Frames 655-657

Correlation of asphalt tests with l.t.car. results.

Frames 658-661

Fuel oil and electrode coke by mild hydrogenation of bituminous coal and l.t.car. of the primary bitumen under pressure. January 6, 1942.

Hydrogenation of bituminous coal with an insufficient amount of hydrogen, and middle oil as a pasting oil, converts the coal into a soluble and fusible product which can be deashed by filtration; the filtrate contains less than 0.1% ash.

L.t.car. under slight pressure (5-20 atm.) at 475-500° C. readily splits the primary bitumen into an ash-free l.t.car. coke from which satisfactory electrode coke can be produced by subsequent calcination. Pressure carbonization is necessary to produce a dense uncalcined coke.

The filtrate itself (with the middle oil used in pasting) and the primary bitumen topped at 300° can be used for pressure charring, and it is pumped in the fused state with the production of somewhat denser coal. With Upper Silesian coal the following results were obtained with pressure charring:

a. Primary bitumen made at 23.5 mv. and 300 atm.
Low temperature carbonization results.

Feed	Oil,%	Coke, %	Gas + Loss	
Filtrate	76.4	19.7	4.9	) The carbonization oil contains the pasting oil
Do.	76.6	16.9	6.5	)
Distillation bottoms	41.8	48.7	9.5	) Pasting oil-free carbonization oil
Do.	41.2	48.8	10.0	)

The composition of the carbonization oils was as follows:

	Carbonization oil & pasting oil	Pasting oil-free carboniation oil	Pasting oil-free carbonization oil
% Water	0.8	2.2	9.6
% Asphalt	2.6	6.7	1.4
% Phenols	11.5	-	8.4
Pour point, °C.	20	+1	-18
Sp. gr./20° C.	1.041	1.069	1.20
I.b.p., °C.	98	90	86
% -200	2.1	3.8	11.2
-250	33.5	11.2	27.3
-300	51.0	19.8	48.2
-325	57.0	23.5	60.3
-350	64.0	34.0	75.6

The two tests without pasting oil show great difference in the quality of carbonization oil, if produced by continuous injection of fused bitumens, or by putting it directly into the l.t.car. retort and then slowly carbonizing. The pour point of the carbonization oil can be strongly lowered by this method, the oil can be almost completely distilled but the oil yield is greatly reduced, with the corresponding increase in the coke yield; the same gasification will, however, result from slow injection of the feed and with somewhat higher carbonization pressure and temperature.

B. Bitumen produced at 700 atm. and 25 mv.

Feed	Carbonization oil, %	Coke, %	Gas + loss	
Filtrate	75.2	17.4	7.4	
Do.	76.8	15.4	7.8	
Distillation residue	33.8	57.6	8.6	Pumped in the fused state
Do.	26.5	61	12.5	**Batch operation**

Properties of the carbonization oil

	Pasting oil-containing carbonization oil	Pasting oil-free, pumped liquid	Pasting oil-free, batch operation
% Water	0.8	5.0	9.2
% Asphalt	0.5	2.5	0.5
Phenols		12.0	18.4
Pour point	-32	+7	-27
Sp. gr./20°	0.996	1.048	0.988
-200° C.	1.0	2.0	14.4
-250	25.6	7.4	30.9
-300	65.6	18.0	50.0
-325	75.7	29.0	60.7
-350	83.7	48.1	75.6

Bitumen obtained at higher temperature is somewhat more difficult to carbonize and the pour point is somewhat higher in continuous l.t.car.; this can, however, be equalized by raising the temperature and slower injection. This bitumen produced at higher temperatures produced a greater amount of coke in batch operations and the l.t.car. tar quality was greatly improved, although gasification also was greatly increased.

The l.t.car. coke still contains 5-10% V.M. because of the low temperature, and cannot therefore be used directly as electrode coke. It will meet the specifications for aluminum electrode production after calcining it at 950-1000° C., as may be seen from the following table:

Ash content, uncalcined	0.1-0.3%
Ash content, calcined	0.20-0.25%
V.M.	0.14-1.34

Calcined coke will therefore meet the electrode coke specifications for use in aluminum production. Production of other desirable properties, in particular density, grain breakdown in grinding, conductivity, requires further studies.

Mention may be made in conclusion that flushing gas tar will also produce fuel oil (60-65%) and electrode coke (abt. 30%) by pressure carbonization.

/s/ Pfirrmann

Frames 662-665

Saturation and splitting hydrogenation of the liquid phase middle oil.
February 26, 1942.

