PATENT SPECIFICATION

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COMPLETE SPECIFICATION

A process for the Conversion of Carbon Dioxide with Hydrogen

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, of Homberg, Niederrhein, Germany, a German Body Corporate, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to a process for the catalytic reduction of carbon dioxide with hydrogen with the production of higher aliphatic hydrocarbons and oxygen containing organic compounds.

It is known to reduce carbon dioxide with hydrogen to methane at atmospheric pressure in the presence of a catalyst comprising a metal of Group 8 of the periodic system or molybdenum or silver (see Franz Fischer, Hans Tropsch & Paul Dilthey, Brennstoffchemie 6, 265/71 (1925)). A great number of experiments have also been made to obtain by the catalytic reduction of carbon dioxide at atmospheric pressure, synthesis products other than methane, such as oxygen-containing organic compounds or hydrocarbons having more than one carbon atom in the molecule (see Herbert Koch & Hans Kuester, Brennstoffchemie 14, 245/51 (1933); Hans Kuester, Brennstoffchemie 17, 221 (1936); Franz Fischer, Theodor Bahr & Albert Meusel, Brennstoffchemie 16, 466 (1935)). In these experiments the formation of hydrocarbons of higher molecular weight than methane was observed when potassium compounds were incorporated in the catalyst. With an hourly throughput of 80 normal litres of $CO_2 + H_2$ per litre of reactor for a run of 80 hours, the maximum yield per normal cubic metre of $CO_2 + H_2$ (normal=at 760 mm mercury pressure and 15° C.) obtained at 200° C., using a cobalt catalyst, was approximately 15 grams of hydrocarbons having more than one carbon atom in the molecule, which would be equal to a space-time yield in "marketable" hydrocarbons of only 28.8 kg. per cubic metre of reactor space in 24 hours. The total synthesis product consisted predominantly of methane its content of higher hydrocarbons being as low as about 24% (Hans Kuester, Brennstoffchemie 17, 221 (1936)).

It is also known to employ elevated pressure in the hydrogenation of carbon dioxide to products other than methane (see Franz Fischer & Hans Tropsch, Brennstoffchemie 5, 224 (1924)). Using coarse iron turnings impregnated with KOH as catalyst, with temperatures exceeding 400° C. and gas pressures in the range 8—136 atmospheres 15 normal cubic metres per hour of a synthesis gas, containing CO_2 and H_2 in a ratio of 1:3 by volume, were passed through the reactor with recycling of the exit in a ratio of 5 volumes of recycle gas per volume of fresh gas. The space velocity through the reactor was 90. In relation to the quantity of catalyst used, only 0.03 normal cubic metre of synthesis gas per kilogram of iron per hour was used. Under the conditions described, the formation of hydrocarbons higher than methane did not occur until the carbon monoxide content of the gas had risen to 19.3% by volume, due to primary reduction of the carbon dioxide to carbon monoxide. The presence in the synthesis gas of a major percentage of carbon monoxide which must first be formed by reduction of the carbon dioxide by hydrogen was therefore considered to be a basic condition for the formation of hydrocarbons. The yield of higher hydrocarbons and alcohols obtained by this known process was, however, very low as compared with the quantity of methane formed.

The knowledge gathered with this process has afterwards led to suggestions (see Herbert Koch & Hans Kuester, Brennstoffchemie 14, 245 (1933)) first to convert the CO_2+H_2 gas mixture to a $CO+H_2O$ mixture, using copper catalysts for example, to such a degree as to give a synthesis gas suitable for use in the known hydrogenation of carbon monoxide in accordance with the Fischer-Tropsch method.

In another suggestion (German Patent No. 293,787 (1913)) for the catalytic synthesis of hydrocarbons at high pressure, it was emphasised that the use of carbon dioxide instead of carbon monoxide would greatly reduce the formation of the higher, normally liquid hydrocarbons.

A process has now been found which permits the conversion of carbon dioxide to synthesis products which may contain as much as 80% or more of hydrocarbons containing more than two carbon atoms in the molecule. This result is achieved, according to the invention, by contacting a gas mixture containing 0.2—1.5 volumes of CO_2 per volume of H_2 two or more times with a hydrogenation catalyst comprising a metal of the 8th group of the periodic system, and containing 0.1—6% by weight of an alkali-metal compound calculated as the alkali-metal monoxide and based on the metal of the 8th group present in the catalyst, the catalyst being provided as a fixed bed or as a suspension in finely divided condition in a liquid medium, the gas being contacted with the catalyst at a temperature within the range 150° C.—380° C., and at a gauge pressure within the range 1—100 atmospheres and at a rate of at least 100 normal cubic metres per cubic metre of catalyst space per hour, the greater part of the water and heavier hydrocarbons being removed from the exit gases which are thereafter contacted with the same catalyst or with a similar catalyst. In such manner, only partial conversion of the carbon dioxide is effected at each contact of the gas with the catalyst.

The process is preferably effected with an iron catalyst at a temperature within the range 240°—350° C. and at a pressure within the range 10—30 atmospheres. The rate of which the gas is contacted with the catalyst may vary over a very wide range, with a minimum rate of flow of 100 normal cubic metres per cubic metre of catalyst space per hour. In general, rates of flow much in excess of the minimum value are used. Although the rate of flow may exceed 5000 normal cubic metres of gas per cubic metre of catalyst space per hour, it is preferred to operate with rates of flow which do not exceed this value.

The exit gases may be recycled or several stages may be employed in series, the exit gases from one stage being passed to the next stage, the water produced in the synthesis being largely removed from the exit gases before the exit gases re-enter a synthesis chamber.

When proceeding in accordance with the invention, the synthesis temperature, though comparatively high, is within the reaction conditions specified, nevertheless below that at which appreciable amounts of methane are formed.

The removal of water may be accomplished by cooling and/or chemical or physical sorption. The use of chemical sorptives, substantially neutral in chemical reaction with respect to synthesis products, for example, calcium chloride, and physical adsorptives, acting by virtue of their surface active properties, such as activated charcoal, alumina, silica-gel, bauxite, fuller's earth, bentonite, or the like is preferred. The surface active agents also offer the advantage of simultaneously separating from the gas mixture some of the hydrocarbon material, particularly some of the normally gaseous hydrocarbons.

The alkali-metal compound used as promoter in accordance with the invention is preferably one having an alkaline reaction in aqueous solution, particularly the oxides, hydroxides, carbonates, silicates, phosphates, borates of sodium and potassium and the sodium and potassium salts of organic acids, particularly of acetic acid and its homologues.

To carry out the process according to the invention, the catalyst may be used either in the absence or presence of a liquid medium. In the hydrogenation of carbon dioxide the reaction heat per volume of CO_2+H_2 is about a third less than the reaction heat developed by an equal volume of $CO+H_2$ in the hydrogenation of carbon monoxide, and the well-known technical difficulties encounted in disposing of the reaction heat and controlling the reaction temperature in the hydrogenation of carbon monoxide are, in consequence, much less in the process according to the invention. It is possible to use the high gas velocities through the reactor provided in accordance with the invention even when using a fixed-bed granular catalyst in the absence of a liquid medium, and without the deposition of carbon reaching such a degree as to choke the reactor. In doing so, it is desirable to use the fixed-bed catalyst in a particle size of more than 1 mm. The fixed-bed catalyst may also be bathed or enveloped in a suitable liquid medium.

When employing catalysts surrounded by a liquid medium in the hydrogenation of carbon dioxide according to the invention, the percentage of higher molecular hydrocarbons in the total products may be 90% or more. In addition, when using more heavily alkalized catalysts suspended in a liquid medium, products are obtained which predominantly consist of solid hydrocarbons. In contrast to a process employing a dry, dust-like catalyst, these high molecular products will not disturb the technical execution of the synthesis.

Wherever the expression "catalyst space" or one of similar import is used herein, it is intended to designate the space occupied by the catalyst material when used as a fixed bed or the space occupied by the suspension when the catalyst is used as a suspension in a liquid medium.

One of the primary factors for the conversion of a high percentage of the gas according to the invention is the removal from the reaction gas, during synthesis, of at least the major portion of the reaction water which is theoretically produced in a quantity of 400 grams per normal cubic metre of $CO_2 + 3H_2$. This is accomplished by converting only a portion of the gas at any one time, removing the reaction water, or at least the major portion thereof, from the partly converted gas and subjecting the remainder of the gas to at least one, and preferably several more conversions, with water removal before each passage through the reactor or through a stage where a multi-stage process is employed. The exit gases may be largely freed from water by cooling for example, to a temperature below 100° C., or by chemical sorption or by physical sorption. Upon removal of the water, the exit gases are preferably mixed with fresh synthesis gas before being subjected to further conversion. The exit gases, as such, or together with fresh gas, may be recycled to the same reactor, or they may be passed through a second and, if required, through a third reactor in a multi-stage process, with water removal before each stage. Cooling of the exit gas, is suitably effected by indirect water cooling, the steam produced being used to heat up the gas freed from water prior to its re-entry into the reactor or its entry into a further stage.

EXAMPLE I

A conventional carbon monoxide hydrogenation iron catalyst obtained by the reduction of oxidic iron with hydrogen or carbon monoxide and hydrogen in known manner was used, the catalyst containing about 0.5% by weight of copper and 0.8% by weight of K_2CO_3, in relation to its iron content. This catalyst was placed in a pressure-resistant reactor (lamellæ or double-tube type) in a fine granular state with a particle size of less than 0.2 mm. and treated at 280° C.—340° C. with synthesis gas of the following composition: 19.9% of CO_2; 0.4% CO; 58.3% H_2; 0.4% CH_4, and 21% N_2. The gas was passed upwardly through the reactor under a pressure of 20 atmospheres at rates between approximately 100—250 normal litres per litre of catalyst space per hour. Once synthesis was started, the fresh gas was continuously mixed with three times its volume of exit gas from the same reactor. The exit gas issuing from the top of the reactor was cooled to 50° C. or less by indirect water cooling, in which operation the water produced in the reaction and the higher hydrocarbons were separated and drained. Part of the exit gas, now almost free from water, was returned to the synthesis gas inlet of the reactor, where it was mixed in the stated proportion with fresh synthesis gas and recycled through the catalyst.

A quantity of exit gas, corresponding to the contraction of gas volume during synthesis, was passed over active charcoal, with or without previous expansion to atmospheric pressure, for the adsorption of the low molecular hydrocarbons (C_3—C_5).

With an average conversion of 85% CO_2 and 96% H_2, the following products are obtained:—

	grams per Ncbm. $CO_2 + H_2$
Methane, ethane, ethylene - -	17
$C_3 + C_4$ hydrocarbons - - -	15 (including 76% of olefines)
Hydrocarbons boiling in the range 15° C.—200° C. - - - -	37 (including 74% of olefines)
Hydrocarbons boiling in the range 200° C.—320° C. - - -	26
Hydrocarbons boiling above 320° C.	26
Water-soluble alcohols C_1—C_4 -	11

The daily yield of hydrocarbons having three and more carbon atoms in the molecule and oxygen-containing organic products was about 500—600 kg. per cubic metre of catalyst space.

EXAMPLE II

The hydrogenation catalyst used had been obtained in known manner by the precipitation of a solution of ferric nitrate with sodium carbonate, and subsequent reduction with a mixture of carbon monoxide and hydrogen. The catalyst contained 0.5% by weight of copper and 1% by weight of K_2O based on the iron content, and it was used in particles having a size in the range 0.05—0.5 mm. The catalyst was charged into a reactor which was subdivided into four separate gas-tight chambers of the lamellæ type, the four chambers being of different sizes, their volume being in the ratio of 20 : 16 : 13 : 11. The chambers were connected in series by pipes disposed externally of the reactor, the pipes being provided with heat exchangers and condensate separators.

Under a synthesis gas pressure of 20 atmospheres and at an initial temperature in the range 280° C.—300° C., a synthesis gas free from carbon monoxide and containing approximately 20% carbon dioxide and 63% hydrogen together with nitrogen and methane, was passed into the first and biggest reaction chamber at a space velocity through the reactor of 600 normal cubic metres gas/cubic metre catalyst space per hour. The exit gas from the first chamber then flowed successively through the other three chambers, water and higher hydrocarbons being largely removed from the gas between each chamber. The contraction in the volume of the synthesis gas over the four chambers was about 60%. Over an operating period of 600 hours, with gradual increase of the synthesis temperature to 320° C., 82% of the carbon dioxide used was converted at the beginning of the run and 75% at the end of the run. On the average one normal cubic metre of $CO_2 + H_2$ used gave a yield of 126 grams of hydrocarbons of the following composition:—

	% by weight
Methane, ethane, ethylene - -	12
$C_3 + C_4$—hydrocarbons - -	7
Hydrocarbons boiling in the range 20° C.—200° C. - -	24
Hydrocarbons boiling in the range 200° C.—320° C. - -	21
Hydrocarbons boiling above 320° C. - - - - -	33
Alcohols C_2—C_5 - - -	3

The olefine content of the liquid products was 74%. By extracting the high molecular products from the catalyst, the catalyst was then used for a further 300 hours with an average carbon dioxide conversion of 72%.

EXAMPLE III

A catalyst of the same composition and same particle size as that used in Example II was suspended in a quantity of synthesis oil boiling in the range 300° C.—340° C. to give a suspension containing about 20% by weight of iron. This suspension was charged into the reactor used in Example II and used in synthesis with a gas of the same composition as that used in Example II, the gas being passed into the reactor at a rate of about 300 normal cubic metres per cubic metre of suspension per hour under otherwise the same reaction conditions as those used in Example II. Good conversion results were obtained with a somewhat better yield of hydrocarbons of high molecular weight than obtained in Example II.

What we claim is:—

1. A process for the synthesis of aliphatic hydrocarbons having more than one carbon atom in the molecule and of oxygen-containing organic compounds, which comprises contacting a synthesis gas containing carbon dioxide and hydrogen in the ratio by volume of 0.2 to 1.5 $CO_2 : 1\ H_2$ with a hydrogenation catalyst comprising a metal of the eighth group of the periodic system, which catalyst contains an alkali-metal compound in an amount, calculated as the alkali-metal monoxide, of 0.1%—6% by weight of the metal of the eighth group present in the catalyst, the catalyst being provided as a fixed bed or as a suspension in finely divided condition in a liquid medium, the synthesis gas being contacted with the catalyst at a gauge pressure within the range 1—100 atmospheres and at a temperature within the range 150° C.—380° C., and at a rate of at least 100 normal cubic metres per cubic metre of catalyst space per hour, a greater part of the water and of the heavier hydrocarbons formed during the synthesis being removed from the exit gases which are thereafter contacted with the same catalyst or with a similar catalyst.

2. A process according to claim 1, in which the process is carried out in two or more stages.

3. A process according to claim 1 or claim 2, in which the pressure is within the range 10—30 atmospheres.

4. A process according to any one of the preceding claims, in which the temperature is within the range 240°—350° C.

5. A process according to any one of the preceding claims, in which the gas is contacted with the catalyst at a rate not greater than 5000 normal cubic metres per cubic metre of catalyst space per hour.

6. A process according to any one of the

preceding claims, in which the catalyst is provided in a fixed bed and has an average particle size greater than 1 mm.

7. A process according to any one of the preceding claims, in which the metal of the eighth group is iron.

8. A process according to any of the preceding claims, in which the exit gas is cooled, directly or indirectly, to a temperature below 100° C. for the removal of water.

9. A process according to any one of claims 1 to 8, in which water is removed from the exit gases by chemical means, for example, by absorption with calcium chloride.

10. A process according to any one of claims 1 to 8, in which water is removed from the exit gases by contacting the exit gases with a surface active agent.

11. A process according to claim 10, in which the surface active agent is silica gel, active carbon, fuller's earth, bauxite or bentonite.

12. A process for the synthesis of aliphatic hydrocarbons and oxygen-containing organic compounds, substantially as described with reference to any one of Examples 1 to 3.

13. A process for the synthesis of aliphatic hydrocarbons and oxygen-containing organic compounds, substantially as hereinbefore described.

14. Aliphatic hydrocarbons having more than one carbon atom in the molecule whenever produced by the process of any preceding claim.

15. Oxygen-containing organic compounds wherever produced by the process of any one of claims 1 to 13.

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