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PATENT SPECIFICATION

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PROVISIONAL SPECIFICATION

Improvements in the Manufacture and Production of Hydrocarbons from Carbon Monoxide and Hydrogen

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) to be as follows:—

It is known that in the synthesis of hydrocarbons having more than one carbon atom in the molecule from mixtures of carbon monoxide and hydrogen in the gas phase, a subsiding in the action of the catalyst readily takes place by reason of the formation of high molecular hydrocarbons (paraffin waxes) which deposit on the catalysts. In order to regenerate the catalysts it has already been proposed to heat the catalysts in a current of hydrogen or to extract them with liquid benzine at intervals of time. The first measure requires, however, a special plant for the preparation of pure or high percentage hydrogen, while in the second large amounts of benzine are allowed to flow round in the voluminous synthesis chamber and, after the extraction, these must be evaporated again in order to recover the extracted solid paraffin waxes.

My foreign correspondents have now found that the high molecular hydrocarbons deposited on the catalysts may be removed very advantageously therefrom by leading vapours of organic liquids, preferably liquid hydrocarbons, over the catalysts and keeping the latter at temperatures at which at least a partial condensation of the vapours takes place. For this extraction of the high molecular hydrocarbons, chiefly paraffin waxes, it is very convenient to use the vapours of the liquid products formed by the synthesis, for example the benzine fraction thereof.

Contrary to expectation, the time of extraction when working in this way is shorter than when extracting with liquid benzene, and it also has the advantage over the hitherto used treatment with liquid extraction agents that the catalyst after the extraction may rapidly be used again for the synthesis. Whereas after after the extraction with liquid benzine, a special working operation is necessary for the complete removal of the liquid absorbed by the catalyst, after regeneration of the catalyst according to this invention, the synthesis gas mixture may be directly led again into the reaction chamber because the catalyst has adsorbed no liquid hydrocarbons or only a small amount thereof.

The organic liquids to be used may be of different kinds provided they are capable of dissolving the substances to be removed, as for example benzine, benzene alcohols, unsaturated or substituted hydrocarbons, tetrahydronaphthalene, nitrogenous organic compounds, such as aliphatic or aromatic amines and the like. Very readily volatile substances, such as pentane, butane, or propane, may also be used for the extraction and the pressure or temperature so selected that they may be used for the process. Higher boiling solvents may also be used, and any pressure and temperature may be maintained. Two or more extraction agents may also be used simultaneously and/or consecutively. Thus for example extraction may first be effected with benzine and then with aromatic solvents, such as toluene and xylene, or with nitrogenous compounds.

The vapours of the extraction agent may be produced and brought into contact with the catalyst in any way. For example the vapours may be led upwards, condensed in the neighbourhood of the vaporisation point on the catalyst and returned to the vaporisation vessel. The supply of the vapours may also be effected from the top or from the side at one or more places. By a cooling system behind the synthesis chamber, the vapours of the extraction agent may be completely condensed. The liquid used for the extraction may generally speaking be comparatively strongly enriched with the substance to be extracted. After the extraction it may be worked up in any way, preferably by evaporation of the solvent. The vapours thus formed may again be used for regeneration of the catalyst.

An advantageous modification of the process consists in leading the vapours of the liquid together with synthesis gas over the catalyst, a liquid being selected which is condensed under the synthesis conditions. It is not then necessary to interrupt the synthesis for the regeneration of the catalyst, and the same temperature and pressure conditions may be maintained continuously. It is merely necessary from time to time to mix with the synthesis gas suitable amounts of vaporous hydrocarbons, in particular synthesis products, which under the reaction conditions are condensed on the catalyst; if desired the throughput of gas may be reduced. The yield of synthesis products is somewhat less during the regeneration, but after the latter immediately increases again. This kind of regeneration may be carried out at shorter or longer intervals of time independently of other regenerative measures. It has the advantage that reversing of the operation is unnecessary and the extracted paraffin wax may be led away together with the extraction agent and the synthesis product in the usual way.

A great variety of catalysts suitable for the synthesis may be regenerated in the said manner, as for example metals of the iron group in admixture with additions, such as cobalt-thorium catalysts. The synthesis itself may be carried out out under the otherwise usual temperatures and at any pressures, i.e. without pressure or at pressures up to 10 atmospheres or more. The catalyst chamber may be of any shape; furnaces in which the catalysts are arranged between plates may be used, or tubular furnaces and similar apparatus. The leading away of the excess heat may be effected in the usual manner.

The said process may also be advantageous for reactions under pressure; in this case low boiling extraction agents may be used, such as propane or butane, which may readily be separated from the extracted substances by releasing the pressure to atmospheric pressure.

The following Example will further illustrate the nature of this invention but the invention is not restricted to this Example. The parts are by weight.

EXAMPLE.

