PROCESS FOR THERMALLY CRACKING HYDROCARBONS

Filed Sept. 2, 1971 2 Sheets-Sheet 1

FIG. 1

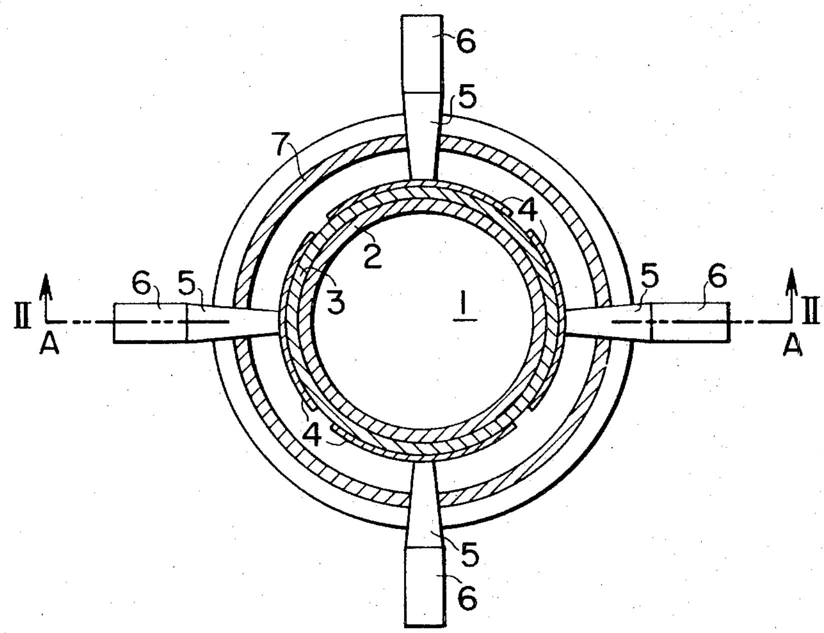
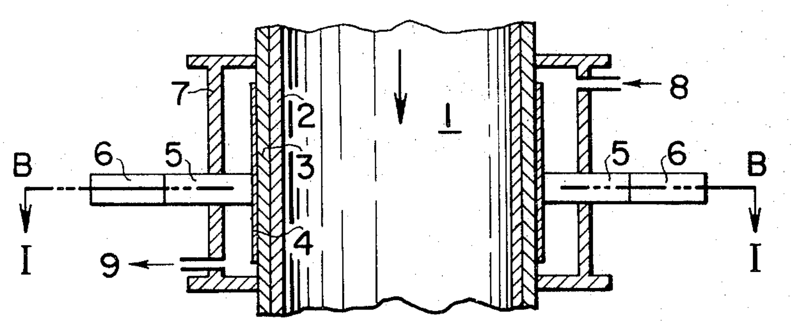


