

### III. METHANOL AND HIGHER ALCOHOL SYNTHESIS

Dr. Halmut Hanisch and Dr. Erich Sackmann, respectively head and engineer of the Organic Division, were interrogated on May 12th.

#### Methanol

The converter was of the cold-shot type, with external interchanger. Each forging had an I. D. of 800 mm. and was 12 m high; the internals were made either of pure copper or of copper-covered steel. The catalyst basket had an I. D. of 650 mm. and contained 5 or 6 equal beds, holding a total of 3 M<sup>3</sup> catalyst. The circulating gas rate was about 100,000 M<sup>3</sup>/hr., giving an output of 120 T/D crude methanol, containing 4 to 5% H<sub>2</sub>O, dependent on the CO<sub>2</sub> content of the gas. The compositions of make-up and circulating gas were:

	<u>Make-up gas</u>	<u>Circulating gas</u>
CO <sub>2</sub>	1 to 1.5%	
CO	30%	18%
H <sub>2</sub>	65 to 68%	
N <sub>2</sub>	1 to 2% )	10 to 15%
CH <sub>4</sub>	0.5 to 1% )	

The maximum catalyst temperature was given as 390°C, reached towards the end of the converter.

A sample of the catalyst was obtained; it was in the form of 9 mm pellets and was based on zinc and chromium. No CH<sub>4</sub> formation occurred to any measurable extent.

Plant output was of the order of 12,000 T/month crude. Reciprocating circulators were used, not centrifugal ones as used for ammonia.

Water-free methanol was used instead of ethanol in motor fuels. Purified methanol was used for formaldehyde manufacture and for solvents.

#### Higher Alcohols

The name given to higher alcohols was "iso-butanol", although this was the main and not the only substance synthesized.

The plant used was very similar to that used for methanol synthesis, although the interchanger was a little smaller, having an I. D. of only 500 mm.

The circulating gas rate was only 35,000 M<sup>3</sup>/hr., giving an output of 40 T/D crude higher alcohols, containing about 12% iso-butanol.

I.C. 7370

The composition of the gases was:

	<u>Make-up gas</u>	<u>Circulating gas</u>
CO <sub>2</sub>	1 to 15%	3 to 5%
CO	30%	25 to 26%
H <sub>2</sub>	65 to 68%	
N <sub>2</sub>	1 to 2% )	10 to 15%
CH <sub>4</sub>	0.5 to 1% )	

Thus higher alcohol circulating gas contained more CO and CO<sub>2</sub> than did methanol circulating gas; CO<sub>2</sub> presumably was produced by reaction between CO and water made in the reaction.

The maximum catalyst temperature was given as 450°C. About 2% methanation occurred. The catalyst was the same as methanol catalyst, but with 2% K<sub>2</sub>O added; a sample was obtained.

Plant output was of the order of 12,000 T/month crude, i.e. about 1,400 T/month iso-butanol.

Methanol made up half the crude and after separation it was injected into the inlet of the interchanger and re-passed through the converter, where it was converted into higher alcohols. By using stocks of crude higher alcohols the synthesis plant could be run for some time without make-up gas, using only this crude methanol as feed. Such methanol was difficult to purify on account of the hydrocarbons, mostly olefins, it contained.

The composition of crude was given as:

50 to 55% methanol  
22 to 25% water  
1 to 3% dimethyl ether  
1 to 2% n-propanol  
11 to 12% iso-butanol  
2% C<sub>5</sub>  
2.5% C<sub>6</sub> and C<sub>7</sub> )  
1 to 2% C<sub>8</sub> and C<sub>9</sub> ) alcohols, ketones, hydrocarbons, etc.  
1% C<sub>10</sub> up to C<sub>14</sub> )  
1 to 2% hydrocarbons (yellow oil containing 70% olefins)

The fraction 110° to 160°C amounted to 3 to 4% and the fraction 160° to 250°C also amounted to 3 to 4%.