Summary

The kiln oil obtained from Scholven H.O.L.D. from 600 atm. operations produced a gasoline by treating with catalysts 8376 and 6434 with practically the same naphthenes and slightly higher aromatics as in the mixed gasoline from saturation and splitting hydrogenation (8376/6434) obtained in processing the Scholven liquid phase middle oil. The octane number of the gasoline so obtained was 1.5 points higher. The difference would become still greater by adding the liquid phase gasoline belonging to it.

Frames 666-668

Reduction of molybdenum consumption in liquid phase operations.
February 3, 1941.

Frames 669-671

Hydrogenation of Scholven coal (Zweckel coal) with iron catalysts and chlorine.
February 11, 1942.

A short test was made of hydrogenating coal at 250 atm. with iron catalyst (iron sulfate and Bayer mass) and chlorine (ammonium chloride) to gasoline and middle oil as a supplement to earlier tests on hydrogenating of the same coal at 600 atm. to gasoline and middle oil and to gasoline and fuel oil. The test was only intended as a brief preliminary test in connection with fuel oil production, and for that reason the length of the test was limited to 8 days because of the absence of facilities to neutralize the products.

The converter was first operated at 600 atm. to gasoline and middle oil without the addition of chlorine, and after 3 days changed to 250 atm. operations, i.e. after the converter had almost reached equilibrium in the distillation curve of the recycle oil. The temperature was somewhat reduced and 1.15% ammonium chloride added to the iron catalyst. The throughput was fairly high for 2 days (0.47) in order to deliberately put the converter into unsatisfactory conditions, and attempts were then made to bring the converter into equilibrium with respect to asphalts at reduced throughput. Results obtained in that way were definitely no better than might have been obtained in a longer test with the same operating conditions. The test proves therefore definitely that bituminous coal can be hydrogenated at 250 atm. with iron catalyst and chlorine without harming the converter or without danger of continuous deterioration in the residue utilization.

The principal results obtained in earlier tests with another Scholven coal are summarized in the table. A comparison of these results with slightly different operating conditions shows that the space-time yield and gasification with iron catalysts are no worse than obtained with tars. The space-time yield with iron is somewhat lower, but throughput could definitely be increased by about 10 percent. The difference of conversion determined by solution in benzene is quite striking. While both tests indicated a 95 percent conversion with tin, it amounts to but 91 percent in tests with iron. On the other hand, asphalts referred to m.a.f. coal amounted to 14 and 17 percent in tests with tin and to only 8 percent in tests with iron. This leads to the conclusion that iron catalysts and chlorine convert coal differently, in that part of the asphalt-like constituents are separated as solids. This is confirmed by the difference in the solids in H.O.L.D. with gasoline and with tetraline-cresol (only 70% solids were found with gasoline of those found with tetraline-cresol). The question was not investigated in greater detail in the short tests. In spite of the high gasoline insolubles in H.O.L.D. amounting to over 30 percent, the residue processing offered no difficulties.

/s/ v. Hartmann

		Test of 9/30/38	Test of 9/8/41
Ash		4.60	4.25
In m.a.f. coal,	% C	82.8	83.2
	% H	5.2	5.3
	% O	10.5	8.9
	% N	0.5	1.5
	% volatile S	1.02	0.96
	% total S	0.96	0.13
	Cl	-	0.2
	Volatile matter	37.4	38.6
	Tar	13.8	14.1

Operating conditions:			
Pressure	250	250	250
Temperature, °C.	460	462	462
Catalysts	0.06% SnO	0.06% SnO	Saturated with 1.2% $FeSO_4 \cdot 7H_2O$
	1.15% NH_4Cl	Referred to paste	1.5% Bayer mass
	Referred to paste	1.15% NH_4Cl	1.15% NH_4Cl

(Cont'd.)

	Test of 9/30/38		Test of 9/8/41
		introduced from below into converter	referred to paste
Throughput, m.a.f. coal	0.442	0.39	0.24
M.^{3} gas/kg. m.a.f. coal	4.05	3.7	4.2
Pasting oil:			
% solids	6.5	12.5	9.2
% -325	10.9	8.5	5.6
% asphalt	9.8	10.2	8.3
Pasting proportion	1:1	1:1	1:1
Coal:H.O.L.D.	1:0.3	1:0.3	1:0.4
Results:			
Conversion (determination with benzene)	96	97	91
% excess pasting oil	29.6	32.0	-5.2
Space-time yield	0.21	0.19	0.16
% gasification	26.4	23.9	24.7
% asphalt to m.a.f. coal	14.1	17.8	8.3
% oil production			
-133°	12.5	-	-
-200°	-	32.4	30.9

Frames 672-699

Earlier tests in 10-liter converters (November-December, 1937) on addition of sodium sulfide to bituminous coal hydrogenation (Gelsenberg coal).
May 28, 1943.

