

HUMBLE OIL & REFINING COMPANY

REFINING DEPARTMENT
TECHNICAL AND RESEARCH DIVISION

LABORATORY
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U. S. GOVERNMENT TECHNICAL OIL MISSION

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Part II

R E S T R I C T E D

Item No. 2 Research

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(A) Comparison of Gasolines Prepared from Hard Coal Liquefaction Oil (Scholven) by the Various Processes (4-9-41)

Gasoline Catalyst Feed	VT 705 5058/634 Gasoline + Gas Oil	C.V. 216 7019 Gas Oil	Experimental Gasoline Ruhroel Process -----K413-----	
			Gasoline + Gas Oil	Gas Oil
Chamber Output		0.15-0.20	0.68	0.48
Gas Yield d15	0.741	0.786	0.773	0.775
Boiling Point Curve				
ASTM -100° (212° F.) Vol. %	60	35	48	49
F.B.P.	150°	160°	165°	165°
Aniline Point	45°	2°	16°	13°
Aromatics + Olefins, %	17	52	42	45
Octane No. (MM) Clear	72	79.5	78	79
+ 0.05% TEL (1.9 cc. por Gal.)	86	87	87	87
+ 0.12% TEL (4.55 cc. por Gal.)	90.5	90.5	90.5	90.5

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(B) Inspection of Gasoline from Hard Coal Sump Phase Gas Oil (Scholven) Prepared by the Ruhroel Process. Sample from Two Drums Made 3-8 and 3-23-1941 (4-1-41) (Table)

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(C) Inspection of Gasoline from Hard Coal Sump Phase Gasoline-Plus-Gas Oil (Scholven) Prepared by the Ruhroel Process. Sample from Two Drums Made 3-8 and 3-11-41 (3-25-41) (Table)

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(D) Inspection of Hard Coal Sump Phase Gasoline from Scholven. Average Sample from Two Drums Made 2-19-41 (2-28-41) (Table)

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(E) Note on the Aniline Point of Hard Coal Sump Phase Gasoline-Plus-Gas Oil from Scholven. See also Note of 1-28-41 (2-19-41)

The aniline points were as follows:

Fraction to 130°	+37.8° C.
Fraction to 150°	+33.5° C.
Fraction to 170°	+30.5° C.

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(F) Inspection of Untreated (Caustic-Washed) Coal Gasoline from Scholven Given by Dr. Urban in Discussion at Welheim on 2-18-41 (2-19-41) (Table)

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(G) Notes About the Operation of the 7019 Chamber in Scholven (1-31-41, Afternoon) (2-1-41)

Temperature	27.5 mV. at 30° Terminal Temp. (Appr. 1020° F.)
Feed	35 Parts Hard Coal A-Gas Oil 65 Parts Self-Produced B-Gas Oil
Abstreifer	25% to 30% Gasoline
Gasoline Phenol Content	0.03% to 0.1%
B Product Phenol Content	0.07%
B Product Anilino Point	-11°
Catalyst Space	16 m ³ (563 Cu. Ft.)
Feed Rate	10 Tons = 0.625 kg./1/hour (10 Metric Tons = 11.02 Short Tons = 63 Bbl.)
Yield	About 0.13 kg./1/hour (Calculated; Not Given by Dr. Schmidt)
Gas Yield	20% to 22%

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(H) Inspection of Sump Phase Gas Oil (A-Gas Oil) from Scholven (1-30-40; Probably Should Be 41) (Table)

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(H) Inspection of Coal A-Gas Oil from Scholven. Average Sample of Four Drums Made 1-15-41 (1-29-41) (Table)

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(H) Inspection of Hard Coal Abstreifer, Gas Oil Plus Gasoline Fraction (335° C. E.P. (635° F.)) from Scholven. Average Sample of a 10 m³ Shipment For Experiments in "Bau 42" (1-28-41) (Table)

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(J) Comparison of Sump Phase Gasoline and Gas Oil from Ruhroel, Scholven,
and Golsenberg-Benzin (11-16-40)

	Ruhroel			Scholven			Golsenberg		
	AP °C.	H ₂ %	C %	AP °C.	H ₂ %	C %	AP °C.	H ₂ %	C %
Frac. - 320° (108° F.) with Phenol and Pyridine	<-25	9.3	89.7	-17.2	10.4	86.5	-23.5	10.3	85.4
Frac. - 320° without Phenol and Pyridine	<-25	9.2	90.4	-12.6	10.5	88.6	-14.0	10.6	87.6
Frac. - 165° (329° F.) with Phenol and Pyridine	-4.4	12.3	87.2	+30.5	14.0	85.7	+27.8	3.2	86.3
Frac. - 165° without Phenol and Pyridine	-5.2	12.6	87.4	+30.5	14.0	85.9	+27.3	13.4	86.5
Frac. - 165°-320° with Phenol and Pyridine	<-25	8.7	89.0	<-25	9.5	86.6	<-25	9.9	85.6
Frac. - 165°-320° without Phenol and Pyridine	<-25	8.8	90.0	<-25	9.8	89.4	<-25	10.2	88.0

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The 320° (608° F.) E.P. was cut from the sump phase Abstreifer in a Hempel column.

	<u>Ruhrroel</u>	<u>Scholvon</u>	<u>Gelsenberg</u>
Density at 15°	0.968	0.923	0.930
Engler Dist.:			
I.B.P.	62° C.	50° C.	60° C.
5 Vol. %	114° C.	78° C.	104° C.
15 " "	185° C.	145° C.	162° C.
25 " "	216° C.	185° C.	195° C.
35 " "	236° C.	207° C.	215° C.
45 " "	251° C.	228° C.	231° C.
55 " "	265° C.	244° C.	248° C.
65 " "	279° C.	261° C.	262° C.
75 " "	290° C.	276° C.	277° C.
85 " "	303° C.	294° C.	291° C.
95 " "	318° C.	320° C.	311° C.
F.B.P.	98.5%/324° C.	97%/323° C.	98%/324° C.
Bottoms, %	0.5	1.0	1.0
Loss, %	0.5	1.0	1.0
% at 100°	3.0	7.5	4.5
" " 170°	12.0	21.0	17.0
" " 185°	15.0	25.0	21.0
" " 200°	19.0	32.5	27.0
" " 300°	84.0	89.0	90.0
"Tiefk" (?), %	0.5	1.0	-
Aniline Point	<25° C.	-17.2° C.	-23.5° C.
Phenol, %	4.3	13.4	17.0
Pyridine, %	4.0	2.4	2.4
Elemental Analysis:			
C, %	89.72; 89.70	86.53; 86.56	85.43; 85.39
H ₂ , %	9.47; 9.34	10.49; 10.59	10.27; 10.36

Pages 549-550, 553-556

(K) Inspection of an Abstreifer Made by Leuna in Experiments on Hydrogenation of Soft Coal A-Gas Oil over Ruhrroel Catalyst (Sample Taken-3-19-41) (4-7-41, 3-19-41) (Tables)

Pages 551-552

(L) Inspection of Leuna - Aviation Gasoline VT 702. Average of a Ten L. Sample (4-7-41) (Tables)

Page 557

(M) Note Concerning the Status of the Experiments on Hydrogenation of Soft Coal Over Ruhrroel Catalyst K-429 in Leuna (3-3-41)

The run is being made at 700 atmospheres gasoline-recycle-gas (= about 600 atm. (8840 psi) H₂ partial pressure) and a temperature of 26.5 mV. The feed rate was left constant for ten days after being slowly brought to 1 kg./k/hour.

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At a feed rate of 1 kg./l/hour pure A-gas oil gave 80 to 85 per cent gasoline (F.B.P. 165° (329° F.)) and a residue of final boiling point 260° to 280° (500° to 536° F.). The ten per cent phenol in the feed was reduced to 0.5 to 0.8 per cent. The aniline point of the gasoline was about +30° (86° F.) that of the residue about +16 to +24° (60.8-75.2° F.).

An improvement in the phenol value and possibly in the aniline point is to be expected by recycling the B-product. The feed rate was increased to 1.5 kg./l/hour to make more B-product. This lowered the gasoline concentration to about 65 per cent and raised final boiling point of the residue to about 315° C. The phenols rose to 1.3 to 1.8 per cent while the aniline point remained practically unchanged. According to the last two reports from Leuna the feed rate was further increased to 1.7 and 1.8 kg./l/hour. The gasoline concentration sank correspondingly to 60 per cent.

The following is proposed for the continuance of the experiment.

1. The own B-product which is now available in larger amounts should be recycled, mixed with the A-product in the ratio of production.

2. Preliminary experiments in the 50 cc. reactor have shown that in order to get a good aniline point of the B-product it is better to obtain the desired 50 to 60 per cent gasoline concentration not by increasing the feed rate but by reducing the pressure. It is proposed, therefore, to reduce the feed rate again to 1 kg./l/hour and at the same time reduce the total pressure until the gasoline concentration becomes 50 to 60 per cent. The feed must in this case be a mixture of A-product and own B-product since too high a phenol concentration at lower pressure can damage the catalyst. (Table of run conditions on the next frame.)

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(N) Inspection of One Barrel (No. 209) of Leuna A-Gas Oil Received
2-18-41 (2-19-41) (Table)

Pages 560-570

(N) Correspondence on Gas Oil Hydrogenation Experiments at Leuna (2-19-41)

Page 560

(N) Letter - Winkler to Schunck

The first four results of the 700 gas phase experiments have been received. From these it is seen that the gasoline yield even at the feed rate of 1 is still too high (85 per cent) so that practically no B-product is produced.

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It was therefore proposed to raise the feed rate until the gasoline yield is 50 to 60 per cent and then mix the corresponding B-product with the A-product. The phenols will thus, as in the first experiment, again be reduced to below 0.1 per cent. It is remarkable, however, that with this catalyst already a stronger aromatization takes place as indicated by the aniline point of the gasoline of 165° E.P. When recycling the B-product the aniline point and therefore also the aromatic content will be improved.

Pages 562-563

(N) Inspection of Soft Coal A-Gas Oil (Sample from Leuna, Jan. 1941)
(2-4-41)

Page 564

(N) Inspection of Soft Coal B Product from the 5058 Chamber (Sample from Leuna, Jan. 1941 (2-4-41)

Pages 565-566

(N) Letter Concerning 700 Atmosphere Experiments with Ruhroel Catalyst
(From Ruhroel to Leuna) (1-27-41)

The following conditions are proposed for the second experiment with Ruhroel catalyst and soft coal gas oil.

1. To prevent unnecessary abrasion use the catalyst as delivered (6 mm. pills).

2. To obtain more quickly a result for the obtainable gasoline quality we proposed to use as feed pure soft coal A-gas oil. The first experiment has indicated that our catalyst with a feed of 5 per cent phenol will reduce that completely. However, it could be possible that a phenol content of 10 per cent in A-gas oil might damage the catalyst. We considered it therefore necessary to use a B-gas oil as soon as possible in recycle.

3. We request to bring the reactor to 26.0 mV. and leave it at this temperature for 24 hours without feed. After feed injection is begun, the temperature is to be brought slowly to 26.5 mV.

4. As product:gas ratio we again recommend 1:3000. The gas is to be gasoline-recycle gas with about 85 per cent H₂.

5. We request to have the feed rate again raised slowly starting at 0.2 kg./1/hour, about as in the first experiment. The feed rate shall be so arranged that the gasoline concentration in the Abstreifer (cut point 165° column distillation or 170° Engler distillation) is not over 60 per cent. If this has not been obtained with a feed rate of 1.5 kg./1/hour, we propose not to increase the feed rate any more but to reduce the pressure.

6. 700 atmosphere is the preferred experimental pressure. This pressure is to be reduced until the desired gasoline concentration in the Abstreifer is obtained if the conditions mentioned in 5 above occur.

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(N) Cover Letter for Note of 1-24-41 Concerning Hydrogenation of Soft Coal Gas Oil in the Gas Phase at 700 Atmospheres (1-27-41)

It is remarked that the high gasoline yield (1.6) cannot be easily handled in a large reactor and that, therefore, for the Louna gas oil a second catalyst has been introduced into the experimental reactor whose cracking activity is less and aromatization properties are stronger. With this catalyst still better results in the desired direction are expected.

Pages 568-570

(N) Notes Concerning Hydrogenation of Soft Coal Gas Oil Over Ruhroel Catalyst (1-24-41)

The following additional report is made for the experiment period of January 7 to 17.

Under the direction of Dr. Doellein an experiment at 700 atmospheres was started on January 7 in the 5 kg. reactor in Building MEA 69 at Ammoniakwerk Merseburg. It was to be tried if soft coal gas oil could be hydrogenated according to the procedure found best at Ruhroel with hard coal pitch gas oil, and what quality gasoline could be obtained by this procedure. Since no experience was available concerning the hydrogenation susceptibility of soft coal product according to the Ruhroel method, the catalyst was first so chosen that in spite of the higher phenol content of the feed (soft coal A-gas oil had about 10 per cent as compared with 3 per cent phenol in pitch gas oil) reduction of the phenol would be assured. In the course of this experiment it was shown that the phenols of the soft coal gas oil are considerably easier to reduce than those of the pitch gas oil. At a feed rate of 2.0 kg./l/hour and a hydrogen partial pressure of 450 atmospheres the phenol content of the Abstreifer was 0.01 per cent. On the other hand the catalyst was so active that in spite of a feed rate of 2.0 kg./l/hour and a reduction of the pressure to 450 atmospheres partial pressure 82 volume per cent gasoline (cut point 165°) was still contained in the Abstreifer. There was no B-gas oil since the total Abstreifer had a final boiling point of 220° to 230°. The residue was a heavy gasoline.

The experiment should, therefore, be only considered as a preliminary experiment. It has shown us that we can weaken the hydrogenation components of the catalyst considerably without having to fear poor phenol reduction. This weakening will then produce a reduction of gasoline yield so that B-product can be recycled. We hope to obtain by this method a considerable increase of aromatics in the gasoline and to increase the octane number which in the preliminary experiments was already 79.5 research.

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The reactor had 5-liter catalyst space. The catalyst K413 was delivered in 6 mm. pills which were crushed into smaller pieces at Louna.

Since it was feared that the high phenol content of 10 per cent in the soft coal A-gas oil might damage the catalyst, the experiment was begun with a mixture of A-gas oil with B-gas oil from the 5058 chamber (1:1). This feed had a density of 0.870, an aniline point of 32°, a final boiling point of 325° and a phenol content of about 5 per cent. The gas was taken from the gasoline recycle stream of the plant. It contains about 85 per cent hydrogen.

The experiment was started on January 7, with a feed of 0.2 kg./l/hour at a temperature of 26.0 and a pressure of 700 atmospheres (about 600 atmospheres hydrogen partial pressure) and a product to gas ratio of 1 to 3,000. The feed was slowly increased to 1.0 kg./l/hour by January 9 and the temperature to 26.5 mV. Since at this feed rate the total Abstreifer distilled at 162°, the feed was raised to 2.0 kg./l/hour by January 13, while keeping the temperature and product to gas ratio unchanged. Also, starting on January 11, the pressure was reduced to 600 atmospheres (about 510 atmospheres hydrogen partial pressure). Even at these reaction conditions 90 per cent of the Abstreifer boiled at 165° and the final boiling point of the Abstreifer was 230° to 250°. The pressure was therefore further reduced to 530 atmospheres (450 atmospheres hydrogen partial pressure) on January 15. The gasoline concentration in the Abstreifer was still 85 per cent while the final boiling point of the Abstreifer remained 225°. At 4 P.M. on January 17 the reactor had to be taken off stream since the pressure differential became too high. Examination showed the lower part of the reactor and the sieve to be full of asbestos fiber which probably came from the packing material of the pump packing gland. The removed catalyst was satisfactory. Abrasion was slight considering that the catalyst had a very angular shape and that it had been exposed to a high feed and gas rate. No conclusion should be drawn from the gasoline quality values obtained so far. As previously mentioned, the activity of the catalyst is too high for soft coal gas oil. A clear picture can be obtained only when the feed contains no 5058 B-gas oil and the self-produced B-gas oil is recycled. Nevertheless, it should be noted that the 165° E.P. gasoline according to an analysis in Louna had 50 to 60 volume per cent below 100, an aniline point of about 40°, and an octano number of 79.5 (research method). Loss calculations must naturally give a higher value at the enormously high activity of the catalyst than when a milder catalyst is used at a yield of about 0.5 kg./l/hour and a gasoline concentration in the Abstreifer of 50 to 60 per cent. The balances for January 16 gave a loss of 16-17 per cent based on total feed, and of 14-15 per cent based on oxygen-free feed. In this calculation the light ends condensed from the Abstreifer release-gas are calculated half as product and half as gas yield.