The working up of the crude can be followed by reference to Figure I. First dimethyl ether was removed in a ring-packed tower working at 10 ats. Then methanol was removed in a bubble-plate column working at 10 ats.; "yellow oil", i.e. the hydrocarbons; was taken overhead and methanol was taken as a side-stream near the top; to obtain an isobutyronone fraction  $[(CH_3)_2CH.CO.CH(CH_3)_2]$ , amounting to 0.5% on crude, a side-still was used as shown. The bottoms from this column separated in two layers; the

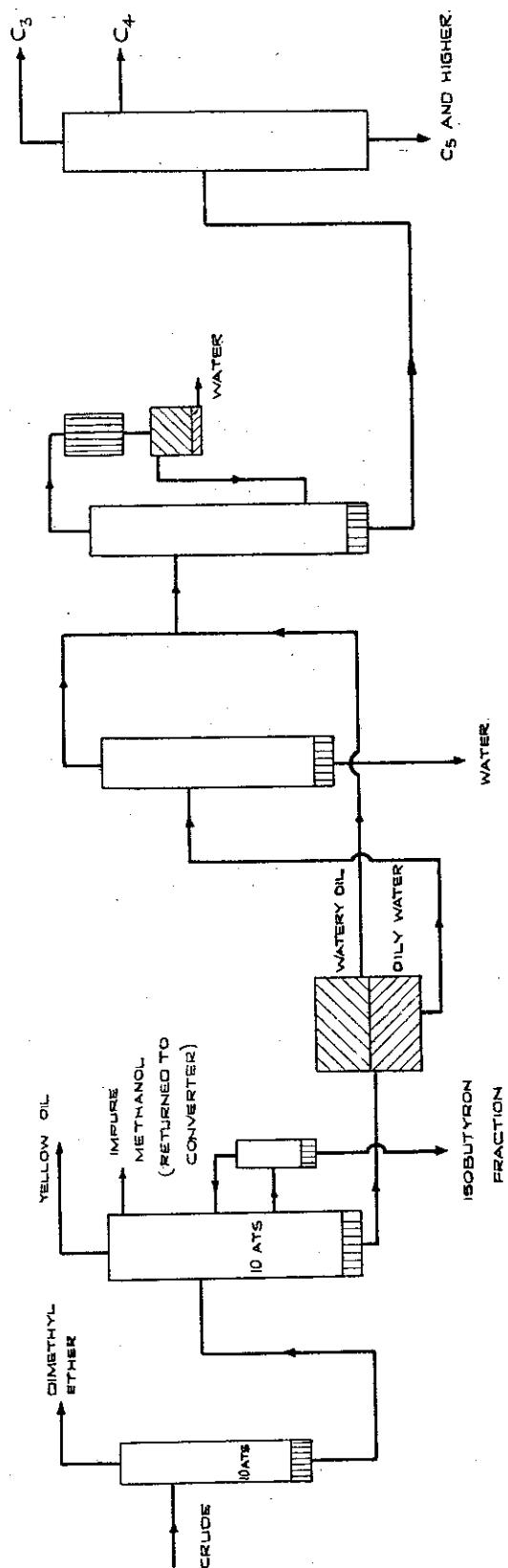
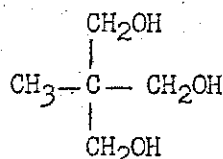


FIG. I. SEPARATION OF CRUDE HIGHER ALCOHOLS

bottom layer, rich in water, was distilled at 1 at. in a ring-packed column to remove water, the overheads being mixed with the top layer, poor in water. Gasoline was added, to form an azeotrope, and the mixture fed to a bubble-plate column operating at 1 at. The overheads from this still on cooling formed two layers; the aqueous one was discarded and the other one was returned to the still. The bottoms from the still were fed to a final bubble-plate column operating at 1 at., with iso-butanol taken off as the main product, propanol taken off overhead, leaving C<sub>5</sub> and greater in the bottoms.

Dimethylether was redistilled in a pressure column and the 98% pure material used for making dimethylsulphate and dimethylaniline.

The propanol fraction was further purified and the purest material was used for cosmetics and in solvents. Other material was converted to propionic acid, but the greater part (100 to 120 T/month) was reacted with formaldehyde to yield trimethylolethane.



which when reacted with higher acids (see below) gave a substitute for castor oil. A small amount was also used in the manufacture of glycerine, but this process was carried out to a greater extent at Heydebreck (Upper Silesia) and Oppau, the former using 300 to 350 T/month propanol.

