Extract from the proceedings of a meeting held at the office of
Continental Oil Company, April 28/29, 1942

Subject: Estonian shale-oil

The following informations were obtained:

(1)   Final capacity of the plants:

590,000 metric tons of shale-oil (comp. appendix 1)

(2)   Types of carbonization systems to be employed:

Pintsch Producer   The hitherto designed producer shows a output of 35-40 metric
tons per day. Experiments with a 100 tons-unit shall be
performed in spring 1943. Approx. 650 cbm gas per metric
tons of shale is liberated, the sensible heat of which is
used for the carbonization. Due to the vast volumes the
hydrocarbons are diluted with combustion gases, thus hampering
their recovery. (gasoline, gasol, H_2S, acetone)

Tunnel kiln   Throughput 200 to 400 metric tons of shale per day per unit.
25 cbm carbonization gas per metric ton of shale due to the
small gas volumes the recovery of the above mentioned by-
products is easy to perform. The heavy dust-containing crude
oil (17-20% of the total recovered oil serves as additional
fuel for the operation of the tunnel kilns)

For the final stage a combination of Pintsch producer and
tunnel kilns has been contemplated (3 Pintsch-producers for
every 1 tunnel kiln) in such a manner that the excess gas of
the Pintsch producers heats the tunnel kilns. The hitherto
used oil is then saved and available for other purposes. Under
those circumstances a by-product recovery from the diluted
gases should be impossible. Such a combination is not favored
by the Estonian specialists, due to the higher oil yield of
the tunnel kilns. It is to be assumed, that the tunnel kilns
can be improved in such a way, that an additional heating source
becomes unnecessary. (compare appendix 2)

(3)   Processing of the crude oils, properties of the finished products. Hitherto
gasoline (end point 200°C) and bunker fuel were produced. The Kivioeli plant is
equipped with a fractionating cooling system and a gasoline extraction installation.
In the future modern methods for oil processing and refining shall be employed. (compare
appendices 3 and 4). Appendix 5 represents a flow sheet of the contemplated refining
system. The results of some analyses performed with Pintsch-oil is presented by
appendix 6.

4.   By-products

(a)   Gasol

The recoverable volumes of gasol can be roughly estimated from some gas
analyses which were performed in London. The permanent gas incl. the topping gases,
and the topping gas proper were analyzed. To get a better economy the 3 largest
plants should be combined for the gasol recovery (plants 1, 3, 6). The plants must
be connected by lines, distances see appendix 1.

Total oil production of the above mentioned plants, 539,000 metric tons per year from 2,700,000 metric tons of shale.

Total quantity of C_3 - C_4 - hydrocarbons available: 14,000 metric tons per year without stabilizer-gas.

Appendices 3 and 4 indicate that additional 3000 metric tons are recoverable from the stabilizer gas.

But should gasol only be recovered from the concentrated topping gases the annual output would be 2,750 + 3,000 = 5,740 metric tons.

Should only tunnel-kilns be employed for the carbonization the yields amount to 32,000 metric tons per year or 10,000 metric tons of the C_3-C_4- hydrocarbons are extracted from the topping and stabilizer gases (compare appendix 7)

50-60% of the hydrocarbons are of the alefinic type which can be easily transformed in polymerized gasoline.

Total yield of hydrocarbons from 100 metric tons of oil shale:
(Tunnel carbonization system)

      19.7 metr tons liquid products
      0.5 " " polymerized gasoline
      0.5 " " gasol

Compare appendix 4.

The recovery of gasol and polymerized gasoline requires an extraction of the H_2S from the permanent gases. Contemplating that a centralyzed sulfur extraction plant is provided for the plants 1, 3 and 6 approximately 2,500 to 5,000 metric tons of elementary sulfur can be recovered.

(b) Acetone has occasionally been extracted from the waste liquor of the tunnel-kilns of Kivioeli. The primitive refining methods leave it doubtful whether a pure acetone has ever been recovered. Acetone yield 0.05% of the crude oil, total contemplated acetone-production = 150 metric tons per year. Besides acetone 150 metric tons of C_4 - C_5 - ketones and 75 metric tons of higher ketone-oils are recoverable per year.

(b) Phenols are recovered during the refining of the gasoline. The composition is 40% cresol and 60% xylenol. Total annual yield 200-300 metric tons (03 - 0.4% of the crude gasoline).

Appendix 1

Plant	Location	Furnace Type	Number (final stage)	Metric tons of crude oil per year			Power Supply
				1940 before destruction	May 1942	End of 1945 final stage	
1	Kivioeli	Tunnel kiln Pintsch	6↑2	70,000	0	122,000 43,000 164,000	from Narva
2	Kuette Joud	-	-	oil-shale-mine, mined shale is sold			
3	Kohtla Tarve	Tunnel kiln Pintsch	2 50	60,000	40,000	52,000 113,000* 165,000	Own power-station
4	Sillamae	Tunnel kiln Pintsch	2	40,000	-	40,000 (fall 1942)	outside sources
5	Kohtlor	Davidson revolv. retorts	8	11,000	5,000	11,000 (fall 1942)	" "
6	Tarve (new plant)	Tunnel kilns Pintsch	15↑3	-	-	104,000 105,000 209,000	own power station " "
Total				181,000	45,000	599,000	Common power net work planned
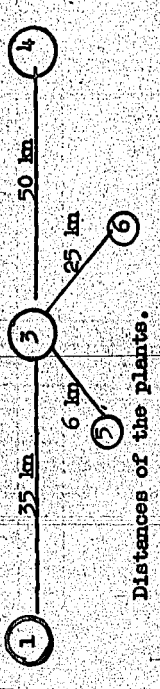
All plants are in want of water (hardness 30°)
Plant 6 shall be located near a lake
Plant 4 has own harbor suitable for vessels up to 2,000 to

*Incl. 7,000 gasoline extracted from the gas (fall 1943)

Distances of the plants.

Comparison of various carbonization systems

| | Pintsch | Tunnel - kilns | |
		With oil heating	With Pintsch gas heating
Output oil-shale metr. tons per day	hitherto 35-40 planned 100	400	400
Heating method	Carb. gas surplus gas	heavy oil fractions 17-20% of the crude oil	carb. gas + Pintsch-excess gas
Recovered products:			
kg per metr. ton of oil-shale — gasoline	15	29	29
middle oil	41	46	46
heavy oil	64	120	61
bitumen ‡	64	-35 85	59
Pitch ‡	184	160	195
		heating purposes	
gasol* from stabilizer	0.5	1.5	1.5
" carb. gas		2.0	-
total carb. gas cbm 1 to shale	650	22→25	22-25
gasoline hydrocarbons in the heating gas present g/m³	20	10	10
Moisture content of the fed-in shale %H_2O	10-12	Pre-drying to 3-5% H_2O (briquetting after wetting to 20-26% H_2O followed by drying to 6%H_2O	
Waste liquor			
crude oil: liquor	1: 0.63	1 : 0.30	
waste liquor cbm 1 ton shale	120	50	
reaction of the liquor	Sour (Hl, H_2SO_4	slightly sour	
phenol content	unknown	unknown	

* recoverable, but not yet performed.

Flow sheet for processing 100 metric tons crude oil or oil shale resp.
Pintsch Producers with (planned) vacuum distillation Kivioeli

Page 1577

Surplus gas
to tunnel-kilns

Approx. 340,000 : 65,000 cbm fuel gas (20g gasol. per cbm) ("Permanent gas")

Pintsch Producers		
Oil-shale output		
524 . 100		

		Products based on 100 crude oil	for sale based on 100 oil shale

Condensing System				Products based on 100 crude oil	for sale based on 100 oil shale
Oil	86.9	16.6			
heaviest oil dust containing	7.5	1.43			
Total	94.4	18.03			

7.5 1.43

Bitumen plant									
Output 7.5 1.43		Bitumen	→				6.8	1.3

84.7   16.15

fuel + carb. gas

Vacuum dist. unit						
vac. crude gas.	5.9	1.13				
" middle oil	16.8	3.21	middle oil →	16.8	3.21
" bunker oil	33.3	6.37	bunker fuel →	33.3	6.37
" pitch	27.0	5.16	pitch →	27.0	5.16
Total	83.0	15.87			

Gas extraction		
(wash oil 25°C)		
Gasoline	5.6	1.07

86.9 16.6 oil   15.82   3.02

Stabilizer					
Stab. crude gasoline					
15.52	2.96	Gasol →	0.3	0.06

Gas holder

Topping System					
Crude gasoline	2.16	0.41			
Crude petrol	2.16	0.41			
Topped oil	82.4	15.73	82.4	15.73
Total	86.72	16.35			

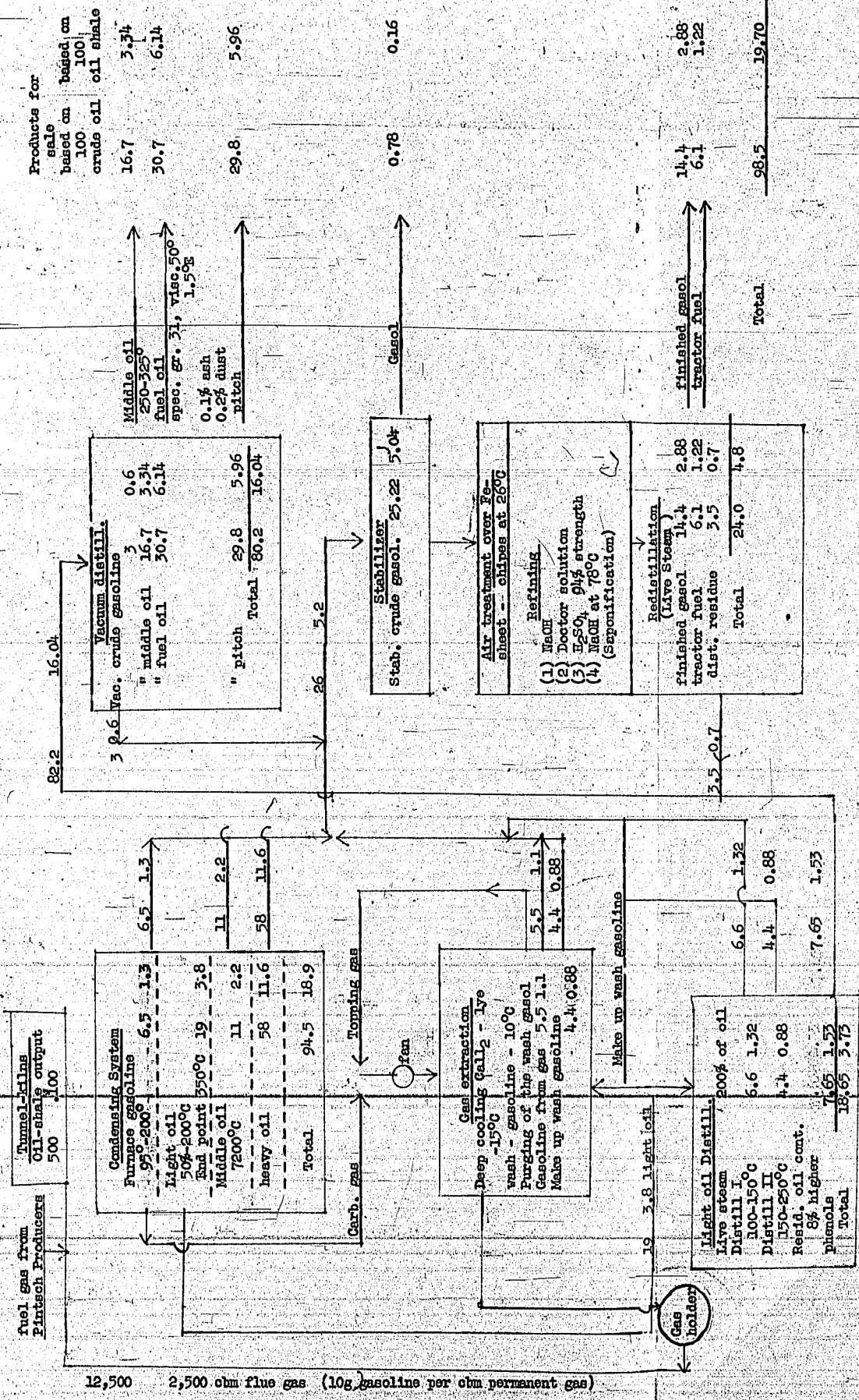| **Air-treatment**					
Refining					
Redistillation					
finished gasoline					
7.69	1.47	gasoline →	7.69	1.47
tractor fuel					
4.72	0.90	tractor fuel →	4.72	0.90
residue					
2.52	0.44				
Total 14.73	2.81				

		Total	96.3	18.47

Flow sheet for processing 100 metric tons crude oil or oil shale respect.
Tunnel-kilns with (planned) vacuum distillation Kiviõli

Page 1578

Tunnel-kilns
Oil-shale output
500   100

fuel gas from
Pintsch Producers

Condensing System

Furnace gasoline	95°-200°	6.5	1.3
Light oil	50°-200°C	11	2.2
End point 350°C	19	3.8
Middle oil	7200°C	11	2.2
heavy oil	58	11.6
Total	94.5	18.9

Topping gas

Fan

Carb. gas

Gas extraction
Deep cooling (AlCl₂ - lye
-15°C
wash - gasoline - 10°C
Purging of the wash gasol.   5.5   1.1
Gasoline from gas   5.5   1.1
Make up wash gasoline   4.4   0.88

Make up wash gasoline

Light oil Distill. 200% of oil
Live steam
Distill I   100-150°C   6.6   1.32
Distill II   150-250°C   4.4   0.88
Resid. oil cont.
6% higher
phenols   7.65   1.53
Total   18.65   3.73

Gas boiler

Vacuum distill.
Vac. crude gasoline   3   0.6
" middle oil   16.7   3.34
" fuel oil   30.7   6.14
" pitch   29.8   5.96
Total   80.2   16.04

Stabilizer
Stab. crude gasol.   25.22   5.04

Air treatment over Fe-sheet — chines at 26°C
Refining
(1) NaOH
(2) Doctor solution
(3) H₂SO₄ 94% strength
(4) NaOH at 78°C
(saponification)

Redistillation
(Live Steam)
finished gasol.   14.4   2.88
tractor fuel   6.1   1.22
dist. residue   3.5   0.7
Total   24.0   4.8

Middle oil
250-325
fuel oil
spec. gr. 3, visc.50°?
1.5%E

0.1% ash
0.2% dust
pitch

Gasol

finished gasol
tractor fuel

Total

Products for sale	based on 100 crude oil	based on 100 oil shale
	16.7	3.34
	30.7	6.14
	29.8	5.96
	0.78	0.16
	14.4	2.88
	6.1	1.22
Total	98.5	19.70

Gas analyses (performed in London)
Permanent gas incl topping gases % vol.
Topping gas (6% of the permanent gas % vol.