Summary

Dr. Kroenig ran some older tests on the effect of Na$_2$S addition to younger Gelsenberg coal. The pasting oil was frequently supplemented with tar and while results are not very definite, they permit drawing the following conclusions:

1. The addition of catalyst 6063 (pure Na$_2$S, Merck) between the paste line and converter causes crust formation at that place. The crust consists in part of Na$_2$S, in part of iron compounds probably derived from the catalyst.

2. The selection of the place of addition of Na$_2$S appears to be of minor influence. The relatively short tests permitted drawing no conclusions on improvements in heat transfer or reduction in crust formation inside the converter.

3. Gasification was lower using the Leverkusen Na$_2$S (6709) than 6063. The product seemed to be somewhat more hydrogenated. 6709 was 97-98% pure, while 6063 contained only 32% Na$_2$S, with greater amounts of sulfide, soda, polysulfide, and thiosulfate.

4. Larger amount of asphalt was found when compared with the usual residue processing when the H.O.L.D. was centrifuged after coming from a stripped hot catchpot and the centrifuge filtrates were topped. Space-time yield and gasification were somewhat better with this middle oil and low solids pasting oil, but not sufficiently so to justify the higher costs of this method. The use of middle oil-containing catchpot bottoms instead of the catchpot heavy oil as thinner does not affect the stability of the untopped centrifuge filtrate.

5. Topping of the centrifuge filtrate instead of the H.O.L.D. did not change results.

6. Mild topping of H.O.L.D. in tubular still instead of retort improved the results.

7. H.O.L.D. let down through an overflow could be more readily filtered than the usual pressure released H.O.L.D. Leading the H.O.L.D. through a valve with a slight excess pressure of 0.5-3 atm. lowered the filtration efficiency.

Frames 700-722

Hydrogenation of mixture of Silesian coal with Silesian bituminous coal tar to excess of heavy oil at 700 atm. in 10-liter converters. November 12, 1942.

Summary

Silesian coal (Heinitz mine) was hydrogenated in a 100:25 mixture with Silesian tar which consisted of 50% hot l.t.car. tar, 36% coke tar pitch and the balance of generator tar. A similar proportion was intended in the planning of production in Blechhammer.

The tar mixture was added to the usual coal paste and contained 1 percent char-iron-titanium catalyst. The usual amount of gas was used for coal and H.O.L.D. was not recycled. The oil production was the same as if coal were processed to gasoline and middle oil, and the tar to heavy oil, i.e. the amount of heavy oil withdrawn from the cycle was that which would be obtained by converting tar in a single pass without coal.

The mixture could be hydrogenated without any trouble and the residue processing gave a good yield of kiln oil. The very high temperature, 473-474°, used in hydrogenation of Silesian coal had to be maintained to reach the recycling equilibrium. The results obtained are compared with the processing of Upper Silesian with 20% hot l.t.car. tar.

	Coal + tar mixture	Coal + hot l.t.car. tar
Converter temperature, °C....	473.5	467
Space-time yield.............	0.36	0.36
Heavy oil in total oil production	10.6	8.9
Gasification, %..............	24.8	21.9
Asphalt, to m.a.f. coal, %...	7.6	10.9
Conversion, %................	95.1	93.8

The conversion of the mixture with tar was somewhat better at the same space-time yield, but gasification was considerably higher. Somewhat less asphalt was produced because of the higher temperature, with no advantages in the residue processing.

Hydrogenation of coal was practically unaffected by the addition of tar, i.e. the advantages offered by the l.t.car. tar were offset by the addition of coking pitch and generator pitch, especially with respect to gasification. The last two additions are favorable by producing more aromatic oils, and the knocking value of the gasoline and on the pour point of the heavy oil were improved.

Frames 723-725

Comparison of results of hydrogenation with different char-iron catalysts. June 13, 1941.

Results with different catalysts obtained at low temperature (23.5 mv. = 450° C.) differed the least.

Differences in splitting (new compounds below 325°) and asphalt reduction became considerable at 24.5 mv. (468° C.), and results are better with the two fluorine-containing catalysts than with iron-char + NaOH. Gasification is somewhat lower with fluorinated catalysts in spite of greater amount of splitting.

Conversion of solids is greatly reduced with iron sulfate-char-NaOH catalyst at 25.5 mv., while the change with fluorinated catalysts is much smaller. Splitting and asphalt reduction are further greatly increased at 25.5 atm. with iron-char-NaOH catalyst. The same splitting and asphalt reduction is produced with fluorinated catalyst at 1 mv. lower temperature. The much lower conversion of solids and the high gasification with char-iron-NaOH catalyst at 25.5 mv. are the result of dehydrogenation and incipient coking.

