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UPGRADING OF ESTONIAN SHALE OIL

3. HYDROGENATION OF PHENOLS

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Estonian shale oil obtained at shale industrial retorting contains up to 26 % phenols. Phenols are highly marketable and could be considered compounds already upgraded on retorting. Production practice includes washing out phenols with water and sodium hydroxide. The question is whether to prefer the hydrogenation of total or dephenolated oil.

The aim of this work was to elucidate both the changes in the composition of phenols occurring during their hydrogenization and distribution of products, to solve the problem of preference stated above - i.e. to obtain the phenols as washed-out final products or additionally decompose them in the composition of total oil to get constituents of the upgraded oil.

Experimental

The phenols were separated from the initial retort oil by treating it with 10 % solution of NaOH.

To obtain comparable data, the same method and conditions as used for hydrogenation of total and dephenolated oils [1] were applied.

In Fig. 1, the dependence of autoclave pressure on hydrogenation time is presented. One can see that the high consumption of hydrogen during the first 30-40 minutes is afterwards replaced with moderate one, this stage lasting for 45-85 minutes, and during the final stage of hydrogenation - last 35 minutes - the pressure is practically constant, indicating the stabilization and the formation of equilibrium between cracking and saturation reactions in autoclave. The optimum hydrogenation time could be a bit shorter than the time used - about 90 minutes instead of 120 at 370 °C. The supply of hydrogen for hydrogenation of phenols in autoclave was sufficient.

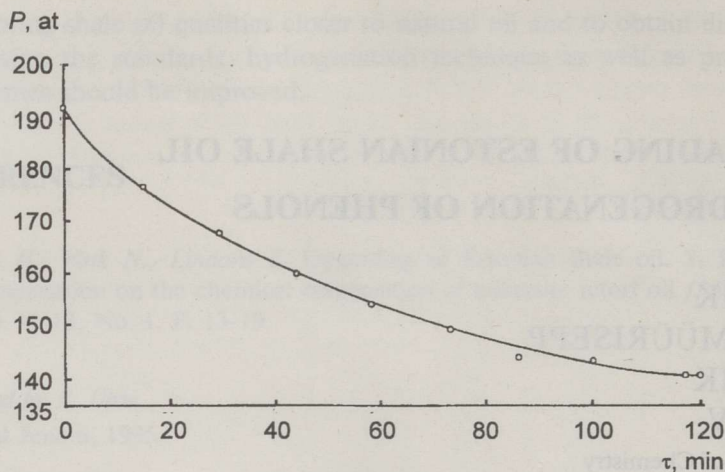


Fig. 1. Changes in the working pressure during hydrogenation of phenols

Table 1. The Yield of Hydrogenation Products of Phenols, %

Product	Yield, wt. %
Oil	81.6
Gas	12.8
Water	5.6
Coke	0

The yield of products removed from autoclave after 2 h hydrogenation is presented in Table 1. As compared with the results of hydrogenation of dephenolated and total retort oil [1], phenols yield as much neutral oil as dephenolated oil on hydrogenation at the same conditions, but no coke.

At the same time total retort oil yields more refined oil and 0.6 % coke, but markedly less gas and water. Therefore, just the phenols give the lion's share of gas and water on the retort oil hydrogenation at the conditions used while neutral oil yields some coke.

Table 2. Chemical Group Composition of Compounds Formed on Hydrogenation of Phenols, wt. %

Compounds	wt. %
Non-aromatic hydrocarbons	15.1
Monocyclic alkylarenes	3.6
Polycyclic (alkyl)arenes	40.9
Neutral oxygen compounds	17.8
Heteroatomic high polar compounds	17.0
Phenols	5.6

