

Frames 288-37

Report on experimental hydrogenation of Silesian coal K 1197 from the Heinitz Mine to gasoline and middle oil at 600 atm. in 10-liter converters, by Kroenig and Hupfer.
March 9, 1942.

Summary

Results of hydrogenation of older Upper Silesian bituminous coal to gasoline and middle oil were unfavorable, and younger coals were experimentally hydrogenated for Blechhammer.

A table shows the properties of the Beuthen and Gelsenberg coal to be rather similar. The former differs unfavorably from the latter by a higher proportion of oxygen and less liquid constituents, especially tar. The C content is somewhat lower. Hydrogenation results were expected to be generally similar, but somewhat less satisfactory. The Silesian coal differs from the Ruhr coal, Gelsenberg, by its higher alkali content in the ash and a lower S, Cl and net hydrogen content, also by its lower l.t.car. tar yield. It was hoped that these unfavorable properties might be compensated by the lower C content.

The coal could be readily hydrogenated in 10-liter converters, using the usual catalyst combination (iron sulfate, sulfurized Bayer mass, sodium sulfide) at different temperature and with different throughputs. Hydrogenation results are presented in a table and show that at the same converter temperature and with the same m.a.f. coal throughput the percentage conversion, gasoline and middle oil space time yields, gasification, and asphalt content differed very little from results obtained with Ruhr coals.

Frames 380-382

Replacing ammonium chloride in the hydrogenation of Ruhr coal (older experimental results).
October 20, 1943.

Summary

Ammonium chloride can be practically completely replaced by the equivalent amount of elementary chlorine, used either as a gas or as chlorinated pasting oil, or by the chlorine content of coal; also by hydrogen chloride. Organic chlorine compounds, such as carbon tetrachloride, produced similar results. Sulfur chloride may also replace ammonium chloride, while sulfur dioxide or ammonium fluoride are undesirable. Practically the same results were obtained with phosphoric acid at 1/2 M.V. higher reaction temperature as with ammonium chloride. The addition of powdered metals (iron, aluminum, zinc, tin, etc.) permitted the reduction of chlorine to 1/2 - 1/3, but somewhat lower temperature is necessary to obtain as favorable asphalt reduction as with ammonium chloride. Results of tests with chlorine-containing water-soluble alumina or with aqueous or spent aluminum chloride have not so far been promising but will be continued.

/s/ Grassl

Experience with the fifth converter, October 20, 1943.

The earlier discussions of March 22 were made for the purpose of bringing about a preheater load reduction.

Properties of N10 steel were not primarily considered in these discussions, but were of importance in connection with possible power economy.

Discussions brought out a few means to reduce the liquid phase preheater load, i.e. to reduce the amount of heat to be supplied to 1 kg. paste, but especially to lower the temperature of the hairpins.

Distinction must be made between plants which operate at present without paste heat exchange and those with heat exchange, or those for which heat exchange is intended.

The former, like Gelsenberg, which still operated without paste heat exchanging were recommended to install it, naturally realizing that this will require time. Poelitz is well satisfied with heat exchanging its thin paste. It involves a somewhat higher equipment cost. No objections were raised, however, to heat all the paste to 320-330° by heat exchange, especially with the already available equipment for which the grinding plant was completely adequate. These temperature limits of around 320° were confirmed by special viscosity measurements by Dr. Hupfer, on which he will make a special report. Gelsenberg has after that successfully heat-exchanged the total paste in 1 or 2 stalls. The expected results were obtained, in particular when connected with gas heat exchange.

Plants already using heat exchange could recover additional heat by heat exchange of precooled products. This was primarily to be used where the feed temperature remained high in the cooler. Such suggestion naturally involves addition of more heat exchangers per stall. Such heat exchangers become, however, rapidly amortized. We went one step still further in Blechhammer. We wish to heat exchange even the thick paste to about 250° C., which is readily possible according to Dr. Hupfer's test.