	H₂	mercapt.	CO₂	CₙHₘ	H₂	CH₄	C₂H₆	C₂H₄	C₃H₈	C₃H₆	C₄H₁₀	C₄H₈	N₂	O₂
	1.4	1.5	18.0	6.1	121.1	11.0	6.3	3.0	3.5	6.0	4.3	5.7	0.1	
	13.0		7.8	0.8	3.2	13.0		25.0	3.3	41.8	3.8	0.4		

12,500   2,500 cbm flue gas (10g gasoline per cbm permanent gas)

Information concerning properties of the oil and refining
procedure of the gasoline

(1) Acid content of the oils

Extraction by means of hot water:

Pintsch Producer:
(without the heaviest fraction)
1.14 mg KOH per 1g of oil for neutralization of H_2SO_4
0.70 mg KOH per 1g of oil for neutralization of HCL

Acid number after extraction by means of hot water: 1.3mg KOH
Saponification number   118mg KOH
Tunnel kiln:
(without light oil or gasoline)

Acid number (acidity): 3.9mg KOH
Saponification number: 19.5mg KOH

(2) Gasoline refining

The gasoline (from tunnel kiln) shows an antiknock value of 64-66 before refining.
The hitherto used H_2SO_4 - refining method shall be replaced by a more suitable method.
It was proposed to use the Rostin-method which applies a Fe-Cu- catalyst over which
the gasoline vapors are passed.

Oil from Pintsch - Producer

Aniline point: not to be determinedd
Flash point: 65°C

Boiling range:

98°	150°	200°	220°	240°	260°	280°	300°	320°	340°	360°
2.6	7.4	12.2	15.4	19.6	24.5	27.2	35.4	42.8	57.8 %

Boiling range using a 30cm - distillation column:

Gasoline to 200°C	Residue above 200°C	H_2O	loss
9.15% wt	89.6% wt	0.7%wt	0.55% wt

Ultimate analysis:
C= 81.85%   N 0.4%
H= 10.05%   S 1.20%

dissolved water 0.7%
Extracted by NaOH (15% solution)   5.13% wt of acidic components
"   " Na_2CO_3 (10%   "   )   1.13% wt of acidic components
Hard asphalt: 7.56%
Soft   "   0.0"
Gasoline topped to 200°C (9.15% wt)

Boiling range:

98°	110°	120°	130°	140°	150°	160°	170°	180°	190°	200°	Residue
0.5	2.0	7.0	330	47	55.5	70	83	92	98.5	1.1

Spec. grav. 0.800
Aniline point 48.8°C
Olefinic + aromatic constituents 75.4%; Olefines (bromine addition) 56%
Gum (glass dish) 56mg per 100 ccm
Quick darkening after distillation

The oil boiling above 200°C showed the following data:

	pour point	Olefines + aromatics	Olefines	% wt. of the crude oil
Oils boiling above 200°C	-18°C			91
fraction 200-250°C (vacuum distil.)	-48°C	73%	60%	6-7
" 250-300°C (" ")	-28°C	80%	73%	10
" 300-350°C (" ")	-13°C	94%	76%	10

<u>Gasol</u> (gas analyses and quantities available compare-appendix 4)

Work 1: 164,000 metric tons per year of oil
"   3: 165,000   "   "   "   "   "   "
"   6: 210,000   "   "   "   "   "   "
Total   539,000 metric tons per year of oil from 2,700,000 metric tons per year
                 of shale = 340 metric tons per hour of shale

C_3-C_4 hydrocarbons present in the <u>tunnel-kiln</u> - permanent gas incl. topping gases:
1,350,000 metric tons per year of <u>shale (170</u> metric tons per hour of shale) x 22 cbm =
30,000,000 cbm permanent gases incl. topping gases
30,000,000 x 20% = 6,000,000 cbm C_3 - C_4 x 2.3 = 14,000 metr tons per year
                 = 1.75 metric tons per hour C_3 - C_4 hydrocarbons

An additional source is <u>the stabilizer gas</u> from stabilizing the gasoline which has
been extracted from the gases which are leaving both carbonization-systems (comp.
appendix 3 and 4)
1,350,00 metr. tons per year of shale = 170 metr. tons per hour of shale (Pintsch) =
                                800 metr tons per $\frac{}{year}$ = 0.1 matr. tons per hours
                                       of C_3 - C_4 - hydrocarbons
1,350,000 metr. tons per year of shale = 170 metr. tons per hour of shale (Tunnel-kiln)
                               = 2,200 metr. tons per year = 0.27 metr. tons per
                                 hour of C_3 - C_4 hydrocarbons

Total amount of C_3 - C_4 - hydrocarbons: 17,000 metr. tons per year
                                       2,1 metr. tons per hour

C_3 - C_4 - hydrocarbons present <u>in the topping gases of the tunnel-kilns</u>
         (comp. appendix 4):
Topping gas = 6% from 30,000,000 cbm = 1,800,000 cbm
1,800,000 x 67% = 1,200,000 cbm   = 2,750 metr tons per year
                                     = 0.35 metr. tons per hour of C_3-C_4 hydrocarbon
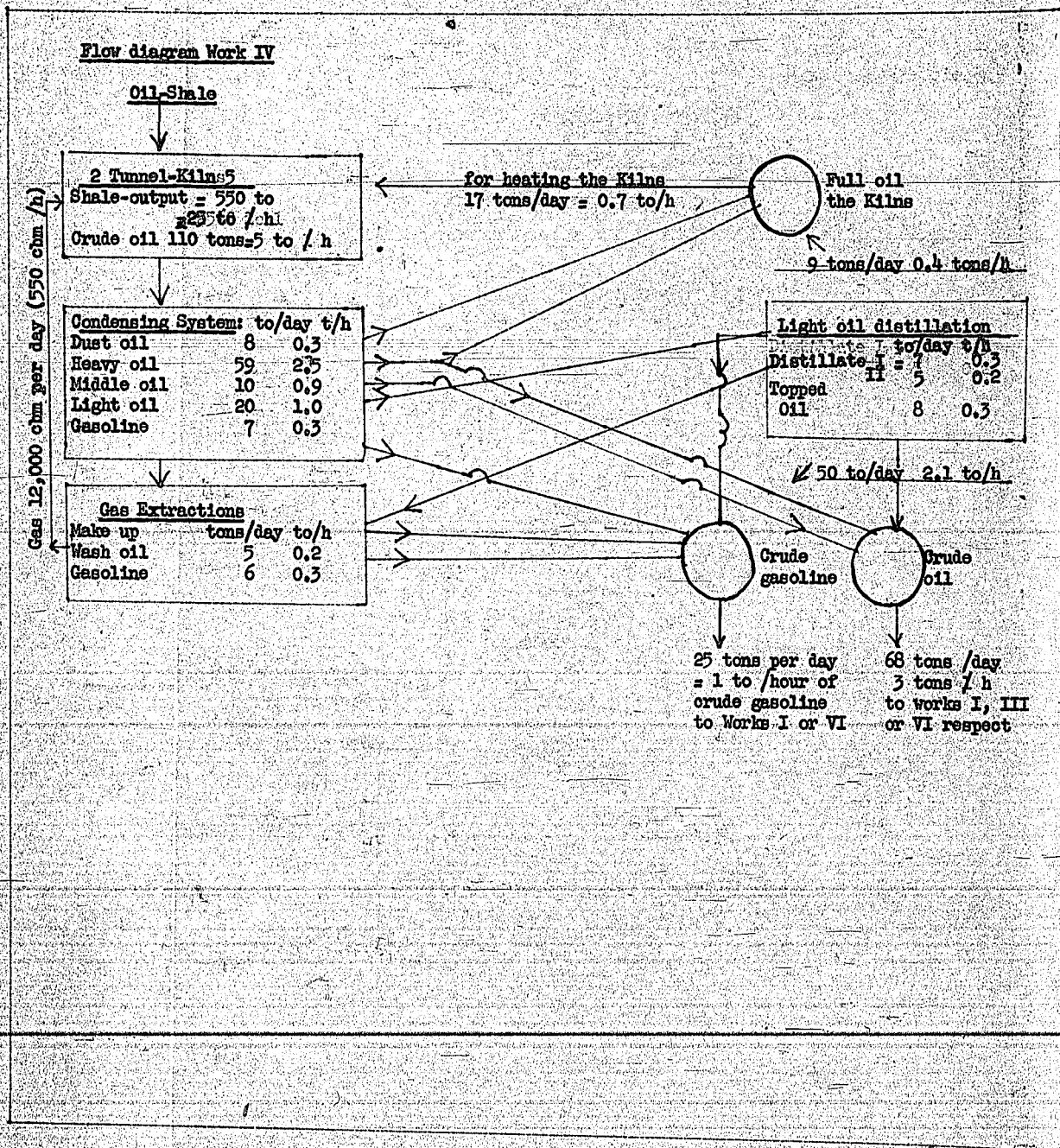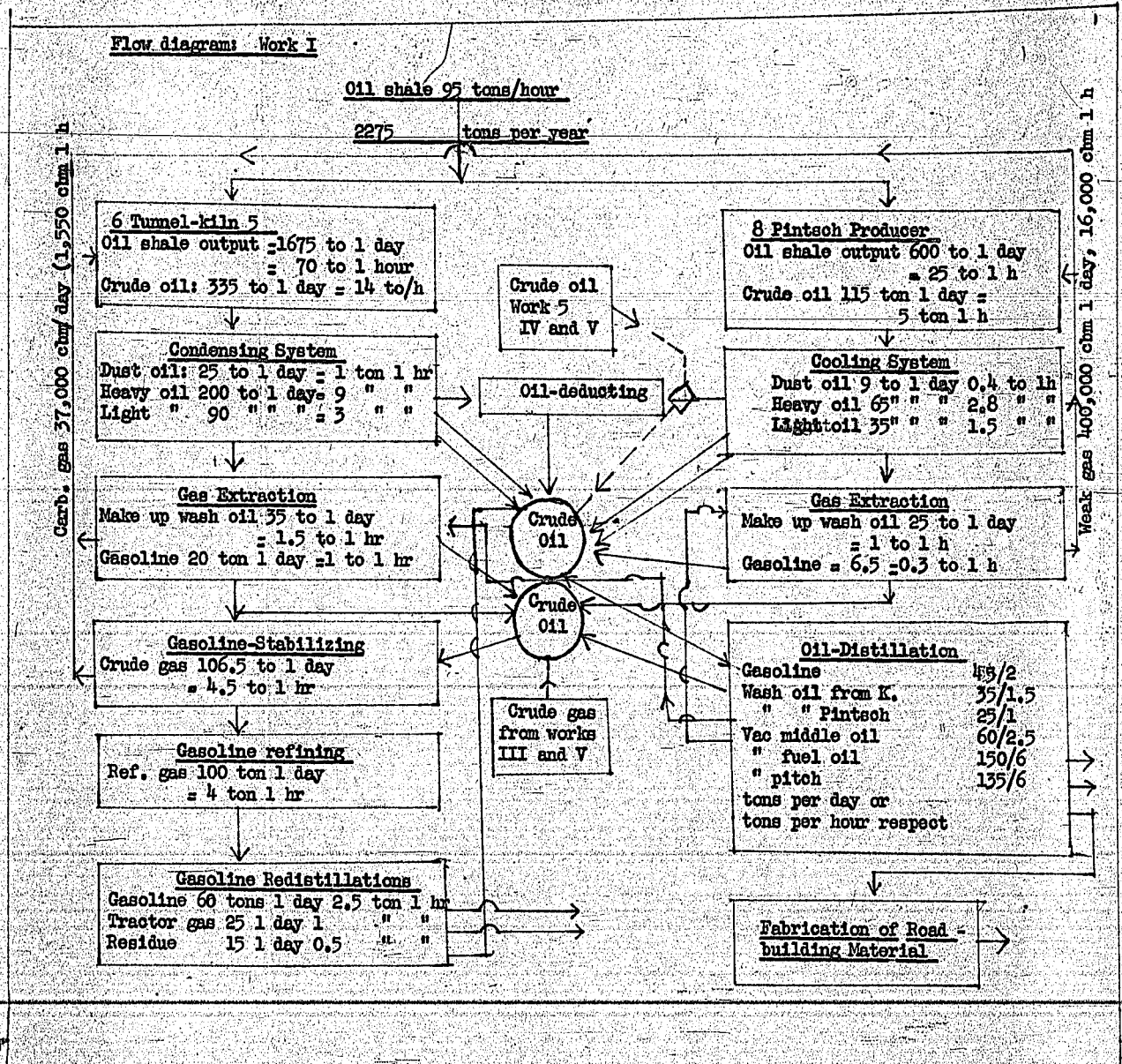
Bag 3,043, Target 30/4.02

