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HYDROGENATION OF ESTONIAN OIL SHALE AND SHALE OIL

Possibilities to produce synoil from oil shales and its upgrading into synfuel have been and still are of interest.

Estonian shale oil (syncrude), produced on thermal destruction of kukersite, is a specific one by its high content of oxygen. Various retorting technologies for syncrude production (chamber and tunnel ovens, vertical retorts, retorts with solid heat carrier) have been used in Estonian oil shale industry and despite of the device used the composition of syncrude obtained is similar (the content of oxygen compounds - neutral ones and phenols - is equal to hydrocarbon content) while effective processes of hydrogenation and thermal dissolution to modify syncrude composition have not been practised in industry yet. Separation schemes known in petrochemistry to get straight-run motor fuels of high quality from crude oil could not be used for retorting syncrude due to the wide boiling range of heterocompounds present not only in heavy fractions but also in lighter ones. For syncrude upgrading different processes could be used among which hydrogenation techniques are the most perspective, enabling simultaneously to remove not only oxygen but also sulphur and nitrogen from syncrude, to elevate its hydrogen-to-carbon ratio, to saturate the unsaturated bonds, to correct the boiling range and group composition of syncrude, so bringing syncrude properties closer to the properties of crude oil and its distillation products.

To make the best use of Estonian shale oil and to find out the most expedient possibilities of its upgrading there exists some historical experience and it is inevitable to return to earlier works in that field to develop updated and better technologies and products. The present review contains the main results of works since 1926 on theory and practice of Estonian oil shale and shale oil hydrogenation as well as the perspectives of shale oil processing and upgrading into motor fuels.

Three periods could be brought forth as oil shale politics and the direction of investigations on oil shale was strongly influenced by the political situation in Estonia.

I. Estonian First Period of Independence

With increasing shale oil production in Estonia possibilities of its utilization and upgrading were under study to widen the assortment of obtainable products [1-14]. More than a score of articles were developed, a lot of them were exported including "diesel oil" and gasoline. The main course was production of syncrude from kukersite and elaboration of technologies for production of motor fuels and other



upgraded articles. In that period an industrial process for shale oil upgrading was worked out and put into use in Estonia - retorting of oil shale was conjuncted with cracking of shale oil obtained in the same industrial process. Vapours of shale oil formed on retorting were submitted to vapour-phase cracking and as a result gasoline was produced which quality did response to the requirements of world market. Before nationalization in 1940 in Estonia 17.3 % of shale oil was processed into motor fuels, viz. 15.3 % gasoline (20,500 t) and 2 % "diesel oil"; the share of oil shale for shale oil production and upgrading was planned still to raise.

Carbon-to-hydrogen ratio in shale oil is high in comparison with that in oil. To elevate hydrogen content in lighter fractions, instead of classical hydrogenation of total oil, its cracking into lighter fractions was taken into industrial use and as a result car gasoline (H 15 %), heavy gasoline, motor kerosine and "diesel oil" were produced from retorting syncrude (H 11-12 %). Composition of Estonian car gasoline: S 0.6-0.8, unsaturates (olefines) 50-60, paraffines 4, aromatics 4 %. Octane number of kukersite-derived cracking gasoline was 68, but for straight-run gasolines from oil it never exceeded 55.

It was established that:

- multiple quantity of gasoline could be obtained on syncrude additional cracking in comparison with that formed on shale retorting;
- total conversion of heavy fractions of syncrude into gasoline, gas and coke could be attained using manifold circle processes;
- coke has autocatalytical properties, and cracking processes at the presence of coke could be carried out at a lower temperature to obtain a higher yield of gasoline;
- retorting syncrude is rich in phenols, and cracking of it in the presence of lime (as well as shale ash containing lime and alumosilicates) results in increase of the yield of gasoline whereas a lot of phenolic oxygen is bound into carbonic acid and so a great deal of hydrogen is released to form gasoline;
- oxygen compounds decompose on syncrude cracking forming CO, CO₂ and H₂O already at low temperatures; at elevated temperatures decomposition remnants of oxygen compounds decompose;
- coke formation is marked already at low temperatures;
- resin donors are stabilized and H₂S is formed on hydrogenation at 400-500 °C in the presence of Fe and Ca oxides or Ca hydroxide;
- Zn dust and H donors have a good effect on syncrude upgrading.

