Conversion of primary bitumen to heavy oil. March 19, 1943.

Results of two-stage conversion of bituminous coal to gasoline and middle oil by first extracting the bitumen are less desirable than direct hydrogenation, in particular with respect to gasification. The bitumen of Silesian bituminous coal was experimentally processed in a single pass. Higher temperatures in this process could be expected to yield somewhat better results without becoming uneconomical because of high gasification.

The H.O.L.D. had to be added in proportion of 1:0.5 to permit pumping the feed, and the middle oil had to be recycled in proportion of 1:0.4. Smooth operations permitted operating at the extraordinarily high reaction temperature of 492°. The slowness of the reaction may be explained by the catalyst not becoming highly concentrated inside the converters because of the viscosity of the contents. Relatively large proportion of catalyst was therefore used (2.0% iron-char + 0.2% sodium sulfide).

The reaction was relatively trouble-free. The space-time yield was 0.8 with 15.9% gasification, and 47% of the oil produced consisted of heavy oil. The bitumen catchpot heavy oil is much less viscous than the bituminous coal heavy oil, while other fuel oil properties are identical in both products. The table below compares the two-stage method of operation with the direct coal hydrogenation to excess heavy oil (at 600 atm.).

	Stage I Extract hydrogenation	Stage II Prim. bitumen hydrogenation	Stage I + II	Direct coal hydrogenation to 35% H.O.
Produced from	1,000 kg. m.a.f. coal	637 kg. primary bitumen	1,000 kg. m.a.f. coal	1,000 kg. m.a.f. coal
Gasoline	53	80	133	134
Middle oil	108	182	290	301
Heavy oil	-	233	233	235
Primary bitumen	637	-	-	-
Total oil production	161	495	656	670
Oil space-time yield	0.135	0.811	0.473	0.480
Gasification, % of to oil production + gasification	34.5	15.9	20.1	20.0

Two-stage conversion of bituminous coal to fuel oil produces practically the same results as direct coal hydrogenation to 35% heavy oil. Direct hydrogenation offers better possibilities for changing the proportion of products in the total oil production, and must be considered preferable as heavy oil production process.

Report on discussions of cracking of hydrogenation gas, Poelitz. 7/8/41

The discussion was held for the evaluation of the Poelitz experience in the construction of the Wesseling plant and for future plants.

The off gas cracking plant consists of 12 units, each with 66 tubes.

The Poelitz cracking plant has caused fewest difficulties of all the units. The cracking plant was supposed to absorb and buffer difficulties in high-pressure section and in the distillation. There existed periods in which almost 100% $C_3 + C_4$ had to be converted.

The liquid and the vapor phase gases are subdivided into rich and lean gases and the two streams subsequently joined. The rich gas is desulfurized with alkazid at 5 atm. The sulfur content at the outlet amounts to about 40 mg./m.^{3}. The lean gas is desulfurized with alkazid at 25 atm. The sulfur content is also equal to 40 mg./m.^{3}. The rich gas is next compressed to 25 atm. and sent for LP-gas recovery. The residual gas from the latter is combined with the lean gas and stored in two 100 m.^{3} spherical containers for 25 atm. pressure. The pressure of the gas is released to 5 atm., the gas purified with Lauta mass to an organic sulfur content of 1-2 mg. The Lauta mass is regenerated as soon as the sulfur content in the gas reaches 2 mg. The use of the Lauta mass depends on the sulfur absorption. A total absorption of at least 20 and up to 40% of the weight of the Lauta mass is expected. Poelitz experience has shown that hydrocarbons condensed in the pipe lines. Traps had to be provided there.

The organic sulfur purification is done with Bayer mass and zinc oxide. Gas was formerly heated to 400° C. in heat exchangers. The organic sulfur content in the Poelitz hydrogenation off gas is surprisingly low. It amounts to $\pm$ 10-12 mg. Variations in organic sulfur content are surprisingly great with completely constant operations of high pressure. It remains as yet unexplained. The present analytical method (precipitation of berium sulfate) is however unsatisfactory. Nor is any dependable rapid method known. Oppau uses, as a qualitative rapid method, the brown coloration of lead acetate paper. Ludwigshafen operational controls is developing an apparatus for continuous measurements.

The total sulfur (organic + inorganic) in hydrogenation off gas in the inlet for cracking should be less than 10 mg. Higher sulfur becomes immediately noticeable by a number of signs (reduced production, higher CH_4 in the cracked gas). Two Bayer-mass towers and two zinc oxide towers are connected in series in Poelitz, next comes a tower in which Bayer-mass and zinc oxide are arranged in layers. According to the I.C.I. experience, such towers should prevent going-through of sulfur. This arrangement is adopted in Poelitz; Poelitz cannot vouch that it answers the purpose. Poelitz reduces organic sulfur to 5 mg. average, with variations between 3 and 7 mg., depending on whether 8 or 15 mg. organic sulfur is present in the feed gas.

