f. Mining costs were too high.

g. Constant lack of technical auxiliary means from the telephone to the lubricants.

h. Last but not least: Working with hungry prisoners instead of robust workers who were interested in their earnings.

Basic faults not to be removable are:

a. Need of large areas of strong foundation.

b. Yield which hardly may reach 60% of Fischer in the average.

c. Bad utilization of the heat.

d. Process is neither regarding the time nor regarding its technical details steerable.

e. Meiler is a plant in permanent fitting.

f. Meiler is dependable on the weather.

g. Comparatively huge amount of poor gas.

It may be of some interest to calculate what the cost price of a water-and-dust-free crude oil obtained by the meiler method under improved conditions could be.

It must be possible to obtain the run of mine shale for RMk 3.0, including crushing, screening and transport until the pile is RMk 3.25. We have produced in Estonia, for instance, several million tons of shale for RMk 2.86 in the average. This corresponds to a normal price of run of mine shale of $0.76 per ton. It will be possible to obtain from a standard meiler of 1700 tons 42 tons of oil, i.e., an absolute yield of 2.5%, or 50% yield according to the Fischer assay. The costs per one ton of oil may approximately amount as follows:

Shale on the pile	RMk 130.-
Wages, salaries	" 45.-
Electric power 450 Kwhs/to	" 9.-
Water, coal, lignite, wooden chips, lubricants	" 10.0
Annuity, interest on capital	" 31.-
Sundries	" 5.-
TOTAL	" 230.-

This amount corresponds to a price of $3.65 per one barrel of oil at the present exchange rate of $1.00 - RMk 10.0. Altho the shale on the pile costs $0.325 only, the estimated cost price of the ready oil is considerably high. This price may be lower in another country, but in general one can say that the meiler-method might be applied under the following presuppositions only: dry and warm climate, vast areas of plain and hard underground at low price, poor and cheap shale, renunciation on good oil yield and on by-products. The electric power must be cheap and the water supply plentiful, the carbonisation plant highly mechanized and the shale deposits situated favorably to the pile field. Principal faults of this system are not removable, as for instance the main error: the meiler misses every continuancy and uniformity necessary for the normal operation of a plant.

A brief summary of the content is given in the following:

Reasons for erection of 10 carbonization plants of the meiler method. First trials on the Metzingen pilot plant seemed to be promising. According to these results 10 plants were designed. Researches continued at the larger Schomberg pilot plant were disappointing. Blunder of transferring perceptions of tiny laboratory tests to industrial stage. No practical experiences of handling the pile. Comparison of regulations for the meiler in summer 1944 with those in summer 1946:

a. Properties of the oil shale of Wurttemberg. Shale sampling later on abandoned. Moist shale.

b. Granulation and crushing practically not performed.

c. Measures of the meiler, grate. Forced to simplify the measures in the industrial stage.

d. Ignition, demand of peat, wooden chips. High O_2-content produced by bad ignition which is dependable on weather. Peat abandoned, ignited by means of lignite.

e. Velocity of carbonisation regulated by means of exhaustor. Oxygen content essential. This was in Metzingen 1.5-4%, rose at the pilot plant to 4-10% and at the standard plants to 7-12%. Duration of carbonisation decreased from 80 hrs to 40 hrs. Comparison of practical data.

f. Trickling and removal of grates appeared to be very troublesome.

g. Lowering of the surface and cooling of the meiler. Wrong times produce a wrong schedule for the continuous carbonization.

h. Theoretical predetermination of carbonisation failed.

i. Piles with perpendicular suction pipes tested.

k. Fixed piles to avoid the removal of grates stipulate handling of residue. Short description of technical devices of standard pile-plant: mine, crusher and screening, meiler-fields, total iron weight of pipe-work 530 tons, condensing plant consisting mainly of natural cooling and Cotrell plant only. Technical devices of the pilot plant which was completed too late. Practical results of the meiler-method. Erection of plants delayed by wrong planning and war influence. Scheduled output never reached. Total approximated output of the shale oil industry of Wurttemberg from November 1944 until July 1946. Estimates on possible production under prevailing circumstances. Interest of the French. Profitableness of the meiler-system as performed in Wurttemberg is out of question. Oil production by means of meilers in the period from November 1944 until July 1946. Return of single meiler's output on the pilot plant Schomberg and on Plant No. 8 from August 1944 until July 1946. Specific consumption of power, water, steam, etc. Comparison of required iron weights for different carbonization methods. The Cotrell-method in collaboration with the meiler did not suffice owing to the instability of the meiler. The "feasible load" depends on O_2-content, amount of gas, temperature and admixtures. Some directions on operating the Cotrell. Power consumption and profitableness of the Cotrell. Conclusion: many faults of the meiler-plants in Wurttemberg were removable, other capital disadvantages are included in the character of the meiler-pile. Attempt to estimate the cost-price of oil produced by meiler-carbonization under ideal conditions.

H. A. Wahl

H. A. WAHL

Graf

Graf

Subject: Information regarding refining methods for shale oil.

A. Experimental experiences

I. The characteristics of shale oils depend on the chemical properties of the original bitumen and on the inorganic substance of the shale. They can be influenced by the applied methods for the recovery of the oils. Therefore, an important step to refine the shale oil must be carried out by the carbonization processes.

II. Characteristics of raw oil produced 1944 from oil shale of Schandelah near Brunswick, Germany, are presented in table 1. The oil samples A and B were obtained in a small scale plant at Vienna and the sample C in a large pilot plant at Schandelah. In both of the plants the oil shale was carbonized at low temperatures by the same gas purging process, which is reported on August 15, 1946 by E. Graf: "Description of a Low Temperature Carbonization Process for Oil Shale." The sample D originated from a meiler-pile which was operated at Schandelah. The samples A and B were tested in the laboratory of E. Graf, whereas the samples C and D were tested by Prof. R. Heinze, director of the Research Institute of Browncoal and Mineral oil of the Technical University of Berlin. The raw oil A was obtained by using air and water steam for the gasification of the shale coke, whereas oil B and C were produced by introducing air and recirculating lean gases into the shaft.

The separation of the recovered oil-water-emulsion was easily to perform with the oils B and C by heating the mixtures to 60°C. The separation of water from oil A was more difficult to perform by heating a relatively long time at 80°C, whereas the oil D was only to separate from water by adding a 3% HCl-solution.

III. The balance of the chemical constituents C, H, S, N and O is an important auxiliary means as to judge the carbonization process. Unfortunately it was impossible to finish the constituent balances of Schandelah oil shale. The results of only one sulfur balance can be presented. The sulfur content of the oil shale, which was capable of being gasified in low temperature carbonization process was 1.66%. 20% of this sulfur content was present in the oil, which had a sulfur content of 4.76%. 34% of the sulfur was present in the gas, 1% in the low temperature carbonization water and 45% remained in the coke.

Trying to extract the bitumen of Wurthemberg oil shale with tetralin at elevated temperature and pressure in a laboratory autoclave 66% of the organic substance was extracted which had the following average chemical composition.

C = 83.4 H = 8.0 S = 3.0 N = 0.60 O = 5.0 %

The balance of the chemical components could not be finished.

TABLE 1 : CHARACTERISTICS OF SCHANDELAH - SHALE OILS

Sample		A	B	C	D
		continuous	Graf-	Iguis-shaft	Meiler- -pile
1) Employed low temperature process					
2) Specific gravity 20°C		0.970	0.973	0.986	1.007
3) Boiling range					
a) Water	% Vol	0.40	0.40	0.00	0.00
b) Light oil -180°C	"	0.00	0.00	0.00	0.00
c) Midde oil -230°C	"	1.49	3.43	2.00	2.50
d) Heavy oil I -290°C	"	11.45	17.59	25.00	25.50
e) Heavy oil II -385°C	"	30.22	39.29	57.50	59.00
f) Heavy oil III -405°C	"	47.76	28.30	9.50	0.00
g) Residue and losses	"	8.68	10.99	6.00	13.00
h) Initial boiling point	°C	190	200	215	220
i) End point	°C	405	403	403	375
4) Phenoles in c)	Wt %	--	4.0	--	--
Phenoles in d)	"	5.2	2.0	--	--
Phenoles in e) + f)	"	2.0	2.0	--	--
Solid paraffins in e) + f)	"	4.5	2.0	--	--
5) Flash point	°C	--	--	122	130
6) Pour point	°C	--	--	-8	+ 0
7) Viscosity at 20°C	°E	8.5	5.9	8.8	14.6
Viscosity at 50°C	°E	--	--	2.1	2.9
8) Conradson test	Wt %	--	--	2.93	5.80
9) Ash content	"	--	--	0.02	0.02
10) Sulfur content	"	--	--	4.8	5.0
11) Insoluble in light gasoline	"	--	--	2.51	8.38
12) Insoluble in butanone	"	--	--	0.06	0.06
13) Corrosion test mg per 16 cm^2		--	--	-0.1	-0.8

IV. The primary interest on Schandelah shale oil of our plant was to use it as diesel fuel. Experiments were made with the crude oil by various technical institutes and I sometimes learned that the oil was satisfactory without any refining for hot bulb engines and even for diesel engines. Due to the short observation time definitive conclusions could not be obtained.

B. Published experiences.

V. Foremost Estonian oil shale and shale oils seem to be investigated. Characteristics of Estonian shale oils are published for example in: K. Luts : "The Estonian Oil Shale Kukersit, its Chemistry, Technology and Analysis," Reval 1944 and R. Zeidler : "New Methods on Oil Shale Utilization," Reval 1933.

VI. As a cooperator of the "German Oil Shale Research Comp." I obtained an I. G. Farben report on a chemical analysis of an Estonian shale oil sample, which was carried out at Oppan in the first months of 1944. This oil sample contained a proportionate amount of gasoline according to the production. It was characterized by the "Baltic Oil Corp." as to asphaltic base with an essential content of unsaturated compounds and a high content of resin, with about 20% of acidic compounds and about 2 to 3% of cresols, but without a content of carbolic acid. The phenoles were higher polymerized compounds, partly hydro-aromatics. Nitrogen compounds were only present in small amounts. The shale gasoline with a boiling range 182 to 200° had the following composition:

62%	olefines
22%	paraffins
9%	aromatics
7%	naphtenes

The oil sample was separated by normal distillation into a light fluid middle oil and a high boiling thick-oil. The boiling range of the middle oil was:

Initial boiling point	182.5	°C	50 cm^3	241.4	°C
2 cm^3	193.0	"	60 "	251.1	"
5 "	198.9	"	70 "	263.7	"
10 "	203.3	"	80 "	289.1	"
20 "	209.6	"	90 "	326.5	"
30 "	215.0	"	93 "	326.5	"
40 "	226.7	"	94.1 " after run		

From this oil a 20% fraction was obtained by distillation at 20 mercury pressure and 115 to 140°C boiling range. The molecular weight of this fraction was 164, that means an average hydrocarbon chain length of 11.7 carbon atoms. The hydrogenation number was 14 according to 6.77% olefines.

Hydro x yl number = 28 equal 8.19% alcoholes
Carbonyl number = 44 equal 12.88% Ketones
Sulfur = 2.6%
Chlorine = 0.008%
Oxygen + nitrogen = 3.23
Hydrogen = 11.49%
Carbon = 82.67%

The high sulfur content caused difficulties for most of the tried refining experiments. The kind of these experiments was not reported.

The thick-oil showed an acid number of 6.13 and a saponification number of 12.40. The vacuum distillation resulted:

at 19 mm.	merc. pr.	4.3%	120 - 140°C
"	"	7.5%	140 - 160°C
"	"	7.8%	160 - 180°C
at 0.2	"	5.7%	110 - 130°C
"	"	10.0%	130 - 150°C
"	"	9.3%	150 - 170°C
"	"	14.2%	170 - 200°C
"	"	7.8%	200 - 220°C

(pressure amounts to 0.5 mm. , destruction of oil)

at 0.5 mm.	merc. pr.	32.0%	residue
		1.4%	losses

VII. During my research works, I obtained the following information on investigation and testing Wurttemberg and Estonian shale oils, which have been reported by others (Dr. Oppelt, Dr. Liebmann).

1) Prof. Theilacker, Tubingen (6.8.1943) " Investigation of low temperature carbonization products obtained from Estonian shale at Metzingen."

2) A. Riebeck-Montan-A. G. Messel/Darmstadt "Comparing investigations of Wurthemberg shale oil from the Dr. Schweitzer-furnace and of oil from Messel."

3) Dr. Obenaus (28.8.1943) "Analysis of shale oil from Wurttemberg and Estonian oil shale".

4) Bureau Frankfurt on Maine (14.7.1943) "Comparing data on shale oil, gas benzine and gas from experiments with Wurttemberg and Estonian oil shale in the pilot plant of Metzingen".

5) Prof. Mally, Tubingen (9.6.1944) "Extraction of resin from shale oil by means of methyl alcohol, pour point lowering of shale oil, separating water from sludge, desulfurication of shale oil (Laboratory experiments)".

6) I. G. Farben-Laboratory (8.3.1944) "Analysis of Wurttemberg shale oil produced in the Otto-Detternhansen furnace."

VIII. The following distillation and refining result applying 8.258 tons of Wurttemberg-meiler-pile shale oil was obtained from the "Ludol-Comp." Esslingen and Prof. Keinze (8.5.1944).

16.625 tons of the oil containing 50.3% water were separated by heating to 60°C at normal pressure and then to 90°C and about 1 at pressure in a batch still. The distillation was carried out by boiling till 200°C at normal pressure, till 270°C (fraction I) with water steam at normal pressure, till 320°C (fraction II) under vacuum and water steam and above 340°C (fraction III) with higher vacuum and water steam and above 340°C (fraction III) under vacuum only. Table 2 represents the results.

The first running gave 2% of a light benzine, 35% heavy benzines and 58% diesel oil. Fractions I and II were assumed to give a good diesel fuel with 70% boiling till 300°C. The fraction III was assumed to be interesting for manufacture of lubricating oil. The united fractions I, II and III were treated with sodium hydrate, whereby a loss of about 1.5% occurred due to phenoles and its homologues and a neutral oil. The latter could be recovered.

IX. Interesting experiments were carried out by the "Physitalisch-Technische-Reichs aust alt" (Reported 28.1.1944) in order to lower the -2°C-pour point of a Wurttemberg shale oil. The admixture of 25% of a naphtenic base supposedly Roumanian fuel oil with a pour point of -35°C gave a mixture pour point of -53°C. The slope of the mixing curve permitted the conclusion that a precipitating of solid compounds of each of the two components is possible, which are easily to be solved by the liquid remainder of the other component. Supposedly the ordinary effect of a natural "paraflow" took not place. Unfortunately, I did not hear more about the continuation of this experiment.

X. The nitrogen content of various fuels is shown in the following table III. Items 1) to 5) are related on ash and water free substance. x) means only data referring to one special sample.

Table 2 : Distillation Results.

	kg	wt %	Specific Gravity	Flash -point °C	Pour- -point °C	Viscosity	
						°E/20°C	°E/50°C
A. First running	277	3.35	0.857	-	-	-	-
B. Middle oil	5539	67.08	0.937	101	-15	2.55	1.42
Fraction I till 270°			0.914	100	-23	1.57	1.20
Fraction II till 320°			0.941	128	-8	2.63	1.42
Fraction III till end			0.983	144	-6	21.80	4.38
C. Asphaltic residue	2343	28.37	Softening point (method Kramer-Sarnow) +32°C, Ash content 0.32 %.				
D. Distillation losses	99	1.20					
Sum	8258	100.00					

Table III. Average nitrogen content of fuels in wt %.

1) Anthracite	0.2 - 1.5	7) Estonian oil shale	0.3 x)
2) Black coal	0.6 - 2.8	8) Estonian shale oil	0.2 - 0.3
3) Brown coal	0.4 - 2.5	9) Scotch oil shale	0.5 - 3.0
4) Peat	0.7 - 3.4	10) Wurttemberg oil shale	0.20 - 0.45
5) Wood	0.04 - 0.1	11) Wurttemberg shale oil	0.6, 0.7 x)
6) Petroleum	0.0 - 0.3	12) Inshim oil shale	0.4 x)
		13) Inshim shale oil	1.35 x)

The manner in which nitrogen, sulfur and oxygen is linked to the hydrocarbons of the shale bitumen and shale oils seems hitherto to be uninvestigated. We know that Estonian shale oils contain about 0.2% of basal compounds foremost pyridine and drinoline compounds. The lower fractions of the basal compounds have more of the latter compounds than the higher ones. The chemical composition of the basal compounds in Estonian shale oil were found as to:

C = 81.53 H = 9.59 N = 8.59 Remainder = 0.29%

In the low temperature carbonization tar of black coals we find 0.5 to 1.0% of pyridine and drinoline compounds, whereas the high temperature tar of the same coals contains only about 0.3% and less, because these compounds are not withstanding the high temperatures.

We know that a great deal of nitrogen is liberated as ammonia by low temperature carbonization and that prussic acid for example is formed of its elements only at high temperatures to which ammonia is not resistant. An unfinished nitrogen balance of Wurttemberg oil shale which was performed in connection with my laboratory experiment of low temperature carbonization showed no prussic acid formation. Another result was the fact that 5 to 9% of the nitrogen content of the shale bitumen was present in elementary form in the gas.

We know that the commercial low temperature carbonization plants of Scotland, France and Manchuria produce important quantities of ammonia sulfate.

✓ The combustion of fuels with high nitrogen content as black and brown coals and peat on grates or as powdered fuels at higher temperatures does not usually cause burner or vessel foulings, whereas numerous results due to corrosion by sulfur combustion products are published.

If nitrogen in shale oil is linked foremost with carbon and hydrogen there is no other effect to be expected than if the mentioned coals are burned. Burning, for example, an oil with 2% harmless nitrogen in good burning conditions with for example 2% of air excess the nitrogen concentration in the flame increases only from 0.740 to 0.755.

A higher formation of deleterious nitrogen oxygen compounds is possible if nitros or nitro compounds are present. An exact determination of the nitrogen compounds of the shale oil is therefore very important. It must be taken attention to small amounts of metals and metal compounds too, which can catalyze the formation of nitrogen oxydes.

Laboratory experiments verifying incomplete combustion of the shale oil under various conditions would be helpful.

Finally it should be pointed out to the necessity of accommodating the combustion spaces, particularly the chamber of internal combustion engines to shale oil.

Graf (28)

28

Description of a Low Temperature
Carbonization Process for Oil Shale

In the summer 1943, I was asked by private enterprise to develop a primitive process to extract oil from oil shale of Croatia which consumes a minimum of equipment. Since it was impossible to provide oil shale from Croatia, I used oil shale from Karnten which is situated in the South of Austria and oil shale from Wurttemburg in Germany.

I. Laboratory Scale Experiments.

After determining their physical and chemical properties I tried to carbonize the shales at low temperatures applying a shaft of 3.28 ft (1 m) height and 8.61 inches (0.22 m) inside diameter. The shaft was filled with oil shale which was crushed to a size of 0.2 - 1.2 inches (5 to 30 mm). The charge did not move during the carbonization. After kindling air was sucked through the charge and the liberated gases and oil vapors were drawn off from underneath a grate.

The progress of the carbonization zone was measured by means of thermocouples and the oil yield was determined. This experiment showed that the carbonization zone did not proceed uniformly because the gases preferred the way of least resistance. An exact separation of the carbonization and the gasification zone was therefore impossible. The following experiments were made with a continuously descending shale in order to imitate the operation of a gas producer.

II. Small Scale Plant.

The small scale plant had an inside diameter of 3.02 ft (92 cm) and a height of 15.1 ft (4.6 m).

Grat (28)

28

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Oil shale from Wurttemberg and Hannover had an oil content of approx. 5 per cent according to the Fischer-Assay. The ignition temperature of the low temperature coke was 734 - 752°F (390 - 400°C). The method for the determination of the ignition point was developed by E. G. Graf. The melting point of the mineral substance was 1922 - 2012°F (1050 - 1100°C). The carbon content of the low temperature coke was approx. 2.5 to 4.0 per cent. We obtained relatively high yields of oil of a good quality by working in the following manner. Sketch #1. Operating with a throughput of 41 - 102.5 lbs. per sq. ft. (200 - 500 kg per m^2) of oil shale we obtained about 90 to 70, average 80 per cent, of the oil, which was present according to the Fischer Assay.

The temperature of carbonization zone was kept between 932 and 662°F (500 and 350°C), because the laboratory experiments had shown that purging with inert gases at 932°F (500°C) secured high yield and good quality of the shale oil, whereby the liberated oil vapors were sucked through zones of lower temperature.

The temperature of the gasification zone must be kept below 1650°F (900°C) due to the low melting point of the shale.

Experiments showed, that the gasification of the fixed carbon was possible using a low speed of the gasifying agents and applying minimal temperatures of 840 - 930°F (450 - 500°C). It was therefore possible to gasify the fixed carbon between 840 and 1650°F (450 and 900°C). For practical reasons the most favorable temperatures were between 930 and 1290°F (500 and 700°C).

To obtain a producer gas with a high content of carbon monoxide and hydrogen and a low content of oxygen if this optimum temperature range was employed it was necessary to use a high gasification zone and a low velocity of the gasifying agents.

In the carbonization zone a higher speed of the hot purging gases was desirable for the decomposition of the oil shale bitumen at the described temperatures. In order to secure the desired different velocities of the gas and the different temperatures in the two zones we introduced recirculating lean gases and air at the bottom of the shaft and blew recirculating lean gases into the shaft approx. 4 ft (1.2 m) below the exit of the carbonization zone (compare sketch #1). The ratio of air and recirculating gas which was introduced at the bottom was between 1:1 to 1:2. The ratio of the sum of air and recirculating gases at the bottom and at the producer wall was from 1 : 2.5 to 1 : 4. 1 lb (1 kg) of oil shale with approx. 4 per cent moisture content and approx. 5 per cent oil content consumed approx. 12 cu ft (0.35 m^3) of air for the gasification. The condensing plant consisted of an indirectly operating water cooler and a tar extractor (disintegrator) system "Theisen Munic."

Properties of the produced oil:

Specific gravity: approx. .98

Viscosity: 8°E = 290 Sec. Time Un. Saybolt = .59 Poises Visc. Kin. at 68°F (20°C)

Pour point: approx. 21°F (-6°C)

Boiling point: approx. 320°F (160°C)

End point: approx. 750°F (400°C)

90% distillate

The separation of oil and water was easily performed by heating the mixture.

III. Pilot Plant at Schandelah.

In the fall of 1944, a pilot plant was designed and constructed at Schandelah near Brunswick with the aid of the "Ignis"-foundry, designing and construction company, Teplice-Sanov, Czechoslovakia.

Because we had to consume a minimum quantity of steel we could not protect the brickwork walls of the furnace by a steel mantle. Sketch #2 shows only one of the two existing ovens chambers, system Dr. Graf-Ignis.

Sizes of the complete furnace:

Height of the oven: 32.8 ft (10 m)

Over-all height : 62.5 ft (19 m)

Oven length : 32.8 ft (10 m)

Over-all length including platforms: 41 ft (12.5 m)

Oven width : 9.2 ft (2.8 m)

Oven width incl. platforms: 18 ft (5.5 m)

The condensing plant consisted of:

1. an indirectly working water cooler.
2. An electric gas precipitator System "Lurgi".
3. A single stage centrifugal exhaust fan.

The results which were obtained with this pilot plant were satisfactory. The oil shale from Schandelah had a moisture content of about 15 to 25 per cent (average approx. 18 per cent). The oil shale was relatively soft and not as hard as the oil shale of Wurttemberg, which has an average moisture content of about 3 - 5 per cent. The used shale was crushed by hand but not screened. It consisted of plates of a length up to 5" maximum 7". The content of dust and of shale pieces below .4" was negligible. The dust formation due to abrasion of the descending shale didn't hamper the carbonization and gasification process, due to a hardening of the shale pieces in the producer shaft. The throughput was 2200 - 3300 lbs per hour (1000 - 1500 kg per hour) or approx. 200 - 300 lbs per sq ft per hour (167 - 250 kg per m^2 per hour). The temperatures in the gasification zone were maintained between 930 and 1290 °F (500 and 700 °C).

Air and recirculating lean gas were blown in at the bottom of the shaft (at "A" of the sketch #2) whereas recirculating gases were introduced through the openings "B", or the grates "C", or the openings "D" respectively.

80 to 90 per cent of the oil which was present according to the Fischer-Assay were obtained if my assistants operated the furnace. Additional test runs which were performed by independent chemists and specialists showed oil yields from 70 to 110 per cent. The plant was operated without any difficulties from November 1944 till April 1945. It was possible to run but one test in order to increase the throughput to 4400 lbs per hour (2000 kg per hour) equals 400 lbs per sq ft per hour 330 kg per m^2 per hour) because the condensing system and the gas exhaustor were not large enough and uncontrolled volumes of air were sucked into the chamber due to a partially cracked wall of the furnace. The experiments showed that it was not commendable to operate the furnace without a steel mantle which protects the brickwork chamber against the influence of the wind. The velocity of the descending ~~oil shale through~~ the furnace was .5 ft per hour corresponding to a throughput of 2200 lbs per hour or 1.0 ft per hour corresponding to a throughput of 4400 lbs per hour. The time which was required for the shale to pass through the furnace was 60 hours or 30 hours respectively. It seems possible to increase the throughput of a commercial plant up to 600 lbs. of oil shale per sq ft per hour (500 kg per m^2 per hour) and even more. The oil yield will supposedly decrease with higher throughputs. But a test which was run with a throughput of 550 lbs per sq ft per hour (460 kg per m^2 per hour) yielded approx. 80% of oil if the small scale plant in Vienna (sketch #1) was employed. It was impossible to repeat this experiment employing the Schandelah plant due to the before mentioned reasons.

It was impossible to determine exactly the volume of the gases which are liberated per lb of oil shale by a gas balance because of the cracked wall of the furnace. The total gas volume (carbonization and gasification gas) amounts to 6.5 to 8 cu ft per lb (.4 to .5 m^3 per kg) of shale. Approximately 4.8 to 6.5 cu ft (.3 to .4 m^3) of air per lb (Kg) of shale are required for the gasification of the fixed carbon. The ratio of air and recirculating lean gas and the volumes of air and gas were approximately the same as we applied when the carbonization was performed in the small scale plant at Vienna. There was no alteration of the quality of the oil to be observed whether we utilized the small or the large scale furnace.

IV. Additional Experiments.

In connection with the development of the described carbonization method the following experiments were carried out:

1. Experiments to find out the best method to preheat oil shales.
2. Experiments to prevent melting of the shale during the carbonization process.
3. Determination of the temperature range which is necessary for a perfect carbonization.
4. Influence of parallel and counter current heat flow of the purging gases on the yield and quality of the obtained oil.
5. Determination of velocity of the temperature rise of oil shale pieces depending on a different thickness and different applied temperatures.
6. Determination of the properties of low temperature carbonization coke of the oil shale.
7. Sulphur balance of the low temperature carbonization process.
8. Extraction of the organic substance of oil shale by various solvents, using an autoclave.
9. Various technical institutes made experiments to use the spent shale for the manufacture of building material, to purify and refine the shale oil and to use crude oils as fuel for hot bulb engines.

V. Planned furnaces.

One of the planned furnaces is represented by sketch #3. The annular shaft (ring shaped shaft) for the carbonization and the gasification is 25 ft (7.5 m) high and has an area of 155 sq. ft. (14.3 m^2). The cylindrical shaft on top is 11 ft. (3.5 m) high and has an area of 87 sq. ft. (8.1 m^2). The over-all height of the furnace is approx. 64 ft. (20 m). The annular shaft is subdivided into 4 sections which are separated by walls "W". Air and recirculating gases are introduced at the bottom, recirculating gases only through openings at the outside and inside of the oven wall (at "B" and "C"). The carbonization zone extends approx. from "b" to "c".

The fundamental considerations which led to the application of a ring shaped shaft are the following: The largest diameter which can be used for cylindrical gas producer shaft is approx. 10 to 11.5 ft (3.0 to 3.5 m with cross sections from 80 to 100 sq ft (7.1 to 9.7 m^2) because of the difficulty to secure uniform distribution of the gasifying agents. But applying a ring shaped shaft it is possible to create a large cross section with a relatively small width. The gasifying agents can be introduced at the inside and the outside of the producer shaft. It is possible to operate a ring shaped shaft which is 4.5 to 6.1 ft (1.5 to 2.0 m) wide. With an inside diameter of 9.8 ft (3 m) the cross section of the gasification zone amounts to approx. 200 to 280 sq ft (18 to 26 m^2). These areas correspond with cylindrical diameters of 16 to 19 ft (4.8 to 5.8 m). The larger cross section of the gasification zone and the increasing cross section of the carbonization zone are in accordance with a desired low gas velocity in the gasification zone and a higher gas velocity in the carbonization zone.

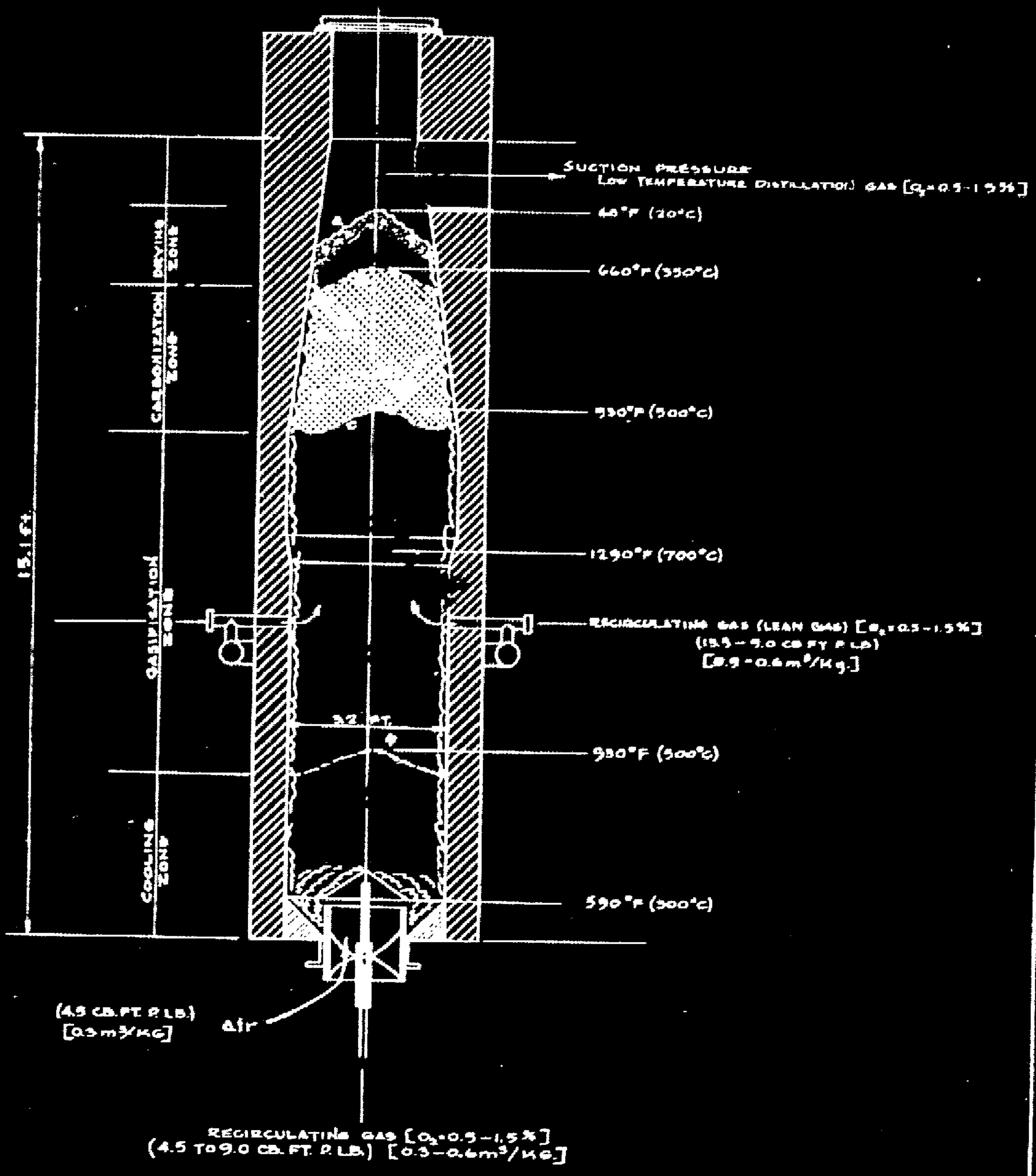
The increasing area is important for the manner in which the shale descends through the shaft. If the charge consists of relatively thin plates the horizontal component of motion directs the plates in a partly horizontal position and keeps the pieces in a better motion than in vertical shaft.