The experiments are being continued with our milder catalyst K429. In this new series of experiments only pure A-gas oil is used as feed in spite of its 10 per cent phenol content, to obtain quicker results. We hope, judging from the previous experiments, that the catalyst will reduce this high phenol concentration without suffering damage. Conditions are to be so arranged that the Abstreifer will contain only 50 to 60 per cent gasoline (to 165°). After recycling of the self-produced B-product final reports about gasoline quality and losses can be made.

Pages 571-573

(0) Current Operating Conditions of the Gas Oil Vapor Phase Hydrogenation at Louna (1-16-41)

1. 5058 Chamber

Catalyst	5058
Feed Rate	0.8 to 1.0 kg./1/hour
Temperature	19-22 mV.
Gas Yield	Slight, Only H ₂ O, NH ₃ , and H ₂ S Splitting Off
Feed:	Soft Coal A-Gas Oil
D ₄₁	0.910
Aniline Point	+15° C.
Initial Boiling Point	70° C.
Final Boiling Point	325° C.
Phenol, %	10
Hydrogen, %	10.0 to 10.5
Abstreifer:	
D ₄₁	0.800-0.805
Cut Point of Gasoline	120°
-120°	20 to 25 Volume %
Aniline Point	
Abstreifer	50°-55° C.
Aniline Point -120°	55° C.
>120°	55° C.
Phenol, Wt. %	<0.5

The chamber is operated to keep the phenol content below 0.5 weight per cent, so that the feed for this chamber in mixture with the recycle oil from the 6434 chamber has a phenol content below 0.2 weight per cent.

2. 6434 Chamber

Catalyst	6434
Feed	0.8 kg./1/hour
Temperature	20-24 mV.
Gas Yield	The total yield from the A products inclusive of losses by O, N, and S is 78 per cent for aviation gasoline (product factor 1.28) and 98 per cent for motor gasoline (product factor 1.11)
Feed:	5058 B-Gas Oil:6434 Feed Gas Oil = 1:1
D ₄₁	0.800
Aniline Point	50°-55° C.
Initial Boiling Point	120° C.
Final Boiling Point	320° C.
Phenol, %	0.2
Hydrogen, %	13.5-14.0
Sulfur, %	0.3-0.4

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The high sulfur content is obtained by introducing H₂S.

Abstreifer

D ₄ ²⁰	0.750-0.760
Gasoline Cut Point	140° (Conditioned by octane number which must be 71)
-140°	45 Volume %
Aniline Point/Abstreifer	50°-55° C.
Aniline Point -140°	50°-55° C.
Aniline Point >140°	50°-55° C.
Phenol, %	0.02

3. Refining of Gasoline

The gasoline is caustic-washed and the wash is so arranged that about 0.02 per cent of the phenols remain in the gasoline as inhibitor. Stabilization follows.

4. VT 702

Feed:

D ₄ ²⁰	0.720
-100°	65 Volume %
Initial Boiling Point	140°-145° C.
Aniline Point	50°-52° C.
Hydrocarbons:	
Aromatics	5-7 Volume %
Olefins	2-3 Volume %
Naphthenes	40 Volume %
Paraffins	50-53 Volume %
Hydrogen	15 Weight %
Sulfur	<0.001%
Octane No. (Motor Method in CFR Motor):	
Clear	71.72
0.8-0.9 TEL*	87
1.2 TEL	90.5-91.5

* Units doubtful.

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(P) Preliminary Notes Concerning Experiments with Ruhroel Catalyst K413 in Leuna (Written by Ruhroel) (1-15-41)

Catalyst Composition: 60 per cent ADV paste, 40 per cent Terrana, 2 per cent Cr as CrO₃, 5 per cent Zn as ZnO, 0.4 per cent Mo as (NH₄)₂ MoS₄ per 100 gram carrier 7.5 grams HF.

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Form 6 mm. Pills, Corrugated

The catalyst pills were crushed at Leuna and used in smaller pieces.

Apparatus

Laboratory of Dr. Doellein, oven 201. The oven consisted of a N_{10} pipe of 45 mm. I.D. and 3620 mm. length. Catalyst volume about 4.9 l. Spaced along the reactor were 6 temperature points. Of these only 4 had the prescribed temperature while the top and bottom ones were 1.0 to 1.5 mV. lower. The reactor was heated by only two heating circuits and one reactor-head heater (We have three heating circuits and one heater each for head, foot, and transfer line. Thus we obtain a constant temperature throughout the catalyst volume.)

The electrical heaters are not insulated. To obtain better temperature distribution compressed air is blown in between the high pressure pipe and the electric heater.

Feed

The feed should not have a high phenol content and therefore a soft coal A-gas oil, and B-gas oil from the 5058 chamber were mixed in 1:1 ratio. Analyses are given for:

Soft Coal A-Gas Oil (for Ka. 9, 10, 11, 16 of 1-4-41)

B-Gas Oil from the 5058 Chamber (Residue? Installation I Me 821 of

6-1-41

1:1 Mixture of A- and B-Gas Oil

Gas (Average Composition)

H ₂ S	0.12
CO ₂	0.0
O ₂	0.0
H ₂	86.3
CO	0.5
Hydrocarbons	6.2
N ₂	6.9

The gas was taken from the gasoline circulation system.

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Operating Conditions

The chamber was brought on stream with a gas throughput of 15 m³ on 1-5-45 and was at 23 mV. on 1-6-45. The temperature was raised to 26.0 mV. at noon and remained there until 5:00 A.M. on 1-7. Feed injection was started at 5:00 A.M. on 1-7. Further progress of the experiment is recorded in a table.

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R E S T R I C T E D

Run Day	Operating Conditions					Analysis of "Abstreifer"						
	Temp., mV.	Throughput m ³ /Hr.	Press., Atm.	Feed Rate, Kg./Hr.	D ₂₀	Engler		Aniline Point		Phenol, Wt. %		
						-100°	-170°	Total	>170°			
7-1-41 (1500)	26.0	15	700	0.2, 0.3, 0.4	0.711	75	91	170	49.4	50.9	-	0.84
8-1-41 (1000)	26.0	15	700	0.5, 0.6, 0.7	0.704	78.4	-	155	48.5	49.2	-	0.04
9-1-41 (1030)	26.5	15	700	0.8, 1.2	0.703	75	-	162	45.1	45.9	-	0.02
10-1-41 (1030)	26.5	17	700	1.2, 1.4	0.718	57	94.5	200	45.7	45.8	-	Traces
13-1-41	26.5	-	600	2.0	0.736	48	89.5	-	-	40.5	38	0.01
26.5				2.1	0.747	36.6	31.6	256	-	39	36	

MSB:art

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Q. Comparison of Catalyst 7019 at 300 atmospheres and 346/349 at 600 atmospheres for the hydrogenation of coal gas oil at Scholven.

After a comparison of the various feeds, Abstreifers, and gasoline from the Scholven hydrogenation at 300 atmospheres over 7019 catalyst on the one hand, and the Ruhroel process at 600 atmospheres over 157/335 catalyst on the other hand, had been reported on 7/27, the Scholven feed for the 7019 chamber was run under various conditions according to our procedure over the newest catalyst K-346/349, as part of a series of tests. The results have been compared with the experimental results which were obtained at about the same time and from the same feed in Scholven in a plant scale experiment with the 7019 chambers.

In Table I, gasolines of various final boiling points have been cut from a 7019 Abstreifer and two 346/349 Abstreifers which were obtained in one case with fresh gas and in the other case with very dense recycle gas. Their most important analytical data were determined.

Table II shows the composition of approximately qualitatively equal gasolines prepared (1) according to the 7019 procedure at middle gas density and (2) the Ruhroel procedure, one with fresh gas, and the other time with very high density gas.

The results can be summarized as follows:

1. The gasoline according to the Ruhroel has more naphthenes and paraffins than the 7019 procedure gasoline. The motor octane number, however, shows even for the original gasoline and particularly for the leaded gasoline equally good knock quality within the limit of measurement.
2. The octane number decreases for both gasolines with increasing cut point, for the 7019 procedure however, considerably faster than for the Ruhroel procedure. (Note: There is a penciled question mark in the margin, opposite 2.)
3. The components boiling up to 100 degrees are much larger for the Ruhroel procedure. This as well as the fact noted under 2 permits cutting the 346/349 gasoline considerably higher than the 7019 gasoline (185-190° versus 160°) for attainment of equal quality; a larger chamber yield can thus be obtained.
4. Under equal treatment of the gasoline (caustic wash) the 346/349 gasoline gives a light stable gasoline while the 7019 gasoline discolorizes after a few days. Other refining tests give approximately equal values.
5. The 7019 gasoline has a higher iodine number.
6. The most significant difference between the two procedures is the gasoline yield per reactor unit and time unit which can be obtained. For preparation of equal quality gasoline the Ruhroel procedure with fresh gas gives a 5.4 and with extremely high recycle gas a three times larger yield than the 7019 procedure at medium gas density. At the same time the reaction temperature for the latter procedure is 10-15° C. higher than for the Ruhroel procedure.

This investigation was to give an approximately quantitative comparison of the two methods. It must be considered, however, that the feed was run only once through. There will be a certain shift in gasoline quality when the Ruhrcoel procedure is run with pure coal A-gas oil and under recycle of the own B-product.

A decrease in output is not to be expected but, since the more aromatic A-gas oil would be present in higher concentration in the feed (because of the greater yield of the process) under approximately equal hydrogen content of the 7019 and 346/349 B-product, the quality of the gasoline would be improved. (Tables given on film.)

Pages 586-588

R. Treating Experiments with Scholven Gasoline Produced Over Catalysts 5058 and 6434 (Bottrop 8/9/40)

The treating experiments which are given in the following table were made on gasolines obtained from the Scholven gas phase stripper as part of our series of treating experiments. The purpose was to obtain treating data to be compared with our gasolines, regardless of motor performance. The gasolines were cut (1) to 190° C. (corresponding to our conditions) and (2) to 160° C. (corresponding to the actual motor requirements). The treat was made in the laboratory under the usual conditions, including rerunning.

Remarks concerning the results: (1) light stability of the samples is very good (in diffuse light), (2) the inhibitor effect noted by us is also present in the Scholven gasoline, particularly the one with the higher cut point. (Tables given on film.)

S. Discussion in Welheim on 1/29/41 concerning the Use of 700 Atmosphere Vapor Phase at Blechhammer for Ausbau II (1/29/41 Schlesien-Benzin)

Dr. Kroenig reported that it had been definitely decided to proceed with the gasoline production (Benzinierung) at Blechhammer in Ausbau* I at 300 atmospheres and that no change could be made in this. For Ausbau II, however, the question of using 300 or 700 atmosphere vapor phase is still open. It would have to be decided by 4/1/41 at the latest. For Ausbau II about 120,000** residual gasoline (Sumpfbenzin) and gas oil (-325°) are available in which, according to our present estimate, there are 48,000** gasoline (-200°.)

Dr. Winkler declared this amount to be approximately right for 2 two-stage aromatization reactors. The high gasoline content in the feed would be a disadvantage.

Dr. Kroenig remarked to this that it seems fundamentally possible to undertake an exchange between Ausbau I and Ausbau II so that Ausbau II gasoline is given to Ausbau I and Ausbau I returns the corresponding amount of gas oil to Ausbau II. The limits for this exchange are to be determined by the following considerations:

1. In Ausbau I the amount of gasoline is not to become so high and the gas oil so low that too mild a Beaufschlagung of the two double 6434 chambers takes place.
2. The exchange between gasoline and gas oil in Ausbau I should not go so far that the octane number of the gasoline from Ausbau I is lowered appreciably.
3. The exchange should not go so far that the heavy gasoline fractions available for DHD from Ausbau I are decreased too much.

Without complete investigation it can be assumed that the gasoline fraction (-125°) from Ausbau II which is about 60 per cent of the gasoline (about 29,000 tons/year) may be exchanged against gas oil from Ausbau I. Concerning the distillation, cutting out the fraction to 125° seems feasible. Dr. Kroenig agreed to notify Dr. Winkler later whether, according to IG, the exchange is possible to this degree. Dr. Winkler would then orient his experiments in that direction. After additional testing and experimental work Dr. Winkler is to submit a report and work-scheme for Ausbau II containing all data necessary for making the decision.

About gasoline VT 706b, obtained at 700 atmospheres from pitch gas oil, having 165° F.B.P., and stabilized at Scholven, Dr. Winkler reported the following data: (the gasoline was treated with 0.5% of 96 per cent sulfuric acid and then with 10 per cent caustic. Then it was rerun with three per cent gas loss.)

*Ausbau expanded unit.

**Units not given; presumably tons.

D15	J.800
Cloud Point	-4° C.
Crystallization begins below	-60° C.
Vapor Pressure	0.4 atm.
Distillation:	
I.B.P.	42 °C.
10%	75.5
20%	83.5
30%	91.0
40%	97
50%	103
60%	113
70%	125
80%	137
90%	153.5
95%	164.5
F.B.P., 98% at	170
Residuum	0.9%
Reaction of Resid.	Neutral
100° Point	45 Vol. %
Index No. (Kennziffer)	114.1
Aniline Point	-4.5
Aniline Point (Aromatics Removed)	47.5
Corrosion	Neg.
Doctor Test	Neg.
Glass Bowl Test	0.02 mg.
Bomb Test	0.12%
Resin not Taken Up	18.4 g/100 cc.
Resin Taken Up Directly*	8.6 mg./100 cc.
Lead Sludge	12 mg./200 cc.
Iodine No.	2.4
Aromatics Plus Olefins	51 Vol. %
Naphthenes	37 Vol. %
Paraffins	12 Vol. %
Elements:	
C	88.38%
H	11.61%
S	0.0072%
Octane Number (Motor Method):	
Clear	81
0.05% lead	87.5
0.12% lead	91.0

* Allowable limit 10 mg.

Dr. Winkler recommends to contact Dr. Dehnlow of the Luftfahrtministerium Berlin, concerning the valuation of the Welheim gasoline and also of the CV_{2b}, and DHD gasoline. As far as he knows CV_{2b} of Scholven does not satisfy requirements of the Luftwaffe concerning iodine number, light stability, and resin test. The DHD gasoline is supposed to be unsatisfactory in the lead sludge test. It is fundamental for this series of high quality gasolines that they have a minimum

aromatic content of 50 per cent. The Welheim gasoline is added to the 87 (octane?) gasolines to the extent of 70 per cent so that the aromatics content of the mixture is 40 per cent.

The Welheim gasoline is prepared in a chamber containing 10.5 m³ catalyst. This chamber consists of:

- 2 "regenerators" (heat exchangers ?)
 - 1 gasheated preheater
(heating gas consumption 4000 m³/hr. with 5,500 heat units (WE))
with 23 return bends (Haarnadeln)
 - 2 Ovens
 - 1 Oven 900 mm ID, 12 m long and
 - 1 Oven 1000 mm ID, 15 m long
- Both ovens have standard insulation.

The ovens have no Blenden (baffles?) but temperature distribution is nevertheless excellent. At a feed rate of:

9 t/hr. fresh oil: B - gas oil = 1:1
28000 m³/hr. inlet gas (72-74% H₂ = 450 atm. H₂ partial pressure)
5000 m³/hr. cold gas

The temperatures were as follows:

Reactor 1	1	2	3	4	5	6
Thermocouple						
Millivolt	25.1	25.5	25.7	26.2	26.2	26.2

Reactor 2	112	111	110	109	108	107	106	105	104	103	102	101
Thermocouple												
Millivolt	25.0	25.1	25.5	25.8	26.0	26.2	26.0	26.2	26.2	26.0	26.2	26.0

Regulation of the temperature at an output of 0.4 presents no greater difficulties than in the 5058-chamber which has been in operation for a long time. Only three times in two years of operation has the chamber "gone high" and in each case mechanical difficulties, not the process itself, were to blame. At a feed of 10.5 tons per hour the amount of inlet gas is 28,000 m³/hour, the cold gas 6,000 m³/hour. The stripper concentration is 50 to 55 volume per cent. In the "Benzinie-rung" of "Sumpf" gasoline and gas oil from the pitch chamber the losses at high pressure are 12.4 per cent, the losses in stabilization and transport to Scholven 3.1 to 5.1 per cent. Dr. Winkler will prepare a C-balance which will show the exact composition of the gas formation, including fixed gases (stabilgas). In a preliminary investigation the composition of the gasified carbon without fixed gas was as follows:

C₁ = 16.2
C₂ = 22.1
C₃ = 31.8
nC₄ = 21.1
~~10₄ = 8.8~~

The hydrogen consumption is 700 IG m³/ton of unstabilized gasoline. A recycle gas wash is not used. The aromatization chamber serves as gas wash for the "Sumpf" chamber in whose circuit it is.

Dr. Winkler expects catalyst life or at least $\frac{1}{2}$ year, probably 1 year. The longest catalyst life attained in industry until now was 180 days. Checking the catalyst after a run in the small reactor showed that it still had good activity. In any case the loss of catalyst activity, if there is any at all, is considerably less than that of 7019 in Scholven. The catalyst is used in the form of 10 mm. pills. It is practically free of bewirtschaftet metals. The catalyst will be furnished by Welheim. Roughly the cost of catalyst was estimated to be about 1500 Reichsmark/m³. The apparent density (Schuetzgewicht) is 0.65. The hardness is excellent. The new catalyst has been changed from the previous one so that it furnishes aromatic gasoline immediately when put on stream whereas the previous catalyst had to lose a peak (Spitze) before furnishing highly aromatic gasoline.

As to the postwar usefulness of 700 atmosphere gas phase hydrogenation Dr. Winkler remarked that the cut point of gasoline would then be 185° F. He was convinced that even for the use as motor gasoline a premium price could be obtained as compared to 70 (octane number?) gasoline, since the Welheim gasoline at 185 cut point has immediate "Aral-" quality and furthermore is a desirable blending gasoline for Fischer gasoline. If aromatic gasoline should not have a peace-time market there would still be the possibility of preparing a hydrogen rich gasoline using somewhat modified catalyst at a temperature of 22 mV.

Summary

The discussion resulted in the conclusion that for Ausbau II Blechhammer the application of 700 atm. vapor phase hydrogenation seems very advantageous under the following conditions:

1. That the exchange of "Sumpf" gasoline and gas oil between Ausbau I and Ausbau II without changing the performance of Ausbau I is possible.
2. That from Scholven gas oil at 700 atmospheres a high quality gasoline can be obtained which satisfies the requirements of the Luftwaffe.
3. That the lesser yield of isobutane in the aromatization process is permissible.

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T. Aromatization of Gas Oil from Coal Liquefaction (April 10, 1941)

1. Summary

For the preparation of high quality gasoline from hard coal liquefaction products, several processes can be considered. These are essentially aromatization with various catalysts under various reaction conditions particularly under various pressures, and the DHD process in various combinations. This report contains the main results obtained in the aromatization of hard coal liquefaction product with a catalyst of the Ruhrcoel in Ludwigshafen.

Since at 600 atmospheres hydrogen partial pressure a sufficient aromatic content was not obtained, the hydrogen partial pressure was reduced to the value of 450 atmospheres which is frequently used industrially at Welheim. After a lengthy run the following results were obtained.

Starting Material	Without "Sump" Gasoline	With
Spec. Wt.	0.974	0.904
% -200 °C.	9.5	38
F.B.P., °C.	330	323
Reaction Conditions:		
Operating hours	967	1031
H ₂ pressure, atm.	450	450
Temperature, °C.	500	500
Throughput	1.1	1.5
Gasoline output kg/1/hr.	0.41	0.56
Gas yield/gasoline & gas made	19	15.7
Gasoline:*		
Spec. Wt.	0.780	0.771
Aniline point	8.0	15
% -100 °C.	35	47
F.B.P., °C.	167	165
Vol. % Aromatics & Olefins	42	36
Iodine No.	11.5	15.2
Octane No. CFR MM:		
Clear	79.5	75.5
/0.12 Pb	90.5	90.5

*Gasoline from the first operating period of the 2 L. oven at 600 atm. H₂ pressure.

An aromatic content (plus olefins) of 50 volume per cent as obtained from pitch gas oil under equal conditions was therefore not attained from the hard coal gas oil using Welheim catalyst. Contrasted to pitch gas oil the phenol content of the products was high. The content of aromatics plus olefins using hard coal gas oil alone was 42 volume per cent and with addition of "Sumpphase" gasoline corresponding to the operation for heating oil, was 36 volume per cent. It is questionable whether gasolines with this aromatics content are satisfactory. A rich mixture curve is available so far for only one gasoline with 36 volume per cent aromatics plus olefins* from a test with Oppau; it was below the C₃ curve. In other respects the gasolines was satisfactory (except for too high an iodine number); however, the tests have not been concluded.

2. Experiments in the 2-Liter Reactor

In a reactor with 2-liter catalyst volume and attached column for distillation of Abstreifer product aromatization experiments were carried out using

* The gasoline is from the first operating period of the 2-liter reactor at 600 atmospheres hydrogen partial pressure.

catalyst shipped to us by Dr. Winkler, Ruhrcoel, Welheim, on January 28, 1941. A Scholven hard coal liquefaction gas oil* served as starting material for the experiments. It was run with and without "Sumpf" gasoline.

The following table shows the analysis of the starting material after redistillation without "Sumpf" gasoline and with an addition of Scholven "Sumpf" gasoline (approximately the ratio of the heating oil production method).

Starting Material	Without "Sumpf" Gasoline	With Gasoline
Specific Gravity	0.974	0.904
Aniline Point, °C.	-20	-10.5
I.B.P., °C.	173	54
% to 150° C.	-	26
200	9.5	38
225	27	48
250	40	61
300	79	86
325	96	-
F.B.P., °C.	330	323
Phenol Content, %	17.4	13

The run was started with liquefaction gas oil under addition of phenol-free aromatization B gas oil in the ratio of 1:1 at 600 atmospheres hydrogen pressure. After 40 hours run time a change to recycle was made and a temperature of 25 mV (40° terminal temperature) was first chosen. The values so obtained (82 run hours) are shown in the following table. According to this, with 1.1 kg./l/hour throughput at a yield of 0.59 and 14.5% gasification per gasoline plus yield,** a gasoline with 33 volume per cent aromatics*** is obtained. (Table on microfilm, page 5 of the paper) Since this aromatics content was too low, a change was made from pitch and coking tar to gas oil. At 25.5 mV a gasoline of 38 to 40 volume per cent aromatics was thus obtained. After 460 run hours, Scholven gas oil was again used and now (506 run hours) a yield was obtained of 0.44 at a hardly changed aromatics content of 35 volume per cent. Since raising the temperature to 26 mV and the feed to 1.5 kg./l/hour produced no raise in aromatics content, the unit was changed back to pitch gas oil at a feed rate of 1.1 and the hydrogen pressure ratio changed to 450 atmospheres. Under these conditions after 800 run hours, an 0.35 yield of gasoline of about 46 volume per cent aromatics was obtained.

The reactor was again changed to Scholven gas oil and at a 0.41 yield (967 run hours) and 19 per cent gas yield, a gasoline with 39 volume per cent aromatics was obtained.

* The same oil was used as starting material for the experiments in Welheim.
 **C in the C₁ to C₄ per C in C₁ to C₄/C in gasoline.
 ***By the aniline point method of Dr. Hirschberger.

A change was now made to gas oil with "Sumpf" gasoline addition and with 1.5 kg./1/hour throughput (1031 run hours) the yield was 0.56. Gas yield was 15.7 per cent and the aromatics content of the gasoline 33.5 volume per cent. The run was then continued without "Sumpf" gasoline addition at 1.1 kg./1/hour feed rate (1211 run hours) and at a yield of 0.4 per cent with 20 per cent gasification and a gasoline of 41 volume per cent aromatics.

After 1220 run hours pressure was raised to 540 atmospheres. At present the reactor is leveling out under these conditions; at first an 0.41 yield of gasoline of 40 volume per cent aromatics was obtained.

The 165° C. F.B.P. gasolines from gas oil and gas oil plus "Sumpf" gas oil, contained about 35 and 47 per cent, respectively, boiling below 100° C. CFR Octane numbers were 77.5 to 80, respectively, and with 0.12 TEL 88.5 to 91.2. The iodine number of 5.5 to 16 was comparatively high.

The produced B gas oil had a specific gravity of 0.92 and, at 25.5 mV, an eniline point of -20° C. and, at 26.5 mV, of -24° C.; boiling range was about 190 to 320° C.; the color was yellow.

The following table shows the elemental analysis of feed and gasolines

	Feed Gas Oil	Feed "Sumpf" Gasoline	Gasolines	
			Hour 967	1031
			% Aromatics	
			39	33.5
% C	86.73	86.27	87.82	87.35
% H	9.11	13.34	12.30	12.43
% O	3.29	0.21	0.00	0.15
% N	0.79	0.17	0.065	0.063
% S	0.08	<0.01	<0.01	<0.01
Gram H/100 G C	10.50	15.46	14.01	14.33
SH "Disp"*/100 G C	9.85	15.39	13.99	14.20

* Disp. (available ?)

A bomb test for the gasoline from Hour 967 showed no pressure loss. The gum test before aging was 3.1 mg./100 cc., after aging 33.9, unleaded (equal resin) 2.2 mg. and was therefore good. The copper dish was high at 59.7, further tests are not yet available.

The make gas (C₁-C₄) contains an average of 39% total butane.
The butanes contained an average of 33% Isobutane.

From this are calculated the following values for workup of gas oil or gas oil plus Sumpf gasoline.

Feed	Sumpf Gasoline	
	Without	With
Vol. % aromatic in gasoline	39	33.5
% Make gas/gasoline / make gas	19	15.8
Produced per ton of gasoline:		
kg butane	95	75
kg isobutane	32	25

3. Experiments in the 0.2-Liter Reactor

Procedure

A 31-day run was made in a 200 cc. reactor with catalyst Lu No. 7978 obtained from Welheim on January 28, 1941. It was started at a 600 atmosphere total pressure and 25 mV = 475° C. with hard coal "Sumpf" gasoline plus Scholven gas oil and recycle from a previous experiment with the same catalyst in the ratio of 1:1, at a feed rate of 0.6. After 3 days the temperature was raised to 25.5 mV = 483° C. and the feed to 1.0. After 5 days pressure was reduced to 450 atmosphere, on the 12th day the temperature raised to 26.0 mV = 493° C. and after a further 4 days the change made to recycle of the experimental product at a 3:2 ratio. After 23 days the temperature was again raised eight degrees and finally after 24 days a change made to liquefaction gas oil and 7 days run made with this feed. The product was yellow to yellow-brown.

In addition to this a short experiment with hard coal liquefaction gas oil without "Sumpf" gasoline was made. Aromatics are reported as weight per cent (aniline point method according to Dr. Hirschberger.) The analyses of the 5th, 9th, 20th, and 30th day of the run are summarized in a table.

Results

At 600 atmospheres hydrogen pressure, feed rate of 1.0 and 25.5 mV temperature, gasoline with 38 weight per cent equal 34 volume per cent aromatics was obtained from coal liquefaction gas oil with 16.5 per cent Scholven gasoline (-160° C.) at a yield of 0.5. The gasoline had 43 per cent boiling at 100° C. and a motor method octane number of 76. The B gas oil had an aniline point of -11° C. and contained 0.29 per cent phenol. The C- gasification referred to gasoline plus make-gas was 14 per cent, when referring to newly formed gasoline plus make-gas, 16 per cent. Yield and aromatics concentration were constant for 170hr.

After lowering the pressure from 600 to 450 atmospheres to obtain high aromatic concentration in the gasoline the yield dropped from 0.5 to 0.38 within 48 hours and to 0.31 in another 250 hours. The phenol content of the B gas oil increased from 0.29 to 0.64. The aromatics content in the gasoline after the change to 400 atmospheres rose only slightly to 36-38 volume per cent. The fraction boiling at 100° C. dropped from 43 to 33 per cent. Motor method octane number was 75.5. The aniline point of the B gas oil dropped from -11 to -15° C.

In the last 7 days the experiment was continued with hard coal liquefaction gas oil without "Sumpf" gasoline at 450 atmospheres. A yield of 0.31 A gasoline with 42 volume per cent aromatics and 28 per cent boiling to 100° C was obtained. Motor method octane number was 73. Aniline point of the B gas oil was -18° C. A short experiment at 250 atmospheres and 27 mV with gas oil without "Sumpf" gasoline yielded a gasoline with 55 volume per cent aromatics with a quickly decreasing yield (first day 0.3, seventh day 0.17).

Summary Report on Hydrogenation of Coal Gas Oil over Catalyst K413 at Pressures Above 300 Atm., April 1941

Contents:

I. General Experimental Conditions

1. Apparatus
2. Catalyst
3. Gas
4. Feed
5. Run Length

II. Run Description

1. Experiment with Gasoline-Containing Gas Oil from Scholven
2. Experiments with Gasoline-Free Gas Oil from Scholven
3. Experiments with Gasoline-Free and Gasoline-Containing Gas Oil from Upper Silesian Coal

III. Analysis of Liquid Reaction Products

IV. Analysis of Gaseous Reaction Products and Calculation of Yield

V. Summary

I. General Experimental Conditions

1. Apparatus

The reactor consists of an N_2 pipe of 45 mm. I.D. and about 5.5 meter length. It was heated by three electric heating elements; foot, head, and transfer lines from the preheater to the reactor foot each had a further heating element. Inside temperature was measured at 6 points; the greatest temperature difference between the 6 points was 0.3 mV.

The preheater was a coil of 6 mm. I.D. N_2 pipe about 12 meters long in a gas heated lead bath. The separator was a 5-liter high-pressure vessel with a gauge glass. The separator product was continuously released into a low pressure container. The released product gas was measured through a gas meter and a composite sample for 24 hours taken by an automatic sampling device. Product was withdrawn every half hour, measured and gravity tested. A composite sample of product collected during 24 hours was analyzed. For balance experiments the gas dissolved in the product at atmospheric pressure was determined. The gas oil was fed through Hofer pumps which ran without difficulty throughout the experiments. The feed was cleaned ahead of the pumps through a Bosch filter. Temperatures were measured with iron-Constantan thermocouples. Terminal temperature was 40° C.

2. Catalyst

Ruhrroel catalyst K413 was used, in the form of corrugated 6 mm. pills. 3.13 Kg = 5.3 l was used in the reactor.

3. Gas

Fresh gas of the following average composition is used:

H ₂	98.2 - 97.4%
CO	0.1 - 0.3%
N ₂	1.7 - 2.3%

Initially the pressure was 670 atm. The main experiments were run at 500-550 atm. Finally, some were run at 450 atm. The gas-throughput was 15 m³/hr. regardless of feed rate.

4. Feed

The main experiments were made with gasoline-containing and gasoline-free hard coal liquefaction oil from Scholven. Short runs were made with oil from Upper Silesian hard coal, which had been prepared by IG Farbenindustrie, Ludwigshafen. The main analytical data are summarized in Table I on the film.

The A-gas oil was never used alone as feed. At the start of the run it was used in 50:50 mixture with B-product from the run. After equilibrium was attained, B-product from the run was used in the proportion in which it was produced.

