

Separation of undissolved solids from the solutes in hydrogenation products.
August 22, 1941.

So far two methods were used for the separation:

- a. Extraction of the solvent constituents by selective solvents.
- b. Mechanical separation by filtration in thin layer with agglomerating additions.

a. Heavy oils can be readily recovered with gasoline from solid primary bitumen and from centrifuge cakes. When solution is done in pressure vessels at temperatures above 200°, simple settling without filtration produces completely ash-free heavy oils from primary bitumen. The melting point of the ash-containing asphalt residues is greatly increased and their extraction with benzene is difficult; yields with separation by means of solvents is shown on two examples.

| Raw material | Gasoline soluble heavy oil | Benzene extract | Benzene insolubles | Residual coal | Ash |
|--------------------------------------|----------------------------|-----------------|--------------------|---------------|------|
| Primary bitumen from Saar coal | 38.6 | 20.0 | 23.4 | 7.5 | 10.5 |
| Centrifuge cake, Upper Silesian coal | 60.5 | 15.5 | — | 24.0 | — |

Extraction changes the solubility of Poelitz primary bitumen to such an extent, that the fraction usually soluble in pasting oil and the benzene insoluble no longer add up to the original results, and the benzene insolubles are no longer recoverable; they amount to about one-fourth of the total bitumen, and this method of recovery becomes uneconomical. It was important to find solvents (cresol-tetraline-pyridine) which would also extract the benzene-soluble fraction.

b. Filtration resistance was found to be definitely caused only by solid particles, and the solid-free H.O.L.D. could be filtered at over 100 times greater rate. This taught to limit filtration to small thickness of the cake, which was easiest done with continuous rotating filters. In addition to the existing filters, inside pressure filters operating in thin layers can be used, such as are at present being designed by us. In addition, filter cloths of different metals and different weaves are being tested.

Filtration efficiency, measured with a pressure filter of 90 cm.² with thin sheet filtration varied with different methods used between 200 and 2,000 kg./m.², hr. One plant for the production of 30,000 T./annum of primary bitumen requires the filtration of 10,000 kg. hydrogenation products/hr.; assuming an efficiency of 250 kg./m.², hr., a total of 40 m.² filter surface is required, i.e. one filter with 40 m.² surface will be sufficient; two additional filters can be kept as stand-by to meet any possible emergencies.

The filtration efficiency would be satisfactory at least for primary bitumen production, but tests were made for improving filtrability by the addition of agglomerating substances. The best separation is produced by substances which are but poorly dispersed in H.O.L.D. and combine also with oil constituents. Sulfo acids work best, give few side reactions, are oil soluble, and can be readily produced from pasting middle oil by sulfurization. 0.3% of the sulfurized pasting oil was sufficient to increase filtration rate 5 times, and 1% and over caused deposition from primary bitumen solutions. When results were applied industrially, failures occurred at first which could not be explained and were possibly caused by the interaction of sulfo acids with the iron walls of the containers, which introduced iron into solution and made them inactive. Tests are being continued.

Considerable improvement in filtrability could recently also be produced by alkaline additions. Earlier tests with hydroxide resulted in no important improvements; should the more weakly alkaline earth carbonates be used instead of the hydroxide, the effect becomes marked; 1% addition of precipitated CaCO_3 raises the filtrability six-fold. These additions will be tested industrially.

Status of filtration testing unit

Filtration on a large scale test is under construction. At present the suction cell filter from Scholven, the Dorr filter and one ceramic filter candle are being installed; the pressure cell filter has not yet been delivered.

/s/ Pfirrmann

Frames 789-790

Additional tests on filtration of hydrogenation residues. August 29, 1941.

Comparable tests were made on the filtration of H.O.L.D. and centrifuge cake from the gasoline and middle oil process and of solution of the primary bitumens from the 10-liter converter. Filtration times, particle size of the solids, and asphalt components in oils were determined.

Grain size determinations of solids showed that 94-99% passed through the finest screen (360-inch mesh). No size differences could therefore be found with the usual screen analysis. Filtration times were determined on the usual 100 gm. samples with a 7 cm. hot suction funnel at 140-150° C.

