

UNITED STATES PATENT OFFICE

2,628,890

PROCESS FOR THE DECOMPOSITION
OF HYDROCARBONS

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No Drawing. Application June 20, 1946,
Serial No. 678,163

4 Claims. (Cl. 23—212)

1

This invention relates to the catalytic decomposition of hydrocarbons and more particularly to such a process utilizing hydrocarbons containing sulfur in amounts greater than 0.5 grain per 100 cu. ft. of vaporized hydrocarbon.

In the commercial production of hydrogen, as now practiced, a gaseous mixture of steam and substantially sulfur-free hydrocarbon is passed over a heated catalytic agent containing nickel. In accordance with one procedure the process is carried out in a furnace fired through the arch, with flue gases withdrawn from the base of the furnace and with the steam-hydrocarbon mixture passing through the catalyst tubes parallel to and concurrent with the flow of heat media. The cracked gases are then passed through a secondary furnace and air introduced in order to obtain an optimum temperature to reduce the methane content of the exit gases to a value below 1%. There results a mixed N_2-H_2 gas as a necessity by this method. In commercial practice of this process the quantity of steam used is customarily of the order of 4 to 5 mols. per mol of carbon in the hydrocarbon in order to obtain the heat pickup required for the endothermic reaction within the cracking tube without obtaining excessive tube wall temperature.

In accordance with another and more efficient method described in Reissue Patent No. 21,521 to J. H. Shapleigh, the steam-hydrocarbon mixture passes essentially countercurrent to a plurality of firing points spaced along the vertical wall of the furnace, the flue gas in this instance leaving from the top of the furnace. In this process, the CH_4 content of the exit gas is obtained directly, even with hydrogen alone produced, at values from 0.3% downward depending upon the particular manner in which the furnace operation is conducted. The CH_4 content can be 0.1% or less if desired. Steam-gas ratios less than 2 may be utilized when using natural gas as the hydrocarbon and are not limited as in the first procedure described.

When operating with the above processes the cracking efficiency, or per cent cracking obtained, is controlled by the steam gas ratio, the space velocity, the catalyst quality and the reaction temperature. Having selected a suitable steam-gas ratio, space velocity and catalyst, in accordance with principles well known in the art, the per cent cracking is obtained by a suitable adjustment of the temperature within the limitations of the particular process. In practice such processes are conducted at temperatures just sufficient to yield the desired conversion, or cracking efficiency, based upon raw materials comparatively free of sulfur. Higher temperatures are unnecessary and have been judged disadvantageous and have been avoided; lower temperatures place a limit upon cracking efficiency. The lowest temperature required in practice to

2

obtain a given per cent of cracking efficiency with a given steam-gas ratio, space velocity and catalyst quality is herein termed the "optimum temperature."

The use of such processes has proved quite satisfactory in the reaction of hydrocarbons which are substantially free of sulfur or sulfur compounds such as, for example, natural gas used on the West Coast, and in some sections of the South and containing sulfur varying from nil to 0.2 grain per 100 cu. ft.

However, when sulfur is present in even minor amounts there is a disadvantage because nickel catalyst is readily susceptible to poisoning, and when sulfur is present in amounts greater than about 0.5 grain per 100 cu. ft. the disadvantage has been deemed great enough by the hydrogen producer that he has resorted to sulfur removal by NaOH or other means. Thus, where hydrocarbons containing about 0.5 grain per 100 cu. ft. are utilized, sulfur removal systems are employed. On the other hand, where such systems are not employed it is recognized in the art that the hydrocarbon has been substantially free of sulfur. Because of this knowledge the patented art has generally advised against the use of hydrocarbons containing appreciable amounts of sulfur. Thus, one patentee (Williams—U. S. Patent No. 2,119,565) states that certain substances such as the halogens and compounds of sulfur greatly decrease or even completely inhibit the activity of nickel catalysts for this purpose and therefore advises that the presence of these and other catalyst poisons be avoided by using salts other than the chlorides in preparing the catalytic materials and by employing gases which are free from compounds of sulfur. Schmidt and Nieman, U. S. Patent No. 1,882,977, state: "It is advisable to operate with purified gases, especially those which have been freed from sulfur." Wietzel, Haller and Hennicker, U. S. Patent No. 1,934,836, state: "If the initial substances are very much polluted, especially with organic compounds of sulfur, these must be removed . . ." Hanks and Freyermuth, U. S. Patent No. 1,943,821, state: "The flushing gas should be substantially free from substances which are poisonous for the hydrogen-producing catalyst, such as sulfur compounds, halides and the like." The art is full of such warnings and limitations on sulfur content of hydrocarbon gases and well illustrates the prevailing attitude against their use.

