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HYDROGENATION OF ESTONIAN OIL SHALE AND SHALE OIL.*

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INTRODUCTION.

THE study of the chemical constitution of organic matter or kerogen of oil shales is undoubtedly connected with the problem of solubility of kerogen in inert solvents.

The experiments on solubility, carried out by one of the authors¹, showed that the kerogen of "kukersite," as the oil shale is called, is practically insoluble in inert solvents, *e.g.*, ethyl alcohol, acetone, ether, chloroform, benzene, carbon disulphide, toluene and xylene. Even the extraction of kukersite with benzene under pressure at about 250° C. yields only about 1 per cent. of extract.²

On the other hand, the kerogen is easily decomposed and depolymerised by heat, but the decomposition proceeds too far on distillation of the mineral under atmospheric pressure, and a considerable amount of the carbon is obtained in the form of coke.³

The distillation of the shale *in vacuo* decreases the amount of coke, but cannot eliminate entirely the coke formation. As is shown in the present paper, on hydrogenation practically all organic matter of kukersite is converted into gaseous and liquid products and a *soluble residue*. Therefore, besides its practical importance, hydrogenation opens a new possibility for studying the nature of kerogen.

For comparison three series of experiments were carried out:— (i.) heating of the shale under pressure of water vapour; (ii.) heating under pressure of hydrogen; and (iii.) heating under nitrogen pressure. The hydrogenation of shale oil has been studied as well.

THE COMPOSITION OF THE RAW MATERIAL.

The shale contained 1.6 per cent. of moisture, 40.2 per cent. of ash, and 58.2 per cent. of organic matter.

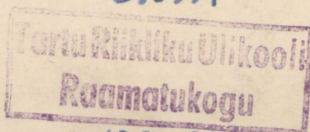
* Paper received January 19, 1932.

¹ P. N. Kogerman, "The Chemical Composition of the Estonian M. Ordovician Oil-bearing Mineral "Kukersite." *Acta et Comment. Univers. Dorpat*, A. III, 6, 1922.

² A. Schneider, "Gesammelte Abhandlungen zur Kenntnis der Kohle," 1922, 5, 41.

³ Compare P. N. Kogerman, "The Present Status of the Oil-Shale Industry in Estonia," *J.I.P.T.*, 1925, 11, 221.

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PROCEDURE.

The experiments were carried out in a revolving, gas-heated, autoclave, made of special steel, having a capacity of about 900 ml. The autoclave was provided with a manometer and a nitrogen-filled mercury thermometer. Charges of shale taken: 200–300 grams. In some experiments 5 per cent. of iron oxide was added to the shale. After about 60–90 mins. a temperature of 370–410° C. was reached, at which temperature the heating was continued for one to two hours. Care was taken to keep the conditions of the operation, *e.g.*, the rate of heating, uniform in all the experiments.

PART I.

PYROLYSIS OF KUKERSITE UNDER A PRESSURE OF WATER VAPOUR.

In this series of experiments about 50 g. of water was added to the shale in the autoclave before starting the experiment. During the reaction a maximum pressure of 190–287 kg./sq. cm. was developed. At the end of the experiment, after cooling, the manometer still showed a pressure of 20–30 atmospheres, *i.e.*, about 20 litres of gas was formed on pyrolysis. (See Fig. 1.)

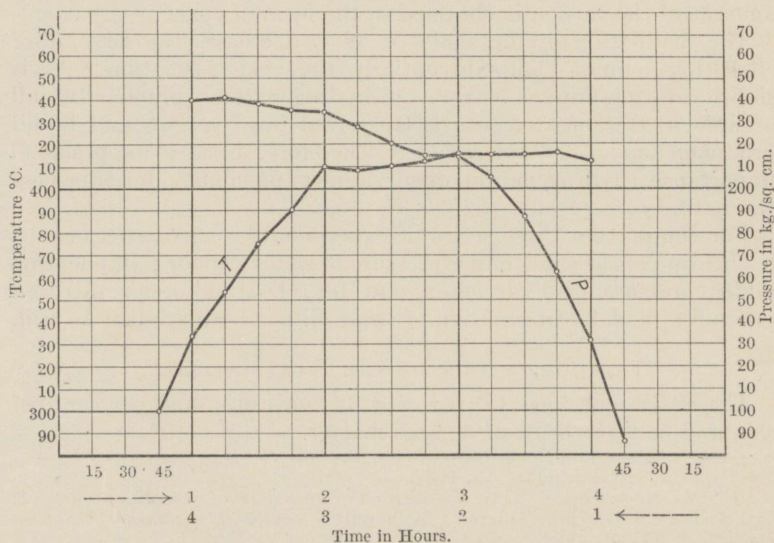


FIG. 1.

