

J. W. DAVISON
THERMAL CRACKING PROCESS WITH AN IMPROVED
HEAT CONSERVATIVE QUENCHING TECHNIQUE
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BY *Hudson & Young*
ATTORNEYS

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THERMAL CRACKING PROCESS WITH AN IMPROVED HEAT CONSERVATIVE QUENCHING TECHNIQUE

Joseph W. Davison, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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This invention relates to a method of and apparatus for forming low molecular weight gases by thermally cracking hydrocarbons.

It is known that ethylene and other low molecular weight unsaturated hydrocarbons can advantageously be produced by the thermal cracking of light hydrocarbons such as ethane, propane or butane. The present invention is concerned primarily with the problem of quenching the effluent gases of such a process in a manner so as to obtain a maximum yield of desired products with a minimum of heat exchanger surface and cooling tower requirements. It is also important to avoid the deposition of coke and tars in the transfer conduits, heat exchangers and other pieces of equipment. It is known in the art to quench the products resulting from the pyrolysis of hydrocarbons by means of fluids such as water and oil. However, the quenching systems employed heretofore have several disadvantages. If water alone is used as the quench medium, the investment in heat exchangers and cooling towers is excessive and, while coking at the primary quench point is avoided, the quenched products tend to carry finely dispersed tars into equipment located downstream from the primary quench. Furthermore, recovery of waste heat cannot be accomplished effectively when using a water quench alone. The use of oil as the quench medium has the advantage of removing tars from the gas stream. However, oil alone is less satisfactory as the primary quench because of coking in the transfer conduits and the relatively large volume of oil required.

The present invention employs a combination of water and oil quenching steps. Also, novel heat exchange steps are integrated with the gas separation system in such a manner as to avoid the difficulties of the systems previously known while accomplishing a maximum heat recovery with a minimum amount of equipment. The invention comprises, generally, vaporizing a hydrocarbon feed stream and directing the vapors into a cracking furnace. The effluent from the cracking furnace is quenched by water and passed to a quench drum where it is contacted by a cool oil. The effluent from the quench drum is cooled, compressed and passed to an absorber column. The hot oil from the quench drum is passed in heat exchange relationship with the liquid in the lower portion of the absorber. This cools the oil and supplies heat to the absorber. The oil is then passed in heat exchange relationship with the incoming feed stream to provide the initial vaporization thereof. The oil can then be cooled further, if desired, and is recirculated to the quench drum.

Accordingly, it is an object of this invention to provide an improved process and apparatus for producing low molecular weight gases by thermally cracking hydrocarbons.

Another object is to provide an improved quench system for use with pyrolysis systems.

A further object is to provide improved heat exchange

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means for hydrocarbon cracking and gas separating systems.

Other objects, advantages and features of the invention should become apparent from the following detailed description taken in conjunction with the accompanying drawing which is a schematic representation of a present preferred embodiment of the invention.

Referring now to the drawing in detail, the feedstream to be cracked is supplied by an inlet conduit 10 which has a pump 11 therein. Conduit 10 communicates with a heat exchanger 12 which provides for the vaporization of the feedstream. The outlet of conduit 10 communicates with the inlet of a cracking furnace 13. A pressure recorder-controller 14 and a flow recorder-controller 15 are associated with conduit 10 to supply the feed stream to furnace 13 at a constant pressure and a constant rate. A diluent, such as steam, is introduced into conduit 10 through a conduit 17 which has a flow recorder-controller 18 associated therewith.

Furnace 13 has an elongated pipe 20 in the upper portion thereof which communicates with a second elongated pipe 21 in the lower portion. Heat is supplied to these pipes by a plurality of burners, not shown, which are mounted in the side walls of the furnace. Pipe 21 communicates with an outlet conduit 22. Quench water is introduced into conduit 22 through a conduit 23 at a constant rate which is maintained by a flow recorder-controller 24. The setting of controller 24 is established by a temperature recorder-controller 26 which responds to the temperature in conduit 22 downstream from conduit 23. The outlet of conduit 22 communicates with the lower inlet of a quench drum 27. A quench oil is introduced into an upper inlet of drum 27 from a conduit 28. A constant flow of oil through conduit 28 is maintained by a flow recorder-controller 29 which is associated with the conduit. The gases from furnace 13 pass upwardly through drum 27 in countercurrent flow with the descending quench oil. These gases are removed from drum 27 through a conduit 30 which communicates through a cooler 31 with a knock-out drum 33. Any liquid which is condensed in drum 33 is removed through an outlet conduit 34. The gases in drum 33 are passed through a conduit 35 to the inlet of a compressor 36. The outlet of compressor 36 is connected by a conduit 37 to the inlet of an absorber column 38.