In addition, commercial practice in the manufacture of hydrogen from hydrocarbons has been (1) to utilize those hydrocarbons which are substantially free of sulfur and/or sulfur compounds, or (2) to provide suitable preliminary treatments for removing the sulfur when it approaches 0.5 grain per 100 cu. ft. of hydrocarbon gas. The practice of (1) severely limits the production of

3

hydrogen both from the standpoint of location of plants and quantity produced, since it avoids the use of many hydrocarbons, particularly liquid hydrocarbons, which aside from their sulfur content, are otherwise quite suitable. In the practice of (2) preliminary treatment to remove sulfur is required and this involves additional equipment, manpower and materials and is both time consuming and expensive. In the case of liquid hydrocarbons such as pentane, vaporization is practiced, with sulfur removal carried out in the vapor phase; for heavier hydrocarbons, the purification process becomes complex. Since "sweet" natural gas is generally sold with a guarantee that it will not have more than 1 grain H₂S per 100 cu. ft. and with contracts generally not available which will guarantee less than this amount, it has been the case that the hydrogen producer has had to protect his production by installing sulfur removal equipment even though the source of the gas might run less than 0.5 grain per 100 cu. ft. for most of the time. So far as is known commercial hydrogen plants using hydrocarbon raw materials containing sulfur in quantity higher than approximately 0.5 grain per 100 cu. ft., do not exist today without sulfur removal systems.

Now in accordance with the present invention it has been discovered that hydrogen may be produced from hydrocarbons containing sulfur by a one-step process and without the necessity for preliminary treatment of the hydrocarbon to remove sulfur. This is accomplished by passing a mixture of the sulfur-containing hydrocarbon and steam over a nickel catalytic agent at temperatures which have heretofore been avoided and which are higher than the optimum temperature heretofore used in the art of producing hydrogen from a hydrocarbon substantially free from sulfur under comparable conditions of cracking efficiency, steam-carbon ratio, space velocity, and catalyst quality. High cracking efficiencies are obtained by this improvement, which have heretofore been regarded as impossible, and from a range of sulfur-containing hydrocarbons, from those moderate in sulfur content, such as propane, to those heavy in sulfur content, such as crude oils.

Thus, in carrying out the process of this invention sulfur-containing hydrocarbons are reacted under specific conditions of steam-hydrocarbon ratio, space velocity and catalyst quality and the temperature of the reaction carried out at above the optimum temperature that would prevail with a sulfur-free hydrocarbon gas under the same conditions of steam-carbon ratio, space velocity and catalyst quality.

Having described the invention generally, the

4

following examples are given to illustrate the advantages thereof.

EXAMPLE 1

A catalyst comprising 25% nickel, 25% zirconium silicate, and 50% magnesia by weight was made up in the form of pellets and placed in the cracking tube of a hydrogen furnace. A sulfur-free hydrocarbon and steam were then passed through the cracking tube under conditions and with results set forth in column 1, Table I, below. A petroleum oil containing 1% sulfur was then atomized, vaporized, mixed with steam and passed through the cracking tube under the same conditions of steam-gas ratio, space velocity, catalyst quality and temperature. The per cent cracking or cracking efficiency fell off to 90% as shown in column 2, Table I. The temperature was then increased 100° C. and the cracking efficiency rose to 98% as shown in column 3, Table I.

