield of the product (dark-brown powder) further denoted as AP/AA was 0.98 g.

2.2.3. Oxidation of Asphaltenes with H₂O₂/CH₃COOH

ET-A asphaltenes were modified using the procedure described in [38]. For modification, mixtures of hydrogen peroxide (HP) (30 wt. %) and AA (100 wt. %) in volume ratios (4 to 10, 8 to 10, 25 to 20) were used. The yield of the products (dark-brown powders) further denoted as HP/AA (4/10), HP/AA (8/10), and HP/AA (25/20), were 0.98 g, 0.97 g, and 0.88 g, respectively, according to the volume of consumed hydrogen peroxide.

2.2.4. Oxidation of Asphaltenes with Na₂CO₃×1.5 H₂O₂

The ET-A asphaltenes were modified according to the procedure described in [40]. Oxidation was carried out in a high-pressure/high-temperature reactor at stirring (in autoclave) (model no. 4570b, Parr Instrument Company, Moline, IL, USA). A total of 5 g of ET-A asphaltenes and aqueous solution of sodium percarbonate (SP) (55 g in 374 g of distilled water) were charged to autoclave. The reaction mixture was maintained at 200 °C under the pressure of 1.8 MPa at constant stirring for 4 h. The mixture of the products (419.1 g) was separated by filtration into water-insoluble products (1.31 g) and water-soluble products (Figure 2). Water-insoluble products were washed with water and dried and further separated using Soxhlet apparatus into the benzene-soluble product SP-1 (0.41 g of dark-brown powder) and benzene-insoluble product SP-2 (0.9 g of black powder). The aqueous solution was acidified with 10% sulfuric acid solution up to pH 2–3, as a result of which carbon dioxide was vigorously evolved and precipitate was formed, which was filtered and washed with water further denoted as SP-3 (1.42 g of dark-brown powder). Water was removed from the filtrate; then, the precipitate was separated into the
acetone-soluble product SP-4 (1.84 g, resin-like) and acetone-insoluble precipitate, namely, sodium sulfate.

Figure 2. Scheme for the separation of asphaltenes oxidation products of the SP series.

2.3. Methods

The elemental composition of the surface of the samples was studied using X-ray photoelectron spectroscopy (XPS) on a HI 5000 Versa Probe II spectrometer (ULVAC-PHI Inc., USA) equipped with monochromatic Al Kα radiation (hv = 1486.6 eV) at 50 W, with a diameter of 200 µm. The instrument was calibrated using binding energy of Au 4f (83.96 eV) and Cu2p3 (932.62 eV). Atomic concentrations were determined from the survey spectra using the relative elemental sensitivity factors of the C1s, O1s, N1s, and S2p lines. Binding energies were determined from high-resolution spectra using a pass energy of 23.5 eV and an energy step of 0.2 eV.

The CHNS analysis was performed on a Vario Macro cube instrument (Elementar Analysensysteme GmbH, Germany). The oxygen content was calculated as the difference between 100 wt. % and the sum of all elements.

Infrared (IR) spectra of the samples were acquired on a Vector-22 IR-Fourier spectrometer (Bruker, Germany) between 4000 and 400 cm⁻¹ with the optical resolution of 4 cm⁻¹.

Electrospray ionization (ESI) mass spectra were obtained on an AmazonX mass spectrometer (Bruker Daltonik GmbH, Germany) with an ion trap. The measurement was carried out in the mode of recording negative ions in the m/z range from 70 to 3000. The voltage on the capillary of the atomizer was ~3500 V. Nitrogen was used as a drying gas with a temperature of 250 °C and a flow rate of 10 L·min⁻¹. A methanol/water solution (70:30, v/v) was used as an eluent at a flow rate of 0.2 mL/min (Agilent 1260 chromatograph, USA). The analyzed sample was dissolved in acetone to a concentration of 10⁻⁶ g/L.

Electron paramagnetic resonance (EPR) spectra were obtained on an Elexys E500 spectrometer (Bruker, Germany) operating at X-band (9.67 GHz) with Bruker ER 049X microwave bridge. The experimental conditions for recording spectra are: microwave power of 0.63 mW, modulation amplitude of 1(4)G, sweep time of 60(240) s, and time constant of 328 ms. The samples under study were weighed and placed in quartz ampoules (d = 3mm) at a height of 13–14 mm, corresponding to the maximum sensitivity range of the resonator.

