

Article

Catalytic Low-Temperature Thermolysis of Heavy Oil in the Presence of Fullerene C₆₀ Nanoparticles in Aquatic and N₂ Medium

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Abstract: Catalytic thermolysis is considered to be an effective process for viscosity reduction, the conversion of high-molecular components of oil (resins and asphaltenes) into light hydrocarbons, and the desulfurization of hydrocarbons. In this paper, we conducted non-catalytic and catalytic thermolysis of a heavy oil sample isolated from the Ashalcha oil field (Tatarstan, Russia) at a temperature of 250 °C. Fullerene C₆₀ nanoparticles were applied to promote selective low-temperature thermolytic reactions in the heavy oil, which increase the depth of heavy oil upgrading and enhance the flow behavior of viscous crude oil. In addition, the influence of water content on the performance of heavy oil thermolysis was evaluated. It was found that water contributes to the cracking of high-molecular components such as resins and asphaltenes. The destruction products lead to the improvement of group and fractional components of crude oil. The results of the experiments showed that the content of asphaltenes after the aquatic thermolysis of the heavy oil sample in the presence of fullerene C₆₀ was reduced by 35% in contrast to the initial crude oil sample. The destructive hydrogenation processes resulted in the irreversible viscosity reduction of the heavy oil sample from 3110 mPa·s to 2081 mPa·s measured at a temperature of 20 °C. Thus, the feasibility of using fullerene C₆₀ as an additive in order to increase the yield of light fractions and reduce viscosity is confirmed.

Keywords: catalytic cracking; thermolysis; aquathermolysis; catalyst; heavy oil; low temperature; fullerene C₆₀



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1. Introduction

Heavy oil resources are becoming a significant contributor to the world energy supply in contrast to depleting conventional crude oil reserves [1]. However, the production of heavy oil is limited under the existing technological and economic conditions. The most unfavorable properties of heavy oil are its high density and viscosity. Moreover, the significant contents of resins and asphaltenes, heteroatom compounds, and metals (such as vanadyl–porphyrin complexes) pose some technical issues during the recovery, refinery, and transportation of heavy crude oil [2,3]. Within the refinery process, different distillation cuts of the recovered crude oil are processed by atmospheric pressure distillation followed by vacuum distillation. Lighter distillation cuts are composed of shorter hydrocarbons, whereas heavier distillation cuts contain larger and higher aromatic hydrocarbons with a larger number of heteroatoms. Consequently, residues of the vacuum distillation contain high aromatic species with a large amount of heteroatoms and metals. In several refinery techniques, such as cracking, hydrotreating and catalytical reforming, the heavier fractions can be transformed into lighter ones. The lighter distillation cuts are gasoline and kerosene.

The middle-weight distillates are diesel oils, marine gas oil and heating oils. The distillation residues are heavy fuel oil for ships, lubrication oils and bitumens/tars. Without any doubt, such complex processes reflect the feasibility of the projects, and therefore, the cost of producing a barrel of heavy crude oil is much higher than that of conventional crude oil. In this regard, new feasible techniques are required to improve the quality of heavy crude oil.

Many methods have been proposed to upgrade heavy oil and reduce its viscosity during production, transportation, and refining, such as microwave-assisted upgrading, ultrasonic treatment, in situ combustion, CO₂-assisted hydrothermal upgrading, thermolysis, vis-breaking, and catalytic aquathermolysis [4,5]. The latter method, which has been applied in many fields, demonstrates favorable results by enhancing oil recovery and, more importantly, partially upgrading heavy crude oil in situ [6]. Catalytic thermolysis and aquathermolysis are important technological processes that convert heavy components (resins and asphaltenes) and heteroatomic compounds of heavy crude oil into light hydrocarbons, thus contributing to an obvious reduction in viscosity. It is thought that overheated water transfers heat energy to the hydrocarbons, and some asphaltene molecules break into small molecules under the high temperature impact [7]. Therefore, the viscosity reduces, and the mobility of the heavy oil improves. Moreover, the additional heat provides a driving force or pressure that makes viscous oils flow easily, and oil production increases. The physical consequences of the steam stimulation techniques have been widely studied. However, the injection of steam into the oil-saturated reservoir formations has chemical consequences. Hydrocracking, hydrogenation, water gas shift, alkylation, hydrolysis, thermolysis and polymerization reactions are the most common reactions that are carried out during steam–oil interactions.