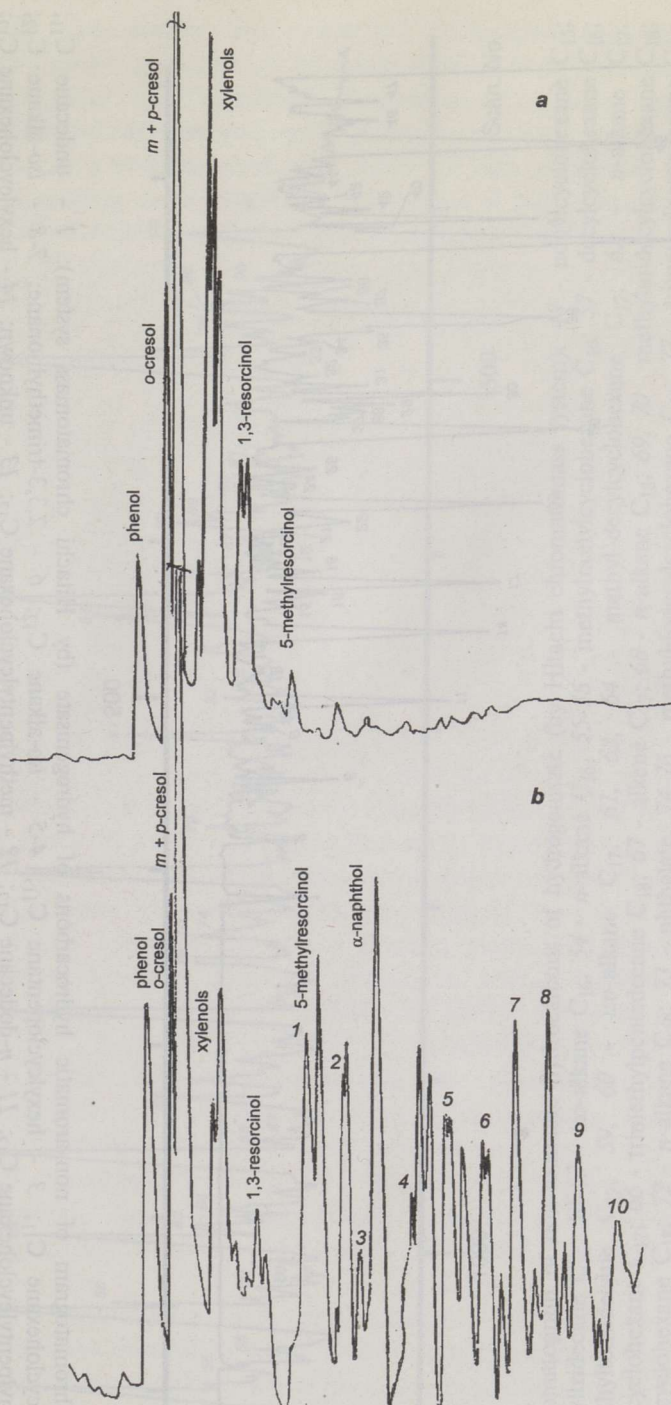


Fig. 2. Chromatograms of phenols: *a* - phenols of hydrogenisate; *b* - total phenols of retort oil, 1-10 - alkylresorcinols