Static exchange capacity (SEC) was determined by ASTM D 2187.

The general scheme of the research methodology is presented in Figure 3.
3. Results and Discussion

3.1. Characteristics of Oxidizing Agents

Peroxide and persulfate oxidants are extensively used for the decomposition of polycyclic aromatic hydrocarbons (PAHs) and other organic contaminants in wastewater and ground purification systems [41–45]. Oxidation potential of HP is higher (E° = 1.77 V) than that of molecular oxygen (E° = 1.23 V) and it was proven that HP is an effective oxidizing agent in a broad range of reaction conditions (from acidic to basic). SP has a similar function to HP, because free H₂O₂ is released upon mixing with water [42,43]. AP is a strong oxidizing agent with a high water solubility and its redox potential (E° = 2.01 V) is similar to that of ozone (E° = 2.07 V) and higher than that of permanganate (E° = 1.7 V). In this case, HP and AP contain identical oxygen bridges but the standard redox potential of AP is much higher than that of HP.

In spite of the fact that HP and AP are thermodynamically stronger oxidizing agents and can decompose organic molecules, a direct reaction with most organic substances is slow. Therefore, H₂O₂ and S₂O₅²⁻ systems are often activated using various physical and chemical methods including alkaline and acidic treatment [45,46]. All these activation processes involve various mechanisms of formation of free radicals due to the cleavage of O-O bond.

Surface modification of carbon materials with peroxide and persulfate oxidizing agents, where acids perform activating functions, are described in [47–49]. O-containing functional groups (carboxylic, phenolic, lactone, and ether) were added using (NH₄)₂S₂O₈/H₂SO₄ and H₂O₂/CH₃COOH reagents onto the surface of various active carbons to improve the sorption characteristics of the materials. Oxidation-sulfonation method with (NH₄)₂S₂O₈/H₂SO₄ as the oxidizing agent was used to prepare ion-exchange materials based on petroleum asphaltenes [32]. The H₂O₂/CH₃COOH oxidizing agent was widely used for the release of occluded hydrocarbons after partial degradation of hydrocarbon skeleton of asphaltenes [34,37,38]. Demetallation of asphaltenes was carried out on exposure to H₂O₂/CH₃COOH oxidant as a result of decomposition of metalloporphyrin complexes [50]. SP, which under experimental conditions [40] decomposed into H₂O₂ and Na₂CO₃ (alkaline medium), was used to prepare water- and benzene-insoluble asphaltenes oxides, which were studied as adhesion additives to road bitumen and sorbents for water purification from phenol.

Some of the oxidizing modification procedures of petroleum asphaltenes with persulfate and peroxide compounds were used for ET-A technogenic asphaltenes in order to compare the products of oxidation and state the similarity and difference of these polyaromatic structures.

3.2. Oxidative Modifications of Asphaltenes

3.2.1. Oxidation of Asphaltenes with (NH₄)₂S₂O₈/H₂SO₄ and (NH₄)₂S₂O₈/CH₃COOH

ET-A asphaltenes, compared to petroleum asphaltenes, are characterized by lower values of molecular-mass distribution (from 100 to 1200 m/z with Mmax = 400–600 m/z) [3,5]. They feature higher aromaticity (H-to-C ratio) and there are almost no heteroatoms (S, O, N), which are intrinsic to asphaltenes OIL-A (Figure 4).
Figure 4. Elemental composition of ET-A and OIL-A according to XPS (a) and CHNS analysis (b).

IR spectra (Figure 5) of ET-A asphaltenes, as well that of OIL-A, show the intense bands of the C=C aromatic carbon framework (1602 cm$^{-1}$), the out-of-plane stretching vibrations of the C-H aromatic region (3046 and 3024 cm$^{-1}$) and substituted benzene rings (964–695 cm$^{-1}$), and vibrations of CH$_3$ (2845, 1376 cm$^{-1}$) and CH$_2$ (2975 cm$^{-1}$, 1453 cm$^{-1}$), as well as O-H groups (3446 cm$^{-1}$). There is also an intense band corresponding to sulfoxide groups at 1029 cm$^{-1}$, which indicates the presence of trace amounts of sulfur, which are not recorded with XPS and CHNS analyses.

Figure 5. IR spectra of ET-A (black) and OIL-A (red).

Investigation of ET-A and the products of its oxidation with AP were performed using XPS technique, where the state of chemical bond of atoms can be revealed by analyzing the bond energy. The specimens were recorded with neutralization and the scale was corrected according to the first peak in the C1s spectrum (with the lowest E$_{bond}$ energy of 284.7 eV), given that asphaltenes contain a large number of carbon atoms in aromatic fragments. This is also indicated by the presence of the peak at 291 eV in the C1s spectra of all specimens. This is a so-called shake-up peak ($\pi$-$\pi^*$ satellite of the peak at 284.7 eV), which is the indicator of sp$^2$ (double) bonds of carbon atoms [51]. Figure 6a shows a survey spectrum of the oxidation product AP/SA, where X-ray induced photoelectrons for C, O, S,
and N are present. The high-resolution spectra for ET-A and oxidation products are presented in Figure 6b–h. Main peaks of the spectra after deconvolution at 284.7 eV and 285.0 eV represent the bond of unoxidized carbon (C=C/C-H aromatic and C-C/C-H aliphatic) and after oxidation involve the peaks due to the bond between O and C. The product AP/SA obtained via oxidation with AP in sulfuric acid contains the peaks corresponding to C-O (C1s 286.7 eV and 289.1 eV, O1s 532.0 and 533.3 eV) in C-OH/C-O-C and O=CO groups. The product AP/AA obtained via oxidation with AP in acetic acid contains the peaks of C-O (C1s 286.9 eV and O1s 532.8 eV) in C-OH/C-O-C groups. In addition, XPS spectrum of the product AP/SA shows the peaks of sulfur (S2p 168.6 eV) in RSOH group and nitrogen (N1s 400.4 eV and 402.0 eV) (Figure 6g,h). The peaks of N1s at 400.4 eV can be rationalized by N-C bonds in functional groups; these usually correspond to pyrrole rings in metalloporphyrin complexes in the case of oil asphaltenes. In the case of the peak at 402.0 eV, a different interpretation is possible; more specifically, there are data for pyridine N-oxide (N=O−) (N1s 402.0 eV) [52,53] and the −NR3+ group (N1s 402.1 eV) [54]. It is likely that ammonium persulfate or product of its decomposition adsorbed on the surface of the product AP/SA.
Exposure of ET-A asphaltenes to AP in sulfuric acid media results in increase in the oxygen and sulfur content, and in the appearance of nitrogen in the products of oxidation (Table 1). It is known from the literature that concentrated sulfuric acid can not only oxidize, but also sulfonate oil asphaltenes [31,33]. On exposure of oil asphaltenes to AP in sulfuric acid, side aliphatic chains are oxidized to carboxylic groups and isomerize, forming sulfonic acid groups [32]. There is also oxidation of sulfide and disulfide sulfur to sulfones and disulfones in native molecules.
Table 1. Elemental composition of ET-A, AP/SA and AP/AA products.

<table>
<thead>
<tr>
<th>Samples</th>
<th>XPS Analysis</th>
<th>CHNS Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>ET-A</td>
<td>99.3</td>
<td>not</td>
</tr>
<tr>
<td>AP/SA</td>
<td>71.6</td>
<td>1.1</td>
</tr>
<tr>
<td>AP/AA</td>
<td>96.5</td>
<td>not</td>
</tr>
</tbody>
</table>

In general, the profile of IR spectra of the products oxidized with AP in sulfuric acid in technogenic asphaltenes correspond to that of oil asphaltenes. IR spectrum of the product AP/SA (Figure 7) shows the bands of hydroxyl (3432 cm$^{-1}$), methyl and methylene (2928 and 2852 cm$^{-1}$), carboxylic (1710 cm$^{-1}$), C-O alcohol or phenolic (1227 cm$^{-1}$), sulfonic acid (1174 cm$^{-1}$), and sulfoxide (1033 cm$^{-1}$) groups. The main differences in the product of oxidation of oil asphaltenes occur in a significantly lower band intensity of carboxylic groups (1700 cm$^{-1}$) and a higher band intensity of methyl and methylene groups (2922 and 2852 cm$^{-1}$) (Figure S1 in Supplementary Materials). In addition, IR spectrum of the product AP/SA shows an additional band at 1401 cm$^{-1}$ associated with the vibrations in phenols or acids and a band at 593 cm$^{-1}$ due to the bending vibrations of SO$_2$ of adsorbed ammonium sulfate or persulfate.

![Figure 7. IR spectra of AP/SA (red) and AP/AA (black) products.](image)

IR spectrum of the AP/AA product prepared in acetic acid (Figure 7) shows the stretching vibration bands of carboxylic groups C=O (1710 cm$^{-1}$) and asymmetric vibrations of C-O groups (1231 and 1287 cm$^{-1}$) due to vibrations of C-O-C and C-O-H groups, including phenols, alcohols, ethers, and acids.

Thus, ET-A asphaltenes are oxidized and sulfonated with AP in sulfuric acid in analogy to petroleum asphaltenes, though to a larger extent. Due to the fact that initially there is no nitrogen in technogenic asphaltenes, in contrast to petroleum ones, we recorded this atom on the surface of AP/SA product as adsorbed ammonium sulfate or persulfate. Exposure to AP in acetic acid leads only to oxidation of technogenic asphaltenes resulting in carboxylic and C-O groups (1231 and 1287 cm$^{-1}$), which are intrinsic for epoxy, phenolic, or alcohol groups.
3.2.2. Oxidation of Asphaltenes with H$_2$O$_2$/CH$_3$COOH

Peroxyacetic acid (PA), which can be prepared in situ during the reaction of hydrogen peroxide with acetic acid, is widely used in organic synthesis. Organic peroxyacids are used for epoxidation of alkenes via Prilezhaev reaction [55] including that of polymeric petroleum resins produced from ET [56]. Petroleum asphaltenes are exposed to PA for the soft destruction and release of occluded hydrocarbons carrying important geochemical information [38,39].

In contrast to petroleum asphaltenes, ET-A do not have occluded hydrocarbons and possess a lower molecular weight and lower stability. ET-A asphaltenes are susceptible to oxidation with air oxygen, which rationalizes the presence of low-intense bands corresponding to carbonyl group in IR spectrum (Figure 5) and the presence of oxygen according to XPS data (Figure 4). ET-A asphaltenes were modified with a gradual increase in HP content in the mixture with acetic acid, as a result of which the oxygen content notably increased in the products (Table 2), while IR spectra of the products showed a broad signal with the vibration bands at 1737 and 1711 cm$^{-1}$ corresponding to carboxylic groups (Figure 8).

<table>
<thead>
<tr>
<th>Samples</th>
<th>XPS Analysis</th>
<th>CHNS Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>ET-A</td>
<td>99.3</td>
<td>not</td>
</tr>
<tr>
<td>HP/AA (4/10)</td>
<td>93.7</td>
<td>not</td>
</tr>
<tr>
<td>HP/AA (8/10)</td>
<td>94.7</td>
<td>not</td>
</tr>
<tr>
<td>HP/AA (25/20)</td>
<td>94.8</td>
<td>not</td>
</tr>
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</table>

Figure 8. IR spectra of HP/AA (4/10) (blue), HP/AA (8/10) (black), and HP/AA (25/20) (red) products.

An increase in the band intensity at 1737 cm$^{-1}$ and a decrease in the band intensity at 1711 cm$^{-1}$ in the products HP/AA (25/20) > HP/AA (8/10) > HP/AA (4/10) are caused by different electronic effects due to the effect of the functional groups formed during chemical modification. These groups are mainly represented by hydroxyl and carboxylic substituents, which affect each other due to inductive, mesomeric, and field effects. With an increase in the H$_2$O$_2$-to-CH$_3$COOH ratio, there is a gradual increase in the relative absorption band intensity values at 1737, 1232, and 1034 cm$^{-1}$ for the products of oxidation of
HP/AA series (Table 3, Figure 8). Absorption bands at 1232 and 1034 cm\(^{-1}\) are associated with vibrations of epoxy ring and asymmetric stretching vibrations of C-O bond, respectively. There are published data on the formation of oxirane (epoxy ring with absorption band at \(\nu\) C-O = 1230 cm\(^{-1}\)) for petroleum asphaltenes oxidized with KMnO\(_4\)/H\(_2\)SO\(_4\) [18]. In the case of PA-epoxidated polymeric petroleum resins, the absorption band is \(\nu\) C=O = 1240 cm\(^{-1}\) [56].

