

The Production of High B.t.u. Gas From Light Distillate
By Continuous Pressure Hydrogenation

Binay B. Majumdar and Brian H. Thompson

Gas Council, Midlands Research Station
Solihull, U.K.

Summary

This paper describes the use of light petroleum distillates for the production of gas of high calorific value. In the process the distillate is converted to methane and ethane by reaction with gas rich in hydrogen. An aromatic condensate is obtained as a by-product.

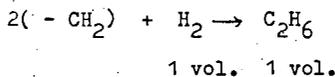
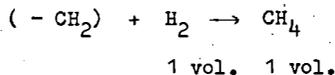
Two methods of carrying out the operation have been used. In the first, a hydrogenator of simple design incorporates temperature control by recycling the reacting gases. The second uses a fluidised bed of coke for the same purpose and can be operated to give an increased yield of liquid products.

I. Introduction

The hydrogenation of oils was developed initially¹ for the enrichment of lean gas produced by the total gasification of coal with steam and oxygen, for example, by the Lurgi Process. In recent years hydrocarbon reformers operating at high pressures have been developed which are capable of gasifying distillate to produce a comparatively lean gas. It is in association with such plants that hydrogenation units are being extensively introduced. The hydrogenation stage is capable of producing gases of high calorific value which can be used as a satisfactory substitute for natural gas.

II. The Hydrogenation Process

When a mixture of distillate vapour and lean gas are exposed to a temperature of 700 - 750°C the hydrogen in the lean gas reacts with the distillate to produce gaseous hydrocarbons, mainly methane and ethane. Little change in gas volume occurs.



The m-thane and ethane arise from the breakdown of the aliphatic constituents of the distillate which usually form the bulk of the feedstock. Further quantities arise from the hydrogenation of the side-chains from aromatic constituents in the distillate. Under the operating conditions normally used the aromatic nuclei themselves survive to give a condensate, free of paraffins, from which high purity benzene can readily be obtained.

The reaction is exothermic and being non-catalytic the distillate need not necessarily be purified before hydrogenation. The degree of preheat required for the reactants can be obtained by heat exchange with the products.

It is necessary to be able to control reaction conditions in order that the exothermicity of the reaction does not lead to hot zones where excessive temperatures cause carbon deposition. Process design has been directed so that this problem does not arise. Initially a fluidized bed was used to maintain uniform temperatures within a reactor but recently the process has been simplified. Rapid recirculation of the reacting gases within the hydrogenator is now used to maintain strict temperature control.

III. The Gas Recycle Hydrogenator

The Hydrogenator is shown diagrammatically in Fig. 1². It consists of a cylindrical vessel with a coaxial tube inside it enclosed within a pressure vessel of sufficient diameter to allow 9" of heat insulation. The mixture of distillate and hydrogen are introduced through a jet at high velocity and directed down the inner tube. The momentum of the jet causes the gaseous reactants to circulate down the tube and up the annulus. The recirculation results in the mixing of the inlet reactants with a relatively large volume of hot gases already at reaction temperature. In the pilot plant, a recirculation ratio, i.e. the number of volumes of recirculating gas per volume of reactants, of 10 : 1 or more has been readily achieved.

The recirculation of gases gives precise control of reaction temperature and the temperature distribution within the reactor is remarkably even. Except in the vicinity of the inlet jet the temperature variation in the reactor is within 3 - 4°C. It is merely necessary to control the preheat temperature to maintain the required temperature. When making gases of high calorific value the preheat temperature required is usually within the range 400 - 450°C whilst maintaining a reaction temperature of 700 - 750°C.

The distillate is converted to hydrocarbon gases, mainly ethane and methane with small quantities of olefines. The proportion of ethane increases as the reaction temperature is lowered. The output of a reactor of a given size varies directly as the pressure. At a given pressure, however, a plant is extremely flexible and output can be controlled over wide limits.

In trouble free operation over long periods carbon deposition must be avoided. This governs the choice of operating conditions especially if the operating pressure is comparatively low. Operation at 350 p.s.i.g. enables a calorific value of 800 Btus/s.c.f. to be readily attained with an operating temperature of 750°C. At lower pressures or when attaining higher calorific values it is necessary to lower the temperature. Below about 675°C however the reaction is slow and operation becomes unstable, 700°C is, therefore, considered to be a safe minimum operating temperature. The presence of 5 - 10% of steam in the hydrogenating gas is usually

sufficient to overcome any remaining tendency for carbon deposition. If a hot potassium carbonate scrubber is used to remove carbon dioxide from the lean gas, there is sufficient steam left in the gases for this purpose.