Page 1582 - 1584

Subject: Estonian shale-oil

The attached sketches represent the flow-diagram of

Work I (Kivioeli) and

of   Work IV (planned Teve-plant)

- 1 -

Flow diagram Work IV

Oil-Shale

Gas 12,000 cbm per day (550 cbm /h)

2 Tunnel-Kilns 5
Shale-output = 550 to
= 23 to / ch1
Crude oil 110 tons = 5 to / h

for heating the Kilns
17 tons/day = 0.7 to/h

Full oil
the Kilns

9 tons/day 0.4 tons/h

Condensing System:	to/day	t/h
Dust oil	8	0.3
Heavy oil	59	2.5
Middle oil	10	0.9
Light oil	20	1.0
Gasoline	7	0.3

Light oil distillation	to/day	t/h
Distillate I = 7		0.3
II = 5		0.2
Topped oil	8	0.3

50 to/day 2.1 to/h

Gas Extractions		
Make up	tons/day	to/h
Wash oil	5	0.2
Gasoline	6	0.3

Crude gasoline

Crude oil

25 tons per day
= 1 to /hour of
crude gasoline
to Works I or VI

68 tons /day
3 tons / h
to works I, III
or VI respect

- 3 -

Flow diagram: Work I

Oil shale 95 tons/hour

2275 tons per year

Carb. gas 37,000 cbm/day (1,550 cbm 1 h)

Weak gas 400,000 cbm 1 day, 16,000 cbm 1 h

6 Tunnel-kiln 5
Oil shale output 1675 to 1 day
= 70 to 1 hour
Crude oil: 335 to 1 day = 14 to/h

Crude oil
Work 5
IV and V

8 Pintsch Producer
Oil shale output 600 to 1 day
= 25 to 1 h
Crude oil 115 ton 1 day =
5 ton 1 h

Condensing System
Dust oil: 25 to 1 day = 1 ton 1 hr
Heavy oil 200 to 1 day= 9 " "
Light " 90 " " " = 3 " "

Oil-deducting

Cooling System
Dust oil 9 to 1 day 0.4 to 1h
Heavy oil 65" " " 2.8 " "
Light oil 35" " " 1.5 " "

Gas Extraction
Make up wash oil 35 to 1 day
= 1.5 to 1 hr
Gasoline 20 ton 1 day =1 to 1 hr

Crude oil

Gas Extraction
Make up wash oil 25 to 1 day
= 1 to 1 h
Gasoline = 6.5 =0.3 to 1 h

Crude oil

Gasoline-Stabilizing
Crude gas 106.5 to 1 day
= 4.5 to 1 hr

Crude gas
from works
III and V

Oil-Distillation
Gasoline   45/2
Wash oil from K.   35/1.5
" " Pintsch   25/1
Vac middle oil   60/2.5
" fuel oil   150/6
" pitch   135/6
tons per day or
tons per hour respect

Gasoline refining
Ref. gas 100 ton 1 day
= 4 ton 1 hr

Gasoline Redistillations
Gasoline 60 tons 1 day 2.5 ton 1 hr
Tractor gas 25 1 day 1 " "
Residue 15 1 day 0.5 " "

**Fabrication of Road -
building Material**

Subject: Estonian shale-oil

The following paragraphs contain the results of analyses carried out with Estonian shale-oils. Due to the complex composition of the shale oil the results concerning the ultimate analysis, bromine figure, olefine ∤ aromatics content may be not quite exact.

1st sample: <u>oil product by Pintsch-producers</u>

<u>Properties of the original oil:</u>

Spec. gravity at 20°C: 0.978
Aniline point: not to be determined
Flash point: 63°C
Boiling range:

98°C	150	200	220	240	260	280	300	320	340	360°C
2.6	7.4	12.2	15.4	19.6	24.5	27.2	35.4	42.8	57.8 ccm	

Distillation by means of a 30 cm column:

Gasoline to 200°C	Residue over 200°C	H_2O	Loss
9.15% wt.	89.6% wt	0.7% wt.	0.55% wt

Ultimate analysis: C: 81.85%
                       H: 10.05%
                       N: 0.4%
                       S: 1.20%

Dissolved water 0.7%
Acidic oils (extr. by means of NaOH 15% sol.): 5.13% wt.
   "   "   ("   "   "   " Na_2CO_3 10% "): 1.13% wt.

Hard asphalt: 7.56%
Distillation applying a 1 meter fractionating column:
      H_2O: 1%
Gasoline to 200°C   9.2%

Fraction 200-250° (vac. dist.)	6.5%
250-300° (" ")	9.6%
300-350° (" ")	9.9%
350-380° (" ")	4.5%
Total distillate	40.7%
Residue	57.0%
Gas & loss	2.3%

Properties of the gasoline fraction (to 200°C)

spec. gravity (20°C): 0.800
aniline point: ∤ 8.8°C
Olefinic ∤ aromatic constituents (100% H_2SO_4): 75.4%
Bromine figure: 71.2   iodine - thiocyanate figure 93.8 (Olefines: 56%)
Residue in the glass-dish: 56mg   Acidic oils 2.47% wt
Boiling range: 98°   120   140   160   180   200   Residue °C
                     2.0   30.0   55.5   83   98.5   1.1

The gasoline shows a brownish-red color after exposition to light and acid.
      Ultimate analysis: C: 84.18%
                         S: 1.47%
                         H: 12.65%

Properties of the fraction which are boiling above 200°C

fraction	spec. grav.20°C	Aniline point °C	Pour point °C	Arom. + Olef. %	Bromine number	Sodine thiocyanate number
200-250°	0.860	+18.8	-51	73	51	--
250-300°	0.919	+25	-28	80.6	50	79.6
300-350°	0.985	-7.2	- 6	94	38	---
350-365°	1.009	-20	+ 5	97	41	63

A portion of the crude oil was topped at 200°C and liberated from asphalt and phenols by diluting the oil with light gasoline and extracting with NaOH. It was now possible to distill 45% of the treated oil which boiled above 200°C. Adding the topped gasoline to the distilled fraction, 55% distillate can be recovered from the crude oil.

Properties of the asphalt and phenol free fraction boiling between 200 and 400°C:

Spec. gravity 0.923
Olef. + Aromat. 85.4%
Boiling range: 218°C

pour point: -3.2
bromine number: 44.8

	218°C	240	280	300	340	380	400	405	Residue
		9.0	30.0	38.0	55.0	76.0	91.0	97.0	2.6 ccm

Estonian shale oil from tunnel kiln
      Barrel: B.O.G.Z.

Properties of the original oil:

Spec. grav. (20°C) = 0.930

Boiling range:
°C	103	130	140	160	180	200	220	240	260	280	300	320	340
ccm	0.1	0.15	2.0	4.0	7.0	10.0	14.3	18.4	24.0	29.2	36.4	36.4	48.0

°C	360	365	370	Residue
ccm	68.4	76.3	86.1	Solid

Aniline point: not to be determined
Flash point: 89°C
Water content 1.9 / 1.95%
Acidic components extracted with NaOH(15% solution): 14.195% wt
Orig. Acids   "   "   NaCO$_3$(10%) "   ): 1.275" "
Acids in the water   0.318" "
Olefines & aromatics extracted with H$_2$SO$_4$ (100% solution) 96.2% wt.
Bromine number   23.9 corresponding with approx. 36% olef. if molecular weight 250
Hard asphalt   8.11%
Ultimate analysis: C: 82.0
                    H: 9.90
                    N: 0.58
                    S: 1.03

A fractionating distillation analysis showed the following figures:
     2% water
     10% gasoline (boiling below 200°C)
     45% oil   (boiling between 200 and 430°C vacuum dist.
     38% asphalt (contains still oil because the distillation was stopped
                  before the point of decomposition)
     5% losses   (The high losses are due to the asphaltic residue
                  which could not measured quite exactly)
The oil fraction boiling between 200 and 430°C was redistilled applying vacuum pressure. The distillate was subdivided into several fraction which showed various boiling ranges.
Analysis were carried out on a fraction boiling between 230-340°C (26% of the original oil) and on another fraction boiling between 200-300°C.

Properties of the gasoline, boiling below 200°C
Spec grav. (20°C): 0.759
Aniline point + 27.1°C
Browning number 25.7
Aromatic + olefinic constituents; 59.9% (24% of olefines if molecular weight 140)
Acidic oil: 0.132%
Boiling range:
°C	74	100	120	140	160	180	190	210	Residue
ccm		15.5	49.5	71.5	81.5	90.5	95.5	98.0	1.4

Ultimate analysis: C: 84.75%   N: 0.11%
                     H: 13.44%   S: 0.90%

Properties of the fraction, boiling between 230 and 340°C (26% of the original oil)

Spec. gravity: 0.917
Aniline point: +29.9°C
Aromatic + Olefinic components: 66.2%
Bromine number: 27.3
Iodine - thiocyanate number 37.8
Acidic oils: 10.4%

Boiling range: °C	232	260	280	300	320	330	339	Residue
ccm		3.0	31.5	67.0	81.0	56.0	98.0	1.5

Ultimate analysis: C: 84.76%
H: 11.2%
N: 0.38%
S: 0.82%

Assuming an average molecular weight of 210 approximately 36% olefines would be present in the oil.

Properties of the fraction boiling from 200-300°C

Spec. grav. 20°C : 0.862
Aniline point +38.2°C
Bromine figure 19.0
Aromatic + olefinic components (by means of 100% H_2SO_4): 52.7%
Acidic oils: 4.05%

Boiling range: °C	208	220	240	260	280	293	Residue
ccm		3.5	39	81	94	97.5	2

Ultimate analysis: C: 85.40
H: 12.27
N: 0.14
S: 0.88

Properties of the fraction boiling from 200-300°C after trating with H_2SO_4 (20% solution) and NaOH (15% solution)

Spec. grav. 20°C: 0.846
Aniline point + 38.1°C
Bromine number: 23.0
Aromatics + olefines (H_2SO_4 100% solution): 50.1%

Boiling range: °C	220	230	240	250	260	270	280	288	Residue
ccm		8.0	35.0	63.0	79.0	89.0	94.0	98.5	1.5

Ultimate analysis: C: 85.46
H: 12.65
S: 0.89

Subject: German shale-oil I
              Sample from the Dotternhausen plant, Wurternberg
              Condensate from condensing system without the dust containing
              heaviest oil

Properties of the original:
Spec. grav.: $(20^{\circ}C)$: 0.950
Aniline Point: $+20.3^{\circ}C$
Color: brownish-black
Boiling range: 160 190 200 220 240 260 280 300 320 340 360 370 Res. $^{\circ}C$
                    2.0 4.5 10.5 15.5 20.0 24.0 31.5 38.5 47.5 66.5 78.5 Solid ccm

Flash point: $85^{\circ}C$
Aromatics + Olefines $(H_2SO_4\ 100\%)$: 52.1%
Bromine number: 36
Acidic oils (extracted by means of NaOH, 15% Solution): 0.55% wt
      "   "   ("   "   "   " Na_2CO_3 "   ): 0.01" "
Dissolbed water   + 0.7%
Hard asphalt   : 1.48%
Ultimate analysis: C: 84.05%
                    H: 10.53"
                    N: 1.02"
                    S: 3.41"

Fractionating distillation by means of a 30 cm column:

        H_2O: 0.7%
        $0-200^{\circ}$: 7.0"
        $200-250^{\circ}$: 11.0%
        $250-300^{\circ}$: 23.0" Slight Decomposition
        $300-400^{\circ}$: 35.3" Vacuum pressure applied
        Residue 35.3"

Properties of the fraction $0-200^{\circ}$

Spec. gravity 0.820, aniline point $+18.7^{\circ}$; Bromine number : 60
Acidic oils: 0.44% wt.
Boiling range: $^{\circ}C$ 120 140 150 160 170 180 190 200 210 226 Residue
               ccm   2.0 13.0 31.5 56.0 74.5 87.0 95.5 96.5 99   0.4

Aromatics + Olefines: $(H_2SO_4\ 100\%)$: 61.5% wt
   Ultimate analysis: C: 82.86%
                      H: 12.38"
                      N: 0.45"
                      S: 4.01"
Properties of the fraction $200-250^{\circ}$

Spec. grav. 0.863, aniline point: $+21.5^{\circ}C$, bromine number 48, acidic oils: 1.03%
Aromatics + Olefines $(H_2SO_4\ 100\%)$: 62.2%
Boiling range: C° 80 120 160 200 230 250 260 270 280 290 300 310 320 330 Res.
               ccm   2.0 4.0 7.0 11.0 18.0 23.5 37.5 58.5 72.0 84.5 95.5 97.5 98.5 1.3
Ultimate analysis:
        C: 83.71
        H: 11.76
        N: 0.35
        S: 3.15

Properties of the fraction boiling from 250 - 300°C

It must be mentioned that a slight decomposition took place during the distillation which usually increases the amount of light products.