/s/ Grassl

Frame 726

Hydrogenation of high-C bituminous coals. June 7, 1941.

Hydrogenability of a coal is measured by the amount of asphalt, and with 0.4% Cl at 600 atm. (or 0.75% at 250 atm.) coal with 86.5% C. could still be readily hydrogenated in 1.5 l. converters.

Frames 727-729

Coal as catalyst in rotating autoclave hydrogenation of pitch-tar mixtures. June 9, 1941.

Coal saturated with 10% iron sulfate used as catalyst with tar-pitch mixture produced results which differed from those with char-iron catalyst by:

Higher splitting and gasification. The oil yield is somewhat lower with coal because of higher gasification; gasoline and middle oil production is increased by it, asphalt reduction somewhat better with Silesian coal as catalyst, with extracted Riebeck coal as good as with the char catalyst. The total conversion of solids is better with coal, because of the greater ease of conversion of coal than of the pitch solids. Assuming that the conversion of pitch solids is unaffected by coal, the conversion of bituminous m.a.f. coal figures to 86.5%, of lignite to 94%.

/s/ Grassl

Frames 730-731

Rotating autoclave tests of catalysts for pitch-tar mixtures.
June 6, 1941.

Comparison of results with char-iron, char-molybdenum and precipitated iron sulfide catalysts.

Equal amounts of precipitated iron sulfide and char-molybdenum catalyst produced practically equal results. Char-iron-NaOH is considerably less satisfactory for asphalt reduction. Char-iron catalyst with double the amount of iron sulfate produces better asphalt reduction and splitting than char-iron-NaOH sulfide, but with somewhat higher gasification (at 0.1-0.2 mv. higher temperature). Iron fluoride (from iron nitrate + NH_4F) upon neutralized char produces as good results as precipitated iron sulfide. The addition of 0.3% Na_2S to this catalyst increases the asphalt production and reduces splitting and gasification. The same catalyst made with iron sulfate instead of iron nitrate was less satisfactory.

/s/ Grassl

Frames 732-734

Effect of the age of coal on primary bitumen production. June 9, 1941.

A number of tests were made at the Uhde plant to determine the suitability of different Ruhr coals to primary bitumen production. Coals arranged in order of age (from memory) were as follows:

Krupp Mine Saelzer	18-20% V.M.
Krupp Mine Amalie	23-24
Gute Hoffnung's Mine	24-25
Lorraine	25-26
Harpen	25-27
Kaiserstuhl	27-28
Harpen Mine Viktoria	32-34
Mont Cenis	34-35
Therese Mine	36-38
Radbod	38-40
Mine Sunen	42-44
Kloeckner	48

Conversion rose from 58% with Saelzer coal to 95% with the Kloeckner coal; the corresponding primary bitumen yields varied between 50 and 88 percent. Only lignite can be converted up to 98%. The primary bitumen yield doesn't vary greatly when volatile matter in the coal varies between 28 and 38%, and amounts to 82-85%. The conversion begins to drop only below 28% V.M. The relation between conversion and V.M. is shown graphically below. It may be mentioned, that the C-content, or the V.M. in coal which runs parallel to the C-content, give definite information on the conversion of coal. Certain beds contain gas inclusions or readily evolved gases, and mixtures of coals from different beds, especially in the deposits further to the north, may be higher in V.M. and be nevertheless but poorly converted, if the composition of coals from the different beds differs greatly. With this limitation in mind we may say that:

The melting point of primary bitumen becomes lower with increasing V.M. in the coal for the same hydrogen consumption; i.e. the same melting point is reached by using more hydrogen with the older bituminous coals than with younger coals; bitumen with melting point below 150° C. is very difficult to obtain from old coal. The older the coal, the lower the proportion of lower hydrogenation products, and with 26-27% V.M. and below, losses in the solvent are no longer covered by the oil produced. Production costs increase, therefore, with the age of coal.

Definite conclusions cannot be drawn on the relation between the C-content of coal and filtrability. While older coal filters more readily, the advantage is balanced by somewhat larger amount of solids to be filtered off; as a general rule, the filtration efficiency decreases with lower C-content.

