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Aquathermolysis of crude oils and natural bitumen: chemistry, catalysts and prospects for industrial implementation

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The results of studies of alterations in the elemental and SARA compositions and physicochemical and rheological properties of highly viscous heavy crude oils upon catalytic and non-catalytic aquathermolysis are generalized. The chemistry of transformations of model hydrocarbons and heteroatomic compounds in aqueous media at high temperature, including subcritical and supercritical conditions, is considered. Comparative analysis of methods for activation of oil conversion *via* aquathermolysis using hydrogen donors, oil-soluble and water-soluble nanodispersed catalysts, ionic hydrogenation processes and various ways for reservoir heating is presented. Problems and prospects of oil-field implementation of catalytic aquathermolysis for upgrading heavy oils and natural bitumen are discussed.
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I. Introduction

Currently, with deterioration of the structure of hydrocarbon reserves and increased consumption of energy commodities, the problem of development of hard-to-recover reserves such as heavy crude oils (HCO) and natural bitumens (NB) has become acute. The exhaustion of oil reserves favourable for production and refining will inevitably make HCO and NB very important resources for stabilizing and enhancing crude oil production.[1,2] According to different estimates, the total world in-place reserves of HCO and NB range from 636–682 billion tons[3] to 1 trillion ton.[4] According to foreign sources, the in-place reserves of NB in Russia are from 47–55 billion tons[5] to 214 billion tons[3] (the latter value includes extra heavy crudes). The largest heavy oil reserves are concentrated in the Volga Ural (60.3%), West Siberian (15.4%) and North Caucasus (11.3%) geological basins.[6] The percentage of the hard-to-recover reserves in the overall balance steadily grows;[3] therefore, in the coming years, the gain in the crude oil production would be provided by HCO and NB to at least 10%.[7]

The lack of possibility of processing HCO and NB at the existing oil refineries designed for traditional crude oils together with difficulty or impossibility of pipeline transportation of these raw materials set the task of field upgrading of HCO and NB. The production of synthetic oil at the field can be based on hydroconversion,[8–11] processes aimed at the removal of excess carbon and heteroatomic and high-molecular-mass compounds from NB[10,11] (deasphalting), thermal processes[12] or combinations of these processes. Also, quite a number of studies are devoted to NB desulfurization and cracking of asphaltites in sub- and supercritical water.[13–16] The interest in this area is due to the quest for a process for synthetic oil production giving no by-products (high-sulfur coke or asphalt upon deasphalting) and consuming no hydrogen. The latter is especially important for the field treatment of HCO and NB, which should have minimum capital and operation costs, *i.e.*, require no construction of hydrogen production plant.

Owing to low mobility of HCO and NB under reservoir conditions, they are often recovered using heat treatment methods, including steam stimulation. In this type of treatment, the temperature of the injected steam can reach 350–400 °C and the productive formation can be heated up to a temperature of 200–250 °C and higher. It is evident that chemical transformations of HCO and NB components can take place under these conditions. The injection of a hot heat carrier and the catalytic effect of rock-forming minerals create a unique 'reservoir reactor', which accomplishes *in situ* chemical transformations of some NB components. In 1982, the high-temperature transformations of crude oil components on treatment with steam (water) in the presence of reservoir minerals were called aquathermolysis by Hyne *et al.*[17] Thus, aquathermolysis is considered as a method for downhole upgrading of heavy oil feedstock in addition to *in situ* combustion, low-temperature oxidation and other methods, common to which is the reservoir heating and injection of chemicals and/or catalysts.[18]

During the last 10–15 years, the interest in aquathermolysis as a process for downhole upgrading of HCO and NB has substantially increased. This is reflected in the large number of scientific publications. The studies consider transformations of heteroatomic compounds in steam or supercritical water, search for intensification methods for the transformations involving catalysts and hydrogen donors, analyze the possible adverse effects of the downhole reactions of crude oil associated with the corrosive action of the hydrogen sulfide formed. The investigation methods used include physical modelling in closed systems and flow type units and field testing. The application of catalysts and hydrogen donors in the aquathermolysis is the subject of a review,[19] while one more review is devoted to the transformations of organic matter into hydrothermal oil.[20]

Meanwhile, data on the changes of the SARA and fractional compositions of crude oils during catalytic and non-catalytic aquathermolysis are rather scattered. There are few data on the effect of rock and aqueous phase salinity on the chemistry of transformations and the overall process performance. The information about the influence of catalyst composition, in particular, the structure of the organic precursor on the degree of HCO and NB conversion during aquathermolysis is contradictory. The contributions of various reactions (cracking, hydrogenolysis, high-temperature hydrolysis) to the alteration of high-molecular-mass and heteroatomic oil components and the possibility of suppressing the condensation reactions without the use of hydrogen donors have not been clarified as yet. This review presents a systematic account of modern data published mainly in the last 10–15 years about alteration of the composition and the physicochemical properties of HCO and NB, the chemistry of transformations of hydrocarbons and heteroatomic compounds and ways of intensification of the downhole upgrading of heavy oils *via* aquathermolysis.

II. Alteration of the composition and physicochemical characteristics of heavy oils under the action of steam

The occurrence of chemical transformations during steam stimulation of the reservoir is confirmed, in particular, by gas evolution. For example, hydrogen sulfide was detected in the product from the steam stimulated area of the Usinskoye oil field.[21] The laboratory modelling of steam stimulation demonstrated that the yields of H_2S and CO_2 increase with temperature rise. Similar experiments were performed to study the effect of the rock on CO_2 evolution, which demonstrated the catalytic action of clay minerals and transition metals.[22] Interesting results were obtained in a study of the effect of physical state of water on the CO_2 yield: catalytic action of steam, resulting in a 4-fold increase in the CO_2 yield compared to liquid water, was found.

The effect of the physical state of water on the H_2S yield in the laboratory model of steam stimulation was also noted in another work:[23] the presence of water as steam and liquid resulted in the formation of twice more H_2S than the presence of liquid water. A possible source of H_2S is the reduction of rock sulfates with hydrocarbons;[24] however, numerous publications (for example, Refs 22, 24–26) describing laboratory models of steam stimulation in the absence of rock attest to H_2S formation upon destruction of organic sulfur compounds. The key pathways of hydrogen sulfide generation include the thermal decomposition of sulfides and thiols, which is intensified in the presence of carbonate rock,[21] and aquathermolysis (high-temperature hydrolysis)[17] of sulfur compounds, which is discussed in Section III.

Both the field data [27, 28] and results of laboratory experiments [29–31] unambiguously indicate that the amount of hydrogen sulfide increases with temperature rise and with increase in the time of exposure of the oil-bearing rock to steam. Researchers report different temperatures of the onset of hydrogen sulfide formation: 250,[29] 200 [27, 30] and even 180 °C.[28] In the latter case, hydrogen sulfide formed in an amount of ~8 litres per m^3 of NB. A study of the aquathermolysis of Athabasca NB (Canada) in a closed system demonstrated that the yield of hydrogen sulfide considerably increases at temperatures >300 °C (Fig. 1).[31] It was noted that above 240 °C, hydrogen sulfide is formed not only upon aquathermolysis but largely as a result of thermal cracking of organosulfur compounds.

High toxicity, corrosive action and environmental hazard of hydrogen sulfide formed upon steam stimulation and produced from wells initiated studies on simulation of the kinetics of its formation during oil field development using stream-assisted gravity drainage (SAGD).[27] Analogous works dealing with the prediction of the produced amount of carbon dioxide [32] were less successful than predictions of the hydrogen sulfide amount. According to the authors cited,[32] this is due to more complex kinetics in the case of CO_2, in particular, the mechanism of carbon dioxide formation *via* decarboxylation of petroleum acids. In order to reduce the atmospheric emission of sulfur dioxide caused by burning of hydrogen sulfide-containing gas coming from producing wells, it was proposed to inject the sulfur dioxide together with steam into the oil formation. In this case, the Claus process to give elemental sulfur takes place in the formation.[33]

Thimm [28] noted that the yield of hydrogen sulfide in a laboratory study of aquathermolysis and during field development considerably depends on the oil origin. In the aquathermolysis of two samples of Venezuela NB, carried out in an autoclave, the yields of hydrogen sulfide differed more than 40-fold.[34] Despite the known opinion that asphaltenes represent a major source of hydrogen sulfide upon steam stimulation,[35, 36] Barrios Coiccetty [34] demonstrated that the content of asphaltenes is not a factor determining these pronounced differences between the hydrogen sulfide yields because the tested NB samples barely differed in this parameter.

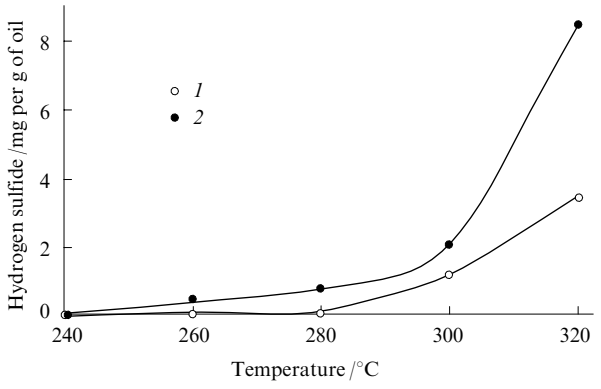


Figure 1. Quantity of hydrogen sulfide formed *vs.* temperature for different durations of aquathermolysis of Athabasca natural bitumen.[31]
(*1*) 24, (*2*) 203 h.

The behaviour of HCO and NB in the reservoir heat treatment, including the amount of hydrogen sulfide formed, is evidently determined by the content and composition of heteroatomic compounds. The reactivity of these compounds is determined by their structure. On the basis of analysis of organosulfur compounds from various crude oils, N K Lyapina [37, 38] proposed a classification of oils including three types: thiophene (I), sulfide (II) and mercaptan (III) oils. The thermal stability of sulfur compounds decreases on going from type I to type III oils. Under steam stimulation conditions, the mercaptan and sulfide oils are likely to be most reactive, because thiols (mercaptans) and acyclic sulfides have lower thermal (and hydrolytic, see Section III) stability, whereas thiophenes are less prone to thermal destruction with C–S bond cleavage.

Before considering the change in the physicochemical characteristics and the possible transformation pathways of HCO and NB under the action of steam, we would like to note that the solubility of organic compounds in water increases with temperature rise, which is due to a decrease in the dielectric constant of water (78.85 and 19.66 at temperatures of 25 and 300 °C, respectively).[20] The dissolving ability of water at 300 °C approaches that of acetone at 25 °C. In turn, the increase in the water solubility of organic compounds facilitates ionic reactions. In the supercritical region, water can be regarded as a nonpolar organic solvent with a dielectric constant of ~6. Moreover, the negative logarithm of the ionic product of water decreases from 14 at 25 °C to 11 at 250 °C.[39] because of the endothermicity of water self-dissociation. Hence, in the subcritical region at temperatures of 200–300 °C, water becomes simultaneously a stronger acid and a stronger base and can potentially act as an acid or base catalyst of, for example, hydrolysis. However, as the critical point is being approached, the negative logarithm of the ionic product sharply decreases, and water is no longer an efficient acid-base catalyst.[40]

Turning to analysis of the changes in oil characteristics during aquathermolysis, note that the mechanisms of transformations of hydrocarbons and non-hydrocarbon oil components in water in the sub- and supercritical regions are different. However, implementation of the downhole upgrading of HCO in supercritical water is impossible. The transformations of oils, NB and asphaltites in supercritical water are subjects of numerous publications, whereas the subject of the present review is catalytic downhole aquathermolysis. Therefore, the transformations of NB in supercritical water are covered here only partly.

Evidently, under the steam stimulation conditions where the reservoir temperature is rarely above 240 °C,[28, 32] transformations do not involve all crude oil components but only the least thermally (and hydrolytically) stable ones. The change in the SARA composition of heavy oil in laboratory steam stimulation, in particular, an increase in the contents of saturated and aromatic hydrocarbons and a decrease in the resin and asphaltene contents,[26, 41] attest to the destruction of resin and asphaltene molecules with elimination of peripheral alkyl or alkylaromatic moieties.

Experiments on aquathermolysis simulation in autoclaves,[26, 41–45] investigations of hydrothermal alteration of heavy oils and asphaltenes in hydrogen and steam [46–51] and studies of the composition and properties of oils produced with and without steam stimulation [52, 53] demonstrated a change in a number of oil characteristics. First of all, a goal

of this research was to elucidate the patterns of decrease in the heavy oil viscosity. A considerable (by 28%–42%) decrease in the viscosity of crude oil from the Liaohe oil field (China) was detected after aquathermolysis performed for 24 h at 240 °C at an oil : water ratio of 3 : 1.[26] It was found[41] that at the aquathermolysis temperature of 240 °C, the viscosity of an oil sample from China (10.98 mass % resin content) decreased most sharply in the first 24 h (Fig. 2 *a*) and then the curve flattened out; the overall decrease in the viscosity was moderate (12%). The most pronounced viscosity decrease is attained when the aquathermolysis temperature is >300 °C.[41] The viscosity of another oil sample with a higher initial resin content (24.81 mass %) decreased in the first 12 h of aquathermolysis at 240 °C by more than 50% (see Fig. 2 *b*).

However, as noted by Song *et al.*,[41] the viscosity of the aquathermolysis product grows during storage, whereas the viscosity of conventional crude oil remains invariable. The increase in the viscosity can be attributed to intermolecular interactions of the aggregate combinations,† which were destroyed only partly under the action of moderate temperature, resulting in an increase in their size and giving rise to a structured oil disperse system (ODS), *i.e.*, to the thixotropic properties of the system.[54] Also, the viscosity may increase as a result of recombination of free radicals of asphaltenes formed upon thermodestruction including detachment of the side groups from polynuclear fused molecules. An increase in the asphaltene paramagnetism under the action of hydrothermal factors was noted by Kiyamova *et al.*,[46] the concentrations of radical paramagnetic centres become similar for asphaltenes of different oils, which initially have different paramagnetic characteristics.

In addition, the viscosity of NB from the Cold Lake field (Canada) increased during too long laboratory aquathermolysis in a closed system. Indeed, the viscosity and the asphaltene content smoothly decreased during the first 50 days of aquathermolysis at 250 °C, and subsequently the viscosity sharply increased and, after aquathermolysis for 75 days, the viscosity of the product was 3 times higher than that of the original NB, while the content of asphaltenes increased only 1.2-fold with respect to the sample obtained in a 50-day experiment and still remained much lower than the asphaltene content in the original NB.[55] However, the SARA composition of NB and its transformation products are not reported in the study. Presumably, intense oligomerization and recombination of free radicals during long-term aquathermolysis gives rise to resins, which account for the substantial increase in the product viscosity.

Comparison of heavy oil samples from the Ashalchinskoye field produced by natural flow and using steam stimulation[52] showed lower density and coking capacity and lower sulfur content of the latter sample. Comparison of NB samples from the Peace River field (Canada) produced with natural flow and with steam stimulation[53] showed some redistribution of the SARA composition towards increased saturate and aromatic contents and decrease in the asphaltene content. The steam stimulated sample contained less sulfur and oxygen, which was due to decarboxylation of acids and destruction of sulfoxides.

Data on the change in the H : C atomic ratios of oil on exposure to steam are highly contradictory. In some studies (see Ref. 41), it is reported to slightly increase, while according to other publications,[9, 26, 53, 56] this value substantially (by 0.3) decreases, thermolysis in the absence of water resulting in the product with higher $H:C_{at}$ ratio than aquathermolysis. This is due to the higher yield of coke upon thermolysis. The $H:C_{at}$ ratios for NB produced under natural flow and using steam stimulation differ insignificantly.[53]

The degree of desulfurization upon aquathermolysis is lower than that attained by anhydrous thermolysis, which has been explained[56] as being due to higher stability of thiophenes under the less rigorous conditions of aquathermolysis than under anhydrous thermal cracking conditions. Generally, even if aquathermolysis is conducted in the presence of hydrogen, the degree of desulfurization cannot be very high and is usually 11%–45%.[51] Even a lower degree of desulfurization (~10%) is attained when NB is treated in a real reservoir.[53] A fairly pronounced decrease in the sulfur content (>85%) was attained in laboratory experiments[26] on aquathermolysis of Chinese oils, which is apparently caused by specific group composition of sulfur compounds, in particular, predominance of sulfides and disulfides over thiophenes.[57]

It is noteworthy that steam stimulation leads to a considerable decrease in the sulfur content of the saturates and a minor decrease in the sulfur content of asphaltenes; in other components, the content of sulfur remains virtually invariable (Table 1). Thus, hydrogen sulfide and hydrocarbons are presumably formed mainly upon thermal or hydrolytic destruction of sulfide bridges in asphaltene

† Aggregate combinations are structural entities of the oil system comprising different types of molecules or molecular fragments.[54]

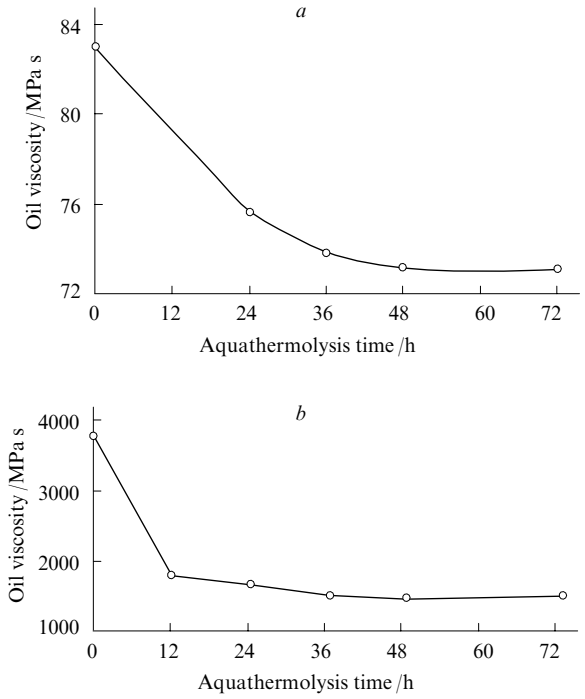


Figure 2. Crude oil viscosity *vs.* time of aquathermolysis at 240 °C.[41]
Resin content (mass %): (*a*) 10.98, (*b*) 24.81.

Table 1. Sulfur content in components of the Peace River natural bitumen produced by natural flow and by steam stimulation.[53]

Component	Sulfur content (mass %)	
	natural flow production	steam stimulated production
Saturates	0.61	0.06
Aromatics	3.65	3.78
Resins		
fraction I	6.36	6.46
fraction II	6.62	6.85
fraction III	7.48	6.78
Asphaltenes	9.63	8.19

molecules. In oil and asphaltenes, the content of sulfide groups decreases, while the content of benzothiophenes increases as a result of aromatization of cyclic sulfides.[53] In the pyrolysis of carbonaceous shale of the Domanik age in the presence of water, the contents of alkylthiophenes and benzothiophenes, which were absent in the initial shale, were found to increase with the increase in the experiment temperature;[58] together with the decrease in the $H:C_{at}$ ratio, this attests to aromatization of the initial organic matter. Cracking and aromatization reactions also lead to lower content of heavy benzothiophene homologues (5 – 15 carbon atoms in the alkyl chain) and higher content of light homologues upon the asphaltite conversion in supercritical water.[59]

Data on the change in the oxygen content during aquathermolysis are ambiguous. Whereas the nitrogen content either decreases [50, 60] or remains nearly the same,[53, 61] the oxygen content of aquathermolysis products can be higher [55] compared to the feedstock; in particular, some components, for example, the ethanol – benzene resins, can be enriched in oxygen;[62] in other cases, the oxygen content of the products can be lower [53, 59, 60, 63] than that of the feedstock. Indeed, the oxidative hydrolytic transformations of sulfides and oxygen compounds, in particular, the retro-aldol reaction,[64] are expected to increase the oxygen content in the conversion products. The loss of oxygen upon aquathermolysis is attributable to the evolution of carbon monoxide and dioxide upon destruction of mono- and dioxygen-containing groups [57] and sulfoxides.

The patterns of variation of the heteroatom contents in asphaltenes may differ from those for crude oil. Most often, the nitrogen content increases and the sulfur content decreases,[59] while the oxygen content either increases or decreases. In the case of aquathermolysis of the natural bitumen from the Bayan Erhet deposit (Mongolia) at 350 °C, the oxygen content of resins increased from 0.31 mass % to 0.74 mass %, while that of asphaltenes increased from 1.26 mass % to 9.72 mass %.[65] This substantial increase in the content of oxygen, which is present in heavy aquathermolysis products as oxo, oxy and carboxy groups, unambiguously indicates that water acts as a chemical reagent in the transformations of resin and asphaltene compounds (RAC). The same is confirmed by increased content of ketones in the resin fraction of the steam stimulated natural bitumen.[53]

Data on the change in the SARA composition of crude oils after hydrothermal treatment in the presence of hydrogen [48, 49] and aquathermolysis in supercritical water,[59] and data for steam stimulation-produced NB [53] attest to the increase in the content of saturates and the decrease in the asphaltene content. The total content of resins decreases, while the amount of benzene or ethanol – benzene resins can somewhat increase because of destruction of asphaltene molecules. These results are consistent with decreased sulfur content in the benzene and ethanol–benzene resins.[43, 47] Thus, hydrothermal treatment results in cleavage of the least stable N – C, S – C and O – C bonds with elimination of peripheral groups from resins and asphaltenes and formation of hydrocarbons, heteroatomic compounds and benzene resins.[66] Some decrease in the content of aromatic hydrocarbons was noted after aquathermolysis performed under drastic conditions (350 °C, 72 h).[41]

As the aquathermolysis temperature is raised, the saturate and aromatic contents increase, evidently, due to the increased contribution of cracking of heavy components. Table 2 demonstrates a change in the SARA composition of the Osmington Mills oil sand (UK) depending on the temperature of aquathermolysis.[67] It can be seen that the formation of hydrocarbons starts at 275 °C, which may be attributed to the increase in the contribution of C – C bond cleavage reactions. This assumption is supported by the formation of methane at this temperature. Hence, the reservoir temperature to be maintained for most efficient steam stimulation is $\geqslant$ 275 °C.

The above data contradict the results of aquathermolysis (for 12 h) for the Usinskoye (Russia) and Liaohe (China) oils.[25] The asphaltene content increased with increase in the aquathermolysis temperature, the content of resins started to decrease only at temperatures above

Table 2. Change in the SARA composition (mass %) of aquathermolysis (24 h) products depending on temperature.[67]

Components	Extract of initial bituminous sand	250 °C		275 °C		300 °C		325 °C	
		oil	extract	oil	extract	oil	extract	oil	extract
Saturates	41	29	10	28	11	33	18	43	16
Aromatics	14	10	19	13	11	19	16	22	18
Resins	15	22	19	25	18	23	16	15	13
Asphaltenes	30	39	52	34	60	25	50	20	53

Note. 'Oil' means aquathermolysis products located above the aqueous phase when the reactor was opened; 'extract' stands for the components extracted from oil sand with a dichloromethane – methanol mixture (97 : 1 v/v).

300 °C, while the content of saturates in the Usinskoye crude oil increased with respect to the initial sample only when the experiment was performed at 350 °C and for the Liaohe oils it did not increase at all. This fact does not find an adequate explanation because in the vast majority of cases, aquathermolysis is accompanied by destruction of RAC to give hydrocarbons.

The formation of hydrocarbons results in higher content of distillates.[52,68,69] The content of the IBP–350 °C fraction (IBP is initial boiling point) in the oil from the Ashalchinskoye field produced by steam stimulation was 5% higher than that in the oil sample from the same well produced under natural flow. According to simulated distillation (SimDis) data, the content of the IBP–550 °C fraction in the Athabasca and Peace River natural bitumens increases by 4% after steam treatment of the reservoir.[68] This increase in the distillate content may appear insignificant at the first glance. However, first, the formation of light fractions can be intensified, as will be shown in Section IV, and, second, even additional 4%–5% of light fractions together with the overall increase in the saturates and aromatics content facilitate the transportation and enhance the commercial value of oil.

Study of the composition of the liquid products of non-isothermal aquathermolysis of asphaltite[42,59,62] demonstrates increased contents (compared to the initial asphaltite) of n-alkylbenzenes, change in the compositions of monoaromatic hydrocarbons, naphthalenes, tetracyclic aromatic sulfur compounds, anthracene and benzocarbazoles, the proportions of different types of compounds varying non-monotonically with temperature. The distribution of n-alkanes shifts to higher molecular mass. The reactions give anthracenes,[70,71] benzenethiols, alkenes[59] and phthalates,[50] which have been absent in the feedstock. This means that the listed compounds occurred as structural moieties in resin and asphaltene molecules. It is noteworthy that in some cases the composition of these compounds 'trapped' in RAC molecules corresponds to lower thermal maturity of the hydrocarbon feedstock than the composition of the saturate fraction of the feedstock. According to Antipenko *et al.*,[63] anthracenes could also result from aromatization of the dihydroanthracene moieties present in RAC molecules, *i.e.*, hydrogen atom transfer from the dihydroanthracene to other moieties (*e.g.*, heteroatomic ones) may take place. It was proposed to use the appearance of compounds absent from the original crude oil[70,71] for monitoring the steam stimulation process in order to optimize oil recovery and reduce the costs.

From the composition of the aquathermolysis products, one can derive the structure of RAC. The formation of unsubstituted polycyclic aromatic hydrocarbons can be due to the presence of biphenyl moieties in the RAC.[53] The number of carbon atoms in the side groups of aromatic hydrocarbons reflects the length of oligomethylene chains linking separate moieties of the resin and asphaltene molecules. Long alkyl chains at the periphery of the asphaltene aromatic nuclei or polymethylene chains containing resin and asphaltene moieties can serve as sources of alkanes and alkenes.

Considering asphaltenes from the standpoint of the presence of 'archipelago' and 'island' models, which differ fundamentally in the molecular structure,[72–74] suggests that the unsubstituted and substituted polycyclic aromatic and sulfur compounds are mainly formed from 'archipelago' type molecules in which relatively small aromatic nuclei are connected by methylene, sulfide and ether bridges.[75] n-Alkanes and alkenes are apparently formed *via* thermal destruction of peripheral substituents of the 'island' type asphaltenes, which comprise only one large aromatic nucleus. In any case, the composition of liquid products of aquathermolysis is always dependent on the composition and structure of RAC molecules[59] and is determined by thermal destruction, cyclization and dehydrogenation reactions,[13] ester and ether bond hydrolysis and alkylation of aromatic rings by reaction intermediates.[76] It was noticed that highly condensed asphaltenes, which have the highest degrees of aromaticity, give more saturates upon thermal destruction than the least aromatic resin-like compounds.[77] The latter compounds are characterized by high abundances of sulfide sulfur in oligomethylene chains. The destruction of sulfide bridges gives rise to light gaseous alkanes and alkenes, while detachment of long chains from aromatic moieties of 'island' type asphaltenes is responsible for the formation of saturated hydrocarbons.

The hydrothermal treatment and steam stimulation affect vanadyl and nickel complexes, which is confirmed by trace elemental analysis and EPR spectroscopy data;[46,48,52] the trace elements are concentrated in the coke residue. The concentrations of trace elements such as Ni, V, Ba, Cd, Co, Ga, Ge, Mo, Sn, Ti, Al, *etc.* in asphaltenes present after hydrothermal experiments sharply decrease, which is indicative of thermal instability of metal complexes.[51]

During aquathermolysis, the $H:C_{at}$ ratio for asphaltenes decreases,[78] the sulfur content decreases, the nitrogen content can either increase[59] or decrease,[50] and the same is true for oxygen. After elimination of the side chains, asphaltene molecules become more compact. The content of free radicals increases, which is evidently a consequence of thermal destruction. Table 3 summarizes the data on the elemental composition, free radical contents and spectral characteristics of asphaltenes of the Tatarstan bitumen after hydrothermal alteration.

The IR spectra of asphaltenes before and after hydrothermal treatment (see Table 3) attest to an increase in the aromaticity, which correlates with the data of elemental analysis, and a decrease in the ester and carbonyl contents (oxidation index) as a result of cleavage of the least stable C–O bonds. The increase in the degree of branching is due to the decrease in the length of alkyl chains and, hence, the aliphaticity decreases. Attention is attracted by the sharp increase in the sulfurization (C_5), which characterizes the content of sulfoxide groups. The hydrothermal processes involve not only destruction of sulfur compounds at the C–S bonds but also oxidation of sulfides to sulfoxides. Furthermore, for asphaltenes of highly oxidized bitumen from the Shugurovskoye field (see the C_2 index), the increase in the C_5 index upon hydrothermal treatment is moderate as compared with other samples, which is due to the high initial content of sulfoxides.

According to determination of the structural and SARA compositions by ^1H and ^{13}C NMR and IR spectroscopy,[53] asphaltenes of the oil produced by steam stimulation contain more phenanthrene and benzothiophene moieties than asphaltenes of the naturally produced oil. The contents of methylene units and sulfide groups in the aliphatic structures were found to decrease, while the content of methyl groups connected to aromatic structures was found to

Table 3. Change in the elemental composition, content of free radicals and spectral indices of asphaltenes of natural bitumens from various Tatarstan deposits upon hydrothermal transformations.[50]

Characteristics	Shugurovskoye		Spiridonovskoye		Ashalchinskoye		Bavlinskoye	
	orig.[a]	alt.[a]	orig.	alt.	orig.	alt.	orig.	alt.
Elemental composition (mass %)								
C	77.85	83.73	72.47	78.40	73.35	83.46	77.06	75.05
H	8.70	3.51	8.68	2.37	8.15	3.35	10.59	3.99
N	1.45	0	1.77	1.34	1.43	0	1.50	0
S	8.30	3.45	7.07	5.18	8.13	3.29	4.12	1.10
$H:C_{at}$	1.34	0.50	1.44	0.36	1.33	0.48	1.65	0.63
Spectral indices[b]								
C_1	7.180	7.580	10.620	33.950	5.61	8.370	2.840	3.830
C_2	0.334	0.004	0.693	0.032	0.080	0.008	0.193	0.055
C_3	0.470	1.080	0.910	0.900	0.640	0.930	0.460	1.400
C_4	0.990	0.880	1.090	1.450	0.940	0.690	1.220	0.760
C_5	0.318	0.489	0.614	0.145	0.193	0.367	0.126	0.759
EPR data[c]								
$R^{\bullet}$	52.48	602.56	83.92	130.91	229.09	645.65	97.72	588.84
V^{4+}	23.99	18.62	25.59	1.83	75.86	14.13	7.94	3.98

[a] 'Orig.' means original asphaltenes, 'alt.' means altered by hydrothermal treatment; [b] spectral indices: $C_1 = D_{1600}/D_{720}$ (aromaticity); $C_2 = D_{1710}/D_{1465}$ (oxidation index); $C_3 = D_{1380}/D_{1465}$ (branching); $C_4 = (D_{720} + D_{1380})/D_{1600}$ (aliphaticity); $C_5 = D_{1030}/D_{1465}$ (sulfurization index) (D is absorbance, the subscript means the absorption maximum /cm^{-1}); [c] the contents of vanadyl (V^{4+}) and free radicals $R^{\bullet}$ in asphaltenes are given in relative units obtained by reducing the EPR signal intensity to the sample mass.

increase. X-Ray diffraction data also attest to an increase in the asphaltene aromaticity and carbonization during the aquathermolysis.[79] The above data explicitly confirm cleavage of the C–C bonds in alkyl substituents and in polymethylene chains, the C–O bonds in ethers and esters and the C–S bonds in aliphatic sulfides.

As shown by Krivtsov *et al.*,[65] the transformations of asphaltene molecules during aquathermolysis of the Bayan Erhet NB (Mongolia) under sub- and supercritical conditions have some specific features. The subcritical process involves the increase in the number of aromatic nuclei in the molecules, destruction of some of naphthene structures and the increase in the abundance of oxygenated functional groups. Under supercritical conditions, elimination of virtually all alkyl groups and complete destruction of naphthene structures occur; the molecules become more compact, the aromaticity of structural blocks grows, the length of methylene chains decreases; and the content of oxygenated functional groups is lower than in the subcritical process. It is worth noting, however, that asphaltene transformations are determined by their origin; therefore, the changes described above may be inherent only in the particular Bayan Erhet NB. Indeed, the oxygen content of asphaltite from the Ivanovskoye oil field was, conversely, found to decrease in supercritical water,[59] as for highly oxidized Tatarstan NB.[50]

The increase in the aromaticity of asphaltenes makes some of them insoluble in toluene, *i.e.*, they are converted to carbenes, carboids and coke, the coke yield increasing with increase in the duration and temperature of aquathermolysis (Fig. 3).[56, 60, 80] Nevertheless, the yield of coke is lower in aquathermolysis than in anhydrous pyrolysis. According to Cheng *et al.*,[60] the role of water is to dissolve and disperse organic products and to decrease the free radical concentration in unit volume, which accounts for the inhibition of

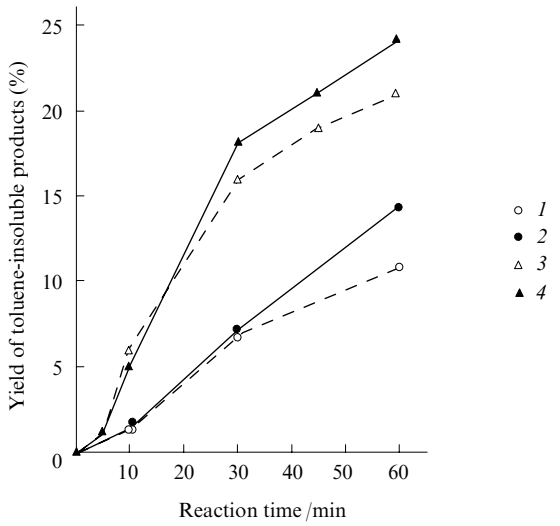


Figure 3. Yield of toluene-insoluble products of aquathermolysis (*1*, *3*) and thermal cracking (*2*, *4*) of Athabasca natural bitumen at temperatures of 430 (*1*, *2*) and 450 °C (*3*, *4*).[56]

coking. In the opinion of Dutta *et al.*,[56] who performed aquathermolysis in D_2O, hydrogen atom transfer from water molecules to liquid products and coke takes place, which is enhanced under more severe process conditions. The D atoms are inserted manly into the α-position of aliphatic substituents in aromatic rings.

The fairly high degree of hydrogen replacement by deuterium (33%–40%) can be attributed[81, 82] to saturation of free radicals by deuterium atoms formed upon oxidation of carbonyl groups with heavy water. In turn, the oxidation

of carbonyl groups is confirmed by the abnormally high (compared with the case of anhydrous pyrolysis) yield of CO_2 formed upon decarboxylation. For ketones and aldehydes, this process can be depicted in the following way:[82]

$$RR'C{=}O + H_2O \longrightarrow HR + HR' + CO_2$$

$$RCHO + H_2O \longrightarrow HR + CO_2 + H_2$$

As noted above, the reaction mechanisms in sub- and supercritical water are different.[40] In the former case, the prevailing process is hydrolysis, while in the latter case, free radical reactions predominate. The radicals can be formed *via* the homolytic decomposition of water molecules or thermal cracking of hydrocarbons.[83]

$$RCH_3 \longrightarrow R^{\bullet} + {}^{\bullet}CH_3$$

This is followed by chain propagation involving water molecules to give hydroxyl radicals.

$$R^{\bullet} + H_2O \longrightarrow RH + HO^{\bullet}$$

$$HO^{\bullet} + RH \longrightarrow H_2O + R^{\bullet}$$

An increase in the concentration of water for the supercritical upgrading of vacuum residue gives a product with reduced viscosity, average molecular mass and sulfur content.[83]

Of special note are papers devoted to the influence of rock-forming minerals on the composition and characteristics of aquathermolysis products.[84–87] In the presence of clay minerals, a more pronounced decrease in the NB viscosity, a change in the SARA composition towards higher content of saturates and a decrease in the $H:C_{at}$ ratio were observed, which is caused by the catalytic action of clay minerals on the cracking reactions. Table 4 presents characteristics of the aquathermolysis products obtained in the presence of rock minerals including quartz, potassium feldspar, plagioclase and montmorillonite and without minerals.[84] The adsorption and catalytic properties of silica gel, bentonite and kaolin[86] are confirmed by the decrease in the density of the Ashalchinskoye oil after hydrothermal treatment in the presence of these minerals and a decrease in the resin content.

Table 4. Characteristics of the oil aquathermolysis products obtained in the presence and in the absence of minerals.[85]

Characteristics	Original oil	Aquathermolysis product	
		no rock	10 mass % of rock
Viscosity /Pa s	88.5	65.7	55.8
Average molecular mass [a]	587	503	475
SARA composition [b]			
saturates	22.2	26.5	27.8
aromatics	27.4	29.3	32.2
resins	43.6	37.7	33.8
asphaltenes	6.8	6.5	6.2

[a] Determined by vapour pressure osmometry; [b] in mass %.

The hydrothermal alteration of oil from the Ashalchinskoye field in the presence of hematite[87] resulted in increased content of saturates, a decrease in the content (almost 2-fold) of the benzene and ethanol-benzene resins and asphaltenes (1.3-fold) (compared to the experiment without hematite) and in the formation of a fraction boiling at 70–120 °C, which is absent in the feedstock. The $H:C_{at}$ ratio of the oil increased from 1.93 to 2.07 and the carbonyl and hydroxyl contents and the oxidation index increased. The latter fact was attributed to the partial oxidation of oil components by the hematite oxygen. In general, these changes should have a beneficial effect on oil recovery and refining, which makes aquathermolysis in the presence of hematite a promising downhole upgrading process.

Meanwhile, Savel'ev *et al.*,[88] who performed aquathermolysis of Argentinian asphaltites in the presence of hematite at 350 °C, obtained opposite results: the content of asphaltenes and carbenes increased (almost 2-fold compared to aquathermolysis without hematite), which was attributed to the activity of iron oxide catalysts in dealkylation of aromatic compounds. This is responsible for the increase in the aromaticity of asphaltenes and for their conversion to carbenes and carboids.

The described differences in the behaviours of oils and asphaltites are apparently caused by different SARA compositions: the relatively low content of asphaltenes (5.8 mass %) and high content of resins (36.9 mass %) in the oil from the Ashalchinskoye field predetermine the resin dealkylation reactions to give saturated hydrocarbons and light fractions. Owing to the high asphaltene content in Argentinian asphaltites (57 mass % – 64 mass %), dealkylation is accompanied by so-called compaction reactions (oligomerization and condensation), which give heavier asphaltenes and carbenes with high molecular mass.

Cracking reactions catalyzed by acidic minerals are suppressed in alkaline medium, as follows from the results of studies[89,90] devoted to alteration of Canadian NB in supercritical water containing potassium hydroxide. The transformation products are characterized by lower content of atmospheric distillates and higher viscosity than the products obtained in neutral medium. Noteworthy are the substantial increase in the hydrogen content and, as expected for the alkali-containing reaction mixture, the absence of H_2S and CO_2 in the gaseous products. The increase in the amount of hydrogen was attributed to some hydrogen formation mechanism operating in the presence of alkali, although the experimental temperature (430 °C) is insufficient for steam reforming reactions. Many researchers[17,39,91] consider the possibility of water gas shift reaction under conditions of aquathermolysis.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Carbon monoxide can appear upon the destruction of aldehydes and ketones, and the presence of alkali in the reaction mixture shifts the reaction equilibrium to the right. Yet another possible reason for the decrease in the conversion in alkaline medium is suppression of hydrolysis of the C–S and C–O bonds, which starts with the protonation of the heteroatom bearing a partial positive charge. This is described in more detail in the next Section.

III. Chemistry of transformations of hydrocarbons and heteroatomic compounds during aquathermolysis

Study of the chemistry of transformations of organic compounds during aquathermolysis is of interest for geochemistry and for elucidation of reactions possible during steam stimulation. The transformations of organic compounds in sub- and supercritical water is the subject of a number of reviews and monographs,[92–98] including the papers by North American researchers Katritzky and Siskin and coworkers. In recent years, catalysis in the hydrothermal processes of fuel production from biomass[99] and coal[100] has started to receive a lot of attention.

Regarding the task of intensification of oil transformations during the downhole upgrading by aquathermolysis, it is of interest to select the conditions, catalysts, reagents and the composition of aqueous phase that would promote some reactions and inhibit other ones. Primary attention should be paid to reactions that are little studied in oil chemistry (high-temperature hydrolysis of heteroatomic compounds, ionic hydrogen transfer involving formic acid) and well-studied reactions (cracking, isomerization, hydrogenolysis), which still have specific features when proceed in the presence of minerals in sub- and supercritical water.

This Section is concerned with the transformations of model oil compounds in hydrothermal systems and the dependence of these transformations on the aqueous phase composition and catalysts.

III.1. Hydrocarbons

In water at temperatures of < 400 °C, alkanes are virtually unreactive. At 400–450 °C, free radical reactions take place to give alkanes and alkenes with lower molecular mass. The addition of clay minerals, for example, bentonite considerably increases the conversion of alkanes even at lower temperature.[101]

The experiments carried out in D_2O demonstrated a significant degree of deuterium substitution for hydrogen in alkanes; after the addition of CD_3CO_2D, the degree of deuterium substitution for hydrogen increased 30-fold.[98] This reaction occurred to the highest extent for n-alkanes, while low reactivity of branched alkanes was explained by steric hindrance.

The insertion of deuterium into hydrocarbon molecules is assumed[102] to follow a free radical mechanism. The $D^{\bullet}$ radicals are formed in the reaction of hydrogen radical with the D_2O molecule. The $D^{\bullet}$ radical reacts with hydrocarbons, for example, with alkenes.

$$R-CH{=}CH-CH_3 + D^{\bullet} \longrightarrow R-{}^{\bullet}CH-CHD-CH_3$$

$$R-{}^{\bullet}CH-CHD-CH_3 + D^{\bullet} \longrightarrow R-CHD-CHD-CH_3$$

An ionic deuteration mechanism has also been proposed.[103]

$$RH + OD^- \longrightarrow R^- + HOD$$

$$R^- + D^+ \longrightarrow RD$$

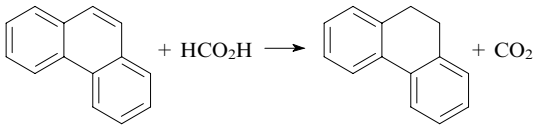
This mechanism is supported by the data on the degree of deuteration of compounds that differ in acidic properties (pK_a): the lower pK_a, the more easy the deuteration in a NaOD solution. The hydrogen atoms attached to α-carbons in pentanoic, hexanoic and palmitic acids ($pK_a \sim 43$) are completely replaced by deuterium atoms in a 0.016 M solution of NaOD at 400 °C over a period of 10 min. Meanwhile, in the case of 2-methylpentane, which has much lower acidic properties ($pK_a \sim 50$), the degree of deuteration achieved in 150 min does not exceed 20% for methyl hydrogen atoms and is zero for other atoms.

Alkenes are hydrogenated in D_2O to give alkanes. Heating of n-octadec-1-ene in D_2O at 330 °C during 3 days yielded n-octadecane with a 60% selectivity.[102] Deuterium atoms were mainly substituted for hydrogen atoms at C-2, C-1, C-3 and C-4, *i.e.*, apart from double bond saturation, its migration followed by saturation took place. According to Siskin, Brons, *et al.*,[104] double bond migration in dec-1-ene in 5.5 days at 250 °C was more pronounced in a 10% NaCl solution in the presence of montmorillonite than in pure water without montmorillonite.

Aromatic hydrocarbons are almost unreactive in pure water.[92] Toluene and benzene do not react at 300 °C for 1000 h. The rate of cracking of *tert*-butylbenzene in supercritical water at 535 °C is almost three orders of magnitude lower than in the absence of water in the gas phase, which is attributable to the cage effect of water and promotion of isomerizarion and substitution reactions in the aqueous environment.[105] In the presence of clay minerals and salts, the conversion of aromatic hydrocarbons increases. In the presence of a hematite–magnetite–pyrite mineral mixture, toluene shows higher degree of conversion to benzene, phenol and benzoic acid than in the presence of the mixture without pyrite.[106] When aromatic hydrocarbons are heated in D_2O, deuterium atoms are inserted, depending on conditions, into either the alkyl group or both the alkyl group and aromatic ring;[103] the latter case is realized mainly in a NaOD solution.

Polycyclic aromatic hydrocarbons (PAH) are unreactive in water below 460 °C.[97] In the presence of formic acid, the conversion of PAH to naphthene-aromatic hydrocarbons exceeds 80%. According to thermodynamic calculations, partial hydrogenation of phenanthrene in the presence of formic acid is possible in the temperature range of 300–800 K (Scheme 1).[107]

Scheme 1



Similarly, at temperatures below 460 °C, destruction of the Ar–Ar, Ar–$(CH_2)_n$–Ar bonds does not occur.[97] In a formic acid solution at 460 °C, the conversion of 1-benzylnaphthalene is 8%, the major products being naphthalene and toluene. The mechanism of reactions in the presence of formic acid is considered in Section IV.

It should be noted that the hydrogen–deuterium exchange, irrespective of the mechanism, is of considerable interest for processes related to heavy crude oil, because this fact is indicative of the possibility of suppressing polymerization and coking reactions or the possibility of ionic hydrogenation and hydrogenolysis.

III.2. Organosulfur compounds

The transformations of organosulfur compounds during thermolysis and aquathermolysis have been studied in detail by the Katritzky, Siskin and Clark group.[108–119] The reactions theoretically possible during aquathermolysis include thermal destruction, high-temperature hydrolysis of heteroatomic compounds, polymerization and radical recombination. In view of the possibility of water gas shift reaction, hydrogenolysis and hydrogenation can also proceed. In the case of hydrolysis, water directly participates in the reaction, which is confirmed by high content of carbon oxides in the gases of aquathermolysis of model compounds (thiophane and thiophene) at 300 °C,[108] although the starting compounds do not contain oxygen, *i.e.*, water is the only source of oxygen in the system.

Song *et al.*[120, 121] conventionally divided all sulfur compounds into 4 groups in terms of their reactivity under conditions of aquathermolysis. Compounds of group A (aliphatic disulfides and thiols) decompose with hydrogen sulfide evolution at temperatures below 200 °C. Compounds of group B, which includes methylthiophenes, benzothiazole, dimethylbenzothiazole and aliphatic sulfides, give off little H_2S at temperatures below 200 °C, the major amount of hydrogen sulfide being evolved at 230–270 °C. Compounds of group C (thiophene) give off a considerable amount of H_2S at 270–300 °C. Finally, compounds of group D are thermally stable even at 330 °C (benzothiophene, dibenzothiophene). Note that owing to very high reactivity of thiols and disulfides at relatively low temperature, mercaptan oils (according to Lyapina's classification)[37, 38] undergo most extensive transformations during steam stimulation giving a large amount of hydrogen sulfide.

Similar studies were carried out by Katritzky *et al.*,[115] who investigated the behaviour of aliphatic and aromatic thiols, sulfides and disulfides, thiophane and thiophene in the thermolysis both in the absence and in the presence of water for 5 days at 250 °C. The degrees of conversion of aliphatic and aromatic thiols are almost equal during anhydrous thermolysis and aquathermolysis (> 50%) and the major products are sulfides. The degree of conversion increases upon the addition of the clay mineral nontronite to the reaction medium and decreases when the aqueous phase is alkaline. Sulfides are converted faster in the case of thermolysis without water than in aquathermolysis. The degree of conversion of dioctyl sulfide is 73% in the former case and only 9% in the latter case, which attests to a free radical reaction mechanism. The aqueous phase decreases the concentration of free radicals in the system (cage effect) and thus hampers the thermal conversion of sulfides. The major transformation products are alkenes, alkanes and thiols. The conversion of disulfides reaches 100% both in the presence and in the absence of water. The conversions of thiophane and thiophene do not exceed 1.5% in both cases.

As has already been noted, the reactions in supercritical water mainly follow free radical mechanism, dialkyl sulfides and alkyl aryl sulfides are most reactive, while diphenyl sulfide, thiophene and benzothiophenes are least reactive, as in the case of aquathermolysis in subcritical water (Table 5).[122] The reactivity is mainly determined by the energy of the α-C–H bond and, to a lesser extent, by the S–R bond energy, *i.e.*, the formation of free radicals upon cleavage of these bonds is the rate-limiting step. Obviously, transformations of heteroatomic compounds during aquathermolysis occur by both radical and ionic mechanisms and, the lower the temperature, the more probable the ionic mechanism. The thermal transformations of thiols lead to the formation of hydrogen sulfide, alkenes and coupling reaction products, for example, thiophenol is converted to diphenyl sulfide, diphenyl di- and trisulfides and thianthrene.[97, 109]

Table 5. Conversion and desulfurization of organosulfur compounds in supercritical water [400 °C, 23.5 MPa, feedstock : water = 1 : 1 (v/v), 31 min].[122]

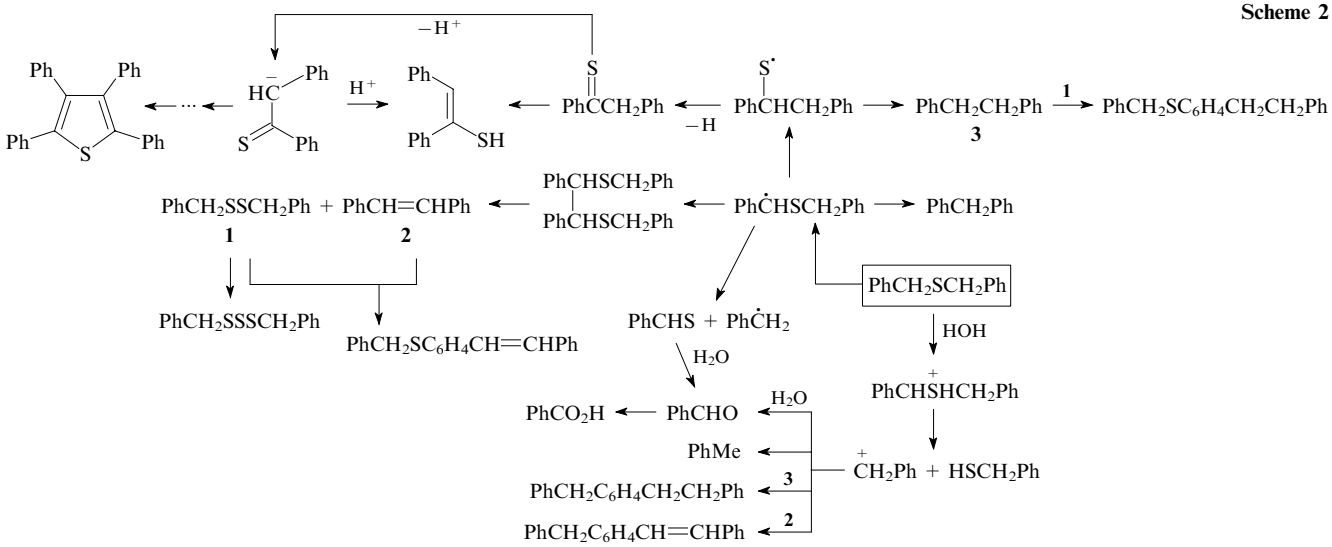
Compound	Conversion (%)	Degree of desulfurization (%)
Dihexyl sulfide	31	25
Thiophane	16	16
Isopropyl phenyl sulfide	31	30
Benzyl phenyl sulfide	97	22
Dibenzyl sulfide	81	60
Diphenyl sulfide	0	< 5
Thiophene	3	< 5
Dibenzothiophene	3	3–5

Naphthalene-1-thiol gives naphthalene and a mixture of dinaphthyl sulfide and dinaphthyl disulfide. The conversion of phenylmethanethiol in the aquathermolysis at 200 °C for 24 h is 13%, while in the thermolysis without water, it is 74% at the same temperature and duration.[116] The reactivity of phenylalkanethiols decreases with increase in the number of methylene groups between the aromatic ring and the SH group. The conversion of thiols to sulfides and disulfides increases 5-fold upon the addition of sodium hydrogen sulfite into the aqueous phase.[109]

Aliphatic sulfides tend to undergo thermal transformations to give alkanes, alkenes, disulfides, trisulfides, thiols and hydrogen sulfide. As has been noted,[104, 110] thermolysis in the absence of water results in higher conversions of aliphatic sulfides and thiols than that in the presence of water at the same temperature. For example, conversion of benzyl phenyl sulfide in 5 days at 250 °C under anhydrous conditions is 31%, while that under the aquathermolysis conditions is only 4%.[117] Nearly the same composition of the thermolysis and aquathermolysis products attests to the homolytic cleavage of the C–S bond in both cases. Thus, in both the presence and absence of the aqueous phase, the free radical mechanism predominates, although some ionic reactions giving minor amounts of products (benzaldehyde) still do proceed. The conversion of dibenzyl sulfide in 24 h at 200 °C is 58% in the aquathermolysis and only 9% in the thermolysis. Despite the higher reactivity in water, the composition of products is nearly the same; therefore, apparently both ionic and radical mechanisms of transformations are involved in aquathermolysis. Free radical and ionic transformations of dibenzyl sulfide during aquathermolysis are presented in Scheme 2.[117] It can be seen that products with molecular mass higher than that of dibenzyl sulfide may be formed, which evidently undesirable for practical implementation of aquathermolysis for upgrading the oil feedstock in industry.

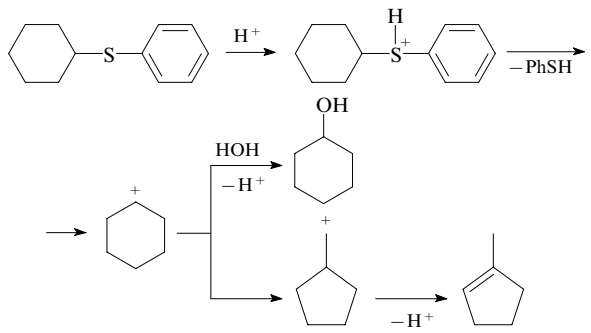
The addition of clay minerals such as nontronite[110] increases the conversion of dioctyl sulfide more than 2-fold (up to 86%) under both aqueous and anhydrous conditions; this is accompanied by evolution of a considerable amount of hydrogen sulfide, while the major liquid products do not

Scheme 2



contain sulfur (heptane, octane, octenes). The effect of clay minerals on the rate of hydrolysis of phenyl cyclohexyl sulfide and the ether and amide counterparts was also noted by Katrizky *et al*.[95] The reactions start with protonation of the heteroatom bearing a partial negative charge (Scheme 3).

Scheme 3



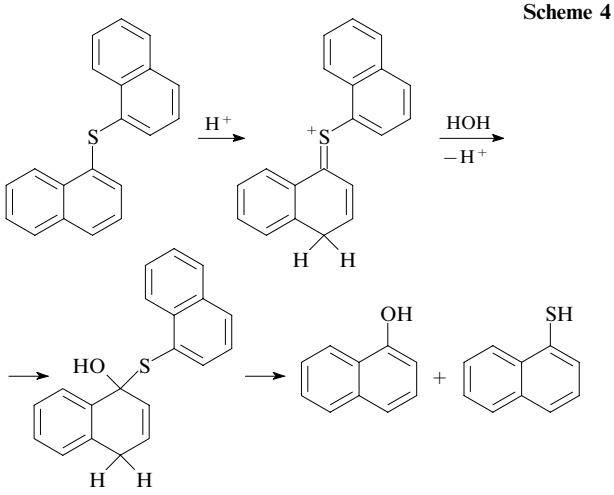
It was ascertained[95] that compounds of this type are virtually unreactive under anhydrous conditions where the ionic mechanism is ruled out. Apart from acidic clays, hydrolysis is accelerated by a 10% NaCl solution, while in the presence of weak bases, for example, $CaCO_3$, it is retarded (for comparison, the conversion of phenyl cyclohexyl sulfide at 250 °C in 5.5 days was 48% in water; 60.2% in 10% NaCl solution; 20.1% in nonane, and 95.7% in nonane in the presence of monmorillonite).[111] The natural clays that form the oil reservoir would accelerate not only cracking but also hydrolysis of sulfides, ethers and other proton-acceptor compounds, thus facilitating transformation of the RAC structures and, finally, a change in the rheological characteristics of the reservoir fluid.

High-temperature hydrolysis of diaryl sulfides also includes the step of sulfur protonation (Scheme 4).[97]

The major liquid products formed from diaryl disulfides are diaryl sulfides, arenethiols and arenes.[97]

From a number of publications,[95, 97, 104, 110, 111] it follows that thiophenes and benzothiophenes as well as cyclic sulfides are least reactive towards aquathermolysis. At the aquathermolysis temperature of $\leqslant$350 °C, thiophenes barely change.[97] However, the addition of acid to the

Scheme 4



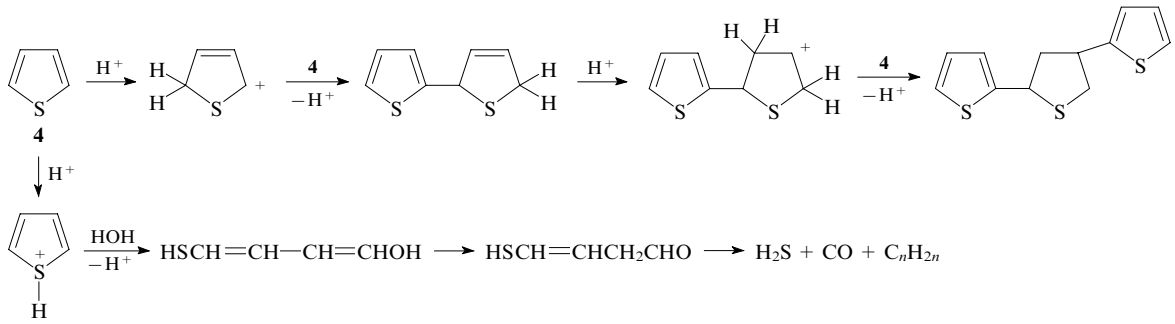
reaction mixture accelerates the acid hydrolysis for which a scheme of transformations including two protonation pathways was proposed[112] (Scheme 5).

Thiophene aquathermolysis performed in 10% H_3PO_4 for 20 h at 250 °C results in 13% conversion; when the reaction lasts for 4 days, it increases to 31.6%. Even this long-term aquathermolysis affords only 0.5% of ethylbenzene — the only product devoid of sulfur.[118] The major products are thiophane, benzothiophene and the products of condensation. Heating of benzothiophene in a H_3PO_4 solution at 350 °C for 5 days results in 37.5% conversion to give ethylbenzene and 2,3-dihydrobenzothiophene as the major products and the products of condensation.

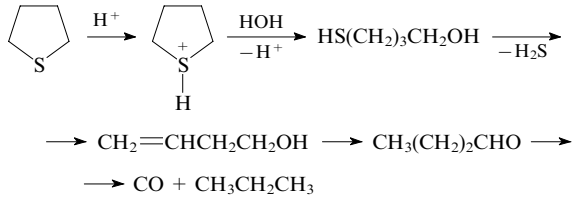
The mechanism of transformations for thiophane is shown in Scheme 6.[112]

Analysis of the gaseous products of these transformations showed the presence of H_2S, CO, CO_2, H_2 and light saturated hydrocarbons. The content of carbon dioxide is in all cases higher than the carbon monoxide content; together with the presence of hydrogen among the gaseous products, this may indicate the occurrence of water gas shift reaction. When aquathermolysis is carried out in acidic medium, the yields of H_2S and CO_2 increase 3 – 50-fold (compared to the neutral conditions), *i.e.*, hydrolysis is more intensive. It is noteworthy that in the downhole aquathermolysis, the

Scheme 5

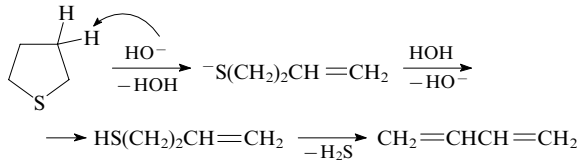


Scheme 6



formation of CO_2 is favourable for oil recovery, as CO_2 being dissolved in oil increases its mobility. When aquathermolysis occurs in an alkaline medium (2 M NaOH), the yield of hydrogen sharply increases. This may be due either to removal of CO_2 formed in the water gas shift reaction from the gas phase, which displaces the equilibrium towards the products, or to the catalytic action of alkali, which is considered in Section IV. The mechanism of the alkaline hydrolysis of thiophane is shown in Scheme 7.[112] This mechanism is supported by the presence of butenes in the gas formed upon alkaline aquathermolysis, whereas the gas formed in aquathermolysis performed in acidic medium does not contain alkenes.

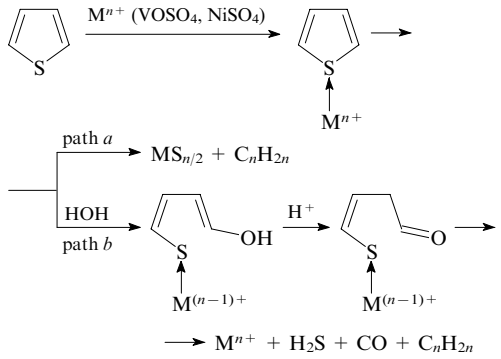
Scheme 7



Sulfonic acids are unreactive in both thermolysis and aquathermolysis at 250 °C.[116]

Hydrolysis of organosulfur compounds, in particular thiophene, is accelerated in the presence of vanadium, nickel[113] and aluminium salts (Scheme 8).[114] The formation

Scheme 8



of metal complexes with a sulfur compound weakens the C–S bond and leads to molecule destruction *via* thermolysis (pathway *a*) or hydrolysis (pathway *b*), pathway *a* being more probable.

In the presence of the mentioned salts, the amount of H_2S formed and, hence, the degree of desulfurization, considerably increase. The highest conversion of benzothiophene in aquathermolysis carried out for 28 days at 240 °C is observed in the presence of Al^{3+}, VO^{2+}, Fe^{3+}, Cu^{2+}, Ru^{3+}, Pt^{4+}, *etc.* (Table 6).[119] A moderate amount of hydrogen sulfide formed with catalysis by VO^{2+}, Fe^{3+} or Cu^{2+} is related to the formation of sulfides of these metals, as evidenced by elemental analysis of the insoluble product of transformations. Platinum group metals ensure a higher degree of desulfurization. It is of interest that Fe^{3+} ions promote higher conversion, whereas Co^{2+} and Ni^{2+} are inactive. The same is true for Pt^{4+} and Pt^{2+} ions, the latter being less active. Thus, most active are metals in intermediate or high oxidation state, which can be reduced during the reaction to a lower oxidation state. Apart from the formation of metal ion complexes with a sulfur atom and/or a π-system, hetereogeneous catalysis by metal sulfides of hydrogenolysis reactions involving hydrogen formed in the water gas shift reaction is possible. As the conversion increases, the quantity of insoluble coke-like residue grows, obviously, as a result of hydrogen redistribution.

The reported[43,52] abnormally high content of carbonyl groups in saturate and ethanol–benzene resin fractions of aquathermolysis products supports the presented mechanisms of transformations, which include steps of aldehyde formation and subsequent conversion to acids and esters.

Evidently, thermal cracking of sulfur compounds to give hydrogen sulfide, hydrocarbons and coupling reaction products should also take place at temperatures of 200–350 °C.

$$C_6H_{13}-S-C_6H_{13} \longrightarrow H_2S + 2C_6H_{12} \qquad (1)$$

In the presence of naphthene-aromatic compounds, hydrogen transfer from these compounds accompanied by hydrogenolysis can be assumed. An example is the reaction of tetralin with thiophane (Scheme 9).

Scheme 9

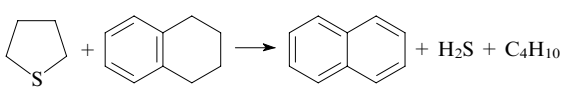
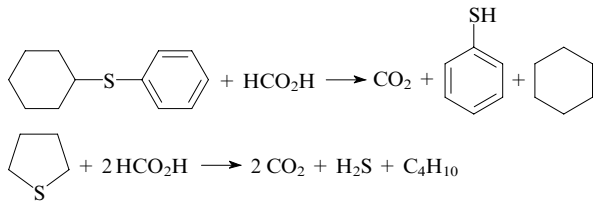


Table 6. Distribution of the products of benzothiophene aquathermolysis (250 °C, 28 days) in the presence of metal salts.[119]

Catalytic additive	Content in the reaction products (mass %)					
	gaseous hydrocarbons	CO_2	H_2S	dichloromethane-soluble organic products	dichloromethane-insoluble products	unreacted benzothiophene
None	0	0	0	0	0	98.0
Al^{3+}	0	1.4	0.2	52.9	0	43.3
Sc^{3+}	0	0	0	0	0	95.0
Ti^{3+}	0	0	0	1.0	0	95.0
VO^{2+}	0	0.9	0.5	25.9	4.6	61.9
Cr^{3+}	0	1.1	0.6	30.5	0.2	66.8
Mn^{2+}	0	0	0	0	0	98.0
Fe^{3+}	0	1.0	0.1	32.6	2.1	63.3
Co^{2+}	0	0	0	1.0	0	94.0
Ni^{2+}	0	0	0	0	0	95.0
Cu^{2+}	0.4	1.8	0.4	58.6	2.4	37.2
Zn^{2+}	0	0.1	0	1.9	0	95.0
Ru^{3+}	0.2	1.8	3.1	80.6	5.1	5.0
Os^{3+}	0.3	2.2	5.1	80.8	4.6	9.8
Rh^{3+}	0.4	1.7	1.4	80.1	4.4	9.0
Ir^{3+}	0.3	1.8	3.8	78.8	4.1	4.9
Pd^{2+}	0.4	2.0	0.1	62.1	2.7	33.3
Pt^{2+}	0.3	0.7	0.3	63.9	1.9	29.4
Pt^{4+}	0.5	1.4	4.6	78.4	5.7	5.1

Hydrogenation of phenyl cyclohexyl sulfide and thiophane can involve formic acid (Scheme 10).[107]

Scheme 10



The change in the Gibbs energy for these reactions was calculated [107] for the 300 – 800 K temperature range, in order to evaluate whether the reactions are thermodynamically possible (Fig. 4). The positive $\Delta_r G^\circ_T$ values for hydrolysis of phenyl cyclohexyl sulfide indicate that these reactions result in low product yields and the equilibrium is shifted towards the reactants. Meanwhile, destruction of phenyl cyclohexyl sulfide to benzenethiol and methylcyclopentene is possible at temperatures above 227 °C. The reaction presented in Scheme 6 is impossible during steam stimulation according to calculations. The thermal decomposition of dihexyl sulfide [reaction (1)] is possible at a temperature of $\geqslant$227 °C. It is noteworthy that the hydrolysis of sulfur compounds in the presence of formic acid (see Scheme 10) is possible over the whole temperature range considered, while hydrogenolysis of thiophane in the presence of tetralin (see Scheme 9) can occur above 120 °C, *i.e.*, it is also possible during steam stimulation.

Thermodynamic calculations of aquathermolysis reactions of thiophane and thiophene [123] taking account of the water gas shift reaction indicate that the yield of gases (CO, H_2, C_1-C_5 hydrocarbons) increases with temperature rise and diminishes with pressure rise; however, within the range

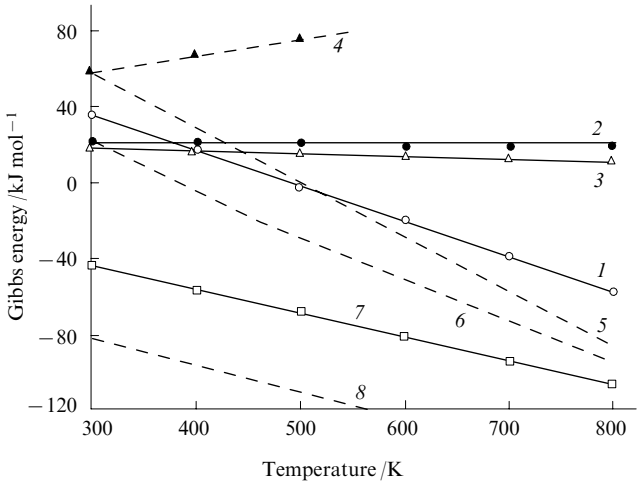


Figure 4. Change in the Gibbs energy for reactions of organosulfur compounds *vs*. temperature.[107]
(*1*) Destruction of phenyl cyclohexyl sulfide to methylcyclopent-1-ene and benzenethiol; (*2*) the same, hydrolysis to phenol and cyclohexanethiol; (*3*) the same to benzenethiol and cyclohexanol; (*4*) reaction shown in Scheme 6; (*5*) reaction (1); (*6*) reaction shown in Scheme 9; (*7*), (*8*) reactions shown in Scheme 10.

of $P-T$ conditions in the reservoir (150 – 300 °C, 6 – 10 MPa), pressure and temperature have an insignificant effect on the product composition. The water : feed ratio is much more significant. The increase in this ratio for thiophane aquathermolysis to 2.5 favours the formation of CO_2, H_2S and CH_4 and conversion of thiophane; further increase in this ratio results in flattening out of the curves (Fig. 5).

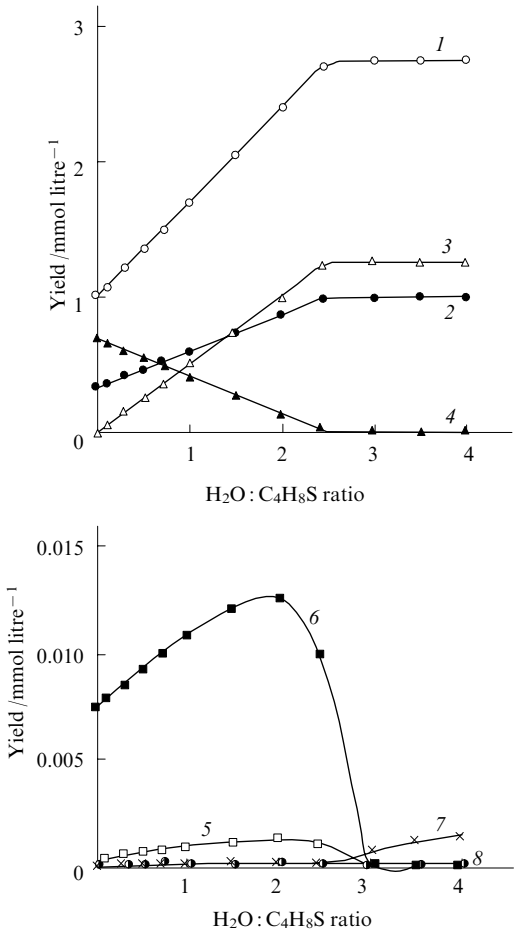


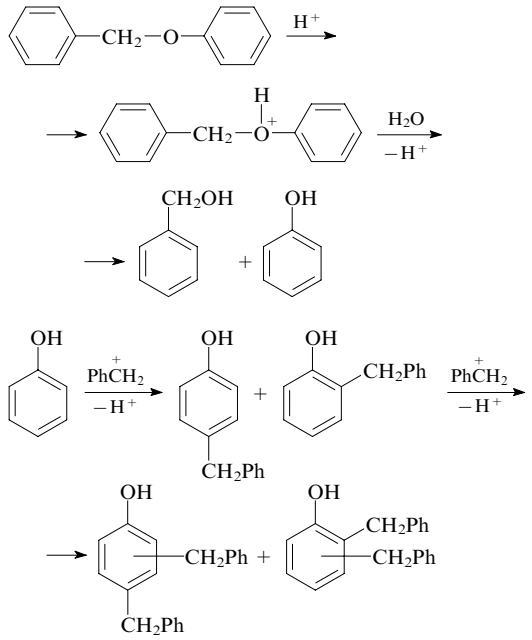
Figure 5. Effect of the water : feedstock ratio on the yield of thiophane aquathermolysis products.[123]
(*1*) CH_4, (*2*) H_2S, (*3*) CO_2, (*4*) C_4H_8S, (*5*) CO, (*6*) C_{2+}, (*7*) H_2, (*8*) thiols.

III.3. Oxygen- and nitrogen-containing compounds

The possibility of C–O bond hydrolysis in polyethylene terephthalate and other polymers at temperatures of 200–250 °C and pressure >1.5 MPa was demonstrated in a patent.[124] The major products of hydrolysis are terephthalic acid and ethylene glycol. Similarly to polymers, depolymerization of the organic matter *via* C–O bond cleavage in ethers and esters can take place for oil shales, kerogen, peat and crude oil. The hydrolysis of benzyl phenyl ether is depicted in Scheme 11.[125] The conversion in the thermolysis under anhydrous conditions (250 °C, 5.5 days) is 26.9%, whereas in water it can be as high as 100%. Phenol formed in this reaction, being a weak acid, acts as a catalyst, *i.e.*, the reaction is autocatalyzed.

The conversion of 1-phenoxynaphthalene at 315 °C for 3 days reaches 95%,[95] although in the absence of water this ether is thermally stable. The rate of hydrolysis substantially increases in the presence of 1% H_3PO_4 or clays,[126] whereas bases (pyridine, $CaCO_3$) and alkali metal chlorides and sulfates inhibit the hydrolysis of diaryl ethers. For example, the conversion of 1-phenoxynaphthalene after 72 h at 315 °C is 94.6% in pure water, while in 1% NaCl, LiCl, KBr and Na_2SO_4 solutions, it is only 7.4%, 4.8%, 3.8% and 0%, respectively.[95, 126]

Scheme 11



However, the rate of hydrolysis of phenyl cyclohexyl ether increases in a 10% NaCl solution. The conversion of phenyl cyclohexyl ether after 5.5 days at 250 °C is 15.1% in pure water and increases to 54.1% in a 10% NaCl solution and to 99.6% in the presence of montmorillonite but decreases to 12.5% in aqueous calcium carbonate.[111]

It is of interest that montmorillonite affects more appreciably the rate of hydrolysis of phenyl cyclohexyl ether or phenyl cyclohexylamine than that of phenyl cyclohexyl sulfide. Indeed, the conversions of phenyl cyclohexyl sulfide and ether after 5.5 days at 250 °C increased upon the addition of montmorillonite to water from 48% to 48.8% and from 15% to 99.6%, respectively.[111] This is caused by a smaller negative charge on the sulfur atom than on oxygen and nitrogen atoms, *i.e.*, the lower proneness of sulfur to proton addition.

The hydrolysis of diphenyl ether in supercritical water unexpectedly demonstrated a regular trend of variation of the conversion and the rate constant (k_H) as functions of the concentration of NaCl solution[127] (Table 7). The increase in the brine concentration from 0 to 0.74 mass % results in a 5.5-fold decrease in the conversion and a 5.7-fold decrease in the rate constant. Further increase in the NaCl concentration induces an increase in the conversion and the rate constant. The researchers attributed this finding[127] to the fact that at low NaCl concentration in water, the Cl^- ions, which appear in the solution upon NaCl dissociation, form the ion pairs H^+Cl^-, *i.e.*, chloride atoms capture protons.

Table 7. Conversion and rate constant for hydrolysis of diphenyl ether depending on the concentration of NaCl solution (430 °C, 5 h).[127]

C_{NaCl} (mass %)	Conversion of PhOPh (% to phenol)	$k_H \times 10^7$
0	1.66	9.49
0.74	0.30	1.66
1.60	1.87	11.0
2.45	2.59	15.1
3.12	3.21	20.1

Since the ether hydrolysis starts from protonation of the oxygen atom, the rate of the overall reaction thus decreases. At higher concentration of NaCl, charge transfer in the water clusters surrounding the Na^+ and Cl^- ions results in the formation of H^+ and HO^- ions in the outer sphere of the clusters and, as a consequence, the rate of hydrolysis increases.

As regards the reactivity of oxygenates of other classes, note that ketones are virtually inert to both thermolysis and aquathermolysis at 250 °C (5 days). The conversion of decan-2-one [104] and acetophenone [128] did not exceed 2% in both cases. Aldehydes are more reactive: the conversion of decan-1-al in the aquathermolysis is >89%, while that in thermolysis is 50%.[104] The major products are nonane, decan-1-ol, decanoic acid and decyl decanoate. In the presence of montmorillonite, the yield of decanoic acid is higher than that of decanol. The conversion of decan-1-ol in water does not exceed 1%, the same is true for thermolysis without water.[104]

The conversion of phenylacetic acid is higher (11.4%) in thermolysis than in aquathermolysis (<1%). Thermolysis gives dibenzyl ketone as the major product.[129] Conversely, 1-naphthoic acid is not converted under conditions of thermolysis (250 °C, 5.5 days) but is decarboxylated to naphthalene during aquathermolysis to 11.6% conversion.[125] At 343 °C in water, 100% of the acid is converted to naphthalene. The increase in the yields of CO_2 and hydrocarbons upon acid decarboxylation in the presence of an aqueous phase was interpreted [130] in terms of the ionic mechanism of the reaction

$$RCO_2H + H_2O \longrightarrow RCO_2^- + H_3O^+$$

$$RCO_2^- \longrightarrow R^- + CO_2$$

$$R^- + H_3O^+ \longrightarrow RH + H_2O$$

As expected, the conversion of esters is higher in water where hydrolysis takes place. In the case of thermolysis (250 °C, 1.5 days), the conversion of decyl decanoate is 24.4%, while in aquathermolysis, the conversion is 80.8%. Decarboxylation takes place in none of cases, the major products being dec-1-ene, decanoic acid, decan-1-ol and dec-2-ene.[104] Dibenzofuran and 2-hydroxydibenzofuran are inert under conditions of thermolysis and aquathermolysis even at relatively high temperature (315 °C, 3 days; 460 °C, 7 min).[131]

The conversion of pyridine in aquathermolysis (350 °C, 3 days) is negligible even in 10% H_2SO_4.[97, 132] Montmorillonite somewhat accelerates the reaction, the conversion increases to 5%, and bipyridines are formed as the major products, while no C–N bond cleavage with evolution of ammonia is observed. Similarly, quinoline does not react at 460 °C under conditions of either thermolysis or aquathermolysis.[133] Acridine is converted by 50.3% to 9,10-dihydroacridine in pure water, while in 10% formic acid (350 °C, 3 days) the conversion increases to 91.3%. Apart from 9,10-dihydroacridine, the products contain 1,2,3,4-tetrahydroacridine.

Analysis of nitrogen-containing compounds in oil samples from the Usinskoye oil field produced by natural flow and steam stimulation showed [61] that these samples virtually do not differ in the total nitrogen content. However, in the case of steam stimulation, the relative content of basic and neutral nitrogen compounds decreases and the content of weakly basic compounds increases. Also, the contents of carboxyl and ester groups in the molecules of strong N-bases increase. Strong N-bases should obviously be more reactive towards acid hydrolysis. In particular, conversions of cyclohexylaniline in thermolysis and aquathermolysis in the presence of montmorillonite can be as high as 99.8% and 70.9%, respectively.[111] The scheme of transformations is similar to that presented above for phenyl cyclohexyl sulfide.

All the reactions of hydrolysis of heteroatomic compounds are autocatalyzed, that is, the acidic products (H_2S, CO_2) participate in the protonation of heteroatomic compounds.[93]

Thus, as noted above, the mercaptan and sulfide oils as well as oils containing a large number of ether, sulfide and amine bridges in RAC molecules will, in all probability, be most reactive under the steam stimulation conditions.

IV. Methods for intensification of upgrading of heavy crude oils and natural bitumens by aquathermolysis

IV.1. Activation of alterations of heavy crude oils by hydrogen sources

As shown in Section II, steam stimulation is associated with the change in the composition and rheological and physicochemical characteristics of feedstock. Unlike the *in situ* combustion, which is accompanied by thermooxidaive cracking, steam stimulation does not decrease the value of the feedstock. Intensification of NB transformations upon steam stimulation implies, first of all, changes of some NB characteristics that promote the bitumen recovery, transportation and process parameters. In order to intensify aquathermolysis, it was proposed to use hydrogen donors, formic acid, formates and hydrogenolysis catalysts as well as physical impacts on the reservoir and alternative techniques of reservoir heating.

Since HCO and NB are depleted in hydrogen and often contain considerable amounts of heteroatoms, numerous studies are devoted to the search for methods of hydrogen supply into the reservoir. The injection of molecular hydrogen proposed in a patent [134] is rarely considered, for its hazard, as a perfect solution to the problem. Possible alternative ways for hydrogen supply to the reservoir fluid include injection of naphthene-aromatics, carbon oxide for water gas shift reaction and injection of formic acid and formates. Strictly speaking, only naphthene-aromatic compounds can be directly classified as hydrogen donors since in the presence of formic acid, ionic hydrogen transfer takes place, which is considered in detail in this Section.

As an alternative to molecular hydrogen, Fedyaeva *et al.*[135–138] proposed conversion of NB or asphaltite in supercritical water using zinc or aluminium. In the supercritical water, the metal is oxidized to give molecular hydrogen and heat (2.2 MJ kg^{-1} for zinc and 17.6 MJ kg^{-1} for aluminium). Apart from this, zinc traps hydrogen sulfide evolved during the conversion of NB, which is also important as regards the safety of the industrial process. The hydrocarbon content in the conversion products increases, so does the degree of desulfurization. The redistribution of the SARA composition of the fluid in the presence of aluminium consists in an increase in the contents of hydrocarbons, including gaseous, and a

decrease in the content of resins, while in the presence of zinc, resin formation is observed with lower formation of gaseous and liquid hydrocarbons, *i.e.*, the efficiency of hydrogenation in the presence of aluminium is higher than with zinc. The yield of the insoluble residue is 44.5% for the experiment without metals, 11.3% for the conversion in the presence of aluminium and up to 26.3% in the presence of zinc. Higher yield of volatile products upon the conversion of asphaltite in the presence of aluminium is due to evolution of a lot of heat upon the aluminium oxidation, which is favourable for the generation of free radicals. It is noteworthy that the conversion products in the presence of zinc contain no thiols, which may be a consequence of zinc-catalyzed destruction of C–S bonds.

The ability of naphthene-aromatic molecules to give off an even number of hydrogen atoms was used in the hydrogen donor diluent cracking.[139] Quite a number of papers dealing with downhole upgrading of NB describe the use of tetralin as hydrogen donor.[140–143] Aquathermolysis in the presence of tetralin ensures more pronounced decrease in the viscosity and density and asphaltene content as a result of saturation of free radicals preventing them from recombination. The latter fact is confirmed by a decrease in the rate constant for thermal cracking and conversion of heavy oil feedstock in the presence of naphthene-aromatic hydrogen donors.[139, 144]

In addition to more a pronounced decrease in the viscosity, this method ensures higher stability of the viscosity during oil storage, whereas the viscosity of the aquathermolysis product obtained without hydrogen donors increases with time (Table 8).[140] The viscosity growth is evidently due to radical recombination, which is also in line with increase in the average molecular mass of both crude oil and asphaltenes during storage of aquathermolysis products. The partial saturation of free radicals with hydrogen from tetralin inhibits free-radical processes in the oil system during storage. It can be seen from Table 8 that the average molecular mass of the oil asphaltenes is higher after the catalytic aquathermolysis with a hydrogen donor than after the catalytic aquathermolysis in the absence of a hydrogen donor, which attests once again to the inhibition of free radical processes, including cracking, in the presence of tetralin. It should also be noted that naphthene-aromatic compounds and bi- or tricyclic aromatic hydrocarbons resulting from its dehydrogenation, which increase the dissolving ability of dispersion medium and disperse the asphaltene aggregates, weaken the intermolecular interactions of aggregate combinations,[54] which also decreases the viscosity (see Table 8). The presence of hydrogen donors also decreases the threshold concentration of asphaltenes for the start of coke formation.[144]

The application of tetralin is held up by its low availability and high cost; therefore, the search for a more available alternative is a topical task. In addition, as shown by measurements[144] of the relative reactivity of various hydrogen donors towards 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), a strong hydrogen acceptor, tetralin is far from being the most reactive hydrogen donor. 1,2,3,4-Tetrahydroquinoline and 9,10-dihydroanthracene are 50- and 28-fold more reactive than tetralin (Table 9). It is worth noting that residual hydrocarbons, resins and asphaltenes, although possess weaker proton-donor properties than tetralin, still surpass tetralin in the reactivity. During thermolysis and aquathermolysis processes, the content of hydrogen donor decreases both in oil (vacuum residue) and in asphaltenes; therefore, the concentration of polycyclic aromatic moieties, *e.g.*, phenanthrene groups, increases.[53]

The theoretical possibility of hydrogenolysis of heteroatomic compounds directly in the reservoir is confirmed by a study[145] in which the transformations of model organosulfur compounds were performed in autoclaves under a synthesis gas and steam pressure using the hydrogenolysis

Table 8. Change in the viscosity and molecular mass during storage of the product of aquathermolysis (240 °C, 24 h, 20% water, 0.8% tetralin, 0.2% catalyst) of Liaohe oil (China).[140]

System	Crude oil before the reaction (oil + tetralin)	After the reaction and storage of the aquathermolysis product for different periods /days				
		0	1	5	10	20
Viscosity (50 °C) /Pa s						
Oil + water	88.5	72.4	73.5	77.4	77.4	77.4
Oil + water + catalyst	88.5	32.4	43.5	47.4	47.4	47.4
Oil + water + catalyst + tetralin	56.4	10.2	10.2	10.2	10.2	10.2
Oil + tetralin	56.4	44.3	44.3	44.3	44.3	44.3
Average molecular mass of crude oil						
Oil + water	648	582	596	603	603	603
Oil + water + catalyst	648	482	482	506	506	506
Oil + water + catalyst + tetralin	648	580	580	580	580	
Oil + tetralin	648	482	482	482	482	482
Average molecular mass of asphaltenes						
Oil + water	6600	6240	6650	6980	6980	6980
Oil + water + catalyst	6600	4260	4280	4720	4720	4720
Oil + water + catalyst + tetralin	6600	6240	6240	6240	6240	6240
Oil + tetralin	6600	4260	4260	4260	4260	4260

Table 9. Content and reactivity of donor hydrogen for hydrogen donors, oil residues and components.[144]

Hydrogen donors and oil residues	Content of donor hydrogen (based on reaction with DDQ)		Reactivity measured against tetralin
	g per 100 g of the sample	% of the total hydrogen content	
Tetralin	3.0	33	1
1,2,3,4-Tetrahydroquinoline	3.0	33	50
9,10-Dihydroanthracene	1.1	17	28
9,10-Dihydrophenanthrene	1.1	17	0.63
Brent atmospheric residue	1.2	11	–
Brent vacuum residue	1.4	13	5.7
Arabian heavy vacuum residue	1.9	19	2.7
Arabian heavy aromatics	2.1	19	2.0
Arabian heavy resins	2.0	21	2.9
Arabian heavy asphaltenes	1.9	25	4.2

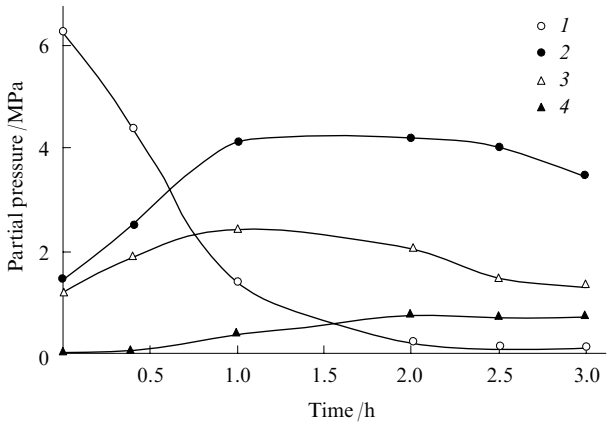


Figure 6. Change in the partial pressure of the benzothiophene transformation products in the presence of carbon oxide and water.[145]
(*1*) CO, (*2*) CO_2, (*3*) H_2, (*4*) H_2S.

catalyst. The distribution of the products of benzothiophene transformation at 380 °C and an initial CO pressure of 4.13 MPa in the presence of water and the MoO_3 catalyst is shown in Fig. 6.

The decrease in the CO partial pressure with time together with the increase in the CO_2 partial pressure confirms the occurrence of the water gas shift reaction, while the decrease in the hydrogen partial pressure indicates that hydrogen is consumed for hydrogenolysis. In the case of sulfur compounds in the system, the curves of formation of hydrogen and carbon dioxide nearly coincide. According to patents,[146, 147] downhole injection of CO together with steam provides more pronounced reduction of the viscosity than injection of steam alone. This effect is enhanced in the presence of hydrogenolysis catalysts (Ni, Mn, Co, Fe, *etc.* salts). Another patent [148] considers synthesis gas injection into the reservoir. It was proposed [149] to use synthesis gas for separation of water–oil emulsions with simultaneous oil upgrading at 300–450 °C in the presence of Mo or W compounds.

The use of formic acid as a source of hydrogen in the downhole upgrading of HCO and NB was proposed in a number of works.[150–152] Formic acid decomposes by the reactions

$$HCO_2H \longrightarrow CO + H_2O$$

$$HCO_2H \longrightarrow CO_2 + H_2$$

As shown by calculations, both reactions are thermodynamically possible over a broad temperature range, in particular, at 300–800 K.[107]

Aquathermolysis of heavy crude oil from the Hamaca oil field (Venezuela) in 9% HCO_2H ensures more pronounced change in the SARA composition towards higher contents of saturates and aromatics and lower contents of resins and asphaltenes as well as the more pronounced increase in the content of light fractions compared with experiments without the additive.[150, 152] The degree of desulfurization increases from 20% (for aquathermolysis in the absence of formic acid) to 38%. As other hydrogen sources, a patent [151] proposed inorganic and organic salts of formic acid and formamides, which can be injected into the steam flow after the steam generator.

The ability of formic acid to participate in hydrogenation and hydrogenolysis reactions is indicated by the fact that on treatment of NB in supercritical water with HCO_2H, the amount of the asphaltenes and coke formed is lower than without the acid.[153] The gases formed upon decomposition of pure formic acid in supercritical water in an autoclave contain 25.4% H_2, 36% CO_2 and 38.6% CO (Table 10). The addition of NB into the autoclave changes the situation: the hydrogen content in the gas phase decreases to 2%–14% depending on the amount of NB, and the CO content drops to 1.9%–22%, *i.e.*, hydrogen is absorbed in hydrogenolysis and hydrocracking reactions, while CO is consumed in the water gas shift reaction. Possibly, in the presence of NB in the reactor, the equilibrium of the latter reaction is more shifted towards the products because of continuous consumption of hydrogen.

Formic acid can decompose by a radical, ionic or molecular mechanism. According to Yu and Savage,[154] the contributions of the two former mechanisms is moderate and formic acid decomposes by the molecular mechanism to give CO_2 and H_2 in the liquid phase or CO and H_2O in the gas phase. The difference between the mechanisms of decomposition of formic acid in the gas and liquid phases

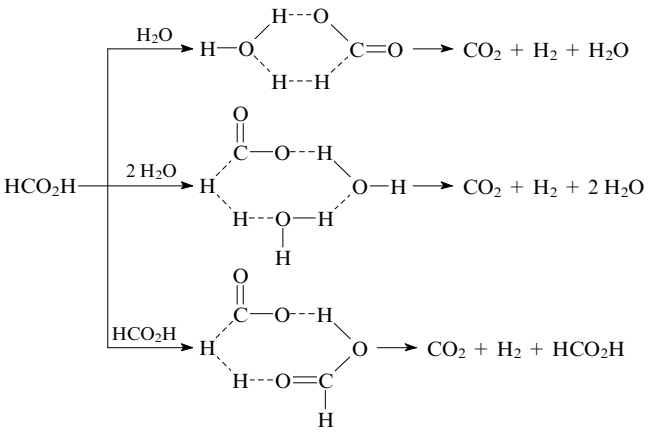
Table 10. Gas composition upon aqueous pyrolysis of natural bitumen (450 °C, supercritical water) in the presence and in the absence of formic acid.[153]

System	Pyrolysis duration /min	Content (mol.%)									
		H_2	CO	CO_2	CH_4	C_2H_4	C_2H_6	ΣC_3	ΣC_4	H_2S	N_2
NB	30	6.3	2.7	1.7	32.3	1.8	28.8	10.0	1.6	12.6	2.2
Water + NB	30	5.3	1.2	5.8	36.3	0.6	18.2	10.9	2.2	16.4	3.1
Formic acid + water	30	25.4	38.6	36.0	0	0	0	0	0	0	0
Formic acid + water + NB	30	14.5	22.0	50.6	2.1	0.1	1.7	2.5	0.7	5.8	0
	60	2.8	5.0	51.4	6.0	0.2	13.6	10.0	2.4	8.2	0.5
	90	2.3	1.9	49.3	2.2	0.1	12.1	18.6	4.6	7.9	1.1

Note. ΣC_3 and ΣC_4 designate the $C_3H_6 + C_3H_8$ and $C_4H_6 + C_4H_8 + C_4H_{10}$ sums of gases, respectively.

is due to the catalytic action of water and formation of the transition complex (Scheme 12).

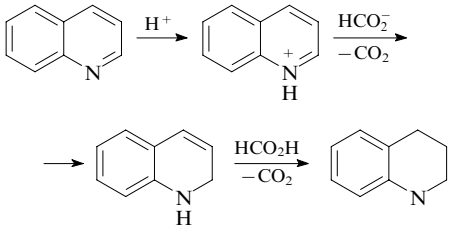
Scheme 12



Quantum chemical calculations[154] demonstrate that that the activation energy for decarboxylation involving one water molecule and formation of the transition complex is 83–105 kJ mol^{-1} lower than that for unimolecular decomposition reaction. The participation of two water molecules in the formation of the transition complex decreases the activation energy by additional ~42 kJ mol^{-1} (see Scheme 12).[155] Catalysis by formic acid itself giving dimeric transition complex is also possible.[155] In this case, activation energy decreases by several kJ mol^{-1} more (see Scheme 12).

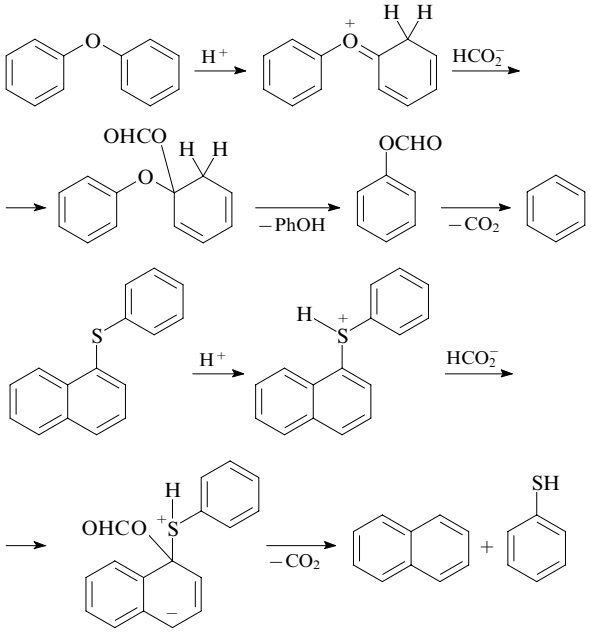
Meanwhile, formic acid can serve as a source of hydrogen in the system without being decomposed to give molecular hydrogen. According to Siskin and Katrizky,[156] formaldehyde and formic acid can transfer hydride ions to oxygen-containing functional groups and polycyclic aromatic hydrocarbons, which results in reduction and hydrogenation of PAH. Indeed, conversion of anthracene in 15% HCO_2H within 1 h at 460 °C reaches 80%, whereas in the absence of HCO_2H, anthracene remains unchanged. The major reaction products are di- and tetrahydroanthracenes. Similarly, acridine is reduced with formic acid to 9,10-dihydroacridine and tetrahydro derivatives without denitrogenation. In 15% HCO_2H, quinoline is converted to 1,2,3,4-tetrahydroquinoline in nearly quantitative yield (Scheme 13).[133]

Scheme 13



Hydrolysis of diphenyl ether and 1-naphthyl phenyl sulfide in the presence of H^+ and HCO_2^- ions is shown in Scheme 14.[97]

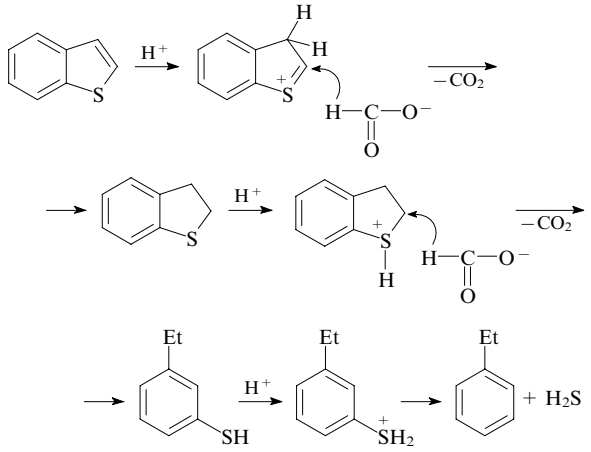
Scheme 14



At 460 °C in 15% HCO_2H, naphthalene and benzene are the major products of hydrolysis of this sulfide; benzenethiol and other thiols are readily desulfurized in formic acid.[97] For example, naphthalene-1-thiol is converted to naphthalene (57.8%) and tetralin (2.2%).

Benzothiophenes have low reactivity under conditions of aquathermolysis in formic acid, the total yield of hydrogenation and thiophene ring cleavage products being not higher than 4% (Scheme 15).[110]

Scheme 15



According to Ross and Nguyen,[157] CO and H_2O react in alkaline media to give formates.

$$CO + NaOH \longrightarrow HCO_2Na$$

Then formates participate in hydrogenation and hydrogenolysis reactions (for example, for compound X).

$$X + HCO_2Na \longrightarrow XH^-Na^+ + CO_2$$

$$XH^-Na^+ + H_2O \longrightarrow NaOH + XH_2$$

The overall reaction: $X + CO + H_2O \longrightarrow XH_2 + CO_2$

Thus, hydrogenation and carbon–heteroatom bond cleavage (depolymerization) occur by ionic mechanism with addition of hydride ion and subsequent regeneration of the hydroxide ion. These alkali-catalyzed reactions do not occur in acidic or neutral medium. It was shown [157–159] that at pH >12.6, the reactive formate form, $[H-O-C{=}O]^-$ (isoformate), which is formed only in the reaction between CO and HCO^-, is present in the system.

The above data can be summarized by stating that the following reactions can proceed during aquathermolysis: hydrogen transfer from naphthene-aromatic compounds, cracking, hydrolysis and hydrogenation if formic acid or carbon monoxide are present in the system and the pH of the aqueous phase is alkaline. The rate of hydrogen transfer and, hence, hydrogenolysis and hydrocracking without catalysts is low; therefore, in recent years, studies of the catalytic treatment of oils under the reservoir conditions have been widely developed.

IV.2. Methods of downhole catalytic upgrading of heavy crude oils

By analogy with the development of industrial catalysts of hydrocracking, this area is widely explored as applied to the downhole treatment of HCO and NB. This is due to the possibility to intensify hydrogenolysis and, hence, to increase the degree of desulfurization and decrease the viscosity as a result of C–S bond cleavage in high-molecular-mass components. As has already been noted, naphthene-aromatic compounds and water gas shift reaction serve as the hydrogen sources.

Strictly speaking, metals and metal compounds introduced in the reaction mixture cannot be called catalysts because they are only catalyst precursors. At certain temperature in the presence of sulfur compounds, they are converted *in situ* into metal sulfides, which catalyze hydrogenolysis. Most often, transition metals (Mo, Co, Ni, V, Fe) and their compounds are taken as the catalyst precursors. It was found [160] that in terms of activity towards hydrotreating, these metals can be arranged in the series Mo > Ni > Co > Fe. The catalyst activity depends also on the particle size of the sulfide formed, which, in turn, depends on the type and method of introduction of the catalyst precursor.

Some researchers propose using bi- and trimetallic catalysts, which are formed *in situ* from bi- and trimetallic precursors or mixtures of two or three monometallic precursors. However, as shown by Panariti *et al.*,[160] the use of organic precursors containing two metals in the molecule (Mo and Ni or Co) provides only a slight increase in the degree of desulfurization over monometallic catalysts. This is due to the fact that in this case, two phases, MoS_2 and sulfide of the second metal, rather than a mixed sulfide, are formed *in situ*. Since MoS_2 is more active than the sulfide of any other metal, the use of bimetallic precursors that do not form mixed sulfides can be justified, first of all, for reducing the catalyst cost. The Mo, Ni, V, Co and Fe sulfides catalyze the water gas shift reaction, molybdenum and potassium sulfides being most active.[161] Figure 7 presents classification of catalyst precursors for downhole upgrading of HCO and NB according to data reported by Mairy *et al.*[19] and Weissman.[162]

Heterogeneous catalysts were proposed for *in situ* combustion with the catalyst bed being located near the wellbore (Catalytic Upgrading Process *in situ* — CAPRI).[163] Owing to the considerable content of metals in NB, these catalysts are rapidly deactivated and deposition of coke and particulates on the catalyst surface leads not only to deactivation but also to plugging of the pore space, which prevents fluid influx to the well. Therefore, below we do not consider this type of catalysts.

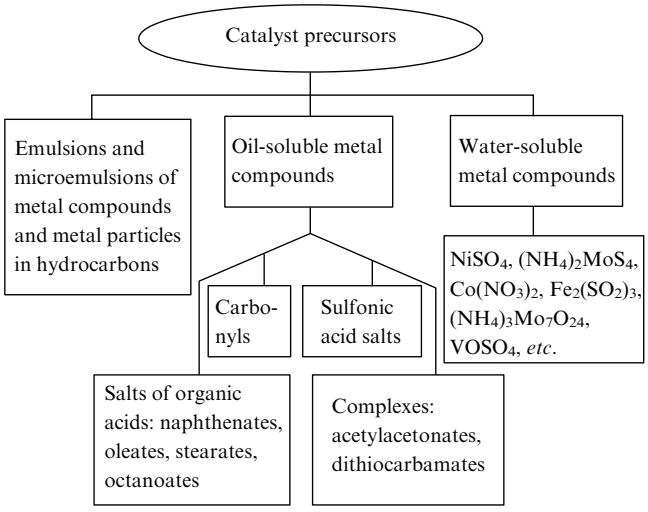


Figure 7. Classification of precursors of downhole hydrogenolysis catalysts (according to Refs 19 and 162).

IV.2.a. Nanosized catalysts obtained from emulsions and microemulsions

Nanosized catalysts are formed *in situ* from hydrocarbon emulsions and microemulsions of aqueous solutions of precursors. The preparation of (micro)emulsions comprises mixing of the organic component (oil fraction or residue) with a surfactant and an aqueous solution of metal salts followed by stirring at ~700 rpm.[164, 165] The inorganic metal salts are represented by nickel, iron and cobalt chlorides, sulfates and nitrates, while molybdenum catalyst precursors are prepared using molybdates, for example, $K_3PMo_{12}O_{40}$.[166] At the hydrocracking temperature, metal salts decompose to oxides, which are then converted to sulfides in the presence of hydrogen sulfide. Often, metal oxide nanoparticles are used as precursors. Noorlaily *et al.*[167] proposed the synthesis of NiO nanoparticles by dissolution of $NiCl_2 \cdot 6H_2O$ in ethylene glycol followed by precipitation of nickel oxide with an aqueous solution of NH_4HCO_3. The precipitate thus formed is dried and annealed; the increase in the annealing temperature from 300 to 500 °C is undesirable, as this results in an increase in the nanoparticle size from 5 to 15 nm according to powder X-ray diffraction data.

It is possible to prepare polymetallic emulsions. A method for the preparation of $Ni_xFe_{3-x}O_4$ nanoparticles as an aquathermolysis catalyst has been reported.[168] The salts $FeCl_3 \cdot 6H_2O$, $FeSO_4 \cdot 7H_2O$, $NiCl_2 \cdot 6H_2O$ were dissolved in water, polyethylene glycol was added as the surfactant, and a solution of $NH_3 \cdot H_2O$ was added. The precipitate thus formed was annealed in a microwave oven. The nanoparticle structure was confirmed by powder X-ray diffraction analysis. The mechanical alloy NiWMoC formed by treating metal (5–25 μm particle size) and graphite (50 μm particle size) in a ball mill was proposed as the catalyst precursor.[169] It is evident that the longer the mechanical treatment the smaller the particle size. Treatment for 240 h gave ~30 nm crystals of NiC, WMoC and WC. More pronounced decrease in the oil viscosity (aquathermolysis at 200 °C, 24 h) with increase in the time of mechanical treatment of the catalyst precursor was noted: from 80% for an untreated mixture to 97% for the precursor after a 240-h treatment. Unfortunately, in the studies that proposed using polymetallic catalyst precursors, no comparison of the catalytic activities of polymetallic and monometallic precursors was performed. As has already been noted,[160] the formation of mixed metal sulfides is unlikely, because it is difficult to conceive the insertion of, for example, Co and Ni cations into the molybdenite crystal lattice in which the Mo coordination polyhedron is a trigonal prism, while Ni and Co form preferably octahedra and tetrahedra.

A microemulsion of metal particles in a hydrocarbon can be prepared. First, a microemulsion of water in hydrocarbons is obtained using surfactants. Then a metal salt, for example $Ni(NO_3)_2$, is added, the mixture is stirred and the cation is reduced to the metal by means of $LiBH_4$. The size of the nickel particles thus formed is ~6.3 nm[170] or, according to another study, 4.2 nm.[171] Direct dispersion of metal particles (*e.g.*, Ru) in an ionic liquid is possible.[172]

Generally, two considerable advantages of nanosized catalysts over traditional ones are the large surface area and the absence of porous structure, which could be plugged by coke, thus ensuring stability of the activity and the absence of diffusion restrictions.[173] Shokrlu and Babadagli[174] compared the catalytic activities of the Raney nickel (microparticles) and nickel nanoparticles towards aquathermolysis. In the latter case, the viscosity of the aquathermolysis product was lower, evidently, because of larger catalytic surface area. There is an optimal concentration of the catalyst in oil (500 ppm) that provides the most pronounced drop of the viscosity (Fig. 8).

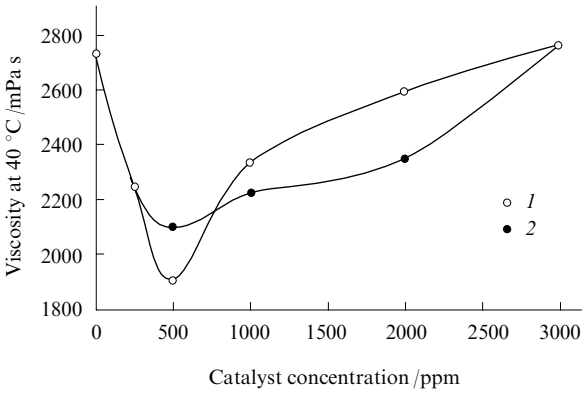


Figure 8. Viscosity of the aquathermolysis product (300 °C, 24 h) obtained using nickel nanoparticles (*1*) and Raney nickel (*2*).[174]

The presence of an optimal concentration of nanoparticles is caused by nanoparticle aggregation taking place at high concentrations to give coarse nanoparticle complexes with asphaltenes, resulting in higher viscosity of the system. At higher concentration of the catalyst precursor, the difference between the viscosities of products obtained with nano- or microparticles becomes insignificant, which was attributed[175] to aggregation of nanoparticles at high concentration. A similar results was obtained with 50 and 500 nm copper particles in 1% concentration (relative to NB): after aquathermolysis (240 °C, 12 h), the viscosity reduced by 75% and 74%, respectively.[176]

Comparison of Ni, Cu, Zn and Fe nanoparticles demonstrated that Ni provides the most pronounced decrease in the oil viscosity upon aquathermolysis.[176] According to Shokrlu and Babadagli,[175] of prime importance is the nanoparticle ζ-potential. Positively charged asphaltene species are attracted by negatively charged copper species, which promotes hydrogenolysis, while the positively charged iron and iron(III) oxide particles would be repelled from asphaltene species. Of course, it is more efficient to use nanosized catalysts together with a hydrogen donor, for example decalin,[176] or molecular hydrogen.[177, 178]

Apart from catalyzing hydrogenolysis, treatment with nanoparticles increases the heat conductivity of crude oil;[175] in view of thermal methods of oil recovery, this would promote faster heating up of the formation. In addition, oxidation of iron particles with oxygen with the participation of water is accompanied by heat evolution, which also promotes heating of the formation. The reaction is accelerated in the presence of acidic oil components, *e.g.*, naphthenoic acids.[179] This fact may be responsible to some extent for the decrease in the oil viscosity upon the introduction of nanoparticles without conducting aquathermolysis. More precisely, the addition of nanoparticles can induce local heating of, for example, asphaltene aggregates with cleavage of weak chemical and hydrogen bonds and partial destruction of aggregate combinations. As shown by

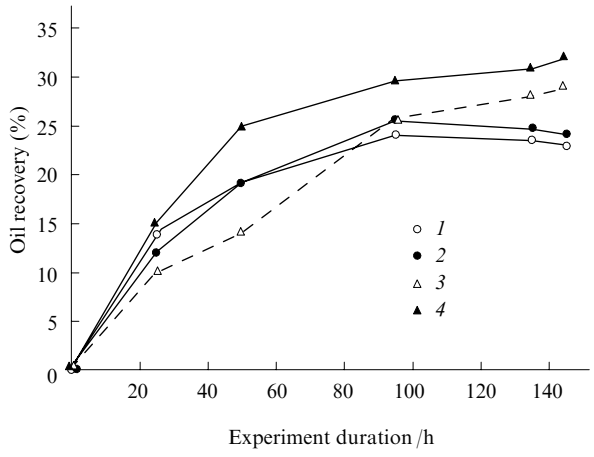


Figure 9. Change in the oil recovery upon injection of hydrogen (1 $cm^3\ min^{-1}$) and steam (0.01 $cm^3\ min^{-1}$) at a pressure of 3.5 MPa and temperature of 320 (*1*, *3*) and 340 °C (*2*, *4*).[178] (*1*, *2*) Without a catalyst; (*3*, *4*) with catalyst injection.

