

## Purification of Synthesis Gas

### Removal of Dust.

Ruhrchemie agree that the most satisfactory solution of this problem is to install an electro-filter, as Brabag have done and as Hoesch proposed doing. They consider that the composition of the dust is of greater importance than its quantity, and they experienced more trouble with it than the other synthesis works because in their case the dust was very sticky as it contained some 40 - 50% elementary sulphur. This made it adhere firmly to the blades of the circulating pumps.

Ruhrchemie went some way towards solving the problem by using the plant for the removal of hydrogen sulphide as a filter to protect the pumps from this dust. To do this, the purification system was arranged in the following order: Removal of  $H_2S$  - Pumps - Removal of organic sulphur. This scheme is by no means perfect, however, because the dust which is filtered out of the gas by the Luxmasse used for removing  $H_2S$  makes the whole of this material sticky, and so increases its resistance to the flow of gas. Hence to prevent the pumps producing a dangerous reduced pressure in the  $H_2S$  - removal plant, the gas flow through the latter had to be reduced from 80,000 to 65,000 cu.m./h.

Essener Steinkohle used a less drastic modification of the normal plant arrangement. They used a low speed pump before the  $H_2S$  - removal plant and a high speed one after it, as they found that less of the sticky dust adhered to the blades of a pump that was being run at a low speed.

#### Removal of Hydrogen Sulphide.

This was done by Ruhrchemie in a plant built by Klönne, Dortmund, consisting of 8 tower purifiers. Each tower was 9.8 m. high and 11.3 m. diameter and contained about 600 t. purification material arranged on wooden frames in sixteen layers, each layer being 400 mm. high. The gas passed through the layers in parallel. The eight towers were arranged in two groups of four, the two groups being used in parallel. Each group had three towers, arranged in series, in use and one in reserve. They are filled either with pure Luxmasse, or with a mixture of 70% new Luxmasse and 30% used material and the temperature is somewhere between 20 and 40°C. Each charge lasts from 6 - 8 months, after which time it contains about 45% sulphur, calculated on the moist material, when it is sold for the recovery of the sulphur. Each group of four towers purifies 40,000 cu.m./h. synthesis gas, reducing the sulphur content from 3 - 4 g./cu.m. to 0.05 - 0.10 g./cu.m. Before the gas enters the purifiers sufficient air is added to bring the oxygen content up to 0.4%. Of this, 0.2% is necessary for the separation of the sulphur in the purification material, and the remaining 0.2% is required for the conversion of sulphur to sodium sulphate in the plant for removing organic sulphur compounds.

Ruhrchemie see no advantage in replacing some of the Luxmasse by exhausted material from the organic sulphur-removal plant, which has been reactivated by standing in moist air for several months, although both Essener Steinkohle and Rheinpreussen do this.

Removal of Resin-Forming Compounds.

The following account of this matter was given by Dr, Grimme of Rheinpreussen:-

When Rheinpreussen first cracked coke-oven gas in the generator, for adjusting their synthesis gas composition, they experienced trouble in the plant for the removal of organic sulphur, which ceased to purify the gas sufficiently. Recognizing that it was the use of coke-oven gas which caused the trouble, coke-oven gas alone was passed over a sample of the purifier material and it was found that all purification ceased in about 30 minutes and the material was left in such a state that it would not purify ordinary water-gas. On continuing to pass water-gas for several weeks, the activity was to some extent restored. This effect was traced to the small amount of oxygen in the water-gas, and the more oxygen present, the more rapidly was the activity restored.

These results gave rise to the idea that the purifier material was coated with some organic substance, resin, for example, which prevented it working properly. This was confirmed as follows: If a piece of purifier material after normal use is broken and the sulphur determined at various depths from the surface, it is found that sulphur does penetrate slowly to the interior of the pieces. For material that has been treated with coke-oven gas, however, no penetration of sulphur into the interior is observed. If the material that has been exposed to coke-oven gas is extracted with benzine at the boiling point nothing is removed, but extraction under pressure at 200°C. removes small quantities of resinous material.

