

CHEMICALS AND OTHER PRODUCTS FROM SHALE OIL

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Summary

Compared to petroleum crude, shale oils obtained by retorting of world's oil shales in their multitude and dissimilarity, are characterized by wide boiling range and by large concentrations of heteroelements and also by high content of oxygen-, nitrogen-, or sulfur-containing compounds. The chemical potential of oil shales as retort fuel to produce shale oil and from that liquid fuel and specialty chemicals has been used so far to a relatively small extent. While the majority of countries are discovering the real practical value of shale oil, in Estonia retorting of its national resource kukersite oil obtained for production of a variety of products is in use for 75 years already. Using stepwise cracking motor fuels have been produced and even exported before World War II.

At the same time, shale oils possess molecular structures of interest to the specialty chemicals industry and also a number of non-fuel specialty products have been marketed based on functional group, broad range concentrate, or even pure compound values. Based on large quantity of oxygen-containing compounds in heavy fraction, asphalt blending material, road bitumens and road oils, construction mastics, anticorrosion oils, rubber softeners, etc. are produced, Benzene and toluene for production of benzoic acid as well as solvent mixtures on pyrolysis of lighter fractions of shale oil are produced. Middle shale oil fractions having antiseptic properties are used to produce effective oil for the impregnation of wood as a major shale oil derived specialty product. Water soluble phenols are selectively extracted from shale oil, fractionated and crystallized for production of pure 5-methylresorcinol and other alkylresorcinol derivatives and high value intermediates to produce tanning agents, epoxy resins and adhesives, diphenyl ketone and phenolformaldehyde adhesive resins, rubber modifiers, chemicals, and pesticides. Some conventional products such as coke and distillate boiler fuels are produced from shale oil as by-products. New market opportunities for shale oil and its fractions may be found improving the oil conversion and separation techniques.

1. Introduction

Taking into account the enormous store of oil Earth's crust, estimated to be more than 65 trillion tons and having shale oil potential about 600 billion tons, it is only a question of time when humankind begins extensive utilization of that still practically unused reserve of fossilized organic matter to produce liquid fuels and various chemicals since petroleum is not a renewable natural resource and its reserves are not inexhaustible. Shale oil obtained on thermal destruction of oil shale is a very specific product and its composition and properties depend both on the chemical composition of the concrete oil shale destructed and the conditions of destruction used. So, even using unified conditions of thermal processing it is practically not possible to produce similar shale oils and to work out any universal acceptance for further utilization of individual shale oils obtained. Being very different by their elemental, group and fractional composition and also by physical-chemical characteristics, shale oils indeed have a great potential for production of various products, but the most expedient and effective utilization of that potential includes as unavoidable application of special technologies for shale oil processing and upgrading, taking into account the singular composition of individual shale oils.

In industrial practice for production of shale oil, hitherto, semicoking of oil shale in special retorts is used. Shale oils obtained by retorting contain a large quantity of hetero-elements—oxygen, nitrogen and sulfur—much more than typical petroleum (Figure 1).



Figure 1. Elemental composition (% on y-coordinate) of Estonian kukersite shale retorting oil (I), Russian Kashpir shale retorting oil (II) and typical for petroleum (III)

As a result of retorting, a lot of unsaturated hydrocarbons are also formed. Phenols and alkenes, missing in petroleum, are typical compounds in shale oils. There exist two positions, different in principle, for utilization of shale oils—one considers in those a petroleum substitute to produce liquid fuels and gives rise to the methods for making the composition of shale oils closer to that of petroleum, abolishing the unique peculiarity of shale oils as substance while the other, emphasizing just on the peculiarity of shale oils finds prospects to produce non-fuel specialty products from shale oil focusing on those particular characteristics which distinguish shale oil from petroleum. Researches on the industrial retorting of oil shales and on the upgrading of shale oil are being carried out in many countries and at present are highly topical in the USA, China,

Australia, Israel, and Brazil. While the majority of countries are taking their first steps on discovering the practical value of shale oil, one of the smallest countries in Europe- Estonia- has the biggest oil shale industry in the world and 75 years experience on making use of its national resource kukersite oil shale, dating back to the 1920's. Also in Russia attempts have been made to benefit by a few of their numerous and different deposits. The present review contains a list of the products already in production from shale oil, including some of those several, which potentially could be produced in future. Various retorting technologies for shale oil production (chamber and tunnel ovens, direct heated vertical retorts, rotary retorts etc.) have been used in Estonian oil shale industry and despite the device used for kukersite semicoking the composition of shale oil is similarly characterized first of all by large concentrations of oxygen-containing compounds, which distinguish it from other ones, e.g. the high sulfurous Russian shale oil (see Table 1)

