Design of Reaction Vessels

Atmospheric Pressure Reactors

As is well known, the reactors for use at atmospheric pressure are of the tube and plate type. They are constructed of ordinary steel, and the tubes are expanded into the plates either by hydraulic pressure or by drawing a steel ball, of slightly larger diameter, through the tubes. Ruhrchemie have reactors made by both methods and they have found that those made in the second way are the most satisfactory.

Two arrangements of the cooling tubes in these reactors have been used. In the 'Sektionalkammerofen' each cooling tube is fitted directly, at each end, into the water chambers at each end of the reactor, whereas in the 'Rohrbogenofen' adjacent or other tubes are combined to give tube coils of different sizes and only each end of each coil is connected to the end water chambers (for further details see B.P. 464 242). In the Ruhrchemie plant the Sektionalkammerofen type of reactor was definitely inferior to the Rohrbogenofen type, but this was said to be due to bad workmanship in their construction. They were supplied by Krupp. Essener Steinkohle's plant contained both types of reactor, and both were supplied by Mannesmann. It was considered that although there was not very much to choose between the performance of the two types, the Sektionalkammerofen was superior as there was less tendency for overheating to occur in this type. Thus the synthesis reaction can get out of control and 'bolting' was actually observed more frequently in the Rohrbogenofen reactors. Against this, it must be remembered that the Rohrbogenofen is RM. 2,000, i.e. 5% cheaper, and is easier to repair in the event of failure than the Sektionalkammerofen. If they had to buy new reactors, Essener Steinkohle say they would buy the Kammerofen type. When they installed new reactors during the war they had to take the Rohrbogenofen type, because these were the only ones being manufactured.

The original reactors in the Gewerkschaft Viktor plant at Castrop-Rauxel had forced circulation at a rate of 120 cu.m./hr. for a water space of 12.5 cu.m. It is estimated that the thermo-circulation in modern reactors occurs at about the same rate. Measurements made by Brabag and Krupp indicated that the temperature in the catalyst is not more than 15°C. higher than the temperature of the cooling water.

Brabag had the older section of their plant (Schwarzeheide-I) arranged with a steam drum for each reactor, but the remainder of the plant (Schwarzeheide-II) was built with four reactors to one steam drum. Essener Steinkohle considered that adequate control could be achieved with this second arrangement. They thought Ruhrchemie's method of connecting six reactors to one steam drum to be definitely worse.

Brabag had an interesting pilot plant consisting of two reactors, so arranged as to copy the conditions in a full-scale plant. Each reactor has a rectangular cross section, 100 x 7 mm. and a length equal to that of a full-scale reactor. These two chambers are embedded in an aluminium block, which is heated electrically, with sectional winding so as to get a constant temperature throughout the length.

Ruhrchemie were asked whether double tube reactors could be used for atmospheric pressure synthesis instead of the tube and plate type now in use. They said that they would be better than the present atmospheric pressure reactors, but pointed out that the double tube medium pressure reactors of the standard pattern could not be used for atmospheric pressure synthesis as they are too high and would have too great a resistance to the flow of gas.

Medium Pressure Reactors, Double Tube Type.

In discussing the standard double tube medium pressure reactors, Ruhrchemie said that although no trouble was experienced due to warping of the double tubes, a great deal of trouble was met with due to welded joints developing leaks, and the reactors supplied by Krupp were the worst in this respect (Ruhrchemie obtained their reactors from Gutehoffnungshütte, Mannesmann, and Krupp; Hoesch-Benzin's reactors were all supplied by Mannesmann and gave no trouble at all). The welds into the tube plates of the Ruhrchemie reactors were all improved by driving in a wedge, after welding, so as to squeeze out any little holes in the weld and so avoid leaks. But it was decided that for any subsequent reactors the design should be so altered as to make the connecting tube 10 cm. above the lower tube plate, because then the joint into the plate could be rolled after welding.

Failure of the welded joints frequently occurs on account of corrosion, and to decrease this it would be advisable to replace the softened water now used in the cooling system by condensed steam. In addition, if a failure does occur and water gets into the catalyst space, the softened water, which is in effect a dilute solution of sodium carbonate, causes the catalyst to set to a solid mass.

The performance of the medium pressure reactors can be judged since each has 0.2 sq.m. cooling surface per litre of catalyst, and whether they are being used in Stage I or Stage II they have to remove the heat evolved by the reaction of 550 – 600 cu.m. ($CO + H_2$) per hour. Of the total heat liberated, some 50% is recovered as steam from the attached steam drums. Although measurements have not been made on the large scale, it has been shown that in the Ruhrchemie semi-technical scale double tube reactors there is a temperature difference of some 10 – 15° between the catalyst and the water, for smooth synthesis.

No difficulties are now experienced due to pressure differences developing across the reactors, or to the gas distribution being bad due to different resistances in the different tubes of the reactor. In the early days of medium pressure synthesis, 1938, the resistances across the individual tubes at the end of the catalyst life sometimes differed by as much as a factor of 3 but this no longer occurs. It was due to partial blockages due to carbon formation caused by faulty technique in conducting the synthesis or by soft dusty catalyst. Since the heat transfer from the very top of each double tube is bad, it was realised that each tube must not be filled to the top with catalyst, but the top 10 cm. must be left empty. Ruhrchemie patented a number of rather elaborate devices for doing this, but they were found to be unnecessary as the desired result is obtained by filling up the tubes to the top and then tapping with a mallet, when the catalyst sinks to the right height in the tubes.

The difficulty about the top 10 cm. of the double tubes being inadequately cooled was also overcome by the so-called 'Wulstofen', in which the steam drum was built into the top of the reactor itself. Ruhrchemie have one such full-scale reactor, and as a result of experience gained with it, they consider that the advantage obtained in this way is negligible. It has the advantage, however, that each reactor can be controlled separately.

The construction of a Wulstofen is more difficult and needs more material that the normal medium pressure reactor and this is not completely offset by the saving in not having to provide steam drums. It is thought that for large plants it would not pay to have Wulstofen reactors, but that it might well be advisable to use them for a small plant, with 20 - 50 reactors, as the extra cost is then not as important. The reactors that were proposed for the plant designed for the Societa Italiana Carburanti Sintetici (Arezzo) for synthesis with iron catalysts at 240 - 260°C. were of this type, but modified to withstand the higher pressure in the water-steam space, which, for such temperatures, must go up to 50 atm. The diameter of the reactor was reduced to 2,570 mm., internal diameter and the wall thickness of the parts exposed to the high pressure increased to 65 mm., as compared with 28 mm. for the ends of the gas space. There were 1,880 tube elements, each 4,800 mm. long. It was the opinion of Lurgi that although double tube reactors are the best type for temperatures up to 230 - 240°C., the tubes might tend to warp at the higher temperatures that were envisaged for the Italian plant.

Other Medium Pressure Reactors.

Several attempts have been made to use reactors in which the catalyst is contained in single tubes. Ruhrchemie found thât a reactor constructed with single tubes 10 - 14 mm. internal diameter would be superior to the ordinary double tube reactor, but it would be far too expensive on account of the very large number of tubes that would be required.

Krupp have always used wide tube reactors with metallic insertions, and Ruhrchemie had a semi-technical scale plant of this type, with tubes 65 mm. internal diameter and insertions of the shape shown in Figure 1 (c). Of the cooling surface, 16% is directly cooled by the water. In this apparatus carbon was always produced at the beginning of a synthesis run and the amount of methane was 10 - 12% more than is normally formed. It is thus definitely worse than the double tube reactors, and the same applies to the wide tube reactors of Schaffgotsch. This company were so convinced of this that they dismissed Kowalski who was responsible for the adoption of these reactors.

It should be emphasized here that although such reactors would be more successful with synthesis gas recirculation, it is not permissible to reduce the cooling surface in this way for water-gas recirculation, because in that case, although methane would not be formed in excessive amounts, the catalyst would be damaged by carbon formation.

Ruhrchemie had one full-scale 'Drucklammellenofen' which was, in effect, an atmospheric pressure plate and tube reactor put in a pressure resisting case. Lurgi had such a reactor, 4/5ths of the normal full-scale size, at their plant at Böhlen and used it for synthesis at temperatures up to 285°C. The plates warped, but it is thought that this may have been due to bad construction - the plates were made double and not single - as warping occurred before synthesis started. Lurgi are still uncertain which type of reactor is best for temperatures of the order of 240°C. which are required for their town's gas-synthesis projects.

They have not yet constructed one of their proposed giant Drucklammellen reactors.

To avoid difficulties due to blockages caused by the formation of carbon, which were encountered in some of their experimental work, K.W.I. introduced the 'Sieve Sleeve' reactor, in which the catalyst is put into the space between the wall of a cylindrical reactor and a coaxial gauze cylinder. The gases pass along the inside of the gauze cylinder and diffuse through it to and from the catalyst. Since with modern catalysts blockages due to carbon do not occur, this reactor is no longer used for synthesis but it has proved very useful for the iso-synthesis in which carbon is always formed on account of the higher temperatures that are necessary. For their work at high pressures on the iso-synthesis the K.W.I. avoid the formation of iron carbonyl by using nickel-chromium steel vessels, fitted with copper liners. Such a reactor has been used for 7 - 8 days without the liner showing any signs of corrosion. It may be mentioned in this connexion, that Ruhrchemie never experienced trouble due to iron carbonyl, either at atmospheric or at medium pressures, although the whole plant was constructed of ordinary steel.

General

Finally, two general points of design should be mentioned. Ruhrchemie said that for synthesis with cobalt catalysts the length of the catalyst tubes was unimportant, there being no difference between 2.5 and 4 metre tubes. For synthesis with iron catalysts, however, changing from 1 to 4 m. altered the direction of the reaction, in the sense that more CO_2 and less olefines were formed.

For a normal type of reactor, they were convinced that most of the synthesis occurs near the top and that the heat liberated there is not dissipated sufficiently rapidly. As a result, there is higher gas formation and shorter catalyst life than would otherwise be obtained. Also, on account of the dilution of the synthesis gas on passing down the reactor, the temperature should be kept higher at the bottom than at the top, whereas with the present design of reactor the temperature is either the same throughout or bigger at the top.

They tested these ideas by using a single catalyst tube surrounded by a steam space, outside which was an electrical winding to compensate for heat losses. If steam were then passed in the steam space in an opposite direction to the synthesis gas in the catalyst tube, synthesis was unsatisfactory, whereas it was excellent if the steam and synthesis gas were passed in the same direction. This result shows the general correctness of the above picture and hence it is reasonable to suppose that in an ordinary reactor there is very much more cooling surface - Ruhrchemie think ten times as much - as would be necessay if the circulation of the cooling medium were only arranged properly.