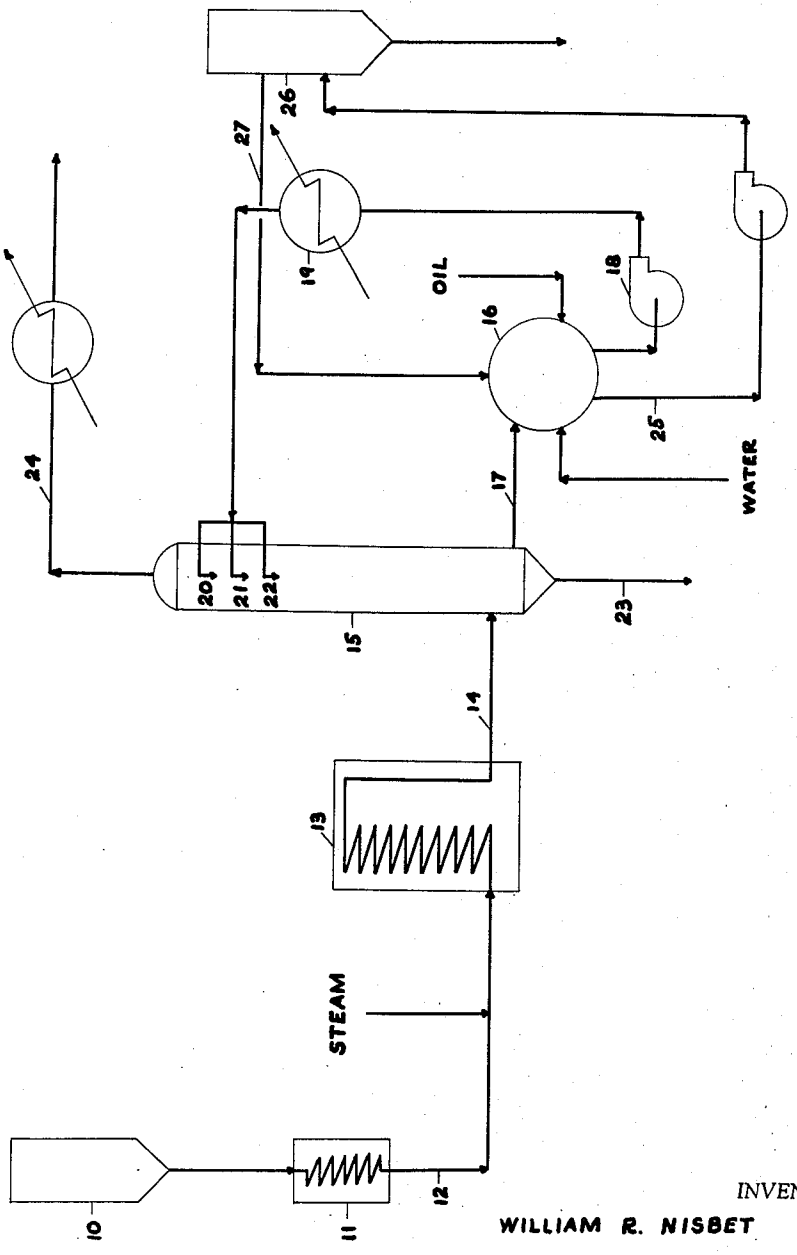
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PRODUCTION OF ETHYLENE

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FIGURE I



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PRODUCTION OF ETHYLENE

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Application August 19, 1955, Serial No. 529,409

3 Claims. (Cl. 260—683)

The present invention pertains to a process for conducting thermal conversions of gaseous material. The invention is particularly concerned with the quenching of cracked gas rich in ethylene resulting from the pyrolysis of hydrocarbons.

The large family of industrially important chemicals and plastics which can be manufactured from ethylene has led to increased demand for this highly reactive unsaturated hydrocarbon. An established method for making ethylene for use in chemical manufacturing involves high-temperature pyrolysis or cracking of a hydrocarbon feed stock such as gas oil or saturated light hydrocarbons such as ethane, propane, and butane. Several practical difficulties arise, however, in conducting such a process. The temperatures required for the reaction are very high and the optimum time during which the feed stocks may be held at the elevated conversion temperature is very short, in the order, for example, of from a few seconds down to a few hundredths of a second. Under the prevailing high temperature conditions, lengthened reaction periods allow secondary reactions, such as decomposition and polymerization or other reactions of the product, to predominate resulting in decreased yield and a troublesome accumulation of tarry substances and finely divided coke in the system. Accordingly, the cracked gas product must, upon completion of the desired conversion, be shock-cooled or quenched immediately.

