PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Synthesis of Hydrocarbons or Admixtures thereof with Oxygenated Hydrocarbons

We, HYDROCARBON RESEARCH, INC., a corporation organised under the laws of the State of New Jersey, United States of America, of 115, Broadway, New 5 York, 6, State of New York, United States of America (Assignees of WALTER GUSTAVE FRANKENBURG and EDWIN TOWER LAYNG), do hereby declare the nature of this invention and in what 10 manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the synthesis of hydrocarbons or admixtures 15 thereof with oxygenated hydrocarbons by the catalytic reduction of carbon monoxide with hydrogen.

More particularly, the present invention contemplates the catalytic manu- 20 facture of hydrocarbons, particularly normally liquid hydrocarbons, in the presence of an iron catalyst at elevated temperatures in the range of about 500 to 750° F., and under elevated pressures. 25 As hitherto proposed, the process is usually accompanied by an objectionable production of by-product carbon dioxide. The present invention contemplates the control of carbon dioxide formation so 30 that the carbon monoxide in the feed is consumed essentially in the formation of the desired products, and contemplates also the controlled conversion of carbon dioxide into useful products. 35 In carrying out the present invention, a stream of reactant feed gas containing carbon monoxide, hydrogen and carbon dioxide is passed in contact with an iron catalyst under reaction conditions such 40 that at least about 80% or more of the carbon monoxide present in the total feed gas is consumed upon passage through

the catalyst.

We have discovered that when the total reactant mixture passing in contact with 45 the catalyst at appropriate reaction temperature contains hydrogen, carbon monoxide, and carbon dioxide in properly regulated proportions, the net production of carbon dioxide in the process is limited 50 to an economical and commercially practical level. We have also discovered that it is possible, by this regulation to cause actual consumption of carbon dioxide in the reaction. Our invention 55 resides in reacting feed gas of predetermined composition and at predetermined temperature effective to control carbon dioxide formation as above.

The total feed gas supplied to the 60 reaction zone most advantageously contains as small a concentration of water vapor as possible. While a gas free from water vapor is ideal, as a practical matter the lower limit is usually determined by 65 the degree of separation commercially practicable when condensing and separating at temperatures and pressures economically available. Accordingly, the present invention particularly contem- 70 plates the use of feed gases wherein the amount of water vapor is very minor, lower, in any event, than about 2 mol per cent., based on the total mols of hydrogen, carbon monoxide and carbon 75 dioxide.

More specifically, the invention contemplates use of feed gas compositions for which the ratio of A of the mols of hydrogen to the mols of carbon monoxide 80 in the feed to the reactor, the ratio G of the mols of carbon dioxide to the mols of carbon monoxide in the feed to the reactor, the ratio G of the mols of carbon

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dioxide to the mols of carbon monoxide in the feed to the reactor, and finally the absolute temperature T of the synthesis reaction, expressed in degrees Kelvin, are selected in such a way that the empirical 5 equation:—

$$K = 279.8e - (0.1548A - 0.1075G + 0.001512T) - 50$$

possesses a K value of 15 or less, preferably less than 10. In the equation, e is the 10 base of naperian logarithms, namely 2.71828 - - - .

A series of experiments has proved that the value of K is, in first approximation, equal to the percentage of total carbon 15 monoxide changed into carbon dioxide, under synthesis conditions. The value of K for any given A, G and T indicates to what extent such a conversion of carbon monoxide to carbon dioxide takes place; negative values of K show the extent to 20 which the reverse process, namely, a conversion of carbon dioxide to carbon monoxide, is occurring.

Stated in another way :—

$$20 \qquad \log_e(K+50) = -0.1548A - 0.1075G - 0.001512T + \log_e 279.8$$

where K, A, G and T have the same meanings as defined above, and A, G and T have to be selected so as to lead to values of K smaller than 15, preferably smaller 30 than 10.

For example, with a feed gas composition and a reaction temperature corresponding to a K value of 15, the net carbon dioxide production will approxi- 35 mate 15 per cent. on the basis of the carbon monoxide supplied to the reactor. Similarly when the feed gas composition and temperature conform to a K value of 10, the net production of carbon dioxide 40 will be about 10 per cent., on the same basis. It is usually preferred, however, to operate under conditions where the value of K is below about 5 whereby the net production of carbon dioxide is 45 restricted to a corresponding low value. It is to be understood that the foregoing specific results contemplate maintenance of a reasonably uniform temperature throughout the catalyst, with elimination 50 of localized hot spots, and high consumption of the carbon monoxide fed to the reactor, preferably substantially above 90 per cent. With a decrease in percentage conversion of carbon monoxide or sub- 55 stantial temperature variation, the net production of carbon dioxide usually tends to increase somewhat above the optimum above indicated.

When it is desired to effect actual con- 60 sumption of carbon dioxide supplied in the feed gas, conditions of temperature and feed gas composition are employed such that K in the foregoing equation has a predetermined negative value. 65 Negative values of K indicate the relative magnitude of the actual net consumption of carbon dioxide, the consumption of carbon dioxide being expressed as a per cent. of the carbon monoxide fed to the 70 reactor. Expressing the carbon dioxide in this way permits using the same general formula.

Obviously this embodiment of the invention is of particular advantage in situations where a source of carbon 75 dioxide is available in addition to the carbon monoxide and hydrogen which comprises the typical synthesis gas.

It is important to note that the foregoing relationships are effective for 80 optimum results when the feed gas comprises from about 8 to about 26 mol. per cent. of carbon monoxide, based upon the total mols of carbon monoxide, carbon dioxide and hydrogen present in the feed 85 gas, and particularly where the value of A is in the range between about 2 and about 6.5, more advantageously between the values of about 3 and about 5.5, and also wherein the value of G is within the 90 broad range from about 1 to about 5, and advantageously within the preferred range of about 2 to about 4. In other words, where the constituents of the total feed gas fall within the foregoing ranges, 95 the present invention affords a reasonably precise basis for controlling the extent of carbon dioxide formation.

Usually the value of A will be greater than 2.5, and the value of G will be 100 greater than 1.5 unless the value of A is substantially above the minimum. However, as clearly established by the empirical equation, increase in the value of G may permit a decrease in the value 105 of A or vice versa where equivalent results are desired.

Maximum production of liquid hydrocarbons boiling in approximately the motor gasoline boiling range, usually is 110 realized with an operating temperature in the range of about 600—650° F., and broadly, from about 550—700° F., depending upon the particular catalyst employed, and the other conditions of 115 operation. For example, with a typical iron catalyst promoted with minor quantities of alumina and potassium oxide, a good operating temperature may

be about 625° F. under a pressure of about 200 pounds per square inch gauge.

The catalyst may comprise granular or powdered iron suitably arranged in heat transfer relationship to appropriate cooling surfaces adapted to hold the operating temperature at the desired value. The catalyst advantageously contains any of the typical activators or promoters such as an oxide of an alkali metal, and in addition may contain oxide of aluminum. The catalyst may be in the supported or unsupported form as desired, although an unsupported type of catalyst is generally preferred. In the supported form, the catalyst may comprise iron, suitably reduced and conditioned, together with the promoter, carried upon silica gel, diatomaceous earth, or the like.

The so-called tail gas from the present process or similar processes, may be recovered and recycled in appropriate ratio with respect to the hydrogen and carbon monoxide feed gases to meet the requirements of the foregoing equation. If desirable, or necessary, the tail gases may be conducted through any suitable gas recovery plant whereby a concentrated carbon dioxide stream is made available for recycle.

As stated above, it is important in handling the recycle stream as well as the other reactant streams, to keep water vapor at a low and preferably insignificant level. Thus, the tail gases may be recovered by passing the gasiform effluent product through a condenser and separator to remove all of the normally liquid constituents. With condensation and separation at temperatures below 100° F. and a pressure of 250 pounds per square inch gauge, the water vapor content will be reduced to an inconsequential value, for example, about 0.36 mol per cent. A material increase in the water concentration, above 1.0 per cent., for example, results in an increased tendency toward net carbon dioxide formation. The residual overhead gases from the separation step constitute the tail gas stream referred to above which may be recycled either before or after removal of undesired normally gaseous constituents.

It is usually desirable from the standpoint of good utilization of available equipment, to limit, in so far as feasible, the proportion of other gaseous constituents in the total feed.

By way of example, feed gas containing carbon monoxide, hydrogen and carbon dioxide, and less than 0.1 per cent. of water vapor, is heated to conversion temperature, and passed at a pressure of from 205 to 250 pounds per square inch gauge in contact with a fluidized iron catalyst of 60 to 400 mesh size, promoted with small amounts of alkali and alumina, in a reaction zone maintained at the temperatures shown in the following table. The table summarizes seven separate runs, showing the mol per cent. of carbon monoxide in the feed gases, and the relative proportions of hydrogen and carbon dioxide to the carbon monoxide. The table also shows the approximate agreement of the calculated value of K, on the basis of the feed gas compositions and temperature, with the respective values of carbon dioxide production or consumption, as the case may be. Moreover, it gives in each case the percentage yield of hydrocarbons having at least three carbon atoms, on the basis of the carbon monoxide fed to the reactor.

EXAMPLES.