The fifth converter was most discussed on 3/22. In what way did this suggestion come about? We received a very detailed reply from Gelsenberg in November, 1942, to an earlier question on the true reactor inlet temperature in hydrogenation plants, or the preheater outlet temperature, which is the same. This letter showed that the preheater outlet temperature could be considerably lowered with the four converter stalls at full load, by as much as 2.20 mv. The temperature was higher in other stalls. We then asked ourselves whether our demands for 22.5 mv. inlet temperature were excessive. We prefer operating at lower limits, if it can be done safely, i.e. at 20-21 mv., even if we use the first converter in part for preheating. Conditions could be equalized by the addition of one more converter, i.e. by changing the 4-converter stall to a 5-converter stall. This should not result in poorer performance. Obviously, increasing the reaction space, and therefore also

the time of residence, must affect the temperature of the last converter, unless throughput is correspondingly increased. Lowering the temperature by that much would anyway materially decrease the load upon the preheater. The load upon the new stall could be increased, as long as the pump capacity is sufficient and the resistance does not become too great; the crusting of the preheater will be reduced, making the fifth converter economical in every way.

We have had for a long time some ideas on flow conditions in the liquid phase converters, and namely that the hotter return flow will raise the temperature of the fresh feed. Whether a definite converter type, e.g. the 1,000 mm. converter is used to capacity with a certain throughput could not, however, definitely tell whether the method suggested by Gelsenberg and involving a strong lowering of the converter inlet temperature would apply also for high throughputs.

It was, therefore, welcome news that Gelsenberg and Poelitz already found a chance to add a fifth converter in one stall and to carry out the necessary tests. Evidently most of these problems, and especially the relationship between converter inlet temperature and throughput could also be solved for a four-converter stall. It required, however, a certain reduction in the output when the first converter is made entirely to operate as a preheater.

/s/ Schappert

Frames 386-389

Discussion of pilot plant experiments in Ludwigshafen, October 25, 1943.

Dr. Peters reports on the success of vapor phase hydrogenation of bituminous coal cold catchpot heavy oil from Upper Silesian coal at 600 atm. over catalyst 8376; the outlet pipeline had to be flushed, however, once a day to remove coronene. In addition, coronene was centrifuged and an anhydrous heavy oil was recycled.

About 0.5% coronene was found in the products.

Frames 390-391

Hydrogenation tests with fly ash of the smelter Kayser A.G., Berlin (Rotating autoclaves).
October 1, 1942.

The tin-containing fly ash was composed of 16.5% Sn, 16.0% Pb, 39.8% Zn, 1.5% Cu, 0.26% S and 0.1% As. This ash contained equal amounts of lead and tin and about twice that amount of zinc, and seemed promising as substitute for the Scholven hydrogenation catalyst because of the ever increasing scarcity of tin oxalate.

The m.a.f. coal was somewhat better utilized with fly ash than with comparable amounts of tin oxalate. Should the fly ash first be converted to sulfide, 0.2% might be sufficient to produce the same results as 0.06% tin oxide. The results are presented in the form of a table.

The formation of caviar-like deposits in the first converter in large-scale tests of fuel oil production from Upper Silesian coal. March 26, 1942.

Summary

Caviar-like depositions were observed in the converter after the completion of fuel oil large-scale tests. The deposits were not normal calcium carbonate caviar but consisted principally of aluminum, iron, sodium, silica, sulfur, and chlorine.

The converter was let down upon completion of the tests on fuel oil production from Upper Silesian coal. About 20 kg. abraided grain (up to 4 mm. in size) were observed upon the let-down of the first converter. The throughput through the converter was good, and it was assumed that the phenomenon was based principally on depositions in the converter funnel. When the converter was opened, its funnel and the middle section of the converter to a height of 2 m. from below were found filled with rather loose grain. A soft deposit 50 cm. in height, was formed above, in which the pieces were dispersed in oil. The upper part of the converter was clean. The total amount of paste which settled weighed about 330 kg. from a total throughput of dry coal of 1,300 tonnes, i.e. it amounted to 0.025% of the weight of the coal. Referred to the coal ash, the deposit amounted to but 0.5%.

The surfaces of the grain were rounded which led to the idea that they represented a caviar formation. They did not, however, exhibit the usual spherical shape, and the grain was oblong.

Cross sections in different axial directions were made and showed a definite conchoidal structure, which is never observed in the lignite caviar in Leuna. The analysis of the deposit is shown in the table below.