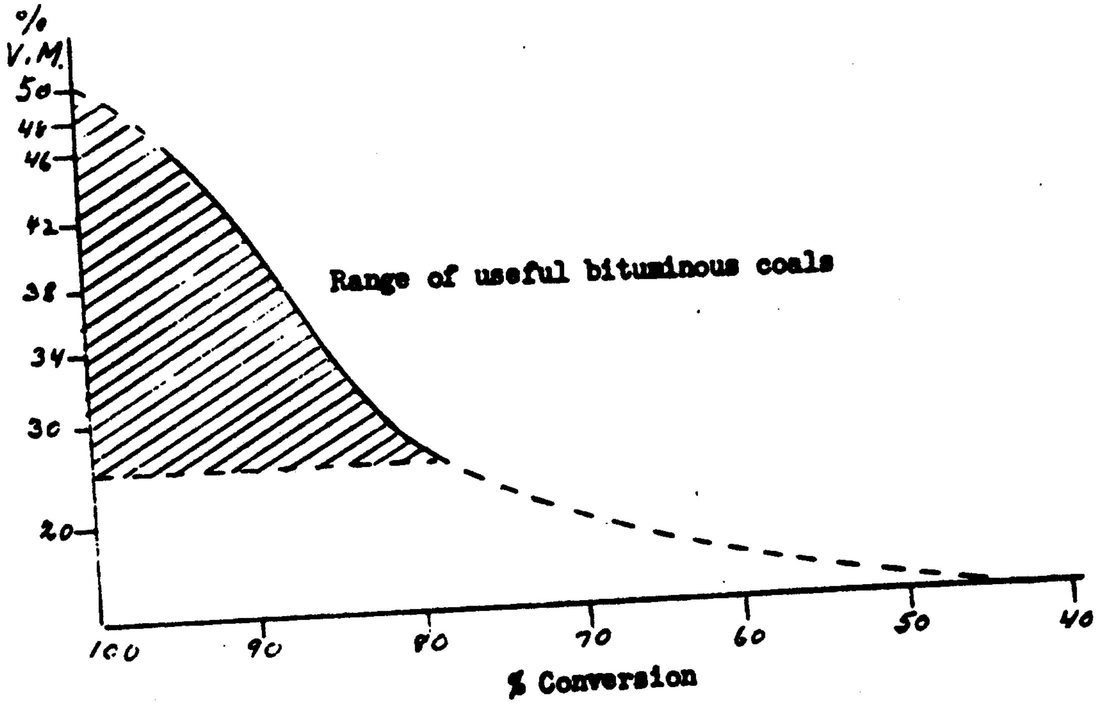
Frames 735-737

Processing of crude coal extract in the Ruhroel G.m.b.H. in Welheim.
March 26, 1941.

The crude extract was filtered in the past in two candle filters with an average throughput of 600-700 kg. feed/m.^{2} filter surface, hr. at 150° C. The filtrate (m.p. 200° C., Kraemer-Sarnow) contains 0.1% ash. The filtrate was experimentally coked in the usual coking oven with the production of a hard lustrous coke.

The filtration installation consists of 32 filter candles with a total filtration surface of 22 m.^{2}. The filtration installation is much too large for the size of the extraction equipment, and no difficulties arose so far in filtration with 8 days' operating periods of the extraction equipment. Some 650 filtrations were made with candle filters. The filtration pressure is about 3-4 atm. gage, the cake about 20 mm. thick and was expelled at 7-8 atm. gage pressure. The life of the filter is 15-20,000 T. production. The gas is CO_2 from the conversion.

A single filter candle is made from flat ground filtration rings (150 mm. diameter, 20 mm. high) of quartz firebrick 30/40 made by Schuhmacher, Bietigheim, with thin Klingerite discs as packing, and



Relation between primary bitumen production and the age of coal.

assembled in an iron tube. A screw at the upper part of the tube compresses the rings against a strong spring at the bottom of the tube. The filter rings are strengthened in Welheim with a double wire ring.

The same method of operation will be shortly used for the production of 110 T./day extract for electrode coke production. This batch candle filter process is intended to be replaced in Welheim by a continuous filtration process. The Imperial Co., Meissen, have cooperated in the design of suction filter with the cake cut off by a string. The filter cloth is to be composed of multiple layers of simple wire cloth of phosphor bronze or monel metal. Three filtrate outlets are provided in the regulating head: The preliminary filtrate is returned to the extract, for pure filtrate collected separately, and washings are returned to the pasting oil. Pressure filter tests will be started with the production of extract.

Oil is expelled from the filter cake in two rotating drums using hot flushing gas. The coal used for hydrogenation contains 6% ash to dry coal, 86-87% C. and 28-30% V.M., calculated to m.a.f. coal. The pasting oil is a middle oil with 4-5% phenols obtained in pitch hydrogenation, 220-320° C. cut. The recycle oil is diluted with 30% make-up middle oil, and the oil obtained is hydrogenated in the vapor phase.