Small amounts of a number of unsaturated compounds which might be expected to form resins were then added to pure water-gas and passed over the purifier material. Styrene, indene, cumarone, hydroxy-compounds, acetylene, mixtures of these substances, and mixtures of them with thiophene and other sulphur compounds were tried and no harmful effect was observed in any case. They simply polymerise to liquid condensates which are harmless. It is to be noted that all these substances react positively to the Egloff test with formaldehyde for resin-formers, but a positive reaction to this test means nothing, as Brabag have found that pure benzene itself reacts in this way.

Dr. Grimme thinks that the formation of resin on the material used for the removal of organic sulphur is due to the polymerisation

of some of the more ordinary unsaturated constituents of the gas under the influence of some catalyst present in coke-oven gas but not present in water-gas. This would explain the negative results obtained by the introduction of pure unsaturated compounds into water-gas. Oxides of nitrogen were tried but they did not act as catalysts, and the latest idea was that diacetylene, which is present to the extent of 0.03% in coke-oven gas, may be the cause of the polymerization.

Rheinpreussen then found that if the synthesis gas made from cracked coke-oven gas, and containing the harmful resin-forming component, is passed through active carbon, the resin-forming compound is removed and the gas no longer poisons the purifier material. If the condensate removed from the active carbon by steaming is re-introduced into the purified synthesis gas in the original proportion, the gas again poisons the purifier material. Rheinpreussen sold this process to Lurgi, and it was on the basis of the work at Rheinpreussen that the active carbon purification plant at Essener Steinkohle was built by Lurgi.

For themselves, however, Rheinpreussen found what they considered to be a more economical solution by changing over to an arrangement in which the coke-oven gas is cracked in a separate unit at 1500 - 1550°C. instead of at 1200 - 1300°C., as is the case for cracking in the generator. All organic compounds are destroyed in this way and the gas produced is completely inactive to the formaldehyde test and forms no resin on the purifier material. The high temperature mentioned is absolutely essential, 1300 - 1400°C. is not sufficient. Schaffgotsch agreed with Rheinpreussen and proposed to alter their plant in the same way.

Essener Steinkohle, however, are firmly of the opinion that the active carbon solution is the preferable one on economic grounds, pointing out that in their case the active carbon plant cost RM. 1,000,000 whereas an external cracking plant would cost exactly three times as much. In connection with the running of the plant, they point out that one of the factors affecting its efficiency is the amount of water vapour in the synthesis gas. In their case this was high and as a result, the absorbers had to be changed every 10 hours, as they rapidly become saturated with water, instead of every 70 hours. They were not certain whether the active carbon plant performed any other useful function in addition to removing the resin-forming compounds. When they installed it the catalyst life increased from seven to nine months, but this may have been due to other changes introduced at the same time.

Erabeg investigated this point in one section of their works. Although they had no evidence for the formation of resins in their plant for the removal of organic sulphur, they installed one active carbon unit and investigated its effect over two years. Only part of their gas could be treated in this way, but catalyst which was run on gas which has been so purified had double the normal life. They thought that this was due to the removal of organic sulphur compounds like thiophene which are present to a large extent in the condensate removed by the active carbon, and which normally pass all the purification stages in considerable amounts. The active carbon plant at Essener Steinkohle also produced condensate containing sulphur compounds, and as this was so small in quantity compared with the final products produced by the synthesis it was mixed with them and sold without in any way harming their quality.

It was generally agreed, however, that the removal of resin-forming constituents, whether done by active carbon or by external cracking, decreases the cost of purifying the gas from organic sulphur compounds considerably, because of the reduction in the amount of labour required for charging the purifier material.

