Research Article

Catalytic Thermal Liquefaction of Oil Shale in Tetralin

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A short review on the publications concerning thermal liquefaction of solid fuels in the environment of hydrogen donor solvents and catalysts is compiled. New experimental results on the catalytic thermal dissolution of oil shale in tetralin as the hydrogen donor solvent in a batch autoclave are presented. The impacts of pyrolysis temperature, duration, and catalyst type on the yields of gas, maltenes, asphaltenes, preasphaltenes, and coke in the presence of tetralin are described.

1. Introduction

Since 1980, discovery of new locations of "conventional" oil sources has fallen below production, and by 2050 discovery of new deposits is supposed to fall to zero [1]. As reserves of conventional crude oil continue to decline, unconventional feedstocks have to be investigated and upgraded to meet the increasing demand for transportation fuels.

In our previous studies [2–5], procedures were developed to increase the extraction yield of liquid products from Estonian oil shale kukersite about 1.5 times. For this aim, the theoretical basis for supercritical dissolution and low-temperature pyrolysis (350–420°C) of the oil shale up to the intermediate product of thermal destruction, thermobitumen (TB), followed by its solvent extraction were worked out. The high molecular and viscous TB obtained needs upgrading to liquid fuels by hydroprocessing. Hydrogenation of the unstable TB [6] has not been systematically studied.

In general, the more asphaltenes present in a fuel, the poorer its burning quality. The ability of hydrogen-donor solvents to depress coke formation releasing hydrogen and thereby converting asphaltenes and heavy hydrocarbons to more valuable lower boiling products has been wellknown. At that, paraffines and single-ring naphthenic compounds are ineffective hydrogen transfer agents, a condensed ring naphthenic compound such as decalin is somewhat more effective, whereas a mixed naphthenic-aromatic condensed ring compound such as 1,2,3,4-tetrahydronaphthalene (tetralin) is much more effective.

In this work, effectiveness of tetralin and several catalysts on the formation of gas, liquid fractions soluble in *n*-hexane, benzene and tetrahydrofurane, and solid residue in thermal decomposition of kukersite, rather on the upgrading of the unstable TB *in statu nascendi*, has been studied.

1.1. Thermal Decomposition of Tetralin Alone. Hooper et al. [7] have shown that tetralin (T_{bp} = 207.6°C) alone is quite stable. In the range of low-temperatures pyrolysis, 300–450°C, tetralin decomposes only insignificantly into naphthalene by dehydrogenation of the saturated ring, and into 1-methyl-indan by rearrangement of the ring. For example, after two hours reaction at 400 and 450°C, the yield of naphthalene was only 0.5% and 0.8% and that of 1-methyl-indan 0.7 and 5%. In the conversion of tetralin, there was a sharp increase, 10% in hour, after 2 hours duration at 450°C.

Benjamin et al. [8] studied the pyrolysis products of 1-^{13}C-tetralin by ^{13}C n.m.r. spectroscopy. He found that heating of tetralin during 18 hours at 400°C caused about 1% decomposition. But at 500°C after 1 hour, only about 25% of tetralin remained. Naphthalene was the major product besides small amounts of 1-methyl-indan, ethyl benzene, toluene, and several other minor compounds. Inspite of the fact that hydrogenation-dehydrogenation reactions of hydrocarbons without changes in carbon skeleton can reach state of equilibrium, it was found that no equilibrium between tetralin and naphthalene in an atmosphere of hydrogen (6.20

and 12.75 MPa) was established without catalysts or in the presence of 30% vitrinite. When tetralin was heated under hydrogen pressure, benzene and its alkyl substituents were formed.

1.2. Reaction of Solid Fuels with Tetralin in Inert Atmosphere. Tetralin, being heated in the mix with a solid fuel, mainly with coals, acts as an active hydrogen donor.

Franz [9] found that when 1,1-d_2-tetralin was added to subbituminous Kaiparowitz coal, the total transformation of the coal into tetrahydrofurane extract and gases from the dry coal reached 80% after heating during 35 min at 427°C. As indicated by ^{2}H n.m.r. results, in the first 10 min introduction of deuterium was favored at aliphatic sites, and afterwards in aromatic structures. At that, varieties of solid fuels differed strongly in reactivity with tetralin.

Pajak and Socha [10] showed on the basis of naphthalene formation that the coals with high content of functional groups being readily reduced (quinones, ketones, certain aromatic compounds) were the most reactive with tetralin, and the rate of the reactions was accelerated by pressure of inert gases (5–50 MPa N_2). The bimolecular mechanism of the reaction of hydrogen with coal was suggested for the low-rank coals (content of O_2 about 20%), whereas the high-rank coals (content of O_2 about 5%) were less reactive, and their hydrogenation was rather unimolecular and not affected by pressure.

Robinson and Cummins [11] studied decomposition of 350 g carbonaceous Colorado oil shale containing 35% of OM in 810 mL tetralin in the range of temperatures 25–350°C and durations 24–144 h. The total yield of extract using subsequently tetralin and benzene increased sharply in the range of temperatures 300–350°C reaching 85% after 48 h and 95% from kerogen after 144 h. The gas yield was about 6% consisting mainly of moles of hydrogen, carbon dioxide, and methane. The extract obtained at 350°C was fractionated between 45–50% of pentane insolubles and pentane soluble material. The latter was fractionated in an alumina column with different solvents as follows: 25–30% of oils, 20–25 % of resins, and 5% of wax. The composition of oil (eluted with pentane) and wax (precipitated in 2-butanone at −5°C) was nearly the same over the temperature range. But oxygen content of the resins (eluted with mix of benzene, ethanol, and acetone) and pentane insoluble fractions decreased with increase in temperature. The average molecular weights of the oil (350–375), wax (355–480), resin (575–650), and pentane insoluble fractions (1200–1300) did not change appreciably with increase in temperature.

1.3. Influence of Catalysts on the Hydrogenation of Coals in the Environment of Hydrogen Donor Solvents and Gaseous Hydrogen. The impact of various catalysts (iron oxide, metallic tin and lead, tin oxide, and supported nickel-molybdenum as reference) on the transfer of hydrogen from the gaseous phase to coal with and without donor solvent tetralin was investigated by Bacaud [12]. It was found that tetralin donated hydrogen in the absence of catalysts but addition of the catalysts increased the consumption of gaseous hydrogen.

Hirano et al. [13] investigated liquefaction of an Australian subbituminous coal under the pressure of 5–7.5 MPa hydrogen at 420°C in batch autoclaves using as solvents 150% of 1-methyl-naphthalene or the hydrogenated mixture of anthracite oil and creosote oil, and as catalysts inexpensive pyrite and synthesized α-FeOOH in the amount 0.02 mmol/g of Fe. The slurry product was distilled under vacuum (ASTM D1160) into moisture, naphtha fraction ($T_{bp} < 220$°C), solvent fraction (T_{bp} 220–538°C), and residue. The oil yield was determined as the sum of the yields of naphtha and solvent fractions, subtracting the solvent amount applied supposed to be invariable during the liquefaction. Both pulverized catalysts increased the coal total conversion (%, d.a.f.) from 49.5 to 80–85% and oil yield from 29% to 44–45%.

Kafesjian [14] investigated in his doctoral work the thermal dissolution of oil shale from US Green River formation Hell's Hole Canyon in cyclohexane and tetralin. The experiments were conducted in a 1-litre autoclave reactor during 24 hours in the range of temperature 274–410°C using 70 gram of the shale and 500 mL of the solvents. Cyclohexane, being in the supercritical state under the extraction temperatures ($T_c = 280$°C, $T_{bp} = 84.16$°C), resulted in somewhat greater yields than tetralin extraction ($T_c = 449$°C, $T_{bp} = 206$–208°C) in runs below 365°C but approximately the same yields as tetralin at higher temperatures. As far the kerogen of Hell's Hole Canyon oil shale was relatively low aromaticy ($f_a = 0.19$), both solvents were found to be capable of removing over 90% of the original organic material at temperatures between 360–375°C, whereas in extraction of highly aromatic Antrim oil shale ($f_a = 0.5$) the oil yield was 71.2% in tetraline and 50.5% in cyclohexane at 364°C. The simulated distillation analysis showed that the high boiling fraction, 375–425°C, was about twice larger for tetralin extracts (35–40%) than that for cyclohexane extracts (19-20%). The difference was attributed to the supercritical phase of cyclohexane penetrating the kerogen longer fragments whereas being cooled to liquid-phase tetralin recovered only kerogen, which had undergone sufficient thermolysis to become soluble. Cyclohexane was easily removed from the extract by distillation at 0.7-0.8 whereas complete removal of tetralin failed. So, an approximate value of the weight percent of the remaining solvent was determined by chromatography and its contribution was eliminated from the results of analysis. The mole ratio H/C being 1.56–1.67 in the organics of the initial samples increased in cyclohexane extracts to 1.65–1.71 and decreased in tetralin extracts to 1.46-1.54. The peculiar hydrogen-donor ability of the reagents was not discussed in this work.

In Colorado School of Mines [15] direct hydrogenation of Australian oil shale (77.83% of ash) with gaseous hydrogen was studied in the environment of tetralin, and hydrogen nondonor solvents as light gas oil (LGO) and heavy gas oil (HGO) produced by fractionation of the pyrolysis oil. The solvent-to-shale ratio was 10 : 1 and initial pressure of hydrogen 2.1–5.5 MPa. Liquids were separated by acetone washing of the product slurry, followed by Soxhlet extraction of the residue with a solution of 50% methanol and 50% benzene. The oil yield obtained under the optimum

conditions of the hydroprocessing (425°C, 5.5 MPa H_2 pressure, and 60 min residence time) surpass that formed in Fischer assay (92.7 L/t) as much as 1.58 times in tetralin, 1.44 times in LGO, and 1.39 times in HGO. The increase in oil yield was explained by two primarily factors: (i) the lower temperatures employed inhibited secondary condensation/coking reactions and (ii) the presence of donatable hydrogen quenched free radicals. Noteworthy is that organic carbon conversion was found to be unchanged in the run in tetralin when hydrogen was replaced by helium. So, it was concluded that no molecular hydrogen is needed, as long as hydrogen donors were present in the liquid phase. Simulated distillation of the product oil obtained in tetralin showed 62% to boil below 343°C and 44% of the oil to be in the diesel oil range (218–316°C). Regrettably, compositions of the oils obtained in helium and hydrogen were not compared, and the procedure of how the high boiling solvents (tetralin—207, LGO—215–321, and HGO—321–391°C) were separated from the oils was not presented in this paper.

1.4. Hydrogenation of Heavy Residues and Asphaltenes in Hydrogen-Donor Solvents. The most research works in the field of hydro treatment by means of hydrogen donors deal with heavy residues and asphaltenes.

It was found [16] that the ratio 2 : 1 of tetralin to Arabian heavy vacuum residuum provided a sufficient excess of tetralin at noncatalytical hydrocracking at temperatures 400, 420, and 435°C and pressure of nitrogen 0.5 MPa. At that, overmuch tetralin was not decomposed under the conditions studied, whereas the spent donor was dehydrogenated. As results, coke formation was inhibited, 50% of asphaltenes were converted to lighter fractions and degree of desulphurization was increased.

Behar and Pelet [17] studied thermal cracking of asphaltenes precipitated from Boscan crude oil. In this work (0-1): 1 of benzene or tetralin and/or water was added to asphaltenes. The temperature range tested was 350–430°C and heating time 0–9 h. The cracking was conducted in sealed gold tubes under initial pressure of nitrogen 0.5 MPa to keep the solvents in the liquid state. The fractions C_6–C_{13} and $C_{14}+$ were extracted subsequently from the cut tube with pentane and chloroform. The maximum conversion degree overcame 90% under the conditions 390°C and 3 h. At that, about 50% from the asphaltenes was transformed into coke without solvents and also in the environment of benzene, water, and their mix. But there was no coke formed in the environment of 10% or more tetralin, whereas the conversion degree of the asphaltenes was only 41–50%. Appearance of naphthalene showed that tetralin had acted as a hydrogen donor. Inhibition of coke formation revealed that hydrogen-transfer reactions were largely dominant over aromatization and condensation reactions. So, when tetralin was present, radicals, once formed, preferentially underwent H-transfer reaction. The resulting hydrocarbons were inactive and had the same carbon number as the initial radicals from primary cracking. In the same way, aromatic moieties did not undergo condensation reactions to form coke but remained small enough to be soluble in chloroform.

The presence of tetralin hindered completely coke formation at 390°C, but at higher temperatures there was a competition between polycondensation and hydrogen-transfer reactions.

The objective of the study of Rahmani et al. [18] was to examine the kinetics of coke formation from Athabasca asphaltenes separated from Athabasca vacuum residue in a closed reactor under a 4 MPa nitrogen atmosphere at 430°C in the environments of 1-methyl naphthalene, maltenes, and tetralin having hydrogen donor abilities 10, 3.44, and 0.12 mg/g of the corresponding solvents. It was shown that the hydrogen donating ability of the solvents and the hydrogen accepting ability of asphaltenes both played an important role in determining the ultimate yield of the target product in the work [18], coke. Tetralin as a donor solvent significantly enhanced conversion of asphaltenes and helped to suppress coke formation. Replacement of one third or more from 1-methyl naphthalene with tetralin decreased the coke formation rate factor from 0.17 to 0.028 min^{-1}.

Upgrading of an extra heavy crude oil (22% asphaltenes, viscosity at 80°C 1810 cP) from Orinoco Belt (Venezuela) was carried out [19] in a 300 mL batch Parr reactor at 315°C during 24 h adding as a radical initiator the mixture of 1 : 1.7 tertamylmethyl ether and methyl-tertbutyl ether, and to the mixture as a hydrogen donor tetralin and water in the ratios 1 : 1 : 10. The presence of the radical initiator had little effect, but the presence of tetralin decreased viscosity at 80°C to 110 cP. After completing the experiment, water and tetralin were separated from the oil and sand by vacuum distillation at 280°C. The remained oil was removed from the sand by solvent extraction with dichloromethane. The content of asphaltenes in the initial extra-heavy crude being 22% decreased up to 18% after upgrading in the environment of tetralin under the low severity conditions tested (315°C, 24 h).

A patent claim was published [20] for pyrolytic upgrading of the Venezuelan extra heavy crude oil (>500°C), to lighter distillates (<500°C) at least at temperature 380°C and pressure 5.5 MPa in the presence of 1–10% (2%) of octyl nitrate, MTBE or TAME as free radical generators having activity towards cracking reactions (resulting both, lighter distillates and coke), and as hydrogen donors 1–35% (33%) of tetralin or other like materials for inhibiting cycling reactions to produce coke.

Already in 1962 Langer et al. [21] have demonstrated that in visbreaking of crude residuum formation of asphaltenes could be decreased from 55% to 12% adding partially hydrogenated (71.2 H_2 n.v/v) tar fraction 371–482°C obtained from catalytic cracking of West Texas gas oil. It was shown that balance between the rates of hydrogen transfer and cracking was very dependent upon temperature, as far residuum cracking was initiated at about 371°C, whereas hydrogen transfer did not become appreciable below 427°C. Consequently, in any thermal cracking operation, regardless of hydrogen donor content, the concentration of polymeric products (asphaltenes) underwent an initial increase until the activation temperature for hydrogen transfer was reached, and polymerization and hydrogen transfer became competitive reactions. Therefore, the temperature range between 371 and 427°C should be spanned as rapidly as

possible. Furthermore, according to [22], with rare exception, no reaction between H_2 and organic compounds occur below 480°C in the absence of metal catalysts.

Gould and Wiehe [23] showed that at thermal conversion of petroleum resid fraction in the presence of a super reactive hydrogen donor, 1,2,3,4-tetrahydroquinoline, increased yield of lighter distillable liquids and formation of polyaromatic cores also. As far the asphaltene core was found not being converted in thermal conversion, the highest hydrogen donation established was rather an unwanted feature. Besides, reactive hydrogen donors greatly reduced the thermal reaction rate by reducing the free radial concentration.

1.5. Catalytic Hydroconversion of Heavy Fractions Using Hydrogen Donor Solvents. Several hydrocracking and -purification catalysts have been investigated and used for intensification of hydrogen transfer activity. Generally heterogeneous catalysts, such as cobalt, molybdenum, or nickel sulphides supported on alumina or silica-alumina and formed into pellets or beads have been used in the upgrading of heavy fractions. One exception to this is Raney-type catalysts, composed of fine grains of an alloy of nickel and aluminum or from various rare earths intermetallic compounds, which are effectively employed in unsupported states. Unfortunately, as a rule, the surface of the catalysts is deactivated by depositing coke. Thereby, the catalysts display short service life and bad operation stability.

Hydrodesulphurization of the heavy fraction (>320°C) of Pakistan petroleum crude containing 1.12% sulfur was investigated in a micro-autoclave in the presence of 0.5–10% various hydrogen donor solvents, and 1% catalysts in the 0.98 MPa inert atmosphere of N_2 at temperature 320°C during 3 h [24]. It was found that desulphurization percentage of the fraction decreased in the row of the hydrogen donors as follows: methanol—53, propanol—47, polyethylene glycol and tetralin—30, formic acid—15, and no donors—8%. As a surprise, it was shown that with decrease of methanol concentration from 1.5 to 0.5%, the desulphurization percentage increased from 22 to 52%. Regrettably, the region below 0.5% of the coreactant was not examined. The desulphurization efficiency of the catalysts tested decreased in the row: Mo-montmorillonite, Zn-ZSM5, Ni, Co-montmorillonite (fresh prepared), montmorillonite, and kaolin.

In [25], the direct liquefaction of a green waste composed of straw, wood, and grass was carried out using Raney Ni as the catalyst and tetralin as the solvent. The experiments were carried out in a 300 mL stainless steel autoclave filled with 70 g tetralin, 5 g green waste (which corresponds to 4.2 g of organic matter), and 1 g Raney Ni. The temperature range was 330–420°C and initial hydrogen pressure 1.6 MPa. The working pressure was between 4 and 7 MPa, depending on the reaction temperature. It was found that the presence of the catalyst had practically no effect on the oil yield being about 30% but amended the oil quality decreasing the oxygen content and increasing the hydrogen content in the oil due to promoting the dehydrogenation of the solvent.

Metecan et al. [26] studied hydroliquefaction of Göynük oil shale in the presence of 2–12% pyrite catalyst and toluene

as solvent under hydrogen initial pressure 2–8 MPa and temperature range 300–450°C. It was found that the pyrite catalyst increased considerably the conversion (from 35 to 58%) and extract yield (from 17 to 33%) at 350°C, however, since 400°C the effect was only some percentages.

In order to eliminate the fast poisoning of catalysts in heavy oils and residues, slurry-phase hydrocracking using water dispersed unsupported catalysts without any hydrogen donor solvent has been developed. Tian et al. [27] studied upgrading of the waxy residue from Petronas Petroleum Refinery in Malaysia in a 300 mL Parr batch reactor heated to 340°C and 7 MPa hydrogen pressure. It was found that a water dispersed Ni-Mo catalyst (prepared from a solution of Nickel chloride and ammonium molybdate in molar ratio 0.5) was effective and comparable with the presulfided supported commercial Co-Mo/alumina catalyst (each loading 0.3 %).

The latest hydrocracking technologies of heavy oil using unsupported heterogeneous solid powders or homogeneous water-soluble and oil-soluble dispersed catalysts were reviewed by Rana et al. [28], Zhang et al. [29], and Maity et al. [30].

It was noted in [28] that high conversion of complicated heavy oils and residua to high value liquids could be achieved when fine particles of hydroprocessing catalysts were slurried/dispersed in feeds. As far the fine catalysts could not be reused, only low-cost, throw-away materials possessing catalyst activity can be practical.

In [29] it was suggested that asphaltenes deactivating catalysts the most should be removed before hydroprocessing. Only after that, the feed oil, hydrogen, and a single used dispersed oil-soluble (molybdenum, cobalt, iron and nickel naphtenates or multi-carbonyl compounds) or water-soluble (phospho-molybdic acid, ammonium molybdate) catalyst should be mixed and went together through the reactor. Despite the oil-soluble catalysts are the most active, high cost greatly restricts their application. Thus, water soluble cheap inorganic compounds have become popular. Sodium molybdate, nickel nitrate, and iron nitrate were used as precursors to prepare water-soluble multimetal composite catalysts for residue hydrocracking. Their coke inhibiting behavior arranged in sequence of Mo-Ni-Fe > Mo-Fe > Ni-Fe > Mo > Fe. In the process, firstly water soluble catalysts are dissolved and then mixed with parts of the residue feed to form an emulsion. Generally, activation of the catalyst via dehydration and sulfurization is the subsequent steps, and finally the catalyst reacts with the residue feed in the reactor.

Maity et al. [30] have published a review on the use of catalytic aquathermolysis of heavy crude oils. The viscosity reduction achieved by these catalysts followed the order: mineral < water-soluble < oil-soluble < dispersed. When tetralin was used with anf Fe catalyst, the viscosity decreased more effectively, and the coke formation was reduced from 3.6 to 0.3 wt %.

Reviewing upgrading processes of a number of different feedstocks, the conclusion was drawn in [31] that there was not a general rule that can give a solution to all refineries, and the final choice should be made by comprehensive

consideration of the feed property, product demand, and economic benefit.

2. Experimental

2.1. Materials. The initial material being hydrogenated was Estonian carbonaceous kukersite oil shale consisting 40.15% of organic matter (OM^d), 48% ash (A^d), and 0.90% moisture (W). The content of mineral matter was calculated as $100 - OM^d$. According to Lille et al. [32], OM of kukersite can be characterized with empirical formula $C_{421}H_{638}O_{44}S_4NCl$. A set of structural elements comprises mainly alkylated phenolic structures particularly alkyl-1,3-benzenediols and condensed alicyclic rings. Up to 80% of methylene groups in kerogen are located in aliphatic chains and the complicated mixture of phenols in the retort oil supposed to result mainly from the thermal conversion of alkyl-1,3-benzenediol units originally present in OM.

During the process of kerogen low-temperature pyrolysis, two types of reactions might occur simultaneously before oil formation: (a) rapid release of volatiles coming primarily from the destruction of carboxyl, carbonyl, hydroxyl, phenolic hydroxyl, and other oxygen functionalities at the periphery of the aromatic and hydroaromatic components of the matrix (b) thermal cracking of the solid kerogen into high molecular semi-product, thermobitumen (TB) where the relatively less rapid release of volatile matters coming primarily from hydrogen produced during the conversion of hydroaromatic portions to aromatic building blocks and coke. The first reaction could be dominant at lower pyrolysis temperature. For stabilization of the free radicals forming in both processes additional hydrogen is required.

The commercial catalysts applied for activation of the hydrogen donation from tetralin to the oil shale decomposition products were in the form of granules. In addition, some local powdered minerals were applied. The nomenclature of the catalysts tested is given in Table 1.

The commercial catalysts were obtained from producers, and were designed as Co, Mo, and Ni supported ones with a maximum number of so-called Super Type II Active Sites (STARS) whose exact composition is confidential technical information. The original granules of the catalysts (3 mm in diameter and 8 mm in length) and presulfided for activation ones using shale oil as a spiking agent were tested.

Marine-type Estonian Dictyonema argillite (also known as dictyonema oil shale, Dictyonema shale, or alum shale) occurs in most of northern Estonia on an area of about 11,000 square kilometers (4,000 sq mi). Although reserves of the dictyonema argillite surpass those of kukersite, its quality is poor as a source for the energy production. The shale consists of 65–70% mostly silicate minerals, 10–15%, organic and 10–20% X-ray amorphous matter. The Fischer Assay oil yield is 3–5% per oil shale. The content of minerals depends on grain size fraction and gradual changes occur laterally as well as vertically. The average to whole rock composition is 37% phyllosilicates (illite, illitic illite-smectite, chlorite), 34% K-feldspar, and 29% quartz [33]. Dictyonema argillite taken from Maardu deposit was applied in this work.

Pyrite crystals, FeS_2, were obtained from the Institute of Geology at Tallinn University of Technology and were powdered in a mortar before addition.

The solvents applied in extractions, tetralin, benzene, hexane, and tetrahydrofurane, were commercial and had purity $\geq 99\%$ (GC).

2.2. Procedures. Reactions were carried out in glass test-tubes inserted into 100 mL stainless steel batch autoclaves. Mass of the initial oil shale loaded was 10 gram. The weight ratio of tetralin to oil shale OM was 1 : 1, and the ratio of catalysts to OM content was 0.1 : 1. The autoclaves were placed into electrical oven heated to the nominal temperature (360–420°C). After the duration prescribed (1–3 h), the autoclaves were left in room temperature and opened on the next day.

All the yields were calculated on the basis of OM.

Gas yield (G) was found from the weight loss of the closed and opened autoclaves. The content of the test-tubes was relayed into weight paper cartridge and extracted with benzene in a Soxhlet extractor. The properly washed cartridge with the insoluble in benzene residue was dried in a drying oven at 105°C and weight (G_{PA}), thereafter extracted using tetrahydrofurane, and dried and weighted again (G_{SR}).

The yield of organic solid residue (SR) was found basing on the initial mass of OM (G_{OM}), subtracting from G_{SR} the corresponding weight of the empty cartridge (G_c) processed likewise and the weight of the mineral matter (G_{MM}, estimated as the ash at 550°C) of the sample, weight of the catalyst (G_{CAT}) as follows:

$$SR = \frac{100(G_{SR} - G_C - G_{MM} - G_{CAT})}{G_{OM}}. \qquad (1)$$

The yield of preasphaltenes (PA), the coke precursors, was estimated directly as the distillation residue after evaporation of tetrahydrofurane from the extract and also as the weight loss in tetrahydrofurane extraction

$$PA = \frac{100(G_{PA} - G_{SR})}{G_{OM}} \qquad (2)$$

agreeing with the direct residue.

Estimation of the amount of benzene extract was somewhat problematic because it was impossible to separate the superfluous tetralin and its decomposition products from shale oil. So, the yield of benzene extract consisting of asphaltenes and maltenes ($A + M$) was estimated as the difference between the weight of initial sample (G_o) and the weights of gas (G_G), and the weight of the insoluble residue after benzene extraction

$$A + M = \frac{100[G_o - G_G - (G_{PA} - G_C)]}{G_{OM}} \qquad (3)$$

presupposing that there are no changes in mineral matter in the process.

The yield of asphaltenes was estimated precipitating asphaltenes in the ratio of hexane to an aliquot of the benzene extract v/w 10 : 1. At that, on the next day, characteristic to the solutions, asphaltenes formed an insoluble lacquer flake

TABLE 1: Catalysts applied.

Catalyst	Producer	Type	Positive features
DN-3100 Th	Shell, US	Universal	Effectiveness
KF-848	Akzo Nobel, Netherlands	Hydropurification	Effectiveness and selectivity
KF-1015	Akzo Nobel, Netherlands	Hydrocracking	
Dictyonema argillite	Another Estonian local shale	Hydrocracking	Cheapness, reach
Pyrite	Estonian local deposit	Hydrocracking	Cheapness, reach

on the glass surface of the beaker being easily washed and decanted. Finally, the washed residue in beakers was dried at 105°C and weighted.

The yield of maltenes was found subtracting from the yield of benzene extract estimated according to (3) the yield of asphaltenes. So, the value of M is somewhat overestimated due to inclusion of water. In some experiments, the water content in the benzene extract was estimated according to the classic distillation method of Dean and Stark [ASTM D95-05 (2010)].

In some hexane extracts the ratio of the peaks area of tetralin and naphthalene (x) was estimated using the GC-MS apparatus Shimadzu QP2010 Plus. The yield of naphthalene (N) resulted from hydrogen donation of tetralin to oil shale was calculated based on the equal quantity of OM and tetralin in the experiments. Neglecting the minor quantity of by-products in the hydrogen-donating reaction [8, 14, 17], and taking the initial content of tetralin as 100%, the sum of tetralin remained (T) and naphthalene formed should be

$$T + N = 100,$$
$$\frac{T}{N} = x, \tag{4}$$
$$N = \frac{100}{(x+1)}. \tag{5}$$

3. Results and Discussion

3.1. Effect of Heating Duration. The effect of time on the yield of the products in "dry" pyrolysis, in the environment of tetralin without any catalyst, and adding the hydropurification catalyst Akzo Nobel KF-848 is depicted in Figure 1.

The catalyst KF 848 was chosen because it had given the highest yield of the diesel fraction 200–360°C (72.7%) and of the total fraction boiling below 360°C (78.4%) in our preliminary experiments where the shale oil boiling above 360°C, was upgraded under initial pressure of molecular hydrogen 7.0 MPa, nominal temperature 380∘C and duration 1 h without tetralin.

The results obtained in this work prove that the main advantage from the addition of tetralin (Figures 1(a) and 1(b)) occurs in an increase in the maximum yield of total extract (curves 5) from 78 to 86%, and in decrease in the minimum percentage of OM remaining in solid residue (curves 0) from 8.4 to 5.2%. At that, unfortunately, formation of the target product, maltenes is higher in the "dry" experiment than in tetralin. The results agree with Behar and Pelet [17] who found that when tetralin was present

in thermal cracking of asphaltenes, radicals, once formed, preferentially underwent H-transfer reaction and the resulting hydrocarbons were inactive to further cracking and had the same carbon number as the initial radicals from primary cracking. The same was confirmed by Gould and Wiehe [23] who explained that reactive hydrogen donors greatly reduced the thermal cracking rate of petroleum resids by reducing the free radial concentration.

Addition of the catalyst KF 848 (Figure 1(c)) in tetralin environment, surprisingly, moderates the decomposition rate of the initial shale (curve 0) and formation of the total extract (curve 5) in comparison with the results in Figures 1(a) and 1(b). Nevertheless, the catalyst evokes continuous increase in the yield of maltenes with time (curve 1), unlike a steady state in the interval 1-2 h without the catalyst (Figure 1(b)), and a maximum between 1–1.5 h without tetralin and the catalyst (Figure 1(a)).

3.2. Effect of Nominal Temperature in the Environment of Tetralin and KF 848. The influence of nominal temperature on the thermal treatment of oil shale in tetralin without catalyst is depicted in Figure 2(a), and with the catalyst KF 848 in Figure 2(b). At that, the insufficient duration for formation of maltenes, two hours, was chosen for better revelation of the temperature effect. The results suggest again that under the conditions studied addition of the catalyst KF 848 being the best in hydrogenation of heavy shale oil with molecular hydrogen rather decreases the yield of total extract in comparison with the test without any catalyst. The maximum extract yield under two hours duration is at temperature 380°C without any catalyst, and at 400°C with the catalyst. But at that, addition of the catalyst amplifies the effect of temperature on the increase in the yield of the target product, maltenes, and decreases the yield of organic solid residue at 360°C.

It can be concluded that tetralin as a hydrogen donor improves liquefaction deepness of oil shale. At that, in the environment of tetralin the rate limiting stage is formation of thermobitumen (TB) resulted from splitting of the kerogen macromolecules, not hydrogen donation from the tetralin to the radicals formed. As far the catalyst KF 848 had unexpected low effect, the variety of catalysts was tested.

