V. D.H.D.(DEHYDRIERUNG-HOCH-DRUCK) PROCESS.

(i) Description of Process and Leuna operating results.

The DHD process was developed in Germany by the I.G. Farbenindustrie A.G. for the catalytic dehydrogenation of naphthenes to aromatics and was intended primarily for the use on hydrogasolines. The catalyst employed is 10% molybdic oxide on alumina and the reaction is carried out with recycle hydrogen under a pressure of 30-40 ats at a temperature slightly above 500°C.

Two DHD units had been completed at Leuna and one of them had operated for 3 months. Two further units were in course of erection.

The method of operating the process is shewn in the simplified flow diagrams in Figs XII. and XIII.

Full boiling range (IBP-185°C) hydrogasoline is first fractionated to remove, as an overhead cut, the lower boiling material boiling up to 85°C. The bottoms from this pre-fractionator are mixed with recycle gas containing 55-65% hydrogen. 1 cu.m. of recycle gas is used per kg. of liquid feed.

The mixture of gasoline and recycle gas is first preheated by heat exchange with the product from the end reactor; then by heat exchange with the material from the fourth reactor, and finally by convection heating to a four-chamber convection heater. The pressure at the inlet of the first exchanger is 42 ats, and at the inlet of the first reactor it is 37 ats.

The feed enters the first reactor at 500°C and passes downward through the catalyst bed and leaves at 450°C. The mixture is then reheated in one section of the heater to 510°C. and enters the second reactor under 34 ats pressure. The material leaves the bottom of the second reactor at 490°C, is reheated in a third section of the heater and enters the third reactor at a temperature of 520°C and under a pressure of 31 ats. The outlet from this reactor at 510°C is again reheated in the fourth section of the heater and enters the fourth reactor at 530°C under a pressure of 30 ats. Each section of the preheater has its own burner and independent fuel gas, air and recycle gas supply. At the outlet of the fourth reactor, the dehydrogenation reaction is completed. The effluent from this reactor at 530°C. is cooled to 300°C by heat exchange with the fresh feed and passes to the fifth reactor for hydrogenation of the olefins. The effluent from this fifth reactor exchanges heat with the fresh feed and passes through a cooler to a receiver for the separation of the gas from the liquid. The gas is principally methane and hydrogen with some ethane and very little C_3-C_4. At the beginning of the cycle, the gas contains about 65% hydrogen, and at the end of the cycle about 55% hydrogen. The density of the recycle gas at 15°C and 735 mm. is 0.38-0.45 kg per cubic metre. A part of this gas is recycled with the fresh feed, as explained above, and the remainder removed from the system as tail gas.

The liquid product from the receiver is let down, fractionated to remove the heavy materials and then sent to a stabiliser along with the IBP-85°C cut from the initial charge. In the stabiliser, the ethane to butane product is taken overhead and the DHD gasoline is made as bottoms.

The total hydrocarbon gas made is purged from the circulating gas and evolved on let down of the liquid product and on its subsequent stabilization amounts to 19-20% by weight of the original hydropetrol, i.e. about 25% by weight of the naphtha fed to the process. The gas is comprised of roughly equal proportions by weight of methane, ethane, propane and butane.

The catalyst used in all five reactors is active alumina on which has been deposited 8-10% MoO_3. It is prepared by the impregnation of activated alumina with ammonium molybdate solution. The catalyst is used in the form of 8-12 mm. cubes and is placed in the reactors in a single bed. It was originally planned to operate the DHD unit with a liquid space veocity of 0.38 kgs of liquid per litre of catalyst. In actual operation, space velocities of 0.25-0.32 were the highest obtainable. The length of the on-stream cycle on the catalyst depends upon the charge stock and varies from 120-240 hours. The regeneration period with the necessary purging operation requires about 24 hours.

At the end of the on-stream cycle, the reactors are first depressured and filled with nitrogen to 10 atmospheres pressure, depressured again and filled with nitrogen to 70 ats pressure. The recycle compressor is then started and air is admitted to the recycle gas stream until the oxygen content at the inlet of each reactor reaches 1%. 20,000 cu.m. of gas are recycled per hour through each reactor. The normal time of regeneration is about 12 hours. Oxygen concentration in the recycle gas is controlled to hold the regeneration temperature to slightly less than 540°C. During regeneration, 1 cu.m. of water is added per hour, either at the second heat exchanger or at the cooler, for removal of acidic compounds produced during regeneration. In some cases, it has been necessary to use dilute caustic at this point. It is necessary to remove SO_2 sulphur dioxide completely from the recycle gas, but the carbon dioxide concentration can go up to 8-13% without harmful effects. At the

TABLE V.

LEUNA D.H.D. PLANT

PROPERTIES OF FEED AND PRODUCTS.

	0-85°C Light Petrol	85°-180°C Naphtha feed to D.H.D. Process.	Stabilised D.H.D. Product.	Final DHD Petrol Blend
Aniline Point	52	45	1.6	6.9
Aniline Point after treatment with sulphuric acid.	55.4	-	63.2	61.0
Wt.% aromatics	4.5	9.5	66.0	52.0
Wt.% Naphthenes	46.2	51.2	7.9	14.4
Wt.% Paraffins	48.7	38.1	25.9	33.0
Wt.% Olefines	0.6	1.2	0.6	0.6
Motor Method Octane No.	73.5	52.0	82.5	80.5
Motor Method Octane No. with 0.12% by vol. TEL.	-	-	-	91.5

TABLE VI

CALCULATED COSTS FOR D.H.D. PETROL

(Based on Works Costs for 1st Qr., 1944)

	Unit	Cost RM/Unit	Per Hour Quantity	Per Hour RM	Per Tne DHD Petr Quantity	Per Tne DHD Petr RM
A. Materials						
1) Petrol	Tonne	170.14 (1)	13.35	2,271.37	1.379	234.6
2) Catalysts & Chemicals.				29.04		3.0
3) By-Products						
Circ.Gas Purge	10^6 Tne Cal.	7.00	14.2	99.40	1.467	10.27
Rich Gas	"	11.35 (2)	20.5	232.68	2.118	24.0
Redistilln. Residue	Tonne	100.00	0.47	47.00	0.049	4.8
B. Running Costs (3) (See Table VI)				594.26		61.3
Production Cost			9.68	2,515.59	1,000	259.8
C. Loading & Evaporation	Tonne	3.00	9.68	29.04	1,000	3.0
D. Oncosts				262.62		27.1
Works Cost (without conversion and oil taxes and other special costs)			9.68	2,807.25	1,000	250.0

(1) This cost has been taken from Table I.

(2) Butane and Propane in Rich Gas valued at Motor Spirit valuation less cost of separation.

(3) It is estimated that for 4 DHD Stalls, the running costs would be 42 RM/Tne DHD Petrol and the Works cost, 270 RM/Tne DHD Petrol.

TABLE VII

BUILD-UP OF RUNNING COSTS FOR DHD PETROL.

		Cost per hour		Per Tne DHD Petrol.	
		Quantity	RM	Quantity	RM
Labour Costs			35.94		3.71
Wages	hrs.	21.76	26.56	2.25	2.74
Salaries			7.07		0.73
Social Insurance			2.31		0.24
Energy Costs			163.65		16.91
Water	M^3	805.38	13.35	83.20	1.38
H.P.Steam	Tne.	21.43	67.44	2.21	6.97
I.P.Steam	Tne.	9.76	20.10	1.01	2.08
L.P.Steam	Tne.	5.63	13.41	0.58	1.39
H.T.Electricity	KWH.	1,881.31	26.47	194.35	2.73
L.T.Electricity	KWH	267.52	5.23	27.64	0.54
Fuel Gas 10^3	Tne.Cals.	6,461.04	58.13	667.46	6.01
Other forms.			0.28		0.03
Repair Costs			49.17		5.08
Wages	hrs.	13.19	15.62	1.36	1.61
Material			6.98		0.72
Workshop and Material on cost.			26.57		2.75
Working Materials			1.71		0.18
Traffic Charges			0.25		0.03
Works General Charges			20.04		2.07
Capital Charges			297.29		30.70
Writing off			192.78		19.90
Obsolescence			104.51		10.80
Taxes			20.88		2.16
Various Costs			6.01		0.62
Credits			0.68		0.07
TOTAL:			594.26		61.39

end of the regeneration cycle, the inert gas is stored in cylinders for re-use on the next regeneration. The catalyst chambers are depressured and then filled with the regular recycle gas from storage for the subsequent on-stream cycle.

The reactors are the usual high pressure reaction vessels having a flanged top head. The inside diameter of the reactor is 1320 mm. The first reactor is 11 metres in length and the remaining four reactors are 13 metres in length. The reactors are lined with firebrick in order that the outer reactor wall temperature does not exceed 200°C. The exchangers are conventional tube and shell units with the fresh feed in the shell in all cases. The convection heater employs flue gas recirculation and all heating is done by convection heat rather than by radiant heat. The fractionating system is the conventional bubble plate tower type.

The finished debutanized DHD gasoline, which includes front ends from the gasoline charge, contains 50-52% by weight of aromatics. The octane number is 80.5 CFR motor method. It appears that some paraffins are converted to aromatics in the process. Other properties of D.H.D. plant feed materials and products are given in Table V.

(ii) Costs.

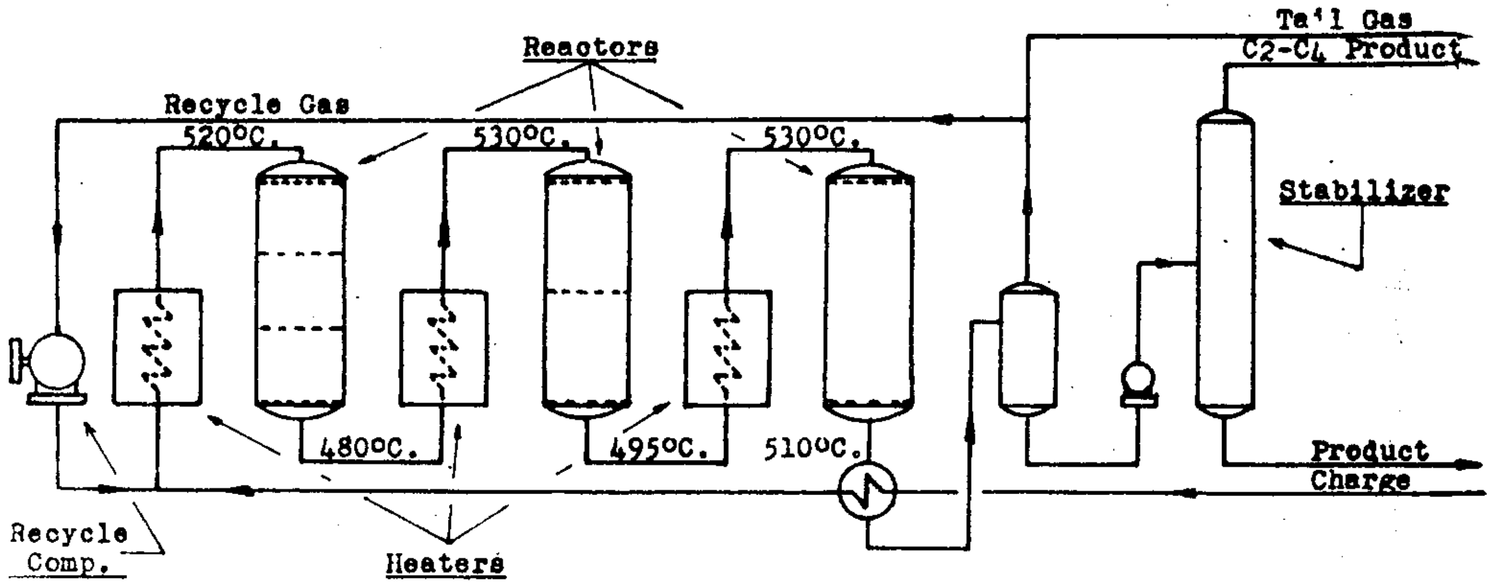
Dr.Pichler provided the following cost data for the DHD process.

The basic flowsheet assumed for the cost calculation is shewn in Fig. XII .

Table VI analyses the cost of manufacture of DHD gasoline in terms of raw material charges and operating costs and shews the credit for hydrocarbon gas.

Table VII gives a breakdown of the operating costs and provides the data on labour requirements, utilities consumption, etc, for calculation of the costs of the process if operated in U.S.A. or Britain.

FIG. XIV



FLOW DIAGRAM - HYDROFORMING PROCESS