The throughput of the planned furnace as represented by sketch #3 is supposedly at least 60 to 85 tons per day. Probably the throughput can be increased to 100 tons per day if an oil yield of approx. 70% of the Fischer Assay is admissible.

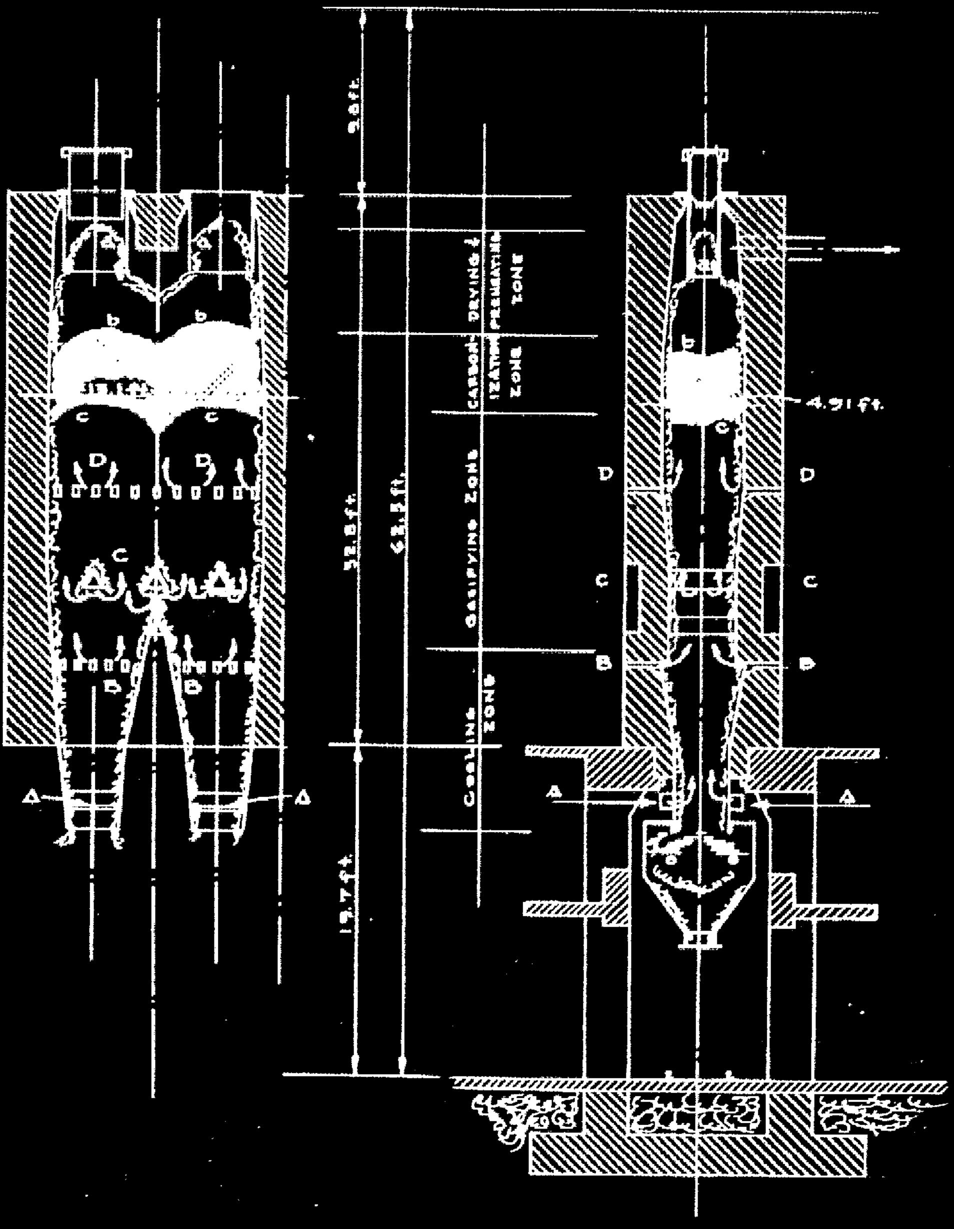
Applying the largest possible dimensions of this type (Shaft width 6.1 ft (2.0 m), inside diameter 9.8 ft (3 m) cross section of the gasification zone 280 sq ft (26 m^2)) a throughput of 150 to 200 tons per day can be expected.

I filed a patent application for the described process which was registered in my native country Austria under No. A 2077-46 and intend to get a U.S.A. patent.

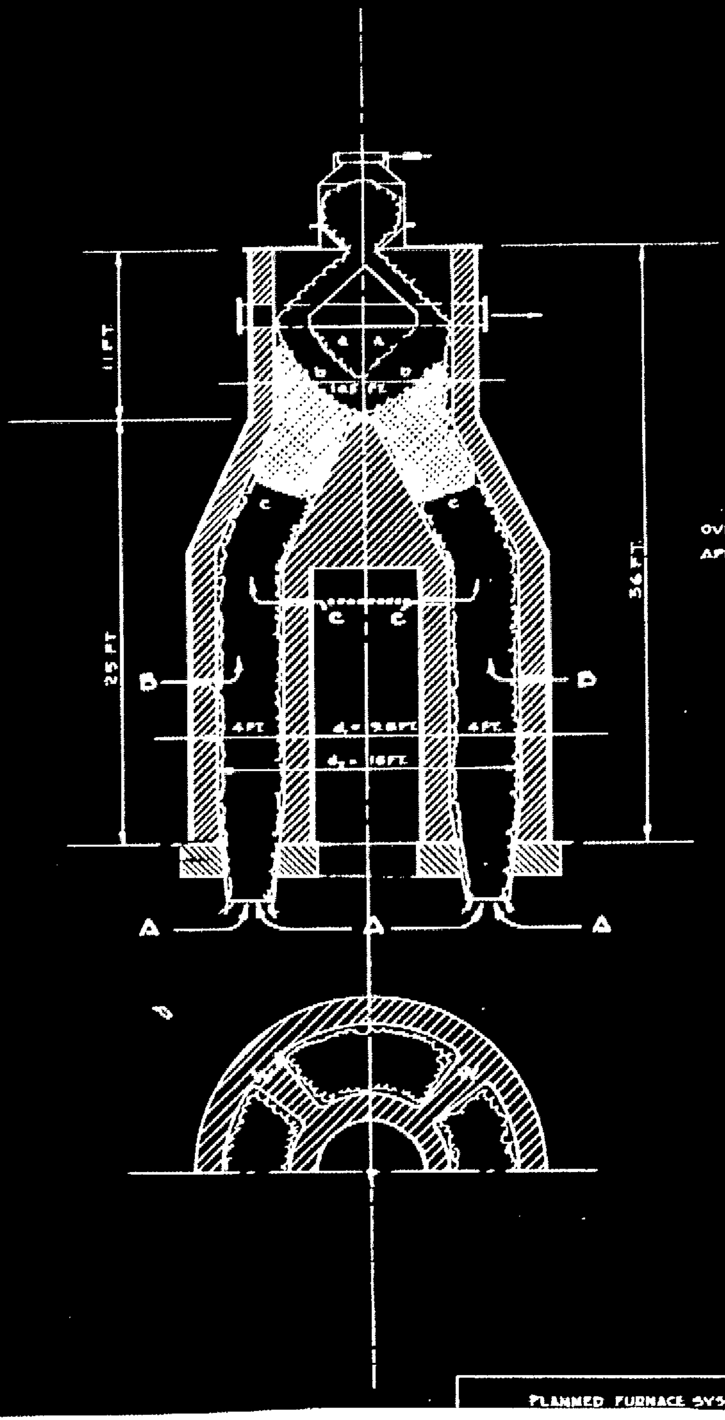
[redacted]



SMALL SCALE PLANT IN VIENNA



PILOT PLANT AT SCHANDELAH NEAR BRUNSWICK. SYSTEM: DR. GRAF-IGNIS.



PLANNED FURNACE SYSTEM : DR. GRAF-IGNIS

(29) GRAF Graf (29)

IDEAS AND PROPOSALS ON OIL SHALE UTILIZATION

In order to recover heat and power from oil shales we can employ the same fundamental methods as are known for coal utilization.

A. Burning of oil shale.

To produce heat by burning oil shale we have to study 1) the behavior of the oil shale during the low temperature carbonization 2) the gasification activity of the obtained shale coke and 3) to take into consideration the high content of ash and its properties.

The relatively high oxygen content of the organic substance, the content of sulfur compounds and the catalytical effect of the inorganic substance cause a comparatively low ignition temperature of the crude oil shale. The well investigated Estonian Kukkersit-bitumen for example with the mean composition as follows:

C = 76.7 H = 9.2 O = 11.2 S = 2.0 N = 0.3 Cl = 0.6%

contain about 40% of the oxygen, which is necessary for the perfect combustion of its C, H and S contents. The ignition temperature of the Kukkersit-shale has been determined to about 200 °C.

Theoretical considerations show that oil shale can be burned even with a minimum carbon content of its coke of about 1%. These computations have been proved true by experiments in the Graf-Ignis pilot plants at Vienna and Schandelah, using low grade oil shales and especially German asphaltic lime stones containing about 3.5% bitumen and yielding 1.7% oil

The ignition temperature of the low temperature coke of Wuerttemberg oil shale with a fixed carbon content of 3.3% could be exactly determined in air atmosphere between 390 and 400 °C. using a small laboratory apparatu

applying 1 gram of coke.

The melting of the inorganic residue at about 1100°C. with a carbon content of 3.3% was performed in the shaft of the pilot plant in Vienna using a 5:1 reduction of the cross section.

The combustion of the relative poor Schandelah oil shale which is no melting during carbonization has been effected in the shaft of a space heater, which is ordinarily used for bituminous coals in Austria. The grate was replaced by an ash pan containing a water sump. The firing principle of this heater consists in dividing the shaft by a fire brick wall into two parts, a filling shaft in which the fuel is preheated and carbonized and the combustion shaft. The gasification takes place in the adjacent lower undivided part of the shaft. The mean air volume partly saturated with water steam is sucked upwards through the gasification zone, a small amount of purging air is sucked downwards through the feeding shaf and the required air volume to complete the combustion is introduced at proper point of the combustion shaft.

With higher throughputs and higher contents of shale bitumen, crackin and burning of the oil vapors becomes incomplete and even more difficulti can be expected if oil shale inclines to melt during the carbonization process and if the inorganic residue inclines to melt below about 1100°C.

In many cases the controlled admixture of water steam produced in a steel water jacket of the furnace might prevent clinkering of the residue.

If melting during carbonization and clinkering of the residue is not to be expected, various grates and equipment known for firing granulated bituminous coals as under feed stokers, tray firings (German: Mulden Feuerung) and combustion equipment for powdered coals are suitable after proper adaption.

The sulfur compounds in the gases and the sulfur oxide odor of the spent shale cause difficulties and disagreeableness.

The consequent development of gasifying oil shales in order to recove a permanent gas leads to the separation of the gasifying and the cracking zones so that the complete cracking of the oil vapors is performed in a separate furnace at high temperatures in the presence of water steam and oxygen.

B. Low temperature carbonization

One of the important factors in recovering optimum quantities and qualities of liquid hydrocarbons by low temperature carbonization is the heat transfer and the manner of conducting the liberated vapors in relation to the heat flow. A high speed of the heat transfer is desirable in order to obtain high throughputs.

Laboratory experiments were made foremost with coal nuts, coal briquettes and at least with oil shale granules and cubes in order to determine the carbonization velocity under conditions similar to those of planned pilot or commercial plants.

Heating for example black coal nuts of 30 to 40 mm in an inert gasflow at a temperature rising from 300 to 650° C. during the process the carbonization time defined by reaching 550° C. in the centre of the nuts was found to take 23 to 15 minutes depending on the velocity of the purging hot gas. In other experiments oil shale cubes with 36 and 48 mm edge length were heated by radiation at 530° C. in a stove without gas purging. The result is represented in the following table: Column a. shows the preheating times of the total carbonization time until the surface temperature reached nearly the temperature of the oven. Column b. contains the time which is necessary to finish the carbonization. Column c. contains the total carbonization times a. and b. Column d. represents the carbonization time which is obtained by plunging the cubes into a molten 75% Al - 25% Zn - bath at 535° C. Column e. contains the estimated carbonization times if the heating is performed by radiation and purging gases. The volume of the inert gas was about 10 times as large as the liberated low temperature carbonization gases.

Table: Carbonization times in minutes

Cubes	a	b	c	d	e
36 mm	15	18	33	17	24
48 mm	23	20	43	25	34

These and other experiments were carried out in order to develop new carbonization furnaces. The experiments were sponsored by the "Ignis" foundry, Designing and Construction Company at Teplice-Sanov, Chechoslova and the Humboldt-Kloeckner Works at Cologne. Several sketches and drawin were made.

With the increase of the gas velocity and the higher throughput it becomes more and more difficult to control the process of carbonization and gasification in a single shaft. It is therefore proposed to perform the processes in two separate pieces of equipment, and iron made carbonizing shaft and a gasifying producer shaft.

The principle of one of the developed carbonization processes is characterized by a relative movement of the shale granules during their descending, heating the charge by radiation of the walls and purging with hot gases at relatively high velocity first in parallel and cross current and in the lower part in counter and cross current. The purging gases are heated by convection and partly by radiation on the inner surface of the non-turning cast iron cylinder. The latter is particularly heated by radiation of a fire brick wall surrounding the carbonizer. The purging gases are moved by a middle pressure fan which is sucking the gases off at proper openings of the rotating inner cylinder and which is blowing the gases in parallel and cross flow to the shale granules.

The purging gases are generated by a gas producer and blown into the carbonizer at the bottom.

The loss of pressure, the dust formation, the quantity and quality of the yielded oil and the throughput in correlation to the gas velocity and heat transfer must be investigated in a pilot plant. It is proposed to use proper granule classes which need different purging gas velocities. The gas velocity is the highest with the largest size of the granules and decreases with the smaller granule classes. Therefore for each granule class a proper minimum carbonization velocity can be expected, according to the laboratory results. The dust and the smallest granules of the oil shale, which cannot be treated in this carbonizer can be carbonized in state of suspension. For example, in a dust carbonizer proposed by R. Zeidl in "New Ways of Oil Shale Utilization", Reval 1933, page 175.

Details of the sketched process and reports concerning own experiences about carbonization processes used in Germany during the last war can be made.

C. Flotation and extraction

The oil shale bitumen seems to be clinging foremostly by adsorption to the inorganic material. Oil shale samples with a higher bitumen content and flotated samples showed that the adsorption is more intimate to clayey than to quartzy substances. Experiments of commercial size by Dr. Winkler in Estonia resulted in a product with about 10% ash content. The cost for pulverizing ~~and~~ are naturally high and they increase from the clayey to the quartzy oil shales.

Because of the clinging by adsorption, the bitumen is difficult to extract by solvents. The extraction by means of benzene, tetraline, decaline, pyridine and oil shale gasoline was tried in my laboratory at normal boiling points and at higher temperature and elevated pressures. At normal boiling points 2 German and 1 Estonian oil shale samples yielded 2 to 8% of their bitumen. The higher quantities were obtained by tetraline. The extraction by three steps with tetraline at 300°C. and 7 atmospheres gave 66% of the bitumen. The extraction at 320°C. and 10 atmospheres resulted in approximately 75 to 80% extracts. The extraction under these conditions is no genuine physical dissolution. A partial hydrogenation by the solvent and a decomposition of the bitumen takes place. The extract is occluded with polymerized tetraline products. The losses of tetraline were relatively high. The solid extracts must be converted into liquid hydrocarbons, so that the method of bitumen extraction seems to offer no advantages in recovering liquid hydrocarbons from the oil shales in commercial plants.

The extraction of the inorganic substance by means of weak inorganic acids is used to obtain concentrated bitumen samples in order to investigate the properties of the bitumen. The commercial use of this method may be considered as without promising prospects.

November 15, 1946

[redacted] 30 Fischer

30 September 1946

Ref.: Information on shale oil, requested by the Bureau of Ships.

My answer pertains to the last question of the letter, which brings up the point of solvent refining. No figures can be given, because all important laboratory files of the Edeleanu Co. were destroyed by fire, and the information below is given from memory.

No large scale plant exists for solvent refining shale oil, but the experience with brown coal tar, which is solvent treated in large scale, can very well be transferred upon the commercial separation of shale oils.

Two shale oils were studied in Edeleanu's lab. chiefly, that was: a) Puertollano oil of Spanish origin, about which I gave some figures in a memorandum of August 23d 1946. b) An Estonian oil, which behaved very differently from the Spanish oil, but which is probably closer in properties to the American oil in question. This oil could be solvent treated with liquid SO_2 at $-25^{\circ}C.$, but decent yield of Diesel fuel was obtained by combined solvent extraction with SO_2 plus aliphatic gasoline only. At that time it was out of the question to obtain the required quantity of suitable solvents and research on that oil was abandoned.

General information about solvent refining and dewaxing of tars and shale oils, giving also data about yield and quality will be found in:

C.I.O.S. Report Target Nr.30/89

Item Nr.30 File Nr. XXXI - 85

Solvent treating of shale oils is rather a separating process, than a refining step. Diesel fuel, various grades of wax and lube oil fractions are obtained as pre-refined products, which require but little after-treatment.

The major part of sulfur and nitrogen compounds is concentrated in the low pouring extract, which (from brown coal tar plants) was considered a satisfactory fuel oil for heating. For reason of its phenolic constituents it gave good blending properties with more paraffinic stocks.

The combination of solvent treatment and hydrogenation should be studied closer. Solvent treatment is comparatively cheap and isolates the more saturated components fairly well from the unsaturated extract. It may be more economical to feed the 50% extract to the hydrogenation only, instead of 100% raw stock with all the saturated and paraffinic compounds in it, which will pass the hydrogenation plant unchanged anyway. (It is understood, that decrease of molecular weight is undesired. If production of gasoline is the aim of catalytic hydrogenation under cracking, however, it might be advantageous to leave the saturated components in the oil, where they are then an additional source of hydrogen and convert to desirable gasoline constituents by dehydrogenation and cyclisation.)

No guesses on yields of different products by solvent treatment of shale oils can be made. These oils are more different than brown coal tars even, and it is by an experimental examination only, that an answer about yield and quality can be given.

31

31

Pittsburgh, Pa.
November 8, 1946

Received NOV 13 1946
FOREIGN SYNTHETIC
LIQUID FUELS DIVISION

MEMORANDUM TO: W. C. Schroeder
A. C. Fieldner
~~L.~~ L. Newman
R. A. Cattell
A. J. Kraemer
H. M. Thorne (6)

FROM: H. H. Storch

SUBJECT: Translation.

I am attaching hereto a copy of a translation of a Russian paper entitled, "Manufacture of Liquid Fuels from Combustible Shales by the Method of Thermal Solution", made by Mr. Harold J. Kandiner, of our staff.

HHStorch
H. H. Storch

1946 NOV 13 AM 7 53

MANUFACTURE OF LIQUID FUELS FROM COMBUSTIBLE SHALES BY THE METHOD OF THERMAL SOLUTION.

by M. K. D'yakova
(Institute of Combustible Minerals, Academy of Science, USSR)

(Bull. Acad. Sci. URSS, Class. Tech. Sci. 1944, No. 4-5, pp. 258-274; submitted for publication May 5, 1942)

Translated by H. J. Kandiner1/

Organic constituents in shales can be used as a source of useful and valuable products, principally liquid fuels. A process for the manufacture of liquid fuels should consist of three stages: (1) Extraction of the organic material, (2) separation of the extract from the insoluble mineral sludge, and (3) preparation of liquid fuel from the extract.

Coking of shale is a primitive method for the manufacture of liquid fuels. Its principle advantage is the simple plant equipment required. The disadvantages include the poor yields and low efficiency of the process, as well as the massive plant necessary for large capacity. On a large scale, no more than 50 percent of the organic matter in the shale is converted to primary tar, the balance being converted into coke and gases. This result is not surprising, because high temperature is employed and because the reaction occurs in the presence of the mineral portion of the shale which behaves as a catalyst. Contact time in the coking oven is several hours. A further disadvantage is that the tars produced are very heavy and yield no more than 9 percent (based on the organic matter in the shale) of light fractions (1).

1/ Chemical Engineer, Office of Synthetic Liquid Fuels, Research and Development Division, Bureau of Mines Central Experiment Station, Pittsburgh, Pa.

The method of thermal solution is characterized by its efficiency in extracting a high (80-95) percentage of the organic constituents of shale. Products of high quality are obtained and large-scale plants of large capacity may be readily constructed. Experiments were started in 1937 on the process of thermal solution, in order to solve certain problems in coal hydrogenation. This work was similar to that of Pott and Broche (2) (3). Subsequently, an extensive program on a laboratory- and experimental-plant scale was outlined and the process is at the present time being investigated in a continuous semi-commercial plant.

The reaction mechanism for a process of converting insoluble organic materials into soluble oils is not completely understood at the present time. In general, it may be regarded as a thermal depolymerization of high molecular-weight polymeric substances, which compose the organic fraction of the shale, into soluble, less complex materials. The average molecular weight of the shale extract, after removal of the gasoline fraction and the solvent, is approximately 325. Apparently, depolymerization is complemented by a simultaneous cracking reaction, catalyzed by the mineral matter of the shale, giving rise to a gasoline fraction with an average molecular weight of 117 and boiling range to 180°C., and a kerosine fraction with an average molecular weight of 155 and boiling range 180-225°C. Removal of sulfur, hydroxyl, and carboxy groups, etc., also occurs, but plays a subordinate role in the reaction chemistry.

McKee and Lyder (4) demonstrated that thermal depolymerization was the most important reaction in the thermal solution of shale. They found that the organic fraction of a Grand Valley, Colorado, shale which was completely insoluble as received in benzene and carbon disulfide, became soluble to the extent of 65-70 percent in the latter solvent after heating at 410-425°C. Further experiments on shale (deposit "A") by V. I. Zhunko, L. E. Lazebnik, and L. S. Zaglodin (5) (6) led to the development of a process involving pyrobituminization of shale followed by benzene extraction of the residue.

As depolymerization occurs even in the absence of solvent, it is reasonable to believe that the choice of solvent employed in a process of thermal solution of shale is not critical. This assumption was confirmed by the author in experiments with phenols and hydrocarbons of various kinds, including solid paraffins; practically complete extraction of the organic fraction of the shale resulted in most tests. The mechanism of thermal solution may thus be regarded as a combination of depolymerization and solution of the depolymerized products in the solvent, followed by cracking (usually catalytic).

The experimental studies described in this paper were, for the most part, technological in nature, directed toward ascertaining optimum conditions for the thermal solution of various typical Soviet shales. A study of solvents and product yields was also undertaken. Finally, pilot-plant investigations were made in order to develop a simple large-scale plant for satisfactory use of the method.

Received DEC 3 1946
FOREIGN SYNTHETIC
LIQUID FUELS DIVISION

1946 DEC 3 PM 2 06

Pittsburgh, Pa.
December 2, 1946

MEMORANDUM TO: W. C. Schroeder
A. C. Fieldner
L. L. Newman
R. A. Cattell, W.O.
A. J. Kraemer, W.O.
H. M. Thorne, Petroleum and Oil Shale Exp. Station
B. Guthrie, Oil Shale Demonstration Plant.

FROM: H. H. Storch

SUBJECT: Translation entitled, "Manufacture of Liquid Fuels from Combustible Shales by the Method of Thermal Solution".

According to information which we have received concerning the translation of the column headings in Table 1, page 4, of the above manuscript, these should read as follows:

Column 1 - Shale.
2 - Moisture content of sample.
3 - Ash (dry basis) + CO_2.
4 - CO_2
5 - Carbon (ash- and CO_2-free basis).
6 - Hydrogen (ash- and CO_2-free basis).
7 - Sulfur (dry basis).

H H Storch rj

H. H. Storch.

EXPERIMENTAL PART

Raw Materials, Shale and Solvents

Shale.

1. Combustible shale of deposit "A" dried and crushed to 35 mesh (.3 mm. diameter).
2. Ditto from deposit "B".
3. Ditto from deposit "V".
4. Sulfur-containing shales from deposit "G", "D", "E", and "Zh", crushed to 80-mesh (.2 mm. diameter).

Analyses of the shales are given in Table 1. These shales are representative of typical deposits of the two principal types of Soviet shales, sulfurous and sulfur-free.

Table 1.- Analyses of Shales Studied.
(percent)

Shale	W^1	A^s + CO_2 mineral	CO_2 mineral	C^g	H^g	S^s Total*
Deposit A, sample 1	3.35	53.45	12.2	77.78	9.21	—
sample 2	2.92	56.43	—	—	—	—
sample 3	.74	51.17	—	—	—	—
Deposit G	8.74	37.81	3.38	61.74	7.7	7.17
Zh	6.97	62.63	10.35	—	—	—
D	5.67	65.13	11.14	—	—	—
E	.5	38.76	.0	61.45	6.51	5.55
B	1.13	66.77	.0	—	8.12	—
V	5.76	56.7	4.9	64.17		2.04

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*These symbols are unfamiliar to the translator. However, the (A^s + CO_2) figures are apparently total inorganics.

Solvents.

The solvents employed were: Anthracene oil, primary shale tar, hydrogenated shale tar, topped shale tar, shale extracts made from primary tars, and petroleum fractions. The properties of the solvents are given in Table 2.

Table 2.- Characteristics of the Solvents.

Solvent	Specific gravity	Initial temp., °C.	Fraction distilled to 350°C., percent	Viscosity, degrees Engler
1. Anthracene oil	$d_4^{20} = 1.1305$	220	70.0	1.52 at 20°C.
2. Residue from primary tars of deposit "A" shale	$d_4^{100} = .9922$	275	23.7	5.8 at 100°C.
3. Extract of deposit "A" shale after removal of gasoline and filtration	$d_{20}^{20} = .986$	220	70.2	16.58 at 25°C.
4. Regenerated solvent (recycle) after extraction of shale "A"	$d_{20}^{20} = .9475$	200	77.5	4.48 at 25°C.
5. Distilled tar from deposit "A" shale	$d_{20}^{20} = .933$	220	90.4	3.4 at 25°C.
6. Tar from deposit "A" shale after removal of gasoline	$d_{20}^{20} = 1.012$	190	72.5	12.6 at 50°C.
7. Surachan(sk) mazut	$d_4^{20} = .963$	290	17	6.38 at 50°C.
8. Ishimbai mazut	$d_4^{20} = .855$	275	25	4.41 at 100°C.
9. Lok-Batan mazut	$d_4^{25} = .941$	285	22.5	- - -
10. Residue from primary tar from sulfur containing shale	- - -	245	48	6.35 at 100°C.
11. Extract of sulfur containing shale, after filtration and removal of gasoline	$d_4^{20} = 1.056$	200	72	- - -
12. Regenerated solvent after extraction of a sulfur-containing shale	$d_4^{20} = .9232$	212	60	- - -
13. Distilled tar from a sulfur containing shale with initial b.p. of 220°C. and containing fractions up to pitch	$d_4^{20} = .918$	200	92	- - -
14. Hydrogenated shale tar	$d_4^{25} = .982$	240	33	8.1 at 50°C. 1.7 at 100°C.
15. Petroleum Diesel fuel	$d_{20}^{20} = .859$	250	100 (to 300°C.)	- - -

Apparatus and Test Method

Experiments with shale from deposit "A" were performed in a 1/2-liter batch-rotating electrically-heated autoclave of the Bergius type, and in a continuous pilot plant. The other shales were tested only in the autoclave. The autoclave tests were performed as follows: 100-150 g. shale + 100-150 g. solvent were charged into the autoclave. The range in shale:solvent ratio investigated was 30:70 to 70:30. Reaction temperature (300-430°C.) was reached in 40-60 minutes, kept at that temperature for the desired length of time, and the autoclave quickly cooled. Reaction time, as shows in Table 3, does not include time for preheating or cooling. After cooling, the liberated gases were measured and analyzed on a V-T-I apparatus*. The solid and liquid products were transferred to a glass distillation flask and two fractions collected, namely, water including moisture originally present and water of reaction and crude gasoline boiling to 200°C. The residue was filtered through a heated (90-110°C.) Büchner funnel and either washed with benzene or shale kerosine or extracted with benzene on a Gref apparatus. After removal of the benzene from the extract by distillation, the portion of the washings that distilled above 130°C. was added to the filtrate. The final residue containing the mineral matter of the shale, together with unextracted organic material, was analyzed for ash (including CO_2). The extraction yield was calculated by the following equation:

$$x = 100\left[1 - \frac{a(100-b)}{b(100-a)}\right]. \qquad (1)$$

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* Possibly "All-Union-Technical Institute", (trans. note.)

where x = organic matter extracted from shale, percent, a = mineral content of original shale, percent, and b = mineral content of residue remaining after extraction, percent. The actual quantity of liquid obtained was less than x by the amount of gas and reaction water formed.

During each experiment, the bulk of the solvent was present in the liquid phase. The reaction pressure (equal to the vapor pressure of the solvent) was 30-40 atmospheres.

Influence of Temperature and Heating Time.

Solution of shale from deposit "A" took place only slowly in anthracene oil at temperatures of 300-375°C. It became very rapid at temperatures of 400-420°C.; maximum solubility (94-96 percent) of the organic fraction of the shale occurred in a very few minutes at this temperature. At temperatures above 430°C., the effective solubility diminished. The same behavior of shale "A" was observed in solvents such as primary shale tars, hydrogenated shale tars, and in Lok-Batan mazut. Shale "B" behaved similarly in anthracene oil.

The sulfur-containing shales "G" and "E" in anthracene oil and Ishimbai mazut began to dissolve at 300°C. At 375-390°C., 85-90 percent of the organic material of shale "G" and 72 percent of that in shale "E" were dissolved in a few minutes. At temperatures higher than 390-400°C. or at longer contact time in the autoclave, the solubility diminished. These shales thus reacted at lower temperatures than sulfur-free shales. Optimum conditions for shales "A" and "B" were 15 minutes at 420°C. for "G" and "E", 5 minutes at 385-390°C.

Influence of Shale:Solvent Ratio.

Experiments on shale "A" were performed using anthracene oil, primary shale tar from this deposit, and hydrogenated shale tar as solvents with 30 percent, 50 percent, and 60 percent shale in the paste. Sulfur-containing shales were tested in anthracene oil in pastes containing 50 percent and 70 percent shale.

With increasing concentration of shale "A" in the paste, the solubility decreased gradually and the concentration of the dissolved organic matter from the shale increased in the extract solution. A 50-percent shale paste was best for industrial operation, resulting in extraction of 90-95 percent of the organic constituents. This paste was fluid and easily pumped and the reaction product was readily filterable. With sulfur-containing shales, using a 15-minute reaction time at 390°C., 87 percent of the organic matter was extracted from a 50-percent shale paste; at 70 percent shale concentration, only 79 percent was extracted.

Influence of Particle Size of Shale.

These tests were performed on shale "A", using Lok-Batan mazut as solvent, at 420°C. and 15-minute reaction period, as well as on sulfur-containing shales, with anthracene oil as solvent at 390°C. and 15-minute reaction period. Range of particle size investigated was, for shale "A", from 0.15 to 5.7 mm in diameter, and for shales containing sulfur, from 0.25 to 5 mm. No effect on the "solubility" was detected that could be ascribed to particle size. For any size in this range, "solubility" of shale "A" was 96.4-96.7 percent, and for sulfur-containing shales, 84.0-86.8 percent.

Relationship Between Shale "Solubility" and Solvent.

In experiments with all shale samples, it was found that virtually all solvents that could be used in large-scale plants gave extractions in the range of 91-96 percent. Hence, suitable solvents could be selected having widely different origins, chemical nature, or physical properties. The most significant factors in selection of a solvent were its physical properties, for example, the solvent must remain in the liquid phase at 400-430°C., and 30-40 atmospheres pressure; it must be thermally stable, and should have a high density (1 or higher). For rapid and easy pasting, the solvent should be free from asphaltic materials (which cause filtration difficulties), and fluid at room temperature. The most satisfactory solvent found was anthracene oil; however, the use of the 220-370°C. fraction of primary shale tars is being studied.

Solubility of Various Soviet Shales.

Table 3 gives the results obtained.

Table 3.- Solubility of Combustible Shales.

Exp. No.	Shale	Solvent	Experiment conditions Time, min.	 Temp., °C.	Percent extraction
259	Deposit A	Anthracene oil	5	420	96.5
612	Deposit B	Anthracene oil	15	430	78.7
660	Deposit V	Anthracene oil	30	400	75.0
338	Deposit G	Anthracene oil	15	390	86.8
583	Deposit E	Anthracene oil	5	390	72.4
476	Deposit D	Ishimbai mazut	10	390	82.2
647	Deposit Zh	Fractions of primary tars of sulfur-containing shales.	10	410	76.0

Cracking of the Shale Extract, Regeneration of Solvent, and Material Balance for Organic Matter in the Shale.