Sample	From Bottom of converter	From Upper middle of converter Soft part	For comparison, Composition of coal ash
% Benzene insolubles	87.0	82.6	
% Ash in the solids	96.1	90.3	
% Asphalt in oil	2.8	3.4	
Composition of ash:			
% SiO ₂	16.72		32.65
% Fe ₂ O ₃	21.80		10.36
% Al ₂ O ₃	30.80		28.11
% CaO	4.23		9.47
% MgO	0.49		4.94
% Na ₂ O	9.43		1.71
% Cl	Trace		-
% SO ₄	13.70		9.59

In the original substance:

% sulfide S	4.95
% total S	5.72
% Cl	6.56

The granules obviously consist entirely of ash. The important ash constituents are alumina, iron, sodium, silica, sulfur and chlorine. Most of the sulfur exists as sulfide, most of the chlorine in volatile form.

Analysis tells, that with the low CaO content the deposit differs from caviar, such as is formed in Leuna. The deposits are different in kind, with about the same Al_2O_3 content as in the coal ash. Silica, iron, sodium, sulfur and chlorine are higher than in the coal ash, and are evidently derived from the catalyst used, $FeSO_4$, Bayer mass, Na_2S . The high chlorine contents of over 6% is surprising.

/s/ Rank

Frames 395-396

A note on a new method of hydrogenation to fuel oil. March 17, 1942.

Frames 398-444

Detailed description of pilot plant hydrogenation of Scholven coal at 250 atm. to gasoline and middle oil with chlorine in different forms and tin oxide. October 10, 1942.

Frames 445-448

Hydrogenation of Rhenish lignite with neutralization of coal. October 12, 1942.

Frames 449-450

Behavior of steam at 450° C. and 700 atm. May 3, 1944.

I have pointed out some time ago that the caviar formation in coal converters leads to the conclusion that steam behaves as a liquid under conditions existing in converters, i.e. at 700 atm. and 450° C., and can dissolve inorganic salts. I have derived from that, that caviar formation can be entirely eliminated. This idea was communicated 2/17/44 to Dr. Pier's collaborators, and finally to Dr. Pier himself. I could in the meantime find several communications in related fields describing analogous phenomena, such as the silica coating of turbine blades or the formation of quartz deposits known to geology.

Professor Otto Fuchs has communicated to the Deutsche Bunsen Gesellschaft on October 25-26, 1940 on work made jointly with Dr. Spillner. This communication was published in Z. Elektroch. 1949, p. 101, and followed by a communication by Dr. Spillner in the Chem. Fabrik, 1940, p. 405. These communications present data on the solubility of several inorganic compounds ($BaCl_2$, KCl , Na_2SO_4 , and $NaOH$) in steam at high pressures and temperatures. Measurements, however, were interrupted at about the critical pressure. Results show, however, that highly

compressed steam dissolves appreciable amounts of inorganic compounds forming true solutions. The solubility greatly increases with increasing pressure. It may therefore be assumed that solubilities are still higher under conditions existing in our hydrogenation converters.

Sufficient water is present in the converters, because 60 kg. of water is present in one tonne coal, and additional water is formed through combination of oxygen with hydrogen; in addition, water is added to the stall. If the solubilities of the salts under conditions existing in the stalls were known, it might be possible to prevent the formation of caviar by suitable additions. When salts are to be deposited in coarsely crystalline form from the liquid phase at atmospheric pressure, a number of factors, such as strong stirring, addition of other salts, etc. may cause them to deposit as undesired fine crystals. It may be possible in this way to cause the caviar to form a harmless fine sludge. Strong stirring inside the converters was, however, found to be inadequate for the purpose.

When the converter contents are cooled, ash constituents are found in the aqueous phase. The assumption appears justified, that salt behavior in the aqueous phase, including the action of CO_2 , is rather unaffected by the oil phase.