Pasting coal:oil	33:66 at the start
Later do.	38:62
Welheim middle oil	8.5-8.9% H_2 9.6-10 parts H_2 : 100 parts C
Scholven middle oil	9.3-9.4% H_2
Nordstern middle oil	9.7% H_2

The Welheim middle oil is high in tetraline homologs. With Scholven or Nordstern middle oil H_2 is required during the extraction (150 m.^{3}/T. coal), with Welheim oil H_2 addition is an advantage.

Extraction pressure	100-150 atm.
(when starting the plant	200-300 atm.)
Extraction temperature	410° C.

No heat exchange is possible with the usual heat exchangers because of difficulties in recycling. Only jacketed tubes can be considered here.

Extraction	82-83% of m.a.f. coal 3% gasification, 40 m.^{3} reaction gas with 20% H_2/l. extract
Yield of deashed extract	72-73% of the coal used
M.p. of extract	200° C., Kraemer-Sarnow

The primary bitumen contains 1% more H_2 than the coal.

Frames 738-741

Study of solution of extract in the Luetzkendorf industrial extraction with phenol. January 4, 1942.

Anhydrous phenol is a selective solvent for aromatic and napthenic hydrocarbons. When oil is extracted with anhydrous phenol, these substances can be completely extracted by using sufficient amount of phenol, leaving a purely paraffinic oil behind. The separation is not quantitative; the purity of the raffinate depends on solution equilibrium at the existing extraction conditions, and some paraffins are accordingly lost. The quality of the raffinate is best with anhydrous phenol but the yield is small.

The dissolved paraffinic constituents can be recovered from the extract by two different methods, and returned at the proper place to the extraction tower, or made to rise through the layer of the extract in the tower. The methods used consist of:

1. Lowering of the temperature of the extract
2. Addition of water to the extract

Both methods operate similarly. Method 1 involves shifting the solution equilibrium and separation of all components which are less soluble at lower temperatures, i.e. the paraffins. Method 2 lowers the solvent ability of the phenol which also results in separation of the paraffinic constituents of the original solution. The recycling of the raffinate increases the yield without noticeable deterioration in quality and increases the specific gravity of the extract through removal of the lighter paraffins.

Both methods were used in the Luetzkendorf installation to increase the yield of products. Determination of the density of the extract is used as control. A maximum yield is sure to be reached when the extract is sufficiently heavy. The tests, however, gave no perfect results so far, and it was never found possible to have the specific gravity of the extract reach that obtained in the Leuna tests under similar conditions. In other words, the maximum yields were never reached so far in Luetzkendorf.

Both methods were used simultaneously during the last operating period by reducing the temperature by 5° and adding 5% water to the solution. A neutral oil, specific gravity 0.900/50°, was separated into a raffinate of specific gravity 0.870 and an extract sp. gr. 0.965, with a calculated yield of 68.5% by volume.

Judging from laboratory tests, the density of extract should have been 0.985 at 50° C. In this case the yield would have been at a maximum with 73.5% by volume. The reason for the poorer yield in large scale operations than in laboratory tests remains unknown. This may have been caused by:

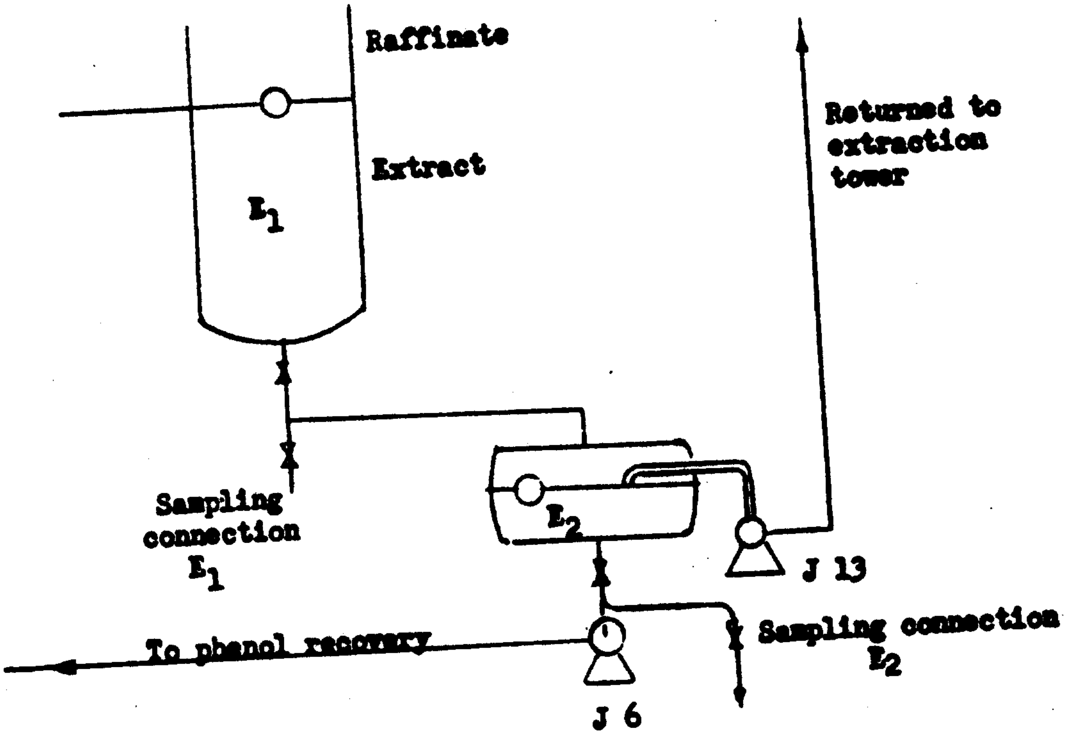
1. Incomplete separation of the paraffinic components from the extract solution at the outlet from the extraction tower.