The progress in petroleum industry is associated with the application of catalysis in enhanced oil recovery methods, processing of natural and associated gases, catalytic conversion of individual hydrocarbons and compounds based on them, processing of oil distillates, gas condensates and many other processes. Catalysts are widely used in various industries of developed countries and are common in nature, even in space. The processes of oil production can be intensified by using catalysts to carry out catalytic processes (for example in situ aquathermolysis of oil in the presence of nanosized organometals) in the formation. These the downstream processes include the catalytic processes of cracking and reforming, desulfurization and isomerization, catalytic pyrolysis and many others. In petrochemical processes, catalysts are used in the vast majority of processes—hydrogenation and dehydrogenation, hydration of olefins and chlorination of hydrocarbons, Fischer–Tropsch synthesis, alkylation reactions and polymerization. Catalysts regulate the rate of chemical (catalytic) processes, change the selectivity of industrial catalysts in the direction of increasing the production of target products and minimizing the output of by-products. The catalysts contribute to the alteration of reactions temperature, pressure and time. Moreover, the selectivity of the end-products depends on the nature of the catalysts. By introducing appropriate catalysts, hydrogen donors, and other additives with water vapor or inert gas N₂ into heavy oil reservoir formations, thermal, catalytic, and aquathermolytic reactions are promoted, so the quality of the heavy oil is further improved, and viscosity is irreversibly reduced. Water dissociates in the presence of the catalysts to produce hydrogen and favors the hydrogenation of oil, which gives stability to the final product, reduces the production of olefins and polyaromatics, and generally increases the ratio of H/C [8]. The most important step in the aquathermolysis of heavy oil is the hydrolysis of sulfide bonds into sulfides and thiophenes. Breaking the C–S bonds in the sulfides will reduce the number of high-molecular-weight compounds such as resins and asphaltenes so that the viscosity of the heavy oil decreases [9]. On the other hand, the reactive species produced upon aquathermolysis can either polymerize in the absence of free hydrogen donors. Catalyzing hydrogenation reactions and increasing thermal conductivity are considered to be important functions of catalytic nanoparticles [10]. The polymerization leads to undesirable viscosity increase. Acid polymerization of heavy crude oil highly depends on the specific molecular structure of the heavy oil and changes in the chemical nature of the

oil. The carbon dioxide gas, which is generally produced in a significant amount from the oilwells producing by steam-based recovery methods, can enhance the acid polymerization. Certain added inorganic salts can also hydrolyze and produce acidic conditions. The crude oils that are sensitive to such acid polymerization should obviously not be subject to acid fracturing conditions. Instead, caustic floods may be useful. Different from the conventional downstream catalytic cracking processes, catalytic nanoparticles are injected with superheated steam into the well, upgrading the heavy oil in-reservoir without highly investing in facilities [11].

To the best of our knowledge, the first use of metals to improve bitumen during aquathermolysis was reported by Clark et al. (1990) [12]. They noted that the use of aqueous metal salts instead of water in steam stimulation improves the properties of the extracted oil, such as viscosity and asphaltene content. They explained that the observed improvements are due to the catalytic action of metals on the above-mentioned aquathermolysis reactions. Homogeneous catalysts based on transition metals, including water-soluble inorganic salts, organic coordination compounds, and ionic liquids, can provide uniform contact with the oil phases, thereby achieving an increased viscosity reduction degree [13]. However, separating these catalysts from the upgraded oil is quite difficult, which not only contributes to an increase in cost but can also harm the refining industry. By contrast, heterogeneous catalysts comprising transition metals and their oxides, sulfides, carbides, phosphides, and solid acids can be easily separated and even reused after aquathermolysis. Kinetic studies of the catalytic aquathermolysis of heavy crude oil are very useful for better understanding the activation energy and reaction mechanisms of the catalytic thermolysis process [14].

The oil-soluble catalysts are injected into the reservoir formations on an industrial scale in order to carry out the downhole upgrading of heavy oil. The results of pilot experiments carried out in the Boca de Jaruco heavy oil reservoir (Republic of Cuba) produced the expected results. The authors reported the decrease in the content of asphaltenes and their molecular masses after the injection of the organosoluble catalysts. Moreover, the viscosity of heavy oil was reduced by more than three times, which was explained by the rearrangement of the high-molecular-weight components of crude oil. Thus, the amount of light distillate fractions increased, and the heavy oil was partially upgraded in the cheapest reservoir formation. The application of the catalytic composition produced an increase in cumulative oil production and incremental oil recovery in contrast to that of the non-catalytic steam injection cycle. After the injection of catalysts, more than 200 samples were isolated to be further investigated in a laboratory by using analytical methods. The obtained results inspired authors to expand upon the pilot testing of the catalyst injection [15]. On the other hand, the industrial application of water-soluble catalysts is highly limited, which is explained by the low efficiency of water-soluble catalysts and the low sweep efficiency of water. Moreover, the poorly studied fundamental phenomena such as the agglomeration of catalyst particles and their adsorption and precipitation on the rock surfaces are the major uncertainties that make the application of such catalysts difficult on an industrial scale.