Table I.—Comparison of cracking efficiencies utilizing sulfur-free and sulfur-containing hydrocarbons

| | 1 | 2 | 3 |
|-------------------------------|-------------------------|--|--|
| | Sulfur-Free Hydrocarbon | Petroleum Oil Containing 100 Grains of Sulfur Per 100 Cu. Ft. of Gas | Petroleum Oil Containing 100 Grains of Sulfur Per 100 Cu. Ft. of Gas |
| Cracking Efficiency percent.. | 98 | 90 | 98 |
| Steam-Carbon Ratio..... | 2:1 | 2:1 | 2:1 |
| Space Velocity..... | 500 | 500 | 500 |
| Catalyst..... | (1) | (2) | (2) |
| Temperature.....°C.. | 800 | 800 | 900 |

1 Ni, ZrSiO₄, MgO
25% 25% 50%

2 Same as 1.

EXAMPLE 2

A catalyst comprising 10% nickel, 10% aluminum oxide, and 80% magnesia by weight was made up and the same procedure followed as in Example 1. Conditions of treatment and results are shown in Table II below. The sulfur-free hydrocarbon gave a cracking efficiency of 99% as shown in column 1. The petroleum oil (same as used in Example 1) containing 100 grains of sulfur per 100 cu. ft. of vaporized hydrocarbon, gave a cracking efficiency of 88% under the same conditions of steam-carbon ratio, space velocity, catalyst quality, and temperature, as shown in column 2. Raising the temperature from 800° C. to 900° C. increased the cracking efficiency from 88% to 98% as shown in column 3. A further increase in temperature to 950° C. gave a cracking efficiency of 99%.

Table II.—Comparison of cracking efficiencies utilizing sulfur-free and sulfur-containing hydrocarbons

| | 1 | 2 | 3 | 4 |
|-------------------------------|-------------------------|--|--|--|
| | Sulfur-Free Hydrocarbon | Petroleum Oil Containing 100 Grains of Sulfur Per 100 Cu. Ft. of Gas | Petroleum Oil Containing 100 Grains of Sulfur Per 100 Cu. Ft. of Gas | Petroleum Oil Containing 100 Grains of Sulfur Per 100 Cu. Ft. of Gas |
| Cracking Efficiency percent.. | 99 | 88 | 98 | 99 |
| Steam-Carbon Ratio..... | 2:1 | 2:1 | 2:1 | 2:1 |
| Space Velocity..... | 500 | 500 | 500 | 500 |
| Catalyst..... | (1) | (2) | (2) | (2) |
| Temperature.....°C.. | 800 | 800 | 900 | 950 |

1 Ni, Al₂O₃, MgO
10% 10% 80%

2 Same as 1.

5

EXAMPLE 3

A catalyst comprising 10% nickel, 40% zirconium silicate and 50% magnesia by weight was made up and the same procedure followed as in Example 1. Conditions of treatment and results are shown in Table III below. The sulfur-free hydrocarbon gave a cracking efficiency of 97-98% as shown in column 1. Under the same conditions of steam-carbon ratio, space velocity, catalyst quality and temperature the petroleum oil utilized in Example 1 and containing 100 grains of sulfur per 100 cu. ft. of vaporized hydrocarbon gave a reduced cracking efficiency of 88% as shown in column 2. However, when the temperature was increased to 900° C. the cracking efficiency rose to 97-98% as shown in column 3. The sulfur content of the oil was then increased to the abnormally high value of 1000 grains per 100 cu. ft. of vaporized hydrocarbon. The resulting cracking efficiency of 93%, when compared with the cracking efficiency of 88% obtained when treating a petroleum oil containing 100 grains of sulfur per 100 cu. ft. of vaporized oil at 800° C. (column 2) well illustrates the improved results obtained in accordance with this invention.

Table III.—Comparison of cracking efficiencies utilizing sulfur-free and sulfur-containing hydrocarbons

| | 1 | 2 | 3 | 4 |
|----------------------------------|-------------------------|--|--|--|
| | Sulfur-Free Hydrocarbon | Petroleum Oil Containing 100 Grains of Sulfur Per 100 Cu. Ft. of Gas | Petroleum Oil Containing 100 Grains of Sulfur Per 100 Cu. Ft. of Gas | Petroleum Oil Containing 1,000 Grains of Sulfur Per 100 Cu. Ft. of Gas |
| Cracking Efficiency percent..... | 97-98 | 88 | 97-98 | 93 |
| Steam-Carbon Ratio..... | 2:1 | 2:1 | 2:1 | 2:1 |
| Space Velocity..... | 500 | 500 | 500 | 500 |
| Catalyst..... | (1) | (2) | (2) | (2) |
| Temperature.....°C. | 800 | 800 | 900 | 900 |

¹ Ni, ZrSiO₄, MgO
10% 40% 50%

² Same as 1.

EXAMPLE 4

The results of tests on heavy oils in plant size apparatus, shown in Table IV below, are illustrative of the highly unexpected results obtained in accordance with this invention. These oils contained from 0.5% sulfur to 2.5% sulfur and gave actual H₂S quantities in the cracked gas of major quantities such as 40 grains and higher per 100 cu. ft. Temperature of the exit gas was taken, and analysis of the gas showed that it contained in the order of 130 grains of sulfur per 100 cu. ft. while obtaining cracking efficiencies in the order of 97%. Considering the volume expansion of gas caused by cracking these sulfur quantities in a nickel catalytic conversion system is illuminating as evidence of what can be accomplished by temperature higher than optimum for nonsulfur-containing gas in catalytic processes poisoned by sulfur.

Table IV.—Results of tests on heavy oils

| | Diesel Oil Containing 0.5% Sulfur | P. S. 300 Fuel Oil Containing 0.93% Sulfur | Crude Oil Containing 2.5% Sulfur |
|----------------------------------|-----------------------------------|--|----------------------------------|
| Cracking Efficiency percent..... | 96 | 97.5 | 96.7 |
| Steam, Oil Wt. Ratio..... | 4.3:1 | 5.3:1 | 5.1:1 |
| Space Velocity..... | 548 | 795 | 595 |
| Catalyst..... | (1) | (2) | (2) |
| Exit Temperature.....°C. | 750 | 800 | 900 |

¹ Ni-ZrSiO₄-MgO

² Same as 1.

6

In accordance with this invention a mixture of steam and sulfur-containing hydrocarbon are passed through a catalytic bed heated to a new and higher level of temperature than previously used in the art to give the unexpected cracking efficiency. Both hydrocarbons which are normally gaseous and those which are normally liquid may be treated.

Steam to carbon ratios and space velocities are those normally utilized in the processing of sulfur-free hydrocarbons. According to usages well known in the art, steam to carbon ratios will generally vary from about 2 to 4.5, based on the number of carbon atoms in the particular hydrocarbon. Space velocities will generally vary from about 300 to 1000 volumes of steam-hydrocarbon mixture per volume of catalyst per hour.

Temperatures utilized will depend on the steam to gas ratio, space velocity, catalyst quality, amount of sulfur present and the desired cracking efficiency. By selecting proper values for steam to gas ratios, space velocities, catalyst quality and cracking efficiency in accordance with the teachings of the prior art in connection with the treatment of sulfur-free hydrocarbons,

the temperature utilized will then depend on the amount of sulfur present. Sulfur content substantially less than about 0.5 grain per 100 cu. ft. of gas being treated normally does not appreciably poison the catalyst and hence requires no substantial increase in temperature. Sulfur content in excess of 0.5 grain per 100 cu. ft. of gas being treated has a sufficient poisoning effect on the catalyst to require sulfur removal equipment in the present day art. Concentrations of 1 grain per 100 cu. ft. have been considered as simply unusable. For concentrations in excess of 1 grain per 100 cu. ft. and even with oils having sufficient sulfur to be customarily expressed on a per cent by weight basis, for example, 1% sulfur, I have found that temperature increase to about 125° C. higher than optimum temperatures utilized for the treatment of sulfur-free hydrocarbons under analogous conditions will give high commercial efficiencies not heretofore obtained without prior sulfur removal.

