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(54) HYDROCARBON SYNTHESIS

(54) SYNTHESE D'HYDROCARBURES

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(57) ABSTRACT

CLAIMS Show the claims

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O.Z.10768 Amer./Can. J/Bo.

The present invention relates to the synthesis of hydrocarbons containing more than one carbon atom in the molecule, especially liquid hydrocarbons from carbon monoxide and hydrogen.

It is already known that gases which are employed for the said synthesis must be purified very thoroughly to remove catalyst poisons. Even a very small sulphur content causes a rapid decrease in the activity of the catalysts. In the case of some synthesis gases, especially those which are obtained by gasification of carbonaceous solid materials more recent than bituminous coal, for example, brown coals, the catalysts do not exhibit their full activity even at the beginning of the reaction, and these difficulties occur even when the said gases have been carefully purified from sulphur compounds.

These latter difficulties in the synthesis appear to be due to noxious impurities other than sulphur compounds present in such gases, such as gum formers, which impair the catalyst activity.

We have now found that the said difficulties can be avoided, if as synthesis gas a mixture of carbon monoxide and hydrogen is used, which after its production has been heated to high temperatures, above 800°C, preferably above 900°C, and simultaneously or thereafter has been freed from the hydrogen

sulphide, which may have been contained in the same in the form of organic sulphur compounds and/or as such.

The best results are attained by heating at temperatures of at least 1000°C, say 1100°, 1200°C or more.

By the said heating the organic sulphur compounds which may be present in the gases are practically completely converted into hydrogen sulphide, which can then easily be removed in any known manner.

Besides the sulphur compounds also the aforesaid other noxious constituents are apparently decomposed at the high temperatures applied in the present process and thus rendered harmless.

It is usually not necessary in the said heating to add substantial amounts of steam.

The surprising effect obtained by the process according to the present invention is particularly striking when employing synthesis gases obtained from solid carbonaceous materials more recent than bituminous coal, more particularly browncoal, since when heating the said gases according to the present invention they are equally suitable as the most suitable synthesis gases obtained from coke from bituminous coal and in some cases even superior to them. However, the process is also useful for the synthesis of gases obtained from other carbonaceous materials, such as for example bituminous coal, coke and the like, if these give rise to the aforesaid difficulties. Also other gases, suitable for the synthesis of hydrocarbons may be treated with advantage in the said manner as for example gases obtained from hydrocarbon gases, as for example natural or re-

finery gases, by conversion with steam and, if desired, carbon dioxide.

The gases employed in the process of the present invention may contain higher or smaller amounts of accompanying gases which do not disturb or may even be desired for the synthesis, for example, carbon dioxide or methane.

Advantageously, the heating of the gases according to the present process is carried out in heat accumulators or heat exchangers provided with filling material or in a combination of these two apparatus, so that part of the added heat is retained and only the heat necessary for obtaining the requisite high temperature must be newly supplied. The high temperature may be attained in any desired manner, for example, by means of direct heating, which may be carried out by supplying oxygen (this heating method is especially suitable for bringing the hot material to the requisite high temperature) or by means of gas burners, electrical heating rods, etc. In many cases it is advantageous to preheat the gas indirectly and to supply oxygen to the preheated material to bring it to the requisite high temperature. It is also possible to heat the gases by passing them over periodically heated heat regenerating masses.

The heated synthesis gases may be cooled by direct or indirect cooling to the temperatures suitable for conversion in the synthesis into hydrocarbons, for example, by means of heat exchange with fresh synthesis gas to be heated for purification, or by injecting water free from oxygen or by utilizing their heat for distilling the synthesis product or for the production of steam.

Advantageously heat exchangers which are constructed

of metals withstanding corrosion by sulphur and decarbonization are used. In case the initial gases contain much organic sulphur, it is occasionally advantageous to use as filling material in the heat accumulator, or, as the case may be, heat exchanger, burnt lime, burnt dolomite, bauxite or like materials, which accelerate the conversion of the organic sulphur compounds into hydrogen sulphide.