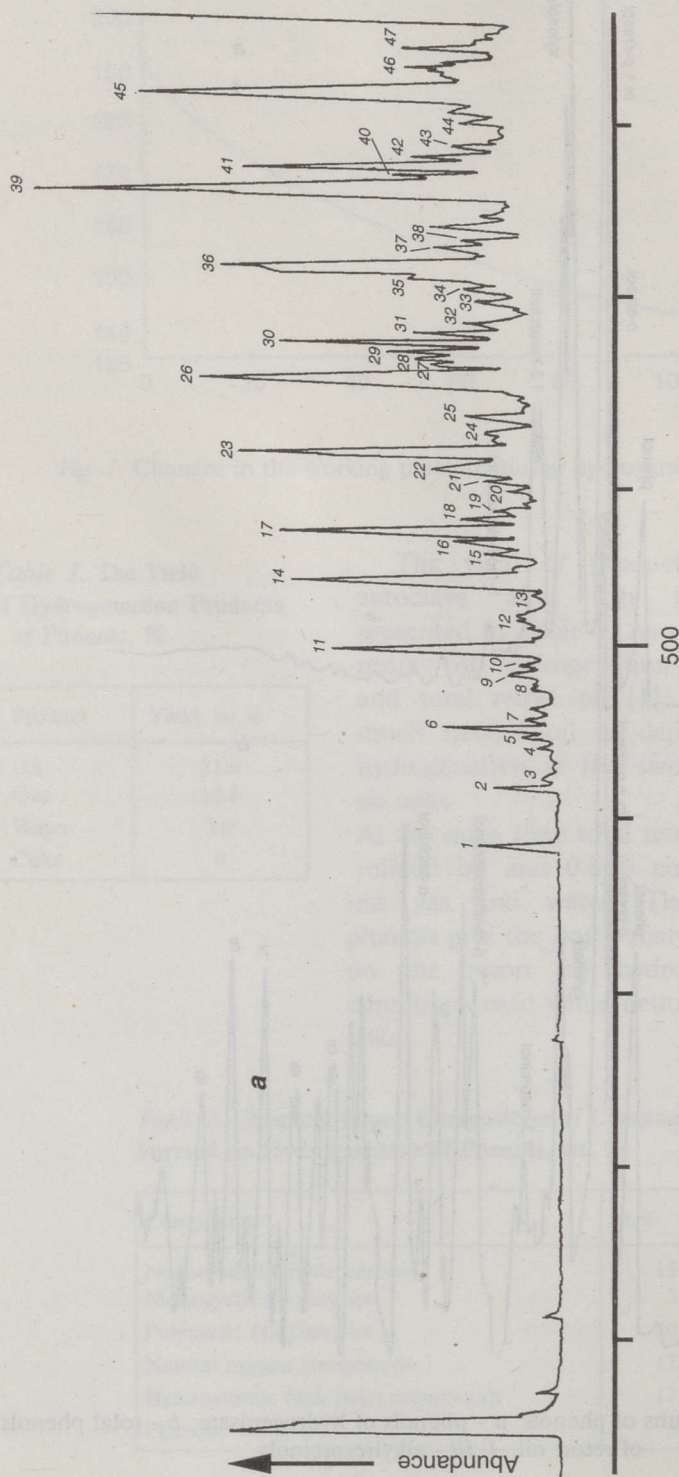


Fig. 3a. Chromatogram of non-aromatic hydrocarbons of hydrogenisate (by Hitachi chromatomass system): 1 - undecane C₁₁; 2 - pentylcyclohexane C₁₁; 3 - hexylcyclopentane C₁₁; 4-5 - iso-alkane C₁₂; 6 - 2,3,3-trimethylnonane; 7-8 - iso-alkane C₁₂; 9-10 - methylpentylcyclohexane C₁₂; 11 - n-dodecane C₁₂; 12 - methylpentylcyclohexane C₁₂; 13 - unknown; 14 - hexylcyclohexane C₁₂; 15, 16, 18-20 - iso-alkane C₁₃; 17 - trimethyldecane C₁₃; 21, 22, 25 - methylhexylcyclohexane C₁₃; 23 - n-alkane C₁₃; 24 - unknown; 26 - heptylcyclohexane C₁₃; 27-29, 31-33 - iso-alkane C₁₄; 30 - trimethylundecane C₁₄; 34, 35, 37 - methylheptyl-cyclohexane C₁₄; 36 - n-alkane C₁₄; 38, 40, 42-44 - iso-alkane C₁₅; 39 - octylcyclohexane C₁₄; 41 - trimethyldecane C₁₄; 45 - n-alkane C₁₅; 46, 47 - methyldecylcyclohexane C₁₅