Until July 1944 isobutanol was mostly converted to isobutylene and thence to iso-octane, but then the demand for Oppanol (polyisobutylene) became so great that the butanol was practically all shipped to Oppau and Frose for this purpose. About 80 to 100 T/month were used as acetates as solvents ("Polysolvan") for lacquers; some iso-butylene was used for making butyl phenol at Ludwigshafen, used for laquer resins. About 80 to 100 T/month were used for making Koresin at Ludwigshafen, a formaldehyde resin. About 100 T/year were converted to isobutylamine.

50 to 60 T/month of the fractions 110°-130° and 130°-160° were used as acetates as solvents (e.g. "Intrasolvane"). 400 T/month of the fraction 110°-160° were used to make Palatinol HS, esters of phthalic acid, used as plasticisers.

The fraction 160°-200° was oxidized to acids and combined with trimethylolethane (see above) to give a substitute for castor oil. The fraction 200°-250° was used in the manufacture of esters, lubricants and drying aids: the available notes on this are not entirely clear but it appears that the fraction was treated with NaOH and in some way made to yield acids (possibly a naphthenic acid, although this is an obscure reaction), which were then esterified with high alcohols and used as plasticisers or used as Co, Mn or Pb salts as drying aids for lacquers.

Higher fractions could not be used.

IV. HYDROGENATIONA. General

Leuna was the world's first commercial scale hydrogenation plant and also the first to operate on coal (brown coal). In its present form, the Leuna hydrogenation plant consists of 10 liquid phase coal or heavy oil stalls, 5 vapour phase presaturation units and 3 stalls for splitting hydrogenation of middle oils to gasoline. In 1943 and the first half of 1944, the average rates of consumption of the various feedstocks were:

Dry Brown coal	1,100,000 Tons/year
Brown coal Tar	120,000 "
Bituminous coal tar oil	40-50,000 "

Production of final liquid products was slightly more than 600,000 T/yr. and, according to Dr. Buterfisch, these products were made up of 40% aviation base gasoline, 20% motor gasoline, and 40% Diesel oil. In addition, some 150,000 Tons/year of by-product hydrocarbon gases were obtained and these were used for synthesis of isooctane or alkylate (butane), for liquefied gas fuels (propane or propane + butane) and for manufacture of synthetic lube oils (ethane).

In July 1944, Leuna suffered a surprise air attack and, because of the absence of facilities for safe emergency draining of the coal hydrogenation converters, the plant was coked up. The coal-paste preparation plant was also badly damaged. At the same time, damage to the nearby Brabag hydrogenation plants prevented them from hydrogenating all the available brown coal tar. It was therefore decided to change over Leuna from brown coal to brown coal tar and 5 or 6 coal stalls were modified for hydrogenation of liquid phase heavy oil. During the second half of 1944 it was possible to operate the normal liquid phase and vapour phase process for conversion of brown coal tar to gasoline but production was interrupted more and more by continued air raids and, following particularly heavy attacks in January 1945 in which the tar fugals were put out of action, operations had to be limited to a single stall working a modified T.T.H. process (see Ludwigshafen and Zeitz reports). Crude tar input was only 250-300 Tons/day.

The information given in the following sections was obtained from Dr. Schunck, Director and Manager of the hydrogenation section of Leuna, Dr. Becker, his principal assistant and stalls manager, Ing. Cron, hydrogenation section engineer, and Dr. Pichler, a costs expert attached to the hydrogenation section.

B. Brown Coal Hydrogenation(i) Outline of present process

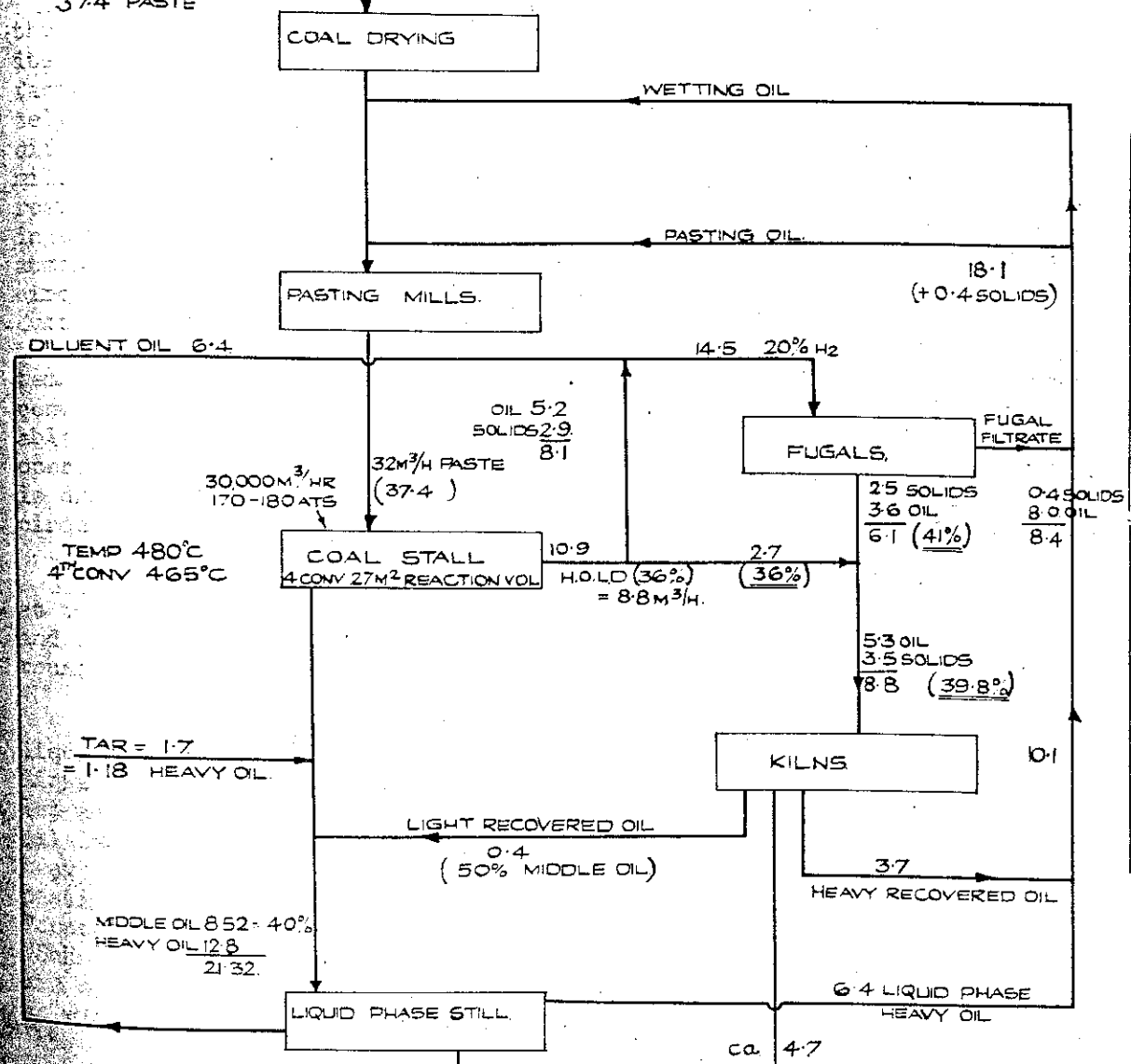
The brown coal hydrogenated at Leuna is obtained from local open workings owned and operated by the I. G. As delivered to the plant, it contains 54% water and 5.5% ash. The ash and moisture free coal substance

14.0% = 16.5 DRIED BROWN COAL  
 1.0% = 1.5 CATALYST  
 1.0% = 0.4 CIRCULATING SOLIDS  
 2.3% = 0.9 WATER  
 49.2% = 18.1 OIL  
 37.4 PASTE

RAW BROWN COAL (54% H<sub>2</sub>O)  
 36.5

CATALYST

MAKE-UP HYDROGEN: 11500 M<sup>3</sup>/H COAL  
 (96% H<sub>2</sub>)  
 380 M<sup>3</sup>/H HEAVY OIL FROM TAR  
 11880 M<sup>3</sup>/H



HEAVY OIL  
 8.0 FUGAL FILTRATE  
 6.4 LIQUID PHASE HEAVY OIL FROM PASTING OIL  
 3.7 HEAVY RECOVERED OIL  
 18.1 HEAVY OIL FOR PASTING OIL

0.2 FROM LIGHT RECOVERED OIL  
 7.8 FROM COAL STALL C.C.P. PLUS TAR HEAVY OIL  
 8.0 MIDDLE OIL FROM COAL LIQUEFACTION  
 0.52 MIDDLE OIL FROM TAR DIRECT  
 8.52 MIDDLE OIL TOTAL

= 70,000 TONS/YR MIDDLE OIL EACH COAL STALL  
 8,000 HRS/YR

MAY 9<sup>TH</sup> 1945

FIG. 11 HYDROGENATION OF BROWN COAL 1944  
 ALL QUANTITIES IN TONNES /HR EXCEPT WHERE STATED



has the analysis - 71% carbon, 5% hydrogen, 5-6% sulphur, 17-18% oxygen and 1% nitrogen. A high proportion of the ash constituents of the coal is sand with very erosive properties.

The hydrogenation process as applied to brown coal is summarised in the flowsheet shown in Fig. II. The wet coal together with about 4% of its weight of catalyst (Bayermasse obtained as a byproduct in the manufacture of aluminium) is dried down to 5% water. The product is immediately wetted with part of the recycle pasting oil in order to avoid dust difficulties and explosion risks and is fed to the grinding and pasting mills where it is mixed with the rest of the recycle pasting oil. The resulting "paste" containing some 44% dry coal (49% total solids) is injected into the hydrogenation stall which operates at a pressure of 230 atmospheres. It is heated together with circulating gas (900 - 1,000 M<sup>3</sup> circulating gas/M<sup>3</sup> paste) firstly by interchange with outgoing vapour products and finally in a gas-fired tube preheater. The reactants then enter the first of (usually) 4 converters at a temperature of about 430°C. This temperature is quickly raised by the heat of reaction to 490°C and is then controlled at this figure, by introduction of cold circulating gas at suitable points, until the reactants leave the third reactor. Under the latest operating conditions, this average reaction temperature in the last reactor is dropped to 475°C by introduction of more cold circulating gas. The total circulating gas used for temperature control is about 1000 M<sup>3</sup>/M<sup>3</sup> paste fed.

A small amount (100 litres/hour) of reactant is continuously drawn off at the bottom of the first reactor in order to prevent the build up of sand and the formation of "Caviar" i.e. small spheres consisting of coke formed round a central sand particle. This draw off is automatically controlled.

The products leaving the last converter pass to a hot catchpot where liquids and vapours are separated at a temperature of about 440°C. The liquid products are cooled by passage through finned air coolers and are let down to atmospheric pressure. Approximately two thirds of this heavy oil let down (Abschläm) is diluted with 75% of its weight of distillate heavy oil and the mixture is centrifuged. The "filtrate" is recycled as pasting oil and the "concentrate" is recycled as pasting oil and the "concentrate" mixed with the remaining "Abschläm" is carbonised in "Schneckenofen" for recovery of its vapourisable oil content. All the ash of the original coal, the unconverted coal and the new formed asphalt is purged as coke from the "Schneckenofen."

The vapours leaving the hot catchpot are cooled by interchange with the incoming coal paste and by passage through a water cooler. Condensed liquids are separated from recycle gas in a cold catchpot and the former are let down in three stages (45 ats., 4 ats. and 1 at.) in order to separate the dissolved gases into "lean" gas for use as fuel and "rich gas" from which butane, propane and ethane are separated. The cold catchpot liquid product is finally distilled together with recovered oils from the "Schneckenofen" (when brown coal tar is hydrogenated simultaneously, this is also introduced at this stage) to give a gasoline + middle oil fraction of 335°C end point as overhead and a heavy oil "bottoms". The light product is passed on for vapour phase hydrogenation and the bottoms are re-

cycled either directly to coal pasting or indirectly as "Abschlamm" diluent oil via the fugals. Gas from the cold catchpot is boosted back to the inlet of the plant via a gas washing plant in which hydrocarbons and nitrogen are dissolved in oil (heavy middle oil ex cold catchpot liquid product) in order to maintain the required hydrogen partial pressure (170-180 ats).

Under these latest operating conditions this paste throughput is slightly under 1.2 M<sup>3</sup>/M<sup>3</sup> of reaction space/hour corresponding to 0.46 Tons ash and moisture free coal/M<sup>3</sup> reaction volume/hour. Throughput and reaction temperature are adjusted so that there is no net make of heavy oil. The yield of 0-335°C light product is 49-50% by weight on the ash and moisture free coal fed. Unconverted coal purged in the Schneckenofen coke amounts to 1.5% on the original ash and moisture free coal. (This is not apparent from the flowsheet in Fig. II since no distinction is made between organic and inorganic solids and no indication is given of the change in weight of the latter due to chemical reduction during the hydrogenation reaction). Gas make in the hydrogenation of brown coal is 25.75% on the amf. coal. This is made up as follows:

Carbon monoxide	1.45%
Carbon dioxide	9.15%
Methane	4.15%
Ethane	3.60%
Propane	4.75%
Butane	2.65%
Total	25.75%

Oil lost in the carbonisation of Abschlamm and Abschlamm concentrate amounts to 8.5% by weight on the ash and moisture free coal.

The following figures show roughly the carbon balance for this process:

IN Carbon in brown coal	100
OUT Carbon in unconverted coal	2.0
Carbon in coke and gas made by decomposition of asphalts in sludge carbonisation.	11.5
Carbon in CO and CO <sub>2</sub>	4.4
Carbon in hydrocarbon gases	17.6
Carbon in sundry losses	1.0
Carbon in Petrol + Middle oil product	63.5
Total	100.0

Hydrogen consumption is 800 M<sup>3</sup>/Ton of ash and moisture free coal hydrogenated or 6.6-6.7% by wt.

(ii) Consideration of process improvements made since the war.

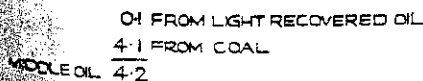


6 Tons  
re-  
vy oil.  
nd  
en coke  
is not  
between  
ge in  
tion  
n the

3

100

1000


$$= 34,000 \text{ TONS/YR. MIDDLE OIL EACH COAL STALL}$$

$$(8,000 \text{ HRS/YR.})$$

ALL QUANTITIES IN TONNES / HR EXCEPT WHERE STATED.

MAY 9TH 1945

The process described above, although much the same as regards yields as that operated before the war, shows a marked improvement in output per stall. Fig. III is a typical Leuna flowsheet for brown coal hydrogenation in a single stall in 1939-1940 and it shows that the coal throughput rate then obtainable was only 0.32 Tons amf. coal/ $M^3$  reaction volume/hour or 70% of that achieved in more recent times. The improvement which has been made is actually greater than this, because in addition to a throughput of 0.46 T. of amf. coal, 0.047 T/hr. of tar heavy oil is now hydrogenated in each  $M^3$  of reaction space.

With fixed pressure and catalyst conditions the only method for increasing the rate of hydrogenation of a given raw material to a given extent is to increase reaction temperature. The extent to which this can be done is, however, limited because of the following considerations:

- (a) For a given extent of hydrogenation, (i.e. in this case, complete conversion of coal to petrol and middle oil with only sufficient new formed heavy oil to replace sludge carbonisation losses) increase in temperature increases the yield of gas, asphalt and unconverted oil at the expense of petrol and middle oil. The increase in asphalt make is particularly serious because, in order to keep the viscosity of the recycle pasting oils down to a workable figure all new formed asphalt must be destroyed in sludge carbonisation and this results in an appreciable loss of carbon from the hydrogenation system. Further, the carbonisation plant itself gets into operating troubles when the asphalt content of the feed is too high.
- (b) Unless special precautions are taken to cool the products before they enter the hot catchpot, increase in reaction temperature leads to a reduction in the amount and, therefore, an increase in the solids content of the Abschlamm. One of the most serious practical difficulties encountered in the brown coal hydrogenation process has been due to coke formation on the hot catchpot walls and this is more difficult to avoid the higher the solids concentration in the liquid product.

The secret of the increase in throughput of the Leuna stalls is that, by attention to a number of process details, the I. G. have been able to get round some of the above limitations and so increase the mean reaction temperature by 20-25°C.

Firstly, automatic controls have been widely adopted. The mixing of Abschlamm and fugal concentrate in the proper proportions for feeding to carbonisation is automatic and this, coupled with the provision of a large buffer storage for carbonisation feed, has led to much steadier running of the Schneckenofen and has enabled a higher average asphalt content feed to be used than was the case when a margin had to be allowed for possible errors in hand mixing. The hot catchpot level is also automatically controlled; this eliminates the danger of the periodic drying out of the walls of this vessel which greatly encourages coke formation and, therefore, allows a higher solids content of Abschlamm to be tolerated.