Synthesis at Medium Pressure

General

Lurgi and Hoesch discovered that for synthesis at medium pressure the best ratio of H_2/CO in the synthesis gas is 1.5 - 1.6, and for their full-scale plant Hoesch use the following ratios, which they say give the best results: Stage I 1.5 - 1.6, Stage II 1.5, Stage III 1.3 - 1.4. The low ratio in the last stage is chosen to suppress methane formation. Ruhrchemie agree with this, and have adopted a similar scheme for their own medium pressure plant.

Lurgi say that if gas rich in carbon monoxide is used from the very beginning of the catalyst life, it damages the catalyst due to formation of carbon, but if used after proper running in it is very good. Hoesch go as far as to say that gas with $H_2/CO = 1$ gives the best results for synthesis on a small scale but cannot be used on the large scale as it causes formation of carbon.

Ruhrchemie drew attention to the fact that the inert content of synthesis gas for medium pressure synthesis will always be less than for atmospheric pressure synthesis gas on account of the ease with which carbon dioxide can be washed out under pressure, and as a result, medium pressure synthesis starts with this advantage over atmospheric pressure synthesis.

In agreement with observations made at the Fuel Research Station, Ruhrchemie also found that if during medium pressure synthesis the gas rate is temporarily reduced and then restored to normal, the activity of the catalyst is permanently ruined. They think that the bad effect is due to the catalyst becoming covered with some products which are not removed by going back to the normal gas rate. It is interesting that the bad effect of low gas rates is not observed during the first few days of synthesis, and during that initial period the high molecular weight products formed at very low gas rates may even be beneficial in protecting the catalyst against the formation of carbon.

These observations have an important bearing on the running of the plant, and if there is a shortage of gas for the Ruhrchemie medium pressure plant some of the reactors are shut down altogether so as to maintain the gas rate for the others.

For a complete shut-down of a reactor the temperature and pressure are maintained at their synthesis levels and the catalyst left in contact with stationary gas. This is for the large plant. For laboratory plant the catalyst is cooled in contact with stationary gas and restarted by restoring the gas flow and then heating up to reaction temperature.

Hoesch-Benzin.

Before December, 1940, this plant was arranged for synthesis in two stages, using H_2/CO ratio of 1.8 -

2.0 for Stage I. The total contraction was 69%, the yield of products 130 g./cu.m. ($CO + H_2$), and the yield/reactor/day was 1.63 t. The catalyst life was about 9 months. Further details for one month's synthesis by this method are given in Table 17.

As a result of experiments carried out at the Hoesch plant in conjunction with Lurgi, Hoesch introduced two independent changes, converting the plant to three-stage working and reducing the ratio of H_2/CO in the synthesis gas. The second of these changes was carried out in spite of Ruhrchemie's advice against it. In this way the methane production was decreased and the specific yield and plant production increased, the latter going up to 2.05 t./reactor/day. Hoesch paid Lurgi a premium on the extra product produced as a result of the change. The big increase much more than balanced the extra expense owing to shorter catalyst life, which was now only 7 - 8 months. The yield of products/kg. cobalt was 550 - 560 kg., which was much higher than that obtained at the other plants. Thus Essener Steinkohle produced 450 kg. and the other plants 300 - 350 kg. Full details of the three-stage synthesis are shown in Table 18, and a comparison of Tables 17 and 18 shows the salient features of the two methods of working. The change made no difference in the boiling range of the products, but it increased the proportion of olefines, as shown in Table 19.

Table 17.

Performance Data for the Hoesch-Benzin Plant
November, 1940. Two Stage Working.

	Stage	
1. Synthesis Gas, N.cu.m./month x 10^6	I	27.600
2. ($CO + H_2$), N.cu.m./month x 10^6	I	23.734

Table 17. continued

		Stage	
3.	$(CO + 2H_2)$, N.cu.m./month 10^6	I	22.950
4.	Ratio H_2/CO	I	1.82
7.	Average number of reactors engaged in synthesis	I II I+ II	43.6 21.6 65.2
8.	Number of reactors started up per month	I+ II	8
10.	Mean catalyst life, h.	I II I+ II	2607 2952 2740
11.	Mean temperature, °C.	I II I+ II	191.0 191.3 191.0
12.	Mean gas rate, N.cu.m./ reactor/h.	I II I+ II	875 666 585
17.	Contraction, %	I II I+ II	61.9 34.4 75.0
18.	Yield of Primary Products, g./N.cu.m. $(CO + H_2)$ — Without Gasol	I+II	135.0
	With Gasol	I+II	150.5

Table 17 continued

		Stage	
19. Yield of Primary Products, g./N.cu.m. ($CO + 2H_2$)	Without Gasol	I+II	193.1
	With Gasol	I+II	155.5
20. Liquid Primary Products, t./month		I+II	3200
21. Production, t./reactor/day		I+II	1.63
24. Conversion of CO, %	Total	I II I+II	70.4 50.2 85.1
25.	to liquid products	I+II	60.3
26.	to gas and gasol	I+II	24.8
27. % CH_4	Synthesis Gas Synthesis Gas Residual Gas	I II II	0.4 9.5 14.3
28. % CO_2	Synthesis Gas Synthesis Gas Residual Gas	I II II	10.6 27.8 42.4

Table 17 continued.