Fullerenes have found wide applications in many fields, such as photovoltaics and photocatalysis, because of their unique electronic properties and structure [16,17]. They are soluble in common organic solvents at room temperature and have strong antioxidant ability and stability. Fullerenes are molecular compounds that belong to the class of allotropic forms of carbon. The most common fullerene is C₆₀, the number of which represents the 60 carbon atoms that form a closed spherical surface composed of regular hexagons and pentagons. It is the molecular analog of a soccer ball. It acts in the likeness of clathrate compounds that can carry with them low-molecular-weight hydrocarbons formed during thermolysis, which allows an increase in the yield of light fractions. C₆₀ has a high electronegativity, which allows it to accept more electrons, and has rich redox properties. At very high temperatures, although the C-C interaction is very high, the structure of C₆₀ molecules remains unchanged, indicating excellent high-temperature stability [18]. C₆₀ is characterized by high electronegativity, which allows it to accept more electrons, and it has excellent redox properties. The large surface

area of the catalyst nanoparticles provides high adsorption and mechanical strength. The conductivity of fullerene C60 is also very high [19,20].

Since Fullerenes (especially C60) have a narrow band gap (approximately 1.6–1.9 eV) and a unique three-dimensional structure, which ensures minimal changes in the structure and salvation associated with electron transfer, fullerenes (especially for C60) are considered to be excellent electron acceptors and transporters. This can result in rapid charge separation on the catalyst, while at the same time, it produces a relatively slow recombination of electrons and holes [21]. The light-induced electron transfer process of fullerene C60 nanomaterials has caused great concern [22–24]. Fullerenes have been successfully applied to many fields, such as photovoltaics and photocatalysis because of their unique electronic properties and structure [25,26]. Although fullerenes have many advantages, the dispersion and solubility of fullerenes in solution are not very good. Therefore, the modification of fullerenes to obtain their derivatives for photocatalytic reactions has received lots of attention. For example, Bai et al. modified a fullerene with a hydroxyl group to obtain a polyhydroxy fullerene, and then, they combined it with titanium dioxide to prepare a photocatalyst for the removal of the organic dye [27]. Djordjevic et al. prepared a composite catalyst of polyhydroxy fullerene and titanium dioxide and studied its degradation efficiency on herbicide mesotrione [28]. In order to obtain more reactivity, the preparation of organic catalysts by a composite of fullerenes and organic compounds has also made some progress [29,30]. More and more research has been carried out on the rapid development of the preparation technology of fullerenes and their derivatives.

In this study, we evaluate the influence of fullerene C60 on the thermolysis of a heavy oil sample in the presence and absence of water. With this in mind, we carried out the thermolysis of heavy oil samples in a high-pressure and high-temperature autoclave. The thermolysis products were investigated by analytical analysis methods and compared with the characteristics of the initial crude oil sample. This article will supply a scientific basis for the application of fullerene C60 and its derivatives in the thermolytic and aquathermolytic upgrading of heavy oil resources in order to achieve large-scale applications in the near future.

2. Results and Discussions

The viscosity parameter is crucial not only for enhancing oil recovery but also for pipeline transportation and other downstream technological processes during heavy oil processing. The viscosity of the fluid determines the pressure difference, and therefore, the amount of energy required to operate the pumps and other aggregates. Therefore, we evaluated the effects of the proposed catalytic systems on improving the viscosity characteristics of heavy crude oil through the acceleration of thermolytic and aquathermolytic reactions. The overall reactions during upgrading processes caused the conversion of high-molecular-weight resins and asphaltenes into low-molecular-weight saturates and aromatics. Moreover, the average molecular weight of the asphaltenes and resins can influence the viscosity of crude oil more than their relative content can. Additionally, the change in the shape of the molecules of the resins and asphaltenes is able to reduce the viscosity of heavy crude oils. In Figure 1, the temperature-dependent viscosity values before and after thermolysis and aquathermolytic of a heavy oil sample are illustrated. The results show that even a small increase in the temperature of the oil bulk significantly reduced the viscosity of all the samples, and this tendency is explained by the destruction of the internal structures of the heavy oil samples. The efficiency of the thermolysis was significantly increased in the presence of fullerene C60 nanoparticles and an aquatic medium (20%), which led to a reduction in the viscosity of the initial heavy oil sample from 3110 mPa·s to 2081 mPa·s (measured at 20 °C). This is explained by the hydrogen-donating capacity of water and the catalysis of dehydrogenation reactions under the given pressure and temperature. There are many studies in the literature that indicate the role of water in the thermolysis of hydrocarbons [31–34]. The generated hydrogen donors participate in the stabilization of free radicals formed after the cracking of the peripheral alkyl substitutes from the polycondensed benzene rings. Moreover, the hydrogen provides an increase in the ratio of atomic H/C, which is specific to upgraded

heavy oils or light crude oils [35,36]. The thermolysis of heavy oil in the absence of water and the catalyst resulted in a reduction in the viscosity by only 5%. However, the additions of 10% and 20% of water to the reaction medium contributed to a further reduction in heavy oil viscosity by 4.8% and 6.3%, respectively.