Dr. Rank informs that with our coal and with 4.5% ferrous sulfate and 4.5% ammonium sulfate a true caviar up to 0.4 mm. in size is formed in experimental converters. The nuclei consist of particles of sand. Their caviar was different from ours and did not consist of calcium carbonate, but of small amount of lime and larger amounts of iron and alumina. The converter desanding equipment was ineffective because salt crust containing calcium carbonate are formed even in our hairpin tubes of the gas preheater, which may also lead to trouble. Most trouble is, however, caused by great accumulation of caviar in the converter, which sinters there at higher temperatures by coking of the oil, reduces the reaction space, and narrows down the passage. Avoiding caviar formation becomes therefore necessary, and it might be desirable to study the solubility of salts in steam at high pressures and temperatures. Results of such investigations would be of interest not only in hydrogenation but also for high pressure steam engineering. It may well be that some inorganic chemical reactions may be made to more readily proceed at high pressures, and that the high pressure engineering is in condition to supply the necessary equipment. The results might therefore be of general interest.

/s/ Moll

Frames 451-452

Rotating autoclave catalyst tests with Scholven coal. October 28, 1942.

Results of tests for substitution of SnO and ammonium chloride because of the scarcity of tin.

The results tabulated show that 1.2% $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$ plus 0.3% zinc oxalate are equivalent in action to 0.06% tin oxalate. Sulfur dichloride differs but little in action from ammonium chloride, and may

even be preferable to the latter in asphalt reduction. The conversion is somewhat lower with zinc catalysts and the gasification somewhat higher, but the asphalt reduction and splitting are somewhat better; gasification is somewhat higher with 0.6% zinc dust instead of 0.3% zinc oxalate. 0.5% precipitated iron sulfide and sulfur dichloride are somewhat preferable to ammonium chloride and practically equivalent to tin oxalate and chlorine. 0.3% antimony pentasulfide produced distinctly more asphalt and gasification than the other catalysts. The high specific gravity of the residue, 1.325 leads to the conclusion on a polymerizing or dehydrogenating reaction of this catalyst.

/s/ Grassl

Frames 453-455

Rotating autoclave hydrogenation tests of Upper Silesian coals.

Frames 456-461

Tests on caviar formation with Rhenish lignite in 10-l. converters.
November 3, 1942.

1. Caviar was found to form from Rhenish lignite in 10-l. converters with stirrers and without desanding. Caviar-like formations may in this way be observed and studied. The 10-l. converter caviar particles are 40-300 μ in diameter and are not strictly spherical. The grain forms layers in which CaCO_3 and SiO_2 can be observed microscopically.

2. Proper desanding methods will overcome caviar formation from Rhenish lignite.

3. Addition of paving tar to coal does not protect entirely against caviar formation, but does retard the deposition in the converter by causing the contents to become more viscous.

4. The substitution of Bayer mass with FeSO_4 to reduce alkalinity by 50% offered no protection against caviar formation.

5. Increasing the amount of pasting oil apparently increases the caviar deposition considerably. This might justify the conclusion that starting operations with much cooling oil in the converter, as was temporarily done in Wesseling, will have a similar effect.

TABLE 1. - Composition of raw materials

	Coking tar	Bit. coal	Low bitumen lignite	Petroleum cracking residue	High bitumen lignite	Lignite l.t.car. tar	Asphalt base petroleum
% C	88.42	82.93	68.72	85.92	71.9	83.41	84.6
% H	6.01	5.28	4.87	9.98	5.3	10.79	10.8
% O	4.28	9.21	25.16	1.37	16.3	3.53	0.5
% N	0.91	1.48	0.74	0.09	0.6	0.28	0.4
% S	0.38	1.10	0.51	2.64	5.9	1.99	3.7
Gm. H ₂ /100 C	6.8	6.37	7.08	11.6	7.4	12.9	12.8
a) Middle oils							
Specific gravity/20	0.988	0.974	0.960	0.907	0.900	0.889	0.876
% phenols	2.5	15.3	20.1	0	13	0.6	traces
% C	88.51	87.28	85.60	87.0	85.7	87.45	87.4
% H	8.95	9.54	9.80	11.07	10.6	11.81	12.0
% O	1.82	3.08	4.00	1.14	2.7	0.37	0.94
% N	0.66	1.06	0.50	0.16	0.6	0.20	
% S	0.06	0.04	0.10	0.63	0.04	0.17	
Gm. H/100 C	10.12	10.93	11.42	12.72	12.4	13.5	13.7
A.p. phenol-free oil, °C.	<-25	-20	+13	+27.7	+34	+41.0	+41
b) Heavy oils							
Specific gravity/50° 1.053	1.038	1.030	1.030	0.994	88.0	0.925	87.8
% C	90.71	89.27	88.62	88.62	88.0	88.47	87.8
% H	7.46	8.26	8.40	9.46	9.7	10.78	9.9
% O	1.10	1.64	1.62	0.64	0.9	0.38	0.2
% N	0.61	0.77	0.28	0.12	0.6	0.12	0.6
% S	0.12	0.06	0.08	1.16	0.8	0.25	1.6
Gm. H/100 C	8.22	9.25	9.46	10.67	11.0	12.18	11.3