FIG. 2

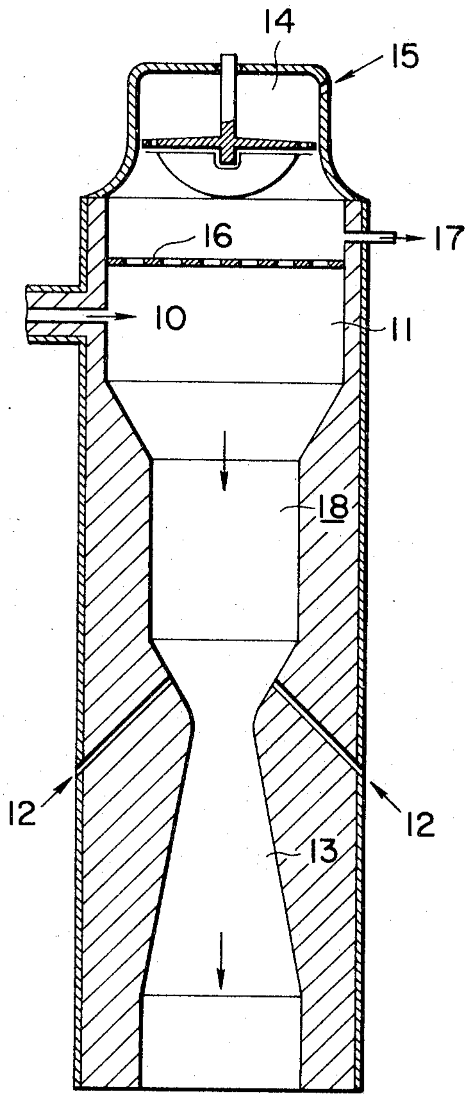


INVENTOR

SABURO HORI

BY Lane, Aitken, Dunner & Ziems
ATTORNEY

FIG. 3



INVENTOR

SABURO HORI

BY Lane Aitken, Dunner & Ziems
ATTORNEY

United States Patent Office 3,819,740
Patented June 25, 1974

1

3,819,740

PROCESS FOR THERMALLY CRACKING HYDROCARBONS

Saburo Hori, Iwaki, Japan, assignor to Kureha Kagaku Kogyo Kabushiki Kaisha, Tokyo, Japan

Filed Sept. 2, 1971, Ser. No. 177,384
Claims priority, application Japan, Sept. 3, 1970, 45/76,654
Int. Cl. C07c *11/24*
U.S. Cl. 260—679 R 6 Claims

ABSTRACT OF THE DISCLOSURE

In thermal cracking of hydrocarbons by bringing petroleum hydrocarbons into contact with a high temperature heat medium to effect thermal cracking of the hydrocarbons, a thermal cracking apparatus equipped with an ultrasonic wave generator is applied to give a mixture of the petroleum hydrocarbons and the high temperature heat medium in the thermal cracking reaction zone ultrasonic wave vibration having a power of 0.01–10 watts/cm.^{2} and a frequency of 1–800 kHz. The ultrasonic wave generator is so designed that it may be protected from the high temperature heat medium by a fluid maintained at a temperature lower than that of the medium. When petroleum hydrocarbons are thermally cracked by application of a thermal cracking apparatus equipped with such an ultrasonic wave vibrator, build-up of carbon or coke on the wall of reaction chamber is effectively prevented and the yield of the thermally cracked product is increased.

BACKGROUND OF THE INVENTION

This invention relates to a process for thermally cracking petroleum hydrocarbons with the application of ultrasonic wave energy and also to an apparatus for conducting such a process.

It is known that in a process for producing useful hydrocarbons such as olefins which comprises blowing hydrocarbon stocks such as petroleum hydrocarbons, especially crude oil, heavy oil and light oil, directly into a high temperature gaseous heat medium maintained at 800° C. or higher thereby subjecting the hydrocarbon mixture to thermal cracking reaction, heavy hydrocarbons are coagulated or built up at the place where said hydrocarbon stocks are mixed with the heat medium or on the wall surface of the cracking reaction chamber, whereby the heavy hydrocarbons are carbonized or coked, thus resulting in clogging of the reaction apparatus.

Application of a variety of devices to the wall surface of the reaction chamber has been proposed in the prior art to overcome the problem described above. However, all of these devices incur heat loss due to introduction of other substances and thus can hardly be dismounted from the chamber after completion of the thermal cracking reaction.

It is an object of this invention to overcome the drawbacks of such known conventional processes and to provide an advantageous process for thermally cracking petroleum hydrocarbons without the thermal cracking reaction being affected.

It is a further object of this invention to provide a thermal cracking apparatus suitable for attaining said object.

SUMMARY OF THE INVENTION

We have found that the above-mentioned objects can effectively be attained by applying ultrasonic wave vibration within a given range of frequencies to a mixture of petroleum hydrocarbons and the high temperature gaseous heat medium.

The ultrasonic wave vibration used in accordance with this invention is within the range of 1–800 kHz. and its power in terms of energy (joule) transmitted per unit area (cm.^{2})/unit time (sec.), i.e. watt/cm.^{2}, corresponds to 0.01–10. In the event ultrasonic wave vibration of a frequency outside the above-mentioned range is applied, the advantageous effect will be reduced and coke formed during the reaction will be accumulated on the wall of reaction chamber. Thus, it is necessary to limit the frequency of ultrasonic wave used according to this invention to said range. This may be attributed to the fact that if the frequency exceeds the above mentioned range, its power will be attenuated in the course of application of ultrasonic wave so that effective vibration cannot be transmitted.