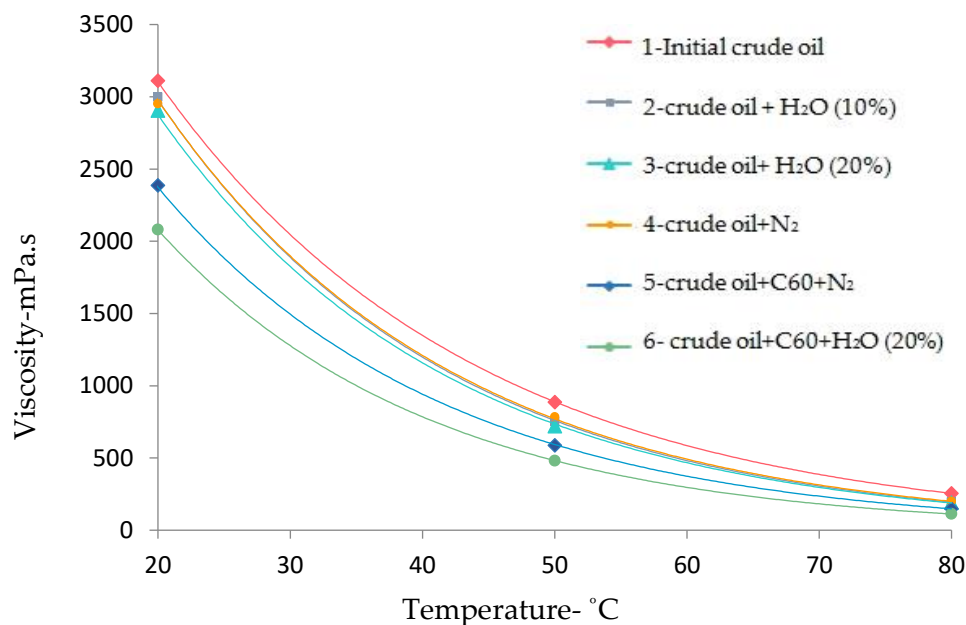


Figure 1. Viscosity–temperature relations in the process of thermolysis in the medium of water and nitrogen.

It is proposed that C₆₀ nanoparticles participate in the dissociative reactions of water and promote the destructive hydrogenation of the most high molecular weight components of oil, which can be judged from the decrease in the content of asphaltenes by 35% (Figure 2). The chemical bond scission in the structure of the resins and asphaltenes initiates with S-S and C-S, which are the weakest ones from the thermodynamical point of view. It is worthy to note that heteroatoms are mainly concentrated in resins and asphaltenes fractions. Hydrodesulfurization reactions trigger other reaction chains such as the rearrangement of hydrocarbons in the composition of resins and asphaltenes, a decarbonylation reaction, which produces a CO intermediate, and a water gas shift reaction, which transforms CO into CO₂ and H₂. Hydrogen gas is involved in closing the formed radicals after the cracking of peripheral alkyl chains from the asphaltene-like fragments. The results of the SARA analysis of the crude oil samples show an increase in the content of asphaltenes in the experiments carried out without water (Figure 2, samples 3 and 6). This supports the above-mentioned proposal regarding the role of water in the conversion of heavy fragments into light ones. The least stable bonds that exist in the composition of the heavy oil structure are S-S and C-S bonds, and, hence, the hydrogen is primarily prone to hydrodesulfurization processes [37–39]. The produced reactive organosulfur species can either polymerize in the absence of protons or react with hydrogen-producing smaller fragments. The former path leads toward increasing the contents of resins and asphaltenes, which are the main challenges in reducing the viscosity and the formation of the light distillate fractions of heavy oil [40]. The significant changes in the compositions of the heavy crude oil samples were observed after thermolysis in the presence of water and the catalyst (sample 5). The results are in accordance with the viscosity values (see Figure 1).