Centrifuge residue, diluted with catchpot bottoms or even with catchpot middle oil to the same dilution as the H.O.L.D. could be filtered at the same filtration rate, when the same thinners were used. The undiluted primary bitumen solution filters at the same rate if diluted with two parts of catchpot middle oil. The filtered products (mixtures) have the following solids and asphalt content:

| | Primary crude bitumen solution | H.O.L.D. + middle oil, 1:2 | Centrifuge residue + middle oil, 1:2 |
|---------|-----------------------------------|-------------------------------|---|
| Solids | 11.4 | 6.8 | 12.7 |
| Asphalt | 11.9 | 5.4 | 3.1 |

A confirmation of the laboratory filtration rates in semi-technical pressure ceramic filters are being tested at present.

Results of asphalt separation of the oils showed that differences in the different products were not as great as to account for the great differences in filtrability of primary bitumen solution, H.O.L.D. and the centrifuge residue. It may follow, therefore, that the effect of different asphalt components will not be too large, even without the production of oil-asphalt equilibrium with the newly formed components.

Filtration time seems to depend far more upon the form of the solids, and naturally upon the viscosity of the thinner, than upon asphalt conditions. Screen analyses down to 40 micron disclosed no differences caused by the size of suspended particles, and the different filtrability of different solids may be caused by increasing the surface of the solids from hydrogenation, forming an asphalt-like product. Less favorable surface relations may be caused by it which will result in poorer separation of solids from oil and also in the sticking together of the solid particles in the filter cakes.

Frames 791-797

Use of hydrogenation pitch for bituminous coal briquetting.

February 17, 1942.

Discussions of attempts to overcome the war shortage of briquette binders by using hydrogenation pitch residues.

Frames 798-840

Production of briquette binder and asphalt-free oil by processing bituminous coal - l.t.car. tar.

January 25, 1943.

Summary

Briquetting binders for bituminous coal before l.t. carbonization were obtained by hydrogenation of bituminous coal l.t.car. tar with coal at 700 atm. This method closely connects the production of briquette binders with the refining of tars. The intended combination of l.t. carbonization and hydrogenation require approximately 1:1 mixture of pasting coal:tar, if an asphalt-free distillate oil is to be produced in an amount corresponding to tar, and a residue with a softening point of about 75° C., i.e. when about equal amounts of oil and briquetting materials are to be obtained.

A few preliminary tests with different tars showed that the coal throughputs can be as high as in processes not dependent on asphalt reduction; the required temperatures are around 480° and 1 m.³ gas is needed per kilogram of coal to produce sufficiently high oil proportion. Converters could not be readily regulated above 479-480°.

The principal tests were made with Lurgi flushing gas tars from Silesian coal, using total tar (P-1504), the hot tar (P-1376), with the topping residue from the total tar, or mixed with Silesian coal. The results are shown in the table.

| <u>Tar</u> | <u>P-1504</u> | <u>P-1376</u> | <u>P-1504, topped</u> | |
|---|---------------|---------------|-----------------------|-------|
| Coal:tar | 45:55 | 50:50 | 50:50 | 50:50 |
| Coal:H.O.L.D. recycling | 1:0.5 | 1:1 | 1:1 | 1:1 |
| <u>Catalyst</u> | | | | |
| Coal saturated with iron sulfate, % to dry coal | 1.2 | 1.2 | 1.2 | 1.2 |
| Bayer mass, % of dry coal | 0 | 0 | 0 | 1.5 |
| M.a.f. coal throughput | 1.01 | 0.69 | 0.69 | 0.67 |
| Converter temperature, °C. | 479 | 478 | 478 | 478 |
| % Yield, to coal + tar | 85.6 | 83.6 | 83.8 | 87.3 |
| <u>Oil production</u> | | | | |
| Space-time yield | 0.98 | 0.62 | 0.61 | 0.72 |
| Oil production to tar, % | 77.7 | 84.5 | 82.1 | 100.0 |
| Heavy oil over 325° in above, % | 20.1 | 30.9 | 20.5 | 27.7 |
| Gasification, to yield + gasification, % | 7.4 | 10.4 | 7.7 | 7.8 |
| Gasification, to oil production + gasification, % | 13.7 | 18.8 | 14.3 | 12.9 |

A space-time yield of about 2.0 can be obtained with the total tar.

Topped tar which requires a higher proportion of recycle H.O.L.D. because of its higher viscosity and greater temperature sensitivity could be used with a total space-time efficiency of 0.2, with slightly higher gasification. Processing of topping residue, which forms 70% of the total tar, permits an oil production of 112% of the total tar, including middle oil, against 78% by the first method.

Hot tar produced the same results as topped tar; it was undesirable in that the oil produced contained more heavy constituents, and gasification was higher.

Surprisingly, l.t.car. hot tar produced a fuel oil (heavy oil: middle oil = 9:1) which met all requirements. The pour point of the oils obtained with topped and untopped total tar were unsatisfactory. The octane number, R.M., of the gasoline -200° C. was 70 and occupied an intermediate position between liquid phase gasolines from bituminous coal and bituminous coal l.t.car. tar. The distillation residue can be used as briquetting binder.

In all tests, coal was saturated with 1.2% iron sulfate. The addition of Bayer mass results in an increased yield and oil production from topped tar, and presumably also with hot tar; the addition would therefore permit higher throughputs with the same yield distribution. The addition of Bayer mass when pasting with total oil had no such great effect. It produced, however, a distinct improvement in the pour point of the oil.

Further tests showed that when the kiln oil was recycled and the amount of tar slightly reduced, the yield consisted of gasoline, middle oil, and briquette binder with somewhat higher gasification.

Tests led one to expect that operations will be free from trouble. Pasting with a very thin Koppers tar causes settling of the coal.

/s/ Hupfer and Leonhardt

Frames 841-842

A large scale briquetting test in Blechhammer.

April 9, 1943.

Frames 843-855

Kilning high asphalt hydrogenation residue mixed with coal.

April 4, 1941.

Summary

High asphalt hydrogenation residue, such as are obtained in fuel oil production, can best be kilned in mixture with 30-40 parts of non-baking coal or carbonization in kilns heated from the outside, and 60-70 parts topped centrifuge cake. The same applies to the residues from brown coal hydrogenation kilned after mixing with brown coal or char.

Frames 856-862

Comparison of results of analyses of H.O.L.D. samples. April 20, 1942.

Maximum scattering of asphalt determinations results is + 15%. Determinations made in one laboratory are, however, uniformly too high or too low, and are scattered less than 15%. Gelsenberg results, e.g. are always the highest and Poelitz the lowest. Results found by Welheim differ from all the rest. Differences in asphalt determination when using different precipitants (Kahlbaum standard gasoline, Merck's standard gasoline, and Rhenania solvan gasoline) differ by 1 to 2%. Differences obtained in Scholven using Kahlbaum gasoline and Rhenania gasoline are striking.

It must be emphasized that when solids are to be determined in H.O.L.D., pure benzene should be used, in particular such which contains no higher boiling aromatic hydrocarbons.

Frames 863-864

Poelitz H.O.L.D. filtration, June 22, 1944.

The Poelitz petroleum H.O.L.D. was found to be difficult to filter.

Poelitz intends to filter the petroleum H.O.L.D. in filter-presses. We have requested Poelitz to send us samples of petroleum H.O.L.D. to bring them in line with our numerous filtration tests with H.O.L.D. from coal, etc.

The sample sent on 6/8/44 consisted of:

19.5% benzene insolubles
49.2% ash in solids
0.4% asphalts
22.4% middle oil -325° C.

Tests were run in a laboratory suction filter, steam heated, 70 mm. diameter, 100 gm. sample) in a pressure cloth filter, (190 mm. diameter up to 5 atm. pressure wire screen + cloth + paper, 180° C.).