TABLE 2. - Properties of liquid phase products from a long-flame coal differently hydrogenated

a) Middle oils

Production Method	100% gasoline + m.o.	35% heavy oil	50% heavy oil	Middle oil + bitumen 70% m.p. 1/	Middle oil + bitumen 100% m.p. 2/
Sp. gr./20°	0.979	0.973	0.964	1.006	1.012
% phenols	12.8	15.0	15.5	11.6	8.6
% C	87.08	86.68	86.54	88.91?	88.90
% H	9.66	9.42	9.57	7.49	7.82
% O	2.59	3.58	3.28	2.96	2.52
% N	0.64	0.30	0.60	0.45	0.59
% S	0.03	0.02	0.01	0.19	0.17
Gm. H/100 C	11.08	10.86	11.0	8.42	8.80
A.p. phenol-free oil, °C.	-29	-25.6	-24.0	-43.5	-43.3

b) Heavy oils or bitumens

Sp. gr./50°	1.042	1.052	1.052	88.87	88.79
% C	89.58	89.37	89.02	5.53	5.72
% H	8.22	7.93	8.21	5.41	3.94
% O	1.46	2.09	2.32	0.06	1.39
% N	0.71	0.59	0.42	0.13	0.17
% S	0.03	0.02	0.03	6.22	6.5
Gm. H/100 C	9.18	8.87	9.25		

1/ 700 atm. extraction hydrogenation.
2/ 300 atm. extraction hydrogenation.

Frames 462-464

Tables of composition of raw materials and of liquid phase products from them, and of liquid phase products obtained by different hydrogenation of a gas flame coal.
March 11, 1942.

Frames 465-467

A letter by Dr. Pier on the hydrogenability of coals (abstract).
November 3, 1942.

Hydrogenability of lignites is limited only by its ash content. A high ash results in large amounts of H.O.L.D. and centrifuge residues, and the oil losses during kilning will be high.

Central German coals with up to 13% ash are presently considered good hydrogenation coals, while coals with up to 18% ash, referred to the m.a.f. coal, may still be considered suitable. Rhenish brown coals are hydrogenated with about 7% ash. Not only the absolute percentage of ash, but also the possibilities of deashing prior to hydrogenation, or the need of neutralization, must be considered.

Aside from ash, no other limitations are set upon lignites. Excessive oxygen content is undesirable because of certain requirements during the heating of paste and smaller yields with high oxygen coals.

Amongst bituminous coals the long flame and gas flame coals are best for hydrogenation, while the gas coals can still be hydrogenated.

Coals with the same carbon content but from different deposits require different conditions during hydrogenation. A good Ruhr coal should have 82-83% carbon with 84% as a maximum, and volatile matter content of over 37%. Ruhr coal with 87% carbon and over 30% V.M. can still be hydrogenated, but requires individual testing.

A good Upper Silesian hydrogenating coal should have less than 82.5% C and over 37% V.M. Coal with 85% C and over 35% V.M. can still be hydrogenated.

A well-hydrogenating Saar coal has less than 83% C and over 37% V.M. Coal with 86% C and over 35% V.M. are still suitable for hydrogenation.

The ash content of bituminous coal must be kept as low as possible, and should be reduced to below 4%, referred to dry coal. The cost of deashing before hydrogenation and of the ash separation in kilning must be balanced.

Petrography of the coal must be considered when judging it; wood content in the lignite and the fusite in the bituminous coal are unfavorable to hydrogenation.