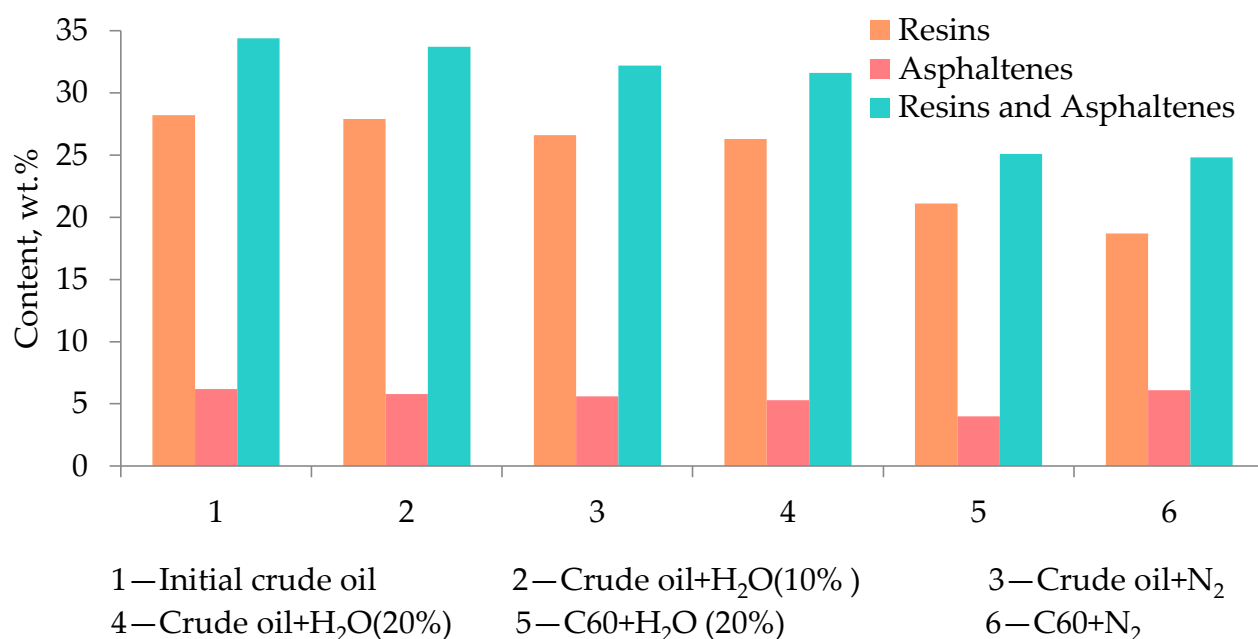
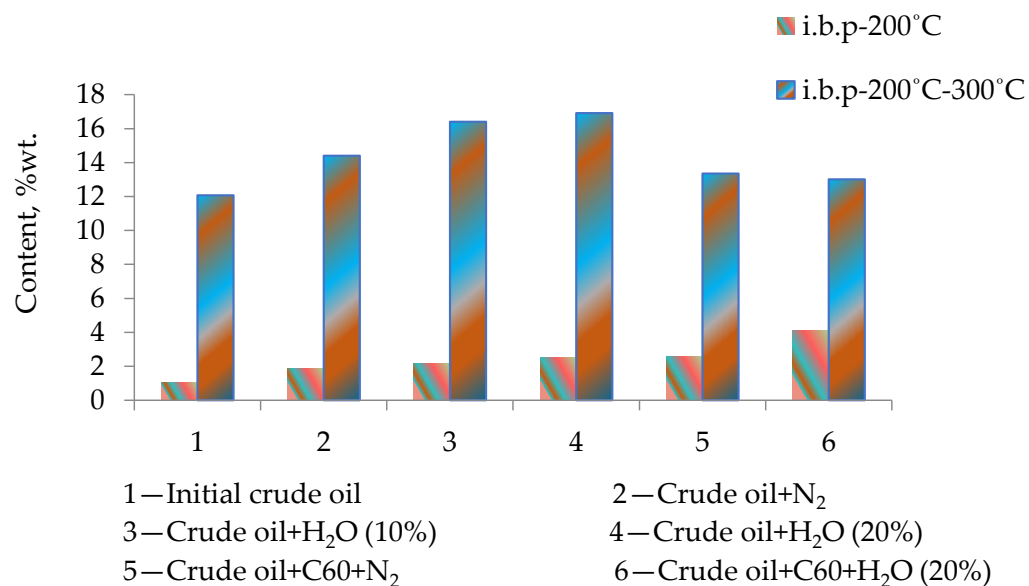


Figure 2. Changes in the contents of high-molecular-weight fragments of oil.

