United States Patent Office 2,859,258 Patented Nov. 4, 1958

2,859,258

PROCESS FOR THE PRODUCTION OF ETHYLENE

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No Drawing. Application October 8, 1954
Serial No. 461,294

Claims priority, application Germany October 10, 1953

6 Claims. (Cl. 260—683)

This invention relates to the production of ethylene and particularly relates to the production of ethylene by the thermal cracking of methane or natural gases which predominately contain methane. This application is a continuation in part of co-pending U. S. patent application Serial No. 432,016, filed May 24, 1954.

Application Serial No. 432,016 is concerned primarily with the production of ethylene by the thermal cracking of hydrocarbons wherein the by-products of the process are recycled for additional treatment to produce additional quantities of ethylene. The process set forth in this prior patent application, however, cannot be used with a raw material such as methane. The reason for this is that the thermal conversion of the methane molecule requires substantially higher temperatures than those necessary for the cracking of the hydrocarbons because of the far greater thermal stability of methane molecules.

It has heretofore been known to convert methane to acetylene at extremely high temperatures, as, for example, by the use of an electric arc. This conversion into acetylene involves a reaction which is unduly expensive and therefore commercially infeasible. The expense is incurred, in the first place, by the high amounts of energy which are consumed during the endothermic formation of the acetylene; in the second place this acetylene formation requires complex and expensive apparatus. Furthermore, since the energy must be removed in the form of hydrogenation heat which is developed during the hydrogenation of acetylene to ethylene; this exothermic reaction, following the previous endothermic reaction, involves a total waste of energy since the energy level at the completion of the process is substantially similar to the energy level at the beginning of the process, even though a great deal of energy has been used during the process. It is, therefore, highly desirable to effect the cracking between such temperature ranges that there is very little formation of acetylene but a substantially large formation of ethylene.

According to the process embodied in this invention, methane may be used as the raw material if, prior to the recycle in which the main formation of ethylene takes place, there is provided a recycle operating at substantially higher temperatures than the first mentioned recycle.

In the recycle at the higher temperatures the methane is partly converted to ethylene and partly to saturated and unsaturated hydrocarbons having two or more carbon atoms in the molecule. These hydrocarbons can then be cracked at lower temperatures.

The raw, cracked gas which is formed in the primary recycle; that is, the recycle operating at the higher temperatures, is separated from the unconverted portion of the methane and the ethylene is then removed therefrom. The unconverted methane is then returned to the primary recycle together with a fresh amount of methane

which takes the place of that consumed during the first reaction. That portion of the cracked gas which remains after the separation of the ethylene is introduced into the secondary recycle, at the lower temperatures, where conversion to ethylene takes place in accordance with the process as described in the above-mentioned copending application Serial No. 432,016.

The combination of a primary recycle operating at a relatively high temperature and a secondary recycle operating at a relatively lower temperature not only serves to simplify the entire process but also acts to save energy. The saving of energy is effected by the use of the heating gases, used in the primary recycle, to heat the apparatus used in the secondary recycle, the temperature of these gases having been lowered during their use for heating the primary recycle. It has been found that a temperature range of between about 800° C. and 1100° C. is required for the primary recycle, while a temperature range of between about 600° C. and 800° C. is required for the secondary recycle. Optimum results have been achieved when the temperature of the primary recycle is between about 950° C. and 1050° C. and when the temperature of the secondary recycle is between about 700° C. and 750° C.

The recovery of the ethylene from the primary cracking step preferably takes place by means of adsorption methods. This is necessary in this case because the yield is relatively small and results in a so-called "lean" gas. It has been determined that adsorption methods are the only economically feasible methods for recovering the ethylene.

It has been found that the primary cracking step provides the highest yields if the cracking is conducted in the presence of suitable catalysts. Such catalysts preferably take the form of oxygen-containing metal compounds wherein the metals are of the second, third and fourth groups of the periodic system. Among the catalysts which may be used are aluminum oxide, magnesium aluminum silicate, and magnesium aluminum molybdate. In order to obtain optimum results, these oxygen-containing metal compounds are preferably activated by the addition of small amounts of heavy metals. Among the heavy metals which may be used are lead, copper, chromium, iron, nickel, cobalt, arsenic, antimony, gold, silver and mercury.

The primary recycle may be conducted either at atmospheric, sub-atmospheric or super-atmospheric pressures. More particularly, the primary recycle is preferably conducted at pressures ranging between one and five kg./cm.^{2}. It is preferable, however, to employ a certain amount of superatmospheric pressure, that is, pressures ranging between one and five kg./cm.^{2}, in order to simplify the adsorption separation process due to the formation of high molecular reaction products.

The secondary recycle may be conducted under the same pressure conditions as the primary recycle; however, in the secondary recycle the application of a super-atmospheric pressure and the employment of catalysts are not necessary. The apparatus for conducting the secondary recycle, therefore, may be relatively simple and inexpensive.

Example

Five cubic meters of methane per hour were introduced at a pressure of two kg./cm.^{2} into a reaction chamber which was maintained at 1050° C. The reaction chamber was filled with a catalyst consisting of magnesium aluminum silicate.

The catalyst was activated by a small amount of chromium comprising about 3%. The exit gas had the following composition in percent by volume:

	Percent
Propylene and butylene	0.2
Propane and butane	2.1
Ethane	1.6
Hydrogen	24.3
Ethylene	2.4
Methane	69.4
	100.0

From this gas mixture the methane and the ethylene were removed by means of adsorption on active carbon, and the methane was returned to the reaction chamber together with 30.6% of fresh methane. The entire remaining gas, after separation of the ethylene and methane, was again subjected to cracking in a coiled tube heated externally to 800° C. and yielded a cracked gas having the following composition:

	Percent
Propylene and butylene	25.0
Saturated hydrocarbons and hydrogen	54.3
Ethylene	20.7
	100.0

From this cracked gas the ethylene was removed by pressure oil washing; it was combined with the ethylene formed in the primary cracking step and the resulting ethylene mixture was then subjected to a purification.

The entire remaining gas, together with the higher hydrocarbons and hydrogen from the primary cracking zone was returned as recycled gas to the secondary cracking step.

After a continuous operation for 24 hours, it was possible to set up the following balance (of amounts):

Introduced, 13.33 kg.
Obtained, 5.25 kg.
Fresh methane=100%
Ethylene=39.4%

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope hereof, it is to be understood that the invention is not limited to the specific embodiments hereof, except as defined in the appended claims.

What is claimed in this invention is:

1. A process for obtaining ethylene in high yields comprising the steps of thermally cracking a gas which is at least predominantly methane at a relatively high temperature ranging between about 800° C. and 1100° C. to partly convert said gas to a mixture of ethylene and saturated and unsaturated hydrocarbons, separating said mixture from the unconverted portions of the gas, removing the ethylene from the mixture, and subjecting the remainder of said mixture to a second thermal cracking step at a relatively lower temperature ranging between about 600° C. and 800° C. to convert the said remainder of said mixture at least partially to ethylene.

2. The process of claim 1 wherein the unconverted portion of said gas is again subjected to the thermal cracking at the relatively high temperature.

3. The process of claim 1 wherein said relatively high temperature comprises a temperature ranging between about 950° C. and 1050° C. and wherein said relatively lower temperature comprises a temperature ranging between 700° C. and 750° C.

4. The process of claim 1 wherein the thermal cracking of the gas at the relatively high temperature takes place in the presence of a catalyst comprising an oxygen-containing metal compound wherein the metal is selected from the group consisting of the metals of the second, third and fourth groups of the Periodic System.

5. The process of claim 4 wherein said oxygen-containing metal compound is activated by the addition of a relatively small amount of a heavy metal.

6. The process of claim 1 wherein the heat for the second cracking step is at least partially provided by the cooled heating gas from the first cracking step.

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