Fig. 2 shows the flow diagram of the pilot plant. The hydrogen was made by the steam reforming of commercial butane followed by carbon monoxide conversion, carbon dioxide removal and compression, approximately 0.9 million s.c.f./ day of gas containing about 9% hydrogen being available. The distillate, which was not purified, was pumped into the hydrogenating gas stream and the mixture preheated so as to maintain the required temperature in the hydrogenator using gas-fired preheaters which would be replaced on a commercial unit by heat exchangers between product gases and reactants. The product gases removed from inside the top of the reactor were water quenched followed by indirect cooling. Samples for analysis were taken from the hot gases before the quench.

The plant was started up using hydrogenating gas, preheated to about 650°C, to raise the temperature in the hydrogenator to 575 - 600°C. Distillate was then introduced into the hydrogenating gas stream at a low rate and as the heat of reaction raised the hydrogenator temperature the distillate rate was increased and the preheat temperature reduced until over a period of about 1/2 hour the final reaction conditions were attained.

IV. Tests in the Gas Recycle Hydrogenator

The results of some three days tests are given in Table 1.

Test 1 represents a run at 350 p.s.i.g. using an hydrogenating gas containing 92.4% hydrogen, obtained by reforming commercial butane followed by carbon monoxide conversion and carbon dioxide removal. A calorific value of 804 Btus/s.c.f. was obtained without difficulty using a comparatively high specific gravity distillate with a final boiling point of approx. 170°C. Analysis of the feedstock gave an aromatic content of 8.1% by volume and on hydrogenation 11.1% of the carbon in the oil appeared as condensate and 88.9% as hydrocarbon gas. There was no trace of unreacted paraffins in the condensate. The gas contained a considerable concentration of ethane, but no trace of higher paraffinic hydrocarbons showing the relatively slow rate of ethane decomposition compared with higher hydrocarbons under these conditions. A small amount of unsaturated hydrocarbons also survived.

A preliminary test showed that at a pressure of 450 p.s.i.g. and a reaction temperature of 725°C a calorific value of 960 Btus/scf, using a similar distillate and a dry hydrogenating gas could not be obtained without an appreciable amount of carbon deposition. Tests 2 and 3 were therefore carried out to make calorific values of 900 Btus/s.c.f. and 1,000 Btus/s.c.f. respectively using an hydrogenating gas to which 9 - 10% steam was added, carbon deposition troubles being then eliminated.

As the calorific value of the gas was increased from 900 - 1,000 Btus/s.c.f. the yield of aromatic condensate increased so that in the latter case 15.1% of the carbon in the oil appeared as condensate and only 84.9% as hydrocarbon gas. With the reduced operating temperature and the low partial pressure of hydrogen in the final gas traces of paraffins appeared in the condensate.

Table 1 - Tests in the Gas Recycle Hydrogenator.

Test No.	1	2	3	4	5
Hydrogenation Pressure, p.s.i.g.	350	450	450	180	180
Inlet Gas Rate, s.c.f.h.	30,790	18,230	18,400	13,855	14,090
Dry Inlet Gas Composition, % by volume:					
CO ₂	0.3	1.0	0.8	12.7	12.8
CO	3.7	3.7	3.7	2.5	2.4
H ₂	92.4	93.6	92.4	83.3	83.9
CH ₄	3.0	1.2	2.4	0.6	0.1
N ₂	0.6	0.5	0.7	0.9	0.8
	100.0	100.0	100.0	100.0	100.0
Steam content of hydrogenating gas vols/100 vols dry inlet gas	Nil	10.2	9.2	7.3	7.2
Distillate Type:	170	170	170	170	115
Specific Gravity	0.71	0.71	0.72	0.71	0.66
Aromatic Hydrocarbon, % by volume	8.1	7.2	6.5	7.4	1.6
Carbon/Hydrogen, w/w	5.7	5.7	5.8	5.7	5.4
Imp. Gals. of distillate per 1000 cu.ft. of dry inlet gas	4.27	5.39	6.87	3.98	3.99
Preheat temperature, °C	441	403	425	503	530
Hydrogenation temperature, °C	750	715	715	715	715
Product Gas Rate, s.c.f.h.	33,600	20,480	21,400	15,330	15,575
Product Gas Composition, % by volume:					
CO ₂	0.4	0.7	0.7	11.35	10.9
C _x H _y	1.1	1.1	2.4	1.4	2.1
CO	3.3	3.8	3.3	2.9	2.8
H ₂	44.6	34.8	23.8	43.1	44.6
CH ₄	32.6	36.8	43.95	23.35	21.3
C ₂ H ₆	17.5	22.1	25.15	16.8	17.5
N ₂	0.5	0.7	0.7	1.1	0.8
	100.0	100.0	100.0	100.0	100.0
Calorific Value, Btu/s.c.f.	804	896	1008	704	713
Calorific Value, Btu/s.c.f. (inert free)	810	909	1022	804	808
Carbon Balance					
Percentage of carbon supplied in distillate appearing as:					
Hydrocarbon Gas	88.9	88.8	84.9	87.3	96.0
Benzene	8.8	7.9	7.9	7.8	3.2
Toluene	1.1	1.5	2.7	2.3	0.3
Xylene and Higher Monocyclics	0.6	0.7	1.7	1.5	0.2
Naphthalene	0.3	0.6	1.2	0.5	0.1
Higher Aromatics	0.3	0.4	1.5	0.4	0.0
Unreacted Paraffins	0.0	0.1	0.1	0.2	0.2
Carbon Deposited	0.0	0.0	0.0	0.0	0.0
Gases Produced and absorbed s.c.f./imp. gallon of distillate:					
CH ₄ produced	76.4	74.4	71.0	63.4	58.7
C ₂ H ₆ "	44.8	46.0	42.6	46.7	48.5
C _x H _y "	2.8	2.3	4.1	3.9	5.8
H ₂ absorbed	102.5	100.9	94.2	89.5	86.8

The use of steam to avoid carbon deposition difficulties enabled the use of lower operating pressures and Tests 4 and 5 were comparative tests at 180 p.s.i.g. Gas with an inert free calorific value of 800 Btus/s.c.f. was made using an initial gas containing about 13% of carbon dioxide. The hydrogen partial pressure was only 135 p.s.i.g. Two types of distillate were used, one the comparatively high gravity distillate used for the previous tests and the other of lesser gravity with a final boiling point of about 108°C containing only 1.6% aromatics. The main feature of the results is the increased yield of hydrocarbon gases with the lighter feedstock, 96% of the carbon in the distillate being converted to gas. A second feature is that taking the increase in volume into account the product gas contains almost as much carbon dioxide as present in the inlet gas. There is no marked tendency for the carbon dioxide to react with hydrogen to give carbon monoxide.

A typical potential heat balance when making a gas of 900 Btus/s.c.f. from 170 distillate is given in Table 2. The efficiency of the process is seen to be high with 88.4% of the potential heat in the distillate appearing in the gas and 9.2% in the condensate, the combined yield being 97.6%.

TABLE 2

Typical Potential Heat Balance when making
900 C.V. gas in Gas Recycle Hydrogenator

Type of Distillate	L.D.F. 170
Potential Heat in Products as percentage of Potential Heat in Distillate:	
Hydrocarbon Gas	88.4
Benzene	6.5
Toluene	1.3
Xylene and other Monocyclics	.6
Naphthalene	.4
Higher Aromatics	.3
Unreacted Paraffins	.1
Heat of reaction by difference.	2.4
	<u>100.0</u>

V. The Fluidized Bed Pilot Plant

The use of a gas recycle simplified the design of a hydrogenator for use with distillate under conditions when carbon deposition is avoided. The fluidized hydrogenator developed for crude and heavy oil, is an alternative and can be used when carbon is deposited. In this process a fluidized bed of coke serves to take up any carbon and also serves to establish the uniform temperature requirement. The large heat capacity of the fluidized bed compared with that of the inlet reactants serves to bring them rapidly to reaction temperature and by absorbing reaction heat prevents excessive temperatures in the bed.

The hydrogenator design is shown in Fig. 3. The reaction vessel consists of a thin walled cylinder 22" dia. and 16 ft. deep terminating at the lower end in an inverted cone. It contained a fluidized bed of coke particles (size range C.C17" - C.C02") and to prevent agglomeration when using heavy feedstocks the bed could be recirculated through a lower fluidized bed via a downcomer and riser about 15 ft. long. The main stream of hydrogenating gas was introduced just below the bottom of the riser. Subsidiary streams of hydrogenating gas were used to maintain fluidization in the lower bed and at the bottom of the downcomer. When using distillate the solid recycle system was not necessary but was retained as part of the development programme of the reactor for use with heavier feedstocks. The latter were introduced through an atomiser located below the riser and coaxial with it. When using distillate it was merely evaporated into the main hydrogenating gas stream fed in below the riser.