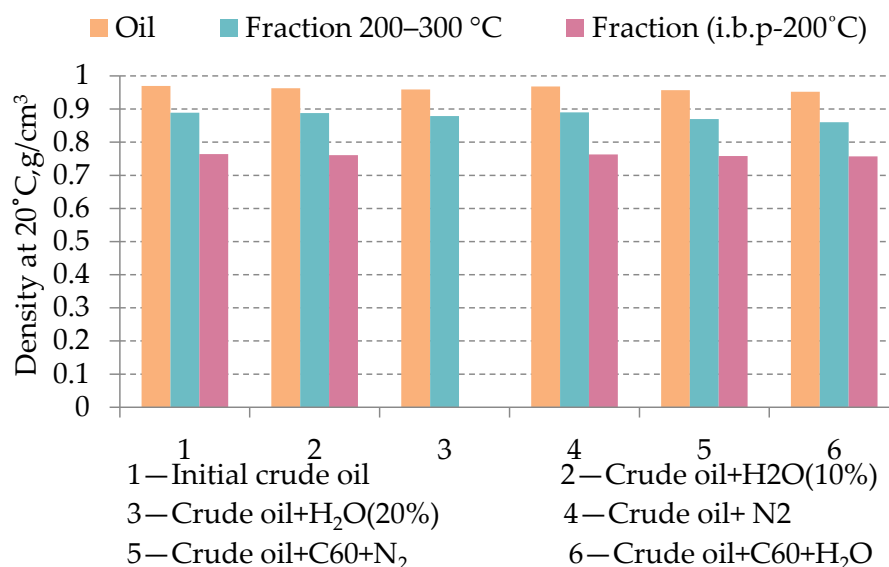
Atmospheric oil distillation is the first step and a very informative approach to studying the chemical composition of heavy oil. The results of the atmospheric distillation of the heavy oil samples before and after thermolytic experiments are summarized in Table 1 and Figure 3. The initial boiling points (i.b.p.) of oil samples before and after experiments vary depending on the content of low-boiling hydrocarbon fractions. In turn, the boiling points of distillate fractions depend on the number of carbon atoms, light fractions, and the chemical structures of the compounds in the following order: normal alkanes < normal alkenes < iso alkanes < iso alkenes < alkyl cyclopentanes < alkyl cyclohexanes < alkylbenzenes < alkyl naphthalenes. The lowest boiling point temperature of an oil sample (98 °C) was observed in the case of catalytic and water-assisted thermolytic upgrading. Apparently, the reductions in the overall length of the side chain, density, and refractive index of aromatic hydrocarbons led to a reduction in the boiling point. The distillates were roughly divided into two fractions in order to evaluate the yield of light components and, hence, the upgrading performance of fullerene C60 nanoparticles. The first fraction is the accumulation of heating products starting from the initial boiling point to a temperature of 200 °C. This fraction corresponds to the gasoline distillates, which are composed of a mixture of alkane, naphthene, and aromatic hydrocarbons. Generally, in such hydrocarbons, the number of carbon atoms varies between 5 and 10. The yield of the gasoline fraction (i.b.p. 200 °C) from the initial crude oil was 1.02%wt., while the catalytic thermolysis in the absence and presence of water (20%) drastically increased the yield by more than 2 and 4 times, respectively. This indicates the proposed mechanism of destructive hydrogenation of the most high-molecular-weight components of heavy oil and their conversion into light low-molecular-weight hydrocarbons such as saturates and aromatics. The second fraction is the gas oil fraction with a boiling point range of 200–300 °C. This fraction is mostly composed of C10–C20 hydrocarbons. The maximum gasoil fraction yield (16.91%wt.) was observed after the thermolysis of heavy oil in the presence of water with a concentration of 20%. The content of total sulfur was almost unchanged for all the heavy oil samples.

Table 1. Atmospheric distillation yields and total sulfur contents.

Samples	i.b.p., °C	Fraction (i.b.p-200 °C), %wt.	Fraction 200–300 °C	Total sulfur, %wt.
Initial crude oil	170	1.02	12.07	4.72
Crude oil + N ₂	140	1.85	14.40	4.27
Crude oil + C60 + N ₂	110	2.60	13.35	4.25
Crude oil + H ₂ O (10%)	142	2.15	16.40	4.28
Crude oil + H ₂ O (20%)	130	2.50	16.91	4.22
Crude oil + C60 + H ₂ O (20%)	98	4.1	13.01	4.25

**Figure 3.** The contents of light distillate fractions before and after thermolysis.

The chemical and structural composition of heavy oil can be indirectly evaluated by the density of the oil and petroleum products. Hence, in Figure 4, we present the density of the initial crude oil sample and its fractions (i.b.p.–200 °C and 200 °C–300 °C) and the thermolytic and aquathermolytic products in the absence and presence of fullerene C60.

**Figure 4.** The density of crude oil and light distillates before and after catalytic thermolysis measured at 20 °C.

Fullerene C60 is a nanostructured molecule composed of sixty allotrope carbon atoms, which form a closed spherical surface with pentagonal and hexagonal faces. The obtained experimental results indicate the activity of these nanoparticles on the following reactions that are carried out during the thermolysis of heavy oil: cracking of C-C bonds into saturated and unsaturated products, acid polymerization, water–gas shift reaction, decarbonylation, hydrogenation and dehydrogenation reactions, hydrogenolysis, isomerization, and desulfurization and alkylation reactions. The C60 nanoparticles promote the overall reactions via radical-chain and carbonic-ion mechanisms that lead to a decrease in the content of unsaturated hydrocarbons and an increase in the yield of light distillate fractions. The overall reaction mechanism is summarized in the graphical abstract.

