

## Atmospheric Pressure Synthesis

### Comparison of Results

Before considering in detail the different methods that have been used for conducting synthesis, a number of rather general points must be stated as they have to be borne in mind when comparing the results obtained.

In the German documents, yields of products are usually given in grams per normal cubic metre synthesis gas, but sometimes per normal cubic metre 'Nutzgas' or 'Idealgas'. Nutzgas is inert-free synthesis gas, and Idealgas is  $(CO + X.H_2)$  where X is the utilization ratio, i. e., the ratio of  $H_2/CO$  reacting in the synthesis.

When comparing results obtained on the full scale with those on the experimental scale, it must be remembered that in an experimental reactor which is worked for the whole of the catalyst life with ordinary synthesis gas, the output/reactor/catalyst life will be some 20% higher than the best result that can be obtained in the large plant, because in the latter case the gas, averaged over the two or three stages, is much more dilute. But the utilization of the gas is worse in the experimental single stage reactor than for multistage working.

When comparing claims for proposed plants with those actually obtained, a statement of Lurgi is of interest, to the effect that the yields quoted by them in claims for their processes are always about 5 g./cu.m. less than the true values because they have to guarantee the figures quoted to possible purchasers. Similarly the temperature range quoted always extends some  $10^\circ$  higher than the true range for synthesis so as to leave a factor of safety for the construction of the reactors.

Again, if a plant is being worked so as to produce benzine as the main product, then it will give more methane

than if wax or Diesel oil is the product aimed at. This must be borne in mind if, in comparing two plants, one is thought to be more efficiently run than the other on the ground that its methane production is relatively lower.

Another point is that if a plant is run with a short catalyst life it will produce more catalyst wax than a similar plant where the catalyst life is long. But in spite of the high value of catalyst wax Essener Steinkohle consider that it is better economically to work to a long catalyst life.

#### Composition of Synthesis Gas Required

Laboratory tests carried out by Ruhrchemie have shown that gas with 93.5% ( $\text{CO} + \text{H}_2$ ) is better than the gas with 80% ( $\text{CO} + \text{H}_2$ ) which is used on the large scale in their plant. They could not carry out the same comparison on the large scale, but they are convinced that any plant having a synthesis gas with a low proportion of inert constituents has a great advantage over the others, and the results obtained by Essener Steinkohle are a striking illustration of this. Although Ruhrchemie's synthesis gas contained a high percentage of inerts, their catalyst was not specially developed to suit this gas.

As far as individual impurities in the gas are concerned, the plants whose synthesis gas contained a high percentage of methane got less gas formation, but Ruhrchemie themselves could not confirm or deny this. Lurgi consider that the methane acts simply as an inert constituent and they obtained the same yields when synthesis gas was diluted with nitrogen and with methane. They stated that the incorporation of methane into the Fischer reaction is thermodynamically impossible, and they explain the fact that the gas formation in the second stage of ordinary synthesis is so small, as being due to different gas compositions and lower surface temperatures. Dr. Ritter, of Krupp, produced evidence that water vapour in the synthesis gas has a specifically harmful effect. Rheinpreussen agree that if the water vapour in the synthesis gas exceeds about 50 g./N. cu. m. the yields of products are worse than if drier gas were used. Both Essener Steinkohle and Rheinpreussen had about this amount of water vapour in their synthesis gas. The other licensees consider that the water vapour acts only as an inert diluent, but as such, should naturally be present in as small amounts as possible. Brabag say that if

the percentage of carbon dioxide in the gas exceeds some 15% it will oxidize the catalyst.

Ruhrchemie said that the ratio  $H_2/CO$  should be as near 2 as possible. Water-gas at atmospheric pressure always gives carbon deposition, and a gas with  $H_2/CO = 1.65$  reduces the catalyst life for the same reason. Essener Steinkohle say that a ratio of 2.1 is usually bad, but that if the catalyst is not too active 2.01 to 2.03 may be used with advantage. They make small alterations in the composition of the synthesis gas to suit it to the average activity of the catalyst in Stage I, lowering the temperature of any reactors which have an activity above the average when a change in the direction of more hydrogen is made.

In general, Ruhrchemie consider that the different methods of working adopted at the different plants were determined by differences in the synthesis gas, particularly in the  $H_2/CO$  ratio and in the proportion of inerts present.

#### Method of Controlling the Synthesis

Careful control of the individual reactors is necessary not only to keep them to the schedules of temperature, gas-rate, conversion, etc. required, but also to detect and suppress bolting. This is the name given to the reaction getting out of control, and zones of high temperature forming in the catalyst, on which all the synthesis gas reacts to give methane and free carbon. Essener Steinkohle consider that the performance of each reactor must be watched, hour by hour, by analysis, and the whole checked by very frequent direct measurements of the products. A 'Mono'  $CO_2$  - recorder was provided for each block of four reactors and was switched from one reactor in the block to the next at hourly intervals. Its reading was checked daily by analysis.