2. Insufficient change in the solution equilibrium or reduction in the solvent power of phenol by the addition of water. To solve this problem the following tests were run.

The drawing shows schematically the bottom part of the extraction tower E_1 with the extraction solution let down to the extract tank E_2.

Samples were first taken from the sampling connection E_1 and the pump J_6, and samples were kept at 50° C. for 1/2, 1 and 2 hours. The amounts of paraffin oil separated are shown in the table below.

Different amounts of water added to the same samples and the mixtures again kept at 50° C. Oil was found to separate from these samples, and the amount of oil is shown in the table.



Sampled at E_1	Sampled at J_6
Kept standing at 50° C.: Separation after 1/2 hr. 1% by vol. of oil 1 hr. 1% of oil 2 hrs. 1% of oil Sp. gr. of extract after separation of oil 0.980	Kept standing at 50° C.: Separated after 1/2 hr. 0.5% by vol. of oil 1 hr. 0.5% 2 hrs. 0.5% Sp. gr. of oil 0.982
Addition of 1% of water by vol. Separation of 1/2 hr. 2% by vol. of paraffinic oil after 1 hr. 2% by vol. oil 2 hrs. 2% by vol. oil Sp. gr. of extract after separation of oil 0.989	Addition of 1% of water by vol. Separation after 1/2 hr. 2% by vol. of oil 1 hr. 2% 2 hrs. 2% Sp. gr. of extract without oil 0.984
Addition of 2% H_2O oil Separation after 1/2 hr. 2%/by vol. 1 hr. 2% do. 2 hrs. 2% do. Sp. gr. of oil-free extract 0.986	Addition of 2% of H_2O 1/2 hr. 3.5% 1 hr. 3.5% 2 hrs. 3.5% Sp. gr. of oil 0.995

The following conclusions could be drawn:

1. Separation of extract solution and paraffinic oil was not complete in either E_1 or in E_2, probably because of too short time. Were it complete, the density of the extract would be 0.980 to 0.982. It actually was 0.965 or lower.

2. A reduction of temperature by 5° and 5% water are insufficient for the extract solution to raise its density to 0.998/50°.

Tests 2 and 3 show that only 2% additional water is necessary to increase separation.

Frames 742-777

Preliminary report on the extraction plant with phenol at Luetzkendorf.
January 4, 1942.

Summary

Tests during five operating periods showed that the intended throughput was reached for both products, the neutral oil and the residual oil.

The question of raffinate yield cannot yet be definitely answered because the intended conditions could not be realized or could only be partially realized. It is nevertheless certain that the intended yield will be reached.

Phenol losses are extraordinarily small as determined by analyses. They amount to about 0.003% of the recycled phenol. Any larger observed losses must be attributed to leaks in the pump stuffing boxes, valves, poor flange gaskets, etc. These losses were greatly reduced by improving the stuffing box packing and selection of the proper flange gaskets. Difficulties encountered were the leaks in the packing, breakage of floats and float chains, leaks in coolers and valves which could not be attributed to corrosion and could be readily corrected; also some difficulties in the level measurements in the extraction tower. The difficulties could be overcome by improving level measurements.