PRESSURE-TEMPERATURE CURVES: P—PRESSURE; T—TEMPERATURE.
THERMAL DECOMPOSITION OF SHALE UNDER A PRESSURE OF WATER VAPOUR.

The particulars of the experiments are given in Table I., which shows the yield of liquid products as well :—

TABLE I.

The Results of Pyrolysis of Kukersite under a Pressure of Water Vapour.

Nos. of Experiment.	Charges in g.	Catalyst.	Pressure in kg/sq. cm.		Reaction temp. °C.	Duration in hours.	Oil, b.p. up to 170° C.	
			Max. pressure.	Final pressure.			Oil in g.	Per cent. of oil based on shale.
1	300	Fe ₂ O ₃	259	34	390–400	1½	23·0	7·7
2	300	„	242	30	370–380	1	23·0	7·7
3	300	„	210	27	380–390	1	23·0	7·7
4	300	„	165	22	380–390	½	20·0	6·7
5	300	„	187	22	380–390	½	19·0	6·3
7	200	„	192	18	375–385	2	16·0	8·0
8	200	„	240	28	400–405	2	21·0	10·5
9	200	none	232	27	400–406	2	23·0	11·5
10	300	„	287	34	390–402	2	32·0	10·7

THE PRODUCTS OF PYROLYSIS.

(1) *Gases.*—The gases were analysed in a modified *Orsat-apparatus*: methane, ethane and hydrogen were determined by partial combustion over CuO in a quartz-tube. The gases contained chiefly saturated hydrocarbons and carbon dioxide.

As an example, the analysis of gases obtained in experiment No. 3 (see Table I.) is given: CO₂ + H₂S, 38·4 per cent.; C_nH_{2n}, 1·0 per cent.; O₂, 0·2 per cent.; CO, 0·5 per cent.; H₂, 9·6 per cent.; CH₄, 21·7 per cent.; C₂H₆, 22·5 per cent.; N₂, by diff., 6·1 per cent.

(2) *Liquid products.*—The products of the pyrolysis which remained in the autoclave formed a mixture of a yellowish-brown oil and a brown asphalt-like sticky substance. The mixture was distilled in a copper vessel, provided with a long Liebig condenser. Up to 170° C. water and light oil passed over. This was called the *gasoline-fraction*.

The yield of gasoline is dependent upon the temperature and duration of the process; *e.g.*, on heating of the shale at 375–380° C. for two hours the yield of gasoline fraction was 8 per cent.; heating at 400–410° C. for the same period increased the yield of gasoline to 10 to 11 per cent. (based on the weight of the shale).

The residue, which remained in the still boiling above 170° C. appeared as a black solid substance. About 30 to 40 per cent. of it was soluble in ether. The coke formation has advanced too far and the residue did not soften on heating.

The gasoline fraction.—The freshly distilled gasoline was almost water-white, but darkened on standing. After treatment with 10 per cent. NaOH solution and dilute sulphuric acid, the fraction

was dried and redistilled. The refined product remained water-white on standing.

The gasoline was refractionated, and the following fractions taken:—60–120° C., 120–150° C., and 150–190° C. The properties of these fractions are given in the Table II. below:—

TABLE II.
Properties of Light Oils.

Fraction °C.	Sp. Gravity at 20° C.	Refract. indices (Abbé Refractometer).
60–120°	0.7137	1.4018 (at 20°)
120–150°	0.7848	1.4357 (at 14°)
150–190°	0.8073	1.4499 (at 14°)

As regards the effect of ferric oxide upon the process of pyrolysis, definite conclusions cannot be drawn; undoubtedly iron combines with sulphur, and the sulphur content of the oils is reduced as had been found in some experiments.

PART II.

PYROLYSIS OF KUKERSITE UNDER PRESSURES OF NITROGEN AND HYDROGEN.

The shale used for this series of experiments had the following composition: moisture, 1.7 per cent.; total ash, 50.9 per cent., and organic matter, 47.4 per cent.