		Stage	
29. Sulphur in Synthesis gas, g./100 N.cu.m.	Inorganic	I	0.04
	Organic	I	0.12
	Total	I	0.16

Table 18.

Performance Data for the Hoesch-Benzin Plant March 1944. Three Stage Working.

	Stage	
1. Synthesis Gas, N.cu.m./month x 10^6	I	33.000
2. (CO + H_2), N.cu.m./month x 10^6	I	28.358
3. Ratio H_2/CO	I	1.84
4. Average number of reactors engaged in synthesis	I	40.0
	II	16.0
	III	8.0
5. Number of reactors started up per month	I-III	16
6. Number shut down per month	I-III	16
7. Mean life of catalyst, hours	I	3020
	II	2033
	III	235
	I-III	2425

Table 18 continued

		Stage	
8. Mean temperature, °C		I II III I-III	198.1 195.4 198.7 197.8
9. Mean gas rate, N.cu.m./reactor/h.		I II III I-III	928 1238 2037 696
10. Contraction, % (from special analysis for N_2)		I II III I-III	56.2 44.2 36.0 78.5
11. Yield of Primary Products, g./N.cu.m. ($CO + H_2$)	Without Gasol	I-III	143.5
	With Gasol (produced)	I-III	161.6
	With Gasol (recovered)	I-III	161.0
12. Liquid Primary Products, t./month		I-III	4070
13. Liquid Primary Products + Gasol, t./month		I-III	4572
14. Production, t./reactor/day		I-III	2.05
17. Conversion of ($CO + H_2$), %	Total	I II III I-III	69.2 68.2 74.2 94.9

Table 18 continued.

		Stage	
18.	to liquid products	I-III	69.9
19.	to gas and gasol	I-III	25.0
20. % CO in	Synthesis Gas	I	33.35
	Residual Gas	I	29.95
	Synthesis Gas	II	27.18
	Residual Gas	II	21.67
	Synthesis Gas	III	19.84
	Residual Gas	III	11.87
21. % H_2	Synthesis Gas	I	52.43
	Residual Gas	I	30.60
	Synthesis Gas	II	38.80
	Residual Gas	II	16.00
	Synthesis Gas	III	29.09
	Residual Gas	III	7.83
22. % CH_4	Synthesis Gas	I	0.40
	Residual Gas	III	14.88
23. % CO_2	Synthesis Gas	I	8.20
	Residual Gas	III	37.57
24. Sulphur in Synthesis Gas, g./100 N.cu.m.	Inorganic	I	0.03
	Organic	I	0.21
	Total	I	0.24

Table 19.

Olefine Contents for Two and Three-Stage Working

Number of Stages	Product	Olefine Content %
2	Gasol	10-12
3	Gasol	20
2	Spirit	15-17
3	Spirit	20-22

Hoesch had 40, 20, 8 reactors in Stages I, II, and III respectively but the pipeline connections were not completely adequate, so that even up to 1944 the best method of working could not be used for all the reactors, namely of starting synthesis in Stage III and then switching into Stage II and finally Stage I. Details are as follows:

Stage III. Freshly reduced catalyst is started here and kept in this stage for 1 month. Synthesis is started at 170°C. and 2,000 cu.m./h. and the temperature is increased to 200°C. in four days. The gas rate is decreased gradually and is only 1,500 cu.m./h. at the end of the month. Hoesch say that it would have been better to have used temperatures of 210 - 215°C., which would not harm the catalyst but which could not be attained with the present reactor fittings. It was proposed to alter these to allow temperatures of 220 - 225°C. to be available if required.

The gas entering this stage had an H_2/CO ratio of 1.3 - 1.4.

Stage II. After switching from Stage III the temperature is reduced to 180°C. and the gas rate set at 1,200 cu.m./h. During the first month in this stage the temperature is increased to 195°C. and the gas rate decreased slowly so as to keep the contraction constant. For the next 4 - 5 months the gas rate is still decreased, down to 900 cu.m./h. at the end of this period. The gas used in this stage has H_2/CO = 1.5.

Stage I. The catalyst spends the remaining 1 or 2 months of its life here, starting at 196 and 900 - 1,000 cu.m./h. and finishing at 200°C. and 600 cu.m./h. The gas for this stage has H_2/CO = 1.5 - 1.6.

The details of how the synthesis proceeded in these stages can be seen from the analyses in Table 20.