The ultrasonic wave generator which is used to transmit ultrasonic wave vibration to the thermal cracking apparatus according to this invention may be an electrical or mechanical generator. A ferrite vibrator or nickel vibrator is preferable from the viewpoint of its strength, heat stability and number of frequency. A rotary siren is suitable as a mechanical ultrasonic wave generator but its use necessitates introduction of pressurized air into the reaction apparatus so that modification of the apparatus is required. In accordance with this invention, there is provided an apparatus which enables effective transmission of ultrasonic wave vibration to the wall of reactor without requiring any special modification of the reaction apparatus itself.

The apparatus used in this invention comprises a thermal cracking reactor and an ultrasonic wave generator disposed perpendicularly to the exterior wall of the reactor and having a diaphragm connected through a horn duct to the vibrator. In practice, the ultrasonic wave generator is protected with a fluid maintained at a temperature lower than that of the high temperature heat medium used in thermal cracking. The ultrasonic wave vibration is transmitted through such fluid.

A thermal cracking apparatus using a rotary siren may also be utilizable for this invention. In this case, a rotary siren is mounted on the top of the apparatus and a porous plate and an outlet provided at the upper part than the porous plate for introducing a pressurized fluid needed to drive the rotary siren are disposed between the rotary siren and an inlet for the high temperature heat medium to be introduced into the reaction chamber. In this apparatus, the pressurized fluid serves to protect the ultrasonic wave generator from high temperature.

In general, ultrasonic wave energy is applied at ordinary temperatures or relatively low temperatures. According to this invention, however, ultrasonic wave can be applied at the high temperatures maintained in the thermal cracking of hydrocarbons with the ultrasonic wave generator protected as described above.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Referring to FIGS. 1 and 2, a mixture of a hydrocarbon stock and a heat transfer medium is passed through a reactive chamber wherein the thermal cracking reaction is carried out in the reaction chamber **1**. The reaction chamber **1** is surrounded by refractory material **2**.

Four ultrasonic wave generator vibrators are arranged symmetrically around the reaction chamber.

Each ultrasonic wave generator comprises a diaphragm **4** mounted to the exterior peripheral side of an adiabetic material **3** present at the outer side of a refractory material **2**, the diaphragm being connected through a horn **5** to a vibrator **6**.

The diaphragm **4** is maintained at a high temperature by supplying steam heated at 800° C. from an inlet **8** in the outer cylindrical jacket **7** and discharging the steam from an outlet **9**. The thermal cracking reaction of crude oil with superheated steam was carried out using such apparatus with the frequency and power of ultrasonic wave energy being varied. The results are shown in the table below. For comparison, the results obtained by performing the thermal cracking under the same conditions but without application of ultrasonic wave vibration are also shown in the table.

Thermal cracking conditions:
Starting material—Ceria crude oil, 1,000 liters/hr.
Steam—2,000° C., 1,400 kg./hr.
Reaction temperature—1,100° C.
Reaction time—0.005 sec.

Ultrasonic wave (W./cm.², 10 kHz.)	Yield of acetylene-ethylene (wt. percent)	Amount of coke built up (kg. feed)
None	48.0	7.2
0.1	54.1	0.8
0.05	50.0	1.1
0.1	52.1	0.9

Referring to FIG. 3, a rotary siren **14** made of a heat-resisting material is mounted on the top of the reactor and a high temperature heat medium is introduced from an inlet **10** above the reaction chamber **18** into a large cavity **11** in the upper portion of the reaction chamber **18**. The high temperature heat medium is brought up to a steady flow rate in the large cavity and then mixed with oily hydrocarbons introduced from an inlet **12** fitted to an entrance of a lower constricted portion **13** of the reaction chamber **18**. The mixture then flows to the lower constricted portion **13** of the reaction chamber **18** where thermal cracking of the hydrocarbons takes place.