Many methods have been proposed for carrying out the quenching operation. The more common of these include quenching with liquids such as water or hydrocarbon oils since passage of the hot cracked gases over water- or air-cooled heat transfer surfaces such as metal plates is, of course, inefficient in bringing temperatures down rapidly. Certain defects, however, are inherent in the use of such media as have heretofore been employed. While water is eminently suitable because of its latent heat characteristics and represents the most economical operation both from the standpoint of capital equipment required and material cost, serious problems are presented when the cracked gas is quenched directly in a spray of water. It is virtually impossible to avoid altogether the formation of some tarry substances and some finely divided coke in the pyrolytic reaction. With a water quench, therefore, tar emulsions are formed which present a serious disposal problem. In addition, much of the coke present being hydrophobic in nature is not "washed down" by water and as a consequence it accumulates in the equipment plugging up orifices, passages, heat exchangers, automatic relief valves, etc.

Certain hydrocarbon oils, on the other hand, are superior to water as a quench medium in that they exert a wetting action on the tar and coke slurrying these materials and keeping them in motion so that they do not settle out in undesirable and inaccessible spots in the system. However, oil is a more expensive quench medium than water and, because of its poorer latent heat characteristics, a significantly larger quantity of oil is required for the quenching operation as compared to water, thus necessitating more and larger equipment as well as additional process or handling steps.

A major object of this invention, therefore, is the provision of an improved practical process for conducting gaseous conversions of the type requiring very high temperatures and rapid quenching of the reaction products.

Another object of the invention is to accomplish quenching of the reaction products from the pyrolysis of hydrocarbon stocks in an effective manner without encountering certain defects found in conventional methods.

A more specific object of the invention is the provision of an improved process for making ethylene by the pyrolysis of light saturated hydrocarbons in which the quench step is carried out without encountering the difficulties which occur with the usual water and oil quench media.

These and other objects and advantages of the invention will be obvious from the following detailed description thereof.

According to the invention, a hot cracked gas effluent is quenched by introducing it into a suitable zone or tower wherein it is sprayed with an oil-in-water emulsion containing from about 5 to about 40% of oil. By using such an oil-water emulsion as a quench medium, the advantages of oil quenching combined with those of water quenching are realized without any of the attendant difficulties experienced in those systems wherein oil or water is used separately as discussed in some detail above. With a water quench alone, for example, shut-downs for the purpose of cleaning coke out of the equipment were necessitated on the average of about once every two or three months. Since employment of an oil-water quench was begun, no such shut-downs have been required and inspection after two- to three-month periods of operation has indicated the system to be essentially free of coke build-up.

For further understanding of the invention, the following description of the process as applied in the production of ethylene from the cracking of a propane charge stock is presented with reference to the accompanying diagrammatic flowsheet of Figure I wherein a preferred arrangement of suitable equipment for carrying out the invention is presented.

The propane charge stock from storage facilities indicated at **10** is passed through a vaporizer **11** where it is heated to approximately 80° C. and thence via line **12** to a cracking furnace **13** designed in accordance with principles well known in the art. While the undiluted hydrocarbon may be pyrolyzed as such, it is preferable to employ an inert carrier gas to lower the partial pressure of the propane in the cracking zone and to improve heat transfer. Steam is admixed, therefore, with the vaporized propane at the point indicated before the gas enters the furnace and generally in an amount such that there is from about 0.05 to about 3.0 parts by weight of steam per part of vaporized propane. The cracked gas effluent containing approximately 20–25 mol percent ethylene together with hydrogen, methane, ethane, propane, propylene, and small amounts of higher hydrocarbons leaves the furnace at approximately 800° C. and 5 p.s.i.g. pressure via line **14**. The effluent is then passed into the lower section of the quench tower **15** whre it is immediately shock-cooled to a temperature of approximately 100° C. by contact with an oil-water emulsion ejected from sprays in the top of the tower, pumped from a quench medium surge tank **16** to which water, as steam condensate, and oil are charged. The oil-water emulsion contains approximately 5–15% oil. Typical of the oils which may be used is one which is aromatic in character containing only 17.2% paraffins, has a specific gravity of 68° F. of 0.9212, a viscosity of 32.2 Saybolt sec., and upon distillation has an initial boiling point of 350° F., a 50% boiling point of 442° F. The oil-water emulsion quench