	1	2	3	4	5	6	7
CO mol % in total feed gas passing to the reactor	11.3	16.8	14.7	31.7	5.3	12.2	12.2
A(H_2/CO)	3.21	3.12	1.27	1.86	3.83	3.05	3.05
G(CO_2/CO)	2.27	1.26	2.14	0.29	5.04	2.12	2.12
Temp. °F.	643	645	638	650	618	505	679
K	2.82	9.60	22.63	30.07	13.61	10.79	3.39
CO_2 Production of Consumption as % of total CO charged	3.78	11.9	21.3	27.3	11.1	12.4	2.97
Yield C_3 and higher hydrocarbons basis % of total CO charged	73.1	59.3	40.1	54.1	87.6	58.1	78.2

Comparison of second example with the first shows that with a decrease in the ratio of carbon dioxide to carbon monoxide (G) in the feed gas, all other variables remaining essentially the same, there is a material increase in the net production of carbon dioxide. The third example, contrasted with the first, shows that operation with a lower ratio of hydrogen to carbon monoxide (A), such that K in the foregoing equation is outside the purview of the present invention, the production of carbon dioxide is excessive, and the yield of C_3 and higher hydrocarbons is low. The fourth example also shows excessive production of carbon dioxide and low yield of hydrocarbons, with low values of both A and G such that K is substantially above 15. Actual consumption of carbon dioxide is shown in the fifth example. The sixth and seventh examples serve to compare the general effect of variation in the reaction temperature.

It should be understood that the hydrocarbon yield referred to in the foregoing table includes small proportions of oxygenated hydrocarbons.

From the foregoing, it is apparent that the present invention provides an effective means for suppressing the net production of carbon dioxide to low levels below 15 per cent. and preferably below 10 per cent., and, in the optimum preferred operation hereunder, not greater than 5 per cent. on the basis of the carbon monoxide consumed. This is accomplished without adversely affecting the product distribution to any material extent, and results in a corresponding overall increase in hydrocarbon production. It may, moreover, be accomplished without great regard to the specific type of hydrocarbon product which it is desired to produce.

In general, a change in the specific iron catalyst employed, the operating pressure, or the contact time, within reasonable limits, will cause only minor variation in desired results.

The invention may be applied to operations wherein the feed gas is contacted with the catalyst in either a single stage, or in a plurality of series stages, with or without interstage condensation or removal of water vapor and/or hydrocarbon products. In general, the intermediate removal of water vapor between stages is beneficial.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What we claim is:—

1. A process for the production of hydrocarbons or admixtures thereof with oxygenated hydrocarbons, wherein reactant gas containing hydrogen, carbon monoxide and carbon dioxide is passed in contact with an iron synthesis catalyst in a reaction zone maintained under a temperature of from about 500 to about 750° F. and a superatmospheric pressure effective to cause consumption of, at least, about 80 per cent. of the carbon monoxide supplied, with formation of desired products of reaction, and the products of reaction are recovered, characterised by the fact that the total stream of reactant gas supplied as a feed for passage in contact with the synthesis catalyst is in conformance with the following equation:—

$$\log_\varepsilon(K+50) = -0.1548A - 0.1075G - 0.001512T + \log_\varepsilon 279.8$$

where K is less than 15; ε is the naperian logarithmic base, 2.71828 - - - ; A is equal to the ratio of the mols of hydrogen to the mols of carbon monoxide in the feed gas to the reaction zone; G is the ratio of the mols of carbon dioxide to the mols of carbon monoxide in the feed gas to the reaction zone; and T is the absolute temperature of the synthesis reaction in degrees Kelvin; and the products of reaction are separated from the effluent gases.

2. A process as defined in claim 1, wherein the value of K is below about 10.

3. The process as defined in claim 1, wherein the value of K is below about 5.

4. A process for the production of hydrocarbons or admixtures thereof with oxygenated hydrocarbons, wherein reactant gas containing hydrogen, carbon monoxide and carbon dioxide is passed in contact with an iron synthesis catalyst in a reaction zone maintained under a temperature of from about 500 to about 750° F. and a superatmospheric pressure effective to cause consumption of, at least, about 80 per cent. of the carbon monoxide supplied, with formation of desired products of reaction, and the products of reaction are recovered, which comprises maintaining the relative molar proportions of hydrogen, carbon monoxide and carbon dioxide in conformance with the following equation:—

$$\log_e(K+50) = -0.1548A - 0.1075G - 0.001512T + \log_e 279.8$$

where K is a negative number; e is the naperian logarithmic base, 2.71828 - - - ; A is equal to the ratio of the mols of hydrogen to the mols of carbon monoxide in the feed gas to the reaction zone; G is the ratio of the mols of carbon dioxide to the mols of carbon monoxide in the feed gas to the reaction zone; and T is the absolute temperature of the synthesis reaction in degrees Kelvin; and the products of reaction are separated from the effluent gases.

5. The process according to claim 1, wherein the mixture of reactant gas supplied in contact with the catalyst contains not above 1.0 mol per cent. water vapor.

6. The process according to claim 1, wherein the mixture of reactant gas supplied in contact with the catalyst contains water vapor in an amount lower than 2 per cent, based on the total mols of hydrogen, carbon monoxide and carbon dioxide.

7. The process according to claim 4, wherein the mixture of reactant gas supplied in contact with the catalyst contains not above 1.0 mol per cent. water vapor.

8. The process as defined in claim 1, wherein the said gas contains about 8 to about 26 mol per cent. carbon monoxide based on the total content of carbon monoxide, hydrogen and carbon dioxide and wherein the value of A is between about 2 and about 6.5.

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