<table>
<thead>
<tr>
<th>Samples</th>
<th>Intensity of the Band Relative to the Intensity of the C=C Aromatic Band (1600 cm(^{-1}))</th>
<th>C=O (1737 cm(^{-1}))</th>
<th>C-O (1232 cm(^{-1}))</th>
<th>C-O (1034 cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HP/AA (4/10)</td>
<td>0.76</td>
<td>0.81</td>
<td>0.58</td>
<td></td>
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<tr>
<td>HP/AA (8/10)</td>
<td>0.93</td>
<td>1.14</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>HP/AA (25/20)</td>
<td>1.08</td>
<td>1.39</td>
<td>0.90</td>
<td></td>
</tr>
</tbody>
</table>

For petroleum asphaltenes oxidized with PA [34], there is no band at 1737 cm\(^{-1}\), while the band intensity of carboxylic (1711 cm\(^{-1}\)) and epoxy groups (1232 cm\(^{-1}\)) is much lower (Figure S2 in Supplementary Materials). Moreover, oxidized petroleum asphaltenes show intense bands at 1298 cm\(^{-1}\) and 1126 cm\(^{-1}\) corresponding to vibrations of S=O bonds, which are formed due to oxidation of sulfur in native molecules to sulfones [57].

Thus, differences in the products of oxidation of technogenic and petroleum asphaltenes during oxidation with PA is related to higher stability and a large amount of sulfur in the latter. In this case, oxidation of polyaromatic molecules with peroxyacetic acid always leads to the formation of carboxylic, hydroxyl, and epoxy groups.

3.2.3. Oxidation of Asphaltenes with H\(_2\)O\(_2\)/Na\(_2\)CO\(_3\):

SP is fully decomposed into Na\(_2\)CO\(_3\) and H\(_2\)O\(_2\) at heating above 100°C, which affords both oxidizing agent and alkaline medium. Asphaltenes ET-A were oxidized under rigid conditions in autoclave at 200°C and pressure of 1.8 MPa. The products of the reaction were separated according to the procedure described for petroleum asphaltenes [40]. Thus, water-insoluble product was obtained, which was separated via extraction with benzene into SP-1 and SP-2. The precipitate was isolated from aqueous solution after oxidation to pH = 2–3—product SP-3, while SP-4 was afforded from the filtrate during extraction with acetone (Figure 2).

Oxidation of ET asphaltenes in water-alkaline medium, in analogy to petroleum asphaltenes [40], forms similar O-containing products (Figures S3 and S4 in Supplementary Materials). IR spectrum of the SP-1 product (Figure 9) showed intense absorbance at 1710 cm\(^{-1}\) (C=O) and a less intense band at 1283 cm\(^{-1}\) (C-O), which identifies this product as the least transformed asphaltenes with carboxyl groups.
There is a large increase in the oxygen content in the SP-2 product (Table 4). XPS analysis recorded oxidized oxygen (C1s 286.3 eV and 288.0 eV, O1s 531.4 and 532.5 eV) in C-OH/C-O-C and O=C groups. In addition, the presence of 1.5 wt.% sodium (Na1s 1067.8 eV) was recorded, which is adsorbed on the surface of the product, presumably in the form of sodium carbonate. IR spectrum of SP-2 indicates the appearance of an intense absorption at 3384, 1710, 1385, and 1272 cm⁻¹, which is intrinsic for hydroxyl, carbonyl, carboxylic group, and C-O groups. An intense band of C=C bond in IR spectrum at 1579 cm⁻¹ indicates a notable increase in the fraction of conjugated polyaromatic structures (Figure 9). It is considered that SP-2 is the product of oxidative condensation of asphaltenes, which becomes insoluble in most solvents. In addition, there was a large decrease in the absorption intensity of the bands at 2858 and 2954 cm⁻¹ corresponding to methyl and methylene groups, which agrees with the formation of crosslinks at cleavage sites of PAHs [58,59].

Table 4. Elemental composition of ET-A and oxidation products of the SP series.

