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RECENT EXPERIENCE IN FINAL GAS PURIFICATION, BY DR. FRANÇOISE,
BRABAG, SCHWARZHEIDE, FROM SYMPOSIUM OF THE SYNTHESIS WORKS
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We have arrived in the course of our development work of the final purification of the synthesis gas in Schwarzeide at some results which must be reported today even if in some respects they are still experimental and do not seem to be sufficiently tested in operations. We have found that an increase of the size of the pores of the final purification mass from about 50 to 70% has resulted in an important improvement in the elimination of organic sulfur, and, second, that this improved purification effect takes place already at temperatures which are on the average 60-70°C lower than the temperature at which the purification mass was formerly used.

We must, however, emphasize that our experience so far extends only to the organic sulfur in the Schwarzeide synthesis gas which is made from brown coal briquettes in Koppers and Didier installations, with dust removal by electrostatic precipitation and elimination of H₂S by dry purification before being subjected to fine purification.

The total sulfur content of the brown coal is 0.5-0.8% of which 50-60% form volatile sulfur, and our synthesis gas contains about 2.5-3.5 gm organic S/100 cbm before the final purification.

This organic sulfur content is not high in comparison with the other synthesis plants, but its composition varies a great deal.

A number of aromatic sulfur compounds have been found in the Schwarzeide gas in addition to carbon bisulfide, mercaptans, e.g. thiophene, thiotoluene, thionaphthene, and in addition we know that an appreciable amount of residual

sulfur exists in unknown combination forms. For this reason our synthesis gas contains a number of condensates, which make final purification more difficult.

With the conditions as they existed, it was impossible to obtain values of below 0.2 gm organic S/100 cfm synthesis gas by using the usual purification mass, and to obtain the required constant results for the synthesis operations.

For this reason a number of laboratory and production scale tests were made, which did not, however, result in any important improvements.

A first indication of possible success was obtained when we investigated also the comparative tests with a coarse grained mass particle diameter about 10 mm with a fine grained mass diameter about 2 mm. During the course of these tests we have found that reduction of the coarse particle size to about 1/5 of its diameter changed not one but two properties, increasing the surface as well as the pore size by about 10%.

We did not know at first to what to attribute the improved purification properties of the fine particles found in these tests.

We now undertook large number of tests on porosity, and they showed us soon that a maximum porosity of the mass is of deciding importance in the final purification.

We must point out two facts before describing the preparation of such a highly porous mass:

- 1) Drying the lanta mass with 50% water, as used as the raw material for the preparation of our final purification mass, to a water content of 4-0%, the average porosity of the particles is 80-85%.

- 2) If a final purification mass is prepared from the same lanta mass by mixing the lanta mass with calcined soda, as is usually done now, an average porosity of 45-50, maximum 55% is obtained.

A new method must therefore be found to avoid this loss in porosity or else limit it to a permissible magnitude.

The lanta mass itself gave excellent results in the fine purification tests in the laboratory when its porosity was 80%, but its use in actual operations did not appear desirable, because the strength of the particles with an 80% porosity amounted to only 1.2 kg/cm², and moreover because its alkali content was too small and varied too much, between the limits of 2-12%, mostly between 5-6%.

We were thus forced to mix the lanta mass with soda to obtain a final purification mass with a definite and higher alkali content and with mechanically stronger particles.

The addition of a fine grained calcined soda to a lanta mass containing 50-60% water, as is commonly done, the temperature rises considerably during mixing because of the interaction of soda with the water, and the mixture becomes pasty to viscous. The granular structure of the lanta mass was largely lost and the porosity dropped by 50%.

Should we, however, avoid the formation of the pasty or the viscous state of the mixture of soda and the lanta mass when preparing the final purification mass, masses with a porosity e.g. of 70% were easily obtained. It is merely necessary for this purpose to limit the reaction between the calcined soda and the water of the lanta mass.

This can be done in a very simple way by mixing the soda with a suitable amount of pre-dried lanta mass, and then adding the balance of the mass. We say, for example, proceed as follows:

100 kg of a lanta mass containing 2% alkali and 50% water are divided into two parts, one part dried, mixed with about 5 kg soda, and then added to part two. The crumbly mixture obtained will contain about 25% of water and is sufficiently moistened by spraying with a water spray until the

consistency becomes suitable for pressing, then forced through screens and finally dried.

The drying is best made in two steps, at first at 60-80°C until the mass has hardened, and finishing the drying at a higher temperature.

55 kg of final purification mass containing about 15% alkali and with a porosity at least 70%, with strength of the particles of about 3-4 kg/cm² is then ready for use. A 15% alkali content has been selected in this example because experiments have shown that this is the most favorable alkali content of the purification mass.

A comparison of the characteristic values of the new and former final purification masses is as follows:

	Filling Weight	Particle Strength kg/cm ²	Soda Content	Fe ₂ O ₃ Content	Porosity
Mass as formerly prepared	0.7	6-7	30%	36%	50%
New Mass	0.5	3-4	15%	44%	70%

The composition differs considerably. A better explanation of these differences can be seen by comparative tests with the old and new mass in two industrial final purification units of the same construction.

	Total Filling of the Unit	Alkali, as Na ₂ CO ₃	Iron as Fe ₂ O ₃
Old Mass	100.8 to	29.5 to	35.7 to
New Mass	76	12.5	33.8

There is evidently a saving per unit volume in the lime mass and soda when using the new final purification mass. These advantages of the lower filling weight and soda content of the new mass go hand in hand with the disadvantage of the lower particle strength.

A few data are already available on this point from tests during operations. We have loaded two railroad cars with the highly porous mass and unloaded them again, weighed the dust produced, 0-6 mm particle size. We

found 13.8 and 17% dust in comparison with the old mass treated in the same way which gave 8.9 and 8.7% dust of the same particle size. We may summarize the results of the comparison of the filling weight and particle breakdown of the masses by saying that one ton of the highly porous final purification mass will fill about 20% more purifier unit space.

The porosity of the new mass is 70%, that is the inner surface of the iron compounds exposed to the gas is about 40% higher than with the mass having a pore volume of about 50%.

The fact that the total amount of iron in the purifier is now reduced by about 8% is of no importance, because our experience in Schwarzheld is that the final purification mass can become saturated on the average only to about 10% with sulfur, because of other effects such as carbon deposition, crust formation on the surface by condensation residues and so forth, will ruin the mass before it is exhausted. The purification results obtained so far with the new mass confirm this impression. A comparison was made in the laboratory test of 8000 hours duration in which masses of 50 and 70% pore volumes were compared at the same temperature and load. The mass with the 50% pore volume had 1.0 gm residual organic S/100 cbm gas, corresponding to an absorption of 70% of the total sulfur; while the mass with the pore volume of 70% absorbed 95.8% of the organic sulfur and transmitted only 0.1 gm organic S/100 cbm of gas. A single purification tower was used in both tests, which was a simplification frequently used in the laboratory when determining the usefulness of a final purification mass.

We soon found in addition that better purification results could be obtained with the new mass at lower temperatures than were formerly used in the final purification. This fact is important for several reasons. It represents a saving in fuel gas, the equipment is less severely used, the undesirable side reactions are avoided with the synthesis gas such as carbon deposition and the re-formation of condensates, which were invariably

observed when the final purification was done in the temperature interval of 230-320°C.

We will illustrate the effects of the lowering of the temperature and simultaneous improvement of the purification of the synthesis gas by reporting here two tests which have not as yet been completed but which already furnish valuable data.

In comparative tests with old and new mass of 100 days duration, the following average temperatures and average sulfur values have been found:

Mass I with 50% porosity was used at an average temperature of 200°C in the A tower and at 187°C in the B tower, while the new mass II was held at only 164°C in the A tower and 158°C in the B tower. The average sulfur values were 0.21 gm/100 cbm behind mass I and only 0.09 gm/100 cbm behind mass II in spite of the same lead and composition of the gas. This permitted us in Schwarzheide to obtain for the first time average sulfur values of below 0.1 gm/100 cbm.

The advantages of the new mass are still more prominent in test operations in more recent times where the final purification system was started at 80°C, i.e. at a temperature about 100°C lower than ordinarily used.

After 23 days of operation the highest former sulfur value in the purified synthesis gas was 0.11 gm/100 cbm, with an average sulfur value of only 0.06 gm/100 cbm, and the average temperatures in the A and B tower were 87 and 81°C. We regret to be able to report results with the new mass over a period of only 23 days, but the results obtained are already very significant. We realize that considerably more material will have to be collected before passing final judgment on the new final purification mass, but the success already obtained shows definitely that the hope is justified of lowering the sulfur values in the Schwarzheide synthesis gas to partial pressures which are harmless to the synthesis catalyst. In the subsequent

discussions questions were raised whether this highly porous mass could be used for the purification for a gas of higher sulfur content, but this was denied. Lutzkendorf at present is making tests on which nothing can as yet be reported.

Feisst asked whether the abrasion of the new mass was higher in operation than of the former mass because the strength of the particles is lower. While the abrasion is higher, no difficulties have been caused by that during operations.

Braunes inquired whether the new mass could be used at the same load per unit as usual, i.e. 14-15000 m³/hr and with an 0.4% by volume of oxygen addition for the final purification. This addition of oxygen is necessary in Schwarzhöhe, although 0.2-0.3% of the oxygen added still remains in the synthesis gas after final purification. No effect has been observed of this amount of oxygen upon the synthesis catalyst. Pilot plant experiments in Schwarzhöhe have shown that only 0.5% oxygen content becomes harmful. These observations agree with the experimental results in the Chemische Werke, Essener Steinkohle and the Bahrenstein.

Schwenke states that an activated charcoal installation is being installed for the preliminary purification of synthesis gas prior to the final purification, and that results will become known before the end of the year. Schwenke asks whether Schwarzhöhe intends the installation of the activated charcoal unit to remove the condensables from the synthesis gas. Hochschwonder denies this because the low sulfur content at present observed no longer makes the question so urgent as it formerly was. Feisst asks whether any change has taken place in the amount of condensables in the synthesis through the use of the new mass. Franschke believes some reduction has taken place, but this subject is still being investigated. It is intended to make a complete report about it at a later date.

~~Martin inquires whether highly porous mass was used in both towers of the final purification system, or whether the usual mass is used in the first tower and the new mass in the second tower, and whether the new mass is appreciably more expensive to produce. Hochschwender and Kollmar have replied that no two stage operation is being anticipated and that the economics have at present not been fully studied. It is, however, pointed out that any possible higher production costs and any increase in cost resulting from the lower charge will be either compensated or possibly exceeded by savings in the fuel gas because of the lower operating temperature and the lower soda contents.~~

Grims has stated that when the final purification mass is used with the usual oxygen addition all the sulfur becomes converted to sodium sulfate. He believes therefore that with a smaller sodium carbonate addition to the new mass, the saturation limits of the mass should be lower. The saturation limits of the mass have not as yet been determined in Schwarzheld.

Lopmans believes that the irregularity in the final purification masses may be the cause of the different behavior of the different final purification systems. The first variations found were in the porosity. Martin explains these variations by the variations in the consistency of the lux mass used as raw material, which varies very greatly chiefly in its moisture content with the only storage possible today, in the open. A testing of this question is recommended.

Weitenhiller states that the higher the load consistently kept on the different systems, the better the total utilization of the mass.

Kolawski says that the removal of the organic sulfur to 0.1-0.15 gm/100 cbm is done successfully in Schaffgotzen (15 gm/100 cbm of synthesis gas) and that the mass becomes completely saturated. The sulfur here is

believed to enter into combination with the sodium carbonate. No combination has ever been found with the iron.

The highly porous mass can as yet not be delivered to other works because the total production is allocated to the end of the year by the present delivery program. According to this program the only outside plant which will get deliveries is Datschendorf.