Spec. grav. (20°C): 0.896   Aniline point ÷ 23.6°C   Bromine number 34

Acidic oils: 0.78   Aromatics ÷ Olefines: 69.1%

Boiling range: C°	80	120	160	200	230	250	260	270	280	290	300	310	320	330	Res.
ccm	2.0	4.0	7.0	11.0	18.0	23.5	37.5	58.5	72.0	84.5	95.5	97.5	98.5		1.3

Ultimate analysis: C: 83.58%
                     H: 11.22"
                     N: 0.53%
                     S: 3.37%

Properties of the fraction boiling from 300-400°C (vacuum pressure applied)

Aromatics ÷ Olefines: 53.6%

Boiling range: °C	325	340	360	370	380	390	400	402	Residue
ccm	8.5	38.5	52.0	67.5	77.5	87.5	91.5		8.0

Ultimate analysis: C: 86.18%
                     H: 10.12%
                     N: 2.76%
                     S: 1.16%

Subject: Description of the oil shale carbonization plants Kivioeli, Kohtlor Taerve
and Kohtlor situation November 1942

A. Description of the Kivioeli-plant (Tunnel-kilns)

The Kivioeli plant is the most important plant of Estonia. With the destructed
installation almost repaired the oil production is 2/3 of the prewar quantity.
In order to increase the capacity of the plant additional furnaces (tunnel kilns,
Pintsch producers) stills, refining equipment, installation for the recovery of
acetone and phenols, and a research laboratory are under construction.

Prewar production: 70,000 metric tons of oil, 4 tunnel kilns
Present   "   50,000   "   "   "   "
Contemplated "   164,000   "   "   "   "   ", 6 tunnel kilns
                                                 8 Pintsch producers

The oil shale is worked by underground mining 12 m below the surface. The shale
forms horizontal layers 20 cm thick which are interrupted by limestone layers
of almost the same thickness. After loosening the rock the shale must be packed
out and loaden by hand. The shale is predried from 12 to 5% water, screened and
separated into the fines (approx 1/3) and nuts which are fit for carbonization. The
fines are burned and furnish additional heat, which is required for the carbonization
process.

Tunnel-kilns available for the carbonization:
2 Tunnel-kilns 330 tons capacity per day each (max. cap. 400 tons)
2 "   "   190 "   "   "   "   "   " (max. "   250 ")

The heating of the furnaces is performed by recirculating carbonization gases which
have been preheated by passing through heat exchanges.
The spent shale contains 6-8% fixed carbon. The liberated gases are passed through
the condensing system which consists of 2 preliminary air coolers followed by 3
water coolers.
The condensate of the two first coolers (heavy - and middle oil) are united whereas
the condensate of the water coolers is drained off separately. Ordinarily the
carbonization gases are stripped from the gasoline after having been cooled to
-10°C by means of a $CaCl_2$-lye. The lean gas saves as fuel for heating the
recirculating gases. The future recovery of sulfur and C_3-C_4 - hydrocarbons is under
consideration.

Refining of the recovered oils:
The middle and heavy oil is delivered to the navy without further treatment. Dedusting
the oils by means of centrifuges and fractionating the crude oil shall be provided
in the near future.
Hitherto the light oil is separated into two cuts, the gasoline fraction with an
end point of 200°C and a higher boiling one, which goes to the bunker fuel. The
gasoline fraction incl. the gasoline extracted from the gas amounts to approx. 20%
of the total recovered oils.
The gasoline is refined by means of NaOH, H_2SO_4 and NaOH. The finished gasoline
(spec. gravity 0.740) contains
            62% Olefines
             7% Aromatics
            22% Paraffins

Waste Liquor:
Due to the absence of carbolic acid in the oil, the phenol content of the waste
liquor should be low. The liquor smells like ether - compounds which is due to
ketones. The quantity of recoverable ketones is estimated to be 12-18 tons per
month (corresponding with an oil recovery of 70,000 tons per year. Half of the
ketones are supposed to be acetone.
The recovered acetone was treated with NaOH and distilled. It was easy to sell
despite its bad odor.

Description of the Kohtlor-Taerve-Plant

The Kohtlor-Taerve-Plant which is situated 30 km distant from Kivioeli carbonizes the oil-shale which has been worked by means of open cast methods utilizing Pintsch producers.

    Prewar production: 60,000 tons of oil per year
    Present   "   40,000 " " " " "
    Contemplated "   165,000 " " " " "
      (Combination of tunnel kilns and Pintsch producers

The plant consists of 6 producers with a capacity of 35 tons each and 22 producers which carbonize 55 tons per day of oil-shale.
A producer with an assumed capacity of 100 tons per day is under construction. The size of the shale to be carbonized is at least 16mm, it is fed in by means of hand-operated feeding gadgets. The condensing system consists of air-and water-coolers. Due to the vast volumes of diluted gases the cooling surface of the condensing system is inadequate. The spent shale contains 4% fixed carbon.

Oil Treatment

The dust containing "SS-oil" is blown to asphalt by means of hot air. The middle oil is sold as bunker oil without further treatment (0.5% dust).

Description of the Kohtla-plant

Kohtlor is situated a few miles south from Kohtla Taerve. It is an experimental plant more than a commercial plant. The prewar production was 11,000 tons of oil per year. There is no enlargement of the plant under consideration.

The carbonization is performed by means of 8 revolving furnaces, 4 of which are in operation at the present time.

The Sillamae-work formerly owned by Sweden is still completely destructed. The prewar production was 40,000 tons of oil.

The Teve-work (Plant 6) which is supposed to produce 209,000 tons of oil is in the first stage of construction.

Distribution of the recovered tunnel-kiln-products   Appendix 1
based on the years 1938-1940

500 tons moist shale containing 36% organic substance and 10-12% moisture yield the following products:
    100 tons liquid carbonization products (without water) corresponding with 20% oil recovery based on shale.

    69 tons heavy & middle-oil ("S + M") spec. grav. 1.040
                            viscosity 23-26°E at 50°C
                                2.38-3.27°E at 100°C
                                2% are boiling below 250°C

    19 tons light oil ("L")   spec. grav. 0.850
                        in boil. p. 70°C 25% 167°C
                                5%   115 " 35" 180"
                              15"   144 " 70" 250"
                                    End point 360°

    6.5 tons furnace - gasoline ("OB")   Spec. grav. 0.760
                                 80% <180°, 95% <250°

    5.5. tons gasoline extr. from the gas spec. grav. 0.700
        (from the deep-cooling plant) in boil. p. 27°C
                                80% to 100°C
                                End p. appr. 150°C

11,000 cbm "Permanent gas" i.e. 22 cbm p. ton of shale containing:
    0.11 tons C_5- hydrocarb. and higher ones (i.e. 10g per cbm "Gasol"
    3.3-3.5 tons C_3-C_4- hydrocarbons   (i.e. 300-500g per cbm)
                                            (i.e. 240g H_2S per cbm)

Additional products:
30 cbm waste liquor
      14 cbm carbonization water
          12.5 " liquor from the light-oil-distillation-unit
          3.5 " liquor from gasoline refining

Distribution of the recovered Pintsch-Producer-Products
520 tons of moist shale containing 36% of organic
material and 10-12% moisture

100 tons liquid carbonization products (without water) = 16-18% based on shale

7 tons dust containing heavy oil ("SS") spec. grav.=1.03 - 1.04
2% boiling < 250°C

93 tons middle oil ("M")   spec. grav. 0.980; 4.5°E at 50°C
in boil. p. 150°C
5% -200°C
15 " 250°C
28" 300"
57" 350"

400,000 cbm diluted gases containing :   i.e. 640 cbm to oil shale

10 tons C_5 - hydrocarbons and higher
(-200°C)   i.e. 25 g per cbm "Gasol"

Recovery of C_3 - C_4 - hydrocarbons and of H_2S impossible due ot the diluted gas.

The composition of the waste liquors have not yet been determined.

Estimated quantity of waste liquor: 60 cbm.

Composition of the Wurteenbergian oil-shale

The figures are based on 100g oil-shale as received:

1. Analysis of the shale:
   (a) CO_2 calculated as gr C which is liberated by means of Hll: 4.4g
   (b) Carbon which is present in the organic material   8.5"
   (c) Total sulfur (sulfides are not present)   3.5"
2. Fischer Assay
   (a) H_2O 2.6g
   (b) Tar   5.2"
   (c) Residue   89.49g
   (d) Gases ‡ losses   2.68"
3. Analysis of the spent shale
   (a) CO_2 calculated as gr C liberated by Hll   5.2g
   (b) Carbon which is still present in the organic material   2.5"
   (c) Total sulfur   2.1"
4. Sulfur content of the heated residue of the Fischer Assay   1.7g

Composition of Estonian shale-oil

Tunnel-kiln- products

Gasoline from the furnaces: (3 samples)

Spec. gravity 20°C	0.768	0.756	0.767
Aromatics + Olefines %	66.7	75.8	-
Bromine number	100.1	64.6	64
Boiling range			
initial boiling point °C	47	52	50
to 80°C are vap. %	7.5	9.0	6.0
100" " " "	20.5	25.5	20.0
120" " " "	42.5	50.0	41.5
150" " " "	69.5	76.0	68.5
170" " " "	80.5	86.0	82.0
190" " " "	88.5	92.0	89.5
210" " " "	93.5	95.0	93.0
End point 98% at °C	245	227	234
Residue %	1.2	1.0	1.4
Ultimate analysis			
C	84.00	83.19	84.74
H	13.93	10.93	12.88
N	0.05	0.19	0.42
S	0.39	0.90	1.01
Acidic oils (15% NaOH)%wt.	0.416	0.434	0.486
N - bases %wt.	0.089	0.050	0.059

	Middle oil 70-340°C (3 samples)		
Spec. gravity 20°C	0.831	0.831	0.825
Aromatics + Olefines	-	69.1	-
Bromine number	62	28.2	69.6
Boiling range:			
initial boiling point: °C	71	68	73
to 100°C are vap. %	3.0	3.5	2.5
120 " "	9.0	9.0	8.5
150 " "	25.0	23.0	20.0
180 " "	37.5	39.0	38.5
210 " "	54.0	55.0	54.0
240 " "	70.0	70.0	70.0
270 " "	81.0	82.5	81.0
300 " "	90.0	90.0	90.5
320 " "	92.5	92.0	95.0
End point 98% at °C	334	342	334
Residue	solid	2.5	1.6
Ultimate analysis:			
C:	84.13	83.95	84.10
H:	12.21	12.25	12.37
N:	0.37	0.29	0.28
S:	1111	1.30	1.22
acidic oils (15% NaOH)%wt	0.695	0.699	0.792
N-bases " "	0.068	0.069	0.070

Heavy oil

Spec. grav. 20°C	1,000	0.995
Aromatics + Olefines %	100	-
Bromine number	92	62
Boiling range		
initial boiling point °C	158	
to 210°C are vap. %	2.0	
270" " " " "	9.0	
300" " " " "	16.0	15.5
330" " " " "	28.0	30.0
350" " " " "	45.0	38.5
370" " " " "	59.0	51.0/365
Residue	solid	solid
Ultimate analysis		
C	83.21	83.02
H	9.52	9.63
N	0.44	0.51
S	0.71	0.65
Acidic oils (15% NaOH)% wt	12.070	-
N-bases %wt	0.078	-

Products from the Pintsch-Producer

Spec. grav. 20°C	0.985	0.975	0.980	0.980	0.985	1.039
Aromatics + Olefines %	99.0	99.0	99.0	99.0	99	
Bromine number	106.4	119.6	123.6	95.2	129	91.0
Boiling range						
initial boiling point °C	93	90	90	140	93	130
to 160 are vap. %	4.0	4.0	4.0		5.0	
200 " " "	8.5	9.5	10.0		8.5	
240 " " "	16.0	17.5	16.5		17	3.5
280 " " "	27.0	26.0	27.5		25	
320 " " "	38.5	39.0	38.0	32	34	
340 " " "	48.0	54.0	45.0	38.5	42	
End point % at °C	66/352	77/360	57/350	49/365	58/365	59/370
Residue	solid	solid	solid	solid	solid	solid
Ultimate analysis						
C	82.83	81.79	82.26	82.91	82.50	82.96
H	9.80	9.94	9.66	9.88	9.73	9.82
N	0.46	0.39	0.37	0.40	0.29	0.61
S	1.15	1.08	1.16	1.06	1.33	0.78
Acidic oils (15% NaOH)%wt	3.574	3.609	4.797	5.493	9.208	7.56
" " (10% Na_2CO_3)%wt	3.44	3.59	4.79	5.47	9.1	-
N-bases % wt	0.076	0.083	0.17	0.199	0.23	0.22
flash point °C	71	73.5	58.5	58.0	65.0	158
dissolved H_2O %	1.6	0.8	0.6	0.6	0.7	0.9
hard asphalt %	-	-	-	-	-	-

Fractions of the tunnel-kiln-oil

Fraction 0-100°

Spec. grav. (20°C) 0.705 /aniline point 21.3°C; bromine number 127.3;
Aromatics & olefines: 68.2% acidic oils: 0.03%
Initial boiling point

45°	60°	70°	80°	90°	100°	110°	122°	Residue
	12	35	63.5	82.5	92.5 — 96		98.5	1.2 cm

C: 84.73%   H: 13.85%   N: 0.05%   S:0.66%

Fraction 100-200°

Spec. grav. 0.783, aniline point 19.2°C, bromine number 95.6
Aromatics & olefines: 71.5% acidic oils: 0.66%
Initial boiling point

98°	110°	120°	130°	140°	150°	160°	170°	180°	190°	205°	Residue
	1	6	23	42	57	69	81	90	96	99	0.8

C: 84.93%   H: 13.05%   N:0.08%   S;1.14%

Fraction 200-300°

Spec. Grav. (20°): 0.899; aniline point: +24.5°C; bromine figure: 65
Aromatics & Olefines; 77.0%, acidic oils 10.2%
Initial boiling point

196°	220°	240°	260°	280°	300°	320°	330°	338°	Residue
	1	21	47	66	80	92	95	98.5	1.2

C: 84.39%   H: 11.47%   N:0.17%   S: 1.00

Fractions of the Pintsch-Producer-oil

Fraction to 240°C

Spec. grav. (20°C): 0.851   Bromine number   aromatics + olefines   phenols
                             55.0   61.0   4.996

Pyridine
0.052

Initial boiling point	170	180	190	200	205	210	215	220	225	230	235	240	250	Residue °C
140°	1.2	3.0	6.0	14.0	20.0	27.0	37.0	47.5	60.0	74.0	87.0	97.0	98.7	0.9 com

Fraction 240-325°C

Spec. grav.(20°C) 0.955 Bromine number   Aromatics + Olefines   phenols   Pyridine
                         62.5   80.0   14.150   0.054   oC

Initial boiling point	260	270	275	280	285	290	295	300	305	310	315	320	325	338	Res.
130°	1.2	4.4	11.8	23.0	33.0	45.0	54.0	62.5	71.9	77.5	80.0	83.7	85.7	97.3	2.1 com

Distillation analysis applying a 1m-column:

0-80°	13.0%	20.05	bromine number
80-85°	2.5" vt	15.85	" "
85-165°	57.0 "	13.1	" "
165-170°	3.0 "	17.5	" "
170-200°	10.0 "	16.1	" "

Composition of Schandelah shale-oil (German shale-oil)

Crude oil

Spec. grav. 0.976   aniline point -11.4°   bromine number 7.42
Soluble in H_2SO_4 (100%): 100%
Ultimate analysis:

C: 82.24%
H: 9.80"
N: 1.30"
S: 4.40"

Phenols: 1.9%
Pyridines: 2.275%
Pour point -3°C
Ash 0.1%
Asphalt 0.32%
Conradson carbon
Residue 2.33%
Initial boiling point: 190°C

-200°C - 5.7%
-220" - 9.3"
-240" -15.7"
-260" -22.0"
-280" -28.5"
-300" -35.7"
-320" -42.9"
-340" -48.6"
-360" -57.0"
-380" -74.0"
-400" -80.0"
Residue 15.0"

Fraction boiling to 360°C

Spec. grav. 0.922
Aniline point -5.8°C
Bromine number 9.4
Soluble in H_2SO_4 (100%) 78.9
Phenols 2.21%
Pyridines 4.05%
Pour point -28.5°C
Cloud point -16°C
Ash -
Asphalt 0.0%
Conradson carbon Residue 0.16%
Initial boiling point 124°C

to 160°C - 0.5%
" 180" - 2.0
" 200" - 8.5
" 220 - 20.5
" 240 - 33.5
" 260 - 48.5
" 280 - 62.0
" 300 - 75.5
" 320 - 86.0
" 340 - 93.0
" 360 - 98.5
Residue - 1.1

Fraction boiling to 400°C

Spec. grav. 0.934
Aniline point -6.1°C
Bromine number 10.3
Soluble in H_2SO_4 (100%): 81.5%
Phenols   2.16%
Pyridines   4.10"
Pour point -25.0°C
Flock point -14°C
Asphalt   0.0
Conradson carbon
residue   0.16
Initial boiling point 124°C

to	160	-	0.5%
"	180	-	2.0"
"	200	-	9.0"
"	220	-16.5"	
"	240	-27.0"	
"	250	-42.0"	
"	280	-53.0"	
"	300	-	64.0"
"	320	-	73.0"
"	340	-	82.0"
"	360	-	92.0"
"	380	-	96.0"
"	393	'	98.5"
Residue	1.0	"	

Short report concerning some preliminary tests concerning the production of fuels from Estonian shale oil

A representative sample of Estonian shale oil was decomposed into 3 fractions by distillation:
- (1) boiling from 0-100°C
- (2)   "   "   100-200°C
- (3)   "   "   200-300°C

(A) Fraction 0-100°

The gum content of the light gasoline, as determined in the glass dish was a very high (600 mg per 100 ccm determined in the glass dish). In order to lower its gum content fuller's earth was added and the mixture was boiled for several hours using a reflux condenser and afterwards distilled. Despite the treatment the gum content was still 210mg.

(B) Fraction 100-200°C

It was intended to remove the gum forming components as well as the phenols and sulfur compounds by a slightly acting hydrogenation process without hydrogenating the aromatic compounds in order to obtain a satisfactory gasoline.

A HF catalyst was applied.
Three tests were performed applying 100, 50 and 30 abm and introducing hydrogen

1) 100 abm, 480°C, 0.75 vol. per vol. catalyst per hour and 1000l hydrogen per 1l oil to be treated.
Due to an extremely high gasification the obtained products were not analyzed.
2) 50 atm. 480°C 0.75 vol oil per volume catalyst per hour and 2000l hydrogen per 1 liter oil: Performing a test run of 5 hours the yield of liquid products was 78%. We usually got the same yields if mixed based gasolines were treated. A gasoline with the following properties was distilled from the obtained liquid products.

End point 165°C; vapor pressure 0.4 atm, spec. grav. (20°C): 0.739;
Aniline point +58°C, bromine number 1.8; aromatic + olefinic compounds: 30%
Oxydation test?) = 81.5
or Octane number ?)

3) 30 atm 490°C, 0.75 vol. oil per vol. catalyst per hour and 1000l hydrogen per liter oil:
Performing a test run of 5 hours, the yield was 3% lower but the content of aromatic compounds was higher.
The obtained gasoline had the following properties:

Spec. grav.(20 C): 0.756; aniline point +22°C; bromine figure 2.6; aromatic and olefinic compounds: 41.2%.
Experiments 2 and 3 showed very clearly a rather quick deterioration of the applied catalysts (due to phenol content of the oil). The coke formation (0.3% at 50 atm. and 0.8% at 30 atm. calculated on the volume of the injected oil) was very high.

Fraction 200-300°C

The middle oil was hydrogenated at 26.5mV, 100 atm, applying 5000l hydrogen per liter oil and a specific throughput of 0.6 volume oil per vol catalyst per hour. An aromatizing catalyst containing 5% MoO$_3$ was applied.

Results: Very high gasification; properties of the gasoline as follows:

Spec. grav. (20°C): 0.765; aniline point + 35°C, bromine number: 66; end point 165°C; aromatic + aliphatic compounds: 25%.
Properties of the oils boiling above 165°C
Spec. grav.: 0.874; aniline point + 22.2°C; bromine number: 3.8; aromatic + aliphatic compounds: 56.8%

Translation of Oil Mission Film Reel 15, Pages 1682-4

VOLUMETRIC DETERMINATION OF TWO OLEFIN GROUPS

Improvement on the Method of Tauss (Dr. W. Friedrichsen)

March 28, 1939

In the method worked out by Tauss for the quantitative determination of olefins, these compounds are treated with mercuric acetate and the equivalent amount of acetic acid liberated is then determined volumetrically. This simple method of determination can be improved in several particulars, and more particularly it can be applied to the quantitative determination of branched chain olefins with known position of the double bond along with other olefins. In this connection it has been shown that olefins of the configuration:

and the like will decompose mercuric acetate quantitatively within one minute, while on the other hand, olefins such as react much more slowly. These differences in reaction rate of the two types mentioned are shown in Figure 1. In this connection it should be mentioned that the olefins belonging to the second group (1, 3, 4 and 5 in the curves) are obviously contaminated with various amounts of olefins of the first group according to the method of preparation used.

Method of Determination

Two grams of a mixture of equal parts of 2,4,4-trimethylpentene-1 and -2 were diluted to 25 cc. with methanol in a volumetric flask. Two cc. of solution was placed in a reaction flask, treated with 15 cc. of a saturated methyl alcohol solution of mercuric acetate, and allowed to stand for one minute.

Thereupon the solution was immediately added to 100 cc. of water to which 30 cc. of saturated sodium chloride solution and an excess of 0.1 N sodium hydroxide had previously been added, and the acetic acid liberated in the reaction was determined by back-titrating with 0.1 N HCl using phenolphthalein as the indicator. In the same manner a series of determinations were made after various periods of time. The reaction rate curve determined in this manner is shown in Figure 2. Extrapolating the straight upper portion of this curve to the point of intersection with the abscissa gives the composition of the olefin mixture as 50% of each compound.

In addition to quantitative determinations, in the study of the composition of olefins such as triisobutylene, this method also permits the assignment of the olefin structure to one of these two groups.

The method is particularly useful for determining the purity of synthetically prepared olefins. Thus, for example, in Figure 1 the curves 1, 3, 4 and 5 show clearly the contamination of the corresponding olefins with others, which react with mercuric acetate quite rapidly. These olefins would be obtained from the corresponding tertiary alcohol on splitting out water with oxalic acid or iodine, as follows, using 2,3,4-trimethylpentene-2 as an example:

$$.-\overset{\cdot}{\underset{\cdot}{i}}-.-\overset{\cdot}{\underset{\cdot}{i}}-. + IMgCH_3 \longrightarrow .-\overset{\cdot}{\underset{\cdot}{i}}-\overset{\cdot}{\underset{\cdot}{i}}-\overset{\cdot}{\underset{\cdot}{i}}-. \longrightarrow .-\overset{\cdot}{\underset{\cdot}{i}}=\overset{\cdot}{\underset{\cdot}{i}}-\overset{\cdot}{\underset{\cdot}{i}}-. + .-\overset{\cdot}{\underset{\cdot}{i}}-\overset{\cdot}{\underset{\cdot}{i}}-\overset{\cdot}{\underset{\cdot}{i}}-.$$
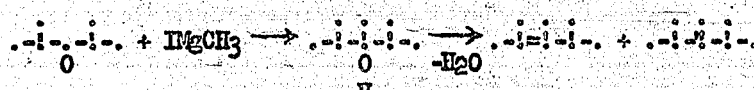
It is seen that the removal of water can proceed in two different directions. An olefin with a configuration corresponding to the last one shown will naturally react with mercuric acetate quite rapidly, and as the curve shows such a structure was present to the extent of 28%.

Translation by H. J. Hall
February 6, 1946

igm-2/8/46
ma-2/21/46

FIGURE 1

I.G. FARBENINDUSTRIE AKTIENGESELLSCHAFT
LUDWIGSHAFEN A. RHEIN 3/28/39
VOLUMETRIC DETERMINATION OF TWO OLEFIN GROUPS

TO: W. FRIEDRICHSEN:

THE GROUP 2 SAMPLES AS
LISTED BELOW OBVIOUSLY
CONTAINED IMPURITIES IN
THE FORM OF OLEFINS FROM
GROUP 1:

Sample	Compound	% Impurity
1	TRIISO-BUTYLENE	5
2	TETRAMETHYL-ETHYLENE	
3	2,2,3-TRI-METHYL PENTENE-3	21
4	2,3-DIMETHYL-PENTENE-2	17
5	2,3,4-TRI-METHYL PENTENE-2	28
6	2,4,4-TRI-METHYL PENTENE-2	

GROUP 1
2,3,3-TRIMETHYLBUTENE-1
2,4,4-TRIETHYLPENTENE-1

GROUP 2

% OF OLEFIN DECOMPOSED IN SATURATED MERCURIC-ACETATE-METHANOL SOLUTION

MINUTES REACTION TIME

FIGURE 2

I.G. FARBENINDUSTRIE AKTIENGESELLSCHAFT
LUDWIGSHAFEN A. RHEIN 3/28/39

TO: W. FRIEDRICHSEN: VOLUMETRIC DETERMINATION OF TWO OLEFIN GROUPS)

1:1 MIXTURE OF 2,4,4-TRIMETHYLPENTENE-1 AND -2

% OF OLEFIN DECOMPOSED IN SATURATED MERCURIC-ACETATE-METHANOL SOLUTION

MINUTES REACTION TIME
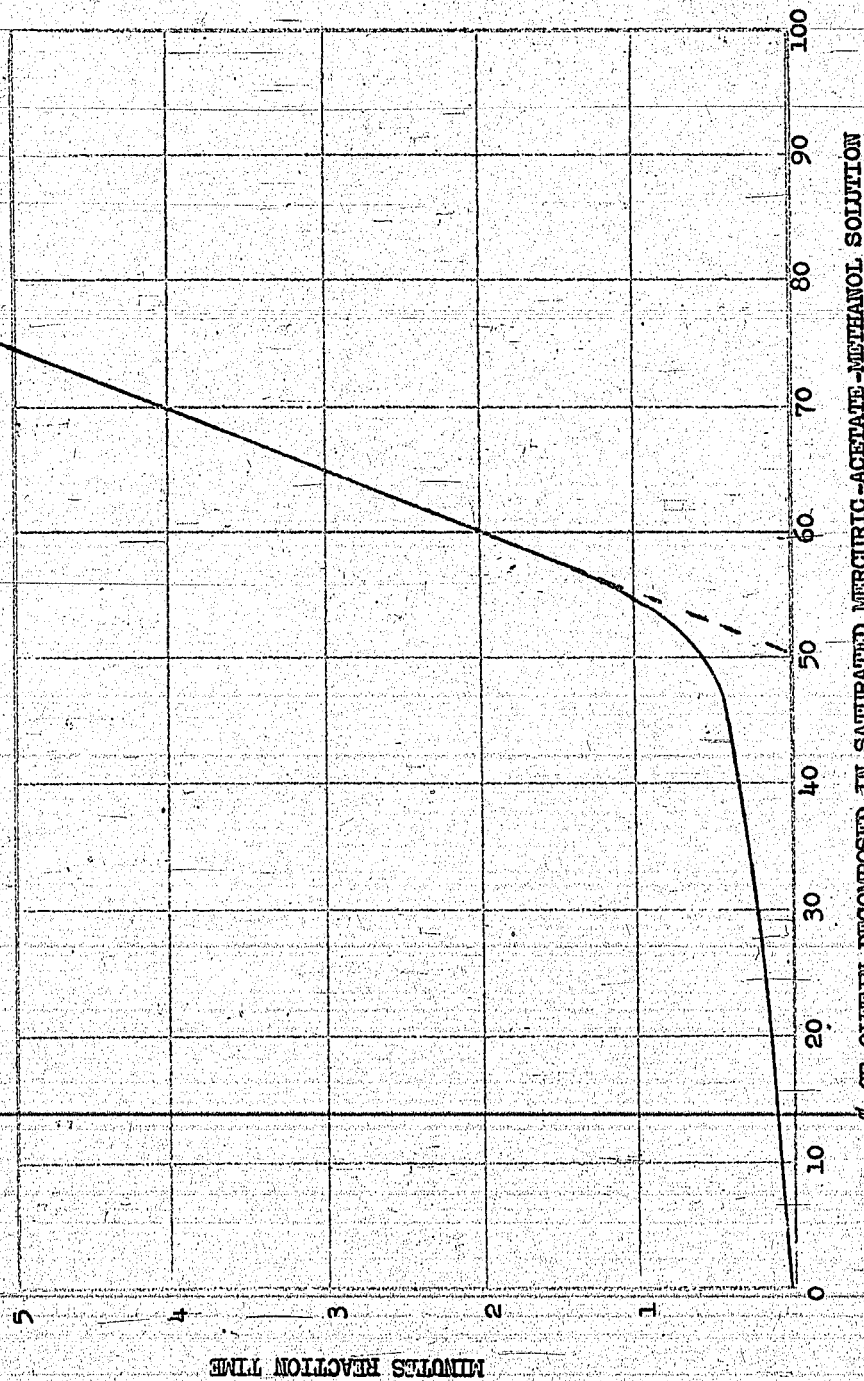
INFORMATION DIVISION TRANSLATION T47-3

The Conversion of Methane With Steam and Carbon Dioxide to Synthesis Gas

Part I: Equilibrium Calculations

The conversion of methane with steam to carbon monoxide, carbon
dioxide and hydrogen is well known as the basis of a technical process for
obtaining hydrogen. The methane is converted according to the equations:

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad 1)$$

$$\text{or} \qquad CH_4 + H_2O \longrightarrow CO_2 + 4H_2 \qquad 2)$$

to a mixture of CO, CO_2 and H_2. These reactions at high temperatures
over catalysts lead to an equilibrium between starting materials and
end-products whose position has been variously calculated, for example,
by W. Klempt and F. Brodkorb[1], Neumann[2] and Padovani[3]. These authors
so proceeded in their calculations that they formulated for the partial
reactions 1) and 2) the equilibrium constants according to the law of
mass action,

$$K_P' = \frac{P_{CO} \cdot P^3_{H_2}}{P_{CH_4} \cdot P_{H_2O}} \; , \qquad K_P'' = \frac{P_{CO_2} \cdot P^4_{H_2}}{P_{CH_4} \cdot P^2_{H_2O}}$$

and reduced the reaction purely schematically to different, well-investigated
single reactions. From the experimentally determined constants for the
methane dissociation, the "Boudouard" reaction and the water gas equi-
librium, the constants K_P' and K_P'' are calculated in known manner. Padovani
had calculated, besides, the equilibrium for the reaction

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2O \qquad 3)$$
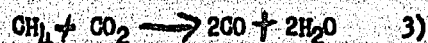
since he had also experimentally proved the possibility to convert methane
with $H_2O + CO_2$ to a mixture of H_2 and CO in the ratio of 2:1 according to
the equation

$$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2 \qquad 4)$$

1. W. Klempt and F. Brodkorb, Ber. Ges. Kohlentechn. 3, 211 (1930).
2. Neumann, Z. Elektr. 34, 218 (1928).
3. Padovani, Chim. & Ind. 32, 517 (1934).

In the comparison of the indicated with the experimentally measured values, one must take into consideration that at lower temperatures, below 600°, the methane is mainly converted according to equation 2, at higher temperatures over 1000°, on the other hand, according to equation 1. In the region between 600°–1000°, which is directly technically interesting, both reactions overlap so that a complete conversion of the methane with water, carbon monoxide and carbon dioxide are obtained in parallel exactly as the water gas equilibrium at the concerned temperature expresses. But one is able to raise[4] the content of exit gas of carbon monoxide to the ratio $CO:H_2 = 1:2$ by addition of carbon dioxide. The required amount of carbon dioxide is calculated when one introduces in the water-gas formula:

$$K_P = \frac{P_{CO} \cdot P_{H_2O}}{P_{CO_2} \cdot P_{H_2}}$$

the ratio $CO:H_2 = 1:2$, for example at about $820^\circ C$ $\quad P_{H_2O} = 2$ $(K_{P820^\circ} = 1)$

$$\overline{P_{CO_2}}$$

At about 820° the excess amounts of H_2O and CO_2 must behave as $2:1$ and the methane conversion then follows the equation

$$3CH_4 + 2nH_2O + nCO_2 \longrightarrow 4CO + 8H_2 + (2n-2)H_2O + (n-1)CO_2 \quad 5)$$
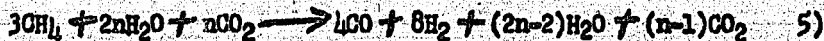
At divergent temperatures the ratio $P_{H_2O}:P_{CO_2}$ displaces in the excess for example, if at 600° one has less water, therefore more CO_2, at 1000° it is just opposite. The conversion equation is then generalized to

$$3CH_4 + 2pH_2O + qCO_2 \longrightarrow 4CO + 8H_2 + (2p-2)H_2O + (q-1)CO_2 \quad 6)$$

For the calculation of the equilibrium constants the present excess of $H_2O + CO_2$ is immaterial, because it is on both sides of equation and disappears. Owing to this equations 5 and 6 have the same constants as equation 4:

$$K_P = \frac{P^4_{CO} \cdot P^8_{H_2}}{P^3_{CH_4} \cdot P_{H_2O} \cdot P_{CO_2}}$$

This constant was further calculated in three different ways, namely, (1) on the basis of experimental data of simple reactions (2) with the help

4. Laboratory Report of Dr. Schiller No. 1448 of October 21, 1936

of the Nernst approximate equation, and (3) according to the formula of Einstein-Eucken. In connection with the first calculation the degree of conversion at different temperatures, pressures and excesses was calculated. In the latter case, with excess of $H_2O + CO_2$ a calculation was made** according to equation 5 instead of equation 6 also at higher or lower temperatures than 820°. This brings an error into the calculation but simplifies it essentially. One can easily estimate that the accuracy is large enough, inasmuch as the methane conversion primarily is influenced by the temperature course of methane dissociation.

1. Calculation of Kp from the constants of simpler reactions

Equation 4 can be described as a series of different simple reactions

$$3 \; [CH_4 \longrightarrow C + 2H_2]$$
$$+ 3 \; [C + CO_2 \longrightarrow 2CO]$$
$$+ 2 \; [CO + H_2O \longrightarrow CO_2 + H_2]$$
$$\overline{S \; 3 \; CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2}$$
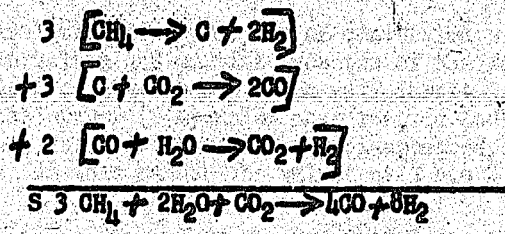
The single reactions have the following equilibrium constants

$$K_{P1} = \frac{P_{CH_4}}{P^2_{H2}} \qquad K_{P2} = \frac{P_{CO_2}}{P^2_{CO}} \qquad K_{P3} = \frac{P_{CO} \cdot P_{H2O}}{P_{CO_2} \cdot P_{H2}}$$

The constant of equation 4 is suitable

$$K_{P4} = \frac{P^4_{CO} \cdot P^8_{H_2}}{P^3_{CH_4} \cdot P^2_{H_2O} \cdot P_{CO_2}} \qquad \qquad 7)$$

Through combination of these three equations one obtains the sought constant;

$$K_{P4} = K_{P1}^{-3} \cdot K_{P2}^{-3} \cdot K_{P3}^{-2} \qquad \qquad 8)$$

** (Trans.: Text is not complete at this point)

For K_{p1}, K_{p2}, and K_{p3} we have inserted the values of Ritschmann, Chem. Met. Zeitschrift "Die Metallbörse" 1928 No.73, 75, 77, Bodmer Schweizer Monatsbulletin 1926, 203, Neumann (loc.cit.). The calculated values of K_{p4} are contained in Table 1, Column I (also see Curve I).

Table 1

Temp.	I	II	III
650°	1.88×10^1	3×10^2	9.55
750°	2.26×10^5	4×10^6	1.55×10^5
850°	9.37×10^8	1×10^{10}	5.50×10^7
900°	1.75×10^{10}	4×10^{11}	6.12×10^9
1000°	8.56×10^{12}	2×10^{14}	2.24×10^{12}

For calculation of the degree of conversion we derive from equation 5 the mole values and partial pressure of the reaction participants, for example, from 3 moles CH_4 which were inserted, X moles are at hand in the equilibrium, (3-X) moles have reacted and 2/3 (3-X) moles H_2O and 1/3 (3-X) moles CO_2 have thereby disappeared, 4/3 (3-X) moles CO are formed. In this manner the values of Table 2 are calculated.

Table 2

Mole Numbers

	Start	in equilibrium
CH_4	3	X
H_2O	2n	$2n+2/3X - 2$
CO_2	n	$n+1/3X - 1$
CO	0	4/3 (3-X)
H_2	0	8/3 (3-X)

Total mole value: $M = 3n - 2X + 9$

The partial pressures of the components are $\underline{\text{single mole number in equilibrium}}$ P

$$M$$

wherein P is the total pressure. By introduction of this expression in equation 7 and several transformations one obtains

$$K_{p4} = \frac{2^{30} (1-1/3X)^{12} p^6}{X^3 (n+1/3X - 1)^3 (3n-2X+9)^6} \qquad 9)$$

This equation we have evaluated for n=1, 2 and 6 besides for P=1 and 10 atms., in that we take arbitrary values for X from which K_{P4} is calculated, and the attending temperatures from Table 1 ascertained. The results are contained in Table 3 (see also page of curves).

Table 3

| | | Equilibrium Temperatures | | | | | | CH_4-content and CO_2 content of the H_2O-free end gases | | | | | |
| | | P= 1 atm. | | | P=10 atm. | | | n=1 | | 2 | | 6 | |
X	CH_4 Conv.	n=1	2	6	n=1	2	6	CH_4 %	CO_2 %	CH_4 %	CO_2 %	CH_4 %	CO_2 %
1	66.7	675°	570°	530°	830°	720°	680°	10.7	3.6	8.6	10.4	6.4	29.9
0.6	80.0	730	650	570	890	800	720	6.4	2.1	4.9	9.8	3.7	29.7
0.2	93.3	820	700	640	>1000	870	790	1.7	0.6	1.6	7.9	1.2	29.6
0.1	96.7	885	735	650	>1000	920	800	0.8	0.3	0.8	7.8	0.6	29.4
0.05	98.3	950	760	675	>1000	960	825	00.4	0.1	0.4	7.7	0.3	29.4
0.02	99.2	>1000	835	700	>1000	>1000	870						
0.01	99.7	>1000	865	730	>1000	>1000	900						

2. Calculation of K_{P4} according to Nernst's Approximate Equation.

About the method and numerical value, see Kuster - Thiel, last edition. The equation reads

$$\log K_{P4} = \frac{-157900}{4.57\ T} + 10.5 \log T + 8.9$$

The results are in Table 1, column II (Curve II)

3. Calculation of K_{P4} according to the equation of Einstein-Eucken

It is treated by the valuation of the following formula for K_{P4}

$$\log K_{P4} = \frac{-W_0}{4.573\ T} + \frac{\Delta \sum C_{Po}}{1.986} \log T$$

$$+ \frac{1}{4.573} \int_0^T \frac{dT}{T^2} \int^T \Delta \sum C_s\ dT + J_K$$

The significance of the singular quantities is the usual. Compare, for example, A. Eucken "Grundriss der phys. Chemie". Table 4 shows the values used by us for heat of formation, chemical constants and specific heat.

Table 4

	Heat of forma-tion at 25°(5)	Chemical Constants(6)	C_p (6)
CH_4	18.0 K cal.	-1.879	$\frac{8}{2} R + 6s \frac{(2000)}{T} + 3s \frac{(4350)}{T}$
H_2O	57.85 K cal.	-1.78	$\frac{8}{2} R + s \frac{(2260)}{T} + s \frac{(5000)}{T}$
CO_2	94.20 K cal.	+0.83	$\frac{7}{2} R + 2s \frac{(970)}{T} + s \frac{(1720)}{T} + s \frac{(3400)}{T}$
CO	26.5 K cal.	+0.157	$\frac{7}{2} R + s \frac{(3100)}{T}$
H_2	——	-3.357	$\frac{7}{2} R + s \frac{(6100)}{T}$

5) Landolt-Bornstein"
6) A. Euken "Grundriss d. phys. Chemie", 4th Edition.

The heat of transformation of the reaction $3CH_4 + 2H_2O \rightarrow 4CO + 8H_2$ is calculated from the several heats of formation to

$$W_{250} = 157,900 \text{ cal.}$$

or $W_0 = 146,850$ cal.

Table 1, Column III (see also Curve III) shows the calculation.

Summary:

The equilibrium constant for the reaction

$$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2$$
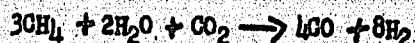
was calculated for 650-1000° in which this reaction was reduced to simple, experimentally well-investigated reactions. In addition the equilibrium constant was calculated according to Nernst's approximate equation and according to the equation of Einstein-Eucken. The agreement between the values of the Einstein-Eucken equation and that secured experimentally is good, while the approximate equation gives little satisfactory results. From the constants secured experimentally the degree of conversion was calculated for various excesses of $H_2O + CO_2$ and for 1 and 10 atmospheres pressure. The results may also be applied to the conversion of methane with oxygen.

/s/ Platz
"Die Umsetzung von Methan mit Wasserdampf und Kohlensäure zu Synthesegas";7pp. 1 illustration

Log K

Temperature °C

700° 800° 900° 1000°

II
I
III

Methane in End Gas

10%

5%

0%

650° 700° 800° 900°

P = 1 atm
n = 2

P = 1 atm.
n = 2

Methane Conversion

100%

95%

90%

100°

P = 10 atm.
n = 2

P = 10 atm
n = 2
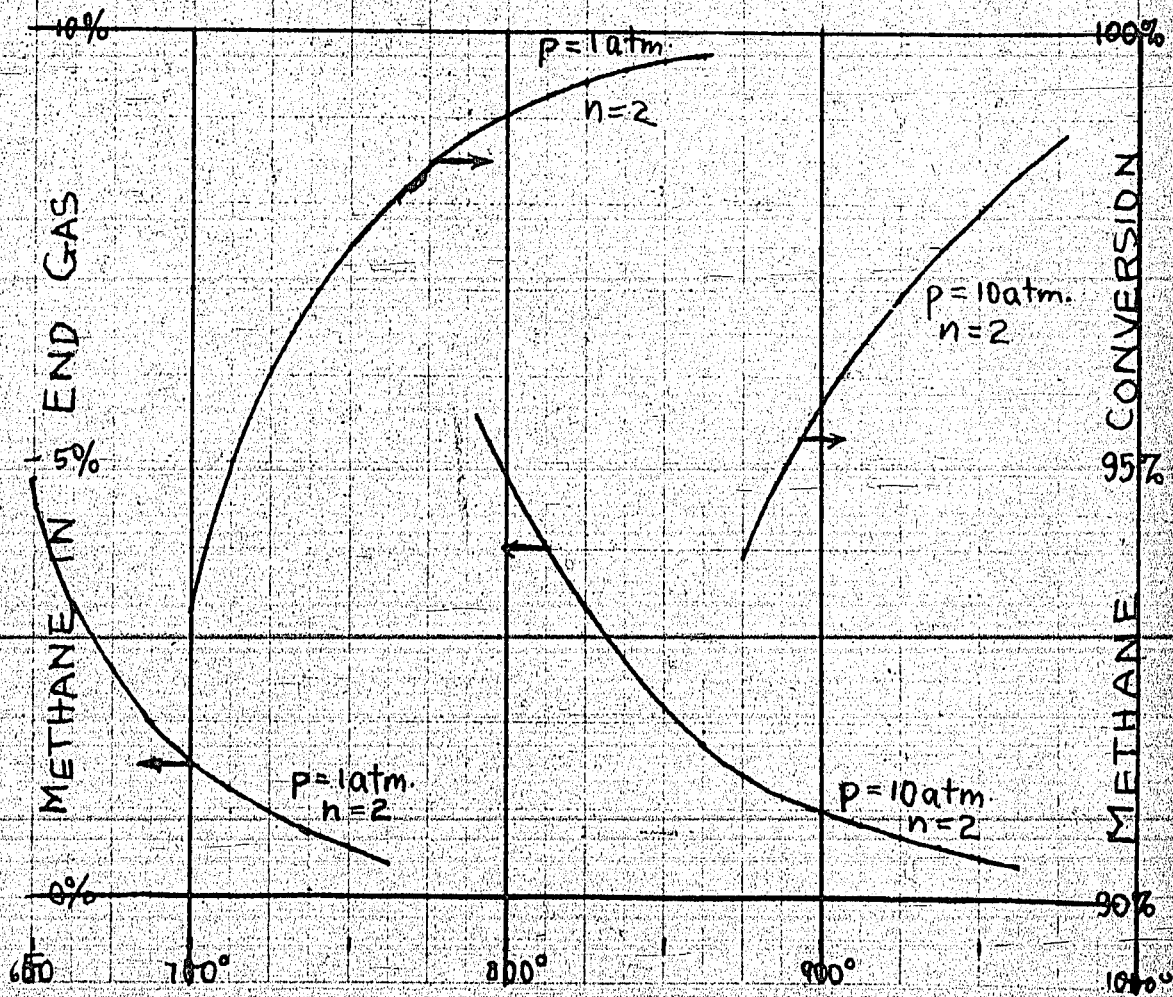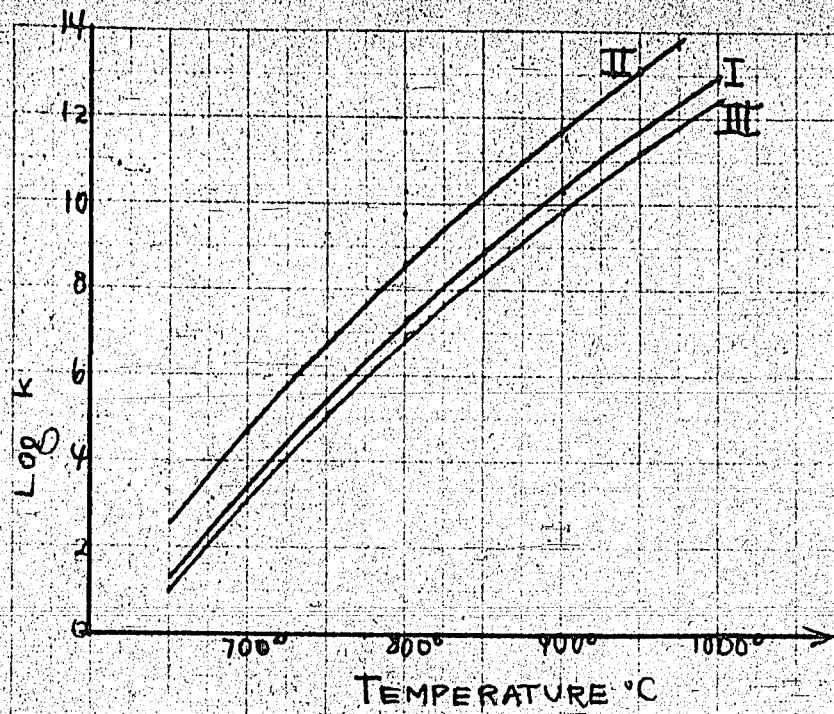
THE TEXAS COMPANY

PORT ARTHUR RESEARCH LABORATORY

TECHNICAL OIL MISSION
REEL NO. 17   ITEM NO. 34
BAG 3041   TARGET 30/4.02
PAGES 606-616

I. G. FARBENINDUSTRIE A. G.
LUDWIGSHAFEN A. RH.
PATENT APPLICATION

PROCESS FOR THE PREPARATION OF VALUABLE OILS

I.G. FARBENINDUSTRIE AKTIENGESELLSCHAFT

　　　　　　　　　　Our Number: O.Z. 11761
　　　　　　　　　　　　　　　Ludwigshafen on the Rhine,
　　　　　　　　　　　　　　　Sept. 6, 1939

Process for the Preparation of
Valuable Oils

　　　　It has been found that valuable oils are obtained if
aliphatic hydrocarbons of at least three C-atoms, are esterified
by means of fatty acids containing at least six C-atoms. The
hydrocarbons must contain two or more primary alcohol groups.