<table>
<thead>
<tr>
<th>Samples</th>
<th>XPS Analysis</th>
<th>CHNS Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>ET-A</td>
<td>99.3</td>
<td>0.7</td>
</tr>
<tr>
<td>SP-1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SP-2</td>
<td>88.3</td>
<td>9.3</td>
</tr>
<tr>
<td>SP-3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SP-4</td>
<td>-</td>
<td>-</td>
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</table>

IR spectra of the products SP-3 and SP-4 show a large number of O-containing functional groups (Figure 10). The presence of absorption bands at 3435 cm⁻¹ (OH), 1800–1700 cm⁻¹ (C=O), and 1306–1010 cm⁻¹ (C-O), as well as 1582 cm⁻¹ (C=C arom), 2923, and 2857 cm⁻¹ (CH₃ and CH₂) could identify SP-3 as the mixture of water-insoluble aromatic and aliphatic mono-, di-, and polycarboxylic acids. Absorbance at 2500—2700 cm⁻¹ is good evidence of the presence of carboxylic acid dimers, where there are bands corresponding to stretching vibrations of O—H bound into dimers of carboxylic groups. Interestingly, the vibration frequency of the carboxylic group is shifted to 1774 and 1736 cm⁻¹, in contrast to
the products SP-1 and SP-2 ($\nu_{C=O} 1710$ cm$^{-1}$), presumably because of the conjugation from donor groups, which could result in a large high-frequency shift of C=O band. For the SP-4 product (Figure 10), the presence of main absorption bands is recorded nearly in the same region though the aromatic C=C band intensity is much lower, which suggests the presence of water-soluble aliphatic and aromatic carboxylic acids.

![Figure 10. IR spectra of SP-4 (red) and SP-3 (black) products.](image)

For the SP-3 product, the salt form SP-3/TEA was obtained using triethylamine (TEA), which was isolated from acetone supernatant as a precipitate. Comparison of IR spectra (Figure 11) show disappearance of intense bands of carboxylic groups at 1774 and 1736 cm$^{-1}$ and a band shift to lower frequency values up to 1769 and 1709 cm$^{-1}$, which is intrinsic for carboxylic acid salts [60]. The bands in SP-3/TEA at 1451, 1375, and 1037 cm$^{-1}$ correspond to the bands of triethylamine, which indicates salt formation. The signals at 2981 and 2843 cm$^{-1}$ correspond to methylene and methyl groups in aryl derivatives and triethylammonium fragment. Reduction in the band intensity at 1125 and 1231 cm$^{-1}$ corresponding to the vibrations of C-OH groups is also related to salt formation. Ordering of the fingerprint area of the product of interaction with triethylamine is presumably caused by various electronic effects and redistribution of electron density of molecules in the salt form.
ESI-MS measured in negative ionization mode gave complex mass spectra for the products SP-3 and SP-4, with a large number of ion peaks (Figure 12). The ESI-MS (−) technique was previously employed for the identification of various carboxylic acids produced through biodegradation of asphaltenes and PAHs with microorganisms [61–63]. From provided information on fragmentation ions formed during degradation of asphaltenes and PAHs [61–63] and the composition of ET [3], we identified some O-containing compounds in the products SP-3 and SP-4 (Table S1 in Supplementary Materials).
Asphaltenes and products of oxidation of SP series were also investigated using EPR spectroscopy. In EPR spectra, petroleum asphaltenes, as a rule, register intense signals of vanadyl complexes (VC) VO\(^{2+}\) and free stable radical (FSR). The FSR signal arises due to the delocalization of lone electrons on carbon \(\pi\)-systems and, accordingly, with an increase in the degree of condensation of aromatic structures, the signal intensity increases [64]. However, the intensity and shape of FSR lines in spectrum are also affected by the local environment of the paramagnetic center. Heteroatoms can conjugate with \(\pi\)-systems of aromatic rings and additionally stabilize paramagnetic particles. For example, the maximum intensity of FSR signal in EPR spectrum is recorded for petroleum asphaltenes, which are rich in heteroatoms (N, S, O) (Figure 13a). The lowest FSR signal amplitude was recorded for the SP-4 specimen, whereas the FSR intensity for the SP-1 and SP-3 specimens changed to a lower extent relative to initial asphaltenes ET-A. In this case, there is a maximum increase in the FSR signal amplitude in the product SP-2, which confirms the increase in the condensation degree of molecules as a result of oxidative condensation (Figure 13a). The VC signals in EPR spectra for technogenic asphaltenes and products of its oxidation are not recorded; however, a hyperfine structure is recorded at high signal amplification for the SP-1 specimen in the sweep range of 800 G, which is intrinsic to petroleum vanadyl porphyrins for OIL-A (Figure 13b). This indicates the presence of trace amounts of vanadyl complexes in technogenic asphaltenes.