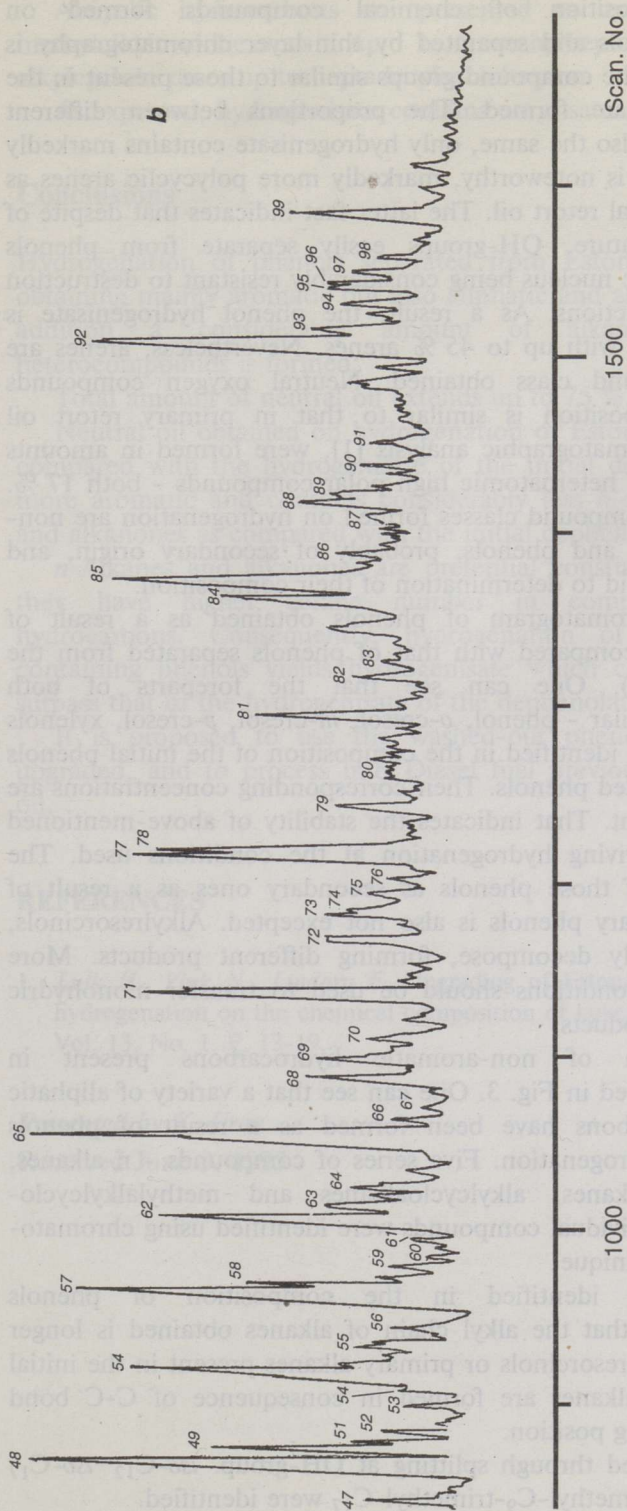


Fig. 3b. Chromatogram of non-aromatic hydrocarbons of hydrogenisate (by Hitachi chromatomass system): 48 - nonylcyclohexane C₁₅; 49 - trimethyltridecane C₁₆; 50-53 - iso-alkane C₁₆; 54 - n-alkane C₁₆; 55-56 - methyl-nonylcyclohexane C₁₆; 57 - decylcyclohexane C₁₆; 58 - trimethyltetradecane C₁₇; 59, 60 - iso-alkane C₁₇; 61, 63, 64 - methyl-decylcyclohexane C₁₇; 62 - n-alkane C₁₇; 65 - undecylcyclohexane C₁₇; 66 - trimethylpentadecane C₁₈; 67 - alkene C₁₇; 68 - n-alkane C₁₈; 69, 70 - methylundecylcyclohexane C₁₈; 71 - dodecylcyclohexane C₁₈; 72 - n-alkane C₁₉; 73 - phthalate; 74-76 - methyl-dodecylcyclohexane C₁₉; 77 - trimethylheptadecane C₂₀; 78 - tridecylcyclohexane C₁₉; 79 - n-alkane C₂₀; 80 - methyltridecylcyclohexane C₂₀; 81 - tetradecylcyclohexane C₂₀; 82 - n-alkane C₂₁; 83 - methyltetradecylcyclohexane C₂₁; 84 - trimethyl-octadecane C₂₁; 85 - pentadecylcyclohexane C₂₁; 86 - n-alkane C₂₂; 87-89 - methylpentadecylcyclohexane C₂₂; 90 - hexadecylcyclohexane C₂₂; 91 - n-alkane C₂₃; 92 - heptadecylcyclohexane C₂₃; 93 - n-alkane C₂₄; 94-98 - methylheptadecylcyclohexane C₂₃; 99 - n-alkane C₂₅ + phthalate

