Patented Feb. 21, 1933

1,898,301

UNITED STATES PATENT OFFICE

WILLY O. HERRMANN AND ERICH BAUM, OF MUNICH, GERMANY, ASSIGNORS TO CONSORTIUM FUR ELEKTROCHEMISCHE INDUSTRIE, OF MUNICH, BAVARIA, GERMANY

PROCESS FOR THE PREPARATION OF UNSATURATED HYDROCARBONS

No Drawing. Application filed July 30, 1927, Serial No. 209,639, and in Germany August 2, 1926.

This invention relates to the production of unsaturated hydrocarbons by the thermal decompositions or partial oxidation of more highly saturated organic compounds. This invention relates more particularly to the production of acetylene and unsaturated compounds of the ethylene series from paraffin hydrocarbons such as methane and ethane and of acetylene from ethylene hydrocarbons such as ethylene.

We have found that aliphatic hydrocarbons can be transformed into more unsaturated hydrocarbons containing the same or a greater number of carbon atoms than the hydrocarbon starting material by leading the materials in contact with heated surfaces. For example, we have found that methane can be transformed into ethylene and acetylene, that ethane can be transformed into ethylene and higher homologues, and that ethylene can be transformed into acetylene etc.

In carrying out this invention we provide a converter preferably containing a packing material. The heated surfaces, such as the packing material may be of coke, porcelain or other inert substances. These heated surfaces may further contain materials catalytic to the reaction; such materials as metals, and oxides and alloys are in general particularly valuable; nickel, copper, and platinum are of especial value as catalysts.

The products of this reaction are in general composed of several materials and I do not wish to be limited to any one product specifically disclosed as having been obtained, but I include the olefine hydrocarbons and acetylene which are obtained in varying amounts under the general term of unsaturated aliphatic hydrocarbons.

The heating of the surfaces which are to act as catalytic material in my reaction may be accomplished in several ways for example, a gas generator filled with coke can be ignited and air blown until the desired temperature is reached; regenerative ovens of brick work or other material acting catalytically on the reaction may be used in connection with the furnaces; molten masses of metal can be used as heat absorbers for regenerative systems by the introduction of an insufficient amount of air for oxidation of the gas which is to be converted, a partial oxidation is obtained which creates the necessary heat for the reaction; or complete oxidation of the gas which is to be converted may be utilized at alternate periods for heat regenerative ovens or gas producers.

The following examples of my invention are given:

Example I

A cylindrical producer having an internal diameter of 100 mm. and about 400 mm. high formed of iron lined with fire resistant material was filled with small pieces of coke, ignited and blown with air until a temperature of about 1000° C. was obtained in the combustion zone. A rapid stream of methane or natural gas was now blown through the glowing mass of coke at a speed of about 500 liters per hour. This amounts to a space velocity of the order of 160 liters of methane per liter of coke or reaction space per hour. The outgoing gas containing 20 to 30% of ethylene and 3 to 4% of acetylene. After a short time when the temperature of the coke mass had fallen below a red heat the introduction of methane was discontinued and the temperature of the producer again raised by blowing with air. The ethylene and acetylene were removed from the outgoing reaction gas by absorption leaving a residual gas. The residual gas contains large amounts of hydrogen which has considerable heating value.

Example II

A quartz tube of about 20 mm. diameter and 380 mm. length provided with an electric heating means was filled with pea size porcelain granules impregnated with vanadic acid. This was then heated by means of an electric current to 700° C. and a rapid stream of a mixed gas containing equal volumes of methane and oxygen was passed through the tube. The outgoing gas contained about 1,5% ethylene and 4% acetylene.

Example III

An inverted incandescent gas light burner

was placed in an iron cylinder provided with a cooling jacket and provided at its lower end with a hood through which the reaction gases could escape. A mixture of 300 liters methane and 177 liters oxygen was fed through the burner in a period of one hour. The high speed of the gases prevented the striking back of the flame. The temperature was above the red heat. The outgoing reaction gases contained 5% acetylene; this corresponds to a yield of about 17% of the theoretical.

Example IV

A Meker burner was placed in a sheet iron cylinder provided with a cooling jacket and a reaction gas exit opposite the burner. This cylinder was provided with a sheet iron partition placed across the cylinder about 10 mm. from the top of the burner and having an opening of about 8 mm. diameter in the cylinder. The Meker burner was fed with a gas mixture of methane and oxygen at a rate of 174 liters methane and 106 liters oxygen per hour. The reaction gas escaping from the cylinder contained about 4% acetylene corresponding to a yield of 15% of the theoretical.

Example V

A quartz tube of about 20 mm. diameter like in Example II was filled with platinated asbestos. The tube was heated to about 700° C. and then a rapid stream of a mixed gas containing two volumes of ethylene and one volume of oxygen was passed through the tube. The temperature was maintained above red heat by the reaction itself. The outgoing gas contained 5–6% acetylene.

In all of the above cases the escaping reaction gas after the removal of the acetylene and ethylene still contained considerable heating value and was for example suitable as a source of hydrogen.

We claim:

1. Process of preparing unsaturated hydrocarbons which comprises passing more highly saturated gaseous aliphatic hydrocarbons in contact with unreactive heated surfaces at temperatures between a red heat and 1000° C. and at space velocities of the order of 160 liters per liter of reaction space per hour, the reaction space being the volume of the reaction tube minus the volume of the filling material present.

2. Process of preparing unsaturated hydrocarbons which comprises passing more highly saturated gaseous aliphatic hydrocarbons and oxygen in contact with heated carbon at temperatures above a red heat and at space velocities of the order of 160 liters per liter reaction space per hour.

3. Process of preparing unsaturated hydrocarbons which comprises passing more highly saturated gaseous aliphatic hydrocarbons in contact with heated carbon at temperatures between a red heat and 1000° C. and at space velocities of the order of 160 liters per liter of reaction space per hour, the reaction space being the volume of the reaction tube minus the volume of the coke present.

4. Process of preparing unsaturated hydrocarbons which comprises passing a mixture of more highly saturated gaseous aliphatic hydrocarbons and oxygen through a burner heated between red heat and 1000° C. at a velocity in excess of that at which flame is propagated in such mixture, the quantity of oxygen being insufficient to completely oxidize the hydrocarbons.

5. Process of preparing olefine hydrocarbons which comprises passing a gas containing methane over carbon at temperatures above a red heat and at space velocities of the order of 160 liters per liter of reaction space per hour.

6. Process of preparing a gas containing ethylene which comprises passing a saturated aliphatic hydrocarbon gas in contact with unreactive heated surfaces at temperatures above a red heat at space velocities of the order of 160 liters per liter of reaction space per hour.

7. Process of preparing ethylene which comprises passing a gas containing methane over carbon at temperatures above a red heat and at space velocities of the order of 160 liters per liter of reaction space per hour.

8. Process of preparing acetylene which comprises passing a gas containing methane over carbon at temperatures above a red heat and at space velocities of the order of 160 liters per liter of reaction space per hour.

9. Process of preparing unsaturated hydrocarbons which comprises passing a mixture of more highly saturated gaseous aliphatic hydrocarbons and a deficiency of oxygen necessary to completely oxidize the hydrocarbons in contact with unreactive heated surfaces at temperatures between red heat and 1000° C. at space velocities of the order of 160 liters per liter of reaction space per hour, the reaction space being the volume of the reaction tube minus the volume of the filling material present.

Signed at Munich, in the county of Oberbayern and State of Bavaria this 13th day of July, A. D. 1927.

WILLY O. HERRMANN.
ERICH BAUM.