![EPR spectra of samples of the SP series, technogenic ET-A, and petroleum OIL-A asphaltenes with a sweep of 100 G (a) and 800 G (b) (the signal intensity of the OIL-A sample is reduced).](image)

Figure 13. EPR spectra of samples of the SP series, technogenic ET-A, and petroleum OIL-A asphaltenes with a sweep of 100 G (a) and 800 G (b) (the signal intensity of the OIL-A sample is reduced).

In EPR, \(g\)-factor is the parameter and is sensitive to the chemical environment of unshared electrons. Even though this parameter could not be related to pure compounds, it reflects the nature of the heteroatomic composition of radicals. The \(g\)-factor values of asphaltenes OIL-A containing O, S, and N heteroatoms is 2.0032, whereas this value is 2.0026 in the case of asphaltenes ET-A. It is considered that oxygen is the atom responsible for the shift of \(g\)-value (2.0029–2.0037) in petroleum asphaltenes due to the formation of quinone or phenoxy radicals [65], which partially localize radical wave function on oxygen. The \(g\)-factors shift during the oxidation of technogenic asphaltenes. For example, for the products of oxidation of SP-3 and SP-4, the radicals with the largest \(g\)-factor values were recorded as 2.0037 and 2.0034, respectively. The shift of \(g\)-factor values for the SP-1 (\(g = 2.0030\)) and SP-2 (\(g = 2.0028\)) products is lowest relative to initial asphaltenes ET-A (\(g = 2.0026\)).

Thus, oxidation of technogenic asphaltenes with SP in analogy to petroleum asphaltenes afford similar O-containing products, which can be soluble/insoluble in water or insoluble in most solvents. During the study, increased sorption characteristics are recorded for the product of oxidative condensation, SP-2, on the surface of which sodium carbonate is adsorbed.
3.3. Application of Modified Asphaltenes

Preparation of effective acidic carbocatalysts and sorbents based on modified petroleum asphaltenes has been extensively investigated in recent years [13–19,31,32]. A rigid carbon framework and facile modification of the polyaromatic core with reactive functional groups could improve the catalytic and sorption ability of modified asphaltenes and allow for their use as effective catalysts in some acid-catalyzed reactions, as well as adsorbents of heavy metals and other ecotoxins. Studies showed that the number of acidic functional groups and their accessibility, as well as the developed surface of carbon carrier, pore size, and the presence of strong electron-withdrawing groups, are the most important parameters for the synthesis of these materials.

To reveal the number of acidic centers in the products of chemical modification of technogenic asphaltenes, the static exchange capacity (SEC) was determined. The higher the SEC value, the larger the number of functional groups capable of acid-base and coordination interactions, which are mainly represented by carboxylic, sulfonic, and hydroxyl groups [66,67].

The SEC values allow us to conclude that oxidation of technogenic asphaltenes is accompanied by the formation of acidic centers displaying diverse activity (Table 5). The maximum value of SEC, 1.54 meq/g, was measured for the product AP/SA, the product of oxidation/sulfonation containing various sulfo-, carboxylic, and hydroxyl groups at the polyaromatic core. In the case of petroleum asphaltenes, there is also an increase in SEC values with a transition from the products of oxidation to the products of oxidation/sulfonation [14,32]. Low-temperature oxidation reaction conditions could not afford a large number of acidic centers and high SEC values, while rigid conditions yielded the product of oxidative condensation, which is insoluble in most solvents and possesses a higher SEC value.

Table 5. SEC of modified asphaltenes.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SEC, meq/g</th>
<th>Modifying Reagent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(NH₄)₂S₂O₈</td>
</tr>
<tr>
<td>Technogenic asphaltenes</td>
<td>1.54</td>
<td>0.46</td>
</tr>
<tr>
<td>Petroleum asphaltenes</td>
<td>2.0 [32]</td>
<td>-</td>
</tr>
</tbody>
</table>

For the SP-2 product based on petroleum asphaltenes (Figure S4 in Supplementary Materials), the SEC parameter is not presented in [40]. However, in this work, its sorption capacity toward phenol in aqueous solution was studied, and the recovery reached 67.5% at the initial phenol concentration of 5 mg/L.

During synthesis, products AP/SA and SP-2 featured increased sorption characteristics, with the adsorption of the products of cleavage of oxidizing agents on the surface, such as ammonium sulfate and sodium carbonate, respectively. However, the SEC value for modified technogenic asphaltenes is slightly lower than that of analogous products based on petroleum asphaltenes. The petroleum asphaltenes possess a more developed spatial structure due to their origin, and they possess a variety of alkyl substituents, which are oxidized during chemical modification. Nevertheless, the choice of optimal conditions of modification could amount to high values of sorption and catalytic characteristics for technogenic asphaltenes.

Thus, based on the SEC values of modified technogenic asphaltenes, they can be considered as sorbents of heavy metals [31] and various organic pollutants in wastewater, such as methyl orange [15], and as heterogeneous catalysts for the acetylation [14] and the Kabachnik–Fields reactions [68]. In addition, technogenic asphaltenes can find practical application as fillers for various polymers [30,69–71]. In the recent work of Eshraghian et al. [71], asphaltenes of various petroleum sources were investigated as fillers for a wide...
range of polymers (polypropylene, polystyrene, polymethyl methacrylate, and polycarbonate). The authors found that better dispersion was achieved for more polar asphaltenes in polymers with a higher polar solubility parameter. Technogenic asphaltenes and their modifications can be used as fillers for polymers with a suitable polar solubility parameter.

4. Conclusions

Ethylene tar, which is the side product of pyrolysis of hydrocarbon crude, can be considered as an accessible source of technogenic asphaltenes, the content of which can reach 22 wt. %. Technogenic asphaltenes are a lower molecular weight than petroleum asphaltenes and can find application in the same areas [30]. The specific features of their composition can contribute to more effective use of these polyaromatic compounds as carbon fillers of polymers with a suitable polar solubility parameter [30,71].

For a number of applications, pre-modification of asphaltenes can be required in order to increase the number of active functional groups capable of acid-base and coordination interactions (for example, during sorption and catalysis). The present work shows for the first time that the methods of oxidative modification previously used for petroleum asphaltenes can be extended to technogenic asphaltenes. It has been shown that, unlike petroleum asphaltenes, technogenic asphaltenes undergo deeper oxidation, although the general patterns of oxidation reactions and the formation of various O-containing groups (carboxyl, phenoxyl, hydroxyl, sulfoxide, etc.) are preserved.

Thus, the isolation and modification of asphaltenes from ET can serve as an effective way to convert this technogenic resource into value-added products.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/en16217376/s1, Figure S1: IR spectrum of products of oxidation of petroleum asphaltenes with (NH4)2SO4/H2SO4; Figure S2: IR spectrum of products of oxidation of petroleum asphaltenes with CH2COOH/H2O2; Figure S3: IR spectra of SP-1 and SP-2 products obtained via oxidation of petroleum asphaltenes with sodium percarbonate; Figure S4: IR spectra of SP-3 and SP-4 products obtained via oxidation of petroleum asphaltenes with sodium percarbonate; Table S1: Ion analysis results according to ESI-MS data (−) for SP-3 and SP-4 products.

Author Contributions: Conceptualization, Y.Y.B., D.N.B. and M.R.Y.; Methodology, M.R.Y.; Investigation, A.M.M., K.V.S. and V.I.M.; Data curation, Y.Y.B. and D.N.B.; Writing—original draft, Y.Y.B. and K.V.S.; Writing—review & editing, Y.Y.B., D.N.B. and M.R.Y.; Visualization, A.M.M. and V.I.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research was carried out with financial support from the government assignment for FRC Kazan Scientific Center of RAS.

Data Availability Statement: Data will be made available on request.

Acknowledgments: The authors are grateful to the researchers of Multiple-Access Spectral-Analytical Center for Physical-Chemical Study of Structure, Properties and Composition of Substances and Materials, KazSC RAS, for their kind cooperation in the examinations conducted for the study.

Conflicts of Interest: The authors declare no conflict of interest.

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Energies 2023, 16, 7376


Energies 2023, 16, 7376


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