In the practice of this invention it is preferred to use a nickel catalyst containing more than 10% nickel by weight. Suitable catalysts of this type are nickel-zirconium silicate-magnesia, nickel-aluminum oxide-magnesia, nickel-zirconium silicate, nickel-aluminum oxide, nickel-diaspore, nickel-magnesia, nickel-pumice, nickel-titanium oxide, etc. These catalysts may be made by any of the methods of the prior art and are desirably given a preliminary tempering treatment with heat prior to use.

The various expressions as used in the specification and claims are defined as follows: "sulfur-containing hydrocarbon" is defined as a hydrocarbon containing more than 0.5 grain of sulfur per 100 cu. ft. of vaporized hydrocarbon treated; "optimum temperature" is defined as the lowest temperature required in practice to obtain a given per cent of cracking with a given steam-carbon ratio, space velocity and catalyst quality; "cracking efficiency" is defined as per cent conversion of the carbon in the hydrocarbon to CO; "steam-carbon ratio" is defined as the ratio of the mols of steam to the mols of carbon in the hydrocarbon being treated; thus in the case of propane a ratio of 2:1 would mean 6 volumes of steam for each volume of propane; "space velocity" is defined as the volume of steam-hydrocarbon mixture per volume of catalyst per hour; "catalyst quality" is defined as the activity of the catalyst under a given set of conditions, i. e., type and age of catalyst and conditions of use.

The process of the present invention is particularly useful in the manufacture of hydrogen by the catalytic decomposition of hydrocarbons. The invention is not, however, limited to hydrogen production but is applicable, as well, to other catalytic processes utilizing a catalyst susceptible to sulfur poisoning.

An important advantage of the present invention resides in the fact that nickel catalysts can now be utilized in the decomposition of sulfur-containing hydrocarbons by use of temperatures higher than those hitherto utilized in the decomposition of sulfur-free hydrocarbons under analogous conditions. As a result, it is now possible, without preliminary treatments of any kind, to crack sulfur-containing hydrocarbons in a one-step process and obtain cracking efficiencies as high as those previously obtained in the cracking of sulfur-free hydrocarbons.

What I claim and desire to protect by Letters Patent is:

1. A one step process for catalytic cracking of sulfur polluted fluid hydrocarbons to produce high weight yields of hydrogen and carbon oxides which comprises passing a mixture of steam and a fluid hydrocarbon containing at least 1 gr. of sulfur per 100 cu. ft. of hydrocarbon in gaseous phase over a heated catalytic body containing at least 10% nickel, at least part of the catalytic body being maintained at a temperature of at least 900° C.

2. A one step process for catalytic cracking of sulfur polluted fluid hydrocarbons to produce high weight yields of hydrogen and carbon oxides which comprises passing a mixture of steam and a fluid hydrocarbon containing at least 1 gr. of sulfur per 100 cu. ft. of hydrocarbon in gaseous phase over an indirectly heated catalytic body containing at least 10% nickel at a space velocity of at least 300 volumes per hour per volume of catalyst, at least part of the catalytic body being maintained at a temperature of 900° C., and said mixture of steam and hydrocarbon having a steam to carbon ratio of about 2 to about 4.5.

3. A one step process for catalytic cracking of sulfur polluted fluid hydrocarbons to produce high weight yields of hydrogen and carbon oxides which comprises passing a mixture of steam and a normally liquid petroleum hydrocarbon containing at least 100 gr. of sulfur per 100 cu. ft. of vaporized hydrocarbon over an externally heated catalytic body containing at least 10% nickel, at least part of the catalytic body being maintained at a temperature of at least 900° C.

4. A one step process for catalytic cracking of sulfur polluted fluid hydrocarbons to produce high weight yields of hydrogen and carbon oxides which comprises passing a mixture of steam and a normally liquid petroleum hydrocarbon containing at least 100 gr. of sulfur per 100 cu. ft. of vaporized hydrocarbon over an externally heated catalytic body containing at least 10% nickel at a space velocity of at least 300 volumes per hour per volume of catalyst, at least part of the catalytic body being maintained at a temperature of 900° C., and said mixture of steam and hydrocarbon having a steam to carbon ratio of about 2 to about 4.5

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