3. Materials and Methods

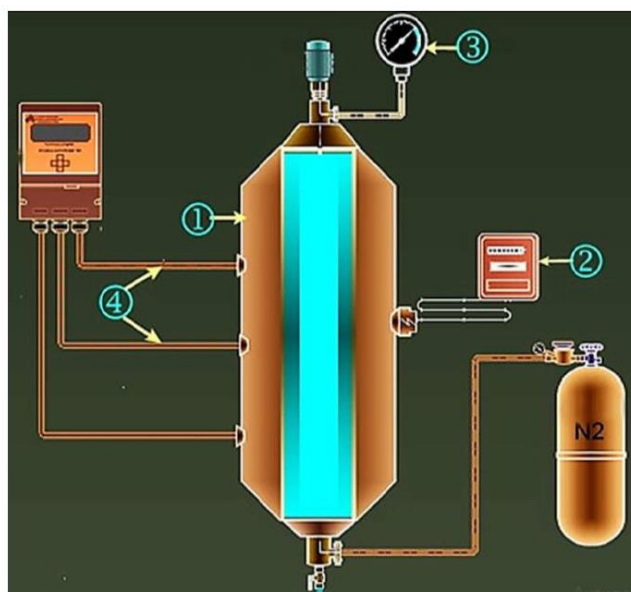
3.1. Experiments in Autoclave

The object of this study was a heavy oil sample obtained from the Ashalchinskoye field, which was characterized by a high sulfur content of up to 4.5%wt. and a significant content of asphaltenes (6%wt.). The dynamic viscosity of the initial crude oil measured at a temperature of 20 °C was 3100 mPa·s. The formation reservoir rocks are referred to as carbonate and terrigenous deposits [41]. A distinctive feature of the object of the study was the small content of light fractions that boiled out at an initial boiling point up of to 200 °C (up to 1.0–1.2%wt.). The main physical and chemical properties of the heavy oil sample are summarized in Table 2. The true vertical depth of the reservoir formation was less than 100 m below the earth's surface. The reservoir temperature and pressure were 8 °C and 0.44 MPa, respectively.

Table 2. Physical and chemical properties of heavy crude oil sample.

Characteristics	Values
Dynamic viscosity at 20 °C, mPa·s	3110
Density at 20 °C, kg/m ³	970
Total sulfur content, wt. %	4.72
Resins, wt. %	26.2
Asphaltenes, wt. %	6.1
Initial boiling point, °C	175
Yield of fractions, wt. %:	
Up to 200 °C	1.0
Up to 300 °C	12.0

Non-catalytic and catalytic thermolysis in the presence and absence of water were carried out in a laboratory unit consisting of a reactor, heating and mixing devices, as well as a control unit to monitor the flow of the process and record the kinetics of the process. The scheme of the autoclave is illustrated in Figure 5. The temperature was raised to 250 °C in less than 1 h and kept at 250 °C for 2 h. Then, the autoclave was cooled down to room temperature. In experiments with water, concentrations of 10% and 20% were chosen to imitate the aquathermolysis process. On the other hand, for the thermolysis processes, the given initial pressure was 1.6 MPa, which was supplied by inert N₂ gas. The introduced fullerene nanoparticles were 70 nm in size, and their concentration was 0.5%wt. in all experiments.



1—Autoclave 2—Temperature-controlling instrument
3—Pressure meter 4—Thermocouple

Figure 5. Laboratory autoclave with catalytic reactor.

3.2. SARA Analysis

A method for the characterization of heavy oils based on fractionation, whereby a heavy oil sample is separated into smaller quantities or fractions, with each fraction having a different composition, was used. The fractionation was based on the solubility of hydrocarbon components in various solvents used in this test. Each fraction consists of a solubility class containing a range of different molecular weight species. In this method, the crude oil is fractionated into four solubility classes, referred to collectively as SARA: saturates, aromatics, resins, and asphaltenes. Saturates are generally iso- and cyclo-paraffins, while aromatics, resins, and asphaltenes form a continuum of molecules with increasing molecular weights, aromaticity, and heteroatom contents. Chromatographic separation was carried out using a silica gel ASA with a grain size of 0.2–0.3 mm. Hydrocarbon fractions were sequentially extracted via desorption using solvents of different polarities (hexane, toluene, and a mixture of methanol and toluene) (Figure 6). The analysis was carried out as per the American Standard Test Method (ASTM) D2007, wherein the details of the apparatus and procedures can be found.

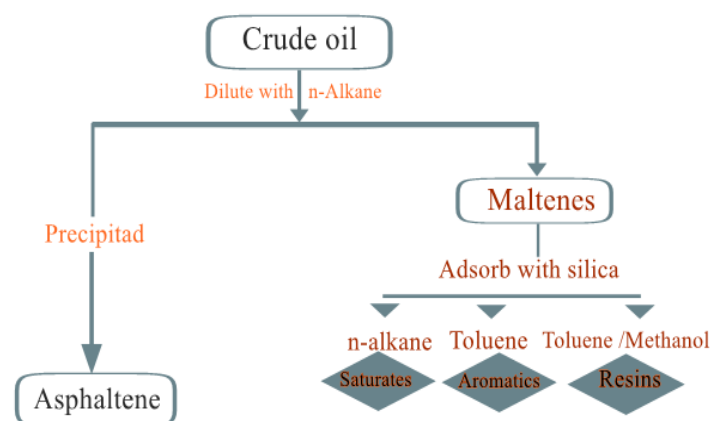


Figure 6. Schematic of SARA fractionation.

3.3. Total Sulfur Analysis

The total sulfur content in the feedstock was determined using the energy-dispersive X-ray fluorescence sulfur analyzer SPECTRO-SCAN SL. The initial crude oil and the thermolysis products in the presence and absence of fullerene C60 in the nitrogen and aquatic medium were analyzed.

3.4. Viscosity Measurements

The viscosity values of the oil samples before and after the thermolytic upgrading were measured using a BROOKFIELD TC500 programmable viscometer at 20, 50, and 80 °C. The constant temperature during the measurements was provided by a “Huber” circulation thermostat, and the measurements were carried out after one day of dewatering (centrifuging) in order to properly compare the viscosity reduction degree of the upgraded oil samples. It is well known that at lower temperatures, the influence of supramolecular asphaltene structures on the viscosity can be complicated [10]. The volume of crude oil samples was 6.7 mL, and the spindle used was TL5. For the viscosity comparison study, the shear rate (s^{-1}), which was calculated by multiplying 1.32 by the RPM, was the same for all of the viscosity values of the crude oil samples. The RPM, in turn, was read when the spring torque was between 50% and 90%. In such conditions, the manufacturers imply that the “Relative Error” and “Repeatability” of the viscosity values should not exceed $\pm 1.0\%$ and 0.2%, respectively.

3.5. Atmospheric Distillation of Crude Oil

Atmospheric distillation of the crude oil and conversion products after the autoclave was carried out using an ARN-LAB-03 distillation plant, consisting of a heater and a condenser. All of the samples were previously dewatered by the centrifuging method, and the absence of water was verified by the FT-IR spectroscopy analysis method. The oil samples were heated up to 300 °C in an atmospheric pressure in order to split up the hydrocarbons into the group of compounds with different compositions, structures, and therefore, boiling point ranges. For the first mixture of hydrocarbon compounds, the boiling point temperature, which is less than 200 °C, refers to the gasoline fraction. The gasoline fraction was collected in the previously weighted graduated flask. The heating rate was adjusted in the range of 5–10 °C/min. After the termination of the distillates with a boiling point of less 200 °C, the heating temperature was increased to 300 °C with the same heating rate, and the collecting flask was replaced with the new one (which had been previously weighted). The mass balance calculations show that the relative error of the process did not exceed 10%.

4. Conclusions

In this paper, we have presented the results of a laboratory study on the thermolytic and aquathermolytic upgrading of a heavy oil sample in the presence of a fullerene C60 catalyst at a temperature of 250 °C. The evidence from the comparative study implies that water exhibits not only a heating medium but also participates in the aquathermolytic cracking of heavy oil fragments, affecting the structure and composition of crude oil samples. Fullerene C60 nanoparticles showed high performance in the upgrading of heavy oil by reducing its viscosity by more than 30%. Moreover, the content of asphaltenes was reduced by 35%. The catalytic aquathermolysis products of the heavy oil sample contributed to the alteration of the initial boiling point and to the significant increase in the yield of the gasoline fraction (four times compared with the initial crude oil). Although the obtained results are promising, future broad studies are required in order to apply fullerene C60 nanoparticles on an industrial scale. Future studies should focus on the catalytic mechanisms of C60 and its transformation during high-temperature hydrothermal reactions.

Author Contributions: Conceptualization, R.F.K.; methodology, A.V.V.; validation, V.E.K.; investigation, Y.I.I.A.; resources, A.V.D.; writing—original draft preparation, F.A.A.; writing—review and editing, Y.I.I.A.; supervision, R.F.K. and A.V.V. All authors have read and agreed to the published version of the manuscript.

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