In the course of thermal cracking, vibration generated from a rotary siren **14** is transmitted to the wall of the reactor **18** and gaseous reaction mixture thereby effects homogeneous mixing action between the oily hydrocarbons and the high temperature heat medium and prevention of build-up of coke and carbon on the wall of reactor through vibration of the wall. A pressurized fluid introduced from an inlet **15** of the rotary siren **14** is forced into the upper part of the reaction chamber **18** by the action of the rotary siren **14**. Mixing of the pressurized fluid with the high temperature liquid must be avoided to prevent disturbance of the temperature distribution in the reaction chamber **18**. To avoid such mixing a porous plate **16** and an outlet **17** are disposed above the inlet **10** for the high temperature fluid to permit transmission of vibration energy to the heat transfer medium while preventing loss of vibration energy in as far as possible. Gases heated as high as possible and capable of protecting the rotary siren from injury, such as steam, are suitable for use as the pressurized fluid in the rotary siren **14**.

When Ceria crude oil was thermally cracked with steam superheated at 2000° C. using the apparatus of this invention, it was observed that the yield of olefins in the experiments where no ultrasonic wave energy was applied was 48% (by weight) based on the starting oils, whereas the yield in the experiments using ultrasonic wave energy was as high as 49–50%. In the latter case, build-up of coke on the wall of reactor was not observed.

The most effective results were obtained in said example where steam heated at 300° C. was used as the pressurized fluid and ultrasonic wave having a power of 0.01–0.3 w./cm.² and a frequency of 1–50 kHz. was used.

As is evident from the foregoing, application of ultrasonic vibration according to this invention serves to minimize remarkably the amount of carbon and coke formed on the wall of the reaction chamber and to increase significantly the yield of olefins formed by the thermal cracking of hydrocarbons.

What is claimed is:

1. A process for thermally cracking hydrocarbons comprising mixing the hydrocarbons with a heat exchange medium at a temperature sufficient to crack the hydrocarbons, and subjecting the mixture to ultrasonic wave vibrations supplied at 0.01–10 watts/cm.² and at a frequency of 1–800 kHz.

2. The process of claim **1** wherein said ultrasonic wave vibration is supplied by a generator and additionally comprising cooling said generator by contacting said generator with a fluid maintained at a temperature lower than that of said heat exchange medium.

3. A process of claim **2** wherein said fluid is superheated steam.

4. A process of claim **2** wherein said superheated steam is at a temperature of at least 800° C.

5. A process for thermally cracking hydrocarbons comprising: mixing the hydrocarbons with a heat exchange medium at a temperature sufficient to crack the hydrocarbons in a reaction chamber; and subjecting the mixture to ultrasonic wave vibration effective to prevent any build-up of carbon or coke on the walls of said reaction chamber.

6. A process for thermally cracking hydrocarbons comprising: mixing the hydrocarbons with a heat exchange medium at a temperature sufficient to crack the hydrocarbons in a reaction chamber; and subjecting the mixture to ultrasonic wave vibration effective to prevent any build-up of carbon or coke on the walls of said reaction chamber by means of an ultrasonic generator; cooling said generator by contacting said generator with a fluid maintained at a temperature lower than that of said heat exchange medium.

References Cited

UNITED STATES PATENTS

3,268,432 8/1966 Nance .... 204—162 S
1,811,195 6/1931 Watson .... 208—130
3,557,241 1/1971 Kivlen et al. .... 260—683

FOREIGN PATENTS

813,319 5/1969 Canada .... 204—162

DELBERT E. GANTZ, Primary Examiner

J. M. NELSON, Assistant Examiner

U.S. Cl. X.R.

204—162.5; 208—48 R, 130; 260—683 R

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,819,740 Dated June 25, 1974

Inventor(s) Saboru Hori

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

IN THE SPECIFICATION:

Column 3, line 20, after "reactor" insert --9--;

line 57, "49-50%" should read --49-54%--.

Column 4, line 25, "claim 2" should read --claim 3--.

Signed and sealed this 17th day of September 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents