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KCBraun
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Industrial Development of the DHD Process

A. - Large Apparatus and DHD Plant.
by Simons, 6 January 1942.

(1) Production of Light Gasoline as a substitute for Iso-Octane by Reduction of Isobutyl Alcohol Residues (CL 100).

Between February and August 1941 about 1800 t of light gasoline was produced in stall 803, (1.6 M^3 catalyst volume), and delivered to the RLM as produced. The Catalyst used was an alumina catalyst poor in molybdenum (7846 with 60 kg Mo/M^3 catalyst space). Since Sept. 1941, this product is made in Oppau, though, for the time being, still with concentrated catalyst (Ni-W with 230 kg Ni + 1500 kg W/M^3).

(2) Prehydrogenation of Brown Coal Middle Oil from Leuna and Bituminous Coal Middle Oil from Upper Silesian and Ruhr Coal with catalysts poor in Mo and W.

Successful trial experiments were made in stall 501 for Leuna and Pölitz prehydrogenation experiments with catalyst 7846 (60 kg Mo/M^3) and catalyst 7846 W 250 (198 kg W/M^3). The catalysts have since been used in Leuna and will be used in Pölitz.

(3) DHD Experiments in $1M^2$ Converter.

Since August 1941, brown coal, bituminous coal and petroleum gasolines have been dehydrogenated in this converter, preparatory to industrial application, and delivered to the RLM for motor tests (abt 900t).

(4) Large Scale Fuel Oil Experiments.

Between July 15th and Sept. 19, 1941, a successful experiment was made in stall 804 (1.6 M^3 catalyst volume) @ 700 atm with Upper Silesian coal to gasoline + middle oil + fuel oil. No difficulty was experienced in running a partial stream of coal paste through the heat exchangers.

B. - Present Position.
by Simon, Ludwigshafen, 14 July, 1942.
(Tables Missing)

Two of the proposed DHD plants are in operation, Pölitz, and Ludwigshafen - Oppau.

The plant at Ludwigshafen - Oppau was built for the processing of 35000 t/anm principally Rumanian gasoline.

This corresponds to a production of 27000 t/a high test fuel.

The building of the plant was started in March 1941 and it was ready for production on Nov. 17 of the same year. The distillation was temporarily done at the experimental plant Lu-35 until December, because the Oppau distillation unit was not ready for operation until that time.

The Oppau tank depot is only partially in use at present, because, since the fire in March, we prefer to use only those parts fully completed. The full use of the Oppau tank depot may be had in about six weeks.

Table I, DHD Stall Lu.

As shown in Table I, the DHD stall consists of 4 reaction converters and 1 refining converter. The reaction converters now have a total catalyst volume of 15 M^3. The main and intermediate preheaters are mainly gas fired. Converters 2 to 4 also have an additional electric preheater each for adjusting the peak temperatures.

The stall, now operating for 8 months, has offered no particular difficulties. Leaks occurred at the start on the heat exchanger covers because of excessive temperature variations when converting from operation to regeneration, but these have been minimized by suitable operating measures. To prevent corrosion by SO_2, which is formed in the regeneration period by oxydation of the sulfur absorbed by the catalyst during dehydrogenation, a soda solution must be injected before the cooler. The catalyst, for which a life of 9 months is calculated, has held up well during the 8 months it has been in operation. Only converter I has had to be refilled twice because of excessive pressure differences. These were caused by a cohesive layer of catalyst, iron oxide, and iron sulfide, about 30 mm thick. It is expected that the soda injection will prevent this trouble in the future.

Table 2, Production of DHD Unit Lu/Op.

Production to date is shown below:

1941,	November	974 t
	December	1654 t
1942,	January	1631 t
	February	1639 t
	March	2288 t
	April	2226 t
	May	2103 t
	June	2249 t

Capacity production was reached in March. It would have been reached in January if it hadn't been for the supply difficulties of raw gasoline from Rumania, due to transportation

difficulties caused by cold weather, and for other reasons.

It has been very difficult to get the desired supply of raw material. Our efforts to obtain purely octanic gasoline from Rumania have been only partially successful. We received only an octanic heavy gasoline in the boiling range 130-170°C. The air force commandeered the light gasoline going with it and we had to be satisfied with an almost purely paraffinic light gasoline, which was often supplied in comparatively undesirably large quantities. Beginning with February we received no octanic gasoline at all and we had to agree to take a raw gasoline rich in paraffin, such as intended for Moosbierbaum. In spite of these restrictions production was maintained both in quantity and quality.

Table 3, Raw Materials Lu/Op.

Table 3 compares the properties of the raw materials. Besides the mixture of heavy and light gasoline and the raw gasoline of Moosbierbaum quality a Hungarian gasoline is shown, of which we are processing experimentally a batch of 850t.

It may be seen from a comparison of the aniline points, paraffin content and knock value that the gasoline mixture and the better quality Moosbierbaum gasoline are almost alike. The Hungarian gasoline, by comparison, is distinctly poorer in paraffin. Unfortunately, it was cut off too low. The following yields were obtained:

77-78.5% from the gasoline mixture
76-78% from the Moosbierbaum gasoline
79-79.5% from the Hungarian gasoline

In the consideration of these figures it must be taken into account that the gasoline is run through the converters without first separating the light constituents at the present time, because of lack of storage tank space.

Table 4, DHD Finished Gasoline Lu/Op.

Table 4 shows the properties of the gasolines obtained from these 3 raw materials.

Table 5, Overload Curves Lu/Op.

Table 5 shows the overload curves compared to CV_2b-RLM.

All 3 gasolines are between 1 and 3 atm above the CV_2b curve. The somewhat poorer behavior of the gasoline from the mixture of heavy and light gasolines is due to the poorer residual gasoline, 2/3 of which originates from the light gasoline component. The octane number of the residual gasoline from the mixed gasoline is 65-66, that from the Moosbierbaum quality is abt. 68.

The following may further be said of the operating conditions:

The thruput was about 0.47 kg raw gasoline/liter catalyst/hour, with 1M³ gas injection per kg. The pressure at the outlet was held to 30 atm. The temperatures during the operating period at the inlet and outlet, respectively, were:

Converter	I,	488 - 468°C
"	II,	502 - 482°C
"	III,	510 - 490°C
"	IV,	515 - 510°C
"	V,	305°C

A mean heat of reaction of -70 Kcal/kg injection is calculated for gasoline of Mocsbierbaum quality.

The mean proportion of operating time to regeneration time was 75:25, where the length of periods varied between 40 and 60 hours. The regeneration time, figured from shutting off injection to turning it on again, was 22 hours at the start, but could be cut to 15 hours, at present, in the course of time.

DHD - PÖLITZ.

The first construction stage contemplated the construction of 2 DHD stalls to produce about 140,000-160,000 t/Anm high test fuel. In order to obtain experience quickly in large scale production a 300 atm stall intended for 6434 operations was first rebuilt for DHD and put into operation in March 1941.

The first new stall, #21, was put into operation on January 23, 1942 and the second, #22, on May 16, 1942.

The rebuilt stall was shut down on May 6, 1942. It had been in operation for a total of 8662 hours without trouble worth mentioning, though it ran with many interruptions due to lack of feed. In October 1941, 2980 t gasoline, equal to capacity production, was produced in 468 operating hours and 112 regenerating hours, with 164 hours of idling. On dismantling it was found that the hairpin coils were heavily scaled on the outside. The hairpins and pipe lines were clean and free of corrosion on the inside. The brick lining of the converters proved satisfactory in operation. On dismantling in horizontal position the inner bricks became loose, because the morter had lost its binding power. The removed catalyst was still in good condition after 14 months operation. It showed only a thin film of iron oxide. In each converter the catalyst on top was covered in a few places with a 3mm layer of dust, consisting principally of iron oxide which, however, did not influence the flow of material in any way.

The new stalls now in operation each have 3 DHD converters with about 25 M³ catalyst volume, plus one refining converter each. Both stalls are to be enlarged to 441 converters. Table 6 shows a diagram of the enlarged stall.

The operation of the 2 new stalls has caused no difficulties so far.

Table 7, Production in Pölitz.

Table 7 shows the development of DHD gasoline production in Pölitz in the first half of 1942:

1942,	January,	2257t,	new stall #21 in operation Jan. 23.
	February,	5317t,	
	March,	6507t,	
	April,	10122t,	
	May,	11573t,	shut down rebuilt stall May 6, new stall #22 in operation May 16.
	June,	13154t,	= about capacity production.

The feed for the DHD stall in Pölitz comes about 40% from petroleum and 60% from coal and tar. A Mixture of 5058 and 6434 gasoline was mainly processed. Later 5058 alone was processed, because the yield was greater.

In the processing of 5058/6434 gasoline from coal and petroleum in the proportion obtained, the supply of low boiling constituents was so great that the light constituents could not be disposed of in the gasoline in the entire plant. The reason for this is that the 6434 gasoline from the mixture of bituminous coal plus petroleum contains a large proportion of light constituents. Furthermore, the problem of the optimum cutting off of these raw materials for the DHD process is still being worked out.

The yields in Pölitz are between 73.5 and 81%, although they have not been definitely determined, because the composition of the feed, the method of cutting off, etc., still vary.

Table 8 shows the properties of the crude and finished gasolines.

Table 9 shows the overload curves of some Pölitz high test gasolines.

The operating conditions applied in Pölitz are the following:

Thruput = 0.4 - 0.6, at present 0.5 so as to obtain highest possible production.
Gas: Product Proportion = 1:1
Pressure (Outlet) = 30-40 atm.
Temperature = 490-515°C.

The operating periods in Pölitz were very long, to 130 hours, with 24 hours regenerating time.

The following DHD plants in the planning stage are:

Works	Start	Capacity
Scholven	March 1943	200,000 t/ann
Pölitz II	April "	160,000
Leuna	Aug. "	345,000
Wesseling	" "	180,000
Bohlen	" "	190,000
Brux	Nov. "	300,000
Zeitz	Dec. "	200,000
Blechhammer	" "	200,000, Total 1,775,000 t/ann

C. Further Development of the DHD Process.
By Löcker, Ludwigshafen, 28 October, 1942.

The subject discussed herein is the applicability to large scale production of the DHD process in the dehydrogenation of naphthenic raw materials. On the basis of results obtained in experiments to date it now appears promising to conduct the process of preponderant naphthene dehydrogenation of paraffinic-naphthenic feeds in a first stage in long periods at elevated pressure, but the dehydrogenating splitting of paraffins of the higher boiling catch pot fractions in auxiliary apparatus under iso-thermal temperature conditions and low pressure.

Since dehydrogenation produces little heat of reaction in the second stage, the development of a converter with product gas recirculation appears promising.

The laws of the DHD process indicate that:

(1) When working with low pressures greater H_2 splitting and coke formation, but lower C-gasification, i.e. increased production, in spite of shorter periods, is observed, than at higher pressures.

(2) The percentage distribution of hydro-carbons shows no essential differences.

(3) The splitting of gasoline at higher pressures is increased by running more circulating gas (H_2).

Thus, the demands for higher yield and lower gasification are opposed by the operating requirements of lower coke separation and longer operating periods. Furthermore, operating results are very much dependent upon the quality of the feed materials.

In the current running of Rheinbraun gasoline at a maximum converter inlet temperature of 26.7 MV (506°C) an operating period of over 600 hours has already been obtained for the original gasoline without apparent deterioration of the catalyst. In running the Rheinbraun gasoline, topped up to 90°C, at a maximum converter inlet temperature of 27.7 MV (522°C) no drop in catalyst activity was observed after more than 400 operating hours. In this case about 80%/wt. of H_2 was found in the recirculating gas, compared to a maximum of 50% for

other gasolines, at partly higher temperatures.

These last figures prove that high naphthenic gasolines can be run almost continuously, whereby easily split paraffins are also dehydrogenated in a manner similar to the naphthenes, without affecting the catalyst. Only after the easily dehydrogenated materials are used up are the more difficult to split paraffins and naphthenes attacked, as is well know, and produce increased gasification and coke formation. Quite often a positive heat of reaction in the last dehydrogenation converter was also observed, particularly when running considerable quantities of circulating gas.

According to experiments by Dr. Donath a higher converter inlet temperature must be used at low than at high pressure in order to obtain an equal percentage of aromatics in the catchpot product. The temperature drop is greater in this case. For this reason, Leuna-Moosbierbaum strove to operate at low pressure but without increased inlet temperature, i.e. iso-thermal. Nevertheless, the large scale process appears economically superior in all cases in which naphthenic raw material promises long operating periods, as well as in those cases in which the greater percentage of the feed is easily dehydrogenated, so that "Scharfe Bedingungen" (high temperature, low thruput) are necessary only in the last converter. Since H_2 is produced in the dehydrogenation of naphthenes, which retards the separation of coke from the simultaniously dehydrogenated paraffins, favoring hydrocarbon gasification, moderate quantities of paraffins dehydrogenated with them have almost no influence on the length of period. From this point of view an admixture of naphthenic materials to inferior feed may even be of decided advantage.

Furthermore, weak dehydrogenation, perhaps up to 30-40% aromatics in the catchpot product, will always be possible in long periods with naphthenic-paraffinic raw materials. It is to be expected, in such cases, that pressure and thruput can be increased, compared to normal, and the quantity of circulating gas decreased. The first product obtained can then be further dehydrogenated easier and with smaller losses, as shown by an experiment with Russian gasoline in stall 504. At that time a finished gasoline with a yield of 74% was produced from a feed containing 53.5% paraffins and 42% naphthenes in the common single stage process. In the two-stage process, however, a total yield of 79.1% was obtained. (The first stage was run to 30% aromatics with 4.3% gasification, the circulating gas contained 87% H_2, dehydrogenation period of 165 hours, limited by lack of feed).

We know from analysis that the higher boiling paraffins are undesirable in the finished gasoline because they decrease the anti-knock value. It should, therefore, be possible to improve the quality, including the formation of lower boiling constituents, by merely dehydrogenating these higher boiling constituents, i.e. the residual gasoline. In the latter case, gasification will be reduced to a fraction of that of even the 2-stage process, since only about half of the product must be

further dehydrogenated. Naturally, the small experiment must decide whether the finished gasoline obtained in this manner is equal in quality to that obtained normally.

The subdivision of the DHD process with paraffinic-naphthenic feed into a pure DHD part and a DHD-cracking process for the catchpot product or a catchpot product fraction of the first operating stage (Arbeitsgang), therefore, promises theoretical success, but there are difficulties in the way of practical application.

These are, primarily, the different lengths of operating periods of the first and second operating stages, which will vary according to the raw material or the operating method (whether running to relatively high or low aromatic content or a fixed circulating gas composition). The second operating stage, which is essentially based on paraffinic feed, will probably have to be run in short cycles, because the coke separation and the deterioration of the catalyst activity demand short periods, wherein the working conditions can be adjusted very accurately to this special material. The material is properly processed at low pressure and equal temperatures, i.e. without much higher inlet temperature (about similiar to the Leuna process). The quantity of circulating gas can probably be reduced in this case, since we are dehydrogenating to coke and not to hydro-carbon gasification.

Judging from experiences to date, aromatics will hardly be attacked at normal temperatures in the DHD-cracking process, no more than low hydro-carbons. In the polyform cracking process, C_3 and C_4 hydrocarbons are even introduced into the process for the new formation of product. Consequently, there again arises the old intriguing problem of controlling this DHD cracking process by recirculating a part of the product of the converter itself. This will be possible here, since the heat of reaction of this particular final process will be only weakly negative, i.e. the heating problem is greatly relieved.

If an improvement in the DHD process may be expected from small experiments on the basis of the foregoing, a technical and economic solution will also be found. When only one gas circulating system is used, this should be conceived about as follows:

(1) Naphthene dehydrogenation and regeneration at about 30 to 50 atm in the first converters.

(2) Catchpot with a short distillation column on it for coarse separation into a light fraction plus gas and a heavy fraction.

(3) Dehydrogenation of the heavy fraction "in parallel" (in Nebenschluss) in several converters, which can be disconnected and regenerated, at low pressures. The necessary circulating gas is supplied as make-up gas. The quantity of circulating gas will be less at lower than at normal pressure, particularly low if the product

could be recirculated in the converter.

(4) The mixture of the products from the first and second stages (Arbeitsgänge) is refined together in the refining converter.

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