medium together with condensable light oils formed in the cracking operation is continuously withdrawn from the bottom section of the quench tower at a point below the cracked gas entry line through line **17** and passed to the surge tank **16**. This oil-water mixture is then pumped from the surge tank by means of the pump **18** which also provides the agitation necessary to keep the oil-water mixture emulsified, through the shell side of the heat exchanger **19** employing cooling tower water on the tube side wherein it is cooled to a temperature in the range from 40–50° C. and recycled for injection into the quench tower **15** through the spray devices, **20**, **21**, and **22**. Heavy tarry matter settles to the bottom of the quench tower **15** and is withdrawn through line **23** periodically for disposal. The cooled cracked gas rises and leaves the top of the quench tower through line **24**, is further cooled and may be passed directly to a suitable purification system.

In order to control the character and composition of the oil-water emulsion which may be altered to some extent by the accumulation of heavy oil, coke, or tar which is necessarily carried over into the quench medium surge tank, a slipstream is withdrawn continuously from the tank through line **25** and pumped to a gravity separator **26** for clean-up. In the separator coke, heavy oils or tarry materials are settled to the bottom and withdrawn while the "clean" oil-in-water emulsion overflows through the line **27** by gravity back to the surge tank **16** where it is recycled to the quench tower.

For optimum effectiveness, the oil-in-water emulsion should contain from about 5 to about 40% by volume of oil and preferably from about 5 to about 15% of oil. Suitable oils are those which are aromatic in character since they must be compatible with the oils or liquid products formed by condensation from the cracked gas being treated. In addition, the oils to be used should be characterized by high latent heat values, a specific gravity of slightly less than 1, being in the range, for example, from 0.9 to about 0.98 at 68° F. and having a boiling range from approximately 350° to 700° F.

While the example given has been directed specifically to the production of ethylene from the cracking of a propane charge stock, the invention is not to be considered as limited to this adaptation. The novel method of quenching herein described is applicable in any process wherein a hydrocarbon or hydrocarbon mixture is cracked at elevated temperatures to form olefins. Ethane, butane, refinery gas and liquid fractions such as kerosene, gas oil and fuel oil may all be used.

What is claimed is:

1. In a continuous process for pyrolytic conversion of hydrocarbon stocks at elevated temperatures to gaseous hydrocarbon products which are unstable at the elevated conversion temperatures, the method of quenching the hot cracked gas which comprises passing said hot cracked gas through a quench zone in contact with a relatively cool oil-in-water emulsion, said oil-in-water emulsion containing from about 5% to about 40% by volume of an aromatic oil characterized by a high latent heat of vaporization, a specific gravity in the range from about 0.9 to about 0.98 at 68° F., and a boiling range from about 350° to about 700° F.

2. In a continuous process of producing ethylene by pyrolysis of hydrocarbons at elevated temperatures, the method of quenching the hot cracked gas which comprises passing said hot cracked gas through a quench zone in contact with a relatively cool oil-in-water emulsion.

3. In a continuous process of producing ethylene by pyrolysis of propane at elevated temperatures, the method of quenching the hot cracked gas which comprises passing said gas through a quench zone in contact with a relatively cool oil-in-water emulsion, said oil-in-water emulsion preferably containing from about 5 to about 15% by volume of an aromatic oil characterized by a high latent heat of vaporization, a specific gravity in the range from about 0.9 to about 0.98 at 68° F., and a boiling range from about 350° to about 700° F., said oil-in-water emulsion containing from about 5% to about 40% by volume of an aromatic oil characterized by a high latent heat of vaporization, a specific gravity in the range from about 0.9 to about 0.98 at 68° F., and a boiling range from about 350° to about 700° F.

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CERTIFICATE OF CORRECTION

Patent No. 2,928,886 March 15, 1960

William R. Nisbet et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 61, for "whre" read -- where --; line 69, for "of", first occurrence, read -- at --.

Signed and sealed this 30th day of August 1960.

(SEAL)

Attest:

ERNEST W. SWIDER
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents