Mr Wilkey

U. S. BUREAU OF MINES 999 T-384
HYDRO. DEMON. PLANT DIV.

ACSraum
6/11/47

Benzination of B-Products from Hydrogenation Works

By Günther, Ludwigshafen, 20 June 1944

Synopsis.

1. B-middle oil from prehydrogenation cold catchpot products from Scholven, Gelsenberg, Wesseling, Leuna and Pölitz, received by us from December 1943 to March 1944, were exceptionally well refined, without exception, and very well suited to benzination. The finished gasolines, produced from the cold catchpot products by benzination of the B-middle oils and mixtures of the 6434-gasolines with the prehydrogenation gasolines, were of 87 octane quality throughout, at a boiling end point of 145° C.

2. In Brüx, B-middle oil (AP 55), well suited to benzination, was produced only in the starting period of the prehydrogenation stalls. In the meantime the activity of the prehydrogenation catalysts has deteriorated very much, so that the AP of the B-middle oil is only 41, in spite of very high temperature. To be sure, the refining is still very good, but the B-product is no longer readily benzinated. Furthermore, the prehydrogenation gasoline has such a low octane number and the quantity is so great that the finished gasoline is not of 87 octane quality at 145° C boiling end point. To produce 87 octane quality the gasoline would have to be cut only at 135-140° C.

3. Tests and experiments with cold catchpot products from the Pölitz prehydrogenation stalls (8376), with and without subsequent 5058, showed that differences exist purely with regard to the quantity of prehydrogenation gasoline in the cold catchpot product, but not with regard to the quality of this gasoline and the B-middle oil. The differences in the gasoline content of the prehydrogenation cold catchpot product have this effect, that with subsequent 5058 in prehydrogenation, the finished gasoline is of somewhat lower anti-knock quality than with pure 8376 prehydrogenation. No easing of the work of 6434 could be observed in our experiments by subsequent 5058 in prehydrogenation.

In the first quarter of 1944 we received prehydrogenation cold catchpot products from Scholven, Gelsenberg, Wesseling, Brüx, Leuna and Pölitz. These were decomposed into gasoline -150°C and middle oil above 150° C. The middle oil and gasoline were analyzed, the middle oil was benzinated over 6434 and the 6434 gasoline, as well as the mixture with the prehydrogenation gasoline belonging to it, was analyzed.

From Pölitz we received an additional barrel each of cold catchpot product from the pure 8376 stall and the 8376-5058 stalls, besides the normal prehydrogenation cold catchpot product from production, for the examination of questions of the effectiveness of 5058 connected behind 8376.

All c.c.p. products were decomposed into gasoline and middle oil at 150° C and the middle oil run over catalyst 6434, with a thruput of 1.5 at 250 atm H_2 and recycling the C-middle oils, to gasoline with 55-60% to 100°C, (boiling end point 140-150° C). The experiments were made in 50 c.c. converters.

Results of investigations of the c.c.p. products and the gasolines and middle oils recovered from them are given in Table I for the normal products of the plants, and in Tables IV and IVa for the Pölitz products. Tables II and V show the results of the benzination experiments, as well as data on the quality of 6434-gasolines. Tables III and VI show the results of investigations of the current mixture gasolines from prehydrogenation and 6434 gasoline in the proportion produced.

I. Discussion of Tables I, II & III.

A. Table I.

The investigations and experiments cover 7 bituminous coal liquefaction B-middle oils (Scholven & Gelsenberg), 2 brown coal liquefaction B-middle oils (Rheinbraun & Leuna), 2 brown coal tar B-middle oils (both from Brüx), and a petroleum (abt. 70)-bit. coal liquefaction (abt. 30)-B-middle oil (Pölitz). The aniline points of the products, compared to each other, are such as would be expected from the starting materials, with the exception of Brüx B-middle oil of 9.3.1944, which must be removed from this series because of its extraordinarily low A.P. All B-middle oils, including that from Brüx with the low A.P., are outstandingly well refined, phenols mostly below 0.01%, all base numbers (Basenzahlen) below 3.0 mg NH_3/l. The products from Scholven, Gelsenberg, Wesseling, Leuna and Pölitz are from stalls with catalysts 8376/5058 or 5058/8376, which have been in operation for some time, over 2 years, in part, and in which the catalyst activity has not yet deteriorated for all practical purposes. The Brüx oils are also from 8376-5058 stalls. The product of the 27.8.1943 is from the starting up period, but was produced at already normal thruput. The middle oil from it has an A.P. of 55. In the course of the following 7 months the activity of the prehydrogenation catalyst in Brüx dropped very much, so that in February 1944 only B-middle oil with an A.P. of 41 was obtained, in spite of a considerable increase in temperature in the meantime.

B. Table II.

Table II shows that the B-middle oil from all plants, except the Brüx B-middle oil at the time, are readily benzinated. The index of benzination varies between 60 and 72. Gasification was high in all cases, over 20%, which is possibly due to the fact that, generally speaking, too high a gasoline concentration was aimed at. All 6434-gasolines generally represent good 87 octane fuels at approximately 55% -100° C in the gasoline and a boiling end point of 145° C and with octane numbers above 72 (motor) and above 89.5 (motor + 0.12% lead).

C. Table III.

In the benzination of B-products from all works, except Brüx, one part of prehydrogenation gasoline goes with approximately 2 parts of 6434 gasoline. Since the prehy-gasoline has poorer anti-knock properties than the 6434-gasoline, the octane numbers of the 6434-gasolines are deteriorated by the admixture of prehy-gasolines. The finished gasolines from the c.c.p. products from Scholven, Gelsenberg, Wesseling, Leuna and Pölitz are still of 87 octane quality, in spite of it. Only in the Brüx gasoline is 87 octane quality not obtained, due to the larger quantities of prehy-gasoline and its especially low octane number at 150° C boiling end point. At a boiling end point of 135-140° C 87 octane quality will probably be obtained.

II. Discussion of Tables IV, V & VI.

The investigations and experiments, the results of which are shown in Tables IV, V and VI, are based on the following starting materials:

1) Prehy c.c.p. products from normal Pölitz production, sample of the end of January 1944. B-middle oil. A.P. 56.

2) C.c.p. products from 8376-5058 stalls 1,6, 7 and 8 in Pölitz. Product collected from daily samples in the period from Nov. 1943 to March 1944, barrel HWP-4356. B-middle oil. A.P. 58.5.

3) C.c.p. products from the pure 8376 stall in Pölitz. Product collected from daily samples in the period from Nov. 1943 to March 1944, barrel HWP-5105. B-middle oil, A.P. 60.5.

The investigations and experiments were primarily to clarify specific differences in analysis and hydrogenation behavior between the c.c.p. products from the 8376-5058 stalls and the pure 8376 stalls.

A. Tables IV and IVa.

Although hydrogenation was somewhat stronger in the pure 8376 stall than in the stalls followed by 5058, the c.c.p. product from the latter stalls contains considerably more gasoline (26.5%) than the c.c.p. product from the pure 8376 stall (19.5%). This indicates that 5058 following 8376 clearly splits, although it is deliberately run at a very low temperature. As might be expected, the gasoline from 8376-5058 stalls also contains a little more paraffins than that from the pure 8376 stalls. But since hydrogenation is somewhat stronger in the pure 8376 stall, it contains less aromatics, 3% in the combined cyclic compounds, compared to 10% with subsequent 5058. Both of these effects are apparently equalized in the octane number, so that no differences could be found here.

In the degree of refining, also, practically no differences can be found. The difference between the base numbers of the 2 products, so slight it is almost within the limits of errors, is in the same class with the degree of hydrogenation. As far as the boiling end points of the B-middle oils is concerned, one might have expected that these would be somewhat lower with the subsequent 5058. However, the analyses show no such effect. On the contrary, the boiling curve shows that the 8376-5058 c.c.p. product is thinner on top than the 8376. This is particularly true of the fractions above 250° C.

The aniline point curves of the 8376-5058 and 8376 c.c.p. products closely resemble each other. The differences, as expected, are that with the supplementary use of 5058, the upper fractions are relatively better hydrogenated than the lower, compared with using pure 8376 alone, i.e. the A.P. curve is steeper with the supplementary use of 5058 than with the pure 8376.

B. Table V.

There are no differences in the index of benzination of the 2 B-middle oils, as well as in the yield and quality of 6434 gasolines pro-

duced from them. The greater degree of hydrogenation in the pure 8376 stall is still recognizable in the 6434-C-middle oil, but no longer in the 6434-gasoline. The slight differences in the octane numbers might be due to small variations in the boiling curves, where they are outside of the limits of errors in the determinations at all.

C. Table II.

The splitting effect of the supplementary 5058 is clearly expressed in the mixture proportion of prehy: 6434-gasoline. With pure 8376 in prehydrogenation the finished gasoline contains 21% prehy-gasoline, with 8376/5058 it contains 29%. Since, however, the prehy-gasoline has lower octane numbers than the 6434-gasoline, a lower octane number in the finished gasolines must result, even with equal octane numbers in the prehy- and the 6434-gasolines, in a mixture with greater prehy-gasoline content, or, in this case, with supplementary 5058 in prehydrogenation. This has also been verified in the motor tests. Even though the measured differences are still almost within the limits of errors, it is significant, that all differences found are in the direction in question.

/fkp

TABLE I

B-Products from Hydrogenation Works

Works	Scholven	Gelsenberg	Wesseling	Leuna	Brix	Brux	Pölitz
Date Reg'd at Lu.	2.2.44	3.1.44	15.3.44	23.12.43	27.8.43	9.3.44	2.2.44
Lu. Designation	P 1422	P 1596	P 1508	P 1521	P 1589	P 1589	P 1475
Spec. Grav.	0.830	0.817	0.827	0.814	0.812	0.800	0.811
A.P.	43.0	46.0	49.0	49.5	51.0	41.5	51.0
Initial Boil	84/00	66/00	59/00	72/00	70/00	62/00	62/00
% - 150	29	31	27	27	26	43	31
180	42	45	36	39	41	55	42
225	69	70	56	62	66	77	69
300	-	-	89	95	93	-	95
Boil. End	296/98	295/98	330/96	305/98	315/98	293/98	305/98
Gasol. -150°: %	29.0	30.0	28.3	23.3	28.8	39.3	28.5
M-Oil >150°: %	71.0	70.0	71.7	76.7	71.2	60.7	71.5
Gasol. to:	-145	-140	-145		-150	-150	-145
Spec. Grav.	0.757	0.743	0.740		0.751	0.748	0.740
AP I/II	40/47	43/52	44/48		43/50	42/52	47/50
Initial Boil	72/00	56/00	52/00		59/00	56/00	55/00
% - 70	-	4	4		2	3	3
- 100	43	56	50		34	44	46
Boil. End	145/99	140/99	153/98		150/98	150/99	149/99
% Paraffins	21	35	26		30	34	31
Naphthenes	69	53	68		60	54	63
Aromatics	10	11	5		9	12	5
Unsaturated	0	1	1		1	0	1
Iodine No.	0.1	0.8	0.4		5.0	0.7	0.4
ON Motor	69.5	69.5	68.0		62.5	65.0	67.5
No 0.12 Pb	86.0	87.5	-		82.5	85.5	85.5
Tests	good	good	good		good	good	good
M-Oil >150°:							
Spec. Grav.	0.860	0.852	0.857	0.841	0.842	0.850	0.842
AP	48	48.5	53.0	54.0	55.0	41.0	56.0
Initial Boil	158/00	156/00	160/00	149/00	156/00	148/00	153/00
% - 180	9	11	7	12	10	13	10
225	44	48	38	55	44	56	48
300	95	96	85	99	93	97	94
325	-	-	98	-	-	-	-
Boil. End	315/99	305/99	326/99	300/99	320/98	310/99	317/99
% Phenols	0.006	0.002	0.007	0.020	0.013	0.003	0.008
Base No. (mg)	0.0	0.0	0.0	2.7	1.5	1.2	0.0
Benzinated in Conv.	5	12	3	5	13	10	11
Record Page	5720	5603	5705	5572	5413	5689	5722
Temp. (MV)	19.5	19.0	19.5	19.5	18.5	20.5	19.5
Index of Benzination	67	72	72	60	99	39	65

TABLE II

Benzination of E-Products from Hydro-Works

Works	Scholven	Gelsenberg	Wesseling	Leuna	Brüx	Brüx	Pölitz
Feed product M-Oil > 150°	P 1422	P 1596	P 1508	P 1521	1589 v.27.8.43	P 1589 v.9.3.44	P 1475
AP	48.0	48.5	53.0	54.0	55.0	41.0	56.0
Phenols	0.006	0.002	0.007	0.020	0.013	0.003	0.008
Base Number	0.0	0.0	0.0	2.7	1.5	1.2	0.0
Boil. End	315	305	326	300	320	310	317
Temperature	19.5	19.0	19.5	19.5	18.5	20.5	19.5
Spec. Grav: c.c.p.p.	0.744	0.755	0.738	0.746	0.742	0.754	0.740
% Gasol. 150 in c.c.p.p.	67	62	72	60	69	56	65
Index of Benzination	67	72	72	60	99	39	65
% Gasol. in c.c.p.p. stabilized	60/145	50/140	62/145	52/145	62/145	46/145	61/145
Gasol.-Yield	0.82	0.70	0.84	0.72	0.85	0.62	0.83
Gasific.	22	22	24	22%	17.5	-	23
Gasol: Spec.Grav.	0.729	0.734	0.726		0.728	0.724	0.722
AP I/II	53/55	51/54	53/55		52/57	52/57	54/55
Initial Boil	55/00	63/00	54/00		58/00	54/00	55/00
% - 70	6	2	6		8	10	5
% - 100	55	55	57		55	56	60
Boil. End	145/99	140/98	147/99		145/98	146/98	149/99
% Paraffins	48	44	48		52	51	48
% Naphthenes	48	53	49		41	42	49
% Aromatics	3	3	3		6	6	2
% Unsaturated	1	0	1		1	1	1
Iodine No.	0.3	0.9	0.4		0.6	0.4	0.2
ON Motor	73.5	73.0	72.5		71.5	72.5	72.5
No 0.12 Pb	90.0	89.5	-		89.0	90.0	90.0
Tests	good	good	good		good	good	good
C-M-Oil:							
Spec.Grav.	0.819	0.814	0.806	0.814	0.808	0.820	0.810
AP	53	52	52.5	57	55	51	57
Boil. End	278/99	250/99	265/99	-	294/99	300/99	284/99
Converter	5	12	3	5	13	10	11
Record Page	5720	5603	5705	5572	5413	5689	5722

TABLE III

Properties of Blended Gasolines from B-Products from Hydro-Works

Works	Scholven	Gelsenberg	Hesseling	Leuna	Brüx (27.8.43)	Brüx (9.3.44)	Pölitz
Mixture:							
Parts Prehy-Gasol.	35	35	33	28	32	45	35
Parts 6434-Gasol.	65	65	67	72	68	55	65
Spec. Grav.	0.737	0.737	0.728		0.735	0.736	0.728
AP I/II	49/52	49/53	51/54		49/55	48/55	51/54
Initial Boil	59/00	62/00	55/00		58/00	55/00	57/00
% - 70	3	2	5		6	7	4
- 100	52	55	54		69	51	56
Boil. End	145/99	140/99	151/98		150/99	150/99	150/98
% Paraffins	38	41	41		45	43	43
% Naphthenes	57	53	52		47	47	53
% Aromatics	5	6	3		7	9	3
% Unsaturated	0	0	1		1	1	1
Iodine No.	0.2	0.5	0.4		2.0	0.5	0.5
ON Motor	72.0	72.0	72.5		69.0	69.0	71.0
Mo 0.12 Pb	89.5	89.0	-		86.5	88.0	88.0
For Comparison:							
ON 6434 Gasol.	73.5	73.0	72.5		71.5	72.5	72.5
ON Prehy-Gasol.	69.5	69.5	68.0		62.5	65.0	67.5
Remarks						Entire column calculated by mixture rule.	

TABLE IV

T-384

Pölitz B-Products

Product	c.c.p.p. product of 2.2.1944, Mixture from all Stalls	c.c.p.p. from 8376-5058-Stalls Bbl. HWP 4356	c.c.p.p. from 8376-Stall Bbl. HWP 5165
Spec. Grav.	0.811	0.810	0.822
A.P.	51.0	54.5	57.5
Initial Boil	62/00	77/00	88/00
% - 150°	31	25	18
180	42	37	30
225	69	61	50
300	95	91	89
Boil. End	305/98	327/99	330/99
Gasol. - 150°:%	28.5	26.5	19.5
M-Oil > 150°:%	71.5	73.5	80.5
Gasol. to:	145	145	140
Spec. Grav.	0.740	0.736	0.739
AP I/II	47/50	48/53	50/51
Initial Boil	55/00	62/00	70/00
% - 70	3	2	1
100	46	45	43
Boil. End	149/99	144/99	140/99
% Paraffins	31	41	36
Naphthenes	63	53	62
Aromatics	5	6	2
Unsaturated	1	0	0
Iodine No.	0.4	0.4	0.5
ON Motor	67.5	65.5	65.5
No 0.12 Pb	85.5	85.0	85.5
Tests	good	good	good
M-Oil >150°: Spec. Grav.	0.842	0.838	0.842
A.P.	56.0	58.5	60.5
Initial Boil	153/00	161/00	150/00
% - 180	10	9	8
225	48	45	39
300	94	91	85
Boil. End	317/99	318/98	318/98
% Phenols	0.008	0.006	0.007
Base No. (mg)	0.0	1.4	0.7
Benzinated in Conv.	11	6	4
Record Page	5722	5710	5709
Temp. (MV)	19.5	19.0	19.0
Index of Benzination	65	71	72

TABLE IVa

A.P. Fractions of Pölitz Products

Product	Vapor Phase Feed	8376-5058- c.c.p. product	8376- c.c.p. product
% Content in c.c.p. product & A.P. of Fractions			
- 80°	51 - 1.5	50 - 2.0	
80 - 100°	42 - 1.5	46 - 6.5	49 - 5.0
100 - 120°	39 - 4.0	46 - 9.5	47 - 8.0
120 - 140°	38 - 3.0	48 - 8.0	50 - 6.5
140 - 160°	38 - 2.0	50 - 5.0	52 - 3.5
160 - 180°	34 - 5.5	50 - 7.5	52 - 8.0
180 - 200°	25 - 6.5	49 - 12.0	52 - 12.0
200 - 225°	13 - 13.0	51 - 13.5	54 - 14.5
225 - 250°	9 - 13.0	57 - 11.5	59 - 10.0
250 - 275°	10 - 10.0	62 - 10.5	63 - 14.5
275 - 300°	13 - 15.0	69 - 8.5	69 - 11.0
above 300°	17 - 23.0	81 - 4.5	81 - 6.0

T-384

TABLE V

Benzination of Pölitz B-Products

Product	B-M-Oil fr. c.c.p. prod. of 2.2.44, Mixture fr. all stalls	B-M-Oil fr. c.c.p. prod. fr. 8376-5058 Stalls Bbl. HMP 4356	B-M-Oil fr. c.c.p. prod. fr. 8376-Stall Bbl. HMP 5165
Aniline Point	56.0	58.5	60.5
Phenols	0.008	0.006	0.007
Base Number	0.0	1.4	0.7
Boiling End	317	318	318
Temperature	19.5	19.0	19.0
Spec. Grav. c.c.p. prod.	0.740	0.742	0.744
% - 150 in c.c.p. prod.	65	59	60
Index of Benzination	65	71	72
% Gasol. in c.c.p. product stabil.	61/145	54/145	56/145
Gasol.-Yield	0.83	0.72	0.77
Gasification	23	22	20
Gasol.: Spec. Grav.	0.722	0.722	0.719
AP I/II	54/55	55/57	56/57
Initial Boil	55/00	54/00	57/00
% - 70°	5	8	7
- 100	60	56	57
Boiling End	149/99	145/99	145/99
% Paraffins	48	54	56
Naphthenes	49	44	43
Aromatics	2	2	1
Unsaturated	1	0	0
Iodine No.	0.2	0.5	0.5
CN Motor	72.5	72.0	73.0
Mo 0.12 Pb	90.0	91.5	92.0
Tests	good	good	good
C-M-Oil: Spec. Grav.	0.810	0.803	0.805
AP	57	57	59
B.E.	284/99	246/99	275/99
Converter	11	6	4
Record Page	5722	5710	5709

TABLE VI

Properties of Blended Gasolines (Prehy. Pölitz - 6434 Lu)

Starting Material	c.c.p. prod. of 2.2.44. Mixture fr. all stalls	c.c.p. prod. fr. 8376-5058 Stalls Bbl. HWP 4356	c.c.p. prod. fr. 8376-Stall Bbl. HWP 5165
Mixture			
Parts Prehy-Gasol.	35	29	21
Parts 6434-Gasol.	65	71	79
Spec. Grav.	0.728	0.726	0.724
AP I/II	51/54	53/56	55/56
Initial Boil	57/00	57/00	60/00
% - 70°	4	5	5
- 100	56	54	53
Boil. End	150/98	144/99	145/99
% Paraffins	43	49	52
Naphthenes	53	46	46
Aromatics	3	4	2
Unsaturated	1	1	0
Iodine No.	0.5	0.3	0.5
ON Motor	71.0	70.0	71.0
No 0.12 Pb	88.0	89.0	91.0
For Comparison			
ON Prehy. Gasol.	67.5	65.5	65.5
ON 6434-Gasol.	72.5	72.0	73.0
ON Mixed Gasoline calculated from it by mixture rule.	70.7	70.1	71.4