The group composition of chemical compounds formed on hydrogenation of phenols and separated by thin-layer chromatography is presented in Table 2. The compound groups similar to those present in the initial retort oil [1] are formed. The proportions between different compound classes are also the same, only hydrogenisate contains markedly less phenols and, what is noteworthy, markedly more polycyclic arenes as compared with the initial retort oil. The latter fact indicates that despite of relatively low temperature, OH-groups easily separate from phenols forming water, aromatic nucleus being considerably resistant to destruction or even saturation reactions. As a result, the phenol hydrogenisate is aromatic by its nature, with up to 45 % arenes. Nevertheless, arenes are not the only compound class obtained. Neutral oxygen compounds (ketones) whose composition is similar to that in primary retort oil established by gas chromatographic analysis [1], were formed in amounts equal to the amount of heteroatomic high-polar compounds - both 17 %. The most interesting compound classes formed on hydrogenation are non-aromatic hydrocarbons and phenols, probably of secondary origin, and special attention was paid to determination of their composition.

In Fig. 2, the chromatogram of phenols obtained as a result of hydrogenation (2a) is compared with that of phenols separated from the initial retort oil (2b). One can see that the foreparts of both chromatograms are similar - phenol, *o*-cresol, *m*-cresol, *p*-cresol, xylenols and 1,3-resorcinol were identified in the composition of the initial phenols as well as in hydrogenated phenols. Their corresponding concentrations are also not greatly different. That indicates the stability of above-mentioned phenols and their surviving hydrogenation at the conditions used. The formation of a part of those phenols as secondary ones as a result of decomposition of primary phenols is also not excepted. Alkylresorcinols, on the contrary, totally decompose, forming different products. More severe hydrogenation conditions should be used to transfer monohydric phenols into neutral products.

The chromatogram of non-aromatic hydrocarbons present in hydrogenisate is presented in Fig. 3. One can see that a variety of aliphatic and alicyclic hydrocarbons have been formed as a result of phenols decomposition and hydrogenation. Five series of compounds - *n*-alkanes, trimethylalkanes, isoalkanes, alkylcycloalkanes and methylalkylcycloalkanes, and several individual compounds were identified using chromatomass-spectroscopic technique.

n-Alkanes C₁₁-C₂₅ identified in the composition of phenols hydrogenisate indicate that the alkyl chain of alkanes obtained is longer than that of initial alkylresorcinols or primary alkanes present in the initial retort oil. Most of *n*-alkanes are formed in consequence of C-C bond splitting in the branching position.

Isoalkanes are formed through splitting at OH-group. *iso*-C₁₂-*iso*-C₁₇ and trimethylalkanes trimethyl-C₉-trimethyl-C₁₇ were identified.

Alicyclic hydrocarbons are presented as cyclohexane derivatives - methylalkylcyclohexanes up to methylheptadecylcyclohexane and alkylcyclohexanes up to heptadecylcyclohexane.

As expected, hydrogenisate contains no unsaturated hydrocarbons.

Conclusions

Hydrogenation of phenols separated from Estonian shale oil results in obtaining mainly aromatic but also aliphatic and alicyclic hydrocarbons. In addition a considerably amount of alkanones and high-polar heterocompounds is formed.

Total amount of neutral oil extends up to 75 %.

Neutral oil obtained on hydrogenation of Estonian shale oil phenols as compared with the hydrogenisate of the initial dephenolated retort oil is more aromatic and contains considerably less *n*-alkanes and less alkanones as compared with the initial dephenolated retort oil.

n-Alkanes and alkanones are preferential constituents of Diesel fuel, as they have higher cetane number in comparison with aromatic hydrocarbons. Consequently, hydrogenation of the initial retort oil containing phenols yields hydrogenisate which cetane number does not surpass that of the hydrogenisate of the dephenolated oil.

It is proposed to use the washed-out phenols as products already upgraded, and to process into Diesel fuel previously dephenolated retort oil.

REFERENCES

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