VI. HYDROFORMING PROCESS.

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 Moosbierbaum. 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 State, 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 molybdena on alumina catalyst containing 5-10% MoO_3.

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 MoO_3 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% MoO_3 and with a particle size of 10-15 mm.; a middle zone, also with a particle size of 10-15 mm., containing 10% MoO_3, and a bottom zone containing 10% MoO_3 but with a particle size of 6-10mm. The second reactor has two zones of catalyst, both with a MoO_3 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% MoO_3.

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 atms. 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 regenorated 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 1-1/2 % 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 76% 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:-

	Charging Stock.	Product.
Sp.gr. @ 20° C.	0.750	0.776
IBP. °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
Aromatics	14	54
Naphthenes	44	8
Paraffins	41.5	36.5
% C.	85.46	87.74
% H.	14.53	12.26
Octane No. MM.	58.5	80
Octane No. MM. 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:-

Charging Stock.	Paraffin Base.	Mixed Base.	Browncoal Hydrogasoline.
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	6.0	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 - Arobin 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 aromatics 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.

VII. AROBIN PROCESS

The Arobin process is a method of manufacture of aromatics from the high boiling residues of the DHD (dehydrogenation of naphthenes) and the HF (hydro-forming) processes. The available charge stock consisted of about 5% residues from the distillation. The process was developed to the pilot plant stage only, with a catalyst volume of 25 cubic ft., and a charge rate of 120 gallons hour.

The following details of the process as applied to HF plant residues were secured from Dr. Herold of Leuna, who is in charge of development work on further utilization of products from existing processes.

Charge to Arobin Plant

Bottoms from HF process charging mixed Rumanian and Hungarian straight run gasoline:

API Gravity	21.2
Engler Distillation	
IBP	316°F.
50%	383
E.P.	676
Bromine No.	14.4
Aromatics & Olefins	98.5%
Pour Point	-66°F.
Elementary Analysis:	
Carbon	90.59%
Hydrogen	9.42
Sulphur	0.08

Operating Conditions

Catalyst Temperature (According to Catalyst activity)	752-852°F.
Space velocity (liquid)	0.65 vol. oil/vol. catalyst/hr.
Gasoline concentration at stripper	50% (by volume)
Pressure	2,940 psi
Circulating gas	1000-5000 volumes/ volume gasoline/hour, to control the heat of reaction (about 0.360 BTU/lb charge)
Chemical consumption of hydrogen	5.45-6.20 cubic ft./lb of finished gasoline.

Catalyst - "KK" catalyst + 1% MoO_3 (see below for method of preparation)

The MoO_3 acts as a hydrogenation catalyst and thus prevents the formation of polymers which would cause coking.

Yield and Quality of the Product

Average Net Yield	Weight %
Methane	0.2
Ethane	1.7
Propane	4.8
Isobutane	3.8
N-Butane	2.4
Gasoline	85.7
	98.6

Quality of the finished product (Arobin)	
API Gravity	43.2
Octane No. (Motor Method)	86
+ 4.55 cc/gal TEL	93.5
Bromine No.	0.84
Reid Vapour Pressure	5.9
Corrosion	Neg.
Freezing Point	Below -76°F.
Gum (Glass dish)	4.0 mg/100 cc
Aniline Point	Below -4°F.
Aromatics & Olefins	65.0 Vol.%
Naphthenes	27.0
Paraffins	8.0
Elementary Analysis	
Carbon	88.50%
Hydrogen	11.45

Engler Distillation	
IBP	117°F.
7.0% at	176
20.0	212
41.0	248
72.0	284
95.0	320
99.0	333
Residue	0.8%

Preparation of the Arobin Catalyst

1. Preparation of alumina. Commercial alumina is dissolved in hot 25% caustic solution, to give about 1.66 lbs. Al_2O_3/gallon. This solution is added to 45% nitric acid to give a pH of 6. Precipitation temperature not over 122°F. After precipitation, the solution is filtered or decanted, the precipitate is washed with pure water until the effluent shows no nitrate, and dried at 248°F, until the ash content is about 70%.

2. Preparation of silica gel. Waterglass solution (Sp. g. 1,333, SiO_2 27%) and 10% sulphuric acid are reacted at 50-59°F to give a 3-4 pH. On heating to 158-176°F, the clear sol congeals. This gel is broken into 1-1/4"-2" pieces and washed until the wash water shows no trace of sulphate. The gel is dried at 248°F to an ash content of about 70% It is pulverized in a mill (Vibratom) until at least 90% of the powder will pass a 10,000 mesh (per unit) sieve.

3. Preparation of the "KK" Catalyst from the gel. The alumina is kneaded in a kneading machine with enough water to make a plastic mass. A [illegible] nitric acid solution is added, the quantity being 10% of that theoretically needed to form aluminium nitrate. Then the powdered silica gel is added with continuous kneading to give a ratio Al_2O_3: SiO_2 = 1:9. The mass if further kneaded for 6 to 10 hours. The mass is then extruded for feed to an adjoining candy manufacturing machine (Franconia), where it is formed into spheres.

4. Preparation of the Arobin Catalyst. The above spheres are soaked with ammonium molybdate solution made up in such proportions that one weight per cent MoO_3 is absorbed. The spheres absorb practically all the liquid. They are then draimed and dried at 356°F.

A 5-pound sample of this Arobin catalyst was secured for further testing.

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FIGURE XV

CATALYTIC CRACKING RESEARCH UNIT DEUBEN

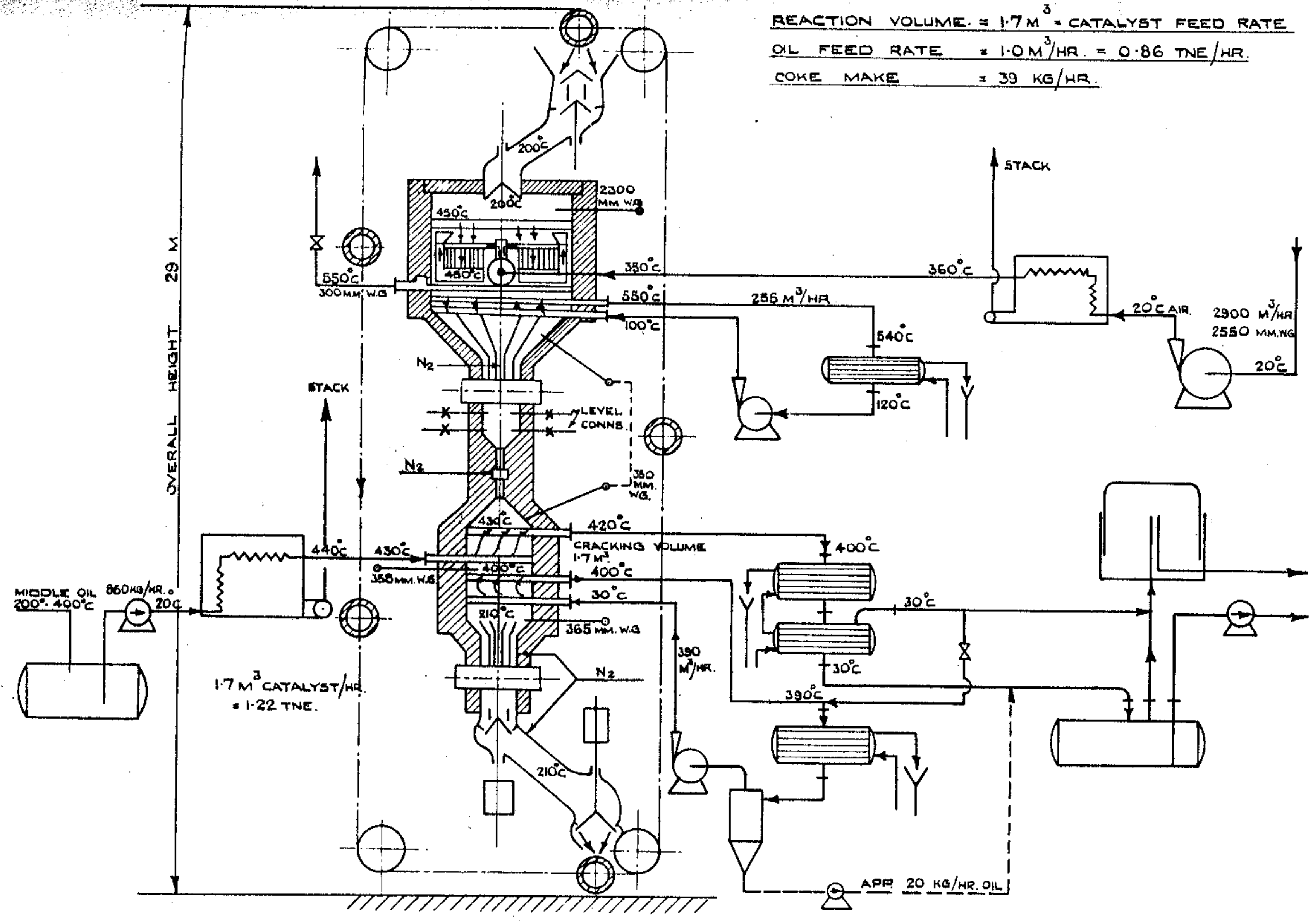
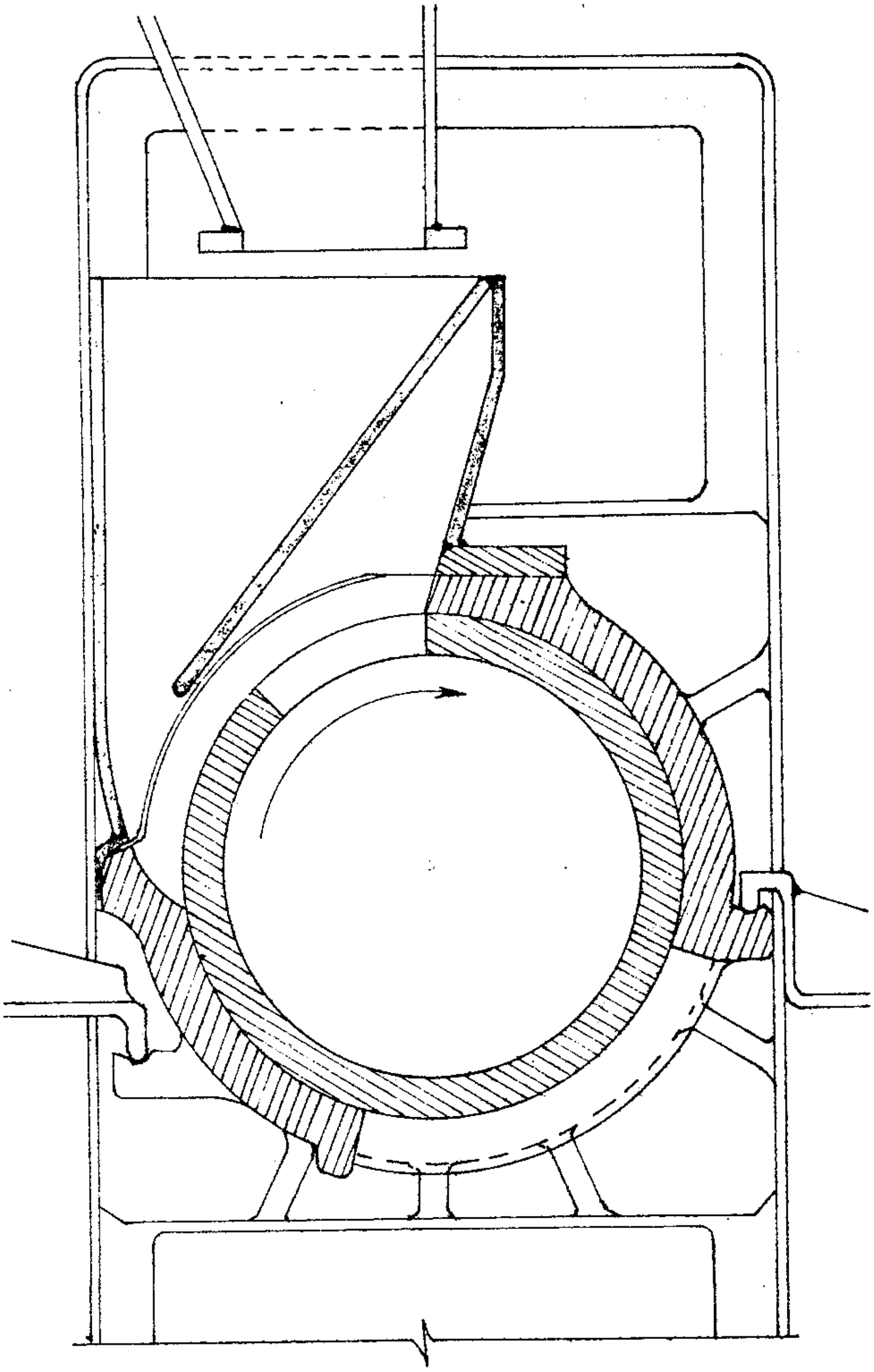

REACTION VOLUME = 1·7 M^3 = CATALYST FEED RATE
OIL FEED RATE = 1·0 M^3/HR. = 0·86 TNE/HR.
COKE MAKE = 39 KG/HR.

FIG. XVI



CATALYST VALVE - CATALYTIC CRACKING UNIT