The amount of gas going to each reactor is measured with an orifice gauge and can be controlled by valves, although naturally big increases in gas rate cannot be made as there is not sufficient gas pressure.

To maintain the best performance of any given catalyst activity, Essener Steinkohle say that the temperature

required depends on the gas rate in the way shown in Figure 2. Thus if the gas rate has to be reduced, on account of shortage of gas, from 1,000 to 800 cu.m./reactor/h., the temperature must be reduced from 195 to 185°C. In order that the amount of synthesis gas available shall always correspond to the amount required by the synthesis it is necessary to arrange a very close liaison between the generation of the gas and the control of the reactors, so that temporary reductions in the gas supply, due to maintenance work correspond to periods over which the reactors require less gas.

At Essener Steinkohle bolting frequently occurred, particularly in the Rohrbogen type of reactors, after revivification. It is now avoided by using a gas rate much less than normal for the first day or so after extraction, or, when the pipe-line arrangements allow, by restarting on synthesis gas diluted by residual gas. A good operator can usually detect bolting in its very early stages and then reduces the temperature of the block of reactors which contains the one that is beginning to bolt. If bolting is not discovered till a later stage, the gas supply to the whole block is cut off and the temperature lowered. They prefer this method of stopping bolting to the method of lowering the gas rate to the individual reactor concerned.

#### Essener Steinkohle

The general principle adopted by Essener Steinkohle was to do as much of the synthesis as possible in Stage II, because the gas is then completely free from sulphur and the loss in activity is very much smaller than in Stage I. This will clearly give a maximum catalyst life. Hence only 40 - 50% conversion is aimed at in Stage I.

A reactor is started in Stage II at a gas rate of 600 - 700 cu.m./h. and the temperature adjusted to give 50% conversion, using 192°C. as a limit which must never be exceeded. It usually stays nearly three months in this stage, and of this time, 8 - 10 days are normally spent below 185°C.

It is then switched to Stage I, the temperature being lowered to 170°C. to begin with, and being increased to 192°C. in the course of some 30 days. The gas rate is 900 - 1,000 cu.m./h. The first regeneration by solvent extraction is then done. After two more weeks synthesis, the second solvent extraction occurred, and after this they were done

at intervals of one week. These latter extractions, the third and subsequent ones, were followed by treatment with hydrogen (86%) at 200°C. The highest temperature allowed for synthesis was 198°C. These principles are illustrated by the data in Tables 14 and 15. Table 14 gives the quantities and compositions of the gas at various stages, and the only comment necessary is that small adjustments of composition are made by adding unwashed converted water-gas before Stage I, and more converted water-gas, from which the bulk of the carbon dioxide has been removed by Alkazid washing, is added for the same purpose before Stage II. Table 14 gives the details of temperature, gas-rate, solvent extractions and hydrogen treatments for one filling of one block of four reactors. The extraction on the 277th day was the final one, and when it was completed the reactors were discharged. This operation together with refilling occupied four days, after which time synthesis was restarted immediately.

The details given in Table 15 are not rigidly adhered to, and the following types of deviations may be made. The actual gas rates, although usually within the limits indicated, vary from block to block of reactors according to the activity of the catalyst in each. If for any reason, such as more reactors than normal being out of commission, more synthesis gas is available than would otherwise be the case and the gas rate has to be increased to utilize this gas. It is not yet decided whether, after switching to Stage I, a reactor should be left for 30 days before revivification, or whether it is better to do the solvent extraction after 10 days. Both methods are used.

Essener Steinkohle are strongly of the opinion that three stage working would be better than the present two stages, and their present practice, already mentioned, of starting up freshly charged reactors with a mixture of synthesis gas - II and residual gas is a step in this direction.

Table 14.  
Gas Compositions. Essener Steinkohle.

	Coke- oven gas	Synthesis Gas (unpurified)	Converted Water-gas (unwashed)	Synthesis Gas I	Converted Water-gas (Alkalid-washed)	Synthesis Gas II	Residual Gas
Gas Rate cu. m./h.	23,800		1,000	72,500	1,000	38,000	21,000
Composition							
CO <sub>2</sub>	2.0	4.7	22.9	4.9	1.0	11.1	21.8
CnHm	1.9	0.3	0.3	0.2	0.2	1.8	0.3
O	0.1	0.1	0.0	0.1	0.0	0.1	0.1
CO	7.3	28.6	2.3	28.0	3.0	20.2	8.9
H <sub>2</sub>	60.5	56.2	65.8	56.1	84.3	38.8	15.5
CH <sub>4</sub>	24.7	4.9	3.2	4.9	4.8	16.4	31.5
N <sub>2</sub>	3.5	5.0	5.0	5.8	6.7	11.6	21.9
H <sub>2</sub> /CO		1.95		2.00		1.92	1.75

Table 15.