#### Removal of Organic Sulphur Compounds.

This is done by passing the gas over alkali-d lumnase at 200 - 260°C. The Ruhrchemie plant for this process was built by Kilmann, Dortmund, and consisted of five groups of towers and one final purification tower. Each group contained a preheater and two towers, each of 4.2 m. diameter and 10.5 m. high. Two types of tower were used. In the 'basket type' the purification material is held in a number of separate containers which are charged externally and then lowered into the tower, which holds 6 or 8 of them. The internal arrangements of the tower are such that the gas passes through the containers in parallel. The second type of tower contains two co-axial vertical sieves, between which the purification material is held in a layer 0.9 - 1.0 m. thick. The basket type of tower can be charged much quicker and the purification material has a longer life in it than in the other type, but difficulty is sometimes experienced in sealing each container into place inside the tower, the gas-tight seals being made with finely powdered purification material. Each of these towers in the Ruhrchemie plant holds 60 t. purification material, but the newer ones of Essener Steinkohle hold 100 t. The only advantage of the screen type of tower is that it is cheaper to construct. The screen type towers of Ruhrchemie hold 70 t.

purification material each. The preheater consisted of a combustion chamber where residual gas from the synthesis was burnt at 600 - 900°C., and a bundle of steel tubes, made of heat-resisting steel at the lower, hot, end, and of ordinary steel at the upper, cooler, end. The incoming gas first passed through a heat exchanger, then through the bundle of tubes of the preheater and then entered the first tower. On leaving this tower it was cooled in the heat exchanger already mentioned to the temperature required for the second tower, which it then traversed. Each group of two towers normally dealt with 17,000 N.cu.m. gas/h. but the rate could be increased to 20,000 N.cu.m./h. if necessary. The space velocity was about 200/h.

On leaving these five groups of purifiers, the gas enters two final purification towers, arranged in parallel. No preheating is required. This last stage of purification is put in as a safety measure, because when a tower in the main purification system is refilled the new material does not begin to work immediately.

The method of working the plant is seen from the data in Table 4.

Table 4.

Method of Working the Plant for the Removal of Organic Sulphur  
(Ruhrochemie)

Days	Temperature °C.		Sulphur g./100 cu.m.					
	Tower 1	Tower 2	Before Tower 1		Before Tower 2		After Tower 2	
			Org.S.	H <sub>2</sub> S	Org.S.	H <sub>2</sub> S	Org.S.	H <sub>2</sub> S
2	200	180	2.30	20.20	< 0.05	4.20	< 0.05	< 0.05
18	230	200	3.10	20.10	< 0.05	5.20	< 0.05	< 0.05
33	255	215	3.40	20.40	< 0.05	5.20	< 0.05	< 0.05
43	270	220	3.50	20.10	0.09	6.20	0.12	0.20

The temperatures given in the table refer to the gas leaving the tower concerned. The data are for gas rates of 16,000 to 18,000 cu.m./h. and for charges of 60 t. purification material in each tower, and they show that for these conditions the life of the material was 45 - 50 days.

As was mentioned in connection with the removal of hydrogen sulphide, the gas entering the plant for the removal of organic sulphur contains 0.2 - 0.3% oxygen. The main function of this is so to direct the reaction that the sulphur is retained in the purifying material as alkali sulphate and not as iron sulphide. Lurgi say that it also has the useful effect of preventing the iron oxide being reduced to metallic iron. If the oxygen content of the gas is too low, or the temperature too high, reduction does occur, and as a direct result of this, carbon formation.

The purification material used consists of Luxmasse with 33% soda, made up into granules of 10 - 15 mm. size, in the Ruhrchemie catalyst factory. The cost of making this material is analysed in Table 5. Capital charges are not included.

Ruhrchemie had done experiments with material containing 50% alkali and these were successful on the laboratory scale. Full-scale tests were inconclusive, however, on account of other disturbances in the works.

They had done no large scale tests with Brabag's highly porous materials. Brabag still used this purifier material in 1944 and considered it to be superior to the normal preparation. In judging this highly porous material, however, it must be remembered that the problem of removing organic sulphur from the Brabag gas was rather different from the problem of the other licensees, because Brabag's gas, prepared directly from brown coal, contained a large amount of condensate - benzene, toluene, naphthalene, thiophene, thiotolene, thionaphthalene and so on - and conditions in their plant for removing organic sulphur were always such that about one quarter of the thiophene and even some of the carbon disulphide passed through unchanged. The Brabag highly porous material was more active, particularly in dealing with aromatic sulphur compounds, but had a considerably shorter life than the ordinary Ruhrchemie preparation.

Table 5.

Cost of Preparation of Purifier Material for Removal of Organic Sulphur (Ruhchemie)

	Quantities		Costs, RM	
	Total	per t.	Total	per t.
Input				
Calcined Soda	2,992,438 kg.	0.274 t.	244,992	22.43
Luzmasse	15,732,690 "	1.440 "	<u>276,143</u>	<u>25.27</u>
			521,135	47.70
Working Costs				
Wages			121,885	11.15
Salaries			16,885	1.55
Electric				
Power	249,290 kwh.	22.799 kwh.	5,816	0.53
Steam (18 atm)	32,567 t.	2.981 kg.	155,018	14.19
Various				
Materials			3,854	0.35
Repairs and				
Maintenance				
Labour			99,637	9.12
Materials			9,566	0.88
Transport				
Charges			13,910	1.27
Insurance				
and Dues			449	0.04
Despatch				
Costs			12,995	1.19
Soda Storage			7,056	0.65
Laboratory			13,063	1.20
General			52,252	4.78
Administra-				
tion			<u>11,379</u>	<u>1.04</u>
			523,769	47.94
Input and				
Working Costs			1,044,905	95.64



All the synthesis plants, whether atmospheric or medium pressure ones, removed the organic sulphur from the synthesis gas at atmospheric pressure in the way described. Lurgi think that for a new medium pressure plant it would be advantageous to remove the organic sulphur after compression and this was to be done in the new plant designed for the Società Italiana Carburanti Sintetici (Arezzo). With this in view, they conducted pilot plant experiments at a space velocity of 400, i.e., twice the normal rate. Their first attempt was made in a wide tube with external electrical heating and this was not successful because the middle of the tube was too cold for efficient purification while the walls were at a temperature high enough for carbon formation to occur. They then stopped using the electrical heating, insulated the tube thermally and preheated the gas. In this way the plant has been run successfully for several weeks, but the life of the purifier material has not yet been determined.

Ruhrcbenia had also investigated the removal of organic sulphur compounds at medium pressure. They carried out laboratory tests using 1/10th the normal gas rate, but with the usual purification material and the same temperature range, and under these conditions the results were satisfactory. Thus at a gas rate of 50 - 100 N.litres/h./100 g. material, and with water-gas containing 17 - 18 g. organic sulphur/100 cu.m., at atmospheric pressure the organic sulphur was reduced to below 0.02 g./100 cu.m. until 25 cu.m. of gas had passed, and after this stage the sulphur passing through increased rapidly. In a parallel experiment at 10 atm. pressure the sulphur rose steadily to 0.10 g./100 cu.m. during the passage of the first 14 cu.m. of gas and remained steady at this figure till 38 cu.m. of gas had been passed, when it increased rapidly.

Finally, it should be mentioned that when the organic sulphur has been removed as completely as possible by the methods described, the Germans consider that it would be advantageous to pass the gas through an active carbon unit to remove condensate formed in the last stage of the purification from organic sulphur. Experimental results have shown that it would pay to have such an arrangement in the large plant.

#### Costs for the Purification of Synthesis Gas.

Ruhrcbenia gave the following figures for the year 1943-4:-

Purification from hydrogen sulphide	0.05 Rpfg./cu.m.
Purification from organic sulphur	0.10 Rpfg./cu.m.

These costs do not include capital charges, which can, however, be estimated from the capital cost of the various items of plant, which are as follows:-

	RM
Circulation Pumps <sup>1</sup>	389,666
Plant for removing hydrogen sulphide	1,021,367
Plant for removing organic sulphur	1,060,521
Crane installation for the above	71,287