Laboratory filtration tests were:

| Sample | Filtration time in minutes for | |
|--------------------------------------|--------------------------------|--------|
| | 100 gm. + 100° | + 180° |
| Original Poelitz H.O.L.D. | 36 | 17.5 |
| H.O.L.D. + heavy gasoline, 170-200° | 12.7 | 7.8 |
| 2:1 | 8 | 5.2 |
| H.O.L.D. + heavy gasoline, 1:1 | 10.3 | |
| H.O.L.D. + xylene, 2:1 | 5.5 | |
| H.O.L.D. + xylene, 1:1 | | |
| For comparison: | 16 | |
| Bituminous coal H.O.L.D. + m.o., 1:1 | abt. 20 sec. | |
| Pott-Brosch extract | | |

The test of 10 kg. H.O.L.D. in a pressure cloth filter at 180° and 4 atm. pressure required about 40 hours.

To summarize, these results show that the Poelitz petroleum H.O.L.D. was found in our small tests to be very difficult to filter. Its filtrability is of the same order as for coal H.O.L.D.

Tests show that samples with 10-12 percent solids was about 20 times more difficult to filter than the Pott extract when the H.O.L.D. was diluted with a suitable solvent in proportion 1:1. We must assume therefore that large scale filtration with filter presses would be uneconomical. We are not familiar, however, with Poelitz laboratory tests on the strength of which industrial filtration was found acceptable.

/s/ Gieg and Rank

Frames 864-870 (duplicate of 871-877)

Testing of H.O.L.D. Samples.

April 20, 1942.

See Frames 856-862.

Frames 878-883

Liquid phase catalysts in rotating autoclaves.

June 20, 1941.

Summary

Molybdenum catalysts are most active and are put at the head of the list. Neutralized char, activated alumina, terrana and gas carbon are the best carriers. Unneutralized char and alkaline Bayer mass are unsuitable for molybdenum catalysts. Steam-activated char is better than unactivated char (generator dust). Neutralization of char with sulfuric acid fails to improve iron catalysts. Char-iron sulfate was improved in quality by saturation with an equivalent amount of NaOH, ^{1/} while acid reacting catalysts, such as fluorine or chlorine-treated terrana or char were made less satisfactory by the addition of sodium hydroxide; the addition of sodium sulfide also resulted in a small deterioration in splitting and in asphalt reduction.

A small addition of chlorine or hydrofluoric acid improves the char-iron catalyst somewhat.

Amongst the Mo-free catalysts, precipitated FeS, 10% FeF₃ upon 90% neutralized char, char-iron-terrana + 0.1% chlorine, aluminum silicate + 0.2% chlorine, SnO + 0.75% Cl and char + 25% FeS + 25% ZnS are nearly as active as char-molybdenum. HF-treated terrana + 20 parts ZnS + 1% MoO₃ and spent 6434 were almost as good. Precipitated iron sulfide can be still further improved by a small addition of chlorine.

Deashing of char introduces advantages, in particular in the conversion of solids and in splitting; charcoal causes much of splitting but is unsatisfactory in the conversion of the solids.

Cerium chloride, iron fluoride and zinc fluoride must be considered about equal, while aluminum chloride is somewhat poorer. Splitting with fluorine-containing catalysts is good and the lower gasification is similar to the chlorine-containing catalysts.

The specific gravity of products formed with silica catalysts is somewhat higher in the heavy oil range, which may indicate polymerization or dehydrogenation.

Elementary sulfur is of benefit with neutral or alkaline reacting catalysts, but causes much polymerization with stronger catalysts such as fluorides.

Terrana, and especially magnesium silicate, are somewhat less desirable as carriers for iron catalysts than is char.

Only few comparative tests are available for brown coal tars, cracking residues, and petroleum residues. Differences between the different catalysts are less pronounced with these feeds than with bituminous coal feed. Such feeds can therefore be hydrogenated with Mo-free catalysts.

/s/ Grassl

^{1/} The improvement probably was caused not by alkalization, but by the precipitation of iron hydroxide upon the char, or by conversion of NaOH with FeSO₄ to Na₂SO₄, which is readily reduced to sodium sulfide in the presence of iron.