5. Run Length

The run at pressures above 300 atm. lasted 70 days (1-25 to 4-4-41). The run is being continued at 500 atm. Run conditions were as follows:

Stream Day	Food	Temperature		Pressure Atm.	Feed Rate Kg/1/Hr.
		mV	°F.		
1	No Feed	Increased		670	0.0
2	" "	24.0	889	670	0.0
3	Scholven Gasoline / Gas Oil with Own B-Oil (50:50)	24.0	889	670	0.3
4	Ditto	25.0	921	670	0.5
5	Ditto	25.0	921	670	0.8
6	Ditto	25.0	921	670	1.0
7	Ditto	25.0	921	670	1.2
8-11	Ditto	25.0	921	670	1.5
12-13	Ditto	25.3	932	500	1.5
14-22	Ditto	25.5	937	500	1.5
23-25	Ditto	25.5	937	500	1.0
26-28	With Own B-oil (60:40)	26.0	954	535	1.0
29-35	Ditto	26.0	954	535	1.5
36-46	With Own B-Oil (65:35)	26.5	969	540	1.5

47-58	Scholven Gas Oil with Own B-Oil (60:40)	26.5	969	550	1.0
59-60	Upper Silesian Gas Oil with B-Oil from 56-58 Day (60:40)	26.5	969	550	1.0
61-63	Upper Silesian Gas Oil / Gasoline with B-Oil from 59-60 Day (60:40)	26.5	969	550	1.3
64-70	Scholven Gas Oil with Own B-Oil (60:40)	26.5	969	450	1.0

The remainder of the report consists entirely of summarizations of the various experiments in tabulated form. The translation of the summary of the report follows:

Summary

1. The yields obtained from gasoline-containing hard coal liquefaction oil (Scholven) at 500 and 540 atm. and a feed rate of 1.45 Kg/l/hr. are:

- at 25.5 mV (937° F.) a yield of 0.58 Kg/l/hr.
- at 26.0 mV (954° F.) a yield of 0.65 Kg/l/hr.
- at 26.5 mV (969° F.) a yield of 0.68 Kg/l/hr.

The yield from gasoline-free Scholven gas oil was 0.48 Kg/l/hr. at 26.5 mV temperature, 1.0 Kg/l/hr. feed rate, and 550 atm. pressure, and 0.41 Kg/l/hr. at 450 atm. pressure.

From the Upper Silesian hard coal liquefaction oil (at 550 atm., 26.5 mV, and 1.3 or 1.0 Kg/l/hr. feed rate) the yield was 0.70 Kg/l/hr. from the gasoline-containing and 0.52 Kg/l/hr. from the gasoline-free feed.

2 From gasoline-containing Scholven gas oil (at 540 atm., 26.5 mV, and 1.45 Kg/l/hr. feed) a gasoline with 42 volume per cent aromatics was obtained. The 165° C. E.P. gasoline has 49 volume per cent below 100° C. Its motor octane number is 78.0 clear, 87.0 with 0.05 volume per cent TEL.

From gasoline-free Scholven gas oil (at 550 atm., 26.5 mV, and 1.0 Kg/l/hr. feed), a gasoline with 45 volume per cent aromatics was obtained. The 165° C. E.P. gasoline has 48 volume per cent below 100° C. a clear motor octane number of 79.0, and 87.0 with 0.05 volume per cent TEL.

From Upper Silesian coal, the gasoline from gasoline-containing gas oil had 41 volume per cent aromatics, from gasoline-free gas oil 47 per cent aromatics. The part boiling below 100° C. was 47 and 45 volume per cent, respectively. ~~Clear octane number 76.5 and 79.5; with 0.05 volume per cent TEL 85.5 and 87.5, respectively.~~

3. The gasolines are easily refined and produce aviation gasoline meeting all specifications.

4. Loss to gas, in the various experiments, was as follows:

From gasoline-containing Scholven gas oil at 25.5 mV, 16 per cent (based on gasoline plus gas yield), and 21 per cent at 26.5 mV. From gasoline-free Scholven gas oil, at 26.5 mV, the loss is still 21 per cent. From gasoline-free Upper Silesian gas oil, the loss is 23 per cent.

Generally, when comparing results from small scale equipment with plant data, the gas loss values in the pilot equipment are found to be about two per cent high.

5. The isobutane content of the total butane is, in all experiments, about 40 per cent at 26.5 mV. It increases with decreasing temperature, to about 55 per cent at 25.5 mV.

V. Investigation of the Desirability of 700 atm. over 300 atm. in Gas Oil Vapor Phase Hydrogenation (4/17/41)

The fact whether 700 or 300 atmospheres is preferable for vapor phase hydrogenation is important in various respects:

1. Generally, that is for the "Benzinierung" and the application of fixed bed catalyst to the greatest possible extent (for example for prehydrogenation, of heavy oil workup, etc.)
2. For the preparation of high quality fuel by aromatization.
3. For the question of combination of "Benzinierung" or aromatization with dehydrogenation for preparation of high quality fuel.
4. Especially for the currently very important case of "Ausbau" II in upper Silesia.

Vapor phase hydrogenation at 700 atm. was undertaken by the IG at Ludwigshafen/Oppau at the same time with liquid phase hydrogenation at 700 atm. and developed catalytically. It has never been applied in industry by IG in spite of the fact that the work indicated that the 700 atm. operations in the vapor phase made it possible to use less noble catalysts, that is to save tungsten and molybdenum, and also to increase the feed and decrease gas make. The reasons are that:

1. Procuring the 700 atm. high pressure reactors creates a bottleneck in the production of high pressure reactors.
2. Because the 700 atm. high pressure material had not been sufficiently developed particularly for the higher temperatures of vapor phase hydrogenation.
3. Because the cost for the 700 atm. process, at least while this process was still in development, went higher than that for 300 atm. in spite of the higher feed rates; therefore 700 atm. was selected only where it was absolutely necessary such as in the hydrogenation of asphalts and liquid phase hydrogenation of coals which are difficult to hydrogenate.
4. Because the 300 atm. vapor phase hydrogenation was developed to the extent that it filled all the practical requirements.

The case was different where, aside from the 700 atm. liquid phase, only a small gas phase is available, particularly if the latter was added at a later date. In such cases there is immediately a considerable advantage in working under equal pressure. Starting with these considerations, 700 atm. has been used for the gas phase both in Welheim and Luetzkendorf. In this manner a common gas cycle could be used for liquid and vapor phase, circulating pumps and compressors could be saved and the recycle gas wash decreased. Catalysts for the 700 atm. vapor phase hydrogenation were developed in Welheim. Pitch was used as raw material; aromatization in this case produces a gasoline with 50 Vol. % aromatics or more which has proved itself as aromatic high quality fuel (VT 706).

Shortly after the beginning of the war the preparation of high quality fuel on an aromatic basis which had been worked on for a long time by Ludwigshafen together with REM became of practical interest. To produce in a short time the necessary amounts of aromatic gasoline, several of the 300 atm. gasoline chambers in Scholven, Poelitz, and Gelsenburg were changed to aromatization. The aromatization gasoline which has been made for some time in Scholven and lately also in Poelitz from hard coal and which contains about 50 Vol. % aromatics (CV₂b) is practically equivalent to the VT 706b (FEP 165° C.) which is obtained from pitch. Both do not have quite the rich mixture rating of the 185° C. cut point VT 706; according to a report from Wilhelm a new, recently installed catalyst produces 165° C. cut point aromatization gasoline with about 50 vol. per cent aromatics whose rich mixture rating is similar to that of VT 706.

With increasing requirements for aromatic fuels the DHD process which had been developed in the meantime in Ludwigshafen/Oppau could be installed in addition to further increase of the CV₂b chambers. In addition to an improvement of aromatization this process has the following advantages according to IG:

1. The DHD installation means an additional processing of the finished gasoline from the present installations and can therefore be installed without disturbing production. For a complete change of the available hydrogenation facilities however, equipment changes (preheaters, oil wash, etc.) would be necessary causing a temporary loss in production.

2. The present iso-octane alkylate program which in case of the production of high quality fuel by aromatization -- because of the different composition of the product gas as compared to "Benzinierung" -- would have to be considerably limited, can be kept going when using dehydrogenation in combination with "Benzinierung".

3. Fundamentally the DHD procedure permits formation of better products and higher aromatics contents from equal raw material when compared to aromatization since the aromatics content can be widely varied according to requirements. DHD gasoline from the "Benzinierung" of hard coal liquid fraction product with 50 volume per cent aromatics corresponds in rich mixture rating to a 185° C. cut point aromatization gasoline from pitch, for example VT 706. Unblended it is a component for the preparation of C₂ fuels and with addition of 20 per cent of light gasoline from hard coal can be brought to C₂ quality without iso-octane.

4. The DHD process permits the production of high quality fuels from a larger number of raw materials than aromatization, which is very significant for an installation such as Poelitz which is to use other raw materials than coal.

5. The DHD process can be combined not only with "Benzinierung" but also with aromatization particularly with a weak aromatization.

From these considerations and after a successful DHD large scale experiment in Ludwigshafen/Oppau, the building of dehydrogenation installations on the basis of hard coal were decided for Poelitz, Scholven, and for Ausbau I of upper Silesia.

For further new installations particularly for Ausbau II of upper Silesia it seems right to reinvestigate the question of the most suitable preparation of high quality fuels on the basis of new experiments. To be able to include the 700 atm. aromatization which proved itself for the pitch processing in Welheim, new data had to be obtained for the aromatization of hard coal liquefaction oil at 700 atm.

According to agreement, therefore, experiments were started in Welheim and Ludwigshafen/Oppau at the beginning of 1941 for hard coal gas oil hydrogenation with Welheim catalyst. These experiments were carried out (a) with gasoline free hard coal liquefaction gas oil from Scholven, (b) with hard coal liquefaction product from Scholven with higher gasoline content (32 to 38 per cent to 200° C.) which corresponds more closely in composition to the gas phase feed available for upper Silesia.

According to checking experiments with Silesia product, no great differences are to be expected compared with the Scholven product. Attention is called, however, to the fact that with increasing gasoline concentration in the gas oil the aromatics concentration necessarily decreases.

Reports about the comparative experiments in Welheim and Ludwigshafen/Oppau are attached. Results from these experiments agree well. (The most important figures are briefly compared.)

If these figures are compared with the results from industrial 300 atm. aromatization, they prove to be somewhat more favorable in yield and gas formation; however in contrast to the 300 atm. aromatization no product with 50 volume per cent aromatics was obtained from the hard coal liquefaction gas oil. In Case (A) the gasoline has 42* and 47** volume per cent plus olefins respectively, in Case (B) 35 and 42 volume per cent, respectively.

According to analysis by DVL the two products from the Welheim experiment will be C₃ fuels. Further determinations have been made to find out if it is possible to increase the aromatics content to 50 per cent as required for a C₂ fuel. The aromatization gasolines at 700 atm. differ from the 300 atm. aromatization gasolines in a higher content of low boiling components (45 per cent against 35 per cent at 100° C.).

To answer the question whether to use 700 or 300 atm. vapor phase hydrogenation, it is not sufficient to consider only the current status of aromatization. Further 300 atm. aromatization experiments at IG have produced catalysts with high yields and lesser gas formation than the currently industrially used aromatization catalyst. In case of the 700 atm. aromatization, experiments in Welheim and in Ludwigshafen/Oppau show signs that by changing the catalyst the aromatics concentration can be increased. It should be mentioned that by comparatively minor changes 300 atm. catalysts can be used for 700 atm. and vice versa.

*Determined according to corrected aniline point method

**Determined according to Kattwinkel (BVM) method

It is more important for a decision whether the 700 or 300 atm. hydrogenation should be used, to consider not only aromatization but also the other vapor phase processes such as processing of heavy oils over fixed bed ("Festangeordnet") catalyst, prehydrogenation, and "Benzinierung,"* and the combination of "Benzinierung" or aromatization with the DHD process. As in aromatization, somewhat higher yields and concentrations are indicated by the results of small scale experiments at 700 atm. compared to 300 atm. It seems more probable that an industrially useful catalyst for the processing of heavy oils over fixed bed catalyst can be developed at 700 atm. than at 300 atm. For the "Benzinierung" there exists the possibility that it can be carried out at 700 atm. in one step rather than in two steps like the 300 atm. "Benzinierung." Opposed to this, the 300 atm. "Benzinierung" has the advantage that it is proven in industry.

A decision can be made about the various processes when the yield (referred to the feed of "Sumpf" gasoline plus gas oil) and the quality of the aviation gasoline produced are compared.

In the following table in addition to the yield of aviation gasoline and aromatic high quality fuels, the yield of these products including aviation alkylate is given. For this not only the butane from vapor phase but also from the liquid phase process is calculated for alkylation. Raw material is a hard coal gas oil with 40 per cent "Sumpf" gasoline such as will eventually be produced in upper Silesia. On the basis of experiments of which the aromatization was carried out in Welheim and Ludwigshafen, the others in Ludwigshafen, the following picture presents itself:

		Yield	
		Without Alkylate	With Alkylate
"Benzinierung" at 300 atm.	Aviation Gasoline Octane No. 87	About 84	About 89
Aromatization at 300 atm.	C ₃ quality; 40 Vol. % aromatics (1)	About 81	About 86
Aromatization at 700 atm.	C ₃ quality with about 35 volume per cent aromatics (1)	About 82	About 86
"Benzinierung" / DHD	Blending stock with 50 vol. % aromatics (1), C ₂ quality (2)	About 76	About 92
Mild aromatization at 300 atm. / DHD	Attains almost the above quality	About 76	About 81
Mild aromatization at 700 atm. / DHD		About 78	About 83

(1) Aromatics by corrected aniline point method

(2) This DHD gasoline can be made to C₂ quality with 20% light gasoline instead of iso-octane.

* Cracking pressure-hydrogenation at about 400° C. (destructive hydrogenation?)

It can be seen that the difference in yield for comparable quality is comparatively slight for the 300 and 700 atm. process. Since the yield is the most important factor for judging the economics of the various methods, no unequivocal decision can be made on the basis of working costs. The differences for working at 300 and 700 atm. will not be great in any case.

The initial cost for aromatization is, according to our estimates, higher for 700 than for 300 atm. in spite of greater yields. The differences are however here also so small that they are in the order of 1 per cent compared to the total installation cost.

If we therefore favor a 700 atm. vapor phase installation for Ausbau II of upper Silesia, it is for the following reasons:

(1) Ausbau I has a 300 atm. vapor phase / DHD installation. In spite of a space separation of the two installations, there is a possibility of exchange of products; however, the exchange of liquid phase gasoline from upper Silesia II against liquid phase gasoline from upper Silesia I is at the expense of the quality of gasoline from upper Silesia I.

(2) In upper Silesia II there may be the necessity later to produce motor gasoline from heating oil. For processing the heating oil over fixed bed catalyst at 700 atm. there are then no changes necessary in the liquid phase, but the gas phase installation might have to be enlarged.

(3) The 700 atm. vapor phase is also very easily converted to the production of motor gasoline or normal aviation gasoline. Here the yield is somewhat larger compared to 300 atm. Furthermore the catalysts at 700 atm. will contain less rare material than those for 300 atm.

We must, however, report that upper Silesia II after installation of the 700 atm. vapor phase hydrogenation will not be in a position to deliver a high quality fuel with 50 volume per cent aromatics. By current estimate, an aromatic fuel of 35% aromatics and 42% olefins will be produced, which has C₃ quality. The preparation of C₂ fuels is however at the present status of aromatization impossible.

The decision for building the vapor phase unit for upper Silesia II is very urgent. As shown however it is very hard to make on a basis of economics since it concerns small differences of large quantities. The question as to the development of requirements of high quality fuels is also still open.

If it is certain that fuel of no more than C₃ quality is required, we believe that 700 atm. aromatization will be sufficient. If however only C₂ quality is desired, then the 700 atm. installation will have to be run for normal "Benzinierung" or light aromatization, and additional dehydrogenation installed. It is to be checked whether the preparation of C₂ fuels is possible by product exchange with upper Silesia I. As long as these various questions are open, the decision about building a DHD installation in upper Silesia II will have to wait.

In the above considerations it was presumed that obtaining suitable construction materials for 700 atm. is no more difficult than for 300 atm., which is considered permissible.

Also the above considerations show that the reasons for recommending a 700 atm. vapor phase installation for upper Silesia II and leaving the decision about a DHD installation open have no general validity. For each new installation it has to be determined which operating method best corresponds to the local conditions, the raw materials, and the requirements for the finished products.

Pages 647-649

W. Note Concerning Regeneration of Extract Solvent from 700 Atmosphere Vapor Phase Hydrogenation* (7/14/1943)

For the confirmation of results on regeneration of extract gas oil (P 64) which have been obtained late in 1942 in a series of experiments in 50 cc. reactors, and to obtain exact figures for the resulting gas formation and obtainable chamber yield, regeneration experiments have again been performed in a five-liter vapor phase reactor.

Unfortunately, the solvent furnished by the extraction division was only slightly used, so that the improvement due to regeneration is only small. Since the original oil still had a good "aufschluss" ability (78 per cent referred to pure coal), naturally only a small increase could be obtained by regeneration (81 to 82 per cent).

It is to be assumed, however, that the favorable reaction conditions and the measured gas formation and yield which have been determined are also applicable to more exhausted solvents.

The result of the experiments and analysis of products are given in the attached table. Determination of the "aufschluss" ability of the oils was made through experimental aufschluss in autoclave by Engineer Reinmuth ... (See note by Reinmuth of 7/1/43.)

In summation, it can be reported today, in agreement with previous communications, that the regeneration of exhausted extraction solvent by mild vapor phase hydrogenation is possible. Application of 700 atmosphere pressure is recommended for equipment reasons even though lower pressures could be used. At a reaction temperature of 13.0 mV, the gasoil molecule is cracked but the phenol is not reduced. The reduction of bases which takes place has no harmful effect on the "aufschluss" ability of the oil.

Since the gas formation is very slight and a high feed rate can be used, a regeneration chamber can be run with the very high output of approximately 1.0 kg. regenerated oil per liter per hour.

* See also notes of 3/31/42 and 11/24/42.

A strong hydrogenation catalyst is required. Most suitable, therefore, is pure molybdenum sulfide or tungsten sulfide (5058). These catalysts are very expensive and cannot be procured at present. One could use the available catalyst 58 II (largely molybdenum sulfide). It also may be possible to develop a catalyst with desired properties according to our procedure.

Experiments on regeneration of extraction solvent are considered closed for the present.

(A table of data is included.)

Page 650

W. Note Concerning Testing of Ruhroel Gasolines at the Testing Laboratory of Gewerkschaft Mathias Stinnes (6/19/1943)

Pages 651-654

X. Concerning the Behavior of Water Injected Ahead of the Furnace in High Pressure Hydrogenation (6/4/1943)

In addition to the usual water injection in the regenerator (after the hot catch pot), a portion of water was injected after the coal paste pumps* of Chamber 52 (ahead of preheater and furnace), starting late in May, 1943. This was to prevent the formation of scale, or at least to diminish it.

This addition of water ahead of the furnaces was not made in Chamber 108.

It was observed that the water separated in the 52 chamber had a considerably higher CO₂ content than the water in Chamber 108. This fact was the more inexplicable, since the dilution of the water of the 52 chamber by the added water injection should lead to a lowering of CO₂ content. Feed and feed gas were also equal for the two chambers. The possibility could be assumed that additional CO₂ is formed by the addition of water ahead of the reactor through a reaction of the water with carbon or carbonaceous material.

To study this problem, several experiments were made in the Technische Versuchsanlage, following Experiment G 71/9 in the Chamber 2 filled with catalyst 534. We chose the vapor phase reactor, since it was currently available and, furthermore, it could be assumed that the reaction to be observed would take place most easily at high catalyst concentration.

First, we injected 1.3 kg. water (approximately 22 per cent) after the furnace, with an oil feed (PIC₂) of 6 kg. per hour. Injecting a lesser amount of water was impossible for mechanical reasons (pump). Furnace temperature was 25.5 mV; pressure, 550 atmospheres; feed gas, fresh gas; and the feed rate, 1.0 kg. per hour. 28.5 per cent gasoline was obtained. After equilibrium had been obtained, the separator water and the reaction gases were analyzed.

* Breipressen

The same experiment was repeated two days later at equal reaction conditions and feed rate and injecting the same amount of water ahead of the pre-heater and furnace. Loss of catalyst activity was observed immediately. Gasoline formation fell to 23.5 per cent.

	<u>Water After Reactor</u>	<u>Water Ahead of Reactor</u>
Separator Water:		
CO ₂	1.4 g/l	21.7 g/l
NH ₃	44.2 g/l	39.1 g/l
H ₂ S	7.0 g/l	5.5 g/l
Phenol	4.8 g/l	7.6 g/l
Cl	6 mg/l	5 mg/l
D ₄ 15	0.94	1.004
Reactor Gas:		
CO (Drechsmidt)	0.2 Vol. %	0.5 Vol. %
CO ₂ (bulb)	0.0	0.0
Product Gas:		
CO (Drechsmidt)	1.4 Vol. %	2.2 Vol. %
CO ₂ (bulb)	0.0	0.0

Most notable is the large increase of the CO₂ content of the water which had been injected ahead of the furnace, which can be explained only by additional formation of CO₂ since no CO₂ escapes in the gases. The reaction in question can be only the conversion of carbon monoxide: $CO + H_2O \rightleftharpoons CO_2 + H_2$ / 10,110 Kcal per Kmole, which is practically complete to the right between 400 and 500° at atmospheric pressure in the presence of catalyst. Under vapor phase hydrogenation conditions (no conversion catalyst, high H₂ partial pressure, very slight CO concentration and CO partial pressure), the conversion according to the above equation is very incomplete as evidenced by the CO content of the reaction gas. Only about 11 grams of water, which is about 0.85 per cent of the injected water, reacts with about 17 grams or 14.5 liters CO to form 27 grams CO₂ per hour.

It cannot be seen from our experiments whether the reacting carbon monoxide is only that introduced with the fresh gas or if additional CO is obtained, possibly by splitting off of CO or COOH groups from the feed oil.

The CO content of the fresh gas varies according to its composition from "Linde" and generator hydrogen between 0.2 and 0.5 per cent. If the CO₂ wash is overloaded, CO contents of above 0.6 per cent have occurred. The difference in the CO content in the reaction gases of the two experiments we explain by different CO content in the respective feed gases.

Assuming an average CO content 0.3 per cent in the fresh gas, 60 liters CO would have passed through the chamber per hour with about 20,000 liters feed gas; only 14.5 liters, or about 25 per cent, were converted. If CO was also formed by destructive hydrogenation of the gas oil, the percentage is still less. This amount of reacted CO is so small that it cannot be determined by analysis of the feed and reactor gases.

It could be assumed that the slight amount of water (11 grams per hour), which reacted with CO in the experiment, is also injected under normal conditions

with the feed or formed in the reaction so that even without water injection an equally large CO conversion would take place. This is so far correct in that a small amount of conversion always takes place. It is also the reason why too high a CO content in the fresh gas is feared since, due to the high exothermic character of the conversion, there is a danger of the furnace going out of control. On the other hand, it is known that the equilibrium of the conversion goes to the right only with a large excess of water vapor. It is therefore easily explained that only with the injection of larger amounts of water ahead of the reactor the large increase in CO₂ formation is noticeable. The danger of the chamber going out of control with a sudden increase of fresh gas CO content is, of course, particularly great when running with water injection ahead of the furnace.

Furthermore, a strong increase of the specific gravity of the separator water due to the high CO₂ content is noticeable. This must be considered if there are difficulties in the water-oil separation.

Pages 655-657

Y. Effect of Product-Gas Ratio in 600 Atmosphere Vapor Phase Hydrogenation
(Main Laboratory of Ruhroel GMBH 6/4/1943)

A product-gas ratio of 1:3000 was used in our work on 600 atmosphere vapor phase hydrogenation, the results of which have been reported in the report, "Ueber die einstufige spaltende Hydrierung von Pech-Mittelöl in der Gasphase bei 600 atü" (about one step destructive hydrogenation of pitch-gas-oil in the vapor phase at 600 atmospheres).

To complete our previous work, experiments have been carried out in the Technische Versuchsanlage to determine the influence of different feed volumes at constant production rate (Experiments G70/1-5). Reactor conditions were as follows:

Catalyst Volume	5.4 l.
Catalyst	K534
Feed	P101/102/302
Temperature	25.5 mV
Pressure	550 Atmospheres
Gas	Fresh Gas
Feed Rate	1.0 kg./l./hr.
Product-Gas Ratio	1:2000
	1:3000
	1:6000

The table presented in the film shows the experimental results at various product-gas ratios. It can be seen that output, gas formation, and analysis of reaction products do not differ significantly and are, within limits of experimental condition, largely independent of the gas input.

The experiment indicated, however, that at the low product-gas ratio of 1:2000, that is, at a high oil partial pressure, catalyst activity drops considerably faster than at a ratio of 1:3000 or higher. The decreased contact time at the

high gas throughput of 1:6000 shows up in a decrease of the phenol- and base reduction, a low gasoline aniline point, and decreased hydrogenation of the feed gas oil. This means, as proved by Experiments G70/4 and 5, a decrease in output for the higher gas throughput when recycling B-gas oil.

The increase in gas formation with increasing gas throughput, as shown by the table, could hardly mean an actual increase in the formation of gaseous hydrocarbons, since decreasing contact time could only lower this formation. The higher figure results from the fact that at the higher gas throughput more low boiling components from the separator are entrained. In the plant where the gas is continuously recycled, gas formation, therefore, would probably be independent of gas throughput within limits of our experimental conditions.

In summary, our experiments have shown that for the single step destructive hydrogenation of gas oil in the vapor phase at 600 atmospheres, a low gas throughput (1:2000 and less) harms the catalyst, while a high throughput (1:6000 and above) decreases output and gives poor reduction of phenols and bases. Most favorable is the gas to product ratio of 1:3000 as used in our previous experiments and in the plant. The limits are considered to be 1:2500-1:4000.

Pages 664-674

BB. Investigation of Dehydrogenation for the Analysis of Naphthenes (Main Laboratory of Ruhroel GMBH)

A report on the dehydrogenation of naphthenes to the corresponding hydrocarbons is attached. This is a short summary of the work carried out by Dipl.-Ing. Hahn from August, 1942, to February, 1943.

The purpose of this work was, first, to work out an analytical procedure for the quantitative separation of naphthenes and paraffins in the gasoline range. The separation of aromatics by concentrated sulfuric acid, nitric acid, or extraction with liquid SO₂ is relatively easy. A separation of naphthenes and paraffins, however, is not made at present and the content only calculated from the aniline point. Aside from the fact that the accuracy of these calculations is doubtful, it has been lately a considerable disadvantage that we never have the pure hydrocarbon classes separated, particularly in the analysis of "rest" gasoline.

It was to be tried, therefore, to convert naphthenes in aromatics-free gasoline quantitatively into the corresponding aromatics. Conversion of paraffins had to be avoided so that they would be available in the original form after separating the aromatics. (Conclusions can be drawn as to the identity of the naphthenes by separating and analyzing the aromatics formed from them.) ~~The work by Hahn can be considered closed in the analytical aspect, since the desirable catalyst and working conditions have been found by making extensive use of previous work, particularly by Zelinski. The undesirable property of the catalysts, that they are quickly poisoned by aromatics and paraffins, is insignificant in analytical work where catalyst is easily changed and gasoline throughput is small.~~

~~The further purpose of our work on dehydrogenation was the preparation of highly aromatic gasoline. I.G. has worked several years intensively on this problem and has developed the two equivalent processes DHD (I.G. Lu) and H.F. (Louna), using, in part, American work.~~

The experiments carried out by Hahn so far are limited to our gasoline VT 330. It can be summarized at this early stage that in this already highly aromatic gasoline a further increase in aromatics can be obtained only with great loss to gas and coke. Furthermore, at the high dehydrogenation temperature, olefins and diolefins are formed which immediately polymerize, in part, to higher boiling oils and resins and, in part, cause decoloration of the gasoline and delayed gum formation. An additional treat would therefore be necessary.

In spite of the fact that the dehydrogenation would never become significant for our present gasoline, the work was continued with a view toward other gasolines which may have to be worked on. Active catalysts were developed and favorable reaction conditions including the usual, such as temperature, feed rate, gasoline partial pressure, and, in addition, favorable catalyst regeneration conditions were determined. The experiments at atmospheric pressure may be considered closed, so that now only experiments at 50 to 100 atmospheres are still to be made, on which I.G. is also working. These are to be carried out first in equipment in the Technische Versuchsanlage.

Dehydrogenation of Naphthenes

The addition of hydrogen is a reversible reaction whose equilibrium is changed with increasing temperature in favor of the unsaturated compounds. With platinum catalyst, benzene can be hydrogenated completely to cyclohexane below 200° C., whereas at higher temperatures the reverse reaction, dehydrogenation of cyclohexane to benzene, occurs quantitatively. Since in such reversible reactions the same catalyst catalyzed the reaction in both directions, it is to be expected that hydrogenation catalysts are also good dehydrogenation catalysts at higher temperatures. Zelinski* has already proved the presence of naphthenes in petroleum fractions using platinum, asbestos and palladium catalysts.

Quantitative Determination of Naphthenes

The dehydrogenation of cyclohexane to benzene was used to determine the effectiveness of dehydrogenation catalyst in the apparatus (Figure 1 on the film). The cyclohexane is injected into the catalyst space from the micro burette. Catalyst temperature is held constant within a few degrees centigrade in an electrically heated iron block. Conversion can be calculated from the gas volume and the density of the cooled reaction product. Gas analyses often show the gas to be more than 98 per cent hydrogen.

An especially effective catalyst was platinized carbon, which was prepared from activated carbon by saturation with aqueous solution of platinum chloride and consequent reduction by hydrazine hydrate. Preliminary experiments indicated that even pure activated carbon has a dehydrogenating effect. At very low feed rates it was even possible to dehydrogenate more than 80 per cent of the cyclohexane to benzene, while other surface active catalysts, such as silica gel and clay, were entirely ineffective. Some conversion was also obtained with charcoal and with cracking catalyst K438. The latter, however, caused considerable carbon formation.

* Bor. 44 (1911) 3123, Ber. 45 (1912) 3678

The curves (Figure 2) of the effectiveness of activated carbon and activated-carbon-platinum catalyst, respectively (0.1, 1, and 10 per cent Pt.) at temperatures of 400° and 450° C., show that at low feed rates, even at 400°, all platinized carbon catalysts give 100 per cent conversion. Most effective, of course, was the 10 per cent platinum catalyst, which gave 100 per cent conversion even at high feed rates. (The benzene, due to its purity, crystallized immediately in the ice-cooled receiver and plugged the gas line so that ice cooling could not be used. The curve is therefore increased, compared to the other curves, by the partial pressure of benzene.)

In the dehydrogenation of pure cyclohexane the platinum activated carbon catalysts show no loss in activity after running for several days. When dehydrating with paraffins (normal heptane and normal hexane) and gasoline (VT 330 and VT 77), the catalyst was soon poisoned. Benzene vapor will also poison the catalyst. When heating these poisoned catalysts in nitrogen at red heat their activity was increased but not brought back to the original activity. Regeneration experiments in air, even below 350°, led to ignition and complete burning of the catalyst. Nevertheless, the platinum-carbon catalysts are useful for the quantitative naphthene determination in hydrocarbons. Up to five analyses can be carried out with the same catalyst in one apparatus. Experiments with synthetic blends of benzene and cyclohexane gave identical results and a limited error of 0.5 per cent. The most useful catalyst is that with 10 per cent platinum. The platinum from used catalyst is best recovered in aqua regia after burning the carbon carrier.

Dehydrogenation of Gasoline Fractions

Platinum catalysts are not suitable for plant scale dehydrogenation of gasoline because they are easily poisoned and very expensive. To find suitable catalyst for this purpose a series of non-noble metals or their oxides were applied on activated-carbon and tested for their activity at 450° with cyclohexane in the apparatus of Figure 1. Metal contents were 10 and 25 per cent of the catalyst weight, respectively. The following metals were effective: Cr, Mo, Ni, and Co. (The cobalt catalyst, however, produced so much cracking that in a short time the catalyst bed was plugged with carbon.) Almost inactive were Cu, Ag, Mn, Fe, and La. The hydrocarbon content of the gas from 96 to 98 per cent according to the catalyst, indicated dehydrogenation with only slight gas formation. Results are given in Figure 5. All heavy metal catalysts, however, show loss in activity. Even the heavy metal activated carbon catalyst could not be regenerated, and a nonburning carrier had to be used. Experiments with silica gel and terrona paste showed a strongly reduced activity, whereas active clay as carrier showed no decrease in activity against carbon. These catalysts could be regenerated by burning with air to their original activity. The curves for the effective heavy metal catalysts are given in Figure 4 and contrasted to the corresponding values for carbon and carbon platinum (one per cent) catalyst. It can be seen that some mixed catalysts surpass the effectiveness of the platinum carbon catalyst considerably. Most effective is the mixture of 20 per cent Cr and 5 per cent Mo on Al_2O_3 . A further increase in the content of effective metal oxides gives only an insignificant increase in dehydrogenation activity. Also considerably better was a chromium catalyst with 0.1 per cent platinum content.

With these regeneratable catalysts, 400 to 800 cc. gasoline (VT 330—topped 175° C.) per dehydrogenation period was run through a 150 cc. reactor. The gasoline was injected by a small pump into an electrically heated preheater, where it was vaporized and heated to reaction temperature (Figure 3). A second feed line allowed the addition of a carrier gas. The reaction product could be withdrawn from a receiver during the run after being cooled and liquefied. Inlet and exit gas were measured by gas meters.

Preliminary experiments indicate that the mixed catalyst with 20 per cent Cr and 5 per cent Mo on Al_2O_3 is the most effective platinum-free catalyst, also, for the dehydrogenation of gasoline. The catalyst can be regenerated in air and regains its previous activity, which at the beginning is even higher than that of the fresh catalyst. If air is fed too quickly, the burning of the deposited carbon may bring the catalyst to white heat. In this case, of course, the catalyst can be destroyed and its activity reduced to one-third of original. It is necessary, therefore, to mix the regenerated air with inert gases for heat removal. Nitrogen or steam is useful for that purpose. The catalyst could be completely regenerated in three hours by using steam-air mixture; the end of the regeneration was determined by quantitative testing for CO_2 .

The purpose of dehydrogenation experiments was to determine the most favorable gasoline partial pressure and to check whether hydrogen as carrier gas shows an advantage over dehydrogenation without carrier gas. The experiments indicated that even a small addition of carrier gas effects a considerable decrease in gas formation. At a gasoline partial pressure of 1.0 (no carrier gas), the tail gas contained 22.8 per cent hydrocarbon, whereas even at a partial pressure of 0.825 only 16.6 per cent hydrocarbons were found. Further increase of the carrier gas leads to a decrease of hydrocarbon components of the tail gas to 14.8 (gasoline partial pressure, 0.265); the dehydrogenation effect, however, is decreased due to shorter contact time. A gasoline partial pressure of 0.8 at furnace temperature of 28 mV seems most useful. The dehydrogenated gasoline so obtained had a density of 0.835 (feed density, 0.813) and an aromatics content of 78 weight per cent (feed, 59 per cent by BVM method).

It is intended to carry out the same process under pressure in a five-liter furnace at the Technische Versuchsanlage, where it is to be expected that dehydrogenation can be carried out at lower temperatures and with lower gas formation.

Pages 675-676

CC. Asphalt Determination in Liquid Phase Separator Product and Heating Oil
(Main Laboratory at Ruhroel GMBH) (7/30/42)

Several series of experiments on the analysis of "asphalt" in liquid phase separator product and heating oil have been carried out. The following results have been obtained: By "asphalt" is meant a material which is soluble in benzene and insoluble in normal gasoline. It includes all those high molecular, dark brown or black amorphous materials whose exact chemical composition cannot be determined. In the lube oil analysis where the concept of asphalt was first introduced, it means products which are formed in thermal and oxidative treatment of the oil by polymerization.

In our separator product and heating oil, however, addition of normal gasoline causes mainly the precipitation of crystalline materials, such as "carbazol," "pyren," anthracene, etc. These can by no means be considered asphalts. This can also be concluded from the fact that asphalt, according to DIN DVN 3660, is not to be alcohol soluble; whereas our precipitates which consist of condensed ring systems are soluble.

Separation of the real asphalt from the coprecipitated crystalline material is analytically almost impossible. We have tried so far to carry this out by heating the precipitated asphalt not as prescribed by the DIN procedure at 105°, but at temperatures (above 200°) where a part of the crystalline material sublimes. This determination, however, is very inaccurate and poorly reproducible.

Therefore in the future asphalt determinations will not be made on the separator product and heating oil. Instead, the benzene insoluble residue will be determined according to Procedure DIN DVN 3792. This will give essentially a measure of the mechanical impurities present. Asphalt determinations will therefore be only carried out (1) in lubricating oils according to Procedure DIN and DVN 3660, (2) in the feed and in the residue of the liquid phase according to Procedure for R-asphalts.

Page 677

DD. Pressure Filtration of Coal Decomposition Products with Addition of Bottoms (5/5/42)

A pressure filter with a ceramic insert "40" (12.5 cm. diameter) was used for the filtration of coal decomposition products with certain percentages of bottoms added. The bottoms contained about 26 per cent solids.

After the filter time for the pure decomposition products had been determined, additions of 5, 10, and 15 per cent bottoms were made, and the increase in filter time was observed. The following table gives a survey of two series of experiments which were carried out using two different decomposition products with different filtration characteristics:

Number	Sample	Filtering Time
		Seconds per 1,000 G.
1	1,000 g. Product of 4/27/42	20
1a	950 g. Product 50 g. Bottoms	43
1b	900 g. Product 100 g. Bottoms	187
1c	850 g. Product 150 g. Bottoms	313
2	1,000 g. Product of 5/1/42	45

Number	Sample	Filtering Time
		Seconds per 1,000 G.
2a	950 g. Product 50 g. Bottoms	131
2b	900 g. Product 100 g. Bottoms	265
2c	850 g. Product 150 g. Bottoms	433

All filtrations were carried out at 5 atmospheres and 150° C.

The experiments indicate that an addition of 5 per cent bottoms of medium solids content lengthens filtration time two to three times; 10 per cent lengthens it six to nine times; and 15 per cent, 10 to 15 times.

Pages 678-680

EE. Explosibility of Oil-Air Mixtures and Its Prevention by Addition of Inert Gases (5/1/42)

These experiments were carried out to determine under what conditions the heavier oils form explosive mixtures when vaporized in a stream of air. Furthermore, it was to be determined under what conditions these explosions could be prevented by adding inert gases such as CO₂ and nitrogen. The following equipment was used: A flask was half-filled with the oil, and a constant air stream of 20 liters per hour was blown through and saturated with the oil at different temperatures corresponding to the vapor pressure of the oil. This mixture was exploded by sparking in a heated flash tube. In this manner the air stream, the oil temperature (and therefore richness of mixture), and the temperature of the gas before explosion could be varied. Gas oil, heating oil, and pitch distillate were tested.

Gas Oil

At constant air rate of 20 liters per hour the gas mixture was explosive at oil temperatures of 120° to 180° corresponding to 90 to 126 grams oil per cubic meter of air, or, assuming an average molecular weight of 150, to about 1.3 to 1.9 volume per cent oil. When the explosion space was below 180°, no explosion could be obtained; whereas at all temperatures above 180° explosions took place easily.

Addition of carbon dioxide to the extent of 20 per cent (i.e., 5 liters CO₂ per 20 liters air) was sufficient to prevent explosion. When nitrogen was added, at least 100 per cent based on air had to be added to prevent explosion.

Gas Oil Plus 10 Per Cent Gasoline

With 10 per cent Wolheim gasoline added to the same gas oil, minimum temperature of the oil for explosibility was 70° and the maximum temperature for explosibility was the initial boiling point of the mixture. Therefore the

explosive mixture was between 320 and 590 grams per cubic meter of air. Assuming an average molecular weight of 110, this corresponds to 6.5 to 12 volume per-cent combustibles in the mixture. Minimum temperature of the reaction space was again 180°. Twenty-five per cent CO₂ was required to prevent explosion.

Heating Oil

Explosive mixtures were obtained at oil temperatures of between 260° and the initial boiling point of the oil, corresponding to 100 to 150 grams oil per cubic meter of air. Assuming an average molecular weight of 220, this indicates 1.0 to 1.5 volume per cent oil vapor in the mixture. Explosions again required a reaction space temperature above 180°. Thirty-five per cent carbon dioxide based on air was required to prevent explosion. One hundred per cent of nitrogen was required for the same purpose.

Pitch Distillate

The required oil temperature was 130° to 170°, 45 to 100 grams oil per cubic meter, or 0.5 to 1.1 volume per cent oil vapor assuming an average molecular weight of 200. Minimum reaction space temperature was 180°. Fifteen per cent CO₂ prevented explosion.

Pages 697-700

NW. Effectiveness of Various Catalysts for Destructive Hydrogenation of High Boiling Pitch from Coal (6/28/44)

The purpose of this work carried out, with interruptions, from June, 1943, to June, 1944, was on the one hand to compare the previous IG Catalyst 11002 (2 per cent MoO₃ on coke) with the substitute IG Catalyst 10927 (approximately 10 per cent Fe on coke) and on the other hand to prepare a more effective catalyst with simpler means and using currently available raw materials.

In our experiments the same pitch and the same mixing oil (heavy oil from pitch liquefaction) were used throughout and at the same reaction conditions*

The reaction conditions were as follows:

Feed	70 per cent coking pitch and 30 per cent heating oil
Catalyst	1 to 4 per cent based on feed
Feed rate	1.0 Kg. per liter per hour
Temperature	24.0 mV
Pressure	About 700 atmospheres
Gas	Fresh gas
Product Gas Ratio	1 to 4500
Run length	5 to 10 days per run
Apparatus	8-liter reactor with "ofen-entschlammung" (bottoms receiver?)

* Feed, reaction conditions, and product workup differ from those in the plant and can therefore not be used for direct comparison.

To prevent enriching the catalyst in the lower part of the reactor some product was withdrawn from the bottoms receiver every two hours. One to two per cent of the feed was thus withdrawn as bottoms.

Workup of Liquid Reaction Products

Bottoms and separator product were recombined. Gasoline and gas oil were distilled off up to 325° C. The residuum was an asphalt-rich highly viscous heavy oil which was tested in the Bitumen viscosimeter at 100°.

A further indication of the degree of decomposition in the product is given by the asphalt content. The C fraction was determined since determination of the normal asphalt produces poor values. It was also attempted to obtain accurate figures for the solids decomposition, but results were doubtful and not reproducible. Solids decomposition was between 30 and 25 per cent based on solids in the feed. Results are given in a table, and the following conclusions are drawn:

(1) The superiority of IG Catalyst 11002 (Exp. S33/1 and 39/1) is obvious. Substitute IG Catalyst 10927 (Exp. S34/1--4) is the next best catalyst. Three per cent of this catalyst has the same effect as one per cent 11002.

(2) Series S34/1--4 shows that catalytic effect increases with catalyst concentration. Three per cent based on feed seems to be the optimum for 10927. This corresponds to a Fe concentration in the mix of 0.25 per cent.

(3) The catalytic effect of 10927 is partially due to the effect of the coke (compare S38/1 and S33/2b) but mainly to the effect of the iron (compare S34/2 or S38/2 with S38/1).

The iron is introduced as FeSO_4 and then precipitated with excess sodium hydroxide. The resulting Na_2SO_4 is not washed out. To determine whether the sodium salt destroys activity, the catalyst before precipitation with sodium hydroxide (Exp. S34/2) is compared with 10927 (S34/1). The effect of both catalysts is very similar, but 10927 is the more effective form.

(4) Other substitute catalysts were made by precipitating either small amounts of very effective hydrogenation metals, such as molybdenum or chromium in small quantities or iron in large concentrations on terrana and Kieselguhr. All these experiments (S33/4--6 and S39/2 and 3) give no positive results.

These experiments for checking of liquid phase catalysts are considered closed for the present.

Pages 701-705

00. Hydrogenation of Coal Extract and Coking Pitch Over Solid Catalysts (March 1944)

A. Hard Coal Extract

A note of March 3, 1942 reported on hydrogenation of hard coal extract with solid catalyst. The conclusion was that this process is not practical since

solids build up on the catalyst, weaken it, and plug the reactor. These experiments were made using solid extract dissolved in heavy oil or gas oil from pitch hydrogenation. Further experiments have now been made from August to October, 1943, using the filtrate. In these experiments also, the reactor was already plugged after thirteen days.

It can therefore be said conclusively that hydrogenation of hard coal extract over solid catalyst is not possible.

The only possibility for hydrogenation of the extract is therefore a "Sumpf" phase hydrogenation. The low ash content of the extract should be advantageous in decreasing the excess solid residuum. This might possibly be added to the raw decomposition before filtration, thus saving a special work up of the residuum. In a note of July, 1943, a summary of Sumpf phase hydrogenation of various raw materials on a hard coal basis has been given. It can be seen from this that hard coal itself should be at least as easily hydrogenated as extract, since in the latter case there is the additional difficulty that the slurry oil must be able to dissolve the extract, which is not always the case.

Even if a workup of the residuum were unnecessary in extract hydrogenation, the process of extraction is more elaborate and expensive than the workup of residuum in coal hydrogenation. We do not believe that the additional expenses are balanced by the better hydrogenation ability of the extract. Hard coal extract therefore, should not be particularly advantageous as hydrogenation feed stock.

B. Coking Pitch

Experiments were carried out to hydrogenate over solid catalyst a solution of coking pitch which had been free from solids and the greatest part of ash by filtration. The results may be summarized by stating that coking pitch cannot be hydrogenated over solid catalyst. The heaviest constituents of the pitch are not decomposed and remain on the catalyst. The catalyst loses its activity and the furnace plugs completely after a short time, though not as quickly as in the case of coal extract.

The above experiments correspond to the experience that heavier materials than gas oil cannot be destructively hydrogenated over solid catalyst without damaging the catalyst quickly and permanently. The case is different when hydrogenation without cracking is to be achieved (for example, TTH process for lube oil preparation). If the feed has only a low asphalt content, this process can be run for a long time without damaging the catalyst.

~~Previous experience was contradicted for the first time by our observation of mid-1942, that heavy oil from pitch liquefaction at 700 atmospheres can be destructively hydrogenated to gas oil over solid catalyst without damaging the catalyst. In that case, an asphalt free feed was used. Hydrogenating an asphalt-rich feed such as pure filtrate (6% R-Asphalt) or pitch solution (5.5% R-Asphalt), however, seemed still hopeless. The results of December, 1943, which indicated that filtered solutions of hard coal low-temperature-coking pitch can be destructively hydrogenated over solid catalyst, were therefore particularly~~

surprising. Even solutions with over 60% pitch (17% R-Asphalt) leave no carbonaceous residue on the catalyst. Our present problem, therefore, is not the hydrogenation of low temperature coking pitch over solid catalyst, since this problem has been solved, but the complete de-ashing of the pitch since the ash naturally remains on the catalyst and causes it to lose activity.

Pages 706-707

PP. Separation of Olefins from Synthetic Gasoline not Quantitatively Successful.

For the separation of olefins from a hydrocarbon mixture two methods can be used, according to Koch.¹

1. Reacting the olefins to form dibromides and decomposition of those by zinc dust-glacial acetic acid.²

2. Reacting the olefins to form the mercury double compound and decomposing this by dilute acids. This complex of olefins with mercury salts, first observed by Deniges³ was first introduced into hydrocarbon analyses by Tausz.⁴ With the improvements of Koch, this mercury acetate method may be considered the only method which permits separation of unsaturated compounds from hydrocarbon mixtures and isolation of the compounds in pure form.

Separation of the olefins from "Kogasin" (synthetic gasoline) was made according to Koch.

250 cc. of Kogasin IV (Iodine No. 66.5) was shaken four hours with 125 g. mercury acetate and 250 cc. alcohol, the undissolved acetate going into solution in a short time. The acetic acid formed was then neutralized with dilute potassium hydroxide, under cooling. The olefin mercury compounds were salted out in a separatory funnel by a saturated solution of 50 g. potassium bromide; they separate as heavy oily liquid. To prevent their resolution in the gasoline layer, shaking must be carefully avoided. From 250 cc. of the Kogasin, 50 cc. of olefin mercury compounds are obtained which are separated from the water layer above them and then repeatedly shaken with water. To separate the dissolved saturated hydrocarbons the material is heated thirty minutes with steaming. 50 cc. concentrated hydrochloric acid is added and the liberated olefin removed by steam distillation. The 250 cc. Kogasin yield thus:

200 cc. hydrocarbon mixture of iodine No. 41.

16 cc. of olefin paraffin mixture of iodine No. 105.

~~26 cc. raw olefin of iodine No. 203.~~

(1) Koch dissertation Jena 1930.

(2) Engler and Lohman, B. 30, 2365 (1897).

(3) Doniges, Comptes rend. academy sciences.

(4) Tausz, Petr. 13, 649 (1918); Ang. Chem. 32, 233 (1919).

From the molecular weight (88) of the obtained raw olefin an iodine number of 288 is calculated, thus indicating a pure olefin content of 70%; the remaining olefin-poor Kogasin still contains a small amount of olefin mercury compounds from which it is best separated by vacuum distillation.

For complete removal of the olefins, this Kogasin of iodine number 41 is then treated with mercury acetate at boiling temperature (275 cc. / 125 grams, mercury acetate / 200 cc. methyl alcohol are kept boiling 10 hours.) With the previously described workup of the reaction mixture, 275 cc. Kogasin of iodine No. 41 yield:

200 cc. hydrocarbon mixture of iodine No. 22.5.

20 cc. olefin paraffin mixture of iodine No. 91.

25 cc. raw olefins of iodine No. 175.

The quantitative separation of the olefins from Kogasin IN was therefore not possible since the iodine number of the final hydrocarbon mixture was still 22.5. The separated olefins still contain 30% saturated hydrocarbons, but they could probably be obtained in pure form after an additional mercury acetate treat.

Pages 708-715

QQ. Determination of Aromatics, Naphthenes, and Paraffins in Gasolines by Dispersion, Refraction, and Density (2/21/44)

This article presents some analytical work to evaluate the method of W. Leigh as written up in Oel Und Kohle 39, 883 (1943). The article itself was based on the paper by Ward and coworkers, Ind. Eng. Chem. Analytical Edition 6, 396 (1934) and 10, 559 (1938). Some analyses of products are given.

Page 716-717

RR. Hydrogenation of Coronen over Catalyst 5058 (2/14/44)

A solution of 6.96 grams Coronen in one liter of xylene was hydrogenated in an autoclave at 270° C. Twenty grams of 5058 catalyst were used with a 13-hour reaction time and an initial pressure of 680 atmospheres (maximum pressure 900 atmospheres).

The xylene solution of the hydrogenated Coronen did not react with alcoholic picrin solution; therefore, no unreacted Coronen remained. The xylene ~~was evaporated, the greenish residue twice recrystallized from xylene, once from~~ glacial acetic acid, and then redissolved in glacial acetic acid and precipitated with water. The purified reaction product melts at 254° C. and crystallizes in yellow plates. Its formula by carbon hydrogen analysis corresponds to dodecahydro-coronen (C₂₄H₂₄). The solution in hot sulfuric acid is deep red with red fluorescence while that of Coronen is green with weak blue fluorescence. ~~Dehydro-~~ generation of the dodecahydrocoronen in naphthalene solution, using platinum catalyst at 300° C., yields pure Coronen with no side reactions.

SS. Naphthene Analysis by Low Temperature Dehydrogenation over 5 Per Cent Platinum on Silica Gel (11/22/43) (Main Laboratory of Ruhroel GMBH)

The accurate estimation of naphthenes subject to dehydrogenation is very important in evaluating hydrogenation gasolines for further processing. The previously used aniline point method is only approximate and gives comparable but not absolute values. The determination of naphthenes according to Zelinsky (Ber. 45, 3678 (1912) and Ber. 56, 1718 (1923)) is based on dehydrogenation of their hydrocarbon mixture with platinum or palladium above 300° C. We found that at this temperature paraffins with long side chains lose considerable quantities of hydrogen and may simulate a naphthene content of as much as 20 per cent. Experiments with platinum on silica gel catalyst (5% Pt) showed a qualitative dehydrogenation of cyclohexane and its homologs even at 230° C., in a recycle apparatus. At this low temperature paraffins are hardly attacked. A 25 cc. cyclohexane produced 1.380 grams hydrogen corresponding to qualitative dehydrogenation to benzene while normal heptane under similar conditions produced only 0.014 gram hydrogen and kept an unchanged refractive index. The cause of the loss of hydrogen from the paraffins seems to be not the dehydrogenation of normal heptane to toluene but formation of high molecular resinous polymers. This polymer may also be the cause of the eventual loss of catalyst activity. By regeneration in a current of oxygen the catalyst regains full activity after several hours. Analyzing the combustion gas for CO₂ and H₂O permits a calculated correction for polymer formation. The following table presents experimental results:

Mixture	% Methylcyclohexane		% Methylcyclohexane	
	Calculated From H	Correction	Calculated	Theoretical Valuc. %
10 cc. Methylcyclohexane)	50.19	-0.10	50.09	50.0
10 cc. n-Heptane)	20.26	-0.19	20.07	20.0
Same	1.01	-1.10	0.00	0.0
n-Heptane	0.19	-	0.19	0.0
Toluene				
10 cc. Toluene)	9.21	-0.20	9.01	9.09
10 cc. Heptane)				
2 cc. Methylcyclohexane)				

The hydrogen was oxidized over CuO and weighed as water.

By this new method the naphthene content of VT 330 gasoline gave a dehydrogenatable naphthene content of 9.6 per cent (calculated as cyclohexane). ~~By the physico-chemical method of Ibing-Ebert (Z. Angew. Chem. 53, 60 (1940)), the pure cyclohexane content of VT 330 was 8.8 per cent. The naphthenes in VT 330 therefore are about 92 per cent cyclohexane. The naphthene content calculated by the aniline point method (40 per cent) deviates considerably from these values. In VT 330, therefore, there must be naphthene-like hydrocarbons which it is difficult or impossible to dehydrogenate. It will be attempted to identify these in future experiments.~~

TT. Investigation of Proposed Naphthene Analysis by Hydrogenation of Paraffins to Methane over Nickel Alumina Catalyst (9/28/43) (Main Laboratory of Ruhrcoel GMBH)

Pfaff and Brunck report in Ber 56, 2463 (1923), that paraffin hydrocarbons can be qualitatively decomposed to methane over a Ni-Al₂O₃ at a temperature of 260° C. with excess hydrogen, while naphthene carbons are not attacked at the same conditions. The NiAl₂O₃ catalyst was prepared as follows:

An aqueous solution of 1 mol Ni(NO₃)₂ x 6 H₂O was mixed with a solution of 1/3 mol Al(NO₃)₃ x 9 H₂O in sodium hydroxide and further sodium hydroxide was added for complete precipitation. Excess NaOH is neutralized by CO₂. This Ni-Al-hydroxide mixture is mixed with 1/5 mol pure Al₂O₃, washed thoroughly, dried at 120° and reduced in hydrogen at 320° to 350° C. Results of several experiments are given and summarized as follows: The NiAl₂O₃ catalyst of Pfaff and Brunck splits paraffin hydrocarbons to methane but under the same conditions naphthenes are also cracked, whereas at lower temperatures or with less active catalyst the naphthenes remain intact but paraffins also are only incompletely attacked. Naphthenes and paraffins cannot be separated in this manner.

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UU, VV, WW

Items UU to WW are three consecutive reports of a series of pilot plant runs on the hydrogenation of hard coal extract, carried out at Leuna between August, 1936 and July, 1937. These reports cover 82 pages of the film. The following presents a translation or resume of the aim of the experiments, the equipment used, and the summaries of the three reports.

Report No. 1

Problem

In the extraction of hard coal according to the Pott-Broche-process a brittle, practically ash free, product with a melting point of about 200° C. is produced. Liquid products can be obtained from this material by hydrogenation. Depending upon the reaction conditions and process, they may be fuel oil or gas oil plus a certain amount of gasoline. In the runs reported here fuel oil was the desired end product.

Process

The hard coal extract was supplied by the experimental unit Karnap in the Gewerkschaft Mathias Stinnes. The material was supplied in lumps (i.e., free of solvent) and had to be crushed to dust. The extract dust is slurried in oil to a 40 per cent slurry. Slurry oil is at first anthracene oil and later the topped separator product oil produced in the run. Dry ground catalyst is added to the slurry to the extent of 5 per cent based on extract. The finished slurry is run through a measuring vessel to the slurry pump which feeds it to the high pressure equipment.

The slurry is heated together with the hydrogenation gas and passed through the ovens which are arranged in series. The equipment works at 300 atmospheres pressure. The chamber is equipped with a gas recycle. The consumed hydrogen is replaced by fresh gas which is compressed by additional compressors from 220 to 300 atmospheres.

The liquid products of this process are bottoms (Entschlammung) and separator product (Abstreifer). Both products are accurately measured after pressure release. The bottoms go to a centrifuge for work-up. The separator product, after water removal, is topped in separate distillation equipment and used as separator-product-residual-oil for slurrying the feed.

Equipment

Low Pressure Equipment Ahead of High Pressure Stage

The extract is precrushed in a crusher (Brecher) then reduced further in a disintegrator and finally ground in a mill (Schlagscheibermuehle). The final extract dust leaves 1.8 per cent on a 400 mesh sieve. The catalyst is ground in a ball mill (Kugelmuehle).

The slurring is done in two containers (5 m³) which are equipped with stirrers. The containers are gas tight and gas blanketed. Under the feed valves through which the weighed extract dust is introduced are coarse sieves to distribute the extract dust slowly and evenly into the slurry oil to prevent lump formation. After adding the catalyst also, the slurry is heated in the slurring vessel to 95° to 105° and pumped out. All lines, slurry- and measuring-vessels must be easy to heat.

High Pressure Equipment

A small catalyst slurry pump with a modified plunger serves as slurry pump. The chamber itself in the first installation was equipped with three ovens of 200 liters each. The oven walls have a length of 8 meters and diameter of 300 mm. There is a 50 mm. layer of insulation inside the ovens, leaving a clear inside diameter of 200 mm. A heat exchanger serves to preheat the entering gas. The actual heating of the product gas mixture takes place in a N₂ double coil, using heating gas. The heating gas is taken from the 200 atmosphere pressure ring of the tar recycle line and returns to the suction side. It is brought on temperature by an electric preheater. In addition to the ovens, the separator and the necessary coolers are in the chamber. The separator receiver is outside.

Further parts of the equipment are a gas circulating pump and two 2-stage fresh gas compressors.

Low Pressure Equipment After the High Pressure Stage

The bottoms (Entschlammung) are depressured in a container which is equipped with a level recording device for accurate measurement. They are pumped out at intervals through an Eckardt meter.

A Haubold centrifuge at 515 r.p.m. (No. 278) is used for centrifuging.

For depressuring the separator product two 5 cubic meter containers are available. They are used separately for 24 hours each. The full vessel is connected to the distillation column and serves as still pot. High pressure steam coils heat the charge stock in the still pot and the reboiler. The column is 7 meters high. Gasoline and residuum are measured in calibrated vessels and pumped out through Eckardt meters to permit a further check on quantities. The released gases from separator and bottoms and the distillation gases go to the "Hy-gas system" after being measured.

Run No. 1

The chamber was started up on 8-29-36. It was first heated with gas circulation alone to 300°, then anthracene oil was fed and the temperature increased to 400°. ~~Here already the temperature distribution in the three furnaces proved very bad.~~ The radiation of the furnaces was so large that the second and third furnace were lower in temperature than the first. It was proved later that the heat of reaction when using extract slurry did not improve this condition. The slurry (500 liter of 30 per cent slurry; feed rate 0.9) was preheated to 450°. Entering the second furnace the temperature was 50° and entering the third furnace 100° lower. Exit temperature from the third furnace was 330°. At the allowable feed rate as indicated by preliminary experiments, the temperature decrease would be still greater. Higher preheat could not be obtained because of equipment limitations in the heating gas line. Difficulties were also experienced in measuring the fresh gas, so that the chamber was taken off stream on 6-9-36 for several changes.

Changes in Equipment

The third oven was removed altogether. A second N_5 coil was built between the first and second oven to reheat the material. Also the lines between coils and ovens were welded wherever possible to avoid flanges. Insulation was increased. The limiting N_4 heat-exchanger coil in the heating gas circuit was replaced by a N_5 coil to permit higher temperatures.

To increase velocity in the furnaces a hot recycle was built in, similar to that of tar chambers.

The scheme of the high pressure equipment is indicated in the flow sheet (1323a). The fresh gas is introduced into the suction side of the gas circulating pump in the 300 atm. line by compressors. In a heat exchanger the gas absorbs the heat of the vapor products of the oven and then combines with the slurry ahead of the first preheater coil. The gas-slurry mixture passes through the preheater into the first oven, the reheater, and the second oven. In the separator, the liquid high boiling oil and solids separate from the vaporized products and gas. These latter go through the heat exchanger to the separator receiver. The combined reaction volume of the two furnaces is 400 liters.

Run No. 2

The progress of this run is discussed in some detail. It is summarized below.

Summary

Run No. 1 (Ran from 8-31-1936 to 9-6-1936)

It was discontinued because of poor temperature distribution. No balances could be made from this run.

Run No. 2 (Ran from 9-14-1936 to 9-27-1936)

Feed: 200 liters/hour. The extract content of the feed was at first 30 per cent, then 40 per cent (starting 9-19-1936).

Gas Throughput: 600 m^3 /hour; later 500 m^3 /hour (starting 9-21-1936)

Throughput: 0.22 (kg extract/liter reactor volume/hour)

Maximum Oven Temperature: 465° C.

Produced Per Ton of Feed (392 kg extract):

<u>Abstreifer</u> (water free)	532 kg
<u>Entschlammung</u>	406 kg
Loss, Based on Feed	6.2%
Loss, Based on Extract	15.8%

Hydrogen Consumption: 900 m^3 per ton extract. After measuring the leakage losses (15 m^3 /hour) the hydrogen consumption was calculated to be no more than 720 m^3 . It may be less than that since leakage of the hot equipment presumably is greater than cold.

The extract was slurried with anthracene oil until 9-22-1936, then with topped Abstreifer. Since the amount of topped Abstreifer will not be sufficient, it is planned to continue the experiments using centrifuge oil and finally Entschlammung.

During the last days, the resistance of the chamber rose from 2 to 8 atmospheres. When an attempt was made to increase the slurry velocity in the exchangers by using the hot recycle, the gas cycling pump cut out and the Entschlammung line from the separator plugged, so that the separator ran over. Since the line could not be cleared, the run was discontinued.

For further runs it is planned to slurry the extract with Entschlammung or with oil from the centrifuge. Therefore a cold gas line will be installed between oven 2 and separator to regulate the ratio of Entschlammung and Abstreifer.

The leakage constant of the chamber will be determined to permit closer calculation of hydrogen consumption.

Report No. 2

Problem

It was the purpose of this experiment to continue the previously reported series of 300 atm. hydrogenation runs on hard coal extract, under modified conditions. The desired end product is still gasoline and fuel oil.

Process

In the previous runs, topped separator product, i.e. a 200 - 350° C. gas-oil, was used for slurry-oil with admixture of fresh catalyst, and the Entschlammung, after centrifuging out the solids, produced a commercial fuel oil; in the new runs, the slurry oil is to consist of topped separator product and Entschlammung in the ratio in which they are produced. The remainder of the mixture, after centrifuging, represents the fuel oil production. The catalyst is recovered and reused after centrifuging. The following advantages are to be realized by this operating procedure:

- (1) Improvement of the pour point, viscosity, and asphalt content of the fuel oil; this necessitates increase of the throughput.
- (2) Using the comparatively low boiling topped separator product as slurry oil created a danger of drying out and consequent coking or scaling due to the slurry, in the heat exchangers. Heavier slurry oil prevents this.
- (3) Savings in centrifuging capacity since a large part of the product is recycled uncentrifuged; also consequent catalyst savings.

Because of the heavier slurry oil, the extract concentration in the slurry was reduced to 25-30%; the feed rate was raised to compensate for this.

Equipment (Flow sheets given on the film)

The equipment is essentially unchanged from that reported in report 1. A cold gas line was inserted between oven 2 and separator to lower the separator

temperature. In the course of the run, a water wash (200 mm. pipe, 4 m. high) was installed in the recycle gas line to remove ammonia and CO₂.

Run No. 3

This run was made from 10-5-1936 to 11-5-1936, without interruptions. It was discontinued after all the available extract (65 cc.) had been worked up. This run is discussed in detail, including discussion of the hydrogenation product quality and of the material balances. Following is a translation of the summary.

Summary

Pilot unit runs on the hydrogenation of hard coal extract at 300 atm. were made at Leuna, to provide a basis for the Welheim hydrogenation plant then under construction. The run lasted from 10-5-36 to 11-5-36. The purpose was to hydrogenate the extract to gasoline and fuel oil.

The feed rate was 0.27 to 0.35 (kg extract per liter reactor space per hour).

Feed: 400 Ltr./hr. with 25 to 30% Extract

Reactor temperature: 26.5 mV

Gas feed: 500 Ltr./hr.

Pressure: 300 Atm.

Yield per ton of extract: Appr. 250 kg Gasoline
 500-550 kg Heating Oil
 200-250 kg Gas

The gasoline is highly aromatic with excellent motor performance characteristics. The octane number is between 75 and 90, depending on the cut point (160 and 200° C. respectively).