It was shown that:

- shale cracking in autoclave gives higher yield of gasoline as compared with the total yield obtained on shale retorting and cracking of retorting syncrude obtained separately in liquid phase;
- hydrogen consumption on syncrude hydrogenation is smaller in comparison with that on shale hydrogenation;

- the efficiency of cracking both in liquid phase at elevated pressure and in vapour phase at reduced pressure depends upon the cracking time and temperature;
- pressure has no effect on the yield of hydrocarbons boiling up to 200 °C formed on cracking.

It was found that:

- shale oil is non-homogeneous, and decomposition rates of its components being different stepwise destruction would be recommendable;
- cracking of shale oil would be carried out at 400-570 °C, at higher temperatures the time of destruction should be shortened;
- the optimum temperature for both liquid and vapour phase cracking is 450-500 °C;
- on shale oil cracking at 480-550 °C, 3.7-7.7 % of shale oil is converted into H₂O and 5.6-17.9 % into gas;
- the high-boiling fractions of shale oil decompose readily, their use as lubricating oil without any special treatment is problematical.

Determined were:

- the chemical composition and main technical parameters of retorting shale oil and its upgraded products including gasoline and "diesel oil";
- the share of the products formed on shale oil coking: coke and gas both 30-35, light hydrocarbons (gasoline) 25 %.

Preliminary investigations were carried out:

- on kukersite hydrogenation (J. Kopvillem, P. Kogerman, H. Waterman);
- on non-catalytical and catalytical hydrogenation and desulphuration of kukersite retorting oil and its fractions (J. Usk, Th. Koern, J. Hüsse, K. Luts);
- on liquid phase hydrogenation of heavy liquid residues of kukersite retorting oil;
- on construction of devices for hydrogenation and technical possibilities for its realization.

According to the general opinion hydrogenation of Estonian shale oil represents successive changes, at first in the composition of oxygen compounds and then in hydrocarbons. Mechanism of shale oil hydrogenation was explained as follows: at the beginning of the process greater molecules are splitted into smaller ones which then join hydrogen giving the final products of hydrogenation. So it was established that thermal destruction precedes hydrogenation and not vice versa.

Economical calculations were made to estimate the cost of upgrading of Estonian shale oil, and it was concluded that:

- on upgrading of debenzineted shale oil about 90 % benzine could be obtained. In addition 96-97 % benzine from the rest 10 % could be obtained on hydrogenation;
- hydrogen consumption reaches 800 m³ per 1 t syncrude and 150 m³ per 1 t gasoline;
- the price of hydrogen was taken 0.1 kroons per 1 m³, and the resulting price of upgrading of syncrude was 10 kroons per tonne;
- on kukersite cracking 8 % benzine (on oil shale basis) could be obtained while on kukersite oil hydrogenation its respective yield is 91.2 % (20 % on oil shale basis);
- 2.5 times less oil shale is used on hydrogenation than on cracking to produce an equivalent amount of benzine, but actually also consumption for hydrogen as well as for production of electricity and vapour and also heating were intended to cover up by oil shale;
- the production cost being taken the same, the lucrateness of cracking unit will be twice higher than that of hydrogenation unit.

II. Soviet Period

As a result of incorporation of Estonia into the Soviet Union united energetics system the claim for liquid fuel was satisfied by Soviet oil which price was kept artificially low. Investigations on possibilities of liquid fuel production from local natural resources - oil shale - still continued to some extent up to mid fifties [14-34], but not as a sequel to previous period, and then practically ceased. Interest and attention paid to kukersite was limited to other topics, e.g. structural and geochemical investigations as well as optimizing the yield of the liquid product from kerogen, and in that context they were carried out at the Institute of Chemistry in Tallinn under the leadership of I. Klesment [35-43]. In Kohtla-Järve the production of benzine A-66 (S ~0.6 %, octane number 68) was stopped.

It does not mean that oil shale reserves were preserved for future; mining bulk increased enormously, the lion's share of oil shale was used for the production of electricity and not only for Estonian needs.

The main scientific results obtained on shale oil upgrading during that period could be summarized as follows.

Examined were:

- dependence of the yield of hydrogenation products (shale oil, coke, gas) upon the reaction conditions (temperature, time, pressure);
- influence of different non-rear metal catalysts and solvents on hydrogenation;
- the properties of hydrogenisates and their distillates;
- processes in flow reactors as well as in autoclave.

Depending upon the object of hydrogenation and conditions used different products with different characteristics were obtained.

It was stated that:

the raw fractions of crude shale oil could not be used as motor fuels without previous chemical treatment, thermal cracking or purification: gasoline fraction contains up to 1 % S and is unstable forming resins; diesel fraction gives high coke residue on combustion and has corrosive properties; octane and cetane numbers are low.

Several multistage upgrading schemes for industry combining the possibilities of simple cracking, hydropurification (~ 50 at, 200-300 °C) and destructive hydrogenation - cracking at the presence of hydrogen (~ 300 at, up to 550 °C) were proposed but did not found practical employment, e.g.:

1. Kukersite enrichment \rightarrow liquid phase hydrogenation of enriched kukersite at 440-470 °C \rightarrow vapour phase destructive hydrogenation of the products of liquid phase hydrogenation at 380-420 °C.

As a result 17.7 % motor fuel was obtained; H_2 consumption in the 2nd stage - 2-3 % on kerogen basis, in the 3rd stage - 1.7 % on shale oil basis.

2. Kukersite enrichment \rightarrow thermal dissolution of enriched kukersite \rightarrow :

\rightarrow distillation \rightarrow hydrogenation of distillation products at low pressure (50-100 at). 15.0 % gasoline and diesel fuel was obtained on dry shale basis ($A^{daf} = 66$ %). H_2 consumption 0.9 % was covered by gas conversion.

\rightarrow destructive hydrogenation of total dissolution product at 50 and 300 at. 24.5 % gasoline and diesel fuel was obtained on dry shale basis. H_2 consumption 4 % was covered by gas conversion.

\rightarrow coking of total dissolution product \rightarrow purification of distillates with NaOH and H_2SO_4 .

3. Distillation of generator oil into two fractions \rightarrow cracking of the heavy distillation residue into oil and coke \rightarrow hydrogenation of wide-boiling fraction together with the cracking oil obtained at 100 at. 26.7 % gasoline, 26.2 % diesel fraction and 24.3 % gas were obtained. H_2 consumption 1.8 % was covered by gas conversion.

4. Vapour phase hydrogenation of wide-boiling shale oil fraction (defenolated or not) \rightarrow gasoline distillation or additional cracking \rightarrow catalytical reforming of pre-hydrogenated gasoline.

5. Thermal and catalytical cracking of defenolated generator oil on alumosilicates. In both 4th and 5th cases the gasoline yield was increased and the octane number was improved.

It was found that:

- cracking of the hydrogenated shale oil yields 1.5 times more gasoline and twice less coke than the unhydrogenated one;

- total conversion of shale oil fraction boiling above 325 °C into compounds boiling below 325 °C is possible at 300 °C using a Fe catalyst;

- the quality of gasoline decreases when phenols have been eliminated from shale oil before cracking, because the potential of the formation of aromatic compounds decreases;
- 20 % of gasoline forms as a result of hydrogenation at 100 and 420 °C of just the neutral oxygen compounds present in fraction boiling at 200-300 °C;
- the following industrial catalysts would be used:
 - ferrous sulfate and ferrous oxides on liquid phase hydrogenation,
 - WS_2 and $WS_2 + NiS + Al_2O_3$ on vapour phase hydrogenation,
 - alumosilicates and $ZnCl_2$ on thermocatalytical cracking,
 - natural and artificial clay minerals, boxite, kieselguhr, pumice, Al_2O_3 and SiO_2 in different proportions, Fe fixed on brown coal;
- solvent extraction by Eleneanu should be applied to improve the quality of obtainable products, also furfural, methanol, acetone and other solvents could be used to remove undesirable compounds or contaminants;
- steep decrease in oil formation begins at 425 °C due to the formation of carboids and gas when distillation residue (above 325 °C) is hydrogenated;
- hydrogen consumption on liquid phase hydrogenation of the generator oil at 300 °C reaches 400-700 m³ per 1 t oil.

Theoretical conclusions and composition of the products:

- Catalytical cracking without H_2 results in redistribution of internal hydrogen in shale oil and as a result hydrogen poor (carboids) and hydrogen rich saturated hydrocarbons are formed. Analogically to destructive hydrogenation, on catalytical cracking the bonds between carbon atoms are activated enabling to carry out the process at lower temperatures (by 100-150 °C).
- S present in shale oil is mainly thiophenic, and on catalytical hydrogenation removal of 60-70 % of sulphur was observed.
- On cracking $ZnCl_2$ effects the transfer of hydrogen into the lighter hydrocarbons, the most of oxygen taking part in coke formation, hydrogen consumption for water formation is limited.
- Formation of the secondary phenols both from primary ones and even from previously defenolated shale oil was observed on hydrogenation. Appearance of acidic properties of shale oil products (neutral fractions, defenolated shale oil) not indicating those before, was explained as a result of dealkylation of neutral phenols and cracking of ether groups.
- The neutral part of shale oil gives a higher yield of liquid products on hydrogenation than the acidic part and the carbonyl groups present in neutral oil are readily hydrogenated.
- The acidic part of shale oil has a tendency towards coke formation.
- Asphaltenes in shale oil decompose totally above 460 °C (460-485 °C).

- A. Aarna has found that the fraction of shale oil boiling at 200-300 °C is a good source for production of lubricating oil on polymerization and diesel fuel could be obtained as a by-product.

III. Estonian Reindependence Period

It is the time for conclusive establishment of the priorities in our oil shale policy. On the one hand, existing material resources, technology, as well as historical experience and traditions must be taken into account, and on the other hand, scientific researches on shale oil optimum upgrading to open its total potential and to work out the most expedient manners of application must be set going. The recent publications of I. Öpik are the trail-blazers in this field [44-46]. In these some economical calculations have been made and an old problem - electricity or oil from Estonian oil shale - has been set up again and discussed.

Some opinions for further development of that problematics are added as follows.

The Author's Conclusions and Proposals

Estonia is geographically situated far from the world's oil deposits. Oil shale is its most important natural resource. The economically mineable reserves of oil shale are estimated to be 3,000 million tons. Up to now 770 million tons of oil shale has been used up - only 8 million tons in pre-war Estonian Republic and 762 million tons in the Estonian S.S.R. At present, 90 % of the oil shale mined are used to generate electricity, but now there is no need for electricity production on the same level as during the Soviet period. On the other hand, oil and its products have become goods in short supply.

The production of synoil from alternative sources such as oil shales is highly topical; researches on the industrial retorting of oil shales and on the upgrading of syncrude are being carried out in the USA, Australia, Brazil, China and other countries. Oil is not a recurrent natural resource and its reserves are not inexhaustible. World's oil reserve in 1984 was estimated to be 91.4 milliard tons, while world's oil shale reserve is estimated to be $6.5 \cdot 10^{13}$ tons having the oil equivalent to 600 milliard tons.

As it is known, oil has been formed as a result of catagenesis of oil shale in the lithosphere under natural geothermal conditions during millions of years. Thermal destruction of oil shales (semicoking, hydrogenation or gas extraction) could be observed as imitated artificial catagenesis of oil shales and as a result oil-like product (syncrude) is obtained within some hours or less. Its composition and properties depend upon the origin of the oil shale as well as on the conditions used on thermal destruction. To produce synoil from syncrude secondary thermal treatment (upgrading or modification) is usually needed. Further processing of synoil into synfuel runs according to general schemes known and practised in oil chemistry.

To lessen Estonian's dependence on oil import from the West or East, and considering the large reserves of oil shale of high syncrude potential Estonia has, it is important just now to carry out the scientific studies to evaluate the possibilities and perspectives of employing it as synoil.

The strategy could be as follows:

Taking into account the specificity of Estonian syncrude produced industrially by the retorting process, upgrading of syncrude just into diesel fuel is preferable, as it enables to separate and preserve highly marketable phenols as components already upgraded on retorting and to maintain also as much neutral oxygen compounds of a high cetane number as possible. In this way a lot of oxygen will be upgraded in valuable separation products and, what is particularly important, the consumption of hydrogen will essentially decrease, oxygen being partially eliminated from syncrude. It would result in a cheaper hydrogenation process.

As the sulphur content of syncrude is slightly higher than has been set by the standards for motor fuels, nitrogen content is negligible and that of oxygen has been reduced, moderate hydrogenation process is to be worked out to obtain synfuel meeting the standards.

The production of diesel fuel from Estonian syncrude should be considered together with the possible production of valuable by-products (gasoline, phenols, gas, mazut, bitumens, chemicals, etc.) formed in the same process partially *in situ* and influenced by the process parameters. The optimum proportions between the products to be obtained must be found out.

Hydrogenation is an expensive process and its cost should be partly covered on account of the by-products formed. The consumption of hydrogen will be partly compensated by the hydrogen present in kerogen. The gases released during oil shale retorting, cracking and hydrogenation of shale oil may be subjected to conversion and used as an H-donor in the industrial upgrading process. Possibilities of redistribution of internal hydrogen into cracking products on shale oil thermolysis must be elucidated.

Estonian syncrude contains different compounds and has a wide boiling range. So the fractionation of syncrude leads to products of very different properties and the potential of syncrude can entirely be realized.

As the present review shows, it is technologically possible to obtain a lot of various products on oil shale and shale oil processing, but the perspectives to produce a certain product industrially depends on the economical expedience.

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