PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Conversion of Carbon Monoxide with Hydrogen into Hydrocarbons having more than one Carbon Atom in the Molecule

I, HAROLD EDWIN POTTS, Chartered Patent Agent, of 12, Church Street, Liverpool, in the County of Lancaster, Subject of the King of Great Britain, do hereby declare the nature of this invention, which has been communicated to me by N. V. Internationale Koolwaterstoffen Synthese Maatschappij (International Hydrocarbon Synthesis Company), a Dutch Company, of 20, Wassenaarscheweg, The Hague, Holland, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

It is known that in the conversion of carbon monoxide with hydrogen into hydrocarbons having more than one carbon atom in the molecule the temperature must be kept within narrow limits, in particular when using catalysts derived from nickel, cobalt and iron. As is known, this is attended with considerable difficulties, owing to the large amounts of heat evolved.

It has already been proposed in order to maintain a constant temperature in the said conversion to operate in apparatus comprising several narrow reaction spaces separate from each other and bathed by a cooling medium. It was found, however, that within a cross-section of these reaction spaces considerable differences in temperature may occur.

It has now been found that in the conversion of carbon monoxide with hydrogen into hydrocarbons having more than one carbon atom in the molecule not only a constant temperature but also a substantially uniform temperature level throughout the reaction space is attained by using narrow tubes bathed by a cooling medium, and containing the catalyst in such a manner, that the reacting gases can stream along the wall of the reaction space through a narrow passageway, which is not or only little obstructed by catalyst, while in the middle of the tube no or only little interstitial space remains not filled by catalyst.

The tubes may be filled with catalyst pieces in the form of tablets or pellets having a diameter which is only a little smaller than the internal width of the tubes or with a catalyst in the form of a rod of corresponding diameter. However, also other forms for the catalyst may be taken in accordance with the present invention, for example, balls or egg-shaped pieces, which have a corresponding diameter or cubes having the corresponding size or prisms with a base of proper size, or also pieces having less regular forms, for example, irregular lumps. The tablets, pellets, cylinders, prisms, balls, cubes and the like need not necessarily be arranged concentrically in the tubes, but may lie more or less toward one side of the tubes. This is generally the case, if the conversion is carried out in inclined or horizontal tubes. When working in vertical tubes the catalyst may, if desired, be arranged in such a manner, that at all places about the same distance between the catalyst and the wall of the tube exists; in tubes with a circular cross-section concentrically arranged cylindrical tablets or rods are used with advantage; with tubes with elliptical or polygonal cross-section concentrically arranged tablets or rods of corresponding form can be used.

The process may be carried out in the gaseous phase or also in the liquid phase in a liquid medium.

When working in the gaseous phase in general tubes with an internal diameter of 5 to 25 millimetres, preferably 5 to 10 millimetres, are used with advantage. The size of the catalyst pieces is then adjusted to the internal width of the tubes in such a manner, that annular spaces between the catalyst and the wall of the tube are formed, the average breadth of which is about 0.2 to 2 millimetres, advantageously 0.2 to 1 millimetre.

When working in the liquid phase wider tubes and wider interstitial spaces between the wall of the tube and the catalyst may be taken, because owing to the higher specific heat of the liquid medium the heat absorbing capacity in the reaction space is

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a larger one.

The process is advantageously carried out under pressure, because in this case the heat may be better withdrawn. Pressures of up to 25 atmospheres or also higher pressures up to 200 atmospheres and more may be employed.

The length of the conversion tubes and the height of the catalyst layer may be selected within wide limits. In general this amounts to more than 1 metre, for example 2 metres.

The conversion may be carried out in a single tube or in a series of tubes connected in parallel or also in several tubes connected one behind the other or several series, connected one behind the other, of tubes connected in parallel. In the case of tubes connected one behind the other the catalysts in the first tube, or first series of tubes connected in parallel are advantageously filled with catalysts in the manner described above; in the following tubes or series of tubes, in which owing to the fact that the conversion has already partially taken place the development of heat is smaller, the devices hitherto usual may also be used.

When operating with tubes connected one behind the other the pressure may be different in the various tubes, for example, 25 atmospheres in the first tube, 10 atmospheres in the second tube or in reverse order 10 atmospheres in the first and 25 atmospheres in the second tube.

When operating with tubes connected in parallel these are advantageously combined to bundles, for example, similarly as with steam producers welded or rolled into a header.

In order to facilitate the filling of the tubes with the catalysts, these may be widened at one end. Sieves or the like may be provided at the other end of the tube to hold the catalyst in the tube. Also at the upper end an obstruction device may be placed, which prevents the catalyst being blown out, when the gases stream from below upwards.