The average C of the present hydrogenation off gas is 2.0. It contains 25-30% hydrocarbons and 60% H_2. The gross calorific value is around 6,000. The gas contained originally no CH_4, as long as only the vapor phase off gases were used. No pure C_4H_{10} was so far cracked, but mixtures containing up to 20% C_4H_{10}. The gas contains at present 5-10% butane.

The cracking plant was put on stream with 300% excess of steam, which was later reduced to 200%. At present, 130% excess is maintained. The catalyst contracted at first by about 10%. Tubes were therefore at first filled rather high. Abrasion of catalyst has so far caused no increase in pressure. The differential pressure in the reactor is about 0.9 atm. The catalyst life is very long. The American catalyst was not replaced since 1933, and merely replenished.

The CH_4 content in the cracked gas is below 2%. Only 0.4% CH_4 was found with a cracking temperature of 750° C. Only 0.8% CH_4 were found in another reactor, and 1% CH_4 in a gas cracked with new catalysts at 690-700° C.

All tests have shown that the $CO:CO_2$ ratio corresponds to steam equilibrium. 7-8% CO_2 and 11-12% CO are found with 130% steam excess. A high CO content is necessary to maintain operations. Operations could be maintained in the winter with 18% CO, but in the summer only up to 16% CO (because of lower radiation losses).

/s/ Becker

Frames 180-215

Translation from the Russian of an article by P. W. Putschkow on destructive hydrogenation, Bull. Acad. Sci. U.S.S.R. 1937, pp. 481-500.

Theory of destructive hydrogenation in the liquid phase based on thermodynamic data and experimental material of the characteristic reactions occurring in the process. Derivation of a hypothesis on the mechanism of hydrocarbon decomposition, and the regulation of processes under different hydrogenation conditions.

Forty-nine references quoted, mostly Russian.

Frames 216-223

Theory of ammonia catalysis, based on the work of I.G.

Frames 224-226

The bauxite residues from Al_2O_3 manufacture, by von Funer. January 10, 1942

Bauxite is industrially dissolved in alkalies by two principal methods. The first, the dry process (pyrogenic process), produces red mud as a byproduct, in which $Fe(OH)_3$ is produced by hydrolysis from the sodium ferrate formed during fusion. Fe_2O_3 in the bauxite remains un-attacked in the second, wet, method of solution under pressure (Bayer

process). According to Dr. Reichert (Giulini Co.) 20,000 T./ann. of hydrated alumina is produced by his concern by the former process (their own process is also used, and is similar to the first). The mass is solubilized by calcining with Na_2SO_4 and coal, with formation of SO_2 which is reconverted to H_2SO_4. Leaching produces the same red mud (Lux mass) as in treating with soda; the solution is stirred, saturated with CO_2, $Al(OH)_3$ is deposited and the soda in the filtrate recovered.

Giulini was recently given an order for production of additional 50,000 T./ann. hydrated alumina by the Bayer process. 80,000 T./ann. of moist red mud with about 50% water is expected to form as a byproduct, and the Bayer mass is similar in composition to that obtained in the Lauta and the Martin plants. Giulini is at present trying to find a market for this mass. If used as catalyst in the liquid phase, this mass must be dried to 10-15% H_2O and preformed (into sausage shape) as in the Lauta works. The unpreformed powdered Bayer mass can be transported dry only in special dust-proof wagons.

The Bayer mass cannot be used for gas purification. Red mud suitable for Lux mass obtained by Giulini by dry solubilization (pyrogenic process) amounts to about 500,000 tonnes (?). Leuna and Ludwigshafen have both found that Bayer mass can be used in hydrogenation. One cannot decide whether Lux mass or the Bayer mass is the better liquid phase catalyst (a minimum price is set on the Lux mass, which may make the Bayer mass the better product for the liquid phase). The approximate amounts of Bayer mass for the liquid phase hydrogenation are at present:

	T./ann.	Delivered by
Leuna	30-35,000	Lauta plant, Lausitz
Blechhammer I	12,000	do. do.
Blechhammer II	(6,000)	do.
Gelsenberg	10,000	?
Poelitz	6,500	Probably Lauta plant
Rheinbraun	13,000	? (probably Martin plant)
Scholven	at present still SnO + Chlorine	
Gladbeck	to start 1943/1944	

Leuna, Blechhammer and Poelitz can be more easily supplied from Lauta works, and moreover, Leuna and Blechhammer are already bound by contract with Lauta works, and only Gelsenberg and Rheinbraun can now be considered as buyers of the Bayer mass from Giulini, and Scholven and Gladbeck at a later date. It is not known whether these concerns already have long-term agreements with their suppliers.

Analyses of Bayer Masses

	Lauta Plants, %	Martin Works, %
SiO_2	7.48	7.28
TiO_2	7.60	5.49
Al_2O_3	17.86	15.27

Analyses of Bayer Masses (cont'd.)

	Lauta Plants, %	Martin Works, %
Fe_2O_3	51.27	57.15
N_2O_3	0.12	-
CaO	0.88	1.25
MgO	0.09	0.46
K_2O	0.12)	
Na_2O	5.46)	1.6 (water soluble alkali)
SO_4	1.2)	
S total	-	0.17
H_2O	0.55	1.44
CI	0.12	-

Frames 227-228

Coal drying in Liévin and Béthune, by Rank and Simon.

1. **Liévin**

The Marly coal was ground in driers for the liquid phase test. A Loesche system dryer grinds 4 T./hr. of coal. The coal feed is 20-40 mm. size and contains 8-10% moisture. The dried ground coal still contains 5% moisture and leaves less than 5% residue on the 3600 mesh screen (per $cm.^2$: = 150 mesh). Recycle gas (from a gas burner) is at 125° C. (15,000 $m.^3$/hr. - 3750 $m.^3$/T. coal). The two grinding stones are mounted on a vertical shaft upon a rotating base. The coal could be dried further with a lower coal throughput. The powdered coal is separated in a cyclone.

2. **Béthune**

Coal is dried in a drum dryer, built like a sulfate dryer. The drum is slightly inclined, 11-12 m. long, 1.8 m. diameter, and is mounted on two bearings. It is electrically gear driven. Inside deflectors are built into the drum. An inclined tube is used for feed. Flue gas is used for drying, mixed with a large excess of air. The gas reaches the dryer at 150-180° C. The flow is concurrent. The feed leaves the dryer at 70-80° C. Most of the coal is moved by a screw conveyor. The dust is collected by the gas and removed in a cyclone, in which most of the coal is deposited. The gas is vented into the air. Powdered coal 0-10 mm. is sent through the dryer. Throughput 3-4 tonnes/hr. Less than 1% water remains in the coal after drying.

Gas consumption 60 $m.^3$ coke-oven gas per hour.
Blower capacity, 1500-2000 $m.^3$/hr.

Frame 229

Use of hydrogenation residues in briquetting.   June 13, 1944

Proposed use of hydrogenation residues as a briquette binder

Frame 230

Employment of foreign help in secret work.

Frames 231-232

Instrumentation in hydrogenation, dehydrogenation and methanol synthesis.
February 17, 1943

List of German instruments.

Frames 233-236

Regulation of converter temperatures with H and B regulators. March 27, 1943.

Frames 237-239

Inspection report in Gelsenberg, April 15, 1943

1. Tar converter

One 3-converter stall was operated experimentally with and without preheaters. The test was satisfactory, even if run for a short time only.

2. Paste heat-exchanging

Different methods of paste heat exchanging were discussed.

Frames 240-243

Paste heat exchange.   April 19, 1943.

Frames 244-247

Increased use of bituminous coal l.t.car. tar plants. Discussion
February 12, 1942.

A proposed installation of bituminous coal l.t.car. to meet fuel requirements.

Frames 248-273

Hydrogenation of Silesian coal to gasoline and middle oil at 600 atm. in 10 l. converters. Report of investigation, January 3 to January 27, 1940. Report dated May 21, 1941.

Summary

Coal from the Preussen Mine for use in Blechhammer is similar to two coals already tested for their hydrogenation qualities and in

their ultimate analysis, chlorine content, bitumen and ash composition.
Only volatile constituents and tar yields are higher with this coal.
This coal might therefore be expected to hydrogenate with better space-
time yield and gasification than the other two coals mentioned, but
will nevertheless be much inferior to the Gelsenberg coal.

Chemical composition of preheater crust.   March 22, 1943.

Distinct layer structure was noticeable in the incrustation
in the preheater tubes, and the different layers might have been formed
during different operating periods. In Gelsenberg the crust formed
three layers, with the outer layer directly upon the tube wall.

1. Outer layer: 1 mm. thick dark mass, sp. gr. 5.2 (pyrite or hex-
agonal FeS, sp. gr. 4.8) and is practically homogeneous.

2. Middle layer: 3.5 mm. thick, gray, very hard mass with many well
formed brass-colored crystals. Sp. gr. 4.8.

3. Inside layer: 8 mm. thick, black heterogeneous mass, less hard than
the other two layers. Mixture of coke and crystalline constituents. Sp.
gr. 3.9, confirming the presence of coke particles.

The tube wall was brittle to a depth of 1/2-1 mm., and its
appearance indicated strong corrosion.

The chemical analyses of the layers of the Gelsenberg crust
show that the principal constituents in the intermediate and inner
layers are Fe and S, present in proportion by weight of the compound
FeS.

The presence of W, Mo, V, Cr in the crust is surprising, and
they were derived from the tube material. Their amounts decrease from
outside to the inside. Their presence may indicate that the metals
diffuse in the solid phase from the surface attacked.

Unlike other crusts, the Poelitz crusts contained only traces
of these metals, showing somewhat different conditions there. Titanium
is also present in Poelitz in much smaller amounts than in Gelsenberg.

Iron in the crust cannot possibly come from the tubes, because
of the very slight reduction in weight of the tubes, and must come from
the coal or the catalyst. The proportion of iron and titanium in the
crust and of the individual iron compounds helps in arriving at this
conclusion.

	Fe : Ti
Ruhr Coal Ash	51 : 1
$FeSO_4 \cdot 7H_2O$	90 : 1
Bayer mass	8.1: 1