The procedure remained essentially the same as described in the introduction. Charges taken about 300 grams, and 5 per cent. of iron oxide was added to the shale. The products of pyrolysis resembled the products described in Part I., but in the case of nitrogen the inner surface (walls) of the autoclave was covered with a very sticky asphalt-like substance.

During the reaction, at a fairly constant temperature, the nitrogen pressure curve showed a tendency to rise. As an example, comparative yields of oil from the shale under nitrogen and hydrogen pressures are given in Table III. below:—

TABLE III.
Yield of Oil on Pyrolysis of Shale.

Experi- ment.	Total amount of shale treated in g.	Gas used.	Liquid products boiling up to 275° C. under 15 mm. pressure; per cent. based on the shale.			Remarks.
			Oil.	Water.	Total.	
1 } 1a }	620	N ₂	23.9	4.2	28.1	Mean figures of two experiments are given.
2 } 2a }	645	H ₂	30.5	4.0	34.5	
3 } 3a }	628	twice treated under H ₂ .	29.2	4.1	33.3	

In the experiments 3 and 3A the shale was heated under hydrogen pressure, then, after cooling, the gases released and the product hydrogenated once more.

The gas from experiments with nitrogen had the following composition (Expmt. 1a) : CO_2 , 7.9 per cent. ; C_nH_{2n} , 0.3 per cent. ; O_2 , 0.0 per cent. ; H_2 , 1.8 per cent. ; CO , 2.7 per cent. ; $\text{CH}_4 + \text{C}_2\text{H}_6$, 5.6 per cent. and N_2 , 81.7 per cent.

The products of pyrolysis, liquid and solid, were introduced into a 2-litre copper flask and fractionated : up to 170°C . under atmospheric pressure, above that temperature under 15 mm. Hg. pressure. With the first fraction water passed over as well. The results of fractionation are given in Table IV. :—

TABLE IV.

Fractionation of Oils.

Experiments.	Percentage yield of Fractions.					
	1 and 1a.		2 and 2a.		3 and 3a.	
Fractions $^\circ\text{C}$.	On organic matter.	On the oil.	On organic matter.	On the oil.	On organic matter.	On the oil.
Up to 170 at atm. ..	18.1	35.8	22.3	34.7	21.2	33.4
„ 125 at 15 mm. ..	6.1	12.2	9.9	15.3	10.3	16.9
125-155	6.0	11.9	8.3	12.9	7.3	11.8
155-185	5.5	10.9	8.1	12.5	8.5	13.8
185-215	4.5	8.0	6.6	10.3	4.6	7.5
215-265	—	—	—	—	9.9	15.9
215-270	—	—	9.2	14.2	—	—
215-275	10.6	21.0	—	—	—	—
Total yield	50.8	99.8	64.4	99.8	61.8	99.3

Comparing the results of conversion of kerogen into oils (Table IV.), one can see that, on “hydrogenation,” about 10 per cent. more of organic matter is converted into oils than on treatment under nitrogen pressure. In order to check some of the previous results, three experiments were carried out under strictly comparable conditions :—

(i.) The autoclave, without shale, was filled with hydrogen up to an initial pressure of 106 kg./sq. cm. and heated at $395\text{--}407^\circ\text{C}$. for $1\frac{1}{2}$ hours. (Blank experiment.)

(ii.) 250 g. of shale was introduced into the apparatus, then hydrogen fed in up to 98 kg./sq. cm. of initial pressure, and the shale heated at $394\text{--}410^\circ\text{C}$. for $2\frac{1}{2}$ hours.

(iii.) 250 g. of shale of the same quality was heated in the autoclave under nitrogen pressure at $398\text{--}411^\circ$ for $2\frac{1}{2}$ hours. Initial pressure of N_2 was 97 kg./sq. cm.

The rate of heating in experiments (ii.) and (iii.) was the same. The temperature and pressure were recorded every 10 mins., and temperature-pressure curves are given in Fig. 2.

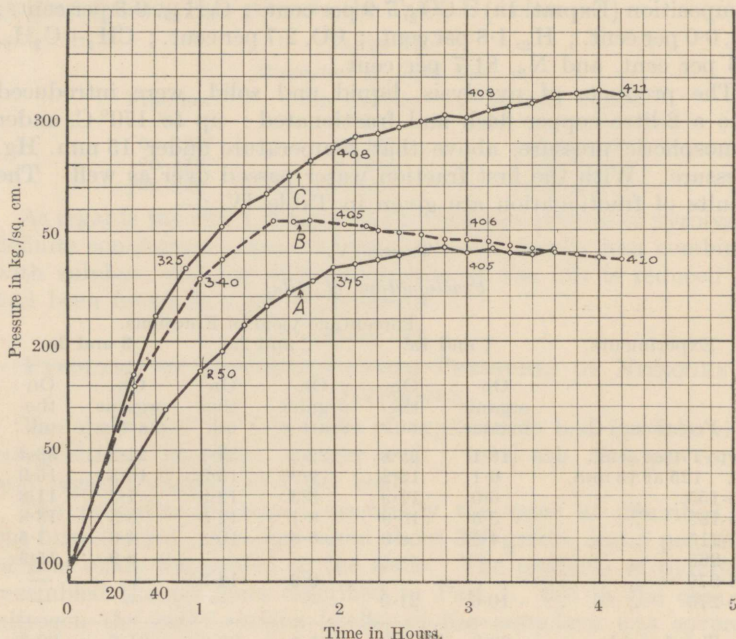


FIG. 2.

TYPICAL PRESSURE - DECOMPOSITION CURVES: A—BLANK EXPERIMENT; B—HYDROGENATION CURVE; C—THERMAL DECOMPOSITION UNDER NITROGEN PRESSURE. THE FIGURES ON THE CURVES REFER TO TEMPERATURES.

In the blank experiment the pressure of gas rises with the temperature and remains constant at constant temperature. After cooling, the manometer showed a pressure of 105 atmospheres—*i.e.*, one atmosphere less than the initial pressure. Although the autoclave proved to be gastight, there might have been some losses on heating at higher temperatures and pressures. Another reason for this discrepancy might be the inaccuracy of readings, because one point of the manometer corresponds to 20 kg./sq. cm.

In the second experiment (hydrogenation) the pressure curve began to fall as soon as the reaction temperature was kept constant. After cooling of the apparatus the manometer showed a pressure of 74 kg./sq. cm.—*i.e.*, 24 kg./sq. cm. less than the initial pressure.

During the third experiment, when the shale was treated under pressure of nitrogen, the pressure curve was steadily rising, although the temperature was kept constant. The final pressure at room temperature exceeded the initial pressure by 8 atmospheres.

Analysis of gases.—The analysis of gases obtained on pyrolysis of the shale under hydrogen (E. 2) and nitrogen pressures (E. 3) are given in Table V. below :—

TABLE V.

Analysis of Gases.

Gas.	Expmt. 2.	Expmt. 3.
CO ₂ ..	4.8%	4.9%
C _n H _{2n} ..	0.3	0.2
O ₂ ..	0.0	0.1
CO ..	1.4	0.2
H ₂ ..	86.2	1.3
C ₂ H ₆ ..	0.8	2.4
CH ₄ ..	2.6	1.4
N ..	3.9	89.5
	100.0	100.0

Liquid Products.—The liquid products of both experiments were distilled in a copper vessel of about 750 ml. capacity. The oil was separated from water, treated with soda solution, then washed with very dilute sulphuric acid and water. The neutral oil was dried over fused sodium sulphate and fractionated under atmospheric pressure.

The light fractions of the oils seem to be very similar in composition, as is evident from the Table VI. below :—

TABLE VI.

Properties of Oils.

Oil.	Fraction °C.	Sp. Gravity at 20° C.	Mean Mol. weight.	Refractive index.
From E.2 : hydrogen pressure	95–160	0.7455	111	1.4167
From E.3 : nitrogen pressure ..	95–160	0.7453	109	1.4179

The water obtained on pyrolysis of the shale showed an acid reaction. The oil boiling up to 160° C. showed a marked solubility in 10 per cent. solution of sodium hydroxide.

PART III.

EFFECT OF HYDROGENATION UPON THE FORMATION OF "FREE CARBON" AND UPON THE SOLUBILITY OF THE RESIDUE.

The product of hydrogenation of the shale is a very viscous, pasty substance with a characteristic smell of kerosine. The

residue remaining in the distillation flask after removal of light oils, forms a soft brownish-black asphalt-like substance. Its penetration values at 25° C. were 94–128, dependent upon the conditions of the experiments.

For the determination of “free carbon” or “coke” in the residue, the latter was extracted with benzene for about 16 hours. The ash contents of the residue was determined in an electric furnace, and CO₂ in Baur’s apparatus. Mineral ash + CO₂ = total ash.

The difference between the percentage of organic matter in the residue (*a*) and that of the portion soluble in benzene (*b*) is regarded here as percentage of “coke” (*a-b*).

The percentage of coke in the residue is dependent upon the temperature of the reaction, pressure of hydrogen, and duration of the experiment.

In Table VII. the particulars of the experiments and percentages of coke in residue are given.

The highest percentage of coke was formed on heating the shale without hydrogen (blank experiment No. 20)—*i.e.*, 20.4 per cent. of the residue.

At temperatures below the “transition interval”—*i.e.*, 360–390° C.—at which the insoluble kerogen is converted into a soluble semi-solid intermediate substance, the “coke” contains undoubtedly a part of unaltered kerogen as well. Below the transition temperature, the decomposition respectively depolymerisation of the kerogen is very slow (experiment No. 6).

On heating the shale at temperatures between 380–410° C. under hydrogen pressure of 250 kg/sq. cm. for 2–3 hours, practically *no coke is formed*.

Above this range of temperature—*e.g.*, 440–450° C.—the secondary decomposition or “cracking” of the intermediate product begins, and the coke contents of the residue increases again.

In hydrogenation we have a new method for studying the nature of the kerogen. Of all the methods applied so far as for coal and shale research, none gives the bulk of kerogen in soluble form. How far the salts of organic acids, a fair percentage of which the kerogen probably contains, affect the transition temperature is difficult to tell at present. But, on the other hand, the transition interval excludes the presence of many aliphatic and particularly aromatic acids⁴, and gives some hints for searching for oxygen-compounds in the shale oil.

⁴ Compare: Hurd, C. D., “The Pyrolysis of Carbon Compounds,” New York, 1929, pp. 475-523.

As an average the hydrogenation product of the kerogen contained:—

About 12 per cent. of gasoline fraction, b.pt. below 170° C.

About 17 per cent. of kerosine fraction, b.pt. 60–170° C. at 10 mm. Hg.

About 20 per cent. of asphalt.

Percentage based on dry shale.

The kerosine fraction contains about 13 per cent. of higher phenols, 32 per cent. of unsaturated and 8.5 per cent. of aromatic compounds.

The yield of oils produced from the shale on treatment under hydrogen pressure in one run does not surpass to any considerable extent the yield of oils, obtainable on distillation under ordinary pressure.

PART IV.

HYDROGENATION OF SHALE OILS.

For hydrogenation the following shale oils were taken:—

(i.) Crude shale oil, obtained from Kohtla plant⁵; sp. gravity about 1.00.

(ii.) A fraction of this oil, boiling from 170° C. at atm. pressure up to 215° C. at 15 mm.

(iii.) The residue boiling above 215° C. at 15 mm.

(iv.) The neutral shale oil, obtained from the crude oil on removal of acidic constituents (phenols and acids).

(v.) Crude phenols, obtained on soda-wash of the crude oil.

Charges taken: 300–350 grams. Initial pressure of hydrogen was about 100 atmospheres. Reaction temperature: 400–410° C., and duration of reaction 90–150 mins.

The temperature-pressure curves were similar to those obtained on hydrogenation of the shale.

The products of hydrogenation were distilled in a round-bottom flask, provided with a Liebig condenser, and five fractions were taken—*i.e.*, one up to 170° C./atm. and four under 15 mm. Hg. pressure.

The particulars of these experiments are given in Table VIII.

In the experiment No. 17, the crude oil was twice treated under hydrogen pressure.

⁵ For particulars, see: *P. Kogerman*, "Oil Shale Industry in Estonia," *J.I.P.T.*, 1925, **11**, 221–222, and by the same author, "On the Chemistry of the Estonian Oil Shale 'Kukersite,'" *Archiv für die Naturkunde Estlands*, 1931, 1. Ser., 10, Bd., 2 Lief.

TABLE VIII.
Results of Fractionation of Hydrogenated Shale Oils.