Synthesis Details for one Filling of one  
Block of Reactors, Essener Steinkohle, 1944.

	Time days	Temp- erat- ure, °C	Gas-rate, cu. m./h.	Solvent Extraction	Hydrogen Treatment	Wax recovered, kg.
Stage II	36	190.5	1010			
	66	190.5	840			
	95	191.5	820			
	105	192.0	820			
Stage I.	106	185.5	980			
	113	190.5	980	*		9310
	114	182.5	1070			
	134	191.8	1020	*		8830
	135	185.5	1050			
	160	193.0	960	*		6380
	161	184.0	960			
	177	194.0	1050	*		2560
	178	188.0	960			
	196	195.0	1030	*		2450
	197	192.8	1040			
	214	195.5	1050	*		2270
	215	193.7	1100			
	218	195.2	1100		*	
	219	181.3	1050			
	232	195.0	1070	*		5400
	233	191.5	920			
	238	193.2	900		*	
	239	180.5	1070			
	251	195.5	1090	*		3130
252	194.5	940				
253	186.0	1000		*		
273	197.3	870				
274	194.1	900		*		
277	195.5	1020	*		640	
						40960

Rheinpreussen.

The original method of working used by Rheinpreussen was to aim at a big conversion in the first stage and a smaller one in the second stage, and to use a high gas rate and obtain a high plant output. During the war years Rheinpreussen tried to work their plant with the Essener Steinkohle method, but the comparison was not a fair one for a number of reasons. Firstly they had not sufficient reactors available to allow them to use the very low gas rates recommended by Essener Steinkohle. Then, since their hydrogen plant was destroyed early in 1942 they could not follow up solvent extraction by hydrogen regeneration, as Essener Steinkohle did, and as a result, the catalyst life was only some 5 months and the specific yields were rather low. For the same reason they could not adjust the  $H_2/CO$  ratio in the gas for Stage II to 2 by adding hydrogen. And finally they could not start synthesis with residual gas before putting the reactor into Stage II, as the pipelines were not suitably arranged.

These differences are probably responsible for the different effects observed at the two works. For example, Essener Steinkohle said that the longer a catalyst was kept in Stage II the longer its total life, since it is not poisoned at all in Stage II. Rheinpreussen could not confirm this, and found, in fact, that the catalyst was poisoned as quickly in one stage as in another. This difference may be due to the lower  $H_2/CO$  ratio used by Rheinpreussen for Stage II, which was 1.7 - 1.8 instead of 2. The same explanation may also cover the fact that Rheinpreussen never observed 'bolting' whereas Essener Steinkohle frequently did. And this in spite of the fact that Rheinpreussen used a gas with 40% ( $CO + H_2$ ) for starting synthesis in Stage II, which is a much richer gas than that used by Essener Steinkohle. Another difference is that the residual gas at Rheinpreussen had  $H_2/CO = 1.3$ , whereas for the other atmospheric pressure plants this ratio never fell below 1.5 to 1.6. Thus, during the synthesis, the water-gas shift reaction occurred to a greater extent at Rheinpreussen than elsewhere.

The result of this attempt of Rheinpreussen to divide the conversion equally between the stages in the Essener Steinkohle way was that worse yields were obtained. Hence they concluded that for their plant, and with its limitations, their original method was the better one, and they



went back to it before they were finally shut down, and the yields obtained increased again to the former values. But in spite of this, Rheinroessen think it is probable that if a new plant had to be built, it would be best to plan it for the Essener Steinkohle method of operation.

#### Ruhrchemie.

A freshly charged reactor is always started up in Stage II, where it is put under gas pressure and heated to 100 - 125°C. and kept for 5 hours at that temperature without gas passing through. Gas is then passed at 250 cu.m./h. and the temperature increased at a rate of 5°C/h. till 160°C. is reached, and then at 1°C/h. till the contraction reaches 60%. The gas rate is then increased to 500 cu.m./h. and as a result the contraction falls to 40%. The temperature is then increased at 1°C/h. until the contraction reaches 45%, when the gas rate is increased to 1,000 cu.m./h. As before, this causes the contraction to drop to 40% and it is again restored to 45% by increasing the temperature at the same rate as before. The gas rate is then put up to its final value of 1,400 cu.m./h. and the temperature increased, still at the same rate, to give a contraction of 55 - 60%. Whichever the temperature is only increased to maintain the contraction. Further details are given by the full curves in Figure 3.

