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PROCESS FOR PRODUCING STYRENE

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This invention relates to a process for the synthesis of styrene from benzene and acetylene.

It is known that styrene is formed when a mixture of benzene and acetylene is heated to high temperatures (Berthelot 1867, Liebigs Annalen 142, 259). This method has not been proved applicable for the technical production of styrene because the largest part of acetylene reacts in another undesired way. For the verification of Berthelot's method a mixture of 75 g. of benzene and 20 liters of acetylene was passed per hour with equal speed at a temperature of 600° C. through a tube of 20 mm diameter heated at a length of 600 mm which consisted of a chromium-iron alloy rich in chromium (Sicronal 12" of the firm Vereinigte Stahlwerke A. G., Düsseldorf). After two hours' trial the tube had been filled up with sooty coal. Only 2 g. of styrene were formed beside a larger amount of substances boiling at a temperature of above 180° C. An experiment on the same conditions but at a temperature of 800° C. yielded 3,6 g. of styrene. 35 g. of high-boiling substances were formed besides. In the tube 16 g. of coal were found. The waste gas did not contain any acetylene left. In applying a tube of quartz instead of chromium-iron the results were similarly unfavorable.

It has now been found that the heating of a mixture of acetylene and benzene in the vapour phase takes a surprising favorable course if the heating is performed at diminished pressure instead of an ordinary one.

Example 1

Per hour a mixture of 90 g. of benzene and 20 l of acetylene (measured at a pressure of 760 mm) was passed at a temperature of 900–950° C. through the above named tube of chromium-iron alloy. The tube and the conjuncted arrangement for condensation were brought by a pump to a pressure of 40 mm. The vapours after having passed the heated tube entered a water cooled condenser and receiver. This condenser was connected with two low cooled receivers into which benzene condensed containing still some styrene. After two hours all the condensates were fractionally distilled. 9,5 g. of styrene were obtained. 6. g. (mostly diphenyl) distilled at a temperature of above 180° C. The tube contained only few soot. The unchanged benzene was regained practically quantitative. The waste gas contained 85% of acetylene beside hydrogen formed partly by the by-reaction of the formation of diphenyl. This gas may be used again in circulation or it may be used for another purpose.

On the same conditions of working but without using diminished pressure the tube choked already after a quarter of an hour by coaly separation.

Example 2

The apparatus was the same as in Example 1. At a pressure of 18–32 mm. a mixture of 45 g. of benzene and 20 l of acetylene (measured at ordinary pressure) was passed per hour through a tube heated at a temperature of 950–1000° C. After two hours 8,5 g. of styrene and 4,5 g. of high-boiling substances were obtained. The tube contained very few soot. A gas of 80% of acetylene was regained. By further diminishing the pressure the formation of by-products could be reduced further-more.

Example 3

Through the same apparatus a mixture of 45 g. of benzene and 5,5 l acetylene (760 mm) was passed per hour at a temperature of 900–950° C. and a pressure of 11 mm. In two hours 3,6 g. of styrene and only 0,7 g. of high-boiling substances were obtained. The gas was 80–90% of acetylene.

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