No. of Experiment.	Oil.	Catalyst.	Specific gravity at 20°C.			Fraction up to 170°/atm.; % by weight.		Fractions under 15 mm. pressure; % by weight.		Residue per cent.
			Original oil.	Hydrogenated oil.	Water.	Oil.	Total.	60°-215°.		
1	Crude oil	None 5% Fe ₂ O ₃ Fire clay 5% Fe ₂ O ₃	—	—	1.4	6.8	8.2	36.9	54.5	
4			1.000	0.957	1.8	14.7	16.5	44.3	37.8	
5			—	—	2.3	9.8	12.1	44.8	—	
17			1.000	0.945	1.5	14.6	16.1	44.6	—	
7	Fraction b. pt. 170° C. at atm. press. to 215° C. at 13 mm.	None 5% Fe ₂ O ₃	—	—	0.8	9.1	9.9	66.7	22.5	
8			0.954	0.912	0.4	11.4	11.8	72.4	15.7	
13	Neutral oil Residue Crude phenols	5% Fe ₂ O ₃ Fe ₂ O ₃ 13% Fe ₂ O ₃	—	—	—	7.1	7.1	42.3	49.7	
11			—	—	1.3	3.5	4.8	17.6	—	
18			—	—	4.7	24.3	29.0	—	—	

The results of experiments on the desulphurisation of shale gasoline by hydrogenation have been published elsewhere⁶, and show that on hydrogenation the complete desulphurisation of shale petrols is achieved.

The results of hydrogenation of Estonian shale oils can be summarised as follows :—

(1) On hydrogenation of shale oils, with the formation of light oil, polymerisation occurs with the formation of heavier, higher boiling oils. (Compare experiments Nos. 7 and 8.) For instance, the fraction of oil boiling between 170° C. and 215° C. at 15 mm. yielded, after hydrogenation, 11·4 per cent. of oil boiling below 170° C., and about 17 per cent. of residue boiling above 215° C., at 15 mm.

(2) The crude phenols, boiling above 170° C., yielded 24·3 per cent. of light oil and 4·7 per cent. of water.

(3) The residue obtained on distillation of the crude oil, from which all constituents boiling below 215° C. at 15 mm. had been removed, yielded, on hydrogenation at 380° C., 4·8 per cent. of light oil. At higher reaction temperatures—*e.g.*, 427° C.—the coke formation advanced too far.

(4) The lower boiling fractions of oils, obtained on hydrogenation of crude shale oil, were almost identical with those obtained on hydrogenation of the shale.⁷

GENERAL SUMMARY AND CONCLUSIONS.

(1) The amount of kerogen of the shale liquefied on hydrogenation in one run does not exceed to any considerable extent the amount of liquid products obtained by ordinary distillation.⁸

(2) On hydrogenation of kukersite an absorption of hydrogen is observed : about 1·8 per cent. by weight of kerogen. Below

⁶ Paul N. Kogerman, *J. Inst. Fuel.*, 1932, **5**, 278.

⁷ After this paper had been written, a paper on cracking and hydrogenation of shale oils was published by Tilicheev and Seledgeev ("Oil Shales and their Technical Utilisation," Leningrad, 1932, pp. 449-481; in Russian). The authors claim that on "repeated" or total hydrogenation of Estonian shale oil about 70 per cent. of gasoline, *i.e.*, oil boiling below 200° C., is obtained. Their procedure was : after each run (experiment) the light fraction, boiling up to 200° C., was distilled off, and the residue treated again under hydrogen pressure. Initial pressure of hydrogen about 200 atms., reaction temp. about 450° C.; duration : first run 3 hrs., second and third 6 hrs. each. Ten per cent. of nickel oxide was used as catalyst.

Compare also : H. I. Waterman, S. C. de Jong and A. J. Tulleners' "Contribution to the Knowledge of the Treatment of Estonian Oil-Shale," *J.I.P.T.*, 1932, **18**, 183-186.

⁸ Compare : A. W. Nash, "Torbanite and its Treatment by the Bergius-Method," *J.I.P.T.*, 1926, **12**, 568-581.

the decomposition point of kerogen practically no hydrogenation is taking place;⁹ of the decomposition products or the "products of cracking" of kerogen mainly the lighter products are hydrogenated.

(3) The hydrogenation of the shale prevents the coke-formation.

(4) On hydrogenation, under the same conditions, the shale and the crude shale oil yield oils, of which the lower boiling fractions are almost identical.

(5) The heating of kukersite or its crude oil at temperatures 400–410° C. under 250 kg./sq. cm. hydrogen-pressure favours the formation of oils with lower boiling points, mostly paraffin-, and naphthene-hydrocarbons; at higher temperatures and on long-continued heating the formation of aromatic hydrocarbons is observed.

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⁹ The amount of chlorine giving addition-reaction to the shale is very small as well. See P. N. Kogerman, *Sitzungsberichte d. Naturforsch.—Gesellschaft, Tartu, 1927.*

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