The process of thermal solution is accompanied by catalytic cracking of the extract slurry. The mineral fractions of the shale contain, among other constituents, aluminum silicates. Products of cracking are crude gasoline, gas, reaction water, and heavy pitch-like residue. The 220-370°C. fraction is used as recycle solvent.

An optimum relation exists between the degree of cracking and the completeness of extraction. Too much cracking reduces the extent of extraction. In addition, with excessive cracking, insufficient recycle oil can be regenerated and make-up solvent is required. Too little cracking (for example, heating shale "A" to 380-400°C.) results in highly viscous solutions which are difficult to filter.

Extensive experiments have demonstrated that optimum results are obtained when the shale slurry after passage through the reactor contains 9-12 percent crude gasoline with a boiling range to 220°C., calculated on the total product, including the inorganic material. Under such conditions, moderate gas loss (about 5 percent of the organic matter of the shale) is obtained, and the yield of reaction water is low. The solvent can be completely recovered, eliminating the need for makeup. Recycle of regenerated solvent can be continued indefinitely if the solvent is obtained by distillation.

It is not possible to recycle the gasoline-free slurry (when freed of solids) which boils above 220°C., as asphaltic materials accumulate in the system reducing extraction yield and interfering with filtration. Recycle of the 220-370°C. fraction of the slurry eliminates this difficulty.

The following data are based on batch autoclave tests:

<u>Shale A</u>: 35-40 percent of the organic matter becomes converted to crude gasoline with boiling range below 220°C., 35-40 percent to pitch, 3-4 percent to reaction water, 5-10 percent is lost as gases, and 5-10 percent is lost with the ash. The gas contains 31.5 percent CO_2, 3.1 percent H_2S, ?.0 percent C_nH_{2n}, 13 percent CO, 7.8 percent H_2, and 43.2 percent C_nH_{2n+2}.

<u>Shale B</u>: Using petroleum Diesel oil as solvent and reaction conditions of 20 minutes at 430°C., 57.8 percent gasoline, 11.4 percent extract*, 5.8 percent gas, 4.1 percent H_2O, and 20.9 percent organic insolubles (based on organic fraction of shale) are obtained. The gas contains: 20.7 percent CO_2, 3.8 percent C_nH_{2n}, 7.7 percent CO, 16.4 percent H_2, and 51.5 percent C_nH_{2n+2}.

<u>Sulfur-containing shales</u> give yields similar to shale A. Using anthracene oil (15 minutes, 400°C.), 8.7 percent of gas was obtained containing 47.4 percent CO_2, 74.1 percent H_2S, 1.8 percent C_nH_{2n}, 1.2 percent CO, 11.2 percent H_2, and 24.5 percent C_nH_{2n+2}.

<u>Solution of Shale in a Continuous Experimental Plant.</u>

After the laboratory investigation on thermal solution of combustible shale was completed and optimum conditions of temperature and length of reaction time ascertained, experiments on a large-laboratory continuous scale were undertaken. Flow rates ranged from 10 to 30 kilograms of raw materials per hour.

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*Definition of term uncertain, (trans. note).

The equipment consisted of: (1) mixer (capacity 100 liters), (2) gear pump, (3) high-pressure paste pump, (4) coil preheater (50 meters of 10-12 mm. I.D. tubing), (5) reaction vessel (capacity 4 liters in first set of experiments and 8.6 liters in second set) which was fitted with an agitator in the second set of experiments, (6) motor, (7) throttling valve, (8) condenser, and (9) product receiver.

Experiments, using shale from deposit A only, were performed in this equipment. The raw shale, crushed to 35-mesh and dried, was mixed in the blender with solvent (either in 2:3 or 1:1 ratio) using topped gasoline-free shale tar in experiment series 1, or in a 1:1 mixture with the 220-370°C. fraction of distilled shale tars (in series 2). Paste at a temperature of 20-70°C. was pumped, through the electrically heated preheater where it was heated to 400-420°C., into the reaction vessel where it remained for 5-20 minutes at 400-430°C. Products of solution of the shale (gas, gasoline, heavy solution, reaction water, and inorganic minerals) together with the solvent were throttled through the cooler into the receiver, where the liquid and solid materials collected and the gaseous fractions were separated. Temperatures were measured at 4 points (inlet to preheater, and 3 points in the reactor). Pressures were held at 33-38 atmospheres by a specially constructed throttling valve.

The most serious operating difficulty was rapid wear of the paste pump. No accumulation of solid residues was observed anywhere in the system. Equipment of this general type, with some minor modification, can be used in a large-scale plant for the liquefaction of combustible shale.

Extraction of 85-90 percent of the organic fraction of the shale in gasoline-free shale tars was obtained at 400-420°C. in 5-20 minutes in the reactor. It was found expedient, in order to increase the gasoline yield and to produce an easily filtered slurry, to operate at 420°C. for 15-20 minutes with a 40:60 shale:tar feed. Solvent was continuously regenerated and the need for makeup solvent thus eliminated.

Data for two runs are given below in Table 4.

Table 4.- Data on Thermal Solution of Shale in a Continuous Pilot Plant.

	Test 3		Test 7	
	Parts by weight	Percent of shale	Parts by weight	Percent of shale
Feed				
Dry shale	40		40	
Solvent (tar)	60		60	
Total	100		100	
Products				
Recycle solvent	60		60	
Crude gasoline	8	20	6.3	16
Shale extract	3.2	8	4.6	11.5
Insoluble including ash	24.8	62	24.2	60.5
Gas, water, and losses	4.0	10	4.9	12

As the shale used (sample 2, Table 1) had 43.5 percent organic matter, and as 27-28 percent of the shale was obtained as crude gasoline and shale extract (filtered), the yield of liquid fuel was about 62-64 percent of the organic fraction of the shale.

Certain disadvantages are present in the use of topped shale tar as a solvent: (1) slurry is difficult to filter and is very viscous at room temperature, (2) asphaltenes accumulate in the system on recycle, (3) concentrated shale pastes cannot be used as feed, so that the capacity of the unit is lowered, and (4) certain constituents of the tar are cracked on passage through the reactor, increasing the gas and water loss. For example: gas and water loss is less than 15 percent (based on organic fraction of shale) when a 1:1 mixture of shale and anthracene oil are treated. Under the same conditions of temperature, pressure, and reaction time, gas and water loss is 25-27 percent (same basis) when a feed of 2 parts shale to 3 parts gasoline-free tar is used.

Because of these shortcomings, other solvents were tested on pilot-plant scale.

The 220-370° C. fraction of primary shale tar (from shale A) was used as a solvent in the second series of experiments. It had the following specifications: d_{20}^{20} = .933, E_{25} = 3.4°, initial boiling point = 220° C., 47.8 percent (by weight) distilled to 300° C., 78.8 percent to 330° C., 90.4 percent to 350° C., and 97 percent to 370° C. Average molecular weight = 222.

A throughput of 30 kg./hr. of paste (equal parts of shale and solvent, d_4^{20} = 1.18), was maintained in these tests. Contact time in the reactor was 20 minutes. Paste temperature at the exit of the preheater was 415-420° C. and in the reactor 425-430° C. Operating pressure was 32 to 34 atmospheres. Material balance calculations were based on 100 kg. feed. The raw shale analyzed W = .74 percent, A^s = 51.47 percent (including mineral carbonates), A^s of the residue after extraction = 91.95 percent. The organic material in the shale was 91.65 percent extracted as follows: 39.3 percent converted to crude gasoline, 2.9 percent to Diesel oil, 0.6 percent to hydrocarbon gases, 30.2 percent to pitch, 8.75 percent to gas, 6.3 percent to reaction water, and 8.4 percent insoluble. A material balance is shown in Table 5.

Table 5.- **Material Balance**

Input			Output		
	Kg.	Percent		Kg.	Percent
Solvent	50		Regenerated solvent	50	
Organic constituents of shale	24.23	48.46*	Crude gasoline to 220°C.	9.53	19.06* 39.3**
Mineral fraction of shale	25.40	50.8*	Gaseous hydrocarbons	0.15	.3* .6**
Water (in shale)	0.37	0.74*	Diesel fuel	.70	1.4* 2.90**
	100.00	100.00*	Gas	2.12	4.24* 8.75**
			Pitch	7.30	14.6* 30.2**
			Organic insoluble	2.04	4.08* 8.4**
			Inorganic matter	25.4	50.8*
			Water (as moisture)	.37	.74*
			Water (reaction)	1.52	3.04* 6.27**
			Loss	.87	1.74*
				100.00	100.00*

*Based on shale.

**Based on organic fraction of shale.

Thus, starting with a metric ton of dry shale from deposit A containing 48 percent organic matter and using the 220-370°C. distillation cut of primary shale tar as an initial solvent under the indicated conditions, 190 kg. crude gasoline boiling below 220°C., 3 kg. gaseous hydrocarbons, 14 kg. Diesel fuel, 42 kg. gas, and 146 kg. pitch were obtained. Hydrogenation of the latter will give about 110 kg. gasoline and kerosine. Solvent was completely regenerated by distillation of the filtered gasoline-free slurry. A balanced flow sheet for the process (using shale A) is given in Figure 1.

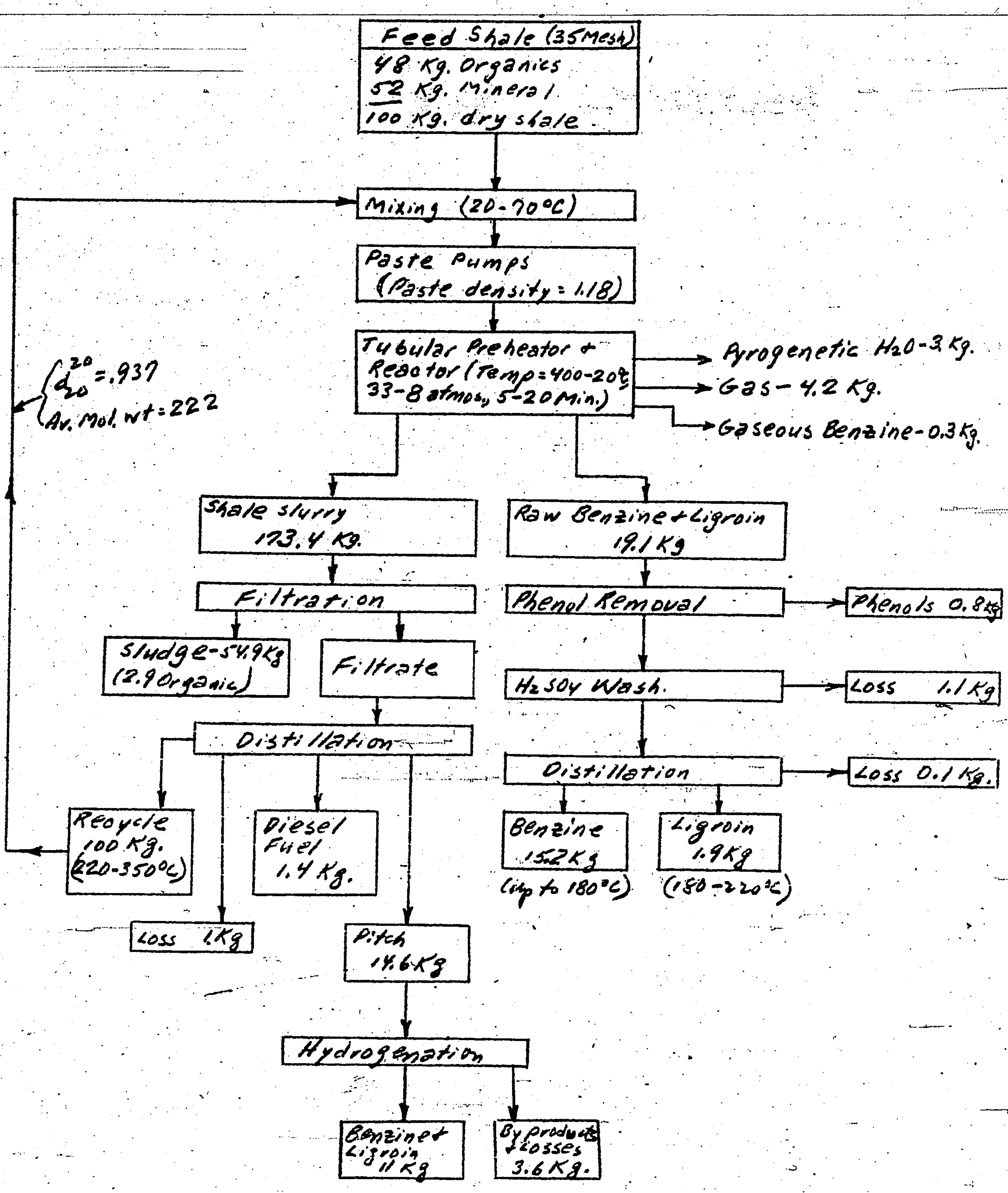

Figure 1: Material Balance on Thermal Solution of Shale from Deposit "A".

Treatment of the Shale Extract.

The gasoline-free shale solution is a dark, more or less viscous liquid, containing insoluble ash which settles on prolonged standing. Shale solutions made from gasoline-free shale tar are extremely viscous at room temperature. The filterability of the extract depends on the completeness of extraction and degree of cracking and can be qualitatively estimated from the appearance of the slurry. Solutions only slightly cracked and very difficult to filter have a brownish shade and high viscosity. Dark black, comparatively fluid extracts are particularly easy to filter.

The raw plant extract contained "cracking gasoline," excess solvent, dissolved organic constituents of the shale, solid residue containing mineral matter and undissolved shale, and reaction water. The composition varied quite widely, depending on the initial shale and the operating conditions employed.

In practice, it was quite easy to separate the products into liquid and solid fractions. The gasoline-kerosine fraction could be readily removed. On a laboratory scale, insoluble material was removed by filtering the residual extract (distilling above 220°C.) through paper in a heated funnel. At 100-110°C. filtration was satisfactorily rapid.

On a plant scale, various methods were tried for filtering the slurry. Slurries made from shale A and primary shale tar and a distilled shale tar were tested in centrifugal filters and supercentrifuges. The supercentrifuge (at 12,000 rpm.) gave good and rapid separation, but the drum quickly became clogged with residue. Very good results were obtained using a centrifugal filter (3,000 rpm, feed temperature 140-150°C.) even on highly viscous shale extracts.

Slurry made from shale A and distilled shale tar (220-370°C. boiling range) was tested in a filter press.

Good results were obtained using feed at 130-140°C. The cake was washed in the press with kerosine, boiling range 180-220°C. (wash liquor equal in volume to the filtrate). The residue, after steam drying, contained 91.76 percent ash.

The filtrate is an oily liquid at room temperature having the following properties: d_{20}^{25} = .989, viscosity 16.58° Engler at 25°C., initial boiling point 220°C., 54.1 percent distilled below 320°C., 70.2 percent below 350°C., and 83.3 percent below 375°C. Vehicle is regenerated by distilling the filtrate to 370°C., leaving a high-melting pitch residue.

Composition and Quality of Products from Shale A.

Gases: About 2.1 percent of the feed mixture appeared as gas when shale A was treated with distilled shale tar at 430°C. for 20 minutes. The gases had the following composition: 37.5 percent $CO_2 + H_2S$, 22.3 percent CO, 7.9 percent H_2, 13.3 percent C_nH_{2n}, and 19 percent C_nH_{2n+2}. Its heating value was 6,000 cal./m^3. Accordingly, it contains 77.5 grams of hydrocarbon gases per cubic meter.

Gasoline and Kerosine: 9.7 percent of the extract was gasoline, or 39 percent based on the organic fraction of the shale. The crude product was fractionated into a gasoline cut boiling below 180°C., (17 percent of the shale, or 35 percent of the organic fraction of the shale) and into a kerosine cut boiling from 180° to 220°C. (2 percent of the shale or 4 percent of its organic content).

Table 6.- Properties of Products from Shale A.

Material	Specific gravity d_4^{20}	Phenols	Sulfur	Acids	Hydrocarbons, percent by weight		
		percent by weight			Unsaturates	Aromatics	Naphthenes and paraffins
Crude gasoline boiling below 180°C.	.7575	3.6	—	—	—	—	—
Neutral fraction boiling below 180°C.	.7555	—	.77	6.7	30.0	15.5	47.8
Gasoline, washed with 5 percent H_2SO_4	.7492	—	.45	.96	28.5	20.4	50.14
Crude kerosine boiling from 180° to 220°C.	.847	7.7	—	—	—	—	—
Neutralized kerosine boiling from 180° to 220°C.	.8304	—	.77	10.8	28.6	19.6	41.0

Table 6 gives proximate analyses of the crude and neutralized gasoline and kerosine fractions, as well as on gasoline which was washed with 5 percent (of its weight) of H_2SO_4 (density = 1.84). The loss on this treatment was about 6.2 percent of the gasoline. The octane number of the purified gasoline was 63.9, and with the addition of 3 cc. lead was increased to 75.6. In the standard oxidation test, the induction period of the purified gasoline was 70 minutes. Using 5 cc./l. of α naphthol as an inhibitor, a value of 380 minutes was obtained. The purified gasoline was a colorless stable liquid. Treatment with 5 percent acid was not sufficient to remove sulfur-containing compounds, as the sulfur content of the neutral fraction dropped from .77 percent only to .45 percent following treatment. Distillation of purified gasoline gave the following cuts: Initial boiling point, 69°C., 4.5 percent by volume boiled below 90°C., 17.0 percent below 100°C., 27 percent below 110°C., 39.5 percent below 120°C., 54.0 percent below 130°C., 67.5 percent below 140°C., 78 percent below 150°C., 86.5 percent below 160°C., 92.0 percent below 170°C., 95.5 percent below 180°C., and 98 percent below 185°C.

The purified gasoline differed somewhat from the crude gasoline which had the following distillation analysis:

Temp., °C.	Volume percent, cumulative
52	initial point
60	1.5
70	2.5
80	5.0
90	11.0
100	19.0
110	28.5
120	39.8
130	50.8
140	62.8
150	74.5
160	83.0
170	90.0
180	93.0
193	97.0

The crude kerosine contained 7.7 percent (by weight) phenols which could be recovered for use in the plastic industry. (The crude gasoline contained 3.6 percent phenols.) Average molecular weight of the crude kerosine was 155. The following distillation analysis was obtained:

Temp., °C.	Volume percent, cumulative
152	initial point
160	1
170	2
180	7
190	31
200	55
210	72.8
220	86.0
230	94.5

Recovered Vehicle: The distillate from the shale extract boiling below 370°C. had a density d_{20}^{20} = .9475, viscosity = 4.48° Engler (25°C.), average molecular weight = 232, phenol content = 15.5 percent. Analysis of this material by distillation was:

Temp., °C.	Weight percent
below 220	3.5
220-300	44.0
300-350	30.0
350-360	11.1
above 360	11.0
loss	.4

The recovered vehicle was recycled through the plant with fresh shale. Repeated experiments by P.N. Melentyev showed no decrease in quantity of shale dissolved or in amount of light fractions on continued recycle.

Pitch: Solid pitch with a melting point of 155°C. was obtained from the vehicle regeneration distillation.

The insoluble residue contains 92 percent ash and 8 percent organic matter. This mineral residue may be used as a cement raw material. It is a fine, easily crushed powder, with the following screen analysis:

Size, mm	Percent by weight
> .208	19.4
.175-.208	2.7
.124-.175	8.84
.104-.124	5.9
.088-.104	23.22
.074-.088	8.32
.061-.074	8.48
.053-.061	12.76
.043-.053	0.0
< .043	1.7

Plant for Large-Scale Thermal Solution of Shale.

On the basis of the above experimental data, the following scheme may be employed for large-scale thermal solution of shale:

Shale as mined, after concentration to 50-60 percent organic matter, is dried to 1-3 percent H_2O; it is ground to 0.2-0.3 mm. and mixed with recycled distillate (boiling range, 220°-370°C.) in a 1:1 ratio. The feed is pumped through a tubular preheater (415°-420°C.) into the reaction vessel where it is kept for 20 minutes at 425°-430°C. and 30 atmospheres pressure. Reaction product is throttled into a flash evaporator where gas, gasoline, and kerosine are separated from the heavier fractions (boiling above 220°C.). Residual slurry at 130°-140°C. is pumped either through a filter press or a centrifugal filter to remove undissolved solids. Kerosine, at 130°-140°C., is used to wash the filter cake and is recovered from the cake by steam drying. The 220°-370°C. fraction of the filtrate is recycled as vehicle. The gases, after recovery of gaseous hydrocarbons by adsorption, are burned for heat. Gasoline and kerosine, condensed from the gases, are washed with alkali to recover phenols, and then with H_2SO_4 or "contact purifier"*.

In a plant handling 100 Tonnes of shale A per 24 hours, about 18 Tonnes gasoline and kerosine will be obtained. Such a large-scale plant will utilize easily available equipment common to the petroleum industry. The cost of the plant would be about 2.5 million rubles (not including power plant, housing facilities, etc.).

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*Possibly clay treatment (trans. note).

If such a plant is built, including provision for destructive hydrogenation of the pitch, and stabilization of gasoline and kerosine by hydrogenation, a minimum of a 30-percent yield of gasoline and kerosine will be obtained, based on dry shale containing 48 percent organic matter.

(A one-page comparison between thermal solution and semi-coking and an extensive summary of the entire paper were not translated.)

LITERATURE

(1) Transactions of Shale Institute (reference incomplete).
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(4) McKee, R.H. and Lyder, E.E., Ind. Eng. Chem. 13, 613 (1921).
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(7) Egorova, O.I., unpublished work, at Institute of Combustible Minerals of the Acad. Sciences, USSR.**

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*Compt. rend. acad. sci. URSS

**This reference cannot be located in original text.

Part 6.

Ingenior Ake Esbjernsson
Bromolla Sweden

The Carbonization of Oil-Shale in situ

The first method:

Applying this method at first the wells are drilled into the layer. The borings are arranged on the parallel lines. The loosening of the layer is performed by explosion.

The oil-shale is ignited by blowing the hot gases and air through the layer.

After a certain time the carbonization is continued by utilizing steam, which is removed through the layer.

For carrying on the process new wells are drilled and the same treatment is repeated.

This kind of carbonization needs comparatively long time, therefore great areas must be distilled in the same time.

The carbonized oil-shale embodies great amount of the heat, which could be maintained for producing steam and hot gases (generator gas).

The necessary heat for carbonization is produced by:

1. Shale oil
2. Fixed carbon
3. Sulphur
4. Hot gases of shale distillation

The second method:

The same carbonization could be performed by utilizing only one row of borings.

The third method:

This is the well-known "Miler" process applied in Germany (notice of translator).

Notice of Translator:

This method was tested in Germany and was found to be too expensive, while large amount of explosive was necessary.

The producing of generator gas seems to be impossible, while most of the fixed carbon is burned by carbonization.

32

Utvinning av olja etc. ur skiffer in situ.

A. Oljeutvinning genom elektrisk upphettning enligt Dr Ljungström, efter uppgifter i dagspressen.

Bearbetning av 10 m² bergyta pr borrhål lämnar 400 ton skiffer. Detta svarar mot en mäktighet hos fyndigheten av 20 m.

För upphettning av berget till 400° angives åtgå 40,000 kWh. Detta svarar mot 34,400 kal. och en spec.värme av 0,215 hos berget.

Utvinningen av olja angives till 3 à 4 gånger ovan anförda kalorital och utvinningen till 75 % av skifferns oljehalt. Uträknat svarar detta mot en utvinning av 10,5 à 13,7 ton olja pr borrhål resp 400 ton berg och en oljehalt hos skiffern av 3,5 à 4,5 %. Dessutom urvinnes icke angivna mängder värmegaser varjämte bergvärmet tillmätes ett visst ekonomiskt värde. I anslutning härtill uppställes följande

Kalkyl

Utgifter		Inkomster	
		18.0	
40,000 kWh à 2 öre	kr 800:-	13,7 ton olja à 50:-	kr 650:-
Driftkostnader		Värmegaser	
Ränta och amortering		Bergvärme	
Vinst			

B. Oljeutvinning etc. genom förbränning i berget enligt Ing. Esbjörnsson:

Antagen sammansättning hos skiffern:
Analyse des Schiefers

Olja	5 %	motsvarande	500	kal. pr. kg skiffer
Kol	7 "	"	1,370	" " " "
Svavel	6 "	"	130	" " " "
Aska	82 "	"	0	" " " "
	100 %		2,000	kal. pr. kg skiffer

Skifferns upphettning sker genom förbränning under större eller mindre medverkan av följande 4 extrema fall, vilka uträknats pr kg skiffer. Beräkningarna basera sig i övrigt på som förut en yta av 10 m² bearbetat berg resp. 400 ton skiffer.

Erhitzung ausschliesslich durch Verbrennung von Öl

1. Upphettningen sker genom förbränning uteslutande av olja.

Upphettning $0{,}25 \cdot 450^{\circ}$ = 100 kal. = 20 % av oljeinnehållet
Resterande olja 400 " = 80 " " "
Utvunnen olja pr 400 ton skiffer antagen till 75 % av återstoden:

$0{,}75 \cdot 400 \cdot 0{,}8 \cdot 0{,}05 =$ 12 ton olja pr borrhål.

Erhitzung ausschliesslich durch Verbrennung von Kohle

2. Upphettningen sker genom förbränning enbart av kol.

Upphettning $0{,}25 \cdot 450^{\circ}$ = 100 kal. = 7,5 % av kolet
Resterande kol = 1,270 " = 92,5 " " "

Erhitzung ausschließlich durch Verbrennung von Schwefel

③ Upphettningen sker genom förbränning enbart med svavel.

Upphettning . 0,25.450 = 100 kal. = 77 % av svavlet
Resterande svavel = 30 " = 23 " " "

Erhitzung ausschließlich mittels der erhaltenen Heizgasen

④ Upphettningen sker enbart medelst de vid destillationen erhållna icke kondenserbara men brännbara värmegaserna.

Hur stor medverkan vardera av dessa reaktioner i verkligheten komma att lämna för upphettningen torde endast praktiska försök kunna giva besked om. I första hand avdestillerar troligen oljan, men genom luftinblåsningen stiger temperaturen lokalt, varför även endel kol och svavel torde komma att förbrinna. Man torde därför kunna antaga, att oljan lämnar blott halva värmetillskottet och att således 13,5 ton olja utvinnes pr borrhål resp. pr 10 m² yta.

4[illegible] Schiefer mit 3% [illegible] 13,5 [illegible]

Utom olja torde även avsevärda mängder generatorgas kunna utvinnas genom blåsning av luft i borrhålet och delvis förbränning av kolet i skiffern seden oljan avdestillerats. Om det antages, att 25 % av kolet kan överföras i generatorgas skulle detta motsvara

0,25. 1370 = 340 kal. eller c:a 0,1 m³ generatorgas pr kg skiffer.

Ett borrhål om 10 m² ytomfattning eller 400 ton skiffer skulle härvid medelst gasmotorer kunna generera en energimängd av

400 ton Schiefer [illegible]

c:a 40,000 kWh.

Vid blåsningen av generatorgasen antager berget en relativt hög temperatur. Denna torde kunna sättas till i medeltal 800°. Genom införandet av vatten i berget som får avdunsta till vattenånga och överhettas till t.ex. 150° samt utsugas och tillvaratagas medelst accumulatorer e.d. kan följande värmekvantitet tillvaratagas:

(800- 150). 0,25. 400,000 = 60,000,000 kal.

Detta svarar mot en ångmängd av 100 ton, för vilket annars skulle erfordras 10 ton stenkol.

[illegible]

Sammanföras dessa siffror kan man ställa upp följande preliminära

Kalkyl.

Utgifter	Inkomster	
Driftkostnader	13,5 ton olja à 50:-	675:-
Ränta och amortering	40,000 m³ gengas à 1 öre	400:-
Vinst	100 ton ånga à 1:50	150:-
		1,225

De anförda båda kalkylerna kunna givetvis icke göras fullständiga. Metoden med elektrisk upphettning ställer sig givetvis högst väsentligt dyrare än metoden med förbränning av en ringa skiffermängd.

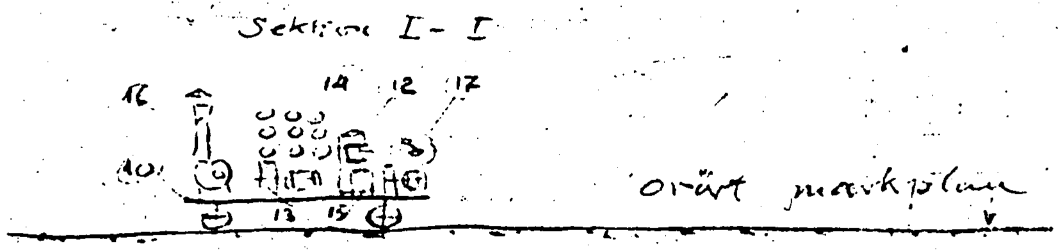
Den senare metoden är visserligen icke utprovad, men synes vid riktigt utförande vara fullt genomförbar och även i fredstid kunna lämna ett gott ekonomiskt utbyte. Metodens genomförbarhet må kanske ännu ifrågasättas, men förslaget kan däremot icke lämnas obeaktat på grund av de stora möjligheter det ställer i utsikt.

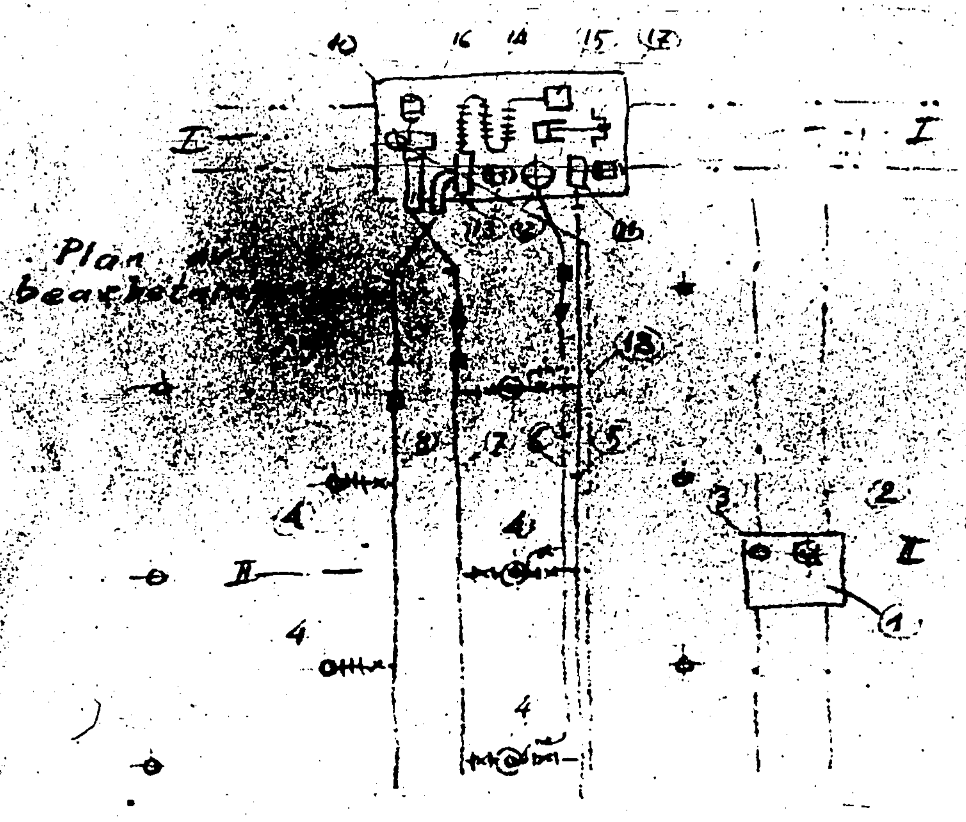
Bromölla åren 1940 - 1941

Zeichn. N:o 2. I

Schema för oljeutvinning
direkt ur lössprängt Berg.

Sektion I – I





Beteckningar:

Borrning & sprängning

1. Kran på räls
2. Kompressor
3. Luftbehållare

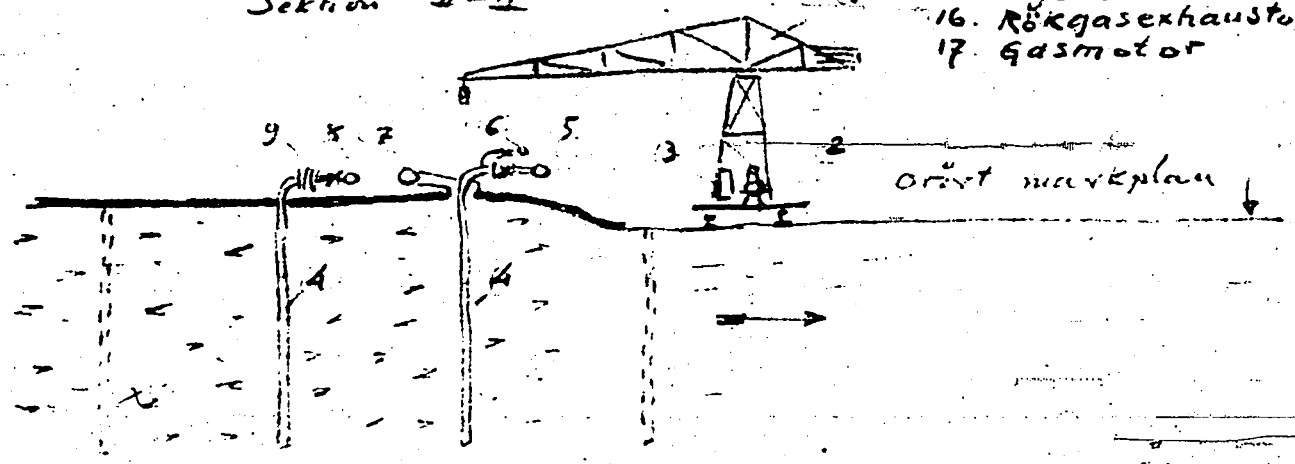
Rörledningar.

4. Sänkrör
5. Luftblåsning
18. Brännqasledning
6. Ångblåsning
7. Rökutsugning
8. Oljegasutsugning
9. Kylrör

Uppsamling.

10. Vagnsrede
11. Luftfläkt
12. Ångpanna
13. Oljegasexhaustor
14. Kondensator
15. Oljebehållare
16. Rökgasexhaustor
17. Gasmotor

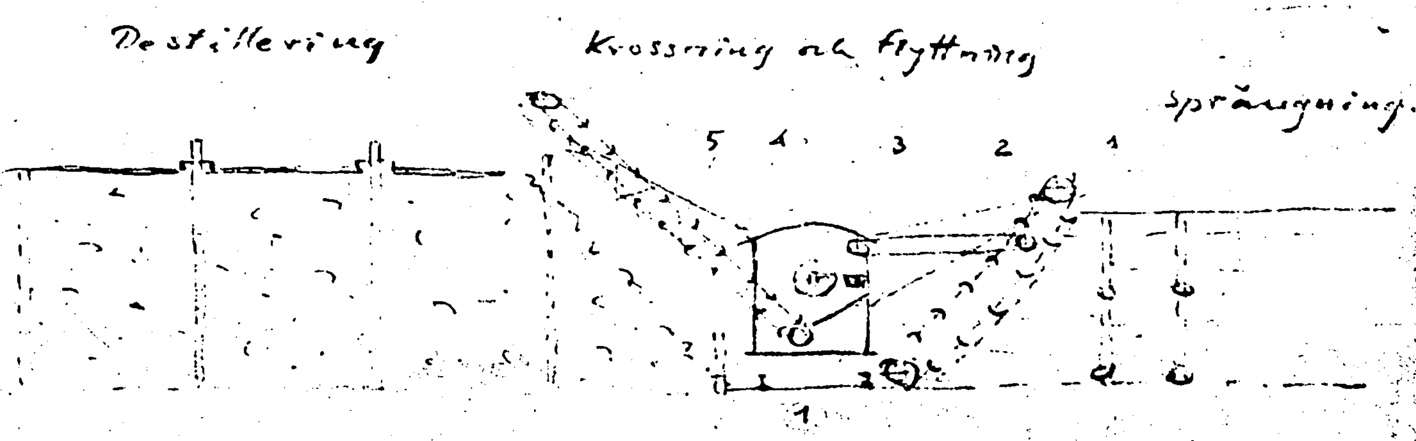
Sektion II – II

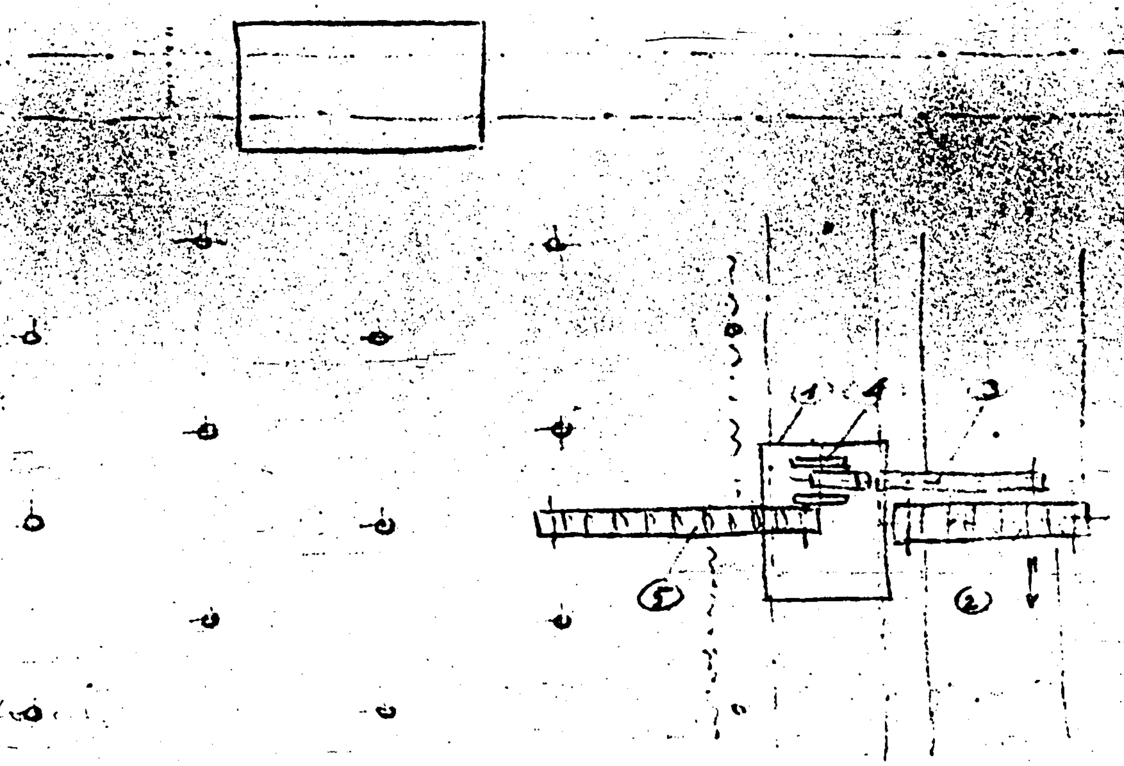


Bromölla i augusti 1946
Åke [illegible]

Zeichn. N:o 3 II ㉜

Schema för oljeutvinning
ur lössprängt, krossat och på marken upplagt Berg.





Beteckningar

1. Vagnsrede
2. Skopverk för lössprängt material
3. Transportband.
4. Stenkross
5. Skopverk för krossat material

Rörledningar för, och Uppsamling av olja äro desamma som under I anfört.

Bromölla i augusti 1946
Åke [illegible]

33

Wahl

33

SUBJECT: **ANSWERING OF QUESTIONS OF THE BUREAU OF SHIPS REGARDING SHALE OIL TREATMENT**

1. I'm not a chemist and regret to be able to give information partly only according to my experiences of 8 years working in the Estonian Oil Shale Industry and to my private files and some data about Sweden.

2. **Nitrogen Content of Shale Oil**

Neither in Estonia, nor Sweden nor Germany we had any trouble with the nitrogen content of shale. On the other hand there were difficulties with the sulfur content. How these were overcome may be taken out of the following.

The Swedish Alum-Shale contains more than 2% of nitrogen and 3.3% of sulfur. The nitrogen is reduced to 0,9% in the raw-oil by means of leading steam into the last stage of the carbonization furnace. The steam combines with the nitrogen of the shale to ammonia of which ammoniumsulfate is made for agricultural purposes.

The percentage of sulfur is reduced in the gas stage by means of the s.c. Alcazid-method. The gas contains up to 25% of H_2S. The refined gasoline has less than 0,20% of sulfur. The annual gain of sulfur of a chemical purity of 99% by this method averages on 20.000 tons annually in Sweden.

The Estonian Kukersite-Shale has the following composition:

C	76.8%
H	9.3%
S	2.2%
Cl	0.7%
N	0.5%
O	11.9%

The average Estonian crude-oil of a spec. gravity of 0,976 composes:

C	82.27%
H	10.44%
N	0.25%
O	6.19%
S	0.85%

This small amount of nitrogen does not cause trouble any more. The contents of sulfur is minimized to 0.2% by various, below mentioned methods.

The desulfurization of the gasoline in Sweden was furthermore carried out by different other methods, as for instance:

(a) Oxydizing agents - poor results.

(b) Inorganic chlorids - adequate results, the gasoline contained 0,10% of sulfur but became chlorine containing and the necessary amount for the desulfurization amounted to 10 wt % of gasoline to be treated with.

(c) Highly activated metals, as for instance Ni which gave a practically sulfur free gasoline. The necessary amount of nickel was 15 wt % of gasoline. These methods fall out of competition on the long run. The gasoline contained before the treatment 2,75% sulfur.

The magnitude of the difficulties by the high sulfur content of the Swedish and Estonian shale oils as well as gasolines consisted in corrosion of motor parts caused by the bad gasoline and diesel fuel as well as of burners of ships and of the Estonian railroad engines which were driven by this domestic bunker oil since 1929 only. The sulfur content amounted then for:

Bunker oil	0.80%
Diesel fuel	0.85%
Gasoline	0.58%

The corrosion test was prounouncedly positive.

The sulfur content reaches its peak in the fractions between 140 and 160°C, as the following shows:

Crude Oil			Crude Gasoline		
Fraction	Sp. Grav.	% S	Fraction	Sp. Grav.	% S
-175°C	0.7557	1.26	28 - 60°C	0.6746	0.55
175-200	0.8438	1.11	60 - 80	0.6770	0.75
200-225	0.8808	1.08	80 - 120	0.7200	1.09
225-250	0.9224	0.97	120-140	0.756	1.30
250-275	0.9509	0.80	140-160	0.784	1.53
275-300	0.9589	0.74	160-180	0.805	1.56
300-325	0.9589	0.78	180-200	0.824	1.50
325-350	0.9904	0.78	over 200	0.868	1.05

In the early thirties one began to reduce the sulfur content by special steering of the carbonization process and by improvement of refining. The sulfur percentage depends on the intensity of cracking and the presence of materials reducing thereby the sulfur. All oil shale gasolines are crack-gasolines. No straight run gasoline is produced in Estonia. In two works the carbonization gases are cracked in the gaseous stage at once by means of passing over heater pipes, in two other zones the cracking takes place in fluid stage by means of special cracking devices. Later on, in 1943, one company induced the Alkazid-process in order to decrease the sulfur content and to obtain pure sulfur.

By doing so the average sulfur percentage was decreased since 1932 for:

Bunker oil	0.50%
Diesel oil	0.75%
Gasoline	0.44%

On the other hand the huge consumption of these fuels proved as well in Estonia as in Sweden and Finland the magnitude of certain sulfur contents as of not being disastrous or even harmful to the motors and burners. The destructiveness depends highly on the active forms of the sulfur which must be kept under 0.01% Gasoline with 0.49% of sulfur was used for test purposes in several private motor cars for years without causing any trouble in the inner parts of the motor merely producing a slight corrosion of the rear chromium coated bumpers after long use in severe climate of the North. Further details of gasoline and refining methods are given later on.

3. Hydrocarbon compounds in Estonian Shale Oils

The Estonian shale oil belongs to the group of asphalt oils corresponding to the composition of the Kukersite-shale. It contains very little parafine components. Regarding the content of phenole the shale oil stands between the coal tar and the petroleum. It contains in the average 27% of phenoles, whereby the simplest phenole, the carbolic acid, is absent. It differs from the petroleum by higher content of phenoles and a much higher content of unsaturated hydrocarbon compounds. The medium fraction of the petroleum is an oil mainly used for heating purposes, the medium fraction of the shale oil is a first rate impregnating oil. It depends therefore on the intensity of cracking and the way of distilling only which hydrocarbon compounds might be obtained. A reduction and oxydation process runs parallel with the cracking. The extreme results of the cracking process are hydrogen and coke. The cracking of great molecules does not produce immediately light benzines and coke molecules. Intermediate molecules are formed which change gradually into light gasoline and gas on the one side and into coke on the other side. Whilst cracking of normal hydrocarbons of the parafine row a large part of the molecules decomposes in one olenfine and one hydrocarbon of the parafine row with a smaller molecular weight. The Estonian shale crude oil showed cyclical hydrocarbons with 7-10 hydrocarbon atoms, hydrocarbons similar to the hexaterpenes and open rings with 9-10 hydrocarbon atoms. (According to K. Luts: "Der Estländische Brennschiefer Kükersit", Tartu, Estonia 1934). The empirical formulae of the products are:

Light gasoline	sp. grav.	0,71	C_6H_{12}
Gasoline	" "	0,745	C_7H_{14}
Naphta	" "	0,84	$C_{10}H_{18}O$
Kerosene	" "	0,86	$C_{13}H_{21}O$
Diesel fuel	" "	0,90	$C_{14}H_{22}O_{0.5}$
Bunker fuel	" "	0,99	$C_{21}H_{29}O_{1.2}$

The constitutional separation regarding the hydrocarbon groups shows the following average proportion of a crude gasoline of sp. grav. 0.75 of Estonian shale origin:

Parafine	27.3%
Naphtene	4.3%
Unsat. Hydrocarbons	62.9%
Aromates	5.5%
	100.0%

Two methods applied in Estonia (A & C see below) allow to regulate the intensity of cracking in a very wide range. Owing to the market conditions the carbonization in Estonia was adjusted mainly to the gain of bunker oil and light gasoline, other products as diesel fuel, kerosene and bitumens were comparatively neglected because of the limited susceptibility of its customers. Corresponding to the structure of the shale, to the cracking and the eventually present matters, to the way of distillation and refining products of varying hydrocarbon compounds were obtained. Therefore I should like to give in the following a sketch of the carbonization methods with their respective products in brief.

4. Characteristics of Raw Shale Oil Special Performances of Production. Details of Treatment. Its Yields and Losses. Obtained Products.

The Estonian raw oil consists - owing to the condensing process - of heavy, medium and light oil and light gasoline. The total oil yield consists in the average of 10% heavy, 60% medium, 25% light oil and 5% of light gasoline.

The heavy oil has a spec. grav. of 1.02-1.05, flash point 190°C, pour point - 12°C, insoluble in benzine 0,17%, heating power 9500 Cal., viscosity at 50°C. 77°E., initial boiling point about 190°C.

The heavy oil is superior to the coal tar because of its little content of matter insoluble in benzine. The content of sulfur and of ash is small too.

The medium oil has a spec. grav. of 0,98, heating power 9400 Cal., viscosity at 20°C. 5,6°E., i.b.p. 135°C.

The light oil has a spec. grav. of 0,825, heating power 10500 Cal., initial boiling point 70°C. The light oil is distilled, the light fractions are added to the gasoline.

The cracking of the shale oils is more difficult than the cracking of the petroleum, because the latter has a spec. grav. of 0,85-0,90 when taken for cracking purposes. The spec. grav. of the shale oil to be cracked is 0.99. The gain of gasoline is smaller at the shale oil compared with the petroleum, because of its smaller combustion heat. The obtained light gasoline differs in many regards from the normal gasoline: it has a very low spec. grav. the boiling curve is favourable to the requests of the combustion in motors, the content of unsaturated hydrocarbons is striking and makes it much more knock proof than the average gasolines. Content of sulfur was minimized. The heavy fraction of the gasoline can be considered as some kind of solvent-naphta and is used largely for denaturizing of spirits.

The four main systems of carbonization in Estonia were:

A.

Method: Kivioli Tunnel Kilns
Company: "Eesti Kivioli A. S."
(Estonian Shale Oil Corporation)

Location of Works: Kivioli, Estonia

Kind of Method:

(a) Carbonization based on indirect heating and scavenging gases. Classified shale during carbonization not moved. Practically no dust in crude oil. Oil gases in superheater pipes of kilns partly cracked leave at 470°C.
(b) Precooling with hot heavy oil, gases leave at 300°C.
(c) Aircooler, gases leave at 230°C obtained heavy oil of sp. grav. 1.02-1.05, yield 2% of shale.
(d) Watercooler I, gases leave at 105°C obtained medium oil 0,99
(e) Watercooler II, gases leave at 60°C obtained light oil 0,85
} yield 15% of shale with 53% of gasoline
(f) Desulfurization by Alcazid method.
(g) Watercooler III, gases leave at 25°C
(h) Watercooler IV, " " " 15°C gases with 450 gr/m3 gasoline are lead to refrigerating and wash benzine plant.
} obtained gasoline of sp. grav. 0.76 yield 3% of shale
(i) 2 Calcium chloride sprinkler towers at -15°C obtained 60% of gas benzine gases leave with 100-120 gr/m3 gasoline
(k) 3 counter current wash benzine towers at -12°C obtained 40% of gas benzine gases leave with 10 gr/m3 gasoline (= 0,125% of total oil = 0.025% of shale) and return to the furnace of the carbonization plant.
} yield 1% of shale
(l) refinery; saponification continuously by Laval centrifuges, treatment with sulfuric acid, addition of Alpha-Naphtol as prevention of gums.
(m) redistillation in 3 stages.

(n) Sweetening by means of litharge
53% of gasoline are obtained in the condensing plant.
47% of gasoline are obtained in the refrigerating plant.
Wash benzine is distillation - residue of light oil.
Gasoline extraction out of the wash benzine in stream-still. Bunker oil is mixed of 49.5% heavy oil + 41.4% of medium oil + 9.1% light oil distillation residue.

The total yield of oil averages between 19 and 21% of shale.
The total yield of gasoline averages between 15 and 22% of oil.
The total losses amount an 2.96% of the total oil production.
The refining and redistilling losses amount an 2.1% of the total gasoline production.

The consumption of chemicals for refining is:

Sulfuric acid	3.4	wt % of the treated gasoline
Caustic soda	1.8	wt % of the treated gasoline
Alpha naphtol	0.043	wt % of the treated gasoline

By redistillation obtained:

	Light Gasoline	Heavy Gasoline	For Comparison Crude Gasoline
Spec. grav.	0.739	0.766	0.762
Colour	Water white	Light Yellow	Yellow
Knock value	68 (73 with lead)		
Heating power	11.000	10.800	10.800
Sulfur	0.26(0.08 with Alcazid)	0.58	1.09
Iodine number	130	143	140
Corrosion Test	negative	negative	highly positive
Doctor Test	"	"	" "
Gum Test	10 mg/100cm^3	600 mg/100cm^3	1270 mg/100cm^3
Constitution:			
parafines	26.8%	8.8%	8.1%
naphtenes	5.7%	9.5%	9.0%
unsat.hydrocarbons	62.1%	75.6%	74.4%
aromatics	5.4%	6.2%	8.5%
Initial boiling point	43.5°C	78°C	45°C
Boiling acc. ASTM:			
up to 50 C	1%	-	-
60 C	10.5%	-	4%
70 C	27.5%	-	9%
80 C	44%	-	13.5%
90 C	59%	1%	23%
100 C	71%	6%	32.5%
110 C	80%	17%	42%
120 C	87%	29.5%	49%
130 C	91%	41%	58%
140 C	94.5%	54%	64%
150 C	96%	62.5%	70%

	Light Gasoline	Heavy Gasoline	For Comparison Crude Gasoline
160°C	98%	72.5%	75%
170°C	-	79.5%	79.5%
180°C	-	85. %	82.5%
190°C	-	90 %	85%
200°C	-	93 %	87.5%
210°C	-	95 %	90%
220°C	-	97 %	92%
230°C	-	-	95%

In 12 working years 1932 to 1944 17% of crude oil in the average wer made to:

Gasoline	Denaturing Gasoline	Diesel Fuel	Losses
75% 315,000 barrels	15 % 63,000 barrels	8% 33,500 barrels	2%

Crude oil produced from 1932 to 1944: 3,040,000 barrels.
Production capacity in 1940: 450,000 barrels per year.

Other products were:
1. Road bitumen - good
2. Dust fixing oil for roads - very good
3. Roofing board tar - sufficient
4. Roofing board varnish - sufficient
5. Carbolineum - good
6. Fruit tree carbolineum - very good
7. Ash oil - rather bad
8. Kerosene - barely sufficient
9. Sulfur - 99% pure
10. Acetone - very good
11. Bacelito - very good
12. Fly tox - good

Licences of this patent of this carbonization system were sold to Germany and England. Kilns according these patents were built: 8 additional in Estonia, 2 in Germany, and 2 in Australia. An improvement of the kiln is patented in England by the K. T. O. Patents Ltd.

B.

Method:	Pintsch Vertical Rotating Generator
Company:	"Esimene Eesti Polevkivi Toostus A. S." (First Estonian Oil Shale Industry)
Location of Works:	Kohtla-Tarve, Estonia.
Kind of Method:	Carbonization based on direct heating.

(a) Classified shale moved during carbonization.
Dust in oil. Gas slightly cracked. Leaves furnace at 450°C.

(b) Aircooler, gases leave at 250°C
obtained heavy oil

(c) Cyclonic tar catches
} obtained oil 16% of shale

(d) 3 Water coolers, gases leave at 25°C with
25 gr/m^3 gasoline
obtained medium oil

(e) Gas washing in 2 scrubber towers in counter-current with wash oil (Crude oil) at 20°C. Wash oil heated in oven at 5 atm. pressure up to 150°C, goes then to evaporizer and fractioning column to extract the gasoline from the wash oil. Gasoline condensed. Wash oil starts over cooler again the circulation. Gases leave at 20°C with 10 gr/m^3 gasoline (abt. 800 calories) and are lead to the power station furnaces.
obtained gasoline 1,5 - 2% of the shale.

(f) Oil settled in separators to break the water oil emulsion.

(g) Neutralized with sodium hydrate.

(h) Separation of the washing water.

(i) Cracking plant. Crude oil is pumped thru [illegible] pipe stills at 20 to 30 atmosph. and 400 to 500°C. Stills heated with cracking gases and residue gas from carbonization plant. Gases go to evaporizer and to fractionating column to separate the gasoline from the recycling oil and the cracking (residue) gas. Gasoline lead to condenser. Cracking plant works also as distilling plant. Cracking adjusted to obtain: Crude gasoline of sp. grav. 0,81, medium oil (recycling oil) of sp. grav. 1.00 and cracking residue with flow point of 10-45° K & S. Capacity of this plant 70 tons per day.

(k) Refinery: by means of 25% caustic soda solution treatment with sulfuric acid, washing out of acids and lyes.

(l) Redistillation in 4 stages
obtained: gasoline, naphta, kerosene, diesel fuel.

(m) Sweetening by means of litharge.

(n) Washing and drying.

The total yield of oil averages between 17 and 19% of shale. The total yield of gasoline averages between 2 and 3% of oil. The total losses amount an 1.81% of the total oil production. The refining and redistilling losses amount an 8% of the total gasoline production.

By redistillation obtained:

	Gasoline	Naphta	Kerosene	Diesel fuel
Spec. grav.	0.745	0.825	0.86	0.87
Colour	Water white	—		
Knock value	68			

	Gasoline	Naphta	Kerosene	Diesel Fuel	
Heating power	11,150	10,500	10,300	10,200	
Sulfur	0.49%	1.0%	1.0%	1.0%	
Iodine number	114				
Corrosion test	negative				
Doctor test	"				
Gum test	20mg/100cm^3				
Constitution:					
parafines	35%	84.9%	84.5%	84.1%	C
naphtenes	4%	12.3%	11.6%	11.3%	H
unsat. hydrocarbons	56%	1.7%	2.9%	3.6%	O
aromatics	4%				
Initial boiling point	60°C	150°C	200°C	250°C	
Boiling acc. ASTM:					
up to 100°C	25-35%				
140°C	60-70%				
160°C	75-85%	finished at			
200°C	95%	260°C	300°C	320°C	

In 13 working years 1931 to 1944, 2,4% of crude oil were made to:

Gasoline	Naphta	Kerosene	Diesel Fuel
55%	30%	7.5%	7.5%
72,500 barrels	41,000 barrels	9,500 barrels	9,500 barrels

Crude oil produced from 1931 to 1944: 2,600,000 barrels
Production capacity in 1943: 750,000 barrels per year

Other products were:

1. Road bitumen - good
2. Dust fixing oil for roads - very good
3. Roofing board tar - sufficient
4. Roofing board varnish - sufficient
5. Carbolineum - very good
6. Fruit tree carbolineum - excellent
7. Plastic pitch - good
8. Asphalt iron lacquer - good
9. Lubricants - sufficient
10. Crude phenolate - sufficient
11. Asphalt emulsion - sufficient
12. Fly-tox - good

The Pintsch Company built by this system a huge carbonization plant in Manchuria. 3 additional plants were built later in Estonia.

C.

Method: Groendal-Ramén Tunnel Kiln
Company: "Eestimaa Oli Konsertium AS"
(Oil Company of Estonia)

Location of Zones: Sillamae, Estonia

Kind of Method:

(a) Carbonization based on indirect heating and scavenging gases. Classified shale, but utilization of the fines too by making of nodules. Shale and nodules during carbonization not moved. Dust free oil. Oil gases in superheaters cracked, leave kilns at 500°C.
(b) precooler with oil, gases leave at 300°C. obtained some heavy oil 0,5% of shale.
(c) drizzling cooler with Raschig rings
gases cooled by heavy oil of 100°C entrance temp.
gases leave at 150°C
obtained heavy oil of sp. grav. 1.02
(d) Theissen-washer with drop catchers
gases rotated by centrifugel power
gases leave at 125°C
obtained medium oil

yield 14% of shale

(e) 2 water coolers gases leave at 25°C
obtained light oil 0,81 yield 5% of shale
(f) Ströder-washer and wash tower
counter-current with wash oil
(g) residue gas returns to kiln furnace
(h) in two stills the light oil (up to 300°C) and the wash oil (up to 150°C) separately heated and gasoline extracted. Pipe stills are heated up 300°C at 5 atmosph. pressure.
(i) wash oil expands in evaporizer and goes to fractioning column when separation takes place:

Distillate I	Distillate II	Residue
Crude gasoline Fractions below 200°C	Used as wash oil Fractions between 150 and 300°C	sp. grav. 0,90

obtained gas benzene 0.7% of shale.
(k) refinery: caustic soda solution and litharge continuously by means of Laval-centrifuges. Treatment with sulfuric acid. Treatment with hydroquinone to prevent the formation of gams
(l) redistillation in 3 stages
obtained gasoline, heavy (Tractor) gasoline and residue
(m) sweetening by means of litharge

The total yield of oil averages between 18 and 20% of shale.
The total yield of gasoline averages between 17 and 18% of oil.
The total losses amount an 2.5% of the total oil production.
The refining and redistilling losses amount an 4% of the total gasoline production.

By redistillation obtained:

	Gasoline	Heavy Gasoline
Spec. gravity	0.746	0.822
Colour	water white	Yellow
Knock value	67	
Heating power	11.200	10.500
Sulfur	0,33%	0,8%
Iodine number	114	
Corrosion test	negative	negative
Doctor test	"	"
Gum test	2 mg/100cm^3	2 mg/100cm^3
Constitution:		
parafines	29.2%	
naphtenes	4.5%	
unsat. hydrocarbons	56.8%	
aromatics	9.5%	
Initial Boiling point	50°C	80°C
Boiling Analysis: 1 drop	52°C	1 drop — 150°C
5%	73°C	160°C
10%	81°C	163°C
15%	85°C	165°C
20%	90°C	167°C
30%	98°C	171°C
40%	106°C	175°C
50%	114°C	179°C
60%	121°C	184°C
70%	129°C	188°C
80%	138°C	194°C
90%	150°C	204°C
95%	160°C	210°C

The consumption of chemicals for refining is:

Sulfuric acid	4.19 wt %	of the	treated	gasoline	
Caustic soda	1.40 wt %	"	"	"	"
Lead oxyde (Litharge)	0.07 wt %	"	"	"	"
Sulfur	0.01 wt %	"	"	"	"

In 6 working years 1936 - 1943 in the average 18% of crude oil were made to:

	Gasoline	Tractor Gasoline
	70%	20%
range	50-160°C	160-200°C
	95,000 barrels	44,000 barrels

Residue 6%
Losses 4%

Crude oil produced from 1936 to 1943: 770,000 barrels.
Production capacity in 1940: 315,000 barrels per year.
Other products are similar to A and B.
By the Swedish Company "A. B. Industrimethoder" similar kilns are built in Sweden.

D.

Method: Davidson Rotating Retort

Company: "The N.C. Gold Fields Ltd."

Location of Works: Kohtla, Estonia

Kind of Method: Carbonization based on external heating.

(a) Non-classified shale moved during carbonization. Dust in crude oil. Heating performed by means of carbonization residue. Thereafter ash contains less than 1% of oil. Gas slightly cracked leaves the retort at 400°C.
(b) Dust catcher
(c) Aircooler, gases leave at 300°C
(d) Water cooler I, gases leave at 150°C obtained heavy oil.
(e) " " II, " " " 60°C
(f) " " III, " " " 25°C
(g) Scrubber tower
(h) Bubble tower
Gas is washed by medium oil
Obtained light oil, gases leave at 15°C

Medium and Light Oil is lead thru roto-jector-centrifuge to extract the dust

Refrigerating plant consists as mentioned under A
of (i) 2 Calcium chloride sprinkler towers at -15°C
(k) Counter current wash benzine towers at -12°C
(l) Residue gas returns to the retorts furnaces
(m) Cracking plant consists of 4 pipe stills working at 400°C and 20 atm. pressure. Stills heated by combustion of cracking residue gas and various oil residues. Cracking plant works as distillation plant too. The gas benzine extracted from the wash oil and the cracking gasoline (maximal gain 24.5% of oil) were treated together
(n) Refinery: caustic soda and litharge
sulfuric acid treatment
sweetening
Treatment with Fullers earth gave no results.
(o) Redistillation in 4 stages
(p) Second sweetening

The total yield of oil averages between 20 and 21% of shale.
The total yield of gasoline averages between 17 and 19% of oil.
The total losses amount an 2,3% of the total oil production.
The refining and redistilling losses amount an 6% of the total gasoline production.
By redistillation obtained:
Gasoline, heavy gasoline, tractor gasoline, residue.

The characteristic data of the gasoline are:

specific gravity	0,740
color	water white

knock value	68	
heating power	11.000 Cal.	
sulfur	0.30	
iodine number	121	
corrosion test	negative	
doctor test	"	
gum test	35 mg/100cm^3	
distillation test:	10%	90°C
	20%	98°C
	30%	105°C
	40%	112°C
	50%	116°C
	60%	123°C
	70%	131°C
	80%	142°C
	90%	155°C
	95%	165°C

In 9 working years 1932 - 1940 in the average 17% of crude oil were made to:

Gasoline	Heavy Gasoline	Tractor Gasoline
85%	5%	4%
70,000 barrels	4,100 barrels	3,800 barrels

Residue 3% and losses 3%
Crude oil produced from 1932 to 1944: 630,000 barrels
Production capacity in 1940: 75,000 barrels per year.
Other products are similar to A, B & C.

The characteristic data of the Estonian bunker fuel for 1943 and the average per 1943 are the following:

Producers:	A	B	C	D	Average
Spec.gravity	1.006	0.991	1.049	1.028	1.001
Heating power Cal.	9485	9540	9520	9600	9500
Viscosity at 50°C	8.1°E	4.82°E	19.4°E	20°E	6.6°E
Pour point °C	-21	-25	-6	-13	-20
Flash point °C	+88	+61	+100	+87	+75
Water Content %	1.6	1.1	1.4	1.2	1.3
Ash Content %	0.03	0.17	0.02	0.70	0.13
Bensol insoluble	0.15	0.37	1.08	1.025	0.37
Phenole Content %	18.9	18.8	25	23	19.3
Distillation Test:	%	%	%	%	%
acc.Engler +200°C	0.0	6.0	0.0	0.0	2.0

Producers:	A	B	C	D	Average
+225	2.5	10.5	0.0	1.0	4.5
+250	4.5	15.5	5.0	2.5	10.0
+275	9.0	22.0	12.0	4.0	16.0
+300	16.5	29.0	22.5	7.5	24.0
+325	27.0	38.0	38.0	20.5	33.5
+350	42.0	53.0	55.0	45.0	45.0

Since 1940 the characteristic data of gasoline were standardized. The average Estonian gasoline showed data as for instance may be taken from the standard for 1943:

Spec. gravity at 20°C: 0,738
Steam pressure acc. Reid at 40°C: 0,24 mg/cm^2
Corrosion test: negative
Doctor test: "
Gum test (Copper): 2 mg/100cm^3
Total sulfur: 0.43%
Iodine number: 114
Acid value: 0.0
Knock value in CFR: 66 (without lead)
Knock value in CFR: 72 (with~~out~~ lead)
Distillation test acc. ASTM:

Initial boiling point	60 C		
up to	75 C	-	4%
"	100 C	-	24%
"	150 C	-	80%
"	188 C		final boiling point

5. Hydrogenation of Estonian Oils

This was not performed in Estonia. Samples were sent to Germany when different hydrogenations were performed. Dr. Frese writes a report on this subject.

6. Refination. Information on Acid Treating

Treatment with caustic alcali. Used is caustic soda of 25 - 30%. The necessary amount depends on the content of phenoles in the crude gasoline.

The refining with sulfuric acid is generally applied in the oil shale industry of Estonia. This process is carried out now mainly by means of Laval-centrifuges to enable a continuous treatment of the gasoline. Sulfuric acid of 90% improves the color, smell, gum test and decreases the content of sulfur. The latter must be kept as small as possible for the crude gasoline because of the decreasing effort is proportionally much more effective at low sulfur contents. As above mentioned this is possible by means of respective carbonization and new methods of desulfurization of the gases. The acid treatment must be performed at low temperatures. During the last years the saponification process was applied with very good results. This method was developed in Estonia and resulted in saving of litharge and sulfur. Further details are not familiar to me. The washing and neutralization after acid treatment has to be performed at once and with small quantities of water to prevent the formation of emulsion. We did not have any trouble with the latter. The treatment with litharge was applied in most cases twice: before and after the redistillation, for it was noted after that the doctor test, once after refining was negative, became positive by the heat of the redistillation. During the sweetening sulfur powder is added to the distilate. The powder produces colloidal particles which promote the oxydation. To improve the gum test various materials were added to the gasoline. Best results of stabilization were achieved by adding of Alpha-Naphtol and Hydroquinone. Nevertheless it must be mentioned that the Estonian oil shale gasoline was not stable: gasolines with a excellent gum test after treatment with different stabilizators showed after one year storing remarkable gums. These researches need time and were interrupted by the happenings of war after 1940.

Very good results of the desulfurization were achieved by means of the Alcazid-method: the sulfur containing carbonization gases were washed in a sprinkler tower with the alcazid-lye. The sulfur is recovered in a heated topper, the lye is regenerated and returns over an heat-exchanger to the sprinkler tower. The sulfur is burned in a special oven. Sulfur and sulfur acid are obtained. The reduction of the sulfur content of the gases amounts an 40-70%.

Solvent extraction processes for shale oil refining were started in order to obtain different lubricants in the laboratory scale only.

7. Summary

The above draft contains the following items. No trouble in Sweden and Estonia with nitrogen. Little difficulties in these countries with the sulfur content of oils and gasolines. Ways to subdue these. The active sulfur only is harmful to motors and burners. Composition of the Estonian shale oil. The hydrocarbon compounds and the nature of carbonization products depends vastly on the shale used, the presence of other materials (lime etc), the carbonization methods, the intensity of cracking, the condensation and the refining treatment. Special performances of four low temperature distillation processes described. Yields and losses. Obtained products. Some details of treatment mentioned. Bunker oil and gasoline standards. Hydrogenation in Estonia not performed, allusion on Germany given. Some hints on refining, saponification, sweetening and desulfurization. Solvent extraction in industrial scale not performed, ought to be research records.

If this report should be of any interest at all, may I suggest to turn to me with special questions which I - as a non-chemist - might be able to answer per chance. Further detailed information may be obtained about carbonization devices and practice, output and working costs, investments and profitableness, comparison of the methods applied in Estonia, proper data about the consumption of water, steam and power. It should be mentioned exactly what items are of interest.

SITUATION AND PROSPECTS OF DEVELOPMENT OF THE OIL SHALE TREATMENT

By Dr. Byron Wehm and H.A. Wehl

1. Basic Problems

It is rather difficult to give suggestions on the shale treatment in the U.S., because we are little informed about the problems prevailing.

The oil shale as raw material comprises a wide range of specific properties. Further the geological deposits, the fuel situation of the respective country, the trend towards bunker-,diesel-or otto-fuel, the value of byproducts as well as the power- and labor-situation are of outstanding influence on the utilisation of shale in general and application of special methods of treatment. Systems successfully proved in Estonia or Sweden for instance may not be advisable in the States or South Africa.

It seems to us of importance to the United States to get as much as possible comparable data on the practice experienced abroad in order to be able to develop according to these lines one or several methods of oil shale treatment which due to the specific conditions prove to be the most efficient.

In connection herewith we like to warn the American reader against one wrong inference only: to draw conclusions regarding the oil shale treatment from a small pilot plant on the commercial size of a profitable industry.

Therefore the submitted paper might be considered as a general survey of the European development only. We shall gladly provide further details, if of interest.

Comparing critically the different ways of oil shale treatment it is obvious, that the produced unit of crude oil, implied by the high ash content of all shales, is by necessity loaded always with the mining, hauling, dressing, transportation and heating of comparatively huge amounts of raw materials unless the treatment does not take place in situ. This underlines the outstanding importance of the mining costs of shale. These seem to average the world over on about $0.70 to $1.00 per ton. By this fact the economical treatment of poor shales is limited at once, except in cases like Fushun where the poor shale is a "byproduct" of coal mines.

Further the high ash percent and the relatively high content of hydrogen of the kerogene of the shales effect, that the crude oil is the main product of the distillation and that the residue of the carbonization process rich in ashes and poor of hydrogens is hard to utilize. The residue becomes very often a troublesome ballast, contary to the low temperature carbonization of the coal, where the valuable coke must be considered as the main product and the tar is taken for a secondary byproduct.. The high hydrogen content of the kerogene on the other hand, especially at very kerogeneous shales, is the reason for the fusion of the shale. The latter causes manifold difficulties of plant operation at the termical treatment owing to the plastic state of shale which is much more pronounced compared with coal or lignite.

Finally one must consider that the shale crude oil is prevailingly of strongly unsaturated nature, stands behind the petroleum regarding the quality and can be refined only by means of comparatively high expense.

Out of these reasons it may be assumed that the utilisation of the oil shales on a wider scale might be performed in connection with the high pressure hydrogenation only.

In conclusion of the above the following principal demands are to be put on a method of oil shale exploitation, first not taking into

into consideration the technical and commercial details:

1. Plant with daily throughput of as large as possible amounts of raw material should be choosen. The material should be classified and not too coarse. The intense impart of heat on the resting shale should be applied by scavenging gases. The utilization of heat should be complete. The process in itself should be steerable.
2. The most complete yield of the kerogene is desirable, especially of the hydrogen of the latter in form of a high value liquid main product and the utilization of as much as possible by-products.

In the practise there occure various obstacles to suffice to all these demands owing to the diversity of the original materials, technical and commercial possibilities and required final products thus making necessary flexible solutions by compromise.

II Existing systems of Distillation

A. General older systems

The greatest part of the carbonization methods developed for coal and lignite is scarcely fit for the distillation of oil shales, since these do not correspond to the under (I) described demands: an exception form the well constructed and practically tested vertical scavenging gas generators by Lurgi (mainly for lignite briquettes, daily throughput per unit up to 400 tons) and by Jul. Pintsch (modified by the Russian Prof. Klimow, chiefly for distillation of peat, throughput per day up to 70 tons). Buth both the systems are at the disadvantage, whilst develope for the production of coke, not to enable the utilization of the distillation residues of shale. Furthermore a homogeneous lowering and equal carbonization of the charge of strongly fusing shales is not waranted.

The distillation methods developed for the Scotch shale (Pumpherston, Young etc.) are designed for special conditions (distillation at 700°C in order to smolt the nitrogen) and did not satisfy at other places for the treatment of much richer shales (South African Torbanite, Australia). Out of this reason and because of their very limited throughput also they hardly can be of any interest for the future development of the oil shale distillation in general. Out of the same reason the Berg-oven, developed for the Swedish shale and very well designed, does not come under consideration for general employment. Likewise, the Salerni-generator which was applied in South Africa, but did not suit for instance the Estonian shale, is not of general interest. That, to be sure, more for reason of other, so to say principal considerations.

B. <u>Newer in Estonia developed constructions</u>

The methods developed in Estonia specially for oil shale have confirmed more or less good results during an operation period covering 15 to 20 years and claim therefore, for a wider interest as the visits of numerous experts of different countries showed (Russia, Germany, Great Britain, South Africa, Australia, Manchuria etc.).

A detailed description of the methods is given elsewhere (Reports of the Glasgow World Congress of Shale Treatment, "Oel und Kohle" and many others).

Therefore a short comparison of the methods only may be submitted in the following.

1. Davidson Rotating Retort

   Principally detrimental to this system is the circumstance, that it does not possess any features of further development. According to the hitherto prevailing experiences with rotating retorts these cannot be enlarged. Special trials with Davidson retorts in Estonia confirms this fact. It means, that a plant with an annual output of 200,000 tons of crude oil at 20 per cent yield of oil had to consist of 120 to 150 retorts. That is practically out of question or at least not advisable. Although the existing construction utilizes the distillation residue almost completely and enables the carbonisation of the total fines (a remarkable advantage in operation on the long run, since there exists no waste shale problem), this method resulted in a higher cost price for the fuel oil owing to the high investment and repair costs compared with the tunnel kiln systems. The yield is excellent, the products of medium quality and the plant operation must be tender and experienced.

2. Pintsch Vertical Generator

   The advantages of this system are the low working expenses (little repairs only) and the utilisation of the distilling residue for producing gases. This surplus of heat in form of gases can be used for power and steam purposes. The disadvantages are; small throughput per unit (only 35 to 40 tons daily), the impossibility to carbonize the fines below 18mm grain size and to use fat shales of more than 35 to 40% kerogens, also less yield of crude oil and gasoline compared with other methods (disturbances by plastic state, local superheating zones, losses of gasoline in the gases). In the final conclusion the higher costs of erection (large condensing plant and gasoline recovery plant), the smaller yield of oil and lower gain on sales products exceed the lower working expenses in such amount, that the price of fuel oil is higher than at the other systems experienced.

3. Kiviöli Tunnel Kiln

In spite of the higher working expenses and comparatively complicated apparatus this system produced the cheapest fuel oil even in the present not perfect design owing to the smaller costs of erection (seemingly contradictory), and due to the satisfactory yield of oil as well as to the good quality and gain of its sales products.

This system is superior to both of the above mentioned owing to the large carbonization units (400 tons and even more per day), to the well controlled conduct of the charge loaded in trucks, to the possibility to extract in a simple manner secondary products out of the concentrated gases and waste waters and finally owing to the highly mechanized operation. Not taking in consideration these advantages this system contains other possibilities of development, by which a further lowering of the cost price by aid of technical improvements can be achieved (particulars see below).

4. Groendal-Ramén Tunnel Kiln
This method is in the basic features very similar to the last proceeding and distinguishes mainly from the latter by details of the construction only.

III Prospects of Development

A. Improvement to existing systems

1. The Davidson Rotating Retorts hardly contain any prospects as above mentioned.
2. Technical improvements to the Pintsch Vertical Generator are not excluded. Researches made in Estonia with enlarged units (100 tons per day) did not show any positive results. If it may even succeed to build larger units there still remains the disadvantage of this system not to be able to utilise the fines (also briquetted) and the difficulties to be overcome distilling shale of high contents of organic matter.
3. The feasible improvements to the Tunnel Kilns are the following: It is possible to raise the yield of oil by means of technical improvements and classifying or pre-treatment of the shale. Tests with the K.T.O.-Kiln in Estonia resulted in a yield of 30% of crude oil from a shale of 43% kerogene instead of 20% of crude oil from a shale of 34% kerogene in the average in the Kivioli works. (K.T.O. method see further below).

It is possible to lower the erction expenses and therewith the cost price of products by means of a more concised design of the whole kiln (see K.T.O. method also).

It is possible to utilize the fines in the Tunnel Kilns completely by means of forming waste-shale-briquettes or nodules (respective tests were performed in Kivioli and Germany; operation experiences gained successfully in Sillamae, Estonia, with the Greendal-Ramen system).

It is possible to derive secondary products in a far wider scale from the concentrated and thence simple handled gases and waste waters (liquid gas, sulfur, ketone, phenolats, nitrate combinations etc. in some countries this is decisive on the overall efficiency).

It is possible to improve the heat-balance-sheet by utilization of the entire heat of the residue by heating the kilns (like the Davidson retorts) or by gasifying the residue.

Almost all these improvements are practicable without any further research since the necessary presumptions are available or in form of actual operating experiences or in form of paramountly successful tests.

The most essential improvements are applied in the K.T.O. kiln of Mr. Kulzinsky who is also the inventor of the Kivioli kiln. Tests of the K.T.O.kiln were performed in Estonia until the out break of the war. The inventor lives in Bavaria. The patents and records are deposited in London.

4. Of the various methods not yet tested in the industrial stage there seems the Lugi-Schweitzer-System (to be applied in Wuerttemberg) to be of the most outstanding interest. Tests were successful up to now.

The Schweitzer Generator appears to be a further development of the N.T.U. Retort, surely familiar to the American reader.

A vertical, on the top open cylinder of sheet iron (respectively a tub slightly enlarged to the top) with double bottom, filled with shale undergoes the carbonization process in a discontinuous course after ingnation of the shale on the top.

The carbonisation process in the succession: drying and preheating zone, distillation zone, combustion and cooling zones passes slowly and very equally the charge (30 to 50 tons) in 48 hours from the top to the bottom in such manner, that actually the distillation residue only is subject to the combustion.

The tubs have diameters of 3 to 4 meters at a height of 3 to 5 meters, are united to groups and connected to a common condensing plant with electrostatic tar precipitators. Since the vapours pass the collecting tube at a temperature of about 40 to 60°C the water cooling stage may be omitted. Thus cooling water is required actually for the gasoline recovery plant only.

The ready tubs are lifted at taps alternatively by means of a traveling crane from their respective places, taken to a tilting device, emptied, filled from hoppers anew and replaced again. The charge lies on the upper sieve bottom of the tub. The lower bottom is connected to a duct. To the latter corresponds another duct joining a water sealing pot. This leads the gases through the gasmain and condensing plant to the exhaustor. As mentioned results of the industrial stage are not yet available. The only doubtful item of this method seem to be the lifetime of the tubs and the depletion when tilting trickled carbonisation residue. On the other hand the following advantages of the method are remarkable:

Simple design, consisting of technically proved elements of construction.

Good utilisation of heat and kerogene, therefore satisfactory yield of oil and always a surplus of heat in the gases.

No moving parts working at high temperature.

Resting charge, therefore diminished content of dust in the tar as well as the chance to carbonise fine shale briquettes and shale of comparatively high content of kerogene.

The feasibility to lead the caronization or combustion process in that way as to perform the possibility of adding inert gases or steam to the air intake. By doing so there arises the chance of using the ashes for cement production, for instance the Lurgi-Trickling-Process (compare the Dotternhausen cement works).

Low erection and operation expenses.

Estimates showed for instance regarding the (poorer, not picked out) Estonian shale cost prices of the crude oil amounting to almost one half of the cost prices of crude-oils obtained by the other systems (compare part II 1,2,3,).

Other detriments would have been taken in account. This system seems to be very prospective and economically practicable for the future of shales with a small content of organic matter as for instance the shales of Sweden and Wuerttemberg. Test were performed with Estonian normal piece shale, briquettes made of Estonian fine shale, especially kerogene poor Estonian shale and with shale of various German origin. All results were satisfactory.

5. The Meyer-Otto-System is of interest only on account of the model made construction, utilization of heat and use of the distillation residues for the manufacturing of cement according to the Lurgi-Suctiongas-Trickling-System. From the point of view of the carbonization process only the large expenditure on material and working expenses are hardly justified for the production of oil.

6. The Meiler-Pile-System depends basically on the same principle as the Schweitzer method, the walls of the retorts are abandoned and the charge is poured in heaps on the soil. But it seems to us that this system is after one years practice hardly worth while mentioning. The expected advantages by this outmost simplicity and by saving the buildings, cranes, removal of ashes are certainly compensated by the following disadvantages:

The dependency on the climate and weather.
The handiwork whilst pouring and ingating the pile.
The great expenditure on ignating material.
The huge expense for pipe work

The difficulties by replacing the suction pipes

The bad yield owing to the shock-effect of the shale on the oil vapours, owing to burning of oil, owing to oozing of oil into the soil.

The resignation on using the internal heat and the ashes.

The lack of any predetermination of the process.

Therefore it is rather difficult to give any chances of economical prospects to this system. It is a rush-development of the war.

B. New Ways of Oil Shale Treatment

There are too little exact data and practical experiences of most of these systems to make any final conclusions for the time being. A short return of the methods might suffice at this place.

One can divide them in four groups:

a. Modern carbonization devices
b. Subterranean carbonization systems
c. Carbonization by electric heating in situ
d. Extraction of hydrocarbons of oil shale without carbonization.

a. Modern carbonization devices

1. Metal-bath-distillation-oven (O.Schmidt-Dr. Oppelt).

This system has its predecessor in the actually not proved nor really tested metal-bath-cracking-ovens of Bluemner (lead), Melamid (tin) and the metal-bath-distillation device of H.Ford (lead). The metal-bath is supposed to consist of Silum, an aluminum-silicium-alloy. The latter enables the advantage not to be seized by sulfur. The great surface tension keeps the moistening of the oil shale at a minimum. This proceeding is promising and elegant, if actually feasible in the industrial stage. The success depends probably of the amount of the oilum losses mainly and the practicable throughput per time unit.

2. Distillation of oil shale dusts in gas streams (Zeidler). Theoretically the distillation of sufficient small grains of oil shale had to be performed very quickly in a hot gas stream. The trials made up to now in Estonia, Sweden and elsewhere showed, that the main difficulties arose at the dust separation.

b. Subterranean carbonisation systems

3. Carbonisation of bursted shale in the mine (Huebener, Kohle und Oel Union). The bursted shale is heaped in depleted adits, ignated by wood and wooden chips, suction applied by dra[illegible]-fan. Condensing plant as mentioned under "Schweitzer" and "Meiler Pilo". The arisen difficulties are the like as at the Meiler system. Trial carbonisations are running in Wuerttemberg, the average oil output amounts on 300 tons per month. It is permature to make any conclusions about this system just as about the following. Surely a lot of research work is completed which might be observed at further development elsewhere.

4. Subterranean carbonization in situ (Dr. Schneiders). Promising test were performed in Estonia and Wuerttemberg They proved the dependency of its application on the local shale deposits. Obstacles arose in preventing of fire-damps and explosions, further in limiting the area of carbonization.

c. Carbonization by electric heating in situ.

5. Carbonization by means of sunk heating elements (Dr. Ljungstrom). Since 1941 these trials are performed in Sweden in collaberation with the Royal Water-Power-Utilization-Committee especially as a means to improve the load factor. Each perforated collector rod reaching for 12 to 17 meters into the shale deposits is surrounded by 6 heating elements with electrical resistances corresponding to a capacity of 22KW each. One set covers the heating of about 400 tons of shale. Several such sets are applied to a large field. The collector rod and piping are connected to a condensing plant and exhaustor as usual. Owing to the layer of soil covering the shale there is no quick cooling of the heated deposits when the electric intake is decreased for the peak load hours in order to adapt to the load factor of the power system. Nevertheless, the Swedes quote a power price of RMK. 0.02 per KWh (i.e. about 8 mills USA/KWh). Required electric power amounts on about 2200 KWhs per one ton of crude oil for heating purposes only, that corresponds to about RMK. 44-per ton of oil. This system is supposed to have entered the industrial stage in the meantime. The heating of the surface is used for agricultural purposes also.

6. The electrical carbonization methods "Electrocarbonization" (Sarapuu) performs the heating of oil shale in situ. Also in this case as advantage the application of peak-off power is to be utilized mainly. The aims of this method could be summarized as follows: loosening the bulk layer by carbonization, applying the ground resistance for converting the electrical current into heat, performing the process through borings from the surface, gasifying the fixed carbons after the carbonization of the oil shale. This system seems to be promising too, especially as it allows for several other applications.

It is to be regreted that large scale tests in the field are not performed up to now.

d. <u>Extraction of hydrocarbons of oil shale without carbonization.</u>

The following methods are very prospective, on the other hand their importance is surely limited to special kinds of oil shales.

7. The thermical melting of the kerogene.

Strongly bitumenous and fusing shales (for instance the Estonian Kukersite) can be transformed in absence of air at temperatures of 300 to 400°C in an homogeneous bitumen in the first stage rich of ashes. The ash can be separated by extraction or dilution and following filtration or separation by centrifuges. The bitumen can be used as such or for the hydrogenation. Advantages are: excellent yield- about 85% of the kerogene instead of 65% at the best by carbonization.

Obstacles arise, as the tests in Estonia and trials on commission of the writer (Wehm) in Ludwigshafen, Germany, proved, at the operating actually by insufficient filtration velocities or temporary by slinging effects respectively.

8. Ash removal of kerogene by flotation and direct hydrogenation of the enriched paste.

The trials performed on commission of the writer (Wehm) with Kukersite in Estonia and in Germany by the "I.G. Farben" in Poelitz, Griesheim, and Ludwigshafen gave very good results. The flotation yielded to 90% kerogene with 15% ash content. The hydrogenation proved at various tests an average yield of 80% of kerogene. The distillation tests acc. ASTM showed 95% up to 325°C boiling of the total yielded by hydrogenation. The overall yield amounted to 68% up to 325°C boiling parts in reference to the original kerogene. This result seems to be granted in the industrial stage also. Owing to the high hydrogen content of the kerogene the consumption of hydrogen as the main expenditure in the actual process is lower as with the coal hydrogenation, the sling ng effect of the waste sludge is good and at any rate better as the expectations suggested.

This proceeding is for certain shales very promising and developed by research work so far, that there no obstakles are to be seen regarding the appliance of the latter in actual large scale demonstration units.

CONCLUSION

Resuming it might be stated, that a decision on the existing new methods of oil shale treatment seems to be premature for the time being.

To give a councel regarding the American development from our point of view is not advisable.. But on the other hand three more exactly researched methods out of the multitude of proceedings might be especially effective for the practice of the next time on account of theoretical reflections, successfully performed tests and actual operation results. These are:

1. The Kulzinsky-Tunnel-Kiln for the carbonisation of fusing shales of very high content of kerogene as well as for oil chalk, asphaltic stones and strongly bitumenous kinds of coal.
2. The Lurgi-Schweitzer-Generator for the distillation of shales of small content of kerogene.
3. The Flotation-Hydrogenation for special shales and in accordance with the local circumstances.

The choice depends on various basic, local and commercial considerations, as mentioned above. We gladly would appreciate to provide you with further particulars suggesting to you to state the respective questions in as proper a limitation.

This report was addressed to Col. Foran and dated Ratshausen, Wuerttemberg, Germany, June 26, 1945..

If this report should be written at all, may I suggest to the distributing office to send kindly one copy to Col. Foran as to the initiator of this paper ~~mostly~~ originated in the thoughts of my former colleague Mr. Wehm.

H. A. W

H. A. Wahl

Generation of Electric Power as a byproduct of Oil Shale Carbonization in Estonia

During the last years of the independence of the Estonian Republic the whole hauling of shale amounted to nearly 2 million tons per annum. Of this quantity were utilized in the average:

For carbonization purposes	1,100,000 tons
As burning material sold	550,000 tons
As heating material for power stations	350,000 tons

The latter amount consisted of 35% piece shale and 65% of fine shale which to the greatest part could not be used for carbonization without making nodules or briquettes. In the average 128,000,000 KWh per year were produced of shale in Estonia and 38,000 tons of shale were sold annually to Latvia for power stations. The fine shale had a heat value of 2200 to 2300 cal/kg. In the average we calculated 1 MWh = 2.5 tons of fine shale. The price of fine shale was standardized according to the heat value: 1000 calories (4000 BTU) cost 0.17 Estonian cents(0.045 USA cents). The heat value fluctuated in dependence of the hauling in open cut or underground mines. Estonia was a poor and small country with an industry which only in the late thirties started a rapid rise. The power stations were comparatively small, the biggest installed unit of a turbine was 10,000 KW. It may be mentioned that we generated by direct combustion of fine shale in power stations by means of condensing turbines 400 KWhs of one ton of shale in the average. The specific consumption was 2.5 kgs x 2300 cal = 5750 cal per KWh, the total efficiency 15%. The best efficiency achieved in a condensing turbine by combustion of shale waste over a period of years was 4550 cal/KWh (18,300 BTU/KWh) or 19%. The corresponding heat costs were 0.98 E cents (0.260 USA cents) for the average and 0.77 E cents (0.205 USA cents) for the cheapest KWh made of fine shale. The best boiler efficiency was 83%, the average 76%. All boilers combusting fine shale were equipped with the special Lomshakow-grates. These grates were developed for fine shale and gave very good results at the strongly caking burning material. The licences were sold to Sweden and Latvia.

Much better efficiencies were achieved in the power supply of the oil shale industry by using bleeder turbines, fine shale and permanent gas combustion.

In connection herewith some examples of the heat economy of three carbonization methods in Estonia and for comparison the heat balance sheet of the Meiler-carbonization system in Germany may be published in the following. To my knowledge heat balance sheets of shale carbonization processes based on facts of the average operation over a longer working period are not made public up to now. These examples are not very favourable and exclude all kinds of estimates. They ought to show the experiences of the carbonization industry of Estonia of the years elapsed until 1940. Within the past months nobody has spoken with me about the shale development in this country. But I suppose that conditions different from those in Estonia are prevailing in the United States. Nevertheless, I guess that these details taken as data of comparison may be of some value for this country in the future.

After the occupation of Estonia by Russia the whole industry was working under other conditions. The following examples are derived from the period up to 1940 and are regarding the efficiency by no means ideal. Therefore each precedent is concluded by a critical opinion considering the disadvantages. The examples rely on positive samples and measurements with the exception of "C" (N.C. Gold Fields Ltd.) where the losses are summarized, because of missing my respective papers which remained in Germany probably.

A.

Rough heat balance sheet and utilization
of residue gases for electric power generation
by means of the
Pintsch Vertical Generator
at Kohtla-Jarve, Estonia
Plant III, 16 Generators

Production during one month of 30 days.

Throughput of shale	18,200 Tons
Daily throughput of shale per one generator	38 "
Moisture of shale	11%
Contents of organic substance of shale	35%
Oil yield from the organic substance	48.9%
" " " " " " by Fischer assay	60.3%
" " according Fischer assay	81 %
" "	17.1%
Output of oil	3,120 Tons
Water contents of oil	1.1%
Gasoline output	75 Tons
Amount of gas per one kg of shale	0.644 m^3
Total amount of gas	11,700,000 m^3
Heat value of shale acc. samples	3,450 cal/kg
" " of oil	9,450 "
" " of gasoline	11,150 "
" " of gas after condensing stage	1,220 cal/m^3
" " " " " wash oil plant	1,100 "
" " " total gas	14,200,000,000 cal
" " " gas for gasoline extraction	910,000,000 "
" " " " " generator heating	1,770,000,000 "
" " " " " cracking plant heating	1,770,000,000 "
" " " " " power station available	9,350,000,000 "
" " " " " " " consumed	6,010,000,000 "
" " " " disposed off	3,340,000,000 "
" " " " losses	400,000,000 "
Electric power to be produced	1,180,000 KWhs
" " actually generated	760,000 KWhs
" " not "	420,000 KWhs
Steam regained by bleeding	1,680 Tons

After the occupation of Estonia by Russia the whole industry was working under other conditions. The following examples are derived from the period up to 1940 and are regarding the efficiency by no means ideal. Therefore each precedent is concluded by a critical opinion considering the disadvantages. The examples rely on positive samples and measurements with the exception of "C" (N.C. Gold Fields Ltd.) where the losses are summarized, because of missing my respective papers which remained in Germany probably.

A.

Rough heat balance sheet and utilization of residue gases for electric power generation by means of the Pintsch Vertical Generator at Kohtla-Jarve, Estonia Plant III, 16 Generators

Production during one month of 30 days.

Throughput of shale	18,200 Tons
Daily throughput of shale per one generator	38 "
Moisture of shale	11%
Contents of organic substance of shale	35%
Oil yield from the organic substance	48.9%
" " " " " " by Fischer assay	60.3%
" " according Fischer assay	81 %
" "	17.1%
Output of oil	3,120 Tons
Water contents of oil	1.1%
Gasoline output	75 Tons
Amount of gas per one kg of shale	0.644 m^3
Total amount of gas	11,700,000 m^3
Heat value of shale acc. samples	3,450 cal/kg
" " of oil	9,450 "
" " of gasoline	11,150 "
" " of gas after condensing stage	1,220 cal/m^3
" " " " " wash oil plant	1,100 "
" " " total gas	14,200,000,000 cal
" " " gas for gasoline extraction	910,000,000 "
" " " " " generator heating	1,770,000,000 "
" " " " " cracking plant heating	1,770,000,000 "
" " " " " power station available	9,350,000,000 "
" " " " " " " consumed	6,010,000,000 "
" " " " disposed off	3,340,000,000 "
" " " " losses	400,000,000 "
Electric power to be produced	1,180,000 KWhs
" " actually generated	760,000 KWhs
" " not "	420,000 KWhs
Steam regained by bleeding	1,680 Tons

Heat balance sheet per 1000 Kgs

	C	Calories
Input:		
1000 kgs shale		3,450,000
97 m residue gas		106,000
Total Input		3,556,000
Output:		
171 kgs Oil		1,620,000
4.1 " Gasoline		45,500
460 " Ash		400,000
Gas to Power Station		476,000
" to Generator Heating		106,000
" to Cracking Plant Heating		106,000
Sensible Heat of Oil		12,000
" " " Gasoline		500
" " " Ash		21,000
" " " Total Gases		4,000
Evaporization Heat of Moisture		72,000
Decomposition of $CaCO_3$		51,000
Losses:		
Radiation of Generators	355,600	
Burning of Ashes	71,000	
Gas losses in Wash Oil Plant, " " by Filling Generators, " " etc.	22,000	
Various undeterminable losses	192,900	
Total losses	641,500	641,500
Total Output		3,556,000

(see attached diagram A)

Condensing bleeder turbine

Steam rates:

at full load working as condensing turbine	5.7 kgs/kwh	(12.6 lbs/kwh)
" " " bleeding 2200 kgs/h steam	6.5 kgs/kwh	(14.4 lbs/kwh)
" " " " 4000 kgs/h "	6.9 kgs/kwh	(15.2 lbs/kwh)
" " " " 6000 kgs/h "	7.7 kgs/kwh	(17.0 lbs/kwh)
Initial Steam Pressure (Gage) 30 atü		(440 lbs/sq. in.)
" " Temperature 400 °C		(750 deg. F)
Bleeding at 9 ata		(118 lbs/sq. in. g.)

The single components of the total efficiency were the following:

Efficiency at main gas line	90%
" " boilers with gas burners	85%
" " steam pipes	97%
Thermal Efficiency as condensing turbine	24.8%
" " as bleeder turbine (bleeding 2200 kgs/h)	44%
" " " " " (" 4000 kgs/h)	55%
" " " " " (" 6000 kgs/h)	67%

Internal Efficiency of turbine	85%
Mechanical " " "	98.5%
Efficiency of the generator	95%
" considering station service consumption	92%

The overall efficiency of the power station including all losses was in dependence of the bleeding:

no bleeding	13.5%	corresponding to	6350 cal/kwh
bleeding 2200 kgs/h	24 %	" "	3600 "
" 4000 "	31.7%	" "	2700 "
" 6000 "	38.3%	" "	2250 "

The demand on bleeded steam amounted on 85.5 kgs per 1000 kgs of shale (189 lbs/ 1 ton) or 7,000 kgs/h. The annual steam consumption was 50,000,000 kgs for the whole work consisting of 4 complete carbonization plants. The corresponding consumption of electric power was 13,100,000 kwhs per year. Under these conditions we had to run one turbine at full load and full bleeding which resulted in the best overall efficiency:

$$7.65 \text{ m}^3 \text{ Gas} = 1 \text{ KWh plus } 4.15 \text{ kgs steam}$$

i.e. 43%

and the second turbine at 75% load and 17% of full bleeding thus achieving a much worse efficiency. The annual average efficiency was 29% corresponding to

$$7.2 \text{ m}^3 \text{ Gas} = 1 \text{ KWh plus } 2.20 \text{ kgs steam.}$$

The carbonization plants delivered per annum roughly 387,000,000 m^3 gas or 426,000,000,000 calories. The utilization of this amount was according to the above data:

Gasoline extraction	6.5%
Carbonization generator's reheating	12.5%
Crack plant heating	12.5%
Power Station utilized for plants supply	24.4%
Power Station utilized for sold power	17.8%
" " disposed of	23.5%
Gas losses	2.8%
TOTAL	100.0%

It means 91,000,000 m^3 gas per annum were disposed of until the reorganization of the heat economy of this factory.

The cost of one tone of bleeded steam was credited to the power station with EKr. 2.90 of which the investment costs were EKr. 1.90. Taking in consideration the heat costs per ton steam of EKv. 1.- the heat costs of the KWh amounted to 0.35 Estonian cents (0.093 USA cents) at the best efficiency, to 0.58 Est. cts. (0.16 USA cents) when working as condensing turbine and to 0.5 Est. cts. (0.13 USA cents) under the annual average conditions, i.e. at 7.2 m^3 steam consumption for 1 KWh plus 2.2 kgs bleeding. The heat price per hour averaged on EKr 10.50, producing 1450 KWh and 3.2 tons steam. The critical examination of the combined process of carbonization and power generating may be expressed as following:

The carbonization method has a comparatively little yield of oil of 16.5 to 18.5%. The throughput per unit of shale is small, fine shale with a granulation less than 18 mm can't be utilized, neither nodules nor briquettes. Fat shale with a content of organic substance of more than 40% produces lumps owing to the strongly caking Estonian shale. The high amount of gas postulates a big condensing plant and huge cooling water demand. The yield of gasoline is small. The building costs are high. The residue (ash) happens to be not completely degasified often and burns on the ash dump. The total of thermal losses is remarkable. Under various undeterminable losses one has to comprehend the losses by cooling down of the carbonization chamber by steam and added residue gas, losses by heat convection, losses by gasoline extraction, etc. The disadvantages of the power station were: very long and insufficient insulated gas main lines (up to 400 m) from the single carbonization plants to the power station. Some condensate was caught in these pipes. Calorimetric measures (acc. Junkers) of the received gases were performed and resulted in a heat value varying between 1080 and 1150 cal/m^3. For being on the safe side the losses of the pipe line were assumed to be 10%. The unit of the turbines was small: the available amount of gas could not be utilized and the efficiency was naturally less than at big units. The amount of bleeding did not correspond to the effective steam demand of the plant. Lack of a distance heating system for the surrounding communities. Hence the turbines had to be run with a smaller efficiency. The vacuum of the turbine condensers was not the best one due to temporary shortage of cooling water. The compound operation of this power station with the general high tension network was impossible due to the lack of an interconnection. Thus the sale of electric surplus power was limited.

B.

Rough heat balance sheet and utilization of fine shale for electric power generation.

Groendal - Ramén Tunnel Kilns
at Sillamae, Estonia
Kilns A and B

The utilization of hauled shale for carbonization, power generating, etc. for one month was the following:

Piece	shale	for	carbonization	17,000 Tons
"	"	"	sale	2,850 "
Fine	"	"	carbonization	4,400 "
"	"	"	power station and bled steam	3,000 "
"	"	"	boilers for process steam only	750 "
Total per month				28,000 "

Production during one month of 30 days:		
Throughput: piece shale	17,000 tons	
nodules	4,400 "	
Total	21,400 "	21,400 tons
Daily throughput of shale of kiln A		450 "
" " " " " " B		250 "
Moisture of shale		10%
" " nodules		14%
Contents of organic substance of shale		37%
Oil Yield from the organic substance		52%
Oil yield from the organic substance by Fisher assay		57%
Oil yield according Fisher assay		92%
Oil yield		19.4%
Output of oil		3,400 tons
Output of gasoline		750 tons
Amount of gas per one kg of shale		0.04 m^3
Total amount of gas		880,000 m^3
Heat value of shale acc. samples		3,450 cal
" " " nodules		2,300 "
" " " oil		9,400 "
" " " gasoline		11,200 "
" " " gas		7,200 "
For heating of the kilns consumed:		
880,000 m^3 gas		$6.35 \cdot 10^9$ cal
230 tons oil		$2.16 \cdot 10^6$ "
Steam Consumed:		
4150 to oil x 1.7 to/to		7,050 tons
	i.e.	9,800 kgs/h,
Electric current consumed:		
Mine including electric excavator for 28,017 tons shale hauling		100,000 kwhs
Plant: 3,400 tons of oil	620,000 kwhs	
750 tons of gasoline	188,000 kwhs	
Total	808,000 kwhs	808,000 kwhs
Electric current produced:		
1200 kw x 720 h =	865,000 kwhs	
minus station service	55,000 kwhs	
	810,000 kwhs	810,000 kwhs

The mine was supplied by the general high tension system.

Heat Balance Sheet per 1000 kgs

	Calories
Input	
800 kgs shale	2,760,000
200 kgs shale nodules	460,000
10.6 kgs oil	100,000
40 m^3 gas	290,000
Total Input	3,610,000
Output	
159 kgs oil	1,500,000
35 kgs gasoline	392,000
40 m^3 gas	290,000
592 kgs residue (coke)	710,000
Sensible Heat of Oil Vapours	57,800
" " " Gas	6,000
" " " Coke	59,200
" " " Water	27,000
Evaporization Heat of Moisture	82,000
Preheat of Shale on 500°C	140,000
" of Shale Lorries	60,000
Losses:	
Radiation of Kiln, Furnace, Heating Channels	88,000
Chimney Losses	48,000
Transmission losses and various	150,000
Total output	3,610,000

(See attached diagram B)

Condensing bleeder turbine

Steam rates:
At full electric load (1200kw) and full bleeding (5500 kgs/h steam) the specific consumption is 7.6 kgs/kwh (17 lbs/kwh). Running as condensing turbine the specific consumption is 6.3 kgs/kwh (14 lbs/kwh).

Initial steam pressure	25 atw
" " temperature	360°C
Amount of bleeded steam	5500 kgs/h at 6 ata
Efficiency of boiler	82%
Efficiency of steam pipes	97%
Thermal Efficiency as condensing turbine	23%
Thermal Efficiency at full bleeding	76%
Internal Efficiency of Turbine	84%
Total Efficiency of power station at full bleeding	44.5%
Total Efficiency of power station as condensing turbine	13.4%

The specific consumption at full load and full bleeding was regarding the kwh 1930 cal/kwh or 7300 BTU/KWH and taking into consideration the bleeded system 3.4 kgs of shale or 7800 cal/kwh (31,500 BTU/KWH).

At full load the fine shale consumption for combustion amounted to 4.05 tons per hour. The shale price was booked with Ekr. 3.95 per ton. The steam heat costs were booked with Ekr. 1.-- per ton. The heat price per hour averaged on Ekr. 15.90. Thus the heat costs of one kwh amounted to 0.86 Estonian cents (0.22 USA cents/kwh). On the other hand, the investment costs of the kwh were owing to commercial circumstances so high, that this small power station was shut down later on and the consumption covered by the general high tension supply.

As a critical examination the following may be mentioned:

The heat losses in the coke (1100 - 1500 cal/kg) were rather high. It was foreseen to gasify the hot coke whereby about 450 to 500 calories per one ng shale were expected to be obtained. By means of these gases the kilns were to be heated and the high value permanent gas was to be used for other purposes as well as the oil saved. Owing to expected war, the Swedish did not invest any money in Estonia furthermore and this remained unsettled.

One big kiln is better than two smaller ones regarding losses, preheating of shale lorries, radiation, etc. The heating oil demand of 5.5%, as above shown, is high. Mostly the latter averaged on 2.5 to 4% and fluctuated strongly depending on the season. The above example is taken of a winter month which used to be in Estonia very severe.

The oil consumption varied depending on the intensity of carbonization. The more intensive the carbonization, the more gasoline obtained by cracking insides the kilns the more calories remained in the residue gas. The oil contents of the shale, the moisture and the not complete and continuous utilization of gas due to the lack of a gasholder produced sometimes a rather high demand on additional oil for heating purposes. But these faults were simple to overcome.

The specific heat demand averaged to 300 to 410 calories per one kg to be carbonized. The nodulization of the fines was very effective and allowed the complete utilization of the hauled shale. The not nodulized fines were used for heating in the boiler house on the s.c. Lomshakov moving grates. The electirc power demand for the nodulization amounted to 2.85 kwhs per ton shale. Thus, the comparatively high power consumption of this plant per one ton of shale before the carbonization is explained:

Mine	18 kwh	/to Oil
Dressing	10 "	"
Nodulization	15 "	"
Total	43 kwh	/to Oil

C

Rough Heat Balance Sheet
of the
Davison Rotating Retort
experienced
at the N. C. Gold Field, Ltd.
Kohtla Oil Works, Estonia

Production during one month of 30 days:	
Throughput of shale	4800 tons
Daily throughput of shale per one retort	23 "
Moisutre of shale	11%
Contents of organic substance of shale	40%
Oil yield from the organic substance	52.5%
" " " " " " by Fisher assay	59%
" " according Fisher assay	89%
" "	21%
Output of oil	850 tons
" " gasoline	160 tons
Amount of gas per one kg of shale	o.02m^3
Total amount of gas	96,000 m^3
Heat value of shale acc. samples	3,500 cal.
" " " oil	9,600 "
" " " gasoline	11,000 "
" " " residue gas	1,000

Heat Balance Sheet per 1000 kgs

	Calories
Input	
1000 kgs shale	3,500,000
20 m^3 residue gas	20,000
530 kgs residue (coke)	580,000
Total Input	4,100,000
Output	
175 kgs oil	1,700,000
35 kgs gasoline	390,000
450 kgs ash	270,000
20 m^3 residue gas	20,000
110 kgs evaporated moisture	84,000
Sensible Heat: oil vapours	50,000
gas	5,000
ash	27,000
water	28,000
Preheat of shale on 500°C	140,000
Total of losses	1,386,000
Total Output	4,100,000

(See diagram C attached)

The above data are regarding the losses undefined due to the lack of the once made calculations I can't find at present under my papers,

As a critical judgement of this carbonization system the following might be intimated: -

The utilization of the coke on moved grates for retort heating is nearly complete. The retorts work up unclassified shale, crushed but not screened. The unit of carbonization is little and cannot be enlarged, as tests in Estonia with 8-feet retorts proved. The good results are due mainly to the elaborated heat control and to the robust construction of the counterrotating scrapers. The retorts are very sensitive on the degree of the moisture of shale as well as on the oil contents of shale, the latter has to be kept below 40%. The method is connected with a lot of handiwork, therefore, the application in large industrial stage seems to be not advisable. On the other hand, the specific yield is excellent.

D

For comparison with the above methods experienced in Estonia, for nearly two decades, I would like to show an approximated heat balance sheet of the s.c. "Meiler" - carbonization method which was applied in the Oil Shale Industry of Wurttenberg, Germany, to a poor shale for two years. The average of 38 Meilers carbonized at the Pilot Plant in Schomberg gives an oil yield of 18%.

Heat Balance Sheet per 1000 kgs

	Calories
Input	
1000 kgs shale	1,200,000
4.5 kgs peat	12,000
1 kg wooden chips	4,000
Total Input	1,216,000
Output	
18 kgs oil	171,000 cal.
0.4 kgs gasoline	4,400 "
500 m^3 residue gas	250,000 "
870 kgs residue	105,000 "
110 kgs water	84,000 "
Sensible heat of gas	9,000 "
" " " ash	158,000 "
" " " water vapour	3,600 "
Decomposition of $CaCO_3$	39,000 "
Losses:	
1.8 kgs oil oozed in the bottom	17,000 "
3.6 kgs oil roasted in pile	35,000 "
Radiation (roughly 28%)	340,000 "
Total output	1,216,000 "

(See dttached diagram D)

I have described this carbonization method in a lengthy paper two months ago. So it may be emphasized that only such items as residue gas, shale residue and sensible heat are to be reckoned as losses completely.

A comparison of the thermal efficiencies may be taken of the following table:

Compared Heat Balance Sheets
(All Data given in Per Cents)

	A	B	C	D
Oil	45.5	41.5	41.5	14
Gasoline	1.3	11.0	9.5	[illegible].04
Residue	----	19.6	----	8.6
Ash	11	----	6.5	----
Gas disposed of	----	----	----	21
Gas utilized	19.4	8	0,005	----
Sensible Heat:				
in oil	0.35	1.6	1.2	-----
in gasoline	0.0001	----	----	-----
in residue	----	1.6	----	13
in ash	0.6	----	0.65	0.11
in gas	0.12	0.92	0.8	0.08
Evaporization of moisture	2	2.3	2.05	7
Decomposition of Ca CO_3	1.5	----	----	4
Preheat of Shale	----	3.9	3.4	----
Losses:				
Radiation	10	3.9	----	28
Oil losses	----	----	----	4.3
Gas "	3	----	----	----
Various "	5	3.9	34	----
Total Losses	18	7.8	34	53.3
Efficiency regarding utilized matter	abt 66.2	60.5	51.0	15.0
Efficiency regarding matter to be utilized	abt 67	71	51	15

The under B mentioned carbonization method is the Swedish Grondal-Ramen Tunel Kiln. The average total efficiency fluctuated between 58 and 63% and can be increased as above mentioned by utilization of the hot coke -- on 70 to 72% without any difficulties. The application of superheated scavenging gas, the advantages of not moving the shale during the distillation process, steering

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in gasoline	0.0001	----	----	-----
in residue	----	1.6	----	13
in ash	0.6	----	0.65	0.11
in gas	0.12	0.92	0.8	0.08
Evaporization of moisture	2	2.3	2.05	7
Decomposition of Ca CO_3	1.5	----	----	4
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The under B mentioned carbonization method is the Swedish Grondal-Ramen Tunel Kiln. The average total efficiency fluctuated between 58 and 63% and can be increased as above mentioned by utilization of the hot coke -- on 70 to 72% without any difficulties. The application of superheated scavenging gas, the advantages of not moving the shale during the distillation process, steering of the respective termperatures, concentration of gases, comparatively small building costs, good and adaptable oil and gasoline yields and a far reaching mechanization of these methods produced at least in Estonia the admitted superiority of the two scavenging processes Grondal-Ramen and Kivioli Tunel Kiln. The latter offered a great number of improvements regarding the mechanical construction as well as the heat economy and yield which were tested already in 1937/39 in a Pilot Plant in Estonia. The results of these tests are available.

May I suggest therefore to the respective authorities in this country not to omit to study at least one of these scavenging processes, if onee in the future the oil shale treatment in the United States will become of notable importance. The conditions here may be very different, but if really large amounts will be spent for research of oil shale utilization one should not forget to erect a unit of at least demonstration size even risking that the results might be disappointing. I cannot help but I'm inclined to suppose sometimes that the Estonian carbonization methods might be put in a disadvantageous light by some European sources who are purposely interested in doing so.

Oil Production and Power Supply after 1940.

Concluding the above sketch, it seems to be advisable to give a few data about the last partly not completed development in Estonia.

By the nationalization of the Estonian Oil Shale Industry performed by the Russian government in 1940 the power supply as well as the utilization of waste shale and residue was put on a new base. The output of oil was to be increased considerably. In summer 1941, the Russians had to leave and destroyed the plants partly. The Germans occupied the country and started at once with a plan similar to the Russian one. The effective erection started in late 1942. The oil output was scheduled to amount to 651,000 tons a year instead of 200,000 tons in 1939. This rated capacity was to be reached in May 1945. In connection with this enlargement, the power problem was fundamentally altered. The Russians as well as the Germans used the onflay and calculations, I had prepared during the years 1939 - 1941. I had the satisfaction to see accomplished the bulk of my plans up to 1943/44. During the retreat of the German forces in September 1944, the whole shale oil industry including all power stations was blown up throughoutly. Nevertheless, the Russian Five Year Plan proclaimed in late 1945 the reestablishment and a huge enlargement of that industry until 1950.

The output and consumption of the 1941 plan were the following:

WI per annum:

hauled shale	1,150,000 tons
produced oil	200,000 tons
consumed power	52,000 MWH
consumed steam	290,000 tons

W II

hauled shale	145,000 tons
consumed power	800 MWH

W III:

hauled shale	1,300,000 tons
produced oil	156,000 tons
consumed power	35,000 MWH
consumed steam	156,000 tons

W IV:

hauled shale	350,000 tons
produced oil	42,000 tons
consumed power	11,000 MWH
consumed steam	72,000 tons

W V:

hauled shale	65,000 tons
produced oil	11,500 tons
consumed power	1,300 MWH
consumed steam	21,000 tons

W VI:

Hauled shale	1,500,000 tons
produced oil	240,000 tons
consumed power	65,000 MWH
consumed steam	277,000 tons

W VII:

hauled shale	2,500,000 tons
consumed power	15,000 MWH

Total power demand of the industry	180,500 MWH
Total power losses including trnasforming line losses, idle running 8%	14,400 MWH
Power sale to the other industries, towns and communities	47,500 MWH
Power losses of the latter consumers	4,500 MWH
Total Demand	246,500 MWH

Power Producers:

Turbines No.	Installed Capacity K.W.	Source of Energy	Kind of Turbines	Annual Production MWH	Efficiency %	Specif. Consump. BTU/KWH	Annual Production BTU
NABC	4,500	Water	Kaplan	28,000	80	4,300	1.2×10^{14}
SLABC	8,750	Fine Shale	Condensing & Bleeder	21,000	10.4	33,500	7.2×10^{14}
JABC	30,000	" "	Bleeder	128,000	41	8,400	10.8×10^{14}
PBC	8,200	" "	Condensing	37,500	16	21,500	8.2×10^{14}
KJABC	4,500	Gas	Bleeder	32,500	40	9,000	2.85×10^{14}
Total/Average	55,950	---	----	246,500	28.2	12,200	30.25×10^{14}

The given overall efficiency includes all losses from the delivery of the source of energy to the power plant up to the included consumption of the power station service.

The area of power supply was 7,500 km^2 or 3,500 square miles. The total transmission losses amount for the Oil Industry 8%, i.e. the KWH at the consumers busbar amounted on 3,300 calories or 13,200 BTU. This results in a total efficiency from energy source up to consumer busbar of 26%. The transmission losses for the power customers were 9.5%, one KWH equaled to 3,400 calories.

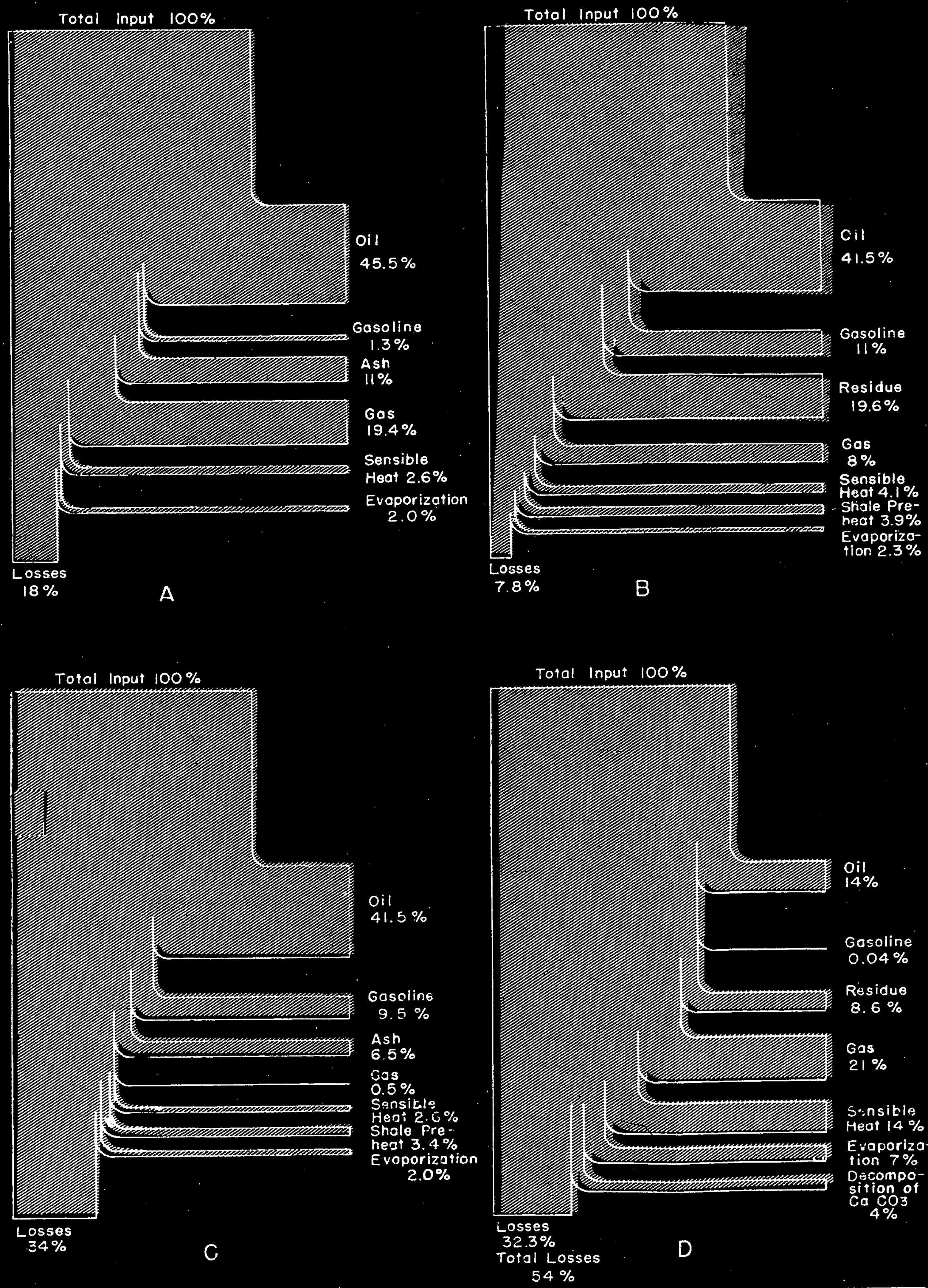
"The source of energy cost price of the 5 power stations was in the average 0.56 Estonian cents or 0.15 cents USA at the power stations busbar. This cost price corresponded to a price at the consumers busbar of 0.61 E Cents. The Oil Works were charged with 1.5 to 2.5 E. Cents/kwh considering the individual characteristics (power factor, etc), of the respective consumer. The outside customers paid 2 to 3.5 cents/kwh.

The total steam demand was to be roughly 815,000 tons per annum, of this amount 450,000 tons or 55% were gained as bleeded steam.

In the meantime, I had developed a second plan of completion of power generating together with foreign colleagues. This plan was based on the elimination of peat and coal as sources of power, abandonment of uneconomical shale based stations and the substitution of these by water and fine shale bleeder turbines. The outlay was to match a further enlargement of the Estonian oil industry. This plan was not terminated and came never in being. Provided was the annual generation of 300,000 MWHS of water energy and 260,000 MWHS of fine shale. The fine shale demand rose on 650,000 tons a year. The total production of the concerned Estonian power stations was expected to amount to 640,000,000 kwhs per annum. Therefrom 340,000,000 kwhs were to be consumed in the local shale oil, phosphorite, diatomite, pulp wood and cellulose industries, 300,000,000 kwhs were surplus and free for exportation. It was considered together with the huge hydro-power stations of Finland and the Russian Swirstroi plant to supply likewise the great consumers of Leningrad in the east or the customers in Riga and Smolensk in the South. The principal details were calculated but the events of war did not allow the realization.

[redacted]

Attached 4 diagrams



DIAGRAMMATIC HEAT BALANCE SHEETS
OF FOUR DIFFERENT CARBONIZATION SYSTEMS

36 TROCKEL Trockel 36

Oil Shale Carbonization Plant at Kivioli, Estonia

The Estonian oil shale district is situated along the northern shore from Taps to Narwa. It is approximately 120 kilometers (75 miles) long and 30 kilometers (19 miles) wide. Assuming that 1.5 metric tons (1.25 short tons) of oil shale are present per sq. m (sq. yd) the whole district contains about 5,000,000,000 tons of oil shale but the Kivioli district contains 1.8-2.0 m. to (1.5-1.7 short tons) per sq. m. (sq. yd). A tunnel kiln is used for the low temperature carbonization of the shale. The laboratory experiments having been finished a pilot furnace for a daily throughput of 75 tons was constructed in 1946. Due to the satisfactory results two more furnaces, for a daily throughput of 250 tons each, were constructed in 1930. Another two furnaces for a daily throughput of 400 tons each were added six years later. The design of all furnaces is approximately the same.

Description of the Kivioli Plant

The oil shale is delivered from the mine with a limestone content of 8% whereby another 7% of limestone has already been removed at the mine. The oil shale is crushed by a roll breaker to a maximum size of 100 mm (4 inches) and screened into three different sizes after the rest of the limestone has been picked out by hand (1) fines below 10 mm (0.4 inches) (2) nuts 10-25 mm (0.4-1 inch) (3) coarse shale 25-100 mm (1-4 inches). The fines can not be carbonized but must be briquetted. Experiments were performed in order to find out the most suitable briquetting method. Due to its high moisture content of 15%, the shale must be dried before it is fed to the furnaces. At first a rotating drum was used but due to a considerable abrasion the results were unsatisfactory. Therefore, the drums were replaced by a belt conveyor. The drying plant has to solve two problems: (1) to dry the oil shale (2) to remove the dust which is attached at the surface of the moist shale pieces. The shale is filled 1 m. (1.093 yds) high into a special lorries called "wagonetts". The load consists of 75% of coarse shale and 25% of nuts according to the proportion of the sizes which are delivered from the crushers. Two short connection pipes are welded at the bottom of the lorry. They can be connected with corresponding gas inlet pipes which are arranged at the bottom of the tunnel. A perforated metal sheet, which bears the shale is inserted a short distance from the bottom of the lorry. The loaded wagonetts are introduced into the tunnel kiln by means of a hydraulic operated reel. The tunnel kiln consists of a large pipe which has a diameter of 2.186 yards. This pipe is subdivided into three zones. The drying chamber is 13 m long (41.5 feet), the carbonization chamber 26 m long (85 feet) and the quenching chamber 5.5 m long (18 feet). The total length of the tunnel kiln is 53 m (174 feet) including those sluices. The sluices are arranged at the entrance of the drying zone and between the three chambers of the kiln. They prevent the flow from one zone to the other. The loaded wagonett is pushed into the front sluice and from there into the drying chamber. A fan of 20 H.P. for each wagonett is situated underneath the furnace. The drying of the shale is performed by recirculating hot steam which is superheated by flue gases which pass through a heat exchanger. The necessary steam is furnished by the vaporization of the moisture of the shale. Excess steam is bled off. The heat exchangers of the drying chamber are situated in a special corridor underneath the tunnel. After a certain time the wagonett passes through the sluice into the carbonization chamber. The heat units which are necessary to carbonize the shale are furnished by recirculating hot gases which flow through the shale charge in an upwards direction. The recycling gases are superheated by flue gases which pass through the heat exchanger and blown into the kiln by means of fans which are situated underneath the furnaces. The recycling gas volume is kept constant and the liberated carbonization gases and oil vapors are drawn off and led to the condensing system. The lorries which contain the carbonized shale are pushed through the following sluice into the quenching chamber. Now the low temperature carbonization is finished. The cooled lorries are discharged, emptied, refilled and brought back to the entrance of the tunnel-kiln. The furnace contains 24 lorries. The lorries are moved at an interval of 8 minutes. The residue is brought to the dumps by a rope way. The stocker which produces the flue gases are arranged close to the drying chamber. Fine shale is used to operate the furnaces. A chamber in which the permanent carbonization gases are burned is combined with the stoker. The walls of the chamber are equipped with some additional gas and oil burners. The latter are used to start the tunnel kiln. The combustion gases which leave the stoker at a temperature of 1600°C (2912°F) are mixed with coal spent flue gases before they pass through the heat exchanger. An exhaust fan draws off the flue gases, one part of which goes directly to the stack whereas the rest is used to superheat the recycling steam of the drying zone before it is disposed of.

Condensing System

The carbonization gases leave the tunnel at approximately 480°C and flow to a primary cooler where they are cooled to 300°C (572°F). Afterwards the gases are led to the condensing system which consists of an air cooler and some water-coolers. Heavy oils with a specific gravity of 1.03 are condensed in the air cooler where the gases are cooled to 230°C (446°F). The heavy oilspass through a second cooler and flow into a tank. A water condenser cools the gases to a temperature of 150°C (302°F) whereby a middle oil with a specific gravity of 0.99 is stripped from the gas. The middle oil is cooled by a final cooler, separated from water and flows into the before mentioned tank. The gases are passed through three additional coolers. The first one condenses light oil, the following two condense benzine. After separating water from oil, the oil fractions flow into benzine and light oil tanks. The gas, which contains still 450 g per cbm benzine is led to the deep cooling system.

The Deep Cooling System

The gases are cooled by an ammonia refrigerating apparatus to a temperature of -15°C (5°F) whereby most of the benzine is condensed. The cold gases are scrubbed in towers with wash oil -5°C (23°F). The benzine yield is 0.8-1% of the oil shale. The permanent gases are used for heating the gas-fired chamber.

Carbonization Process

Due to the thermical properties of the shale, the carbonization process is not easy to perform. The color of the shale changes from a light into a dark brown one at a temperature of 200°C (392°F). The liberation of oil vapors begins at a temperature of 350°C (662°F). The application of higher temperatures is thereby not necessary. Due to the melting properties of the shale between 360°C (680°F) and 410°C (770°F) great precautions must be taken during this period in order to overcome the difficulties which arise from the melted substance especially if rotary kilns or shaft furnaces are employed. Since a slow temperature rise increases the melting of the shale, an exactly controlled velocity of the temperature rise must be applied. Even with the correct heat units furnished, the melting of the shale cannot be avoided if uniform temperature cannot be maintained inside the shale charge. Since "fines" prevent the correct distribution of the gases during their flow through the shale charge only carefully screened shale can be fed to the furnace. Vast columes of recirculating gases secure the most favorable distribution of the temperature inside the shale bed.

