Heat Treatment Apparatus

Operation of Endothermic Gas Generators and New Catalysts for Them

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Machine parts that require high wear resistance, contact fatigue resistance, and bending strength are usually heat treated in gas carburizers. The Taganrog Combine Plant has had considerable experience in carburizing and carbonitriding such machine parts in continuous muffle-free apparatus. The basis of the controlled atmospheres used in the apparatus is endothermic gas prepared in gas generators. A diagram of a gas generator is shown in Fig.1.

The gas generator consists of two retorts (tubular) of the straight-through type made of high-nickel steel filled with the catalyst. The retorts are 230 mm in diam., 15 mm thick, and 1900 mm high. The pipes are heated with six mixing burners 7 with smooth temperature control. Part of the air (60-80%) is supplied from the blower 1 into the mixer through the encircling air line and the rest of the air required for combustion in the mixing burners enters the mixer through valves controlled by a pyrometric device.

The gas flow into the mixer is controlled by a null-regulator of the diaphragm type with feedback (pulse from air input). The mixture of gas and air ($\alpha \approx 1$) enters the six mixing burners and heats the retorts to $1050 \pm 10^\circ$C.

Natural gas is used to produce the endothermic gas. The approximate composition of the gas (vol.%) is $2.72$ CO$_2$, $1.6$ N$_2$, $88.73$ CH$_4$, $4.95$ C$_2$H$_6$, and $2.0$ for C$_3$H$_8$ and higher. Air is added to the gas in an amount to supply the necessary quantity of oxygen calculated from the reaction:

$$CH_4 + \frac{1}{2} O_2 \rightarrow CO + 2H_2.$$  (1)

The oxygen in the natural gas and the carbon in C$_n$H$_{2n+2}$ compounds are also taken into account. Usually, one volume of natural gas is mixed with 2.1-2.4 volumes of air.

During the process of catalytic conversion of natural gas with a small quantity of oxidizer the following reactions can occur in addition to reaction (1):

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2.$$  (2)
$$CH_4 \rightarrow C + 2H_2.$$  (3)
$$2CO \rightarrow CO_2 + C.$$  (4)
$$CH_4 + 2O_2 \rightarrow CO_2 + H_2O.$$  (5)

It is necessary to ensure that reaction (1) occurs primarily to the right and, when the natural gas contains CO$_2$, also reaction (2) to the right.

To obtain an endothermic gas with the minimum amounts of CO$_2$, O$_2$, CH$_4$, and H$_2$O the mixture of reacting gases is passed through a nickel catalyst at a temperature of about $1050^\circ$C. The GIAP-3 catalyst, which is used in domestic industry for conversion of gaseous hydrocarbons, is used to obtain standard controlled atmospheres containing $20\%$ CO, $40\%$ H$_2$, $40\%$ N$_2$. In the conversion of gaseous hydrocarbons, with the oxygen from the air ($\alpha \approx 0.25$) the GIAP-3 catalyst has a high stability, high dynamic resistance, and is not broken down by regeneration, being converted into powder.

Taganrog Combine Plant. Translated from Metallovedenie i Termicheskaya Obrabotka Metallov, No.11, pp.54-56, November, 1968.
A new type of catalyst has been developed to obtain controlled atmospheres on the basis of catalytic conversion of natural gas with air at $\alpha \approx 0.25$.

Atmospheres of standard composition are obtained with the new catalyst: $20.3-21.4\%$ CO, $39.3-41\%$ H$_2$, the rest N$_2$; no CO$_2$, O$_2$, or CH$_4$.

The dynamic resistance of the new catalyst is one-third to one-quarter that of GIAP-3, which makes it possible to increase the output of the generator considerably. The catalyst is easily regenerated. It has been regenerated three times in 15 months (blown through with air for 16 h at 850-900$^\circ$C with an air flow of 3-4 Nm$^3$/h). After regeneration the generator immediately produced gas of the required composition and the dynamic resistance of the catalyst was equal to the original value (about 150 mm water gage at a generator output of 60 Nm$^3$/h of endothermic gas).

The stability and activity of the new catalyst exceed those of GIAP-3. Under the operating conditions at the Taganrog Combine Plant the GIAP-3 catalyst has a useful life of no more than two to three months; the new catalyst has been in operation 16 months and has remained highly resistant to temperature changes (20-1100$^\circ$C). Per unit weight, the catalyst withstands a considerably higher gas load than GIAP-3. Changes in the total output of the generator do not affect the composition of the gas.

Thermal dissociation of methane with formation of carbon in the presence of the nickel catalyst at low oxidizer concentrations ($\alpha \approx 0.25$) begins as low as 400$^\circ$C, i.e., reaction (3) proceeds to the right. At 600-800$^\circ$C carbon is formed on the surface and within the pores of the catalyst, leading to mechanical damage of the grains. To prevent such damage, a layer of E95 electrocorundum or green carburundum 280-350 mm thick with 15-30 mm of granules is placed on a heat-resistant grid in the lower part of the retort (Fig. 2). This arrangement makes it possible to heat the mixture of gas and air to reaction temperature without formation of sooty carbon, thus preventing mechanical damage of the lower face of the layer of catalyst. Over the layer of electrocorundum is placed a layer of catalyst 1200-1250 mm high.

The natural gas enters the retort under a pressure of 1000 mm water gage, passing through the rotameter and entering the mixer (see Fig. 1). The air entering the mixer is also controlled by a rotameter. The gas:air ratio is regulated with a microscrew in the mixer. The secondary air supply is regulated by an isostatic servomotor controlled by a dew point instrument.

The gas — air mixture is transported from the mixer to the retort (Fig. 2) by a rotary compressor (Fig. 1).

The composition of the mixture entering the retort (% by volume) is 0.4 CO$_2$, 15.5 O$_2$, 0.6 CO, 0.7 H$_2$, 25.9 CH$_4$, the rest N$_2$.

The gas mixture passes through the layer of E95 electrocorundum and catalyst and then through the free space 250-350 mm in height into the vertical cooler 3 (Fig. 2). The cooler is a pipe 700 mm high with the same diameter as the retort, to which it is joined by a flange, and has 30 filler tubes 14 mm in diam, and 450 mm high. The gas passes through these tubes, which are surrounded by running water, and enters the gas collector.

The sudden cooling of the converted endothermic gas stops the $2\text{ CO} \rightarrow \text{ C} + \text{ CO}_2$ reaction.

After filtration, the cooled gas is monitored by a dew point instrument at the generator outlet.

The humidity of the gas is determined, along with the activity and carbon potential, on the assumption of a quantitative relationship between the dew points of the components. The dew point instrument regulates the amount of air needed for the reaction. The generator produces gas with a dew point of $+4$ to $+7^\circ$C, which enters the blender, where the endothermic gas, natural gas, and ammonia are measured out in the required proportions and distributed to the apparatus.