For synthesis, the aim was to get the same yield of products/reactor/day - about 2 t. - both for Stage I and Stage II. The same contraction was obtained, to within some 5%, in the two stages, and the detailed method of working was given as follows:-

The freshly charged reactors are started in Stage II, as described, and remain there till the temperature has reached 150 - 175°C. Regeneration by extraction with solvent, which may be followed by treatment with hydrogen, is then carried out and the reactor put back into Stage II at 175°C. for 2 days. It is then transferred to Stage I. There the first regeneration is done when the temperature has reached 192°C. and synthesis restarted at 180°C. The programme of regenerations in Stage I is as follows:-

1st Regeneration when synthesis temperature reaches					
					192°C.
2nd	"	"	"	"	193°C.
3rd	"	"	"	"	195°C.
4th	"	"	"	"	198°C.
5th	"	"	"	"	200°C.
(6th	"	"	"	"	203°C.)

In both stages the normal rate of increase of temperature is 1° every 2 - 3 days.

During the period in Stage I the maximum gas rate is 1,000 - 1,200 N. cu.m./h. at the beginning, and this is decreased at about 100 cu.m./hour/month until at the end of four months the rate has fallen to 800 cu.m./h. Further details are given in Figure 4.

The working of the whole atmospheric pressure plant is illustrated by the following data for the period 1943-4. A volume of 17,200 cu.m. synthesis gas-I was available per hour and was passed through Stage I, which was worked to a contraction of 49.3%. The residual gas was used directly in Stage II where the contraction was 35.9%. Analyses are given in Table 16.

Table 16.

Gas Analyses. Ruhrchemie, 1943-4.

	Synthesis Gas-I	Synthesis Gas-II	Residual Gas-II
CO <sub>2</sub>	14.4	29.6	44.2
C <sub>2</sub> H <sub>6</sub>	0.0	1.5	2.0
CO	26.7	17.8	9.7
H <sub>2</sub>	53.2	33.7	16.0
CH <sub>4</sub>	0.4	7.0	13.2
N <sub>2</sub>	5.3	10.4	14.9

It should be emphasized that the method of working just described must not be judged unfavourably on account of the very bad performance of the Ruhrchemie atmospheric

pressure plant. They themselves said that this was due to a number of very different causes, thus they had an insufficient supply of water-gas, and the composition of this gas <sup>variable</sup> was due to variations in the quality of the coke, which came from outside sources. There were also frequent interruptions in the supply of electricity. In addition, since a large amount of experimental work was done on the full scale, the plant could not be run to its maximum efficiency. When insufficient gas was available for the whole plant, the atmospheric pressure plant had to bear the full loss, so as to keep the requisite amount of gas available for the efficient working of the medium pressure plant, which Ruhrchemie considered the more important. They stated definitely, however, that when the supply of gas was satisfactory, so was the performance of the atmospheric pressure plant.

#### Brabag.

Except for a few experimental reactors, no provision had been made by Brabag for switching reactors from one stage to another, so that all catalyst that was to work in Stage I had to be started in that stage. This was done by starting at 160°C. at one third the normal gas rate. The gas rate and temperature were then gradually increased during a period of 10 - 14 days to 12,000 - 1,300 cu.m./reactor/h. and 185°C. respectively and it was important not to keep the temperature low for too long a period or too much wax collects on the catalyst and the activity decreases accordingly.

On the laboratory scale a catalyst may be started successfully with a low gas rate at 185°C., but on the full scale the nearest approach that can be made to this is to increase the temperature to 185°C. in 7 - 10 days.

The plant was arranged with 222 reactors for Stage I and 40 for Stage II, Stage I consisting of the original Schwarzheide-I plant plus part of Schwarzheide-II, and Stage II of the remaining 40 reactors of the Schwarzheide-II plant.

The general principle of working was to have a conversion of carbon monoxide,  $U_{CO}$ , of 60 - 70% in Stage I and about 94% for both stages, the proportion of the reacted carbon monoxide going to form methane being 13 - 16%. To get the best results in this way the temperatures used throughout the whole plant were kept as

low as possible, the increase above 185°C. being made very slowly. Before 1943-4 this was not clearly realized, and the temperatures used were too high, with the result that the specific yield was then only 143 instead of 165 g./N.cu.m. inert-free synthesis gas, the amount of carbon monoxide reacting being the same, on account of a higher methane formation due to the higher temperature. The lowering of the temperature effected in 1943-4 not only improved the specific yield but also the yield/reactor/day, a result which might not have been expected to follow from a decrease in temperature.

Solvent extraction was originally done every 600 hours, but the latest practice was to carry out a solvent extraction followed by an hydrogenation every 400 hours. The more frequent extractions produced more hard wax, but the amount of the soft wax may actually have been reduced.

The catalyst life was deliberately limited so as to keep the output from the plant high, and after 2 million cu.m. ideal gas had been passed through a reactor in Stage I, or 4 million cu.m. for Stage II, the catalyst was replaced by a fresh charge.