　　　　The above mentioned oxy-compounds can contain the
alcohol groups at any desired position; it is, however, important
that none of the alcohol groups be of the secondary or tertiary
type. For instance, compounds such as HO-R-OH, $R \equiv (CH_2OH)_3$ or
$R'_R C = (CH_2OH)_2$ may be considered; R and R' represent hydrocarbon
groups of the straight- or branched-chain type; their chain-length
should preferably not exceed 20 C-atoms. Especially suitable are
the methylol compounds corresponding to the two last formulae.
Such methylol compounds may be prepared by any suitable method;
for instance, by the action of formaldehyde on aliphatic aldehydes
containing at least three C-atoms; the aldehydes may have a
straight or a branched chain, such as propionaldehyde, n-butyral-
dehyde, n-laurinaldehyde, n-oleyl aldehyde, iso-butyraldehyde, 2-
methyl pentanal or 2,4-dimethyl pentanal. The above mentioned
reaction with formaldehyde takes the course illustrated by the
equations given below:

$$R-CH_2-CHO \quad + \quad 3HCHO \quad = \quad R-C=(CH_2OH)_3 \quad or$$

$$\underset{CH_3}{R-CH-CHO} \quad + \quad 2HCHO \quad = \quad \underset{CH_3}{R-C=(CH_2OH)_2}$$
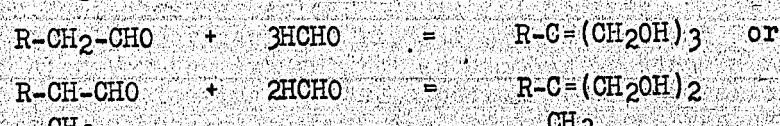
　　　　It will be best to use saturated fatty acids for the
esterification. They may be of straight-chain or branch-chain
structure. Straight-chain acids can be obtained, for instance, by
the saponification of natural fats and oils or, synthetically, by
the oxidation of paraffins or of analogous aliphatic hydrocarbons
in the liquid phase; another synthetic method is given below; the
starting point is acetaldehyde or crotonaldehyde; the reactions
can, for example, be made to run the following course:

$$CH_3-C=CH-CHO \quad + \quad xCH_3=CH=CH-CHO \quad \longrightarrow \quad CH_3(CH=CH)_x-CHO$$

$$\xrightarrow{+H_2} \quad CH_3-(CH_2)_x-CH_2OH \quad \xrightarrow{oxidation} \quad CH_3-(CH_2)_x-COOH$$
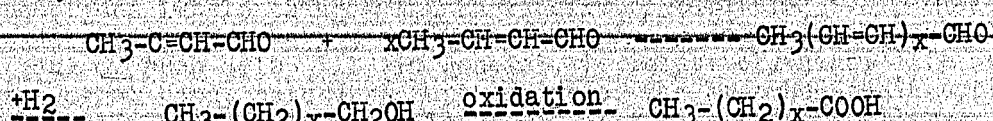
As to the branched fatty acids, they may be prepared, e.g., by oxidation of the corresponding alcohols; the latter in turn may be obtained by the conversion of carbon monoxide with hydrogen. The acids could, furthermore, be prepared from straight-chain aldehydes, as illustrated by the following reaction:

$$R-CH_2-CHO \quad + \quad H_2C-CHO \quad ----- \quad R-CH_2-CH = C-CHO$$
$$\qquad\qquad\qquad\qquad R \qquad\qquad\qquad\qquad\qquad\qquad R$$

$$-------- \quad R-CH_2-CH = C-COOH$$
$$\qquad\qquad\qquad\qquad\qquad R$$
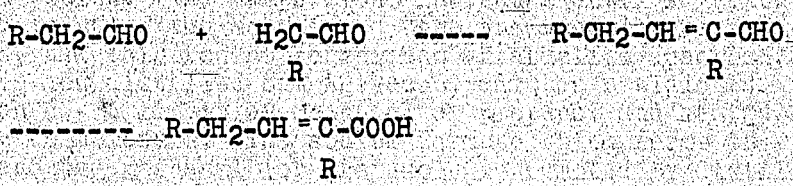
The esterification will take the usual well known course. It is advantageous to heat the methylol compound and the acid in the presence of a substance which is volatile in the presence of steam, such as benzene or toluene; at the same time, a condensing agent such as concentrated sulfuric acid or benzene sulfonic acid is added; the water which is formed is distilled off together with the benzene or the toluene. However, other known esterification methods can be used: one may, for instance, treat the methylol compounds with the anhydrides or chlorides of the suitable acids. In all cases, all the OH groups of the methylol compounds must be esterified.

The esters which are thus obtained have excellent dielectric properties and are therefore highly suitable as insulating oils for electrical purposes, such as the insulation of transformers, switches or cables. Above all however, these oils are very valuable lubricating oils, and may be used for this purpose either alone or in mixture with each other or even in mixture with other lubricating agents, especially the natural or synthetic hydrocarbon oils. Since they distinguish themselves by a very good lubricating capacity while at the same time exhibiting an excellent temperature-stability, they are especially well suited for the lubrication of explosion motors.

By a suitable choice of the esterification components, one can influence the properties of the lubricating oils according to desire and need. If the esterification is carried out with saturated fatty acids of the straight-chain type, especially with those of more than 12 C-atoms, oils are obtained whose viscosity undergoes little change with increasing temperature; i.e., these oils will have a very good viscosity index. However, the pour point of such oils will, in general, be relatively high. If, on the other hand, saturated fatty acids of the branched-chain type are used, oils with a very low pour point (i.e. of a smaller viscosity index) will be obtained. It is, however, possible to prepare an oil which not only has a very good viscosity index, but also a very low pour point; this is achieved by subjecting the methylol compounds to esterification with mixtures consisting of straight- and branch-chain fatty acids.

Example 1

To a mixture consisting of 1 Mol propionaldehyde and 3 Moles formaldehyde, a 50% aqueous solution of 1 Mol sodium hydroxide is added within a period of $\frac{1}{2}$ hour; during this time, the mass is not cooled. The temperature increases until it reaches the boiling point of the solution. Once the reaction has reached termination, the solution no longer has an alkaline reaction. The water is now distilled off in vacuo, and the residue is treated with 3 - 4 liters of methanol or propanol and heated to its boiling temperature. The sodium formate which forms is filtered off and the methanol (or propanol) is removed by distillation. The residue of this distillation is trimethylol-ethane, which can be used directly for the esterification which follows.

1 g-Mol trimethylol-ethane and 3 g-Mol of a mixture consisting of fatty acids with 9 - 11 C-atoms, are heated in the presence of 200 g benzene or toluene after addition of 2 g concentrated sulfuric acid or benzene-sulfonic acid. (The fatty acids are of the type obtained by the oxidation of paraffins: they are the first runnings in the process for the preparation of soap-forming fatty acids). The water which is formed distills together with the benzene (or toluene). After termination of the reaction, the ester is washed with soda solution, and is then subjected to a further treatment with bleaching earth. The characteristics of the product thus obtained are as follows: viscosity at 38°C. = 4.23°E; at 99°, the viscosity = 1.437°E; viscosity index = 133.9; pour point = -29°C.

If, instead of the above mentioned acids, a mixture of branched-chain carboxylic acids is selected (their chain length again being of 9 - 11 C-atoms) such as are obtained by the oxidation of the alcohols of the so-called isobutyl oil* a product of different characteristics is obtained: viscosity at 38° = 6.65°E; at 99°, the viscosity = 1.44°E; viscosity index = 64.7; pour point = -48°.

If the same procedure is used, but with a mixture of aliphatic carboxylic acids of the branched-chain type and with 6 - 13 C-atoms, such as were formed by the oxidation of the alcohols of the iso-butyl oil, one will get an oil of the following characteristics: viscosity at 38° = 4.44°E; at 99° = 1.392°E; viscosity index = 82.3; pour point = -54°.

If the same mixture of branched-chain fatty acids of 6-13 C-atoms is used together with 7.5% soap fatty acids (i.e. with mixtures of straight chain fatty acids containing 12 - 18 C-atoms), an oil of the following characteristics will result: viscosity38° = 4.93°E.; viscosity99° = 1.446°E.; viscosity index = 100.7; pour point = -41°. If 10% of the soap fatty acids be used,

*By the term "isobutyl oil" we mean a mixture of oxygen-containing organic compounds with 4 or more C-atoms, such as is formed by the reaction of CO with H_2, e.g. in the synthesis of methyl alcohol.

the resulting oil will have these characteristics: visc.38^0= 4.38^{O}E.; visc.99^0 = 1.443^{O}E.; visc. index = 100.6; pour point = -28°.

When the esterification of the trimethylol ethane is carried out with a mixture of aliphatic carboxylic acids of the branched-chain type and with 7 - 13 C-atoms (such as the carboxylic acids resulting from the oxidation of the alcohols of the iso-butyl oil), the product will have the following characteristics: visc.38^0 = 4.45^{O}E.; visc.99^0 = 1.384; visc. index = 77.3; pour point = -47°. If the above mentioned branch-chain carboxylic acids are used together with 50% lauric acid, the resulting oil will show the following values: visc.38^0 = 4.72^{O}E.; visc.99^0 = 1.434^{O}E.; visc. index = 101.3; pour point = -57.5^O.

Example 2

1 Mol of n-butyraldehyde is converted into trimethylol propane by means of 3 Mols of formaldehyde; the method used is the same as that described in Example 1. The trimethylol propane is then subjected to esterification, as described in Example 1, with a mixture consisting of the ff. acids aliphatic branched-chain carboxylic acids of C-number 7-13, obtained by the oxidation of the alcohols of the iso-butyl oil; 10% aliphatic carboxylic acids of C-number 7-11, obtained as first runnings in the oxidation of paraffin. An oil of the following characteristics will result from this esterification: visc.38^0 = 4.28^{O}E.; visc.99^0 = 1.397^{O}E.; visc. index = 97.2; pour point = -48°.

A portion of this ester is mixed with 9 parts of a hydrocarbon lubricating oil of the following specifications: visc.38^0 = 47.4^{O}E.; visc.99^0 = 3.68^{O}E.; visc. index = 106; pour point = -23°C. The properties of the mixture are: visc.38^0 = 33.2^{O}E.; visc.99^0= 3.05^{O}E.; visc. index = 109; pour point = -27°C. Comparison of the hydrocarbon lubricating oil with the ester, under the same operating conditions in an Otto-test motor, shows a running period of 11 hours for the former and of 14 hours for the latter. If, instead of adding the above mentioned ester, one adds 5% of a polymerized castor oil to the hydrocarbon lubricant, a running period of only 5 hours, under the same operating conditions, results.

Example 3

To a mixture consisting of 1 Mol lauric aldehyde and 3 Mols formaldehyde, enough methanol is added to achieve a complete solution; then, the properly calculated amount of 50% sodium hydroxide solution is added as described in Example 1, and the resulting mass is processed as described in the same example. Trimethylol-undecane will result, and its esterification is carried out with the same mixture of branch chain C_7-C_{13} aliphatic carboxylic acids as was used in Example 2. The esterification method is the same as that followed in Example 1. The reaction product has the following characteristics: visc.38^0 = 4.62^{O}E.; visc.99^0 = 1.415^{O}E.; visc. index = 92.9; pour point = -50°.

Example 4

A mixture consisting of 1 Mol of 2-methyl-pentanal-(1) and of 2 Moles of formaldehyde is condensed with sodium hydroxide solution as indicated in Example 1. The neutral reaction product is removed (upper layer), washed with water and then distilled. The dimethylol pentane boils between 120 and 140° at 10 mm Hg. Its esterification is carried out with a mixture of branched-chain aliphatic carboxylic acids (See Example 1) of C-number 9 - 13; this mixture was obtained by the oxidation of the alcohols of the iso-butyl oils from the methanol synthesis. The oil which results from the esterification has the following characteristics: visc.38° = 2.86°E.; visc.99° = 1.287°E.; visc. index = 103; pour point = -59°.

Example 5

1 Mol of 2,4-dimethyl pentanal-(1) is converted with 2 Moles of formaldehyde, as described in Example 4. Dimethylol hexane results from this conversion (b.pt. at 10 mm pressure = 125°- 145°); after esterification with a mixture of branched-chain carboxylic acids (C-number 9 - 13), obtained by the oxidation of the alcohols of the iso-butyl oil, an oil of the following characteristic values is formed: visc.38° = 2.42°E.; visc.99° = 1.26°E.; visc. index = 125.3; pour point = -55°.

If the above mentioned carboxylic acids be used together with 15% of a fatty acid mixture prepared by the oxidation of paraffin, the resulting oil will have the following characteristics: visc.38° = 2.94°E.; visc.99° = 1.16; visc. index = 127.3; pour point = -13°.

Example 6

A mixture consisting of hexyl and heptyl alcohols of the branched-chain type, obtained by the conversion of carbon monoxide with hydrogen, is dehydrogenated; the resulting aldehydes are then converted into their corresponding dimethylol compounds by the method described in Example 4. Thus, a mixture consisting of dimethylol pentane and dimethylol hexane is obtained. 60% of this mixture and 40% trimethylol ethane are brought together and subjected to esterification with a carboxylic acid mixture containing 7 - 11 C-atoms (obtained, as first runnings in the oxidation of parrafins into fatty acids); the ester oil resulting from this reaction will have the following characteristics: visc.38° = 2.02°E.; visc.99° = 1.213°E.; visc. index = 146.4; pour point = -70°.

Example 7

1 Mol of 1,4-butane-diol is esterified with 2 Moles of a mixture of aliphatic carboxylic acids of the branched-chain type; these carboxylic acids were obtained by the oxidation, in

alkaline surroundings, of the alcohols of the iso-butyl oils boiling in the range 140 - 250°. The esterification process follows the course described in Example 1. The resulting oil has the following characteristics: visc.$_{380}$ = 1.67°E.; visc. $_{990}$ = 1.17°E.; visc. index = 192; pour point = -76°. A portion of this oil is mixed with an equal volume of a synthetically prepared hydrocarbon oil of the following specifications: visc. 380 = 40.8°E.; visc. 990 = 3.53°E.; visc. index = 112; pour point = -36°; the mixture is characterized by the following data: visc. 380 = 5.25°E.; visc. 990 = 1.59°E.; visc. index = 149; pour point = -57°C.

Patent Claims

1. Process for the preparation of valuable oils, characterized by the fact that aliphatic hydrocarbons containing at least 3 carbon atoms and at least two or three primary alcohol groups are esterified with fatty acids containing at least 6 carbon atoms.

2. Process according to Claim 1, characterized by the fact that, for the esterification, a mixture of straight-chain fatty acids and of branched-chain fatty acids is used.

3. The use, for purposes of lubrication, of esters resulting from fatty acids of at least 6 C-atoms and aliphatic hydrocarbons of at least 3 C-atoms and which contain 2 or more primary alcohol groups, either alone or in mixture with each other, or in mixture with other lubricating agents, especially with the natural or synthetic hydrocarbon oils.

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