Through a chamber for the synthesis of benzine without pressure, which is filled with a catalyst of 85 parts of cobalt and 15 parts of thorium oxide on 85 parts of kieselguhr, a mixture of 30 per cent. by volume of carbon monoxide and 60 per cent. of hydrogen (the remainder being inert gases) is led at about 180° Centigrade.

After operation for 40 days, the yield of liquid hydrocarbons has fallen to half the amount originally obtained. For the regeneration of the catalyst there are led in to the chamber from a vaporising vessel vapours of a fraction boiling at about 180° Centigrade of benzine obtained from the synthesis product, the catalyst being kept at about the same temperature by indirect cooling. The condensed mixture which flows away at the bottom is strongly enriched with paraffin wax. It is returned to the vaporising vessel from which the benzine vapours are again led over the catalyst. The regeneration is interrupted when paraffin wax is no longer being extracted; the benzine vapour is then no longer led over the catalyst, but condensed in a cooler and the paraffin wax remaining in the vaporising vessel is drawn off in the liquid state.

The amounts of benzine in circulation required for the extraction in the said case are about 0.5 cubic metre per cubic metre of catalyst. On the other hand in the extraction with liquid benzene, about 2.5 cubic metres of liquid benzine are required per cubic metre of catalyst. .

Dated this 23rd day of July, 1938.

J. Y. & G. W. JOHNSON,
47, Lincoln's Inn Fields, London,
W.C.2,
Agents.

COMPLETE SPECIFICATION

Improvements in the Manufacture and Production of Hydrocarbons from Carbon Monoxide and Hydrogen

I, GEORGE WILLIAM JOHNSON, a British Subject, of 47, Lincoln's Inn Fields, in the County of London, Gentleman, do hereby declare the nature of this invention (which has been communicated to me from abroad by I. G. Farbenindustrie Aktiengesellschaft, of Frankfort-on-Main, Germany, a Joint Stock Company organised under the Laws of Germany) 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 containing more than one carbon atom in the molecule in the gaseous phase in the presence of catalysts, a considerable decrease in the activity of the catalyst readily occurs, which is due to the fact that conversion products of high molecular weight, such as paraffin waxes, are deposited on the catalyst. In order to regenerate the catalysts it has already been proposed to pass hydrogen at elevated temperature over the catalysts at intervals or to extract them with liquid benzine. However, for the said treatment with hydrogen a special plant for the production of hydrogen or gas rich in hydrogen is required, and for the extraction large amounts of benzine must be circulated through the reaction space, and these must be evaporated after the extraction to obtain the extracted solid paraffin wax.

My foreign correspondents have now found that improvements are obtained in the said conversion by passing over the catalyst at intervals vapours of organic liquids in which the conversion products of high molecular weight deposited on the catalyst are soluble, under such conditions that at least a partial condensation of the said vapours occurs, thereby regenerating the catalyst by extracting the said products.

The time for the regeneration of the catalysts according to the process of the present invention is shorter than in the above-mentioned treatment with liquid benzine, and a further advantage over the said treatment as used hitherto is that after the regeneration the catalyst is at once ready for the synthesis, as no liquid hydrocarbons or only small amounts thereof are adsorbed, whereas in the said extraction with liquid benzine a special operation is required for the complete removal of the liquid which has been adsorbed by the catalyst. Furthermore in the present process much smaller amounts of liquid are required as compared with the amounts used in the said treatment with liquid benzine and usually no more than about one fifth of the latter amounts are employed.

In the process according to the present invention vapours of hydrocarbons which have been produced in the conversion itself, preferably of a fraction boiling within the range of benzine, are employed, with particular advantage. Also vapours of other organic liquids, in which the said conversion products of high molecular weight are soluble, are suitable, for example, vapours of benzine, benzene, alcohols, unsaturated or substituted hydrocarbons, tetrahydronaphthalene, nitrogen-containing organic compounds, such as aliphatic or aromatic amines, and the like. Also vapours of low boiling liquids, such as pentane or normally gaseous hydrocarbons, such as butane or propane may be employed in the present process, under the conditions as stated above. Furthermore vapours of different liquids can be used simultaneously or in succession, for example, vapours of benzine may first be passed over the catalyst and subsequently the catalyst may be treated with vapours of aromatic solvents such as toluene and xylene, or of nitrogen-containing compounds.

The vapours of the said liquids can be produced and brought into contact with the catalyst in any desired way. Thus, for example, the vapours can be taken from a vaporisation vessel and passed through the catalyst space from the bottom to the top, condensed on the catalyst and then allowed to flow back to the vaporisation vessel. The introduction of the vapours can also be effected at the top or from the sides at one or more places. By means of a cooling system behind the conversion space the vapours can be completely condensed. The condensed vapours may generally be enriched to a relatively high degree with the extracted conversion products of high molecular weight. After the extraction the said products can be separated in any desired way, preferably by means of vaporisation of the liquid. When low boiling liquids or normally gaseous hydrocarbons are employed for the regeneration, the said vaporisation can easily be obtained by release of pressure. The vapours obtained may be recycled to the regeneration process.

An advantageous manner of carrying ing out the process of the present invention consists in passing the vapours of the liquid together with synthesis gas over the catalyst. Care is taken in this case to select vapours which are at least partly condensed under the conversion conditions. When operating in this way it is not necessary to interrupt the conversion for the regeneration of the catalyst, and the same conditions of temperature and pressure can be maintained permanently. Only from time to time suitable amounts of the said vapours are added to the synthesis gas, and, if desired, the gas throughput can be correspondingly decreased. The yield of conversion products is somewhat smaller during the regeneration but thereafter increases immediately. This method of regeneration can be effected, if desired, after shorter or longer periods of operation and may also be employed alternately with other regeneration methods.

The present process may be employed for the regeneration of any catalyst suitable for the conversion, for example, metals of the iron group, if desired, in admixture with suitable promoters, such as cobalt-thorium catalysts and the like.

The conversion may be carried out at the usual temperatures, for example, from 170° to 220° Centigrade, and at any desired pressure, for example, reduced pressure, atmospheric pressure as well as at pressures up to 10 atmospheres or higher pressures, for example, 20 to 50 atmospheres or still higher. The catalyst space in the present process may have any desired form, for example, reaction vessels in which the catalysts are arranged between sheets, may be used as well as tubular reaction vessels and the like. The removal of the surplus heat can be carried out in the usual way.

The following Example further illustrates the nature of the present invention and in what manner the same is to be carried out in practice, but it should, however, be understood that the invention is not limited to said Example.

EXAMPLE.

A mixture of 30 per cent. by volume of carbon monoxide and 60 per cent. by volume of hydrogen (remainder inert gases) is passed at about 180° Centigrade and at atmospheric pressure through a reaction vessel for benzine synthesis, which vessel is filled with a catalyst consisting of 85 parts by weight of cobalt and 15 part by weight of thorium oxide to 85 parts by weight of kieselguhr. The temperature is maintained in the reaction vessel by means of indirect cooling.

After an operation of 40 days, the yield of liquid hydrocarbons has decreased to half the amount which was originally obtained. For the regeneration of the catalyst vapours of a fraction, boiling at about 180° Centigrade, of benzine obtained from the conversion products, are passed from a vaporisation vessel into the reaction vessel, the temperature in the reaction vessel being maintained substantially unchanged. The benzine, which is condensed and flows off at the bottom, is enriched in paraffin wax in a high degree. It is passed back into the vaporisation vessel, from which the benzine vapours are again passed over the catalyst. The regeneration is stopped when no further paraffin wax is extracted; the benzine vapours are then no longer passed over the catalyst, but condensed in a cooler, and the paraffin wax, remaining in the vaporisation vessel, is removed in a molten state.

The amounts of benzine, which are necessary for the regeneration, and are therefore maintained in circulation, are about 0.5 cubic metre per cubic metre of the catalyst. In contrast thereto, in the regeneration process by way of extraction with liquid benzine 2.5 cubic metres of liquid benzine are used per cubic metre of the catalyst.

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

1. A process for the conversion of carbon monoxide with hydrogen into hydrocarbons with more than one carbon atom in the molecule in the gaseous phase in the presence of catalysts, which comprises passing over the catalyst at intervals vapours of organic liquids in which the conversion products of high molecular weight deposited on the catalyst are soluble, under such conditions that at least a partial condensation of the said vapours occurs, thereby regenerating the catalyst by extracting the said products.

2. A process as claimed in claim 1, which comprises employing as liquids fractions of products obtained in the said conversion.

3. A process as claimed in claim 2, which comprises employing a fraction boiling within the range of benzine.

4. A process as claimed in any of claims 1 to 3, which comprises separating the extracted conversion products of high molecular weight from the condensed vapours, by vaporisation and subsequently recycling the vapours to the regeneration stage.

5. A process as claimed in any of claims 1 to 4, which comprises passing the said vapours over the catalyst under the same conditions as employed during the conversion.

6. A process as claimed in claim 5, which comprises passing the said vapours at intervals together with the synthesis gases over the catalyst.

7. A process as claimed in any of claims 1 to 6, which comprises employing as catalysts metals of the iron group in admixture with promoters.

8. A process as claimed in any of claims 1 to 7, which comprises carrying out the conversion at a temperature between 170° and 220° Centigrade.

9. A process for the conversion of carbon monoxide with hydrogen with regeneration of the catalyst employed, substantially as described in the foregoing Example.

10. Hydrocarbons with more than one

carbon atom in the molecule, whenever obtained by the process of any of the preceding claiming clauses.

Dated this 7th day of June, 1939.
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