Simplification of the plant for use solely with distillate would leave a single fluidized bed with only the one inlet gas stream containing the preheated mixture of distillate and hydrogenating gas. A system of horizontal and vertical baffles was included in the main fluidized bed to improve the fluidization characteristics. The whole internal assembly of the pilot plant was surrounded by 10 ins. of heat insulation and enclosed in a mild steel pressure vessel.

The flow diagram for the plant is shown in Fig. 4. The hydrogenating gas was produced as for the Gas Recycle Plant by reforming of butane followed by carbon monoxide conversion and carbon dioxide removal. It was then preheated in gas fired preheaters but on a commercial unit heat exchange with the product gases would be utilised. The reaction products were water quenched to about 200°C and then cooled further by direct scrubbing with recycled condensate in a tower packed with raschig rings. Final cooling to 30°C was by an indirect cooler. Gas samples for analysis were taken before the water quench.

The plant was started up with the full flow of preheated hydrogenating gas but at a reduced pressure to give the required fluidizing velocity in the reactor. The coke was then carried in with a subsidiary stream of gas and the plant warmed up further with gas preheated to 650°C. When the reactor temperature reached 350°C air was admitted to accelerate the heating. At 650°C distillate was introduced at a low rate and as the heat of reaction raised temperatures the air rate was reduced to zero followed by a reduction of the preheat temperature of the reactants. As temperatures rose the pressure was increased to maintain the desired fluidizing velocity.

VI. Tests in the Fluidized Hydrogenator

The results of tests carried out in the pilot plant are given in Table 3.

Test 1 gives the results of a run of 14 days duration operating at 25 atmospheres pressure and 750°C. The gas produced had a calorific value of 850 Btus/s.c.f. Operation of the plant was extremely steady and there was no measurable carbon deposition. The elutriation of coke from the bed amounted to less than 65 lbs./day. A comparatively low gravity distillate with a final boiling point of 130°C was used.

Table 3 - Tests in the Fluidised Hydrogenator

Test No.	1	2	3
Hydrogenation Pressure, p.s.i.g.	350	350	720
Inlet Gas Rate, s.c.f.h.	53,240	32,369	32,052
Inlet Gas Composition, % by volume:			
CO ₂	1.2	1.3	1.85
CO	2.6	2.3	3.6
H ₂	93.5	92.0	91.3
CH ₄	2.1	3.9	2.75
N ₂	0.6	0.5	0.5
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>
Distillate Type:			
Specific Gravity	0.67	0.70	0.71
Aromatic Hydrocarbon Content, % by volume	3.6	6.3	7.44
Carbon/Hydrogen ratio, w/w	5.3	5.7	5.6
Imp. Gals. Distillate per 1000 cu.ft. of dry inlet gas	4.88	4.95	7.82
Time of residence, secs.	28	29	66
Preheat temperature, °C	455	454	379
Hydrogenation temperature, °C	755	755	722
Product Gas Rate, s.c.f.h.	37,767	36,343	40,348
Product Gas Composition, % by volume:			
CO ₂	0.85	1.0	1.35
C _x H _y	1.00	1.3	1.05
CO	2.55	2.45	3.15
H ₂	37.9	33.7	16.75
CH ₄	39.1	45.3	54.05
C ₂ H ₆	17.4	15.4	23.05
N ₂	1.2	0.85	0.6
	<u>100.0</u>	<u>100.0</u>	<u>100.0</u>
Calorific Value Btus/s.c.f.	840	859	1024
Carbon Balance			
Percentage of carbon supplied in distillate appearing as:			
Hydrocarbon Gas	94.8	89.4	82.8
Benzene	4.5	8.7	11.2
Toluene	0.1	0.3	1.7
Xylene and higher monocyclics	0.1	0.2	0.6
Naphthalene	0.3	1.0	1.4
Higher Aromatics	0.2	0.4	1.7
Unreacted Paraffins	-	-	-
Carbon Deposited	-	-	0.6
Gases Produced and absorbed as ft. ³ / imp. gallon of distillate:			
CH ₄ produced	86.8	94.3	83.5
C ₂ H ₆ "	40.5	34.7	37.1
C _x H _y "			
H ₂ absorbed	103.4	108.8	89.8

Test 2 was of similar duration and reaction conditions but a higher gravity distillate (S.G. 0.70 and final boiling point 165°C was used.) The performance of the plant was equally satisfactory the most significant difference being the increased condensate yield with the heavier feedstock. In test 1 94.8% of the carbon in the oil appeared in the gas and only 89.4% in test 2.

In comparison with the tests in the gas recycle hydrogenator using the heavier type of distillate the yield of naphthalene and higher aromatics is higher, possibly due to a more sudden heating on entry to the fluidized bed and the absence of dispersion of the reacting distillate in a large volume of reacted gas.

Test 3 shows the results of a run at 50 atmospheres pressure to produce a gas of 1,000 Btus/s.c.f., a calorific value which was reached without difficulty. With an operating temperature of 722°C 0.6% of the carbon in the oil was deposited on the particles in the fluidized bed. In comparison with tests 1 and 2 the effect of increased residence time due to the higher pressure was to reduce the ethane/methane ratio in the gas produced, despite the counteracting effect of a reduced operating temperature. The yield of condensible aromatic hydrocarbons was increased and only 22.8% of the carbon in the oil appeared in the gas.

VII. The Hydrogenation of Light Distillate with the production of Aromatic Hydrocarbons

In the tests described so far the aromatic condensate is mainly derived from that already in the distillate. The ring structure of these aromatics remains intact under the reaction conditions although the side-chains are removed increasing the yield of gaseous hydrocarbons.

However, it is evident that as the distillate/hydrogen ratio is increased in order to obtain a higher calorific value of product gas the yield of condensible aromatic hydrocarbons is increased. The synthesis of aromatics is believed to be due to the fact that, when present in greater concentration, radicals have an opportunity to cyclise before they are hydrogenated. It was considered, therefore, that if the distillate/hydrogen ratio were increased to an even larger extent the production of aromatic hydrocarbons could be very greatly increased, whilst still producing a very high calorific value of gas.

Laboratory experiments³ showed that at an operating temperature of 750 - 775°C and with a distillate/hydrogen ratio of about 20 - 25 imp. gallons/1000 cu.ft. 20% or more of the carbon in the oil could be recovered as aromatic hydrocarbons even when there was virtually no aromatic content in the distillate. Pressure was found to have little effect on the reaction. With the limited partial pressure of hydrogen the condensate contained an appreciable proportion of alkylated aromatic compounds and the gaseous hydrocarbons contained a comparatively high proportion of unsaturated compounds. It was apparent that further hydrogenation was desirable in a second stage to de-alkylate the condensate and to convert olefinic hydrocarbons to methane and ethane.

TABLE 4

The Hydrogenation of Distillate with
Aromatic Hydrocarbon Formation

Hydrogenation Pressure	365
Inlet Gas Rate, s.c.f.h. (90% H ₂)	33,350
Distillate Type:	
Specific Gravity	0.682
Aromatic Hydrocarbon Content	3.0
Carbon/Hydrogen, w/w	5.4
Imp. Gals. of distillate /1000 cu.ft. of gas:	
a) synthesis stage	21.2
b) overall	7.5
Hydrogenation temperature, °C:	
a) synthesis	760 - 765°C
b) de-alkylation	790
Product Gas Rate, s.c.f.h.	45,080
Product Gas Composition, % by volume	
CO ₂	2.9
C _x H _y	0.3
CO	3.4
H ₂	30.0
CH ₄	51.8
C ₂ H ₆	11.0
N ₂	0.6
Calorific Value, Btus/s.c.f.	821
Carbon Balance	
Percentage of carbon supplied in distillate appearing as:	
Hydrocarbon Gas	71.6
Benzene	17.2
Toluene and Higher monocyclics	1.5
Naphthalene	3.6
Higher Aromatics	5.2
Deposited Carbon	0.9

It was realised that the fluidized hydrogenator with the solids recycle is suitable for carrying out this process with very little modification (Fig. 5). The lower fluidised bed was utilised for the 1st stage of the reaction and the 2nd stage was carried out in the main bed.

The whole of the distillate was mixed with the hydrogenating gas used to fluidize the lower bed which was deepened to 5 ft. to give adequate time for reaction. The hydrogenating gas for the second stage was introduced at the base of the riser. The first stage reaction was endothermic and the second stage exothermic. The solids recycle then served to transfer heat from the second stage to the first stage maintaining overall heat balance with a temperature differential between the two stages of 25 - 30°C.

The results of operating the process are given in Table 4 showing that for a distillate containing only 3% of aromatics the yield of aromatics accounted for 27.5% of the carbon in the distillate. The condensate itself was free of paraffins. Carbon deposition amounted to 0.9% of the carbon in the oil and this was deposited as a graphitic coating on the fluidised particles. The overall product gas had a calorific value of 821 Btus/ft.³, a value which could be increased with a reduced supply of hydrogen to the second stage.

Acknowledgements

This paper is published by permission of the Gas Council, and the work described in it was carried out under the direction of Dr. F. J. Dent. The Authors thank their colleagues who were responsible for the experimental work.

Literature References

1. Dent, F.J., Edge, R.F., Hebden, D., Wood, F.C. and Yarwood, T.A. "Experiments on the Hydrogenation of Oils to Gaseous Hydrocarbons" Gas Council Research Communication, G.C. 37, 1956, 51 pp., Trans. Inst. Gas Engrs., 106, pp. 594-643, 1956-7.
2. Murthy, P.S. and Edge, R.F. "The Hydrogenation of Oils to Gaseous Hydrocarbons" Gas Council Research Communication G.C.88, 18 pp., 1962, J. Inst. Gas Engrs., 3, pp. 459-476, 1963.
3. Moignard, L.A. and Stewart, K.D. "The Hydrogenation of Light Distillate with reference to the Production of By-product Aromatic Hydrocarbons" Gas Council Research Communication G.C.51, 36 pp., 1958, Trans. Inst. Gas. Engrs., 108, pp. 528-562, 1958-9.

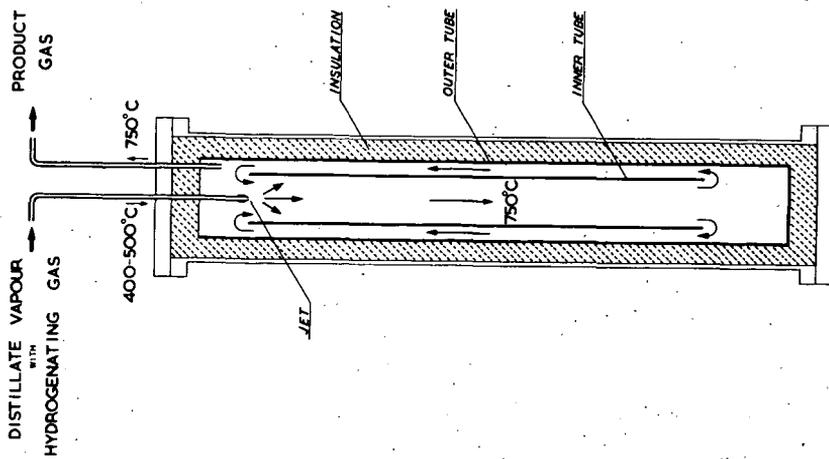


Fig. 1. The Gas Recycle Hydrogenator.

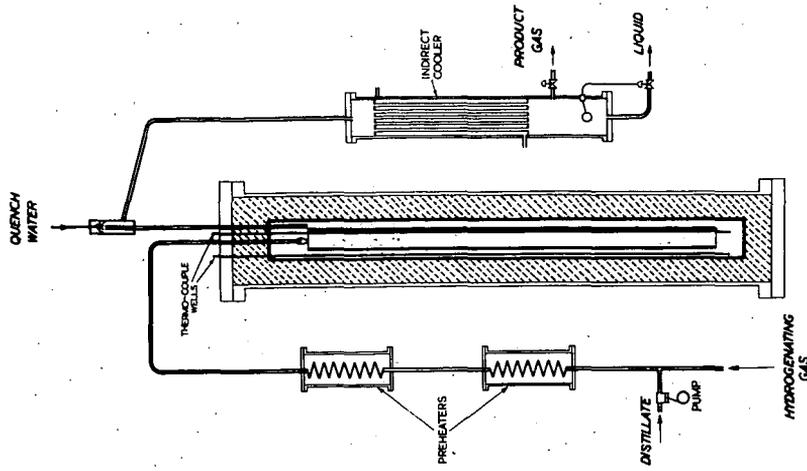


Fig. 2. Flow Diagram of the Gas Recycle Pilot Plant.

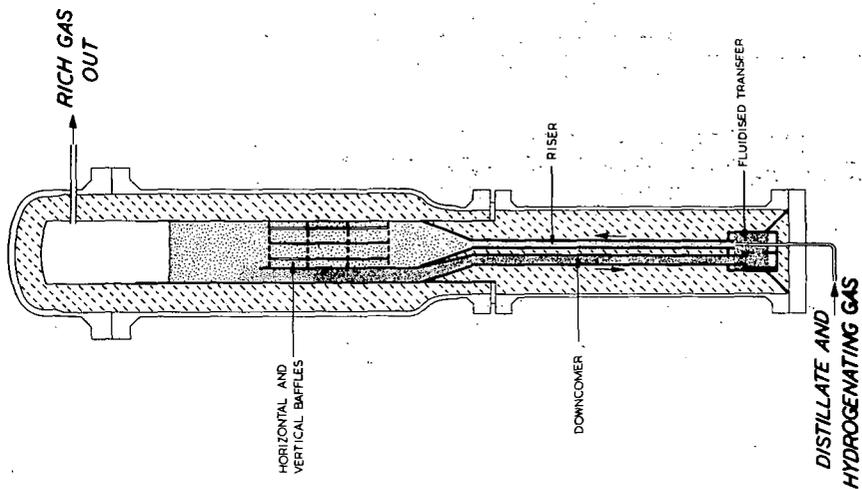


Fig. 3. The Fluidised Bed Pilot Plant.

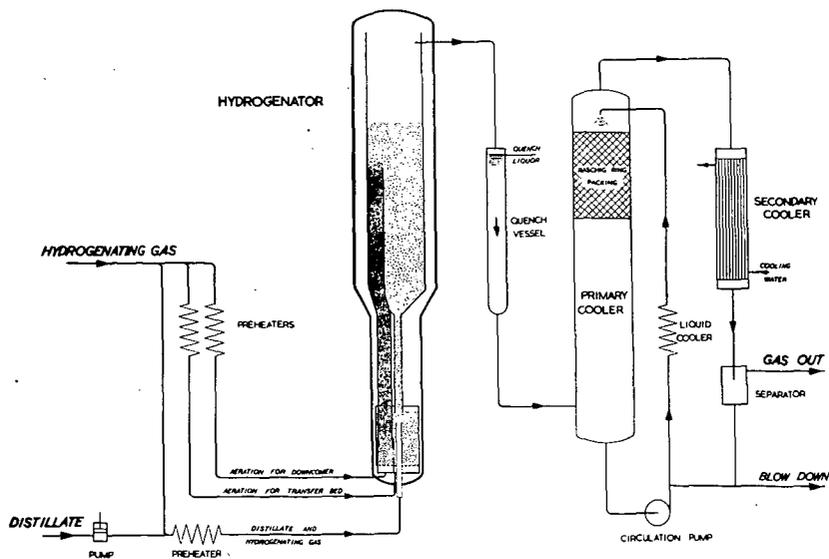


Fig. 4. Flow Diagram of the Fluidised Bed Pilot Plant.

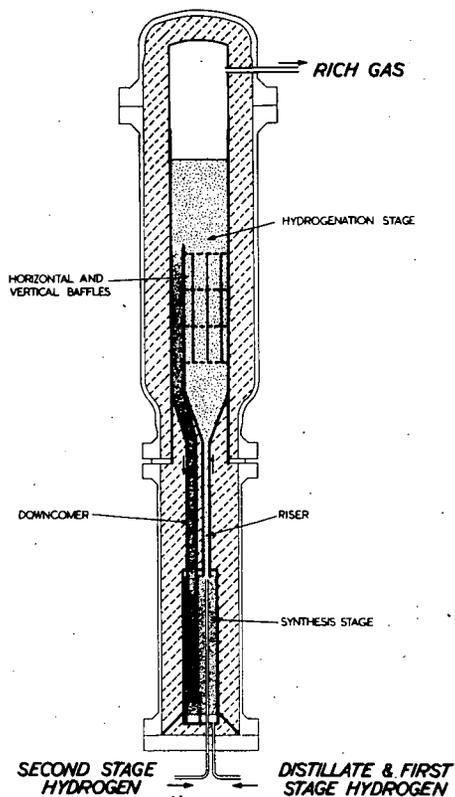


Fig. 5. The Fluidised Bed Hydrogenator used for the Production of By-Product Aromatic Hydrocarbons.