Characteristics	Kukersite shale oil	Kashpir shale oil
Yield, % on dry shale basis	23.3	12.0
Elemental composition, %:		
C	83.0	80.2
H	9.7	9.1
N	0.1	0.9
O	6.4	2.1
S	0.8	7.7
Chemical group composition, %:		
alkanes, cycloalkanes and alkenes	10.3	9.0
aromatics	27.6	26.0
heteroatomic compounds:	57.1	65.0
including		
phenols	30.0	6.0
neutral oxygen compounds (ketones)	27.1	15.0
sulfurous compounds	5	40.0
including		
thiophene derivatives	2.4	33.0
sulphides, mercaptans and others	2.6	7.0
nitrogenous compounds, mainly pyridine and kinoline derivatives	–	4.0
Density at 20 °C, kg m ⁻³	1010	1040
Viscosity at 75 °C, mm ² s ⁻¹	18.7	11.8
Flash point, °C	104	120
Molecular mass	290	250
Congelation temperature, °C	–20	0.5
Calorific value, MJ kg ⁻¹	40	6.6
ASTM distillation:		
i.p., °C	170	180
200 °C, %	2	2
220 °C, %	4	5
240 °C, %	8	9
260 °C, %	12	11

280 _C, %	16	19
300 _C, %	20	28
320 _C, %	30	39
340 _C, %	41	48
360 _C, %	55	61

Table 1. Characterization of Estonian kukersite and Russian Kashpir retorting shale oils

The oxygen-containing compounds represented both by phenolic and neutral oxygen compounds make up two thirds of the total oil content. The most valuable portion of phenolic compounds in Estonian shale oil are the water soluble alkylresorcinols (see Table 2), the unique ones detected in shale oils. The total water soluble phenols component is the only concentrate separated from the kukersite shale oil which is characterized by a distinct main pure compound-5-methylresorcinol; its concentration extends to 35%. In all other broad range concentrates hitherto separated, the content of any single compound usually does not exceed 1-2%. The total water soluble phenols are fractionated by vacuum rectification and the alkyl resorcinol distillates are used to produce a number of valuable chemicals as we see hereinafter.

Compound	Mass %
Monohydric phenols (incl. 0.8–1.2% xylenols)	5–10
Resorcinol	0.5–2
2-Methylresorcinol	0.5–1.5
4-Methylresorcinol	1.5–2.5
5-Methylresorcinol	25–35
2,5-Dimethylresorcinol	8–12
4,5-Dimethylresorcinol	8–10
5-Ethylresorcinol	9–11
2-Ethyl-5-dimethylresorcinol	1–2
2-Methyl-5-ethylresorcinol	4–6
Other identified resorcinol derivatives	10–20
Unidentified resorcinol derivatives	3–7

Table 2. Water soluble phenols (total) of kukersite shale oil

Kukersite shale oil has a wide boiling range in which more than half of the total oil boils above 350 °C. Fractions of a different kind of properties as feedstock for production of various products may be obtained by distillation (see Table 3). At the same time separation schemes known in petrochemistry to get straight-run motor fuels of high quality from shale oil could not be used for retorting oil due to the wide boiling range of hetero-compounds present not only in heavy fractions but also in lighter ones.

Group compounds, %	Boiling range of fractions, _C			
	<200	200–300	300–350	>350
Alkanes + cycloalkanes	11	12	3	1
Alkenes	39	23	3	1
Aromatics	21	29	33	33

Neutral oxygen compounds (ketones)	20	19	30	30
Phenols	9	17	31	35

Table 3. Chemical group composition of Estonian shale oil distillates

Kukersite shale oil is thermally unstable; its distillation proceeds incongruently, i.e. at higher temperatures (200 °C and more) the majority of oil components do not distillate without decomposing. The tendency of shale oil compounds to take part in condensation and sealing reactions has a great practical significance to develop shale oil distillation, coking etc. processes. Kukersite shale oil, consisting mainly of unsaturated compounds and the latter ones containing reactive oxygenous functional groups, is a chemically very active substance. Being readily submitted to chlorination, nitration, sulfurization and condensation reactions with aldehydes the corresponding derivatives could be synthesized from shale oil and its oxygen-containing components and used in different fields. Despite the relatively high hydrogen content (hydrogen-to-carbon atomic ratio is equal to 1.4) and abundance of oxygenous compounds in Estonian shale oil that is easily hydrogenable and oxidizable and as a result of respective processes shale oil physical-chemical properties as density, molecular mass and, in particular, viscosity could be altered within the wide range, enabling us to use shale oil for manufacturing of high-viscous bitumens or liquid fuels meeting international standards. The content of phenols (particularly alkyl resorcinols) and aliphatic chains on oxidation somewhat decreases and that of neutral oxygen compounds increases while on hydrogenation the phenols totally and the neutral oxygen compounds in part decompose and as a result the content of various hydrocarbons in hydrogenisate significantly increases.

As one can see above the shale oils as technogenic products are merely by their heteroelemental composition distinguished not only from natural petroleum but from each other as well by the total concentration of oxygen, sulfur and nitrogen and by their mutual relation. Specific for one or another shale oil heteroatomic compounds being not evenly proportioned into distillation fractions individually diverse technologies for shale oils separation and upgrading to produce liquid fuels have to be created, and the most expedient directions for production of specialty products have to be worked out. Only due to the rareness of the Estonian shale oil, containing such components as water soluble phenols, a lot of non-fuel specialty products from that oil are produced while a variety of different sulfur compounds as a special feature of Russian shale oil makes that a suitable feedstock for production of antibacterial medicine preparations. Shale oil products are usually manufactured by compounding of different fractions, by separation or by additional thermochemical treatment of shale oil.

2. Shale oil cracking products

Petrol, motor kerosene, “diesel oil”, and solvents are by their origin the products of step-by-step cracking of oil shale; shale oil formed on retorting (thermal cracking) of kukersite shale is submitted to further vapor-phase cracking to elevate hydrogen content in lighter fractions and the concentration of desired compounds. Also, a lot of heteroatoms as a result of cracking are removed.

2.1. Petrol

Shale oil cracked petrol consists mainly of hydrocarbons (Table 4) and a slight degree of oxygen compounds and differs from petroleum straight-run petrol by containing aromatic and unsaturated compounds, also by a bit higher specific weight and by specific smell.

Characteristics	Numerical value
Chemical group composition, vol. %:	
alkanes	35
cycloalkanes	4
alkenes	56
aromatics	4
Hydrogen content, mass %	15
Sulfur content, mass %	0.6–0.8
Density, at 20 °C, kg m ⁻³	740–750
Corrosion test	negative
Reaction	neutral
Colour by Stammer	ca 310 water white
Boiling range:	
100 °C, %	25–35
140 °C, %	60–70
160 °C, %	75–85
End point	<200 °C
Octane number	68

Table 4. Characterization of shale oil cracked petrol

One of the heavy fractions of petrol produced by the State Oil Shale Works in Estonia found widespread utilization in foreign markets between World Wars I and II as denaturing agent for alcohol, so-called “denaturation petrol”

2.2. Kerosene

Motor kerosene produced from 1932 to 1966 was used for road-making machines, tractors and motorboats running. Shale oil motor kerosene is yellow-colored having specific weight 820-850 kg m⁻³, heat of combustion 10500 kcal kg⁻¹ and boiling range 150-260 °C. It does not contain phenols and organic acids.

2.3. Diesel fuel

Two types of diesel fuels (Table 5) as refined and fractionated products obtained on raw shale oil cracking were produced in Estonia till 1940.

Characteristics	Diesel fuels	
	I	II
Boiling range, °C	200–300	250–320

Density at 20 °C, kg m ⁻³	850–880	890–910
Viscosity at 20 °C, cP	1.1–1.3	1.3–1.4
Heat of combustion, kcal kg ⁻¹	10200–10400	10100–10200
Phenols content, %	Phenol-free	Phenol-free
Sulfur content, %	1	1

Table 5. Characterization of shale oil cracked diesel fuel

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Biographical Sketch

Hans Luik is head of the department of oil shales and shale oil of the Institute of Chemistry at Tallinn Technical University. He was born on 07. 11. 1954 in Tallinn and his nationality is Estonian. He came

from a family of employees and started his studies at Tallinn Technical University chemistry faculty in 1973. He completed them in 1978 with a degree in chemical engineering. After graduating from Tallinn Technical University he took his postgraduate course on fuel chemistry and organic chemistry. He received Ph.D. (Chem.) degree in 1987. The subjects of his scientific activities are thermal destruction of solid fuels, oils upgrading, chemical modification and liquid products chromatography. He was elected a member of New York Academy of Sciences in 1996. Hans Luik is married and has a child.

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