Oil Shale Results

CO_2 = 18%

Ash = 46%

Organic Substance = 36%
100%

Limestone 7-10% from the mine

Oils = 20% (based on moist oil shale)

Oils = 65% (based on organic substance)

Gas: 25 m/t permanent gases for firing with 10g/m^3 benzine

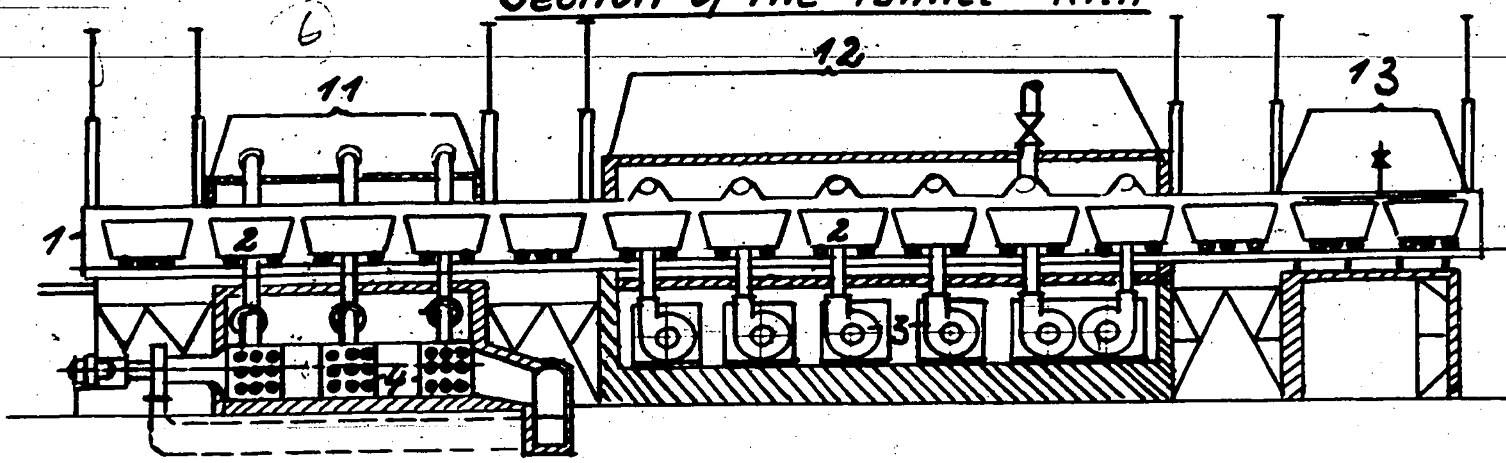
Oil Shale Moisture

Coarse Shale = 12-16% water
Fine Shale = 14-18% water

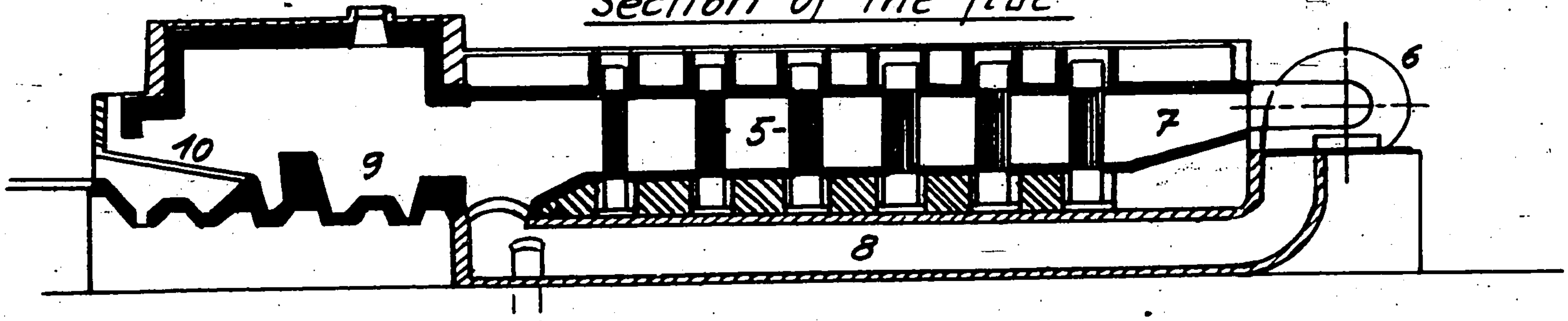
Specific Weights

Oil Shale = 1.5 t/m^3
Gas = 1.23 kg/Nm^3

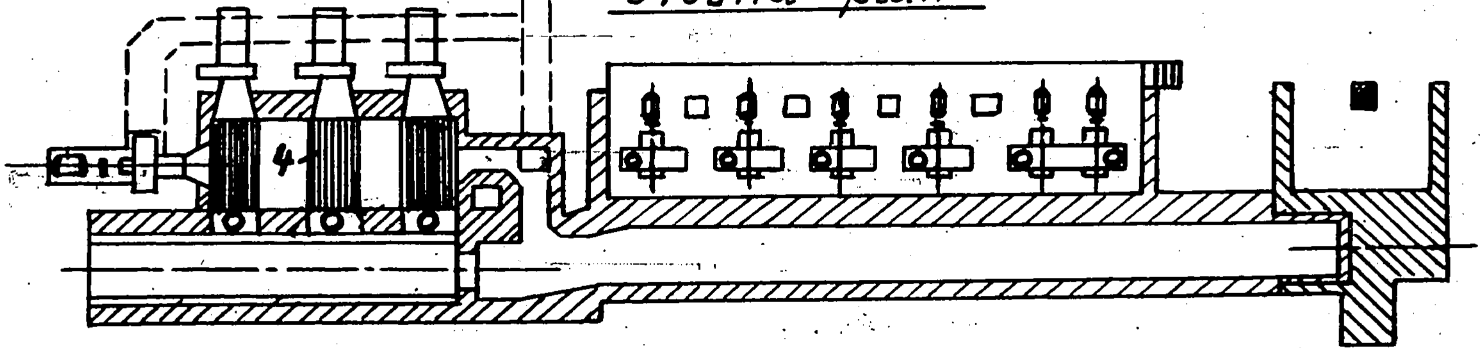
Section of the tunnel-kiln



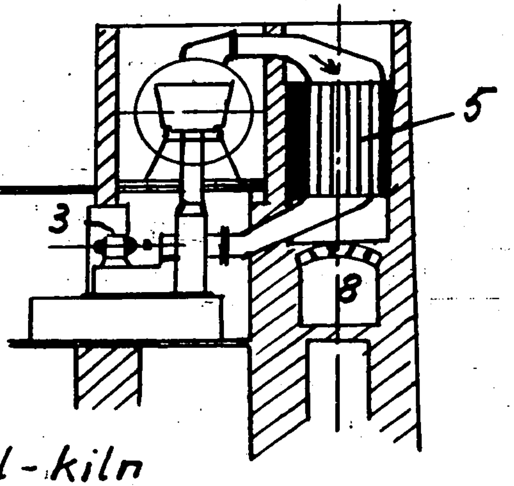
Section of the flue



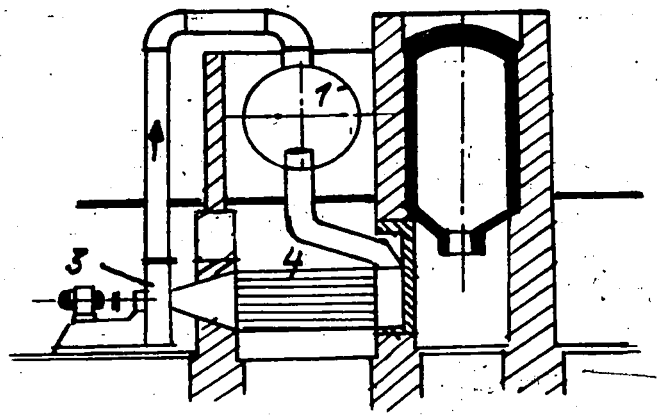
Ground-plan



Section of the carbonization chamber



Section of the drying chamber



1 tunnel-kiln
2 waggonet
3 fans for drying- and carbonization chamber
4 superheater for drying chamber
5 superheater for carbonization chamber
6 fan for circulating combustion gases
7 superheater flue
8 flue for recirculating gases
9 gas fired chamber
10 shale stoker
11 drying chamber
12 carbonization chamber
13 quenching chamber

SARAPUU ㊲ By Erich Sarapuu ㊲

The subterranean Carbonization, Distillation and Gasification of Oil Shale, Coal and Oil-bearing rocks (Secondary Recovery) by Means of Electric Current

I. The Carbonization and Gasification of Oil Shale.

My personal investigations had the aim to clarify the following details of this underground carbonization method:

1. Distillation and gasification of oil shale without removing the shale from the deposit.
2. Application of electric heat due to the electric conductivity of the layer.
3. Utilization of metal pipes as electrodes.
4. Comparison of the proposed method with the Ljungstrom process.
5. Determination of the oil yields.
6. Application of an electric heated furnace for oil shale distillation combined with the gasification of the residue (fixed carbon).

1. Distillation and Gasification of Oil Shale Without Removing the Shale from its Deposit.

a. The gas is drawn off through the electrodes. (Compare sketch #1).

b. The gas is drawn off from between the electrodes. (Compare sketch #2).

c. The gasification of the fixed carbon. After the distillation has been finished air, steam, etc., is blown through the layer in order to gasify the fixed carbon.

d. Loosening of the layer by the current and continuation of the distillation by means of air. The oil shale is distilled until air is able to flow through the layer due to its porosity and looseness. Then the oil shale is ignited near the electrodes by the current and the distillation is continued by means of the combustion of the fixed carbon.

e. Utilization of the heat which is preserved in the layer for the preheating of the surrounding shale. (Compare sketch #3). The distillation begins with "Block" II. The combustion of the fixed carbon raises the temperature to 800°- 1000°C. The heat from "Block" II is transferred to "Block" I.

2. <u>Distillation by Means of Electric Current Using the Electric Conductivity of the layer</u>.

a. The carbonization applying 2 electrodes. (Compare sketch #4).

b. The carbonization employing parallel connected electrodes. (Compare sketch #5).

c. The carbonization by means of various zones of electric conductivity which have been produced intentionally. (Compare sketch #6).

3. <u>Using Metal Pipes as Electrodes</u>:

Usually iron pipes are employed. The current which is transferred to the layer is proportional to the diameter and the length of the electrode. The length of the electrode is of great influence on the transfer of the power. Compare sketch #7. The resistance (R) between the layer and the electrodes may be calculated using the following formula.

$$R = \frac{\ln \frac{2l}{r}}{2\pi\gamma l}$$

l length of electrode

r Radius of electrode

γ conductivity of the layer

4. <u>Comparison of the Proposed Method with the Ljungstrom process</u>.

Advantages and disadvantages of the Ljungstrom process.

a. The heating gadgets are expensive.

b. The power per electrode is low.

c. The progress of the carbonization zone is low.

d. The consumption of the electric current which is necessary for the carbonization is low.

e. The plant is simple.

Advantages and disadvantages of the proposed process.

a. Iron pipes used as electrodes are cheap.

b. Great power per electrode is produced.

c. The progress of the carbonization is accelerated.

d. The current consumption is nearly the same.

e. The plant is simple but transformers for the supply of the current are necessary.

5. <u>Determination of the oil yields.</u>

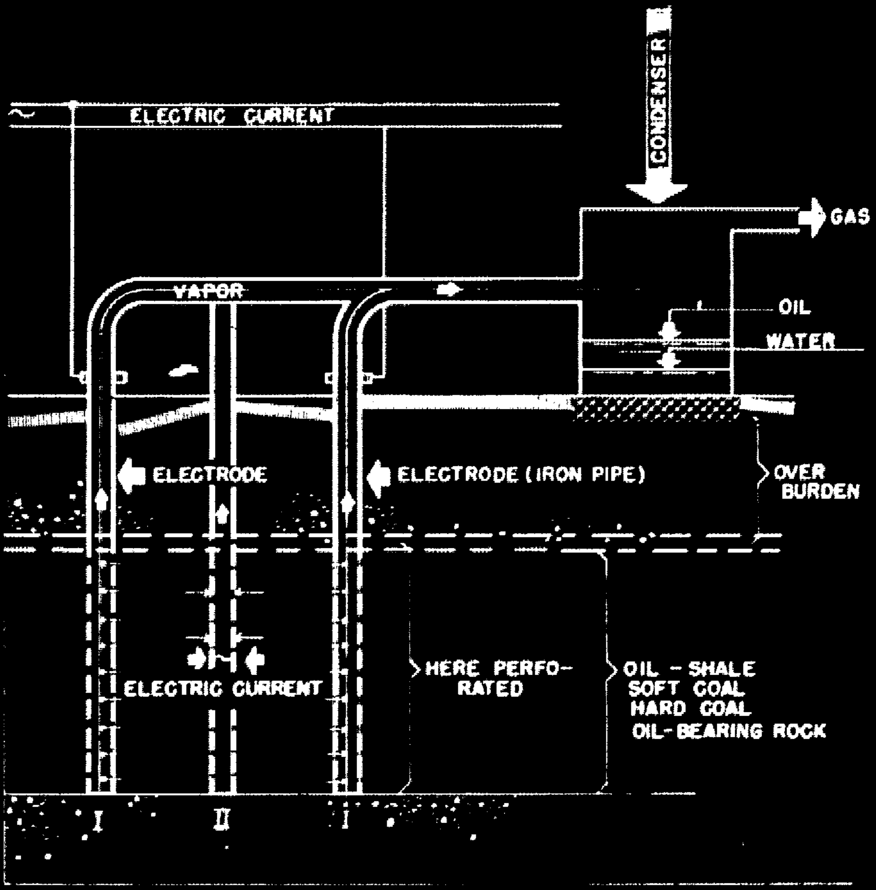
Cracking of the oil vapors influenced the oil yields which were obtained in the laboratory. The yields were 87.3% if they were based on the same cracking effect which takes place in a Fischer bomb.

6. <u>Electrical heated furnace for oil shale carbonization combined with the gasification of the fixed carbon of the residue.</u> (Compare sketch #8).

1. The oil shale is carbonized by means of current. (Zone a). The electric heat is used only for starting process.
2. The fixed carbon is burned. (a)
3. The heat which is produced is transferred to the furnace #II (c) and to the shale by means of vapor (b)

II. <u>Theoretical Considerations and Laboratory Tests were performed which Aimed to Employ the Proposed Method for the Recovery of Crude Oils (Secondary Recovery) and for the Carbonization of Coal.</u>

[redacted]

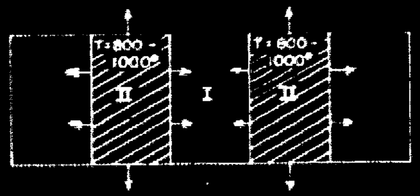


UNDERGROUND CARBONIZATION AND DISTILLATION

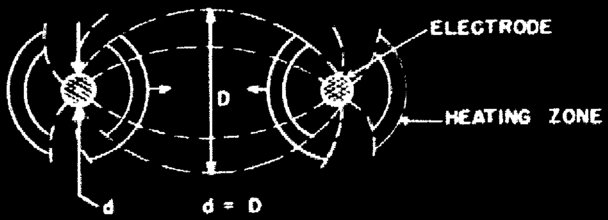
SKETCH 1&2: (1) THE GAS IS REMOVED THROUGH THE PIPES I
(2) " " " " " " PIPE II

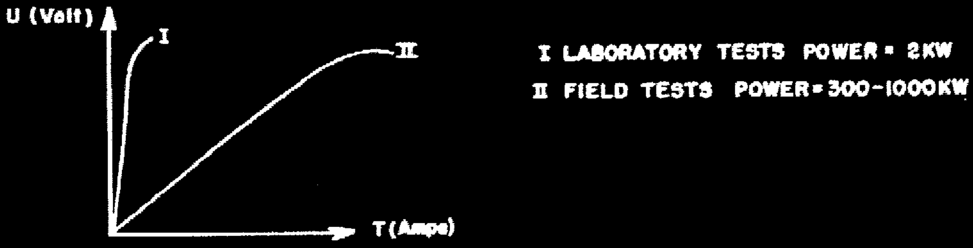
NOTICE: THE GASIFICATION IS PERFORMED EMPLOYING THE SAME PIPES.

SKETCH 3

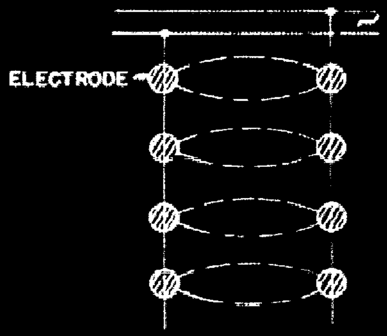


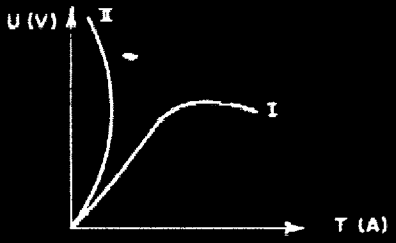
SKETCH 4





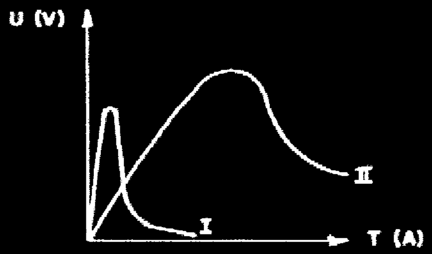
SKETCH 5





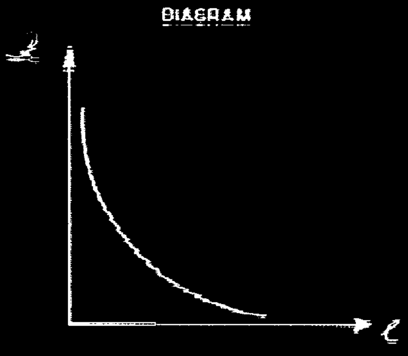
I FIELD TEST POWER = 100 - 10000 KW
II NO CARBONIZATION POSSIBLE

SKETCH 6

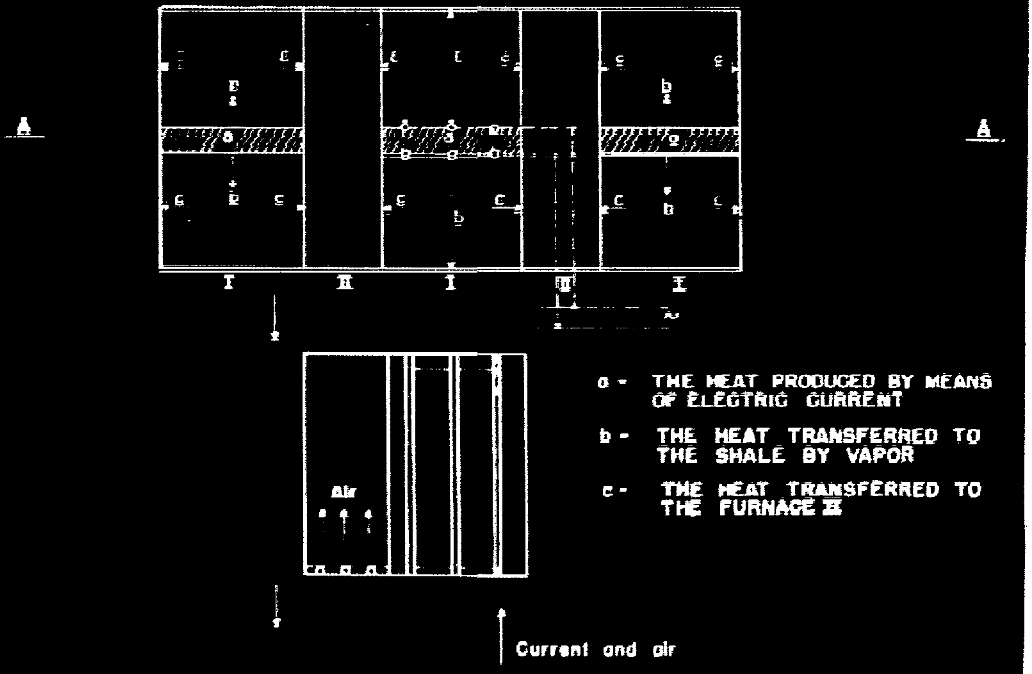

DIAIGRAM

I LABORATORY TEST POWER = 0.5 KW
II FIELD TEST POWER = 700 KW

SKETCH 7



SKETCH 8



a - THE HEAT PRODUCED BY MEANS OF ELECTRIC CURRENT

b - THE HEAT TRANSFERRED TO THE SHALE BY VAPOR

c - THE HEAT TRANSFERRED TO THE FURNACE II

(38) Oppelt

(38)

SC - 102

The Fischer Assay of Oil Shale

The attached flow sheet of the ~~Fischer~~ assay shows the various stages which must be performed if the oil content of an oil shale is to be determined. It is clearly to be seen, that a well considered plan of organization should be established if numerous samples must be tested per day. The following proposal in carrying out the Fischer assay is based on the presumption that the efficiency of a laboratory is improved if the single steps of the process are transferred to specialized groups which operate simultaneously a couple of apparatus which are especially designed for the performance of a single step of the assay. The resulfts of single steps should be reported to a central computing and typing department which compiles the complete analysis and fills out the forms.

Each square of the attached flow sheet represents a group which is in charge of one of the numerous steps of the Fischer assay. The lines represent the flow of the material from one group to the other and the manner in which the results are transferred to the evaluating department.

Daily capacity of the laboratory:

50 Fischer Assays

The samples are delivered to the reception group where they are listed and briefly inspected.

The list contains the ~~following~~ data:

Number of the sample
Date of arrival
Origin of the sample, name of the mine, exact location from where sample has been collected
Roughly estimated size of the pieces
Special remarks

A copy of the list is delivered to the computing and typing department.

Required:
1 supervisor
1 typist
1 unskilled laborer
1 assistant

The inspected and listed samples are delivered to the grinding group -

The samples are ground, bottled and labeled. A complete screening analysis must be made, if already ground shale has been delivered. The label of the bottles carry only the number of the sample.

Required:
1 yaw breaker
1 heavy steel mortar and pestle
2 mills / 1 for emergency purposes
3 complete sets of sieves
1 balance
aluminum dishes
ample supply of flasks
1 laborer / one assistant for the operation of the yaw breaker and the mortar
2 laborers for the operation of the mills.
1 laborer for the performance of screening analyses.

Two bottles are provided of each sample. One bottle is delivered to the weighing section.

Storage

The remaining original shale together with the second of both bottled samples should be stored over a period of approximately 4 weeks.

Required: Ample storage space, shelves
1 laborer for storage and disposal

As mentioned before, one bottle of the crushed shale is delivered to the central weighing station where a couple of balances are set up.

1st: 50 or 100 g of shale must be provided for the determination of the moisture. Glass dishes which are covered with a lid should be utilized. The weighing is performed by an automatically working balance.

2nd: 100 g of shale must be provided for the Fischer assay. Another glass dish equipped with a lid is used. An automatically working balance should be suitable for the purpose.

3rd: An Engler flask which recovers the liberated oils and carbonization water must be carefully weighed. An analytical balance is necessary to determine the correct weight.

4th: The flask is brought back from the carbonization center after the carbonization has been furnished and is weighed again in order to determine the yield of oil and water. An analytical balance is necessary in order to devermine the correct weight.

5th: The cooled shale residue is also transferred from the carbonization station to the weighing department and weighed using an automatically working balance.

Since no computations should be made in the weighing department all weights and figures should be reported to the computing and typing department.

Required: 2 automatically working balances + 1 for reserve
1 analytical balance + for reserve
Ample supply of glass dishes and Engler flasks
3 skilled workers

Carbonization Department

The carbonization center is equipped with numerous Fischer bombs and electrically heated furnaces. The furnaces are automatically controlled in order to secure a definite rise of temperature. Since a Fischer assay must be started with both an almost cold furnace and a cold bomb and it takes approximately 2 hours to heat the shale, it is to be assumed that an apparatus can carbonize but 2 samples per day. 25 complete apparatus must be kept ready for use. 75 Fischer bombs and 10 furnaces should be available in order to secure a constant flow of the tests.

Since the heating system is automatically controlled most of the work to be done consists of preparatory work and supervision of the running tests. Two chemists together with an assistant should be able to handle 50 samples per day.

All determinations of the water content of the shale and the mixture of oil and water are performed by a distillation process after an admixture of xylole. There are 13 water determinations which must be made per hour. Assuming that a complete water determination takes 30 minutes, 14 apparatus must be provided. Since the flasks and burettes must be carefully cleaned and dried, at least 100 complete apparatus should be kept in stock.

Required: 100 complete apparatus
xylole
2 chemists

As mentioned before, all results and figures should be reported to the typing and computing department, where the complete analyses are compiled. In order to secure an unprejudiced performance of the tests, the testing station should know only the number of the sample, whereas the number and the origin and name of the sample are reported to the computing and typing department. All results must be based on shale "as received" and on shale free from moisture. Special forms should be provided which must be filled out in order to facilitate the comparison of numerous shale samples.

With machines and tables for computing purposes provided the work whould be done by 3 chemists and an assistant.

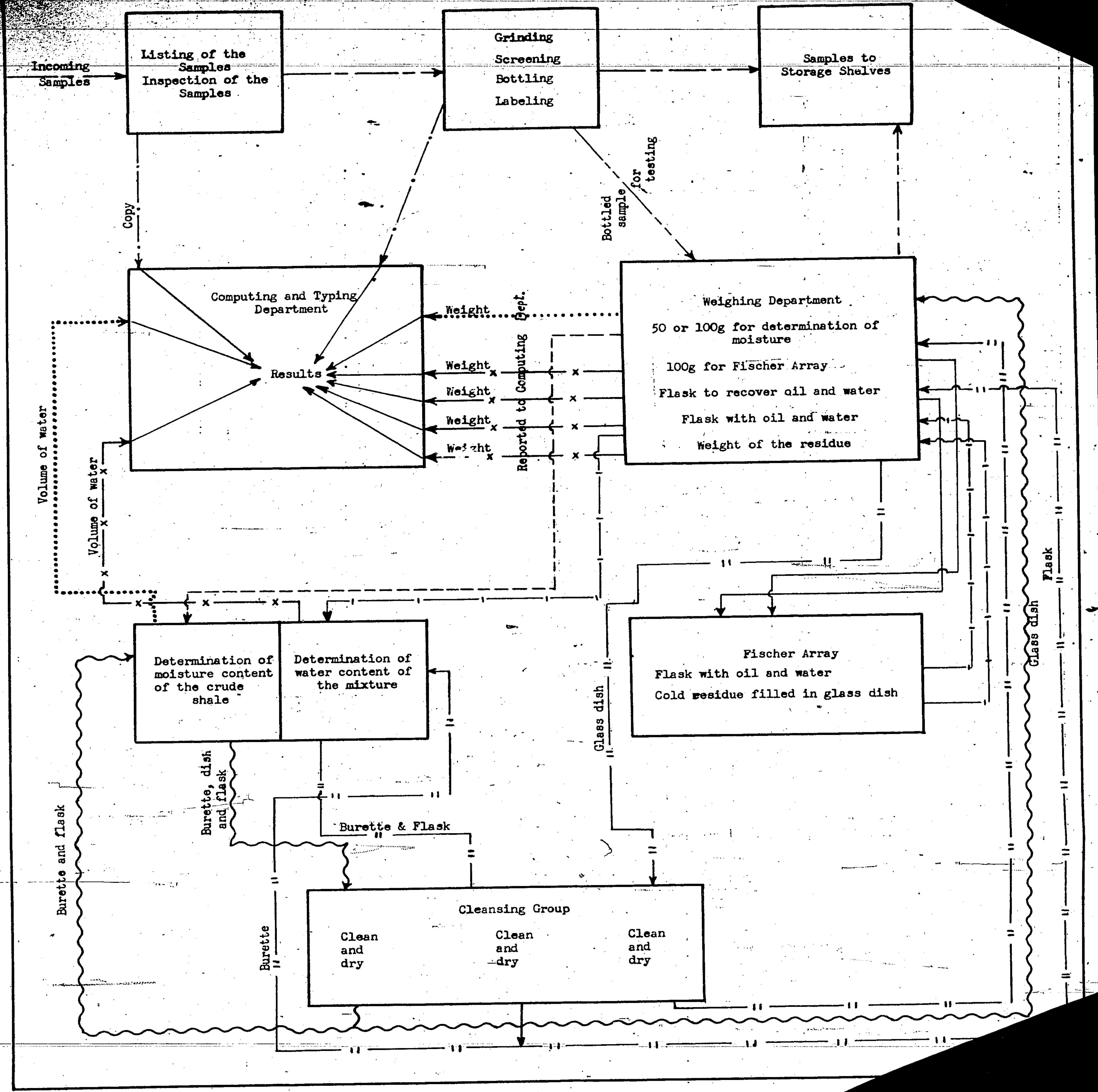
All apparatus, dishes, flasks are cleaned and dried by the cleansing group. A regenerating system, consisting of a still and condenser, which is capable of treating 7 gallons of xylole in 8 hours, should be provided.

Required: dish washing equipment
dryer
still, condenser
1 laborer + 1 assistant

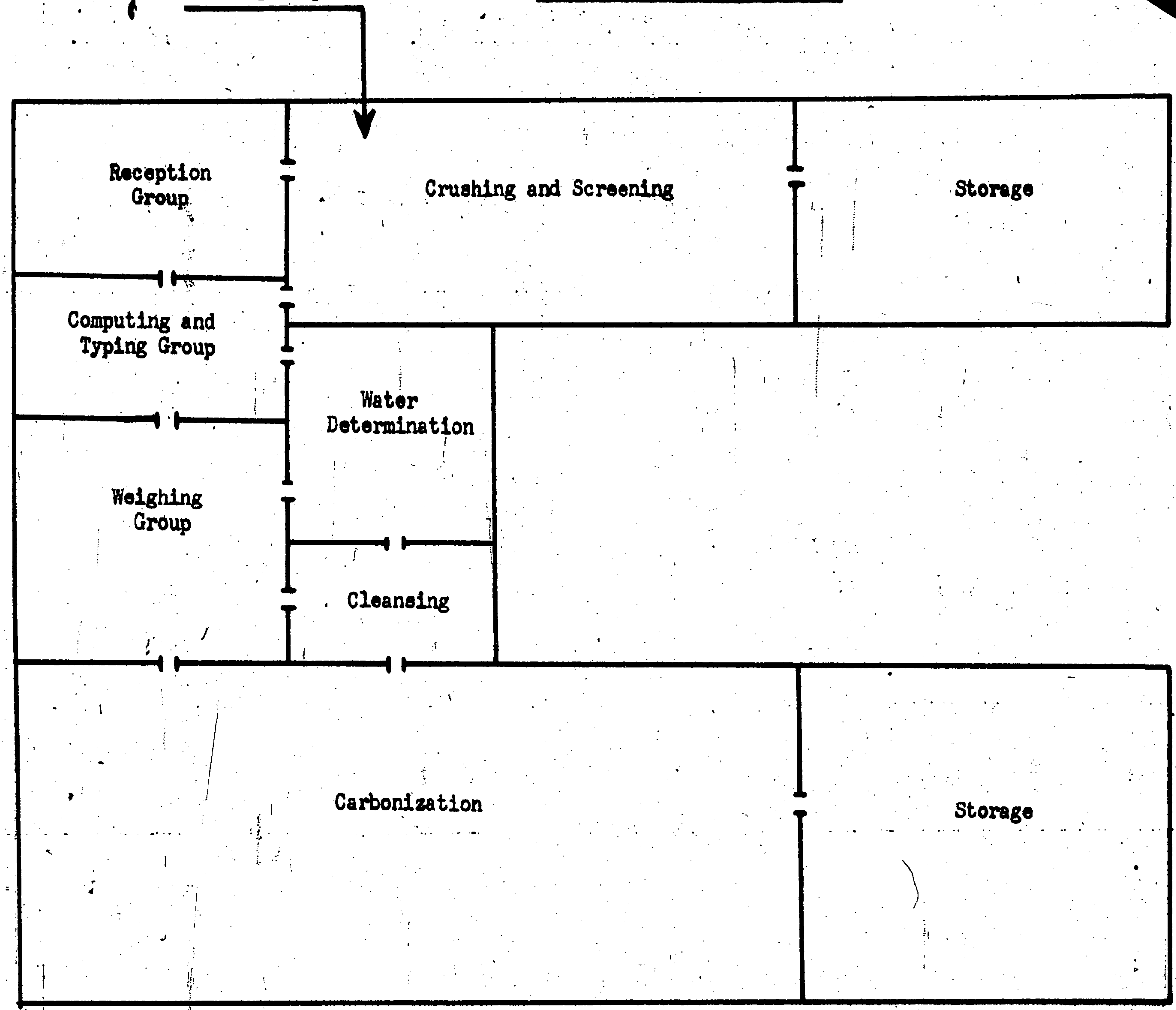
A superintendent (chemist) should be in charge of the laboratory.

Total personnel required: 24.

Efficiency: 2.1 Fischer Assays per man and shift.


Incoming Samples
Listing of the Samples
Inspection of the Samples
Grinding
Screening
Bottling
Labeling
Samples to Storage Shelves
Copy
Bottled sample for testing
Computing and Typing Department
Results
Weight
Weight
Weight
Weight
Weight
Reported to Computing Dept.
Weighing Department
50 or 100g for determination of moisture
100g for Fischer Array
Flask to recover oil and water
Flask with oil and water
Weight of the residue
Volume of water
Volume of water
Determination of moisture content of the crude shale
Determination of water content of the mixture
Fischer Array
Flask with oil and water
Cold residue filled in glass dish
Glass dish
Glass dish
Flask
Burette, dish and flask
Burette & Flask
Burette and flask
Burette
Cleansing Group
Clean and dry
Clean and dry
Clean and dry

GROUND PLAN OF A LABORATORY



OPPELT

Comments on Characteristics and refining methods of shale-oils with reference to the Bureau of Ships questionary.

Since the recovery of oil from German oil shale employing modern carbonization methods began not sooner than 1938 in a comparatively small scale all efforts were made to develop primarily suitable carbonization methods. The small quantities of shale oils which were obtainable were used as raw material for hydrogenation purposes. The Dottershouser plant shipped the oil to the "Union Rheinsche Kraftstubl A.G., Wesseling near Cologne without being furnished any information about the utilization of the oils. With the German oil reserves dwindling near the end of the war the shale oil was supposed to replace the almost not available petroleum oils. The coal-union, Schorzinger (underground carbonization) concluded a contract with the Navy which intended to use the oil as bunker fuel. Small volumes of oils were distilled, treated with caustic soda solution and mostly sold for testing purposes only in diesel-engines, tractors etc. A diesel car which was owned by Portland Cement works was satisfactory operated with the distilled shale oil. Crude oil was employed as fuel for the hot bulb engines which were utilized in the farm work. Commercially used refining methods did not exist. Basic research work was carried out to hydrogenate shale oils but the available quantities were by far to low to run a commercial plant on basis shale oil. The above sketched situation must be borne in mind with respect to the following explanations and considerations.

I. Characteristics of the raw shale oil in foreign installations

The characteristics of the recovered shale oils depends not only on the properties of the shale but also on the employed carbonization methods.

1. According to analyses which have been extracted from the German documents the composition of the Kerogen of oil shale from Wurttenberg and Estonia is as follows:

	Wurttenberg	Estonia
C %	81	77
H "	8.9	9.2
N "	1.3	0.2-0.5
S "	0.4-0.8	1.3-2.2
O "	7.8	11-12

It is obvious that the composition of the recovered shale oils must differ due to the basic differences of the composition of the kerogen. Owning to the low nitrogen content of the Estonian kerogen only small amounts of nitrogen linked hydrocarbons can be expected which should not cause considerable trouble in engine and burner fouling. Inspite of the higher nitrogen content of the Wurttenberg kerogen the nitrogen content of the Dotternhouser-oil (Otto-process) was determined with 0.5 -1.2%. Due to lacking experience no information was available about the corroding influence of the nitrogen compounds on the shale oil operated engines. The higher oxygen content of the Estonian kerogen results oils which contain more creosot oils than the Wurttenberg ones, the creosot content of which is approximately 2%.