3.3. Effect of Different Catalysts. The commercial catalysts applied (Table 1) were oxides of Mo, Co, and Ni supported on alumina or silica-alumina in the forms of granules. The representatives of three types of catalysts, hydropurification, cracking, and universal, were tested in their original forms
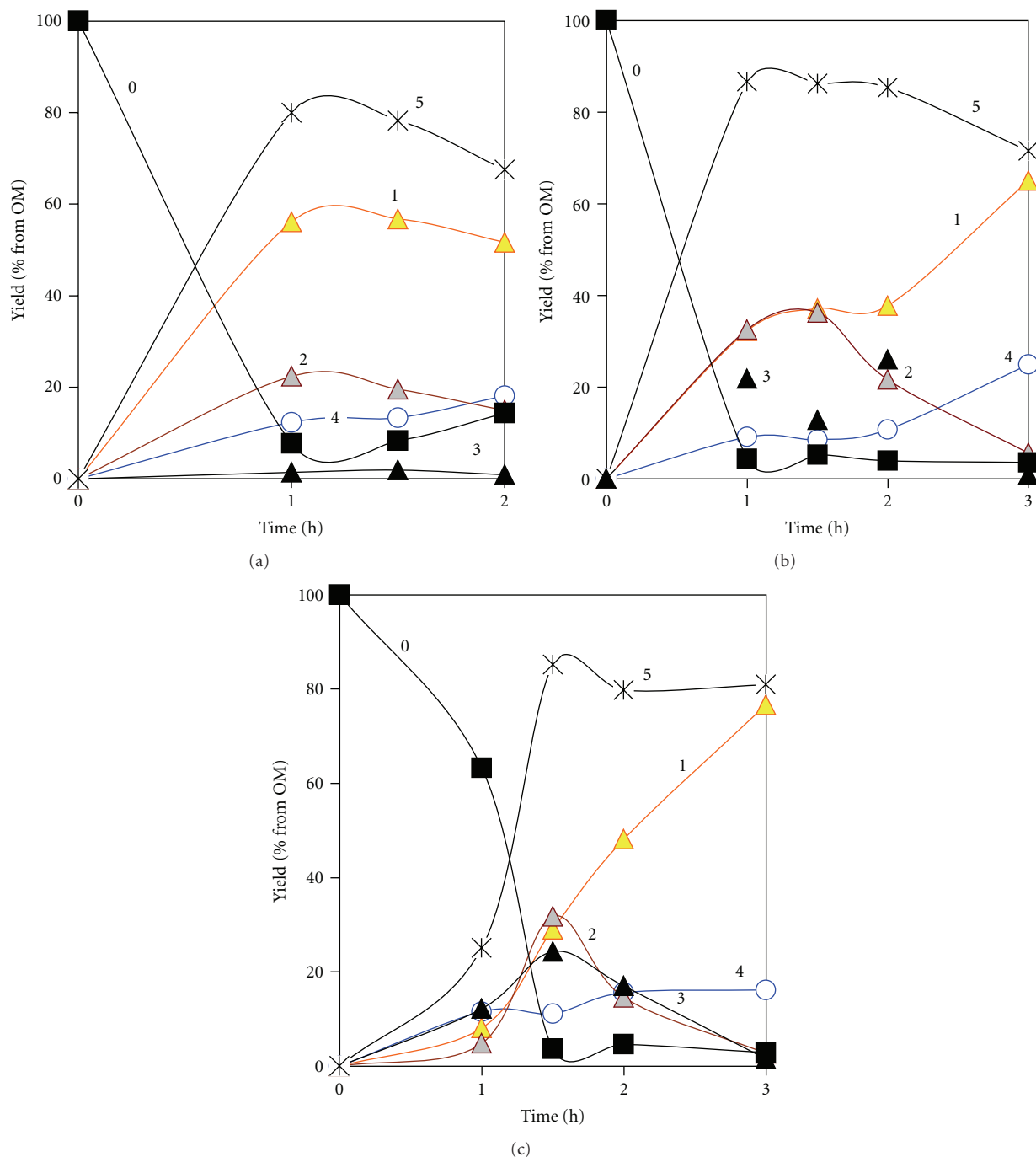
(a)

(b)

(c)

FIGURE 1: Effect of heating duration on the yield of decomposition products in the environment of (a) no tetralin and catalyst, (b) tetralin and no catalyst, (c) tetralin and KF 848. 0: organic solid residue, 1: maltenes, 2: asphaltenes, 3: pre-asphaltenes, 4: gas, 5: total extract. Nominal temperature 400°C.

and after activation using shale oil as a presulfiding spiking agent. The natural catalysts, dictyonema argillite and pyrite, were grinded to powder size. The experimental series with catalysts varieties were conducted at temperature 400°C. The two durations, 1.5 and 2 h, were chosen to found out whether the process is completed or not.

Comparison of the experimental results depicted in Figure 3 reveals the following.