Per ton of extract, about 30 kg of acid oils of a phenolic character are produced, which are included in the higher cut point gasoline. They are mainly cresols and xlenols. These can be either recovered separately or converted to benzene and its homologs by 50 atm. dehydrogenation together with the crude gasoline. Inclusion of these low boiling aromatics further improves the quality of the gasoline.

Compared with the usual gasolines, this product has an excellent miscibility with methyl alcohol, due to its high aromatics content.

The 190-230° C. fraction probably contains appreciable amounts of tetralin in addition to the cresols. Experiments attempting to substitute this fraction for ~~the tetralin-cresol mixture used in extract preparation at Kormap were not unfavorable.~~ Extract production might become considerably cheaper if this fraction could be used for slurring the coal, thus making unnecessary the planned solvent cycle of removal of solvent from extract, naphthalene separation, and naphthalene hydrogenation.

If the present operating scheme remains in effect, consideration must be given to the production of make-up naphthalene by recovering the naphthalene produced by high pressure dehydrogenation.

The fuel oil, a mixture of topped separator product and Entschlammung in ratio of production, shows favorable ignition properties, and burns without carbon residue. It does not quite meet the viscosity and ash requirements of the German navy; however, small scale experiments promise considerable quality improvement when operating at 700 atm.

Hydrogen consumption per ton of extract was 906 m³ at 300 atm. Using 70% H₂ will raise this by about 125 m³/ton.

Report No. 3

Problem:

The purpose of the runs is to obtain chemical and operating data for the hydrogenation plant Welheim. Although Welheim will use 700 atm., the pilot plant can only use 300 atm. These runs are continuations of those previously reported, but under changed conditions.

The variables to be tested are various catalysts in liquid and solid form, and the performance of various feed stocks of hard coal origin, such as pitch, tar, or anthracene oils, which may be used in addition to or instead of the extract. Furthermore, sufficient gasoline was to be prepared to permit further workup by dehydrogenation in a 10 liter reactor.

Not so much emphasis was placed on testing the fuel oil, since the oil produced at Welheim at 700 atm. will be topped Abstreifer and thus contain no solids or asphalt, while the pilot plant fuel oil is of considerably lower quality. That part of the pilot plant fuel oil production not used for slurring was centrifuged and saved as starting oil for Welheim.

Equipment:

The equipment was essentially the same as that described in Report 1. Newly installed was a gas preheater of ten U turns of 24 mm. diam., two of which served as intermediate preheaters between ovens 1 and 2, in Runs No. 4 and 5. Previously, the gas-oil mixture had been heated in two 45 mm. diam. heat exchange coils in series, using a heating gas which had been heated electrically. The change was made because the low velocity in the coils caused deposits and plugging.

The distillation reboiler was changed to electric heating to permit going to higher temperatures, (225° instead of 180°), so that the phenolic components could be distilled overhead for inclusion in the gasoline, to permit subsequent workup by dehydrogenation. Runs No. 4-8 are described in some detail. Following is an abbreviated translation of the evaluation of the runs.

Evaluation:

Concerning catalysts, the Molybdenum-coke catalyst* proved considerably more desirable than the heavier iron-catalyst**. Iron catalysts caused deposits in

* Catalyst 11002, containing 2% Mo on coke (Grude) Sp. gr. 1.85

** Iron catalyst called "Zschimmermasse" Sp. gr. 3.22

the heat exchangers even though the velocity was increased from 3.5 to 7.5 m/sec. In Run 6, at the high velocity, the pressure drop had increased to 11 atm. after 4 weeks. Even at a velocity of 4.6 m/sec., no pressure drop was experienced when using the molybdenum-coke catalyst.

The yield varies with the temperature distribution in ovens 1 and 2, and with the soaking time. Gasoline yield (incl. C₅ and 50% of C₄s) was highest, at 25%, in Run 3, at good temperature distribution and with long soaking time. It went down to about 21% in Runs 4 and 5. Temperature distribution between ovens 1 and 2 became much worse after the intermediate heater was removed, after Run 5. Oven 2 inlet was 20° lower than oven 1. For this reason, results from Runs 3, 4, and 5 can not be compared on one basis with results from Runs 6, 7, and 8.

In Run 6b, the feed contained 35% extract and 20% hard coal tar oil. The high feed rate of 0.6 (based on fresh feed) affected the gasoline yield unfavorably (7.7% based on new feed). No gasoline seems to have been made from the tar oil. Of the 10.7% naphthalene in the tar oil, about 85% was reduced in the chamber.

Comparing Run 7, using the Molybdenum-coke catalyst with Run 6 which used iron catalyst shows that in spite of the higher feed rate (.28 vs. 0.195) a pour of 0° and an asphalt content of 13% are obtained to compare with +17° pour and 17% asphalt in Run 6. Although the gasoline yield of 16-17% including light ends is 2-3% lower than in Run 6, this is probably due to the 12° lower reaction temperature. Disregarding the freedom from iron deposit troubles, the coke catalyst is considered superior on a performance basis.

Run 7a, using pitch for feed, ran without difficulties. The gasoline yield of 10% is 50% less than that from extract. The feed rate of 0.38 kg. pitch per liter oven volume per hour was higher than that used for extract. The pour of the slurry oil was -10°, the asphalt content 6%.

In Run 8, the equipment was converted to be used as a combination chamber, i.e. Oven 1 was operated in slurry operation as usual, but Oven 2, separated from 1 by a separator, was operated in vapor phase with a fixed bed catalyst. Presumably, however, a part of the Abstreifer of which 85% boils below 350° C., passes over the catalyst in liquid phase. The yield, compared with Run 7, increased about 100%, to near 30%. The pour of the slurry oil is comparatively high because of the high feed rate, the asphalt content normal at 10-13%. This operating method is considered of great potential importance since it produces in one step the finished products from the raw material, omitting intermediate distillation and tankage. Several variations of the scheme, to produce different end products, are briefly sketched out.

In Run 8b, anthracene-oil-residue was fed in addition to the extract. This run is compared with Run 6 where hard-coal-tar-oil was fed, to show that the modified operating method leads to an increased gasoline yield.

The hydrocarbon analysis of the product gasolines is summarized in Table 8. The gasolines from Runs 3-7 are approximately identical. They are highly aromatic and have a 10-20% phenol content. They have high octane numbers (Delco Motor) increasing from 80 to 90 with increased cut point. Since chemical treat of the gasolines entails high losses, they were further refined by treatment at 60 atmospheres over NiWo-catalyst (nickel-tungsten ?) at high hydrogen partial pressure. This reduces the phenols to aromatics and dehydrogenates part of the naphthenes to form more aromatics. Octane numbers of 85-93 are thus obtained, the highest occurring in gasolines from Runs 6b and 7a, where hard coal tar and pitch were added. The

gasolines from the iron catalyst runs required caustic and acid wash for color stability, while those from molybdenum catalyst runs required only a caustic wash. This is probably because of stronger hydrogenation by the molybdenum catalyst in the slurry phase.

Gasolines from Run 8 differ fundamentally from the others in that they are highly naphthenic and contain only 1-3% phenols, which could be decreased further by increasing the temperature or decreasing the feed rate of Oven 2. The gasoline is easy to refine chemically. The treated gasoline has an octane number of 70-80, which decreases with increasing cut point. The aviation gasoline is more lead-susceptible than the aromatic gasolines, increasing from 71.5 to 84.5 with 0.08% lead.

Phenol yield is 3-3.5% based on extract with the iron catalyst, 2.2% with the coke catalyst, and 0.7% in Run 8. About 5% of the phenols remains in the water layer. About 70-80% of the phenols are carbolic acid and cresol.

The gas yield depends on several variables, and was from 25-28% based on extract, except in Run 8 where it varied from 17-35%. It is between 4 and 9% based on total feed.

Hydrogen consumption was 700-800 m³ per ton extract, or 120-220 m³ per ton of feed, and about 20% higher in Run 8.

The heat of reaction was 66 Cal./kg. feed in Run 7 with 25% extract in the feed, 80% liberated in Oven 1 and 20% in Oven 2; it was 94 Cal./kg. feed in Run 7a with 35% pitch in the feed, 66% in Oven 1 and 34% in Oven 2. For comparison, the heat liberated in the tar chamber in Leyna is 50 Cal./kg. feed, in the coal chamber 120 Cal./kg. feed.

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Report on the Hydrogenation of Pitch Obtained by the Low Temperature Coking of Hard Coal. Main Laboratory of Ruhröel GmbH, Hugo Stinnes Werke - December, 1944

The contents of this report are well summarized in a "Summary and Critical Evaluation of Results," the translation of which follows:

Our 1½ years of experimentation on the hydrogenation of hard coal low temperature carbonization pitch have indicated a solution of the problem which had not been suspected and which indicates this pitch to be an excellent material for high pressure hydrogenation; this assumes of course that the pitch is of the quality which was used in this work.

During the course of the experiments the surprising fact was definitely proved that a solution of 60 parts of ash and solids-free pitch in 40 parts gas oil can be continuously hydrogenated over fixed catalyst without damage to the latter, in spite of a content of the solution of 20% gasoline-insolubles. Considering the well known sensitivity of used catalyst to asphaltic material, this fact is particularly surprising. It is only explainable by the supposition that the low-temperature carbonization pitch is entirely different in its make-up from regular coking pitch. This difference is partially recognizable from the analytical data; however, such a considerable difference in performance was not expected from these data.

Since a considerably higher catalyst concentration is utilized in the hydrogenation of low temperature carbonization pitch over fixed bed catalyst than obtains in the hydrogenation of regular coking pitch in the slurry phase, the former is completely reduced to asphalt free liquid reaction products. The hydrogenation equipment is similar to a gas-phase chamber; it does not utilize a product separator (Abschneider) and the single product is a yellow-brown oil. In the slurry phase (Sumpf phase) hydrogenation of high temperature pitch only 60% of asphalt free oil is produced while the remainder is taken as asphaltic and highly viscous mud or bottoms (Abschlamm) in the separator.

The complex and expensive workup of the Abschlamm, one of the most unpleasant problems of hydrogenation, is therefore entirely eliminated when working with low temperature pitch. However, it requires the complete removal of gas oil insolubles and total ash, i.e. including the organically bound, prior to hydrogenation. This initially difficult problem was brought to a satisfactory conclusion. The specially developed de-ashing process has the further advantage that the fundamental structure of the low temperature pitch is so modified by it that the reaction products of the consequent hydrogenation are poorer in hydrogen and consequently more valuable.

The de-ashing process is very simple and should produce no difficulties even when applied on a plant scale. Its cost should be slight compared to the workup of Abschlamm.

The use of filtered, solids-free feed to the hydrogenation equipment avoids the cause for all the technical difficulties met in slurry phase operation, such as sedimentation and coking of the preheater, the lines, the ovens, and particularly of the separator. This alone is a great practical advantage.

A further advantage of our process of low temperature pitch hydrogenation over fixed bed catalyst is the doubled output compared to the usual process. This means that twice as much pitch can be worked up and twice as much product made in the same equipment and the same time.

It is particularly surprising that we succeeded in attaining a quality of product which is not essentially inferior to that from high temperature pitch. The primary crude gasoline and gas oil can be processed by the well known Ruhroel one-stage hydrogenation at 600 atm. to produce an aviation gasoline of the same performance rating as that from high temperature pitch gas oil, i.e. a C 3 gasoline.

The heavy oil from thermally pretreated low temperature pitch is produced in a quality which passes the strict navy requirements for fuel oil. By a simple consequent cracking process, its quality can be further improved.

The proposed hydrogenation process is illustrated in a flow sheet which indicates its three main steps:

(1) De-ashing of the low temperature pitch slurry by a treat at 410° C. and 50 atm., with consequent filtration.

(2) Hydrogenation of the solids- and asphalt-free solution at 450° C. and 700 atm.

(3) Hydrogenation of the crude gasoline and gas oil by the Ruhrcoel process in the vapor phase, at 485° C. and 550 atm.

If required, the following fourth step may be added:

(4) Cracking of the fuel oil at 475° and 100 atm.

From the flow sheet, the following material balance is obtained:

FEED: 100 kg. Low Temperature Coking Pitch

MAIN PRODUCT: 44.5 kg. Navy - fuel oil
26 kg. Aviation gasoline
70.5

BY-PRODUCT: 22 kg. gaseous hydrocarbons plus NH₃ and H₂S, which yield 10 kg. Gaseous Fuel (propane-butane)

WASTE PRODUCTS: 6.5 kg. Water
1 kg. Solids
7.5

The results of the experiments have been consolidated into two patent applications.

Circumstances have prevented continuation of the experiments as planned. The long term run had to be discontinued after 28 days, and the planned experiments using low temperature carbonization tar directly had to be postponed.

TRANSLATOR'S NOTE: Following are abstracts of the main topics of the report:

Introduction: This delineates the status of hard coal high temperature coking pitch as hydrogenation feed. It is in large scale operation, particularly with Ruhrcoel. The pitch is preferred to the coal because of its aromatic structure and lower ash content. It is the most hydrogen deficient product subject to hydrogenation and therefore requires higher temperatures and pressures than hard coal. The hydrogenation products are also more hydrogen deficient, more aromatic, and therefore more desirable. The fuel oils have excellent asphalt solvent properties. Suitable treatment of gas oil and gasoline permits production of gasoline of 40-50% aromatic content. The low ash content of the pitch is of advantage since it erodes the equipment less than coal. The remainder of the introduction names the sources of various low temperature carbonization pitch samples which were experimentally hydrogenated.

FEED: The following main differences between high and low temperature pitch were noted:

(1) Hydrogen and oxygen content of the low temperature pitch are significantly higher, carbon content consequently lower. Nitrogen, sulfur, and chlorine are essentially the same.

(2) Fractional extraction analyses show the low temperature pitch considerably more soluble in non-polar solvents. There are only slight amounts of high molecular components, insoluble in boiling tetralin-cresol mixture (4:1). These particularly are what cause deposits in lines and ovens; they accumulate in the Abachlamm.

(3) In the high temperature pitch almost all the ash is present as oil insoluble inorganic material, while in the low temperature pitch 70-80% is oil soluble, presumably chemically bound in the oxygen-compounds. These compounds are very stable, decomposing only above 300° C. This caused them to decompose specifically in the preheater of the hydrogenation equipment, producing hard scales, mostly of iron, and quick plugging of the preheaters. The ash from low temperature pitch contains 70-80% Fe (as Fe_2O_3) and 5-15% water solubles (mostly NaCl), while the ash from high temperature pitch contains about 15% Fe_2O_3 and 5% water solubles.

Slurry Phase (Sumpf phase) Hydrogenation

Two attempts to use slurry phase operation with low temperature pitch feed showed this method of operation to be practically impossible. This is due to the fact that the pitch is much more easily and completely hydrogenated to asphalt-free products which are vapors at reaction temperature. Consequently they cannot carry the powdered catalyst out of the reaction chamber, which leads to operating difficulties; this even under milder conditions than used for high temperature pitch.

Mixtures of high and low temperature pitch with not less than 35-40% of the former can be successfully hydrogenated in slurry phase. Adding the low temperature pitch increases the usual gasoline and gas oil yield somewhat and causes the heavy oil produced to be less asphaltic and less viscous.

It was also found that the low temperature pitch products are more hydrogen rich and contain more oxygenated compounds, particularly phenols.

Fixed Bed Operation

The contents of this section, except for some equipment details, are summarized in the detailed summary. In addition, the catalyst composition is given as essentially consisting of activated aluminum hydrosilicates, on which less than 1% Molybdenum and 2-5% Chromium are deposited.

De-ashing of the Low Temperature Pitch

The finally developed de-ashing process consisted of adding flowers of sulfur (about 0.5%) to the solution of the pitch, and pumping the mixture through a system of pipes at 400° C., without hydrogen addition; however, small amounts of gas are cracked off, particularly methane, ethane, and propane. The reaction is essentially independent of pressure, but the pressure was kept between 50 and 60 atm. to keep the gas dissolved in the oil. Ash could be reduced from 0.3% to 0.006%, by filtration of the product resulting from this treatment, 1% Kieselguhr is required as filter aid to attain practical filtering times.

The remaining three sections which discuss the quality of the hydrogenation products are sufficiently summarized in the detailed summary.