2. Applied carbonization methods

a. Heat transfer by superheated steam
b. Heat transfer by superheated-steam-air-mixture
c. Heat transfer by hot carbonization gases
d. Heat transfer by hot flue gases (combustion of the fixed carbon)
e. Indirect heat transfer

The basic difference of the methods lies in the fact, that the carbonization process of all methods which apply flue gases is performed in the presence of more or less oxygen because a theoretical combustion is hard to maintain. As soon as the oxygen reacts with H_2S, the latter is partly burned to SO_2. The sulfur dioxide reacts with the hydrogen sulfide whereby elementary sulfur is formed according to the following formula

$$2H_2S + SO_2 = 3S + 2H_2O$$

Experience has proved, that oils which contain elementary sulfur have corrosive properties causing fouling of the feed lines, injector pumps, inlet valves, carburetors etc.

The formation of elementary sulfur is cut down if air-free purging gases (steam, carbonization gases) or indirect heating methods are employed. Mostly gaseous H_2S is liberated with, being also corrosive, can be easily removed from the oils by a treatment with caustic soda solution. Substantially more sulfur compounds of the shale are decomposed into H_2S if steam is employed as purging agent than by the application of indirect heat transfer. Since elementary sulfur is fairly good soluble in shale oil, oils which have been extracted by means of oxygen containing gases, contain probably more sulfur than such oils which had never the opportunity to come in contact with oxygen containing oils. Due to secondary influences the true effect of the various kinds of purging gases on the sulfur content of the oil can not exactly by investigated of the composition of oils from commercial plants is compared. The average sulfur content of Wruttenberg oil shale depending on the applied carbonization method is roughly as follows:

	Steam carbonization Dotternhouser	Underground Method	Meiler pile system *
Total S %	3.29	3.63	4.16
O_2 - content of the carbonization gases leaving the chamber %	0-1.3	0.6-5.8	0.3-18

According to the German documents the sulfur content of oils which have been recovered from various types of oil shale employing the Schweitzer carbonization method is as follows:

	Estonia	France (Severac)	Spain (Puertollano)	Bulgaria (Bresuik	(Pirin)
Total Sulfur %	0.75	2.7	0.87	1.2	1.5

Experiments which were carried out from the author of this article concerning the asphalt formation of benzol wash oils (coal for oils) during the benzol extraction process showed that the simultaneous influence of oxygen and hydrogen sulfide is responsible for an extended asphalt formation. The separated asphalts had a very high sulfur content. Considering the highly insaturated character of the shale oils their asphalt content should depend on the composition of the purging gases, whereby a high oxygen content results oils with high asphalts content.

The following figures of the asphalt content were available:

	Steam carb. Dotternhouser	Meiler pile system
Asphalt %	0.88	1.49
O_2 content of the carbonization gases %	0-1.3	0.3 -18

3. Applied carbonization temperatures. -The decomposition of the nitrogen compounds especially the NH_3- formation of a coal depends on the applied carbonization temperature. Carbonizing a Ruhr coal at the normal coke oven temperatures of 1800°F the ammonia yield is 0.3% of the coal, by lowering the temperature to 1100°F not more than 0.1-0.15% ammonia can be recovered. Since the oil shale is subjected to low temperatures not too a high percentage of the nitrogen which is present in the kerogen should be transformed into NH_3. The Scotch oil shale industry makes use of the influence of the temperature on the ammonia formation. Primary the oils are extracted at comparatively low temperatures. The spent shale is heated to 1300°F, approximately 0.350 kg of steam per kg of shale is injected whereby 0.3 kg of ammonia per ton of shale are obtained. Besides ammonia nitrogen containing compounds such as pyridines, amines etc are formed which remain in the condensed oil and are responsible for its nitrogen content. Regarding the composition of coal for most of the nitrogen compounds are present in the middle oil fractions from which they are extracted by means of diluted sulfuric acid. They represent valuable raw material for commercial purposes. Since diluted sulfuric acid has almost no influence on the unsaturated hydrocarbons the removal of a substantial percentage of the nitrogen content of the shale oils should be possible.

4. Condensing system and storage facilities. - The boiling range, especially the initial boiling point and the percentage of the low boiling oils, depends on the temperatures which have been applied in the condensing system. Since the meiler-pile plants were not equipped with a cooling system the light fraction of the oil remained in the gas to a certain extend, resulting in many cases a higher initial boiling point of the recovered oils.

The underground carbonization system applies chambers, which are often 60 and more yards long. It is obvious, that the liberated oils vapors are condensed in the cooler parts of the chamber. With the combustion zone approaching the oils are revaporized, condensed in the cooler parts and revaporized for a second time. Since the pitch cannot be revaporized, mostly distilled oils are recovered by the applications of the underground carbonization method. Since the bottom of an underground chamber is slightly inclined due to the dip of the shale ~~at~~ strata, the condensed oils flow to the exit of the chamber and can be pumped away. The remaining oil vapors are condensed in coolers whereby light fraction are obtained. Owing to the course of the carbonization oils with a low pitch content are recovered by the application of the underground carbonization method. The pitch and the highest boiling oils are partially cracked so that the oil yield in unfavorably affected.

Specification for gasoline prescribe that the finished product must be free from elementary dissolved sulfur which has corroding tendencies. It was found out that elementary sulfur is formed by oxidation of the always present hydrogen sulfide in the crude during storage time. The sulfur formation can be eliminated if the crude condensed gasoline is continously passed through a vessel which is filled with a solution of caustic soda. Since the crude shale oils which originate from the application of a proper carbonization method contain hydrogen sulfide but no elementary sulfur, they should be treated with a caustic soda solution before they are stored. Care must be taken to separate the oils from the condensed water as soon as possible.

The oil-water separation is greatly favored if the condensation of the oils is carried out in two steps. At first the gas is cooled to a temperature which is higher than that of the dew point for water vapors whereby high boiling water free oils are condensed which have the tendency to form emulsions with water. The middle oils are condensed together with the water but due to their properties they can be easier separated.

It is clearly to be seen that the employed cooling method and a pretreatment of the oils may influence the steps which must be undertaken in order to obtain refined shale oils which meet the requirements of the consumer.

II. Physical and chemical properties of various shale oils

1. Oils from Wurttenberg shale

A. Otto process

a. Commercial plant

	thin oil
spec grav. 20°C	0.918-0.95
asphalt	0.49-1.5%
sulfur	3.24 -4.36%
initial boiling point	140-168°C
to 200° are vaporized	3.5-11.0%
" 250° " "	22-39.5"
" 300° " "	40-60 "
" 330° " "	52-73 "

	heavy oil (first step of the condensing system)
specific gravity	0.981-1.01
asphalt	3-4.2%
sulfur	3.05-4.89%
pour point	+ 3 to +15°C
initial boiling point	230-310°C
to 300° are vaporized	3.0-10.3%
to 350° " "	17-75%

	thin oil
spec-gravity	0.950
thermal valve	11,200 kcal per kg
C	84.26%
H	10.31%
N	0.50 %
S	2.90 %
O	2.03 %
to 200°C are vaporized	5.2%
" 250 " " "	20.4%
" 300 " " "	40.0%
" 357 " " "	63.3%

b. Otto-Pilot - Plant

	thin oil
spec. gravity	0.950-0.959
C	86.2-86.5%
H	10.1-10.25%
S	3.3.- 3.4%
Initial boiling point	172-189°C
to 200°C are vaporized	2-6%
" 250 C " "	18 %
" 300 " " "	34-36%
" 360 " " "	63-64%

	thick oil
initial boiling point	274-297°C
to 300° are vaporized	0.4-1.5%
" 320 " "	2.7-3.5%
" 340 " "	9.3-13 %
" 360 " "	24-59.5%

	Total oil
spec. gravity	0.966
net calorific	10,580 kcal kg 1
cetane number	37-43
unit C	84.0%
H	10.2%
S	3.9%
N	1.2%
O	0.6%
Cl	0.07%

B. Meiler pile system

specific gravity	0.949-0.977
viscosity 20°C	1.27-6.79°E
" 50°C	1.12-2.04 "
pour point	-2 to + 20°C
asphalt	0.9 - 3.08%
sulfur	4-5%
flash point	96 - 121°C
ash	0.02-0.16%
insoluble in xylol	0.03-0.52%

paraffine wax	0.5-1.7%
initial boiling point	178-230°C
to 200°C are vaporized	0-3.6%
" 250" " "	4.5-17%
" 300" " "	26-38%
" 350" " "	46-60%

C. Underground carbonization method

a. oil-condensate from the underground chamber

speci. gravity	0.937-0.963
pour point	+ 1 to + 5°C
viscosity 20°C	2.1-3.1°E
50 "	1.3-1.7 "
sulfur	2.3-4.95%
flash point	104-187°C
asphalt	0.25%
conradson carbon	2.64%
initial boiling point	140-200°C
to 200°C are vaporized	0-9.5%
" 250 " " "	8.5-26.5%
" 300 " " "	30-50%
" 350 " " "	62.1-95.0%
" 360 " " "	66.1-100%

b. Oil condensate from the cooling condensing system

specific gravity	0.905-0.951
viscosity 20°C	1.55-3.1°E
" 50°C	1.1 - 1.6°E
sulfur	1.86-4.71%
initial boiling point	125-190°C
to 200°C are vaporized	1.0-20.5%
" 250 " " "	14.6-54.5%
" 300 " " "	41.6-64.0%
" 350 " " "	68.0-100.0%
" 360 " " "	72.0-100.0%

d. Geissen - furnace

specific gravity	0.961
pour point	+ 15°C
total sulfur	4.27%
paraffin wax	1.12%
cresote oils	6%
Thermal valve	10,351 kcal 1 kg
initial boiling point	93°C
to 150°C are vaporized	2.0%
" 200 " " "	6.7%
" 250 " " "	20.8%
" 300 " " "	41.0%
" 350 " " "	77.6%

e. Thyssen - drum

spec. gravity	0.960-0.965%
pour point	-6°C to -10°C
viscosity 20°C	4-5°E
initial boiling point	125-130°C
to 200°C are vaporized	8%
" 250°" " "	21%
" 300°" " "	42%
" 360°" " "	66%

2. Oil from Schandelah oil-shale

spec. gravity	0.9765
initial boiling point	166°C
to 200°C are vaporized	2.0%
" 250°C " "	17.0%
" 300°C " "	38.0%
" 350°C " "	62.5%

3. Oils from European oil shales

Bulgarian shale-oil (Schweitzer process)

	Bresnik	Pirin
spec. gravity	0.946	0.931
pour point °C	+28	+32
cresote %	9.0	7.0
sulfur	1.2	1.5
to 200°C are vaporized %	2.00	2.50
" 260°C " " "	12.0	14.0
" 300°C " " "	26.0	28.0
" 350°C " " "	63.0	58.0
end point " " "	82.0	80.0

Estonian shale-oil

a. Tunnel kiln

heavy oil spec. gravity	1.02-1.05
middle " " "	0.990
light " " "	0.850
gasoline " "	0.760

analysis of a middle oil

spec. gravity	1.004
visc. 50°	5.38°E
insoluble in benzol	0.27%
ash	0.12%
conradson carbon	
residue	5.7%
sulfur	0.75%
thermal valve	9600 kcal per kg
initial boiling point	185°C
to 200°C are vaporized	0.6%
" 250°C " "	10.9%
" 300°C " "	34.5%
" 350°C " "	85.2%

b. Schweitzer furnace

spec. gravity	0.986
to 200°C are vaporized	3.0%
" 260°C " "	14.0%
" 300°C " "	30.0%
" 360°C " "	64.0%

French shale oil (Schweitzer- process)

	Severac
spec.gravity	0.970
cresote %	10.0
sulfur %	2.7
initial boiling point °C	160
to 200°C are vaporized %	5.0
" 260" " " "	24.0
" 300" " " "	43.0
" 340" " " "	77.0

Italian oil from asphalt rock (La Porta furnace)

specific gravity		0.963
viscosity	20°C	13.9%
	50"	24.0%
	100"	1.2%
thermal valve		10,100 kcal per kg
to 250°C are vaporized		6.5%
" 300" " "		18 %

Spanish shale-oil (Schweitzer process)

spec. gravity	0.876
cresote	14.2%
sulfur	0.87%

Swedish shale-oil diesel fuel (Bergh process)

pour point below	50°C
viscosity	1.2°E
cetane number	45

III. Sulfur-nitrogen- and oxygen compounds of shale oil

1. Corrosion trouble originating from S-O-N-compounds. It must be clearly distinguished between the corrosion which arises from the original oils and from the products which are formed by the combustion of the oils.

Especially S- and O compounds are more or less responsible for the fouling of storage tanks, feed pipes, valves, injection pumps etc whereas the nitrogen compounds as for instance pyridines, amines etc are usually non-corrosive.

The presence of corrosive sulfur can be easily determined by the application of polished copper strips which are immersed into the oil. For practical purposes the metals or alloys of which the pipes, tanks, valves etc consist should be applied if the corrosive properties of an oil shall be determined. The often used zinc strips for the detection of the corrosive properties are not very recommendable because almost no part of a diesel engine is made out of zinc.

During the combustion of the fuel in the cylinder of a diesel engine the sulfur compounds are burned to flue gases which contain SO_2 and traces of SO_3. The sulfur compounds of the flue gas become very corrosive as soon as ? water condenser which dissolves SO_2 and SO_3 and forms sulfurous or sulfuric acid respectively. Since the temperatures in the cylinder itself are higher than the dew point for water vapors little danger may be expected except a very cold engine must be started. In this connection it is worth while mentioning that the leaded gasoline contains organic chlorine compounds which are decomposed into hydrochloric acid or chlorine compounds which dissolve the lead originating from the decomposition of the tetraethyl lead. Due to the high temperatures inside a cylinder almost no corrosion can be observed. Sometimes condensation of water vapors takes place in the exhaust pipes due to the low temperatures with which the flue gases leave the pipe. Due to the aggressive properties of the sulfur containing solution, the exhaust pipes are corroded. Remedy in such cases is to operate the engine with slightly higher temperatures or to employ sulfur resistant alloys for the construction of the exhaust pipes. The oxygen containing compounds such as phenols or tar acids are burned to water and carbon dioxide which do not foul the cylinder walls or the exhaust pipes.

Nitrogen containing compounds may be burned to nitrous or nitric acid which as dry gases are not supposed to have corroding properties as far as we know from the manufacturing of nitric acids by the catalytic combustions of NH_3. But as soon as water vapors are condensed corrosion will occur.

2. Sulfur compounds, which are present in the shale oils. The following corroding sulfur components were determined in the Wurttenberg shale oil: elementary sulfur, hydrogen sulfide, mercaptans. The content of elementary sulfur should be kept under control if a suitable carbonization process is employed.

If meiler-pile shale oil showed the following composition with respect to the sulfur compounds:

Total sulfur	3.47% = 100.0%	
H_2S	0.15% = 4.3%	
elementary sulfur	0.29% = 8.4%	
mercaptan sulfur	0.13% = 2.8%	
indifferent S	2,90% = 84.5%	

84.5% of the total sulfur has no corrosive properties, 15.5% cause corrosive trouble.

Corrosive sulfur	0.57% = 100.0%	
H_2S	0.15% = 26.0 %	
elementary sulfur	0.29% = 51.0 %	74.0%
mercaptan sulfur	0.13% = 23.0 %	

Almost 50% of the actual corrosive sulfur is due to the elementary sulfur.

Approximately 70% of the corrosive sulfur remains in the residue after the oil has been distilled indicating that elementary sulfur and high boiling mercaptans are responsible for the corroding properties of the sulfur compounds. Most of the corroding properties are removed by doctor solution which extracts the mercaptide compounds from the oil. (W.F.Farragher, T.C. Morell, G. G. Monroe, Ind. Engin. Chem. 19, 1927, 1281-1289). Since diesel oils are distillates only small amounts of corrosive sulfur will certainly be present. The hydrogen sulfide can be easily removed by a treating the oils with a solution of caustic soda.

From the standpoint of the removal of the corroding sulfur compounds a treatment with caustic soda and doctor solution (sweetening) should be sufficient to produce suitable distilled diesel oils.

3. Oxygen compounds which are present in the shale oils. Depending on the properties of the shale (composition of the kerogen) the shale oils contain more or less organic compounds which can be exhausted by means of caustic soda solutions. Since the alkaline caustic soda transforms the most of the oxygen compounds into water soluble salts, the oxygen compounds are of the phenolic or tar acid type.

4. Nitrogen compounds which are present in the shale oil. Small amounts of hydrocarbons are extracted from the shale oil by means of diluted sulfuric acid indicating that pyridines or amines must be present in the oil. Depending on the composition of the acid soluble nitrogen compounds they are often valuable solvents which can be employed for industrial purposes.

IV. Refining methods for shale-oils

As mentioned before not much work has been done on full scale refining of German shale oils. The oil was distilled, treated with alkaline solutions and sold. It was contemplated to hydrogenate the shale oil which was supposed to be recovered in the Wuste-plants but due to lacking material and manpower the intended production has been never realized until the end of the war. It is to be assumed that basic hydrogenation tests have been made but for the time being no report is available which publishes the results of the tests. The U.S.

Government Technical Oil Mission lists in its catalogue under Bag 3043 Target M 3014.02 Lenna, item 16, pages 1565-1651 a report concerning "shale oil". Since many hydrogenation tests have been performed by the Lenna Works valuable information could perhaps be obtained by studying the report, although the catalogue does not indicate whether the report refers to German shale oil.

The Politz Hydrogenation plant used Estonian shale oil as feed stock. Hydrogenation of the shale oil is the most complete refining method which furnishes under all circumstances good diesel-and fuel oils.

French shale oil is cracked by a Dubles cracking unit but so far as known mostly gasoline is produced.

The shale oil contains saturated, highly unsaturated, paraffine and naphtenic hydrocarbons. Due to the presence of unsaturated compounds precautious must be taken in order to prevent large refining losses.

The modern refining methods which apply selective acting solvents secure high yields and prevent losses. They do not destroy hydrocarbons but separate them according to their chemical composition. Such refining methods have been employed for the refining of lignite tars which contain high amounts of unsaturated hydrocarbons.

Great efforts have been made to cut down losses if crude gasoline originating from high or low temperature carbonization must be refined. The following paragraph contain various methods and experiences which were gathered in the field of gasoline refining.

Instill process:

The instill process applies a mixture consisting of fuller's earth which is impregnated with $FeSO_4$ and small amounts of sulfuric acid. The crude product is pretreated with diluted sulfuric acid and sodium hydroxide solution in order to remove the pyridine like and phenolic compounds respectively. Small amounts of the "Instill agent" are added and carefully stirred. The produced resins are instantaneously absorbed from the fuller's earth and removed from the refined product which is distilled in order to obtain finished products.

Rostin process:

The Rostin process is a kind of catalytic refining process whereby iron oxide is used as catalyst. The hydrocarbons are vaporized and led over the catalyst in the presence of hydrogen containing gases. A slight hydrogenation of the unsaturated hydrocarbons takes place which are not removed but transformed into saturated hydrocarbons.

Aluminum chloride process:

The oils are diluted with an inert solvent as for instance xylol, small amounts of $Al\ 11_3$ are added and the mixture is heated until the development of hydrochloric acid vapors ceases. The refined product must be neutralyzed in order to remove excess $Al\ Cl_3$ and is finally distilled.

Organic acids:

Experiments have been made to replace the often used sulfuric acid by organic acids, which do not affect all kinds of unsaturated hydrocarbons which are present in the products.

The above mentioned processes cover but a few of the proposed or applied methods which have been developed with the aim to cut down the refining losses which are caused by the presence of unsaturated hydrocarbons.

V. Sulfuric acid treatment

The well known method to refine gasolines by means of sulfuric acid has been modified and improved.

The concentration of the acid was lowered resulting in a decrease of the losses. The strength of the applied acid depends on the nature of the hydrocarbons which are present in the oil.

Another efficient method to lower the refining losses consists in applying low temperatures during the refining process. An agitator which was equipped with a water jacket was used for refining of lignite gasoline in order to control the temperatures of the product.

The unsaturated hydrocarbons are polymerized products are either dissolved by the sulfuric acid and drawn off from the refining vessel or they remain in the treated product. It has been observed that during the redistillation the resins are partly vaporized and leave the still together with the hydrocarbon vapors as soon as the higher boiling fraction are distilled.. Since the distilled resins spoil the hydrocarbons the end point of the distillation process is reached when the vaporization of the resins begin despite the fact that valuable hydrocarbons are still present in the still. By lowering the distillation temperature by the application of vacuum pressure it was possible to increase the yield or to apply less and weaker acid.

Lossed are not only due to the influence of the acid on the unsaturated hydrocarbons but also to the formation of emulsions during the neutralizing of the acid treated product. It was found out that, if emulsion were formed by the application of sodium hydroxide as neutralizing agent, a sodium carbonate solution did not form any emulsion and vic. versa.

VI. Generalities

When crude benzol was refined it was of advantage to distill the crude hydrocarbons before they are subjected to a chemical treatment because the single fractions require more or less refining agent. If the total crude product is refined such amounts of refining agent must be employed that the fractions which contain compounds which require a more intense treatment are converted into valuable products, whereas other fractions which do not need much treatment undergo a kind of super-refining which causes high losses.

Specifications for diesel and bunker fuels demand certain figures for the pour point, the asphalt contents, the ash content, the conradson carbon residue and the contents of aggressive or corroding sulfur.

The pour point depends on the content of paraffine waxes, which are present in the crude oil. The amount of paraffin waxes which is formed during the carbonization process depends primarily on the characteristic of the kerogen of the shale. Wurttenberg kerogen does not form high amounts of parafffin waxes whereas the Spanish kerogen is decomposed into a paste-like oil. The paraffin wax content can be influenced by the temperature to which the gases and vapors are subjected. If the gases and vapors are recycled through heat exchangers they can be slightly cracked whereby the content of paraffin waxes is lowered.

The paraffin waxes can be removed by the known extraction processes or by cooling the oils. Both process are more or less expensive. It is also possible to employ certain agents which are able to lower the pour point. (Para flow).

The asphalt content can be controlled by fractionating cooling, whereby the heavy oils contain high amounts of asphalt whereas the middle oils are almost free from asphalt.

The ash content of the crude oil depends on the employed carbonization method, rotating drums, high velocities of the purging gases, high content of fines in the feed stock of the carbonizers result more or less ash in the produced oil. The ash is removed during the distillation process, but it often causes troubles during the distillation. The carbonization process should be carried out under such conditions that a minimum of ash is formed.

The Conradson carbon residue indicates the amount of residue which is formed in the cylinders of a diesel engine, oils from which the asphalts are removed should comply with the specifications.

Mercaptan-sulfur can be removed by "Doctor Solution" but with the application of a high concentrated alkaline solution the possibility of the formation of emulsions arises, since the Wurttenberg shale oils showed the tendency to form emulsions.

A combined refining method is perhaps advisable consisting of the application of selective acting solvents and hydrogenation of the residue, which cannot be used as diesel - or fuel oil.

(40)

Dr. Otto Hubmann

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Re: Refining of Shale-oil

No industrial experience with refining of shale-oil is available. Some experience on a technical scale should be available from the Esthonian Works and also from the Autun Plant in France. Only the Autun oil seems to be of a character similar to that of the Green River shale. The oil from Esthonia-oil shale differs from the Green River shale oil by an extremely high oxygen content. Much laboratory work has been done at Kivioli in connection with the Tunnel-kiln-plant. The refining of the distillation products only concerned the light oils and a kerosine fraction for illuminating purpose. All the heavier oils were sold as bunker oil to the German Navy.

For bunker oil the German Navy never made any prescriptions concerning the contents of nitrogen or pyridine bases. I have never heared of difficulties with oils from Upper Silesia which contained 3 to 4% pyridine. These oils have also been tested many times in the laboratories of the navy. A content of oxygen compounds of 45% (vol.) was not considered objectionable as long as the heating value of the oil was not below 9200 Kcal/ltr.

It is unknown to me if fractions of shale oil have been refined for high-revolution-diesel engines. Oils from Wurttenberg shale-oil have been used successfully in truck-engines and in tractor-engines. These oils contain very little oxygen (2% soluble in alkaline) but 2 to 3% sulfur. The nitrogen content amounts to 1%.

For diesel engines a suitable fraction as condensed in the gas cooler or a fraction obtained by distillation of the tar oil was used without further refining. The Wurttenberg oil contains no paraffin and therefore has a very low pour-point.

Probably no long period experience exists with using shale oils exclusively in a diesel engine. The high content of sulfur should have made more trouble with corrosions and spoiling of the lubrication oil than the nitrogen compounds.

Assuming that the Green River oil contains 0.5 - 0.8% of sulfur and so much paraffin that its elimination cannot be avoided, for diesel oil as well as for bunker oil, a most simple and cheap method of refining is proposed in the attached flow-sheet.

If the oils are condensed with modern methods (electric precipitation above 100°C-surface cooler-oil scrubber) the raw oils are recovered free of water [illegible] a heavy oil which contains all the paraffin wax, a medium oil which contains no paraffin wax, and the benzine-fraction.

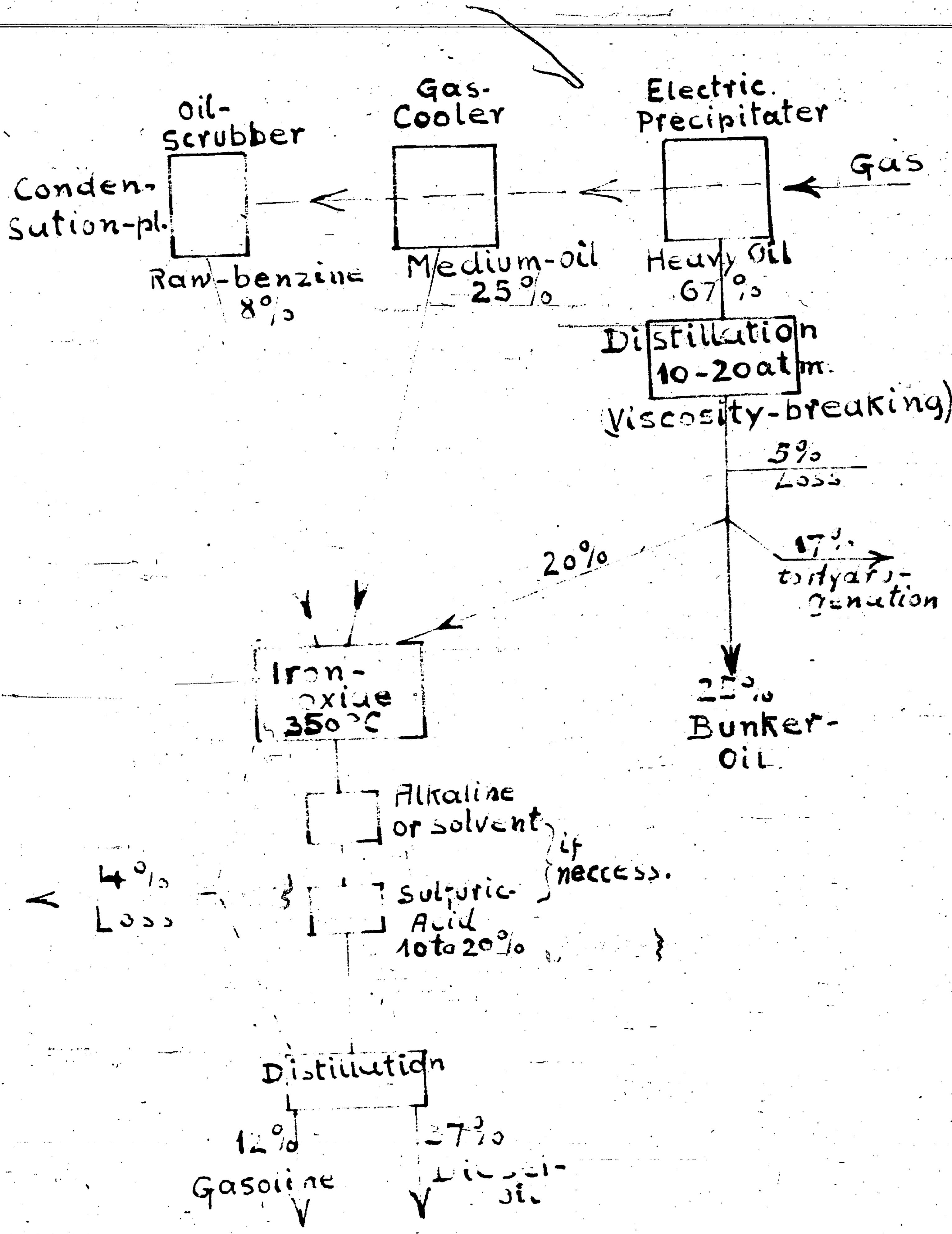
The heavy oil must be treated for an extraction or for a splitting of the paraffin wax. Extraction methods being too expensive in this case, cracking of the paraffin wax by a distillation under 10 to 20 atm. pressure would be much more economical. The heavy oils are divided into three fractions - diesel oil, bunker oil and residue. Possibly the residue could be left in the bunker oil, if necessary, by separately condensing part of the asphalt from the carbonizer gas. Asphaltic residues can be treated by hydrogenation for the production of benzine or diesel oil.

Refining of the benzine and the diesel oil fraction should not be a problem with oils of a low sulfur and a low oxygen content as in the case of Green River oils. The usual washing with sodium-hydroxide solution and sulfuric acid should be sufficient. Possibly a cheaper method, which eliminates more of the sulfur compounds, consists in a catalytic treatment of the oil vapors at 300 to 350°C by an iron-oxide catalyst.

The elimination of nitrogen should be sufficient in the sulfuric-acid wash. The high quality of Green River shale-oil allows a treatment without hydrogenation. Hydrogenation for economical and technical reasons should only be considered for the conversion of heavy fractions of the carbonization and the refining plants into a benzine of high octane number.

Otto Hubmann

Refining of Shale-oil



FRESE (40)

Shale Oil

Concerning Information Requested By The Bureau of Ships

In 1940 or 1941 heavy residues (boiling above 350°C) which originated from the distillation of Estonian shale oil was used during a short period as feed stock at the Rnhroel-Hydrogenation plant at Bottrop. The fraction which boiled below 350°C had been separated from the residue before by another company, which intended to use it for other purposes. The shale oil residue was blended with coal tar pitch and by another at the Rnhroel plant employing a sump-phase reactor which worked under 700 atm. For this reason it is impossible to submit correct data of the yields which are to be expected if pure shale oils are hydrogenated but only rough estimates can be given.

Some difficulties arose during the hydrogenation by the formation of strong foam bubbles in the cold catchpot which separates the circulating hydrogen from the hydrogenated products. The foaming began as soon as more than 10% shale-oil residue was admixed to the pasted pitch resulting a mist of liquid products which was carried away by the circulating gas. Consequently it was not possible to admix more than 10% shale oil residue to the pitch.

But we do not see any difficulties to overcome those difficulties. The foam information is due to the surface tension of various products and can be widely influenced by a proper control of the temperature of the stripper products. For certain reasons we were not able to make experiments which would have jeopardized the daily production of the Rnhroel plant. But we are fully convinced that it is possible to hydrogenate shale oils alone or blended with other similar products if a suitable temperature of the stripper product is maintained.

According to the performed experiments at the Rnhroel plant the following yields may be expected of 100 kg of shale oil residue in hydrogenated employing the sump phase only and applying a preserve of 700 atm.

10 kg gasoline with a boiling range from 40-175°C

40 kg diesel fuel with a boiling range from 180-350°C

35-40 kg completely asphalt free bunker fuel boiling above 350°C

10-15 kg gases + losses.

The gas contains more than 50% propane and butane which can be recovered as wet gas (gaseous fuel) or used for other purposes. Approximately 1000-1200 cbm hydrogen are consumed for the production of 1 metric ton finished product (gasoline + diesel fuel + bunker fuel). We do not doubt that shale oil or shale oil residue is an excellent feed stock for high pressure hydrogenation which produces either high anti-knock gasoline, or diesel fuels of good quality. By changing the hydrogenation conditions the ration of the various kinds of the obtained products can be altered thus meeting the marketing demands. By far most of the N and S- containing compounds which are present in the shale oils are completely removed during the hydrogenation process. During the war the "Poelitz hydrogenation plant" hydrogenated large volumes of Estonian shale oil but for the time being no results of those experiments are available.

It is possible that further information can be furnished by: U. S. Government Technical Oil Mission, Index Reel 15, Page 3043, Target 30/4.02, Leuna, Item Index 16.