

The hydroforming process was invented in Germany by the I.G. Farbenindustrie A.G. before the war and the basic patents were held by the Germans. The process was developed in America for the production of aromatics from straight run gasoline. No commercial units had been built in Germany prior to the war, and the Leuna pilot unit was the forerunner of the only large-scale hydroforming plant now operating in Germany, namely that designed and built by the I.G. at Moosbierbann. The capacity of the plant is 7,000-7,500 tons of finished product per month; this was to be expanded to 14,000 tons per month, but the project did not materialize. The unit at Leuna is similar in some respects to the units in the United States, but in others, quite different. A simplified flow diagram of the Leuna unit is attached as Fig. XIV.

Charging stocks were primarily straight run gasolines and the catalyst used was a molybdenum on alumina catalyst containing 5-10% MoO₃.

The Leuna unit consists of two reactor systems of three reactors each. One system is on stream while the other is on regeneration.

It was thought necessary by the Germans to vary the activities of the catalyst in the different reactors by varying the MoO₃ content and the particle size in order to obtain a uniform coke laydown. The catalyst in the first reactor is divided into three zones, i.e. the top zone containing a catalyst with 5% MoO₃ and with a particle size of 10-15 mm.; a middle zone, also with a particle size of 10-15 mm., containing 10% MoO₃, and a bottom zone containing 10% MoO₃ but with a particle size of 6-10 mm. The second reactor has two zones of catalyst, both with a MoO₃ content of 10%, but with a 10-15 mm. size in the upper zone, and a 6-10 mm. size in the bottom zone. The third reactor contains one bed of 6-10 mm. catalyst with 10% MoO₃.

The charge first exchanges heat with the effluent from the third reactor and is then mixed with 600-1000 cu.m. of recycle gas per cu.m. of charge containing 50-60% hydrogen preheated to 520°C. under 15 atm. pressure. The material leaves the bottom of the first reactor at 480°C., is reheated to 530°C., passes down through the second reactor and leaves at 495°C. It is then reheated to 530°C., passes through the third reactor containing the more active catalyst.

The effluent from the third reactor at 510°C. exchanges heat with the charge and passes to a receiver where the recycle gas is separated and the gas made is removed. The liquid is then charged to a stabilizer where ethane, propane and butane are removed as an overhead product and the debutanized hydroforming gasoline is made as bottoms.

The throughput is 600 gr. of liquid charge per litre of catalyst volume. The three reactors are on-stream 6-12 hrs. and on regeneration for 6-12 hours when straight run gasolines are the feed stocks. It was reported that, if hydrogasolines are charged to a hydroforming unit, an on-stream time of 100 hrs. would be obtained with 25 hours required for regeneration. With such an operation it would, of course, be necessary to arrange the unit in a different manner from the other two systems of three reactors employed at Leuna.

The catalyst is regenerated in situ by recirculation of inert gas and the introduction of controlled amounts of air. At the beginning of the regeneration cycle, the gas contains 1-1½% air, and at the end 10-15% air. The regeneration air is controlled so as not to exceed 550°C. during any part of the cycle. It was believed by the Germans that this is highly important in order to obtain a long catalyst life, although the catalyst life obtained was only in the order of 6 months.

The catalyst was prepared by impregnation of activated alumina with ammonium molybdate solution. It was reported that the catalyst was relatively inactive during the first on-stream cycle until the last traces of ammonia were removed by the first regeneration.

The feed stock was prepared by first distilling overhead 10-15% of a material boiling below 90°C.; the remainder was then hydroformed, the hydroformate was blended with the overhead cut from the primary distillation. A yield of 75% hydroformate based on the total straight run gasoline charge was obtained with a yield of 72-73% based on a case charge. The length of the cycle was controlled to maintain a minimum of 50% concentration of aromatics in the final product. Typical inspection of the charge and product obtained from a mixed base charge is as follows:-

	<u>Charging Stock.</u>	<u>Product.</u>
Sp.gr. @ 20°C.	0.750	0.776
IHP. °C.	62	44
% over at 100°C.	18	36
% over at 160°C.	95	94
RVP atms.	-	0.4
Bromine Number	0.51	2.3
Olefins	0.5	1.5

	<u>Charging Stock.</u>	<u>Product.</u>
Aromatics	14	54
Naphthenes	44	8
Paraffins	41.5	35.5
% C.	85.46	87.74
% H.	14.53	12.26
Octane No. 100L	58.5	80
Octane No. 100L plus 0.12% TEL.	79.0	91

Information was obtained on the results from the hydroforming of paraffin base, mixed base and brown coal hydrogasoline in the pilot unit. These are as follows:-

	<u>Charging Stock.</u>	<u>Paraffin Base.</u>	<u>Mixed Base.</u>	<u>Brown coal Hydrogasoline.</u>
^o API gravity of charge	51-52	48-50	44	
Products % by weight:				
H ₂	1.35	1.45	1.5	
C ₁	3.5	5.1	2.8	
C ₂	5.0	5.25	4.0	
C ₃	5.0	5.4	4.1	
i-C ₄	1.7	4.75	1.1	
n-C ₄	3.2		2.1	
Coke	1.2	0.7	0.2	
Gasoline, IBP 165°C.	74.5	78.3	80.9	
Residue	3.6	3.4	3.4	

It was proposed to subject the heavy hydroformate boiling above 165°C. to a hydrocracking operation described in section VII - Arcbin Process.

It should be noted that the Leuna people were not too well satisfied with their present hydroformer design and have made experiments on hydroforming in a tubular reactor. The experimental unit employed consisted of five tubes with a 60 mm. diameter, each tube containing some 25 litres of catalyst. The tubes were heated by flue gas from an auxiliary burner, and a temperature of 510°C. was maintained throughout the length of the tube. In actual operation, of course, the temperature was varied with the charging stock used to give a desired aromatic concentration in the product. The space velocity used in the tubular reactor was 0.8 kg. of feed per litre of catalyst, as compared to 0.6 kg. of feed per litre of catalyst used in the present unit. The same recycle gas to feed ratio was maintained. It is claimed that the use of the tubular reactor resulted in a 5 percent increase in yield for the same aromatic concentration in the product. Furthermore, it was possible to increase the on stream time using straight run to

20-50 hours, the ratio of on stream to regeneration times being 4-5 to 1. It should be emphasized that the above results are those of a relatively small pilot plant, but it is significant that the I.G. had decided on a plant of this type for the projected Moosbierbaum extensions.