In order to obtain good results in the synthesis of hydrocarbons, the synthesis gases preferably contain carbon monoxide and hydrogen in certain definite proportions, dependent on the particular reaction conditions adopted and the products which it is desired to obtain, for example a proportion of carbon monoxide to hydrogen of between about 2:1 to 1:3, say 1:1,2 to 1:2. The proportion of carbon monoxide to hydrogen in the synthesis gases may, if necessary, be brought within the desired range after the purification according to the process of the present invention, by conversion of a portion of the carbon monoxide with steam to hydrogen and carbon dioxide, and, if desired, removing the latter, and/or by mixing the synthesis gases with hydrogen or gases containing hydrogen and carbon monoxide in other proportions.

The synthesis of hydrocarbons with the gases purified according to the process of the present invention, can be carried out under the conditions usual for this reaction, for example, at temperatures between 175° and 220°C and under ordinary or elevated pressure, in the presence of catalysts. The catalysts may be washed with an oil continuously or at intervals, in which latter case the synthesis may be continued or interrupted. In the case of interruption of the synthesis conditions different from

those during the synthesis proper may be employed, for example, lower temperatures and higher pressures, especially temperatures down to 50° C and high pressures up to 150 atmospheres or more.

The synthesis may be carried out in the liquid or in the gaseous phase.

The following Examples will further illustrate the nature of our said invention, but it should be understood that the invention is not limited to the said Examples.

Example 1.

Water gas which has been obtained by gasification of brown coal and which contains per cubic meter about 100 milligrams of organic sulphur, is passed at 1200°C over bauxite, thereupon freed from the hydrogen sulphide formed by means of a mass absorbing hydrogen sulphide and after cooling passed over a cobalt-thorium oxide catalyst at ordinary pressure and at about 180°C. The average yield of liquid hydrocarbons produced in one passage amounts to about 113 cubic centimeters per cubic meter of carbon monoxide - hydrogen mixture in contrast to only about 90 cubic centimeters per cubic meter of the gas when using the same initial gas after purification from organically bound sulphur in the usual manner with alkalized iron oxide mass at about 300°C. The "half-value-time" of the catalyst (i.e. the time in which the catalyst activity decreased to half its original activity) when the reaction has been started with preheated gas is about 20 per cent longer than with the gas which has been purified in the usual manner.

Example 2.

A carbon monoxide - hydrogen mixture obtained from brown coal briquettes by gasification with oxygen is passed at

1100°C over fragments of quartz and is used for the hydrocarbon synthesis after removal of the hydrogen sulphide formed by means of gas purifying mass. The gas which is passed on to the synthesis is completely free from sulphur and an average yield of liquid hydrocarbons is obtained which per cubic meter of the gas is by 25 cubic centimeters higher than in a synthesis which for purposes of comparison has been carried out at the same time and in the same furnace (the furnace contains two separate catalyst tubes in the same block of aluminium) and in which a portion of the same initial gas was used, which has been purified from organically bound sulphur only in the usual manner.

When purifying a carbon monoxide - hydrogen mixture obtained from coke or bituminous coal in the usual manner and then subjecting it to synthesis under the same conditions, a yield of liquid hydrocarbons is obtained which per cubic meter of the gas is by 8 to 10 cubic centimeters lower than with the same gas mixture which has been heated to 1100°C as described in the preceding paragraph.

What we claim is:-

1. A process for the synthesis of hydrocarbons containing more than one carbon atom in the molecule from carbon monoxide and hydrogen, which comprises heating a synthesis gas, essentially comprising carbon monoxide and hydrogen after its production to a high temperature above 800°C, simultaneously or thereafter freeing it from hydrogen sulphide when it contains the same and then converting it into the said hydrocarbons.

2. A process as claimed in claim 1, which comprises heating the synthesis gas at a temperature of at least 1000°C.

3. A process as claimed in claim 1, which comprises heating the synthesis gas at a temperature within the range of 1000° to about 1250°C.

4. A process as claimed in claim 1, which comprises heating a synthesis gas obtained by gasification with a gasifying agent of a solid carbonaceous material more recent than bituminous coal.

5. A process as claimed in claim 1, which comprises heating a synthesis gas, obtained from a hydrocarbon gas by conversion with steam.