United States Patent Office

2,912,475

Patented Nov. 10, 1959

2,912,475

# MANUFACTURE OF LOW MOLECULAR UNSATURATED HYDROCARBONS

**Walter Krause, Frankfurt am Main, Hans Krekeler, Konigstein (Taunus), and Rudolf Wirtz and Herbert Kamptner, Frankfurt am Main, and Ditmar Bachmann, Hofheim (Taunus), Germany, assignors to Farbwerke Hoechst Aktiengesellschaft vormals Meister Lucius & Brüning, Frankfurt am Main, Germany, a corporation of Germany**

**No Drawing. Application April 17, 1956**
**Serial No. 578,581**

**Claims priority, application Germany April 28, 1955**

**14 Claims. (Cl. 260—679)**

Various processes have already been described which relate to the production of low molecular unsaturated hydrocarbons, wherein gaseous or liquid hydrocarbons are reacted with a carrier gas at high temperatures. As carrier gas it has been proposed to use, for example, steam. In these known processes, the gas used as a carrier has been heated in various ways to a high temperature. Thus, for example, a tower filled with ceramic material is first heated by combustion gases of carbon-containing compounds and, when the combustion is terminated, the tower is cleansed by means of inert gases, e.g. steam, so as to remove the combustion gases and the steam is then heated up on the heated ceramic material. This process, however, involves the disadvantage that the steam temperature varies during the cracking process and diminishes in each period until the heating tower must again be heated up; therefore, a non-uniform reaction product is always obtained. This process, furthermore, requires thorough and constant control and involves great losses in energy.

According to another known process, the hot combustion gases from an oxyhydrogen flame are used as a carrier; these gases are mixed in a nozzle with a hydrocarbon that is gaseous at room temperature and under normal pressure, and the mixture of gases is chilled after a short time of reaction. However, this process involves the disadvantage that the hot combustion gases of the oxyhydrogen flame contain a considerable proportion of oxygen-containing radicals, oxygen atoms and oxygen molecules which react with part of the hydrocarbon to form carbon monoxide and carbon dioxide.

Our present invention provides a process for the manufacture of low molecular unsaturated aliphatic hydrocarbons, especially acetylene and/or ethylene, in which a hydrocarbon containing at least two carbon atoms is pyrolized by contacting it for a short time with a carrier gas consisting of hot combustion gas containing hydrogen, wherein the oxygen- and oxygen-containing radicals, oxygen atoms and oxygen molecules which are formed by dissociation and are contained in the hot combustion gas are first recombined by the introduction of at least one secondary gas having a lower temperature than the combustion gas and which is advantageously of the same chemical nature as the combustion gas, and the hydrocarbon to be pyrolized is then contacted with this carrier gas which has thus been substantially freed from oxygen. The unsaturated hydrocarbon products which chiefly contain 2 to 4 carbon atoms are obtained in a good yield.

The aforesaid disadvantages inherent to the known processes are substantially overcome by the process of the invention and at the same time the formation of carbon monoxide and carbon dioxide has been substantially reduced. The recombination heat set free upon introduction of the less heated gas is used for heating up the secondary-gas and the dissociation energy contained in the carrier gas used is converted to kinetic energy. It has been found that the oxygen-containing radicals, the oxygen atoms and the oxygen molecules contained in the carrier gas favour the formation of carbon monoxide and carbon dioxide in the subsequent cracking process. If, however, according to this invention, the carrier gas is freed from such radicals, then a considerably smaller quantity of these by-products is formed.

The process of this invention can be conducted with advantage by so selecting the amount of the hydrocarbon introduced that the temperature of the gas mixture still amounts to at least 700° C. after the gas has been mixed and reacted with the hydrocarbon or hydrocarbons within the conventional time of reaction which, preferably, amounts to $10^{-1}$ to $10^{-4}$ seconds, and prior to the chilling of the reaction mixture.

When it is desired to produce ethylene as the main product, it is advisable to effect the reaction within $10^{-1}$ to $10^{-3}$ seconds; in this case, the amount of the hydrocarbon introduced is so selected that the temperature of the gas mixture still amounts to at least 700° C. after the gas has been mixed and reacted with the hydrocarbon and prior to the chilling of the reaction mixture obtained. When, however, it is desired to produce acetylene as the main product, it is advantageous to perform the reaction within a shorter time, i.e. within $10^{-2}$ to $10^{-4}$ seconds, and so to select the amount of the hydrocarbon introduced that the temperature of the gas mixture still amounts to at least 1000° C., after the gas has been mixed and reacted with the hydrocarbon or hydrocarbons and prior to the chilling of the reaction mixture obtained.

As starting hydrocarbons there are used aliphatic hydrocarbons. As such compounds there may be mentioned, more especially, ethane, propane, butane, ethylene, propylene, the butylenes and commercial mixtures of these gases; as hydrocarbons which are liquid at room temperature there can advantageously be used any hydrocarbons, such as hexanes, heptanes, octanes, decanes, the mono-unsaturated aliphatic hydrocarbons, commercial mixtures of hydrocarbons, such as petroleum distillates, fractions of benzine, topped oils, diesel oils etc. There can also be used hydrocarbons which are solid at room temperature and contain up to 30 or more carbon atoms; these latter compounds are advantageously used in the form of a solution in less heavy hydrocarbons or in a melted form. The aforesaid hydrocarbons are contacted in the vapor or liquid or gaseous state with a current of combustion gases which are free from oxygen and contain hydrogen.

The process according to this invention can be conducted with particular advantage without application of superatmospheric pressure. It is, however, also possible to perform the pyrolysis both with application of elevated pressure or under slightly reduced pressure. It is advisable to introduce the secondary gas under a pressure of at least 1 atmosphere (absolute). However, it is advantageous to introduce the secondary gas at least under the same pressure as prevails at the inlet where the carrier gas is introduced.

As carrier gas there may be used with advantage the combustion gases of oils, coal dust, gaseous hydrocarbons, hydrogen, etc. to which free hydrogen is added, if not yet contained in these compounds. As carrier gas there may also be used mixtures of hydrogen with steam and carbon monoxide, if desired in admixture with carbon dioxide or small amounts of other substances which do not affect the reaction and as obtained by combustion of the aforesaid substances or by the addition of hydrogen. In the preparation of acetylene it is, generally, not advisable to use as carrier gas nitrogen or carbon dioxide alone or gas mixtures rich in nitrogen or carbon dioxide. These mixtures exhibit a detrimental effect, that is, in the presence of carbon dioxide it is especially the subsequent separation of the gas that is rendered difficult, and in the presence of nitrogen the formation of acetylene is retarded.

As secondary gases there may also be used the gases that are formed by the combustion of the substances described in the preceding paragraph. For the purpose of this invention, it has proved to be particularly advantageous to use steam as carrier gas, and to use steam and/or hydrogen as secondary gas. If hydrogen is used as secondary gas, the hydrogen can be introduced into the carrier gas at any temperature desired; if, however, steam is used as a secondary gas, such steam is required to have a temperature which at least corresponds to the boiling point of the water under the corresponding pressure. When mixtures of steam or mixtures of steam and hydrogen are used, it is, however, advantageous to introduce these mixtures at a temperature of at least 150° C.

The quantity of the secondary gas used may vary within wide limits; furthermore, the amount is dependent on the temperature of the carrier gas and the secondary gas. The amount of the secondary gas used, generally, amounts to between 1 and 80 percent by weight, preferably 30 to 70 percent by weight, and is in each case calculated upon the sum of carrier gas and secondary gas.

The hydrocarbon is introduced according to methods known per se; it is preferable to introduce the hydrocarbons at a temperature not in excess of 400° C., so that no cracking occurs prior to the reaction. It is, however, also possible to introduce liquid hydrocarbons by injection.

In the process of this invention the carrier gas is produced, as has already been mentioned above, by combustion of a combustible substance immediately before contacting the hydrocarbon. To this end, it is advisable to provide for a fairly small distance between the combustion flame and the reaction chamber in order to keep the heat losses caused by dissipation as limited as possible. Preferably a nozzle is arranged between the combustion flame and the reaction chamber, it being of advantage to mix the hydrocarbon with the gas used as carrier gas immediately behind that nozzle.

The significance of the process steps according to the invention is apparent from the fact that in a hot current of steam of 2000° C. about 1.0 percent by volume of steam is present in the form of the OH-radical, 1.0 percent by volume in the form of the $O_2$-molecule, and 0.06 percent by volume in the form of the oxygen atom. At a temperature of 2850° C. which is the temperature of the oxyhydrogen flame without admixture of secondary steam, the OH-radicals, O-radicals and $O_2$-molecules are present in a proportion of 11.5:4.5:5.8 percent by volume. It will be understood that the higher the temperature of the combustion gas, the greater is the advantage offered by the process of this invention.

It has already been proposed to mix a superheated carrier gas with heated methane, ethane or propane in a nozzle and to react the mixture obtained in a reactor. In this known process the propellant has a temperature of about 2200° C. and, when it is mixed with said hydrocarbons, a temperature of about 1650° C. At 2200° C. there are still present noteworthy quantities of oxygen-containing radicals, oxygen atoms and oxygen molecules which favour the formation of carbon monoxide from the hydrocarbons to be reacted. Besides, according to this known process, the gases to be reacted are preheated on the filling material to temperatures of about 1000° C. and more prior to being mixed up, whereby distinct cracking occurs. This process is very complicated and

can only be conducted, if at all, with the use of hydrocarbons which are gaseous at room temperature because of the high temperatures required for pre-heating and owing to the special mode of pre-heating the aforesaid hydrocarbons which are to be reacted; this pre-heating operation involves pumping the cooled filling material into a second container to be heated up.

The following examples serve to illustrate the invention, but they are not intended to limit it thereto:

## EXAMPLE 1

(A) To the hot combustion gases obtained by combustion, per hour, of 26 normal cubic metres (cubic metre at 0° C. under atmospheric pressure) of hydrogen and 12 normal cubic metres of oxygen, ethylene is added in an amount such that the temperature in the reaction zone is about 1100 to 1300° C. The gases are reacted within about 0.005 second and then chilled.

(B) The same amounts of hydrogen, oxygen and ethylene are reacted as indicated sub A with the exception, however, that, per hour, 9 kilograms of steam are added prior to the mixing operation with ethylene.

(C) The reaction tower is charged with the same amounts of oxygen, hydrogen and ethylene as indicated sub A and B with the exception, however, that, per hour, 35 kilograms of steam are added prior to the mixing operation with ethylene. The test results obtained are indicated in the following table. The quantities determined by analysis are given in percent by volume:

*Table*

| A<br>Without steam | | B<br>Steam introduced, 9 kilograms/hour | C<br>Steam introduced, 35 kilograms/hour |
|---|---|---|---|
| $CO_2$ | 2.3 | 1.6 | 0.4 |
| $C_2H_2$ | 14.2 | 22.2 | 22.0 |
| $C_2H_4$ | 4.2 | 9.8 | 20.8 |
| CO | 14.0 | 8.2 | 4.9 |
| $H_2$ | 62.3 | 52.8 | 48.0 |
| $CH_4$ | 3.0 | 5.4 | 3.9 |

## EXAMPLE 2

To the hot combustion gases obtained by combustion, per hour, of 27.5 normal cubic metres of hydrogen and 13.5 normal cubic metres of oxygen are added first 19.5 kilograms of steam of 180° C. and immediately thereafter benzine (boiling range: 50–220° C.; superheated to 350° C.) in an amount such that the temperature in the reaction zone amounts to 1100–1300° C. The components are reacted in the reaction zone for 0.002 second and the reaction mixture is chilled.

From the benzine introduced is obtained 95 percent of a gaseous product of the following composition, (Quantities in percent by volume): 0.8% of $CO_2$, 17.0% of acetylene, 0.8% of higher unsaturated hydrocarbons, 14.9% of ethylene, 9.1% of carbon monoxide, 44.8% of hydrogen and 12.6% of saturated hydrocarbons consisting substantially of methane.

## EXAMPLE 3

To the hot combustion gases obtained by combustion, per hour, of 27.5 normal cubic metres of hydrogen and 13.5 normal cubic metres of oxygen are added, per hour, 3 kilograms of steam of 180° C. and immediately thereafter a petroleum fraction (boiling range: 54–360° C.; superheated to 400° C.) in an amount such that the temperature in the reaction zone amounts to 1100–1300° C. The components are reacted in the reaction zone within 0.002 second and the reaction mixture obtained is chilled.

From the petroleum fraction used is obtained 78.5 percent of a gaseous product of the following composition (quantities in percent by volume): 2.1% of $CO_2$, 15.1% of acetylene, 0.8% of higher unsaturated hydrocarbons, 11.8% of ethylene, 9.9% of carbon monoxide, 47.5% of hydrogen, and 12.8% of unsaturated hydrocarbons.

### EXAMPLE 4

Under the conditions applied in Example 3 are reacted the same amounts of hydrogen, oxygen and hydrocarbons of the same petroleum fraction (boiling range: 54–360° C.) with the exception, however, that the combustion gases are mixed, per hour, with 19.5 kilograms of steam prior to being mixed up with the hydrocarbons.

From the petroleum fraction used is obtained 76 percent of a gaseous product of the following composition (quantities in percent by volume): 1.6% of $CO_2$, 17.5% of acetylene, 13.9% of ethylene, 8.8% of carbon monoxide, 45.6% of hydrogen and 12.6% of saturated hydrocarbons.

What we claim is:

1. A process for the manufacture of low molecular weight unsaturated aliphatic hydrocarbons which comprises (*a*) forming a stream of hot combustion gas containing oxygen atoms, oxygen molecules and oxygen-containing radicals formed by dissociation; (*b*) introducing a secondary gas into said stream of hot combustion gas for recombining the oxygen atoms, oxygen molecules and oxygen-containing radicals therein and thereby forming a stream of carrier gas which is substantially free from molecular oxygen and contains hydrogen, said secondary gas having a temperature of at least about 150° C. but a lower temperature than the combustion gas and the amount thereof being about 1 to 80% by weight, calculated upon the total amount of carrier gas; (*c*) passing the carrier gas through a restricted opening into a reaction zone for accelerating said stream of carrier gas; and (*d*) contacting the accelerated stream of carrier gas with a hydrocarbon containing at least two carbon atoms in the molecule for $10^{-1}$ to $10^{-4}$ seconds for pyrolysis of said hydrocarbon, the rate of feed of hydrocarbon being adjusted to maintain the temperature of the reacted gas mixture at at least about 700° C.

2. A process for the manufacture of low molecular weight unsaturated aliphatic hydrocarbons rich in unsaturated $C_2$ hydrocarbons which comprises (*a*) forming a stream of hot combustion gas obtained by combustion of an excess of hydrogen with oxygen and containing oxygen atoms, oxygen molecules and oxygen-containing radicals formed by dissociation; (*b*) introducing a secondary gas into said stream of hot combustion gas for recombining the oxygen atoms, oxygen molecules and oxygen-containing radicals therein and thereby forming a stream of carrier gas which is substantially free from molecular oxygen and contains hydrogen, said secondary gas being selected from the group consisting of hydrogen, steam and mixtures thereof and having a temperature of at least about 150° C. but a lower temperature than the combustion gas and the amount thereof being about 1 to 80% by weight, calculated upon the total amount of carrier gas; (*c*) passing the carrier gas through a restricted opening into a reaction zone for accelerating said stream of carrier gas; and (*d*) contacting the accelerated stream of carrier gas with a hydrocarbon that is liquid at room temperature for $10^{-1}$ to $10^{-4}$ seconds for pyrolysis of said hydrocarbon, the rate of feed of hydrocarbon being adjusted to maintain the temperature of the reacted gas mixture at at least about 700° C.

3. A process for the manufacture of low molecular weight unsaturated aliphatic hydrocarbons rich in acetylene which comprises (*a*) forming a stream of

hot combustion gas obtained by combustion of an excess of hydrogen with oxygen and containing oxygen atoms, oxygen molecules and oxygen-containing radicals formed by dissociation; (*b*) introducing a secondary gas into said stream of hot combustion gas for recombining the oxygen atoms, oxygen molecules and oxygen-containing radicals therein and thereby forming a stream of carrier gas which is substantially free from molecular oxygen and contains hydrogen, said secondary gas being selected from the group consisting of hydrogen, steam and mixtures thereof and having a temperature of at least about 150° C. but a lower temperature than the combustion gas and the amount thereof being about 1 to 80% by weight, calculated upon the total amount of carrier gas; (*c*) passing the carrier gas through a restricted opening into a reaction zone for accelerating said stream of carrier gas; and (*d*) contacting the accelerated stream of carrier gas with a hydrocarbon that is liquid at room temperature for $10^{-2}$ to $10^{-4}$ seconds for pyrolysis of said hydrocarbon, the rate of feed of hydrocarbon being adjusted to maintain the temperature of the reacted gas mixture at at least about 1000° C.

4. A process as defined in claim 1 wherein steam is present in the secondary gas and said secondary gas has in addition a temperature at least equal to the boiling temperature of water under the conditions of operation.

5. A process according to claim 1, wherein the hydrocarbons to be pyrolized are preheated before they are contacted with the combustion gas.

6. A process according to claim 1, wherein ethylene is produced as a main product by adjusting the temperature of the gas mixture after the reaction within $10^{-1}$ to $10^{-3}$ sec., to at least 700° C. by regulating the amount of the hydrocarbon to be pyrolized.

7. A process according to claim 1, wherein the reaction is carried out substantially at atmospheric pressure.

8. A process according to claim 1, wherein the secondary gas is introduced under a pressure of at least 1 atmosphere.

9. A process according to claim 1, wherein the secondary gas is a compound selected from the group consisting of hydrogen, steam and mixtures thereof.

10. A process according to claim 1, wherein the secondary gas is used in an amount of 30–70% by weight, calculated upon the total amount of combustion gas and secondary gas.

11. A process according to claim 1, wherein a combustion gas is used which consists substantially of steam.

12. A process according to claim 1, wherein the hydrocarbon to be pyrolized is liquid at room temperature and is contacted with the combustion gas in the geaseous state.

13. A process according to claim 1, wherein steam is used as secondary gas.

14. A process accordingto to claim 1, wherein a combustion gas is used which consists substantially of a mixture of steam, hydrogen and carbon monoxide.

**References Cited in the file of this patent**

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,371,147 | Burk | Mar. 13, 1945 |
| 2,520,149 | Keeling | Aug. 29, 1950 |
| 2,706,210 | Harris | Apr. 12, 1955 |
| 2,767,233 | Mullen et al. | Oct. 16, 1956 |
| 2,816,941 | Goins | Dec. 17, 1957 |
| 2,823,243 | Robinson | Feb. 11, 1958 |