Shokrlu and Babadagli,[179] the viscosity of heavy oil decreases from 8292 to 7900 mPa s (25 °C) upon the introduction of 0.1 mass % of nickel nanoparticles and to 7897 mPa s upon introduction of the same amount of iron nanoparticles. The degree of decrease in the viscosity is determined by the type of oil and, first of all, the content of asphaltenes: the higher this content, the greater the decrease in the viscosity.

Lower oil viscosity is favourable for enhancement of the oil recovery.[178, 180] The results of physical modelling of the production of Athabasca NB from an artificial sand core by injecting steam, hydrogen and vacuum gas oil containing trimetallic Mo–Ni–W nanoparticles are shown in Fig. 9.[178] The increase in the oil recovery is mainly caused by the fact that hydrogenolysis and hydrocracking afford gases and light fractions, which migrate throughout the reservoir model. Bitumen is dissolved in light hydrocarbons and, hence, its mobility increases. Apart from steam injection, electromagnetic heating of the formation can be used.[180]

However, the downhole application of the considered catalysts requires investigation of their flow in porous environments and deposition on rock particles. Experiments supervised by Pereira Almao on the flow of molybdenum oxide nanoparticles in vacuum gas oil through pure sand and Athabasca oil sand demonstrated[173, 181] that pure sand retains ~36%, while oil sand retains ~54% of the catalyst. This difference can be attributed to inhomogeneity and porosity of the Athabasca sand surface. Nevertheless, deposition of the catalyst particles in the rock does not bring about a pressure drop and does not prevent the fluid flow.

According to Zamani *et. al.*,[182] rock permeability does not affect the amount of the retained particles. However, the amount of Ni–Mo–W trimetallic catalyst particles retained by Athabasca NB-saturated sand was ~30% for high-permeability sand (248 D)‡ and ~45% for low-permeability sand (8.9 D).[183] Most of the particles were deposited at the entrance of the model porous medium, *i.e.*, in the injection zone without penetrating into the catalytic zone. The retention of the particles is also determined by the type of the metal: Ni and Mo are less prone to deposition in the sand than W or the Ni–Mo–W trimetallic precursor.

The propagation of nanoparticles in the reservoir is affected by a number of forces, including van der Waals, electrostatic and gravity forces.[174] The van der Waals forces induce particle agglomeration and retention of agglomerates in the porous medium; the catalyst does not propagate throughout the bed. Polymers and surfactants, *e.g.*, xanthan gum, alkylbenzenesulfonates, cetyltrimethylammonium bromide (CTAB), are used to prevent agglomeration. It was proposed[184] first to inject a CTAB solution promoting oil emulsification in water and formation of positive charge at the interface and then to inject nanoparticles stabilized in a xanthan gum solution. Owing to the electrostatic interaction of xanthan gum and CTAB, nanoparticles migrate towards the oil–water interface. The particle injection rate is a highly important parameter. If the rate is too high, particles are non-unifirmly distributed in the reservoir, while at a too low rate, they are retained in the injection zone and plug the pores.[174]

The behaviour of nanocatalyst particles in carbonate reservoir rocks has not been studied. The use of nanosized catalysts for the downhole treatment of NB requires further investigations using model reservoirs, in particular, carbonate rocks and NB with different characteristics and optimization of the injection parameters and particle size as regards the availability and minimized retention in the injection zone.

IV.2.b. Water-soluble catalyst precursors

As noted above, the first publications of Clark *et al.*,[114, 185] devoted to the behaviour of organosulfur compounds in the presence of water-soluble Fe^{2+}, Co^{2+}, Ni^{2+}, Ru^{3+}, Pt^{2+}, Pt^{4+}, *etc.* salts revealed considerable activity of Pt^{2+}, Pt^{4+}, Pd^{2+}, Al^{3+} and VO^{2+} towards thiophene and thiophane transformations in water at 200–240 °C. However, it is noteworthy that intense hydrogen redistribution reactions taking place in the case of thiophene in the presence of Pt^{4+} give a considerable quantity (27%) of a hydrogen-depleted coke precipitate insoluble in dichloromethane and also gases (mainly butanes). In a study of the transformations of Canadian NB in water containing metal chlorides ($RuCl_3$ and $FeCl_3$), the same authors[186] ascertained that Ru provides a higher degree of desulfurization (15.3% at 375 °C) and a higher yield of coke, while iron is less active in desulfurization (11%) and provides a minimum yield of coke. Both metals catalyze the water gas shift reaction. The lower asphaltene content in the product of Rh-catalyzed NB reactions attests to high activity of this metal in hydrogen transfer reactions giving coke. The supply of hydrogen to the reaction mixture decreased the yield of coke several-fold.

The methods for downhole upgrading of oils using water-soluble catalyst precursors developed at the laboratory stage are briefly characterized in Table 11. The comparison of metals in terms of influence on the NB viscosity during aquathermolysis is not quite correct because the rheological properties of the transformation products are determined by the SARA composition of the initial crude oil and by the time passed since the end of treatment. Generally, the most pronounced decrease in the viscosity is

‡ The permeability is measured in Darcy (D): 1 D = 1.02×10^{-12} m^2.

Table 11. Methods for downhole treatment of natural bitumen using water-soluble catalyst precursors developed at the stage of laboratory research.

Catalyst precursor	Feedstock	Experimental parameters	Miscellaneous additives	Result	Ref.
$VOSO_4 + NiSO_4 + Fe_2(SO_4)_3$ [$VO^{2+} : Ni^{2+} : Fe^{3+} = 1:1:5$ (mol.)]	Chinese heavy oils (oil field not indicated)	Autoclave, 240 °C, 24 h	Minerals (montmorillonite, kaolinite, quartz, calcite, *etc*.)	Compared with the experiment without a catalyst or additives: decrease in the contents of resins by 12.7 mass % and asphaltenes by 1.5 mass %; 1.5-fold increase in the H_2S yield; decrease in the average molecular mass of oil and asphaltenes; ~85% reduction of viscosity relative to native crude oil samples	187
Fe^{2+}	Liaohe and Shengli oils (China)	Autoclave, 240 °C, 72 h	Tetralin	Compared with the experiment without a catalyst or additives: increase in the $H : C_{at}$ ratio by 0.19; decrease in the contents of resins by 6.9 mass % and asphaltenes by 5 mass %; increase in the C_7-C_{14} fraction of saturates. A ~66% desulfurization; and up to 90% reduction of viscosity relative to the feedstock. The change in the characteristics is more pronounced in the presence than in the absence of tetralin	188, 189
Iron(II) sulfate + + phosphoric acid + + phosphomolybdic acid	Not indicated ($\rho_{15}^{15} = 0.9759$,[a] sulfur content 5.2%)	Autoclave, 350 °C, 72 h	–	Decrease in the viscosity by 96%, density by 32.5%, coking capacity by 47%; 53.8% desulfurization and 46.2% denitrogenation, decrease in the content of RAC	190
$NiSO_4$	Liaohe and Daqing (China)	Autoclave, 240 °C, 36 h	Minerals (kaoline, montmorillonite, quartz, calcite, *etc*.), tetralin	A 25% decrease in the average molecular mass of oil, reduction of viscosity by 61.32% (Daqing) and 84.39% (Liaohe), decrease in the content of RAC. The change in the characteristics is more pronounced in the presence than in the absence of tetralin and minerals	191
Phosphomolybdic acid	Benzothiophene	Autoclave, 300–360 °C	CO pressure	A 24%–90% conversion of CO (increasing with temperature); 2.4%–90% desulfurization (increasing with temperature and duration); the degree of desulfurization and selectivity to ethylbenzene are higher under CO pressure than under H_2 pressure	192
$VOSO_4$, $NiSO_4$, *etc*.	Core (oil field not indicated)	Autoclave, 240 °C	CO pressure	The reduction of oil viscosity is more pronounced under CO pressure with a catalyst than in the case of their separate action. The maximum reduction of the viscosity is provided by Fe^{2+}. The highest degree of desulfurization is achieved with Co^{2+}, Ni^{2+} and Zn^{2+}	146

[a] Density at 15 °C relative to water also at 15 °C.

provided by Co^{2+}, Ni^{2+}, Fe^{2+}, MoO_4^{2-} and Al^{3+} (Refs 146 and 188).

In all cases, the introduction of hydrogen donors or CO into the reaction mixture provides a higher degree of conversion as HCO and NB are depleted in hydrogen. Furthermore, there is the optimal concentration of hydrogen donors in the reaction mixture above which the product characteristics no longer change. It was hypothesized that the VO^{2+} and Ni^{2+} ions can be adsorbed on the clay mineral surface bearing negative charge, which results in the formation of catalysts similar to the industrial hydrocracking catalysts.[193]

IV.2.c. Oil-soluble catalyst precursors

Comparative experiments on aquathermolysis of resins and asphaltenes of the Liaohe oil showed [194] that the degrees of resin and asphaltene conversion were higher in the case of oil-soluble catalyst precursors (Ni and Fe naphthenates) than with sulfates of the same metals (Fig. 10). By the degree of conversion is meant the conversion of asphaltenes and resins to hydrocarbons, a decrease in the average molecular mass and heteroatom content. Apparently, the higher activity of metal sulfides formed from oil-soluble precursors is due to their smaller particle size.[160] Apart from this, oil solubility allows these precursors to penetrate into

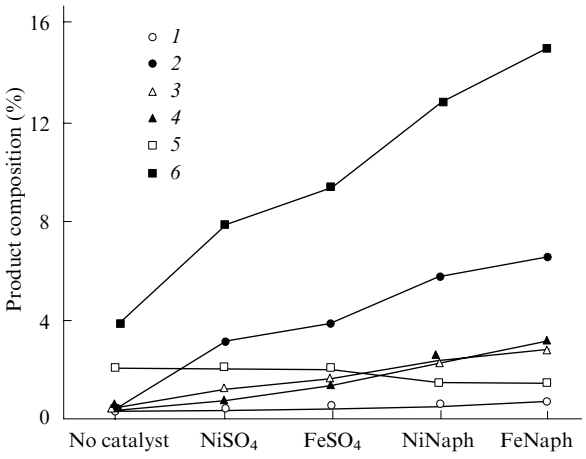


Figure 10. SARA composition of the products of asphaltene aquathermolysis (280 °C, 48 h) in the presence of various catalysts (Naph is naphthenate).[194]
(*1*) Gas, (*2*) saturates, (*3*) aromatics, (*4*) resins, (*5*) toluene-insoluble products, (*6*) total conversion.

small oil-saturated pores, which are inaccessible for an aqueous solution, and propagate together with oil throughout the reservoir rather than be retained in the injection zone.

It was stated[160] that the type of an organic compound bound to the metal does not affect the activity of the catalyst formed *in situ* provided that the rate of thermal decomposition of the precursor is not too low and does not limit the rate of the whole process. Table 12 presents the brief characteristics of some downhole treatment methods with the use of oil-soluble precursors tested in the laboratory.

It was noted[204 – 206] that Cu and Fe sulfonates provide more pronounced decrease in the viscosity and higher redistribution of the SARA composition towards higher contents of hydrocarbons and lower contents of RAC than the naphthenates of these metals. Similar observations were made in a study of the complex compound of iron and Gemini type surfactant.[207] Study of the aquathermolysis of the Karamay oil (China) in an autoclave at 170 °C for 24 h resulted in the reduction of viscosity by 69.3% for $Fe_2(SO_4)_3$, by 83.5% for iron naphthenate and by 99.3% for the proposed Gemini type precursor. Apparently, the surfactant properties of the catalyst precursors, *i.e.*, their ability to disperse asphaltene aggregates, play a role in this case.

Comparing the catalytic activities of various metals based on the published data is difficult because different precursors and different crude oils are used. No significant differences were detected between Fe, Ni, Co and Cu naphthenates in the change of SARA composition and reduction of the viscosity upon aquathermolysis of the

Table 12. Methods of downhole treatment of natural bitumen using oil-soluble precursors developed at the stage of laboratory research.

Catalyst precursor	Feedstock	Experimental parameters	Miscellaneous additives	Result	Ref.
Molybdenum oleate	Liaohe oil (China)	Autoclave, 240 °C, 24 h	–	Compared with native oil: moderate increase in the H : C_{at} ratio; 1.5 – 1.7-fold decrease in the average molecular mass of oils and asphaltenes; 1.4 – 1.7-fold decrease in the resin content and 1.4-fold decrease in the asphaltene content; decrease in the number of heteroatoms	195
Iron acetylacetonate	Jobo oil (Venezuela)	Autoclave, 250 – 300 °C, 24 – 72 h or flow-type reactor, stream temperature 273 °C, a solution of the precursor is supplied in a hydrogen donor	Tetralin, decalim	Compared with the experiment without the catalyst or tetralin: enhanced oil recovery; oil production starts earlier; decrease in the oil density and viscosity, increase in the H : C_{at} ratio, decrease in the content of V and Ni due to deposition in the reservoir pores. Comparison of tetralin and decalin: the reduction of viscosity and density is more pronounced in the presence of decalin. The degree of reduction of the viscosity increases with increase in the temperature of aquathermolysis in a hydrogen donor	196 – 198
Molybdenum arylsulfonate	Shengli oil (China)	Autoclave, 200 °C, 24 h	–	Compared with the native oil: 5.2 mass % decrease in the resin content, 1.2 mass % decrease in the asphaltene content; 97% reduction of viscosity; 1.15-fold increase in the H : C_{at} ratio; decrease in the nitrogen and sulfur contents, increase in the oxygen content; oxygen and nitrogen organic compounds present in the reaction gas	199
Nickel naphthenate	Liaohe oil	Autoclave, 280 °C, 24 h	HCO_2H (7 mass % relative to the oil)	Compared with the experiment without formic acid: 22.3% greater reduction of viscosity; 4.03 mass % decrease in the asphaltene content, 4.15 mass % decrease in the resin content; 0.26 mass % decrease in the sulfur content	200

Table 12 (continued).

Catalyst precursor	Feedstock	Experimental parameters	Miscellaneous additives	Result	Ref.
Nickel arylsulfonate	Shengli oil	Autoclave, 200 °C, 24 h	–	Compared with the experiment without a catalyst: 5.35 mass % decrease in the asphaltene content, 3.11 mass. % decrease in the resin content; 71.85% greater reduction of viscosity; decrease in the average molecular mass of all groups of components; decrease in the content of heteroatoms; decrease in the content of C_{26+} hydrocarbons in the saturates fraction	201
Nickel formate	Not indicated (viscosity 3716 mPa s at 50 °C)	Autoclave, 240 °C, 24 h	HCO_2H (7 mass % relative to the oil)	Compared with the experiment without formic acid: 22.3% greater reduction of viscosity; compared with the experiment without a catalyst: 55.4% greater reduction of viscosity; as the concentration of HCO_2H increases from 1% to 7%, the contents of saturates and aromatics in the product increase and the content of RAC decrease	202
MOLYVAN (molybdenum-containing additive)	Water–oil emulsions	Autoclave, 425 °C, 4 h	Carbon, CO and H_2	Compared with the feedstock: decrease in the density and sulfur and metal contents; 80.4 vol.% increase in the content of the IBP–524 °C fraction	148
Iron oleate	Shengli oil	Autoclave, 200 °C, 24 h, and reservoir model	–	Compared with the feedstock: reduction of viscosity by 75%, decrease in the content of RAC and heteroatoms; 1.9-fold enhancement of oil recovery in testing of cyclic steam stimulation on the reservoir model	203

Shengli oil (China). The most pronounced viscosity reduction was observed for copper naphthenate (82.9%), while for naphthenates of other metals, it was in the 75%–78% range.[206] A comparison of Cu and Fe^{III} sulfonates demonstrated that the former reduces the viscosity to a somewhat higher degree by promoting the C–C and C–S bond cleavage reactions in asphaltene molecules, whereas iron naphthenate catalyzes more efficiently ring opening reactions of heterocycles and isomerization.[208] The SARA composition of the products and the viscosity reduction were nearly equal in the presence of Fe^{II} and Ni dodecylbenzenesulfonates.[209] At aquathermolysis temperature of 150–175 °C, Fe^{III} can increase the oil viscosity by 3%–7%, probably, as a result of oxidative reactions.

As has already been shown, aquathermolysis changes characteristics of crude oil and oil components even without a catalyst. When a catalyst is added, these changes become more pronounced. For example, the IR spectra no longer exhibit bands corresponding to carboxy groups or C–O–C, S=O and C=N stretching bands.[205, 210, 211] Data of the thermal analysis of oil asphaltenes before and after catalytic aquathermolysis indicate [210, 212] that the TGA curves of converted asphaltenes shift to higher temperature. In other words, asphaltenes become thermally more stable, the proportion of aromatic nuclei increases and the proportion of peripheral alkyl substituents decreases.[213]

According to ^{1}H NMR spectroscopy data, the aromaticity of resins and asphaltenes increases after catalytic aquathermolysis owing to decrease in the content of alkyl chains, while the aromaticity condensation (the number of aromatic and naphthene rings in the nucleus) decreases [204, 205] owing to partial hydrogenation of the rings. The average length of alkyl chains and the degree of substitution of hydrogen atoms in aromatic rings also decrease. According to another study,[211] the aromaticity of resins and asphaltenes decreases as a result of partial ring hydrogenation and hydrocracking.

Gas chromatography/mass spectrometry (GC/MS) of saturated and aromatic hydrocarbons of heavy crude oil after catalytic aquathermolysis revealed increased contents of $C_{13}-C_{28}$ n-alkanes and naphthalene homologues with C_1-C_6 alkyl chain and appearance of C_2-C_{13} carboxylic acids.[213, 214] Figure 11 presents the selected ion mass chro-

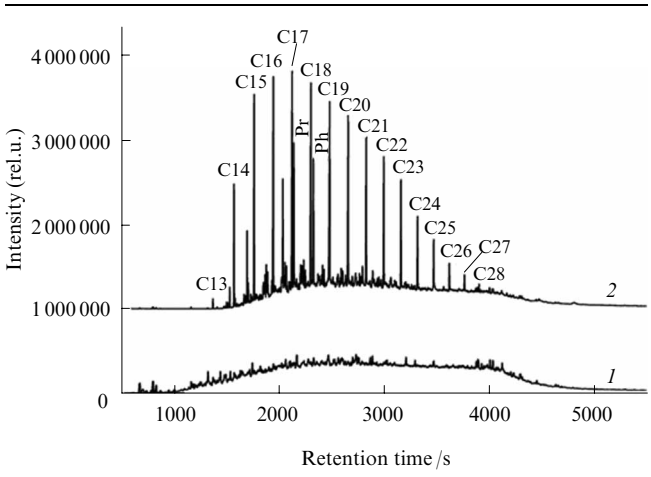


Figure 11. Selected ion mass chromatograms (m/z 57) of saturated hydrocarbons of oil before (*1*) and after (*2*) catalytic aquathermolysis.[213]

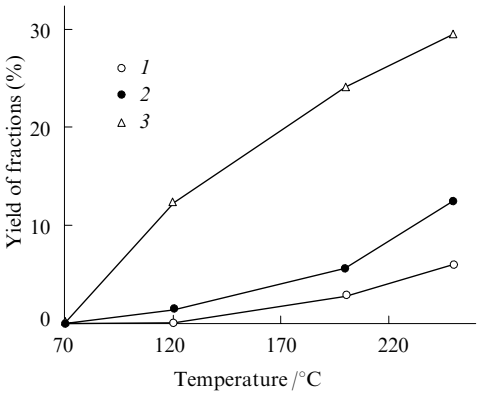


Figure 12. Curves of atmospheric fractional distillation of the original crude oil from the Ashalchinskoye deposit (*1*) and the product of non-catalytic (*2*) and catalytic aquathermolysis (*3*).[215]

matograms (*m*/*z* 57) of saturated hydrocarbons before and after catalytic aquathermolysis of heavy oil from a Chinese oil field. The chromatogram of the initial oil shows a continuous 'naphthene-aromatic crest'. After aquathermolysis, intense peaks of $C_{13}-C_{27}$ n-alkanes and isoprenoids appear. Intense formation of naphthalenes with shorter alkyl chains compared with the initial oil is observed. The catalytic aquathermolysis is also accompanied by substantial formation of n-alkylbenzenes,[215] alkylcyclohexanes and alkylnaphthalenes.[213] The content of C_{12}, C_{16} and C_{18} n-alkylbenzenes increases ~5-fold after the catalytic aquathermolysis of oil of the Ashalchinskoye field.[215] The aqueous phase separated from the oil after the reaction contains carboxylic acids, phthalates, phenols, alcohols and aldehydes. The volatile products of aquathermolysis contain C_7-C_{12} alkanes, C_9-C_{13} ketones, fatty acids and aldehydes. Apparently, compounds with oxygen-containing functional groups, possessing surfactant properties, would promote oil displacement from the reservoir but may complicate oil dehydration in the field.

After aquathermolysis, the fractional composition of oil changes. The catalytic aquathermolysis of the oil from the Ashalchinskoye field increases the content of the 70–200 °C fraction 6-fold (Fig. 12),[215] and after aquathermolysis of the vacuum residue in the presence of molybdenum naphthenate, the total yield of IBP–500 °C distillates increases from ~8% to 60%.[216] The formation of light hydrocarbons is one of the causes of reduction of oil viscosity and increase in oil recovery and, undoubtedly, this justifies the use of downhole upgrading.

IV.3. Auxiliary chemicals and physical impacts proposed for intensification of aquathermolysis

Of certain interest are studies[212,217] in which it is proposed to increase the gas–oil ratio§ and, hence, enhance oil displacement by injecting the catalyst together with carbamide, ammonium carbonate or ammonium hydrogen carbonate, which decompose at temperatures of 158, 58 and 35 °C, respectively, to give CO_2 and NH_3. The dissolution of CO_2 in heavy oil additionally increases the oil mobility. Ammonia reacts with petroleum acids to give surfactants, which are involved in oil displacement.

An extensive investigation area is combination of wave and catalytic impacts on NB in the reservoir. It was shown[210,218,219] that combining catalytic aquathermolysis with sonication has a more pronounced influence on the reduction of viscosity, redistribution of the SARA composition and decrease in the content of heteroatoms than the catalytic aquathermolysis alone. Probably, ultrasound can change the structure of asphaltene aggregates with evolution of immobilized hydrocarbons, which induces a change in the SARA composition. The acoustic treatment also increases the dispersion effect by promoting better mixing of the chemicals with oil, which is important under downhole conditions. Cavitation in the liquid is also possible, which additionally facilitates dispersion and mixing.

Vibration-assisted aquathermolysis of the Shengli oil in an autoclave (vibrostand experiment) with a 20 Hz vibration frequency and 3 m s^{-2} vibration acceleration results in greater (by 6.6%) reduction of the viscosity, decrease in the contents of resins (by 1.6 mass %) and asphaltenes (by 1.6 mass %) and increase in the $H:C_{at}$ ratio of the oil compared with the experiment without vibration.[220] In the vibration-assisted reservoir model experiments, oil recovery increased by 6.7%. Vibration cannot induce a new reaction mechanism but can enhance the degree of destruction of side chains, hydrogenolysis, *etc*.

In the case of aquathermolysis without hydrogen donors, it is expedient to use catalysts of water gas shift reaction. As shown by Jia *et al.*,[161] Ni, Co and Mo catalyze the water gas shift reaction (391 °C); however, alkali metals (K, Na, Li) are the most efficient catalysts.[99] As has already been noted, in the presence of alkalis, CO is converted to the formate, which is involved in hydrogenation. However, potassium completely inhibits the reactions. Therefore, it is necessary to choose between ionic hydrogenation and water gas shift reaction catalyzed by alkalis and cracking and hydrolysis processes suppressed in alkaline medium.

When NB is extracted using steam stimulation, up to 5 tons of steam per ton of NB is injected into the reservoir, which is, first, expensive and, second, results in water encroachment. This makes the development of the given field site unprofitable. In this connection, to decrease the steam consumption for downhole upgrading, it is topical to investigate alternative reservoir heating methods: microwave,[180] radiofrequency[221] and electric[222] ones. The reservoir can be heated by the heat of reactions in binary mixtures the components of which are injected *via* two separate channels in the cold state and react when meet in the producing formation.[223] These binary mixtures can contain, for example, ammonium nitrate, carbamide or hydrazine combined with sodium nitrite or alkali metal hypochlorites.[224] The exothermic reaction yields a gas, which also enhances oil recovery. Hydrogen and heat can be generated in the reservoir upon the reaction between aluminium or calcium and water. Water encroachment of the reservoir is reduced owing to binding of water into metal hydroxides, and hydrogen thus formed participates in hydrocracking.[223,225] The reaction of aluminium with water in alkaline medium gives 16.8 mJ of heat per kg of Al, while the reaction of calcium in water in acidic medium gives 12.6 mJ per kg of Ca.[225]

To conclude this Section, we would like to note that despite quite a number of laboratory studies of the catalytic

§ Gas–oil ratio is the amount of gas (m^3, STP) per ton of produced oil.

downhole treatment of HCO and NB, in our opinion, currently, the transformation pathways of RAC are not adequately analyzed. No long-term field tests of catalytic aquathermolysis are known and no data are available on the distribution of hydrogen donors or catalysts in real reservoirs. Little attention is also paid to coke formation in catalytic and non-catalytic aquathermolysis.

V. Problems and prospects of implementation of catalytic aquathermolysis under reservoir conditions

While considering the prospects for investigations dealing with aquathermolysis, it is important to mention the works that describe the results of testing of the downhole catalytic treatment in the field using water-[188, 189, 193] and oil-soluble [195, 204, 205] catalyst precursors. First, steam was injected into the well to heat the reservoir and, after that, the catalyst precursor (and hydrogen donor [189]) was injected. After 5–10 days, oil production was started. The produced oil differed from the native one by lower (~4-fold) viscosity, lower contents of RAC, sulfur, nitrogen and oxygen, and higher $H:C_{at}$ ratio. Furthermore, enhanced oil recovery was detected and the steam-to-oil ratio could be reduced in comparison with testing without catalysts. Table 13 summarizes the results of field testing of the water-soluble catalyst based on VO^{2+}, Ni^{2+} and Fe^{3+} salts at the Liaohe oil field (China).[193] First, 400 m^3 of steam, then a catalyst solution and again 1600 m^3 of steam were injected. After 5–7 days, oil production was started. It can be seen that oil recovery per cycle increased by 30%–60% and oil viscosity markedly decreased, which is of high importance for the field conditioning and pumping of oil.

The commercial implementation of downhole aquathermolysis requires solving a number of problems, most important of which are the following:

— optimization of the dosing rate and search for available hydrogen donors and catalysts; for the use of nanoparticles, study of the particle distribution in various rocks;

— testing of methods of reservoir heating that would be more cost efficient than steam injection;

— detailed study of the distribution of various types of catalysts (nanoparticles, oil- and water-soluble catalysts) in real oil fields and prevention of atmospheric emission of hydrogen sulfide formed in the aquathermolysis.

The fact of sorption of metals of oil-soluble catalysts by the rock (kaolin) found by Petrukhina *et al.*[215] suggests that the quantity of the catalyst may be decreased and heterogeneous catalysis may be realized within the rock, similarly to the CAPRI process but without placing the heterogeneous catalyst around producing wells. If catalyst precursors are used as suspensions or microemulsions, particle size optimization for the catalyst is required. Suspensions of microparticles are less stable; therefore, microparticles are inferior to nanoparticles not only in the catalytic activity but also in the uniformity of distribution and the reservoir coverage. However, the synthesis of nanoparticles, as noted by Shokrlu and Babadagli,[174] is quite expensive and, hence, microparticles are not rejected either. It is of considerable interest to study in-depth the non-catalytic effects of nanoparticles and metal organic compounds having surfactant properties on the rheological characteristics of oil.

Currently, there is no cost-effective method for delivery of hydrogen into the reservoir, because tetralin proposed in many publications can hardly be used on an industrial scale due to poor availability. Catalytically cracked gas oils, hydrogenated coker gas oil and heavy straight run diesel fractions could serve as more readily available sources of naphthene-aromatic hydrocarbons.

A possible trend of development of aquathermolysis is upgrading the produced oil–water emulsions on the surface. This provides both the separation of emulsion and production of synthetic oil. The process can be performed under synthesis gas pressure [149] and in super-[179] or subcritical water similarly to the Aquaconversion process developed by the Foster Wheeler company (USA).[226] However, for implementation of the ground-level aquathermolysis, it is necessary to consider the problem of equipment corrosion in sub- and supercritical water even in the absence of salts, acids and alkalis.[40]

Yet another possible trend for the development of aquathermolysis is a combination with other methods for HCO and NB recovery: low-temperature oxidation (LTO) and *in-situ* combustion (ISC). Conducting LTO in the presence of water was shown [130, 227] to smooth down the adverse effect of oxidation such as an increase in the crude oil viscosity and acid number and a change in the composition towards increased content of heavy fractions. The content of coke, carbenes and carboids in oil after oxidation in the presence of water is lower than after dry LTO but still somewhat higher than after aquathermolysis. The total acid

Table 13. Results of field testing of aquathermolysis in the Liaohe oil field.[193]

Well No.	Steam stimulation cycle without a catalyst		Steam stimulation cycle with catalyst injection		Oil recovery enhancement		Reduction of oil viscosity (%)
	oil production /tons	duration of oil production period /days	oil production /tons	duration of oil production period /days	tons per cycle	ton day^{-1}	
DU 67	825	58	1105	74	280	0.7	95.0
Shu 1-32-41	1678	70	2041	130	361	−8.3	74.9
Shu 131-40	904	44	1199	67	295	−2.6	60.1
Shu 1-38-32	381	69	1080	120	699	3.5	73.6
Shu 1-7-51	538	146	822	66	285	8.8	75.6
Shu 1-31-24	843	49	1200	62	357	2.2	88.9
Qi 108-23-15	788	141	1322	150	534	3.2	63.1

number[¶] of oil and the oxygen content of oil after LTO in water are close to these characteristics of the original oil. In the presence of aqueous phase, the yield of CO_2 increases, which was attributed[130] to decarboxylation of acids by ionic mechanism.

The lower crude oil viscosity and density and the yield of coke, *i.e.*, the degree of oxidation, in the case of LTO in the aqueous phase may be caused by hydrogen bonding between peroxide radicals and water molecules.

$$RO_2^{\bullet} + HOH \longrightarrow RO^{\bullet}\cdots HOH$$

The hydrated peroxide radicals retain the ability to eliminate hydrogen from hydrocarbons but the rate constant for this reaction decreases by a factor of several tens with respect to non-hydrated radical, and the activation energy increases.[228]

$$RO^{\bullet}\cdots HOH + RH \longrightarrow ROOH + R^{\bullet} + H_2O$$

In addition to mitigation of the adverse effect of oxidation on oil characteristics, the combination of LTO and steam stimulation enhances the oil recovery compared with that induced by steam stimulation alone.[229] This is due to the fact that oxidation generates more heat and gives rise to displacing agent (surfactant). Apart from these effects, one should take into account the possible acceleration of thermal cracking upon steam stimulation as a result of free radical generation during LTO. The hydroperoxides formed upon oxidation in the first stage (LTO) split into radicals in the second stage (steam stimulation) at a lower temperature than hydrocarbons. The radicals thus generated react with hydrocarbons and thus propagate the chain. As a result, cracking leads to higher yield of distillate fractions.[230] The longer the second stage, the more pronounced the viscosity reduction after LTO.

The ISC process with the arrangement of a bed of the $Co-Mo/\gamma Al_2O_3$ heterogeneous catalyst (CAPRI process) in the zone of steam injection into the model reservoir inhibits the coke formation and coke deposition on the catalyst (from 27.53 mass % to 11.3 mass % at a steam-to-oil ratio of 0.1 ml ml^{-1}); enhances the reduction of oil viscosity, desulfurization (from 3.4% to 25.6%) and demetallization (from 16.8% to 70.5%); decreases the asphaltene content (from 5.1 mass % to 2.4 mass %) and produces light fractions.[231] The researchers attributed these results to water gas shift and coke gasification reactions giving hydrogen and to inhibition of radical recombination by hydrogen saturation of the radicals. The contents of asphaltenes, sulfur and V and Ni in crude oil and the content of coke on the catalyst decrease with increase in the steam-to-oil ratio; hence, steam appears to have mainly a physical action as it dilutes the reaction mixture and thus reduces the probability of radical recombination. Furthermore, steam merely 'steams out' the high-molecular-mass coke precursors from the catalyst surface. Thus, the works dealing with downhole catalytic transformation of HCO and NB by combining LTO or ISC with steam stimulation are of practical interest. It should be borne in mind that the optimal air : steam ratio ensuring the highest oil recovery is specific to each crude oil. A too high ratio would give rise to excessive oxidation and, hence, a considerable increase in the oil viscosity, which would hamper the oil production. Conversely, with a low proportion of injected air, the degree of oxidation is insufficient for the formation of the required amount of the displacing agent, surfactant and heat for oil displacement.

* * *

The material summarized in the review demonstrates the diversity of the proposed engineering solutions and good prospects for the development of research into the downhole upgrading of HCO and NB. Generally, the interest in this area increases from year to year, although, despite numerous studies, the results are largely empirical. The details of transformation of oils that differ substantially in the SARA composition and contents of sulfur compounds of various classes are still unexplored. Studies of this type were carried out for LTO, which demonstrated fundamental differences in the changes of physicochemical and rheological characteristics and SARA compositions and identified a number of serious problems hampering LTO of heavy resinous crude oils.[232] Most of studies in the catalytic aquathermolysis deal with Chinese sweet oils. It is of both theoretical and practical interest to compare the aquathermolysis behaviours of paraffinic and resinous, sulfide, thiophene and mercaptan crude oils, and crude oils with substantially different contents of 'archipelago' and 'island' asphaltene fractions, which differ in the structure and molecular mass as well as to study the mechanisms of viscosity reduction, generation of hydrocarbons, redistribution of the SARA composition and coke formation.

A significant phase of the research into the downhole upgrading is testing of the processes in pilot units, *i.e.*, reservoir models, because numerous experiments in autoclaves form the first phase, which only discloses the transformations of crude oil. Only using pilot units, it is possible to study the process of distribution of the catalyst and chemicals throughout the reservoir and the real-time variation of oil characteristics during the test, to monitor the reservoir damage caused by the formation of carbon deposits and so on.[233] This research area is multidisciplinary, it requires integrated approach and coordination of specialists of various fields of knowledge in order to create a scientific base.[234] The existing knowledge is quite sufficient for performing further fundamental research not only for the gaining scientific data but also for full-scale implementation of the catalytic aquathermolysis in oil fields.

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