Frames 772-781

Rotating autoclave experiments for the extraction of primary bitumens.
September 5, 1941

Summary

1. Young bituminous coals can be more readily extracted for primary bitumen production than old coals, as in hydrogenation to gasoline and middle oil. Conversion and filtration time depend on the age of the coal. Older coals may give unfilterable products at lower pressures, but raising the pressure and temperature improves the conversion and the products become filterable.

2. Hydrogen content of the pasting oil affects greatly the filtrability of the reaction products; tar oils are therefore preferable to hydrogenation middle oils but good filtration time could also be maintained at slightly higher temperature using bituminous coal middle oil from Scholven. High hydrogen oils with over 10% hydrogen gave coke-type deposits. The phenol content of the pasting oil seems to be less important.

3. A rise of temperature from 415 to 435 improves filtration time and conversion. The optimum filtrability seems to lie between 435 and 445° C. because the filtration time rises again above 435° C. and coke-like deposits are formed above 450° C.

4. Hydrogen pressure also affects extraction of coals. Increasing the pressure from 200 to 300 atm. improved the conversion and filtration time of Saar coals. Above 400 atm. the filtration time is again longer, because hydrogenation presumably becomes too great, since the products of normal coal hydrogenation are poorly filtrable. An old coal with 89% C gave, however, a filtrable extract at 460 atm. pressure.

Frame 782

X-ray investigation of caviar from the brown coal liquid phase.
February 4, 1943.

Caviar particles were found to be calcite crystal aggregates a few thousandths of a millimeter in size. The size was determined from the inside lines of the diagrams which begin to dissolve into points. A sample of grain isolated microscopically consisted of very coarse crystalline calcite.

Precipitated calcium carbonate of Dr. Whitman was also calcite. A comparison of these samples show that when calcite crystals already formed are treated with oil at 300° C. the crystal lattice is not changed. The size of the crystallites is 10^{-4} to 10^{-5} mm.

/s/ Schneider

Frames 783-785

August 22, 1941.

Filtration tests in 1937.

Preliminary tests were run in 1937 in connection with the study of filtration to determine what constituents in asphalts affected filtration rate of asphalt-containing oils most strongly.

For that purpose, filtration rates of a petroleum residuum which contained only asphalt (20%) and practically no solids were studied and compared with the filtration rate of the same residuum from which different asphalt components were either not removed, or else added after being removed. The individual constituents separated by selective solvents were:

1. Oil
2. Oil gums adsorbed on fullers' earth after precipitation of asphalts
3. Asphalt gums
4. Asphaltenes
5. Carbenes

3, 4, and 5 were precipitated with pentane.

Tests on the effect of addition of different components upon the filtration rate show, as was to be expected, that oil alone as well as oil with addition of oil gums was much better filtrable (at 100-200°) than the original residuum before separation. There was practically no difference in the filtration rate of the oil itself and oil with oil gums.

The addition of separated asphalt gums to oil, or to oil with oil gums, required the use of solvents (e.g. pyridine). The asphalt gums were dissolved in pyridine, the solution added to the oil, and pyridine carefully vaporized on the water bath. When no solvents were used, suspensions were formed, showing fairly coarse dispersion under microscope. (Agglomerized asphalt gums floated in oil and could not be dissolved even at higher temperatures, e.g. 150° C.). Suspensions were appreciably finer when solvents were used without forming completely homogeneous picture in a microscope. The asphalt gums were therefore assumed to undergo changes by chemical precipitation, and the altered asphalt gums can not be used for the preparation of colloidal system of asphalt gums in oil.

Filtration rate of solutions of asphalts in oil, or in oil with oil gums, was appreciably poorer than of the oil itself. It was, however, better than the rate of filtration of petroleum residuum before separation.

Difficulties of producing perfect solutions were magnified upon addition of asphaltenes. They were added first to oil alone, then to oil with oil gums, and finally to oils containing oil gums and asphalt gums. Relatively large amounts of solvents had to be used, approximately equal in amount to the oil, to bring them into nearly homogeneous solution when examined under a microscope. Should, however, these suspensions stand for a longer time (e.g. 4 weeks) the concentration of asphaltenes in the liquid was found to be higher near the bottom of the vessel, than on the surface. This confirms the fact that asphaltenes were not proper dispersed, and that the particles of asphaltene introduced into oil could settle out.

The poor distribution of asphaltenes was also proven by the filtration rate, which was lower in many tests than with the original petroleum residuums.

Carbenes were so much altered by precipitation that they could no longer be at all brought into solution, not even with larger amount of solvents. Attempts to find the effect of different substances upon filtration rate were therefore unsuccessful.

It might be advisable to resume these tests. It would, in particular, be of interest to extend these tests to asphalt-containing oils containing also solids, e.g. sludges.

/s/ Jaeckh