As a heat removing medium bathing the conversion tubes a streaming liquid is most advantageously employed, the boiling point of which at the pressure maintained on the said medium lies at or somewhat below the conversion temperature, so that the heat withdrawn from the tubes is removed by development of vapour. But also other cooling liquids may be employed, if they are passed sufficiently rapidly along the tubes. The cooling may also be effected by gases, for example, by those to be introduced into the conversion, whereby, if necessary, an additional cooling medium may still be employed for part of the tube.

The gas may be passed one or more times through each reaction tube or series of reaction tubes.

The reaction tubes may be filled wholly or partially with the catalyst. In the latter case the part of the tube not filled may serve for the preheating of the gases.

The gases to be converted may be diluted with inert gases, such as carbon dioxide or nitrogen. The proportion of the amounts of carbon monoxide and hydrogen in the gas may be selected according to circumstances within wide limits. Thus gases with an excess of carbon monoxide or with an excess of hydrogen may be employed as the case may be. Prior to the conversion the gases may be subjected to any desired pretreatment, for example a removal of dust, a washing with organic liquids or a heating to high temperatures. If the gases contain impurities, such as sulphur or sulphur compounds, they may be previously purified by one of the usual desulphurising processes.

The reaction temperatures may vary according to the nature of the catalyst employed and the prevailing pressure; they usually lie between about 150° and 350° Centigrade.

The following Examples will further illustrate how the invention may be carried out in practice, but it should be understood that the invention is not limited to the said Examples:—

EXAMPLE 1.

A vessel with parallel cooling walls at a distance of 10 millimetres from each other or a tubular vessel with cooling tubes of 15 millimetres diameter is loosely filled with a catalyst, which consists of 85 parts of cobalt and 15 parts of thorium oxide on 85 parts of kieselguhr, in the form of grains having a diameter of 2 to 3 millimetres. If a gas with 30 per cent. by volume of carbon monoxide and 60 per cent. by volume of hydrogen (remainder inert gas) is then passed at 180° Centigrade and under atmospheric pressure over this catalyst, an average yield of liquid and solid hydrocarbons of 85 grams per cubic metre of carbon monoxide - hydrogen - mixture is obtained. The differences in temperature occurring within the catalyst layer amounts to about 15° Centigrade. If on the other hand the same catalyst is pressed to pellets of 5 millimetres diameter, which are arranged in tubes of 6 millimetres diameter, an average yield of 105 grams per cubic metre of carbon monoxide-hydrogen-mixture is obtained. No substantial differences in temperature within the catalyst are observed in this case.

EXAMPLE 2.

If the operation is carried out in the

same manner as set out in Example 1, but under elevated pressure, the differences in temperature when working in the vessel with cooling walls and in the tubular vessel with the wide tubes are still larger, and the formation of undesired gaseous hydrocarbons, in particular methane, becomes still larger. If on the other hand the conversion is carried out in the narrow tubes filled with catalyst pellets in accordance with the present invention at elevated pressure (for example, 20 atmospheres or higher), the yield of liquid and solid hydrocarbons increases to 115 grams per cubic metre of carbon monoxide-hydrogen mixture, and no difficulties with regard to the removal of heat occur.

Having now particularly described and ascertained the nature of my said invention and in what manner the same is to be performed, as communicated to me by my foreign correspondents, I declare that what I claim is:—

1. A process for the catalytic conversion of carbon monoxide with hydrogen into hydrocarbons having more than one carbon atom in the molecule, characterised by carrying out the conversion in narrow tubes, bathed in a cooling medium, and containing the catalyst in such a manner, that the reacting gases can stream along the walls of the reaction space through a narrow passageway which is not or only little obstructed by catalyst, while in the middle of the tube no or only little space not filled by catalyst remains.

2. A process according to claim 1, characterised by the use of cylindrical tubes which are filled with cylindrical catalyst pieces, the cross-section of which is only a little smaller than the internal width of the tubes.

3. In the process claimed in either of claims 1 or 2, operating in tubes with an internal diameter of 5 to 25 millimetres in which the space between the catalyst and the wall of the tubes has an average breadth of 0.2 to 2 millimetres.

4. In the process claimed in any of claims 1 to 3, working under elevated pressures.

5. Processes for the catalytic conversion of carbon monoxide with selected catalysts substantially as described in the foregoing Examples.

6. Products when obtained in processes in accordance with the preceding claiming clauses.

Dated this 10th day of May, 1939.

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Chartered Patent Agents.

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