A lean absorbing oil is introduced into the upper portion of column 38 through a conduit 39. Gases are removed from column 38 through a conduit 40 and are directed to additional separating apparatus, not shown. The rich oil is removed from absorber 38 through a conduit 42 and passed into a stripper, not shown. A portion of the rich oil is directed by a conduit 43 through a heat exchanger 44 and is returned to the lower portion of absorber 38. Heat is supplied to exchanger 44 by passing a heat exchange medium therethrough. A portion of the liquid in the lower region of absorber 38 is passed by a conduit 45 having a pump 46 therein through a heat exchanger 47 and is returned to the column. The hot quench oil from drum 27 is passed through heat exchanger 47 by a conduit 50 which has a pump 51 and a coke filter 52 therein. This oil is passed through conduit 50 at a rate which is maintained by a liquid level controller 53 that responds to the liquid level in drum 27.

The quench oil removed from heat exchanger 47 is passed through a conduit 55 to heat exchanger 12. Additional heat is removed from the quench oil in exchanger 12 and this vaporizes the feedstream delivered to furnace 13. The cooled oil from heat exchanger 12 is passed through a conduit 56 to a storage tank 57. Conduit 56 has a valve 57 therein which is adjusted by a temperature indicator-controller 58 that responds to the temperature of the oil downstream from valve 57. A by-pass con-

duit 59 directs a portion of the oil through a cooler 60 instead of through valve 58. The position of valve 58 thus determines the ratio of oil passed through cooler 60 to the oil passed directly through valve 58. In this manner the oil is delivered to storage tank 57 is cooled to a predetermined temperature. Obviously, the heat of the oil may be used to heat other fluid streams in some applications of this invention, thereby avoiding the loss of heat at cooler 60. The oil is subsequently removed from tank 57 and passed by a pump 61 back through conduit 38 to quench drum 27. A conduit 62 is provided to remove sludge from tank 57.

As a specific example of the operation of the thermal cracking process of this invention, a mixture comprising normal butane and isobutane is introduced into furnace 13 through conduit 10. These two gases are supplied in the ratio of 972 mols of normal butane to 28 mols of isobutane. For each one thousand mols of feed gas, 249 mols of water in the form of steam are added through conduit 17. The resulting mixture is introduced into furnace 13 at a temperature of approximately 150° F. and at a pressure of approximately 85 pounds per square inch absolute (p.s.i.a.). The residence time of the mixture in pipe 20 is approximately 7 seconds and the residence time in pipe 21 is approximately 4 seconds. The gases are heated in pipe 20 to a temperature of approximately 1000° F. and are further heated in pipe 21 to a temperature of approximately 1500° F. The effluent gases leave furnace 13 at a temperature of approximately 1500° F. and at a pressure of approximately 20 p.s.i.a. The effluent from furnace 13 has a composition approximately as follows.

Material:	Moles per 1000 moles feed gas
Hydrogen	200
Methane	830
Acetylene	10
Ethylene	640
Ethane	130
Propylene	250
Propane	12
Butadiene	20
Butylene	25
Normal butane	42
Benzene	38
Water	249
Other compounds	43

These gases are quenched to a temperature of approximately 900° F. by the direct introduction of water into conduit 22. This can be accomplished by introducing 1240 mols of water at a temperature of approximately 100° F. for each 1000 mols of feed gases.

Quench oil is supplied to drum 27 at a temperature of approximately 140° F. and at the rate of 1920 moles per 1000 moles of feed gas. Gases are removed from drum 27 at a temperature of approximately 180° F. and are cooled to 100° F. by heat exchange with water in exchanger 31. The gases are compressed in a several stage compressor having intermediate cooling and finally enter absorber 38 at a temperature of 100° F. and at a pressure of 170 p.s.i.a.

Quench oil is removed from drum 27 at a temperature of 375° F. and passed through reboiler 47. The oil leaves reboiler 47 at a temperature of 315° F. and is passed to feed vaporizer 12. The oil removed from vaporizer 12 is at a temperature of 250° F. and is cooled by cooler 60 to a temperature of approximately 140° F.

It should be noted that the temperature to which the