(i) *Coke (organic solid residue)* formationis decreased in the presence of tetralin (Figures 3(b)–3(j)) in comparison with the pyrolysis without addition of tetralin and catalysts (Figure 3(a)). At that, an increase in the coke yield with time in the "dry" pyrolysis (8.4–14.4%) and a little effect of time in tetralin (below 5%) prove suppression of the secondary coke formation by hydrogen-donating behavior of tetralin.
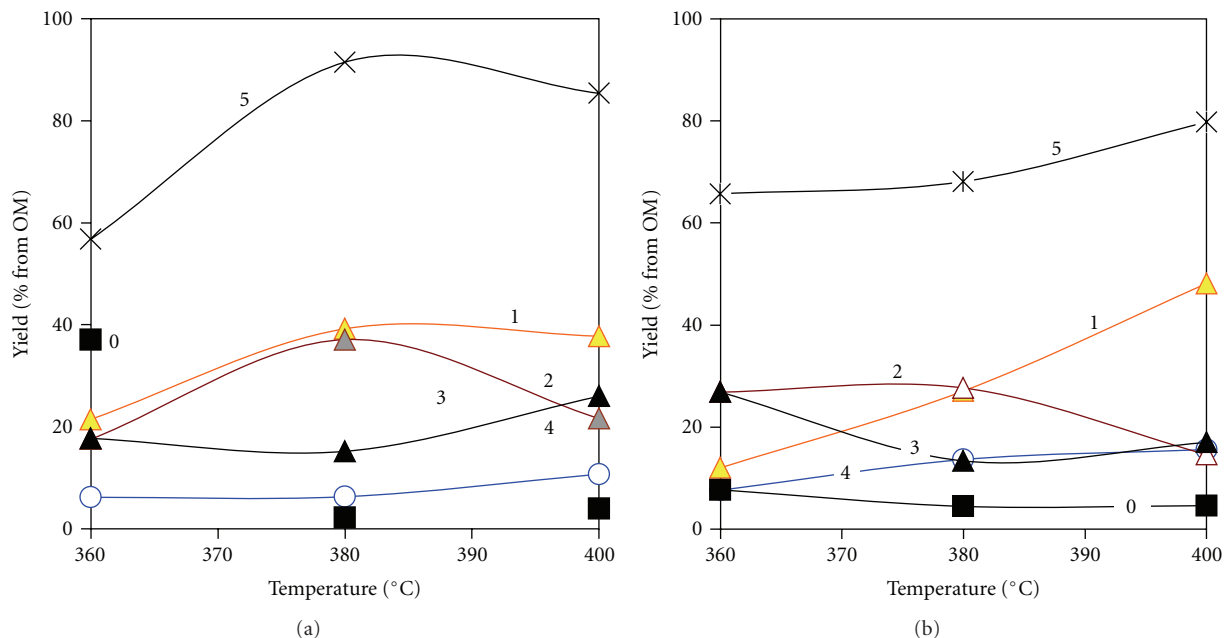
FIGURE 2: Effect of nominal temperature on the yield of decomposition products (see in Figure 1) in the environment of (a) tetralin without catalysts and (b) tetralin and the catalyst KF 848. Duration 2 h.
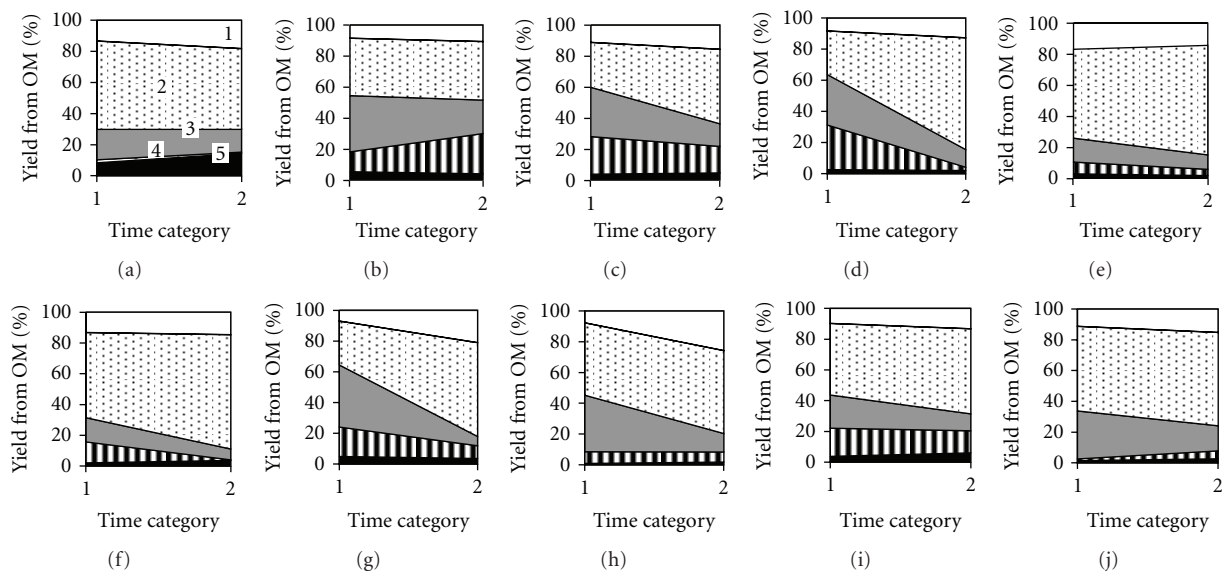

FIGURE 3: Effect of duration and fixings: (a) none, (b) tetralin 1 g/g OM, (c) tetralin and KF 848 pellets, (d) tetralin and activated KF 848 pellets, (e) tetralin and DN 3100 TH pellets, (f) tetralin and activated DN 3100 Th pellets, (g) tetralin and KF 1015 pellets, (h) tetralin and activated KF 1015 pellets, (i) tetralin and Dictyonema, (j) tetralin and pyrite on the yield of pyrolysis products: 1: gas, 2: maltenes (+water), 3: asphaltenes, 4: preasphaltenes, 5: solid residue. Time category: 1–1.5 h, 2–2 h. Temperature 400°C.

The lowest yields of OM in the solid residue, 0.93%, are obtained using the activated cracking catalyst KF 1015 [experiment (h), 1.5 h], 1.46% using pyrite [experiment (j), 1.5 h], and 1.50%, using the not activated universal catalyst DN 3100 TH [experiment (e), 2 h].

(ii) *Gas* formation is quite similar with and without tetralin and catalysts being 8–13% after 1.5 h, and

increasing to 14–18% after 2 h. An exception is the cracking catalyst KF 1015 [experiments (g, h)] resulting a significant increase in gas yield in time not completed during tested two hours.

(iii) *Total extract* of liquid products decreases with time increase from 1.5 to 2 h in the "dry" experiment (a) from 78 to 67%, and using the original and activated cracking catalyst KF 1015 (g, h) from 88 to

75 and from 91 (the maximum in the series) to 72% because of the secondary decomposition reactions. In the other experiments, the yield of total extract overcomes 80%. At that, noteworthy is the high extract yield, 87%, obtained using as catalysts the available local Dictyonema argillite (i) and pyrite (j).

(iv) *Preasphaltenes* yield is the lowest, 1-2%, in "dry" experiment (a) and 1–5% with pyrite (j). In tetralin without catalysts (b), the yield of preasphaltenes increases in time from 13 to 26%. In presence of any catalysts tested, inversely, the yield of preasphaltenes decreases in time, the most drastically, from 29 to 2%, in the test with the activated hydropurification catalyst KF 848 (d). The unique increase in the yield of preasphaltenes in time without catalyst in tetralin (b) is supposed to take place because of the secondary complex formation between the radicals formed, thereby catalytic splitting of the complexes is absent.

(v) *Asphaltenes* act quite analogously to preasphaltenes. Their yield in tetralin in every experiment (b–j) overcomes that in "dry" experiment (a) and thereafter decreases with time. The decrease is the sharpest, from 40 to 6%, with natural KF 848 pellets (g). The total yield of the little decomposed high molecular asphaltenes and preasphaltenes is the lowest, 13.4% and 7.5%, with original and activated DN 3100 Th after 2 h.

(vi) *Maltenes*, the main target product, have in "dry" conditions (a) higher yield, 57–51%, than in the environment of tetraline without any catalyst, 37-38% (b) like it was shown in Figure 1 above and in the work of Behar and Behar and Pelet [17]. Addition of catalysts increases decomposition rate of high-molecular asphaltenes (c–j) and preasphaltenes (c–i) and hereby the yield of maltenes (c–j). So, the positive influence of the longer duration is evident only with catalysts (c–j). The highest yield of maltenes, 74%, is obtained using the activated universal catalyst DN 3100 TH (f) and 72%, using the activated hydropurification catalyst KF 848 (d) at time 2 h. The durations longer than two hours should be tested in further works.

(vii) *Water* is formed inevitably when the oxygen-rich oil shale is hydrogenated. As said above, because of the environment of tetralin and its decomposition product, naphthalene, the yield of hexane extract was evaluated as the weight loss of the initial sample during benzene extraction minus the yield of asphaltenes precipitated in hexane. So, in this work, maltenes contain also the water fraction, estimated not for all samples. It can be seen in Figure 4 that there was no clear relationship between yields of water and any other decomposition products. Yet, the lower water yield at higher yields of solid residue can take place due to the incomplete decomposition of the shale. The dependence of water formation on different
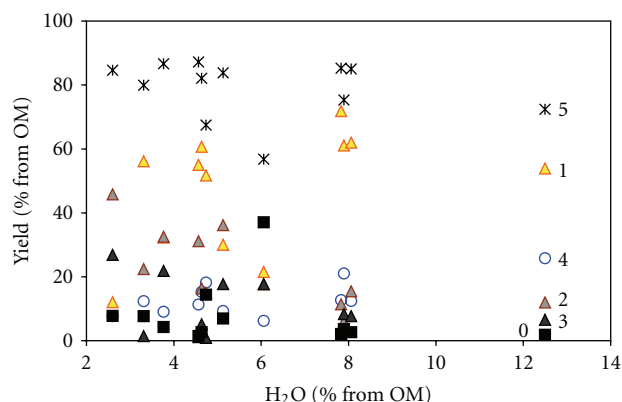

FIGURE 4: Relationship between the yields of water and pyrolysis products (see numbers in Figure 1) in the environment of tetralin.

catalysts, temperature, and duration affecting the oil shale transformation needs further systematic study.

Activation of the catalysts according to the confidential Technical Information instruction of producers increases the total extract yield at 1.5 hours duration to 3-4%. At 2 hours duration addition of the hydropurification catalysts KF 848 increases the yield of maltenes significantly, from 48 (c) to 72% (d), whereas the total extract yield increases only from 80 to 85%. Presumably, the changes take place mainly, due to the favored removal of heteroatoms from asphaltenes and preasphaltenes. Under the condition tested, the effect of activation of the universal catalyst DN 3100 Th (e-f) and cracking catalyst KF 1015 (g-h) on the distribution of products was substantially lower than that of KF 848.

The most efficacious conditions for liquefaction of oil shale were obtained without activation under the environment of tetralin and universal original catalyst DN 3100 Th at 400°C and 2 h (f). Under these conditions the yield of total extract was 84.3%, maltenes 70.9%, asphaltenes 9.3%, preasphaltenes 4.1%, gas 14.2%, and organic solid residue 1.5%.

Considering problems concerning cost, poisoning, and activation of the catalyst, replacement of the commercial catalysts with local natural minerals seems attractive. In this point of view, pyrite (j), just at duration 1.5 h, has promised rather good results. The extract total yield is 87%, of maltenes and asphaltenes 55 and 31%, and solid residue 1.5% only. Like in liquefaction of biomaterials [25], the presence of the catalyst had practically no effect on the extract yield in comparison with tetralin alone (b) but improved the oil quality. The quantity and conditions need for utility of pyrite as catalyst further optimization. The extract, probably, has to undergo further multistep upgrading.

3.4. Transformation of Tetralin in Upgrading of Oil Shale. Appearance of naphthalene shows that tetralin has acted as hydrogen donor. The transformation degree of tetralin into naphthalene characterizes the extent of hydrogen donation to TB. The results given in Table 2 evident that in the series tested approximately one third of tetralin have been used

TABLE 2: Yields of naphthalene (N) from tetralin (T) added, %, and maltenes (M), % from oil shale OM.

	No catalyst		KF 848					KF 1015	
	—	—	Original	Original	Original	Original	Activated	Original	Activated
T (°C)	400	400	380	400	400	400	400	400	400
t, h	1.5	2	2	1	1.5	2	1.5	1.5	1.5
M	37.14	37.76	27.08	8.09	29.06	48.16	27.96	28.55	47.01
T^*/N	3.15	2.26	1.8	3.58	2.66	1.31	2.61	2.38	2.46
N	24.10	30.67	35.71	21.83	27.32	43.29	27.70	29.59	28.90

T^*: tetralin current concentration.

for hydrogenation. Generally, the yield of naphthalene found according to (5) increases with an increase in the yield of maltenes. The relationship is not unilateral because all the variables tested: temperature, duration, type of catalysts and activation of the catalysts, and secondary decomposition of maltenes can influence on the relationship between the yields of maltenes and naphthalene. The systematic interplay of the mutual effects needs investigation in further works.

4. Conclusions

Addition of tetralin as a hydrogen-donor in thermal decomposition of oil shale increases the extract yield and suppresses coke formation. In hydrogenation of the unstable thermobitumen *in statu nascendi* about one third of tetralin per OM of oil shale, g/g, is expended and transformed into naphthalene.

Addition of tetralin avoids the secondary decomposition and condensation of hexane soluble fraction, maltenes, but without catalysts also slows down formation of maltenes in comparison with "dry" pyrolysis. Subsequent distribution of the extract between the fractions soluble in hexane, benzene (asphaltenes), and tetrahydrofurane (pre-asphaltenes) depends on temperature, duration, and type of catalysts. Formation of the target product, maltenes, increases with time and temperature.

Activation of the commercial hydrocracking and universal catalysts KF 1015 and DN 3100 Th using as a spiking agent the shale oil middle fraction has a little effect on the yield of pyrolysis products in comparison with addition of the original pellets. Activation of the hydropurification catalyst KF 848 has a little effect during the first 1.5 h and thereafter increases the formation rate of maltenes from asphaltenes and preasphaltenes.

The best catalyst among the tested ones for liquefaction of oil shale under the environment of tetralin is universal catalyst DN 3100 Th without activation at 400°C and 2 h. Under these conditions, the yield of total extract was 84.3%, maltenes 70.9%, asphaltenes 9.3%, preasphaltenes 4.1%, gas 14.2%, and organic solid residue 1.5%.

Quite promising catalytic effect gives addition of 1% of an available local mineral, pyrite. In the environment of tetralin at duration 1.5 h, the extract total yield was 87%, of maltenes 55%, asphaltenes 31%, gas 11%, and solid residue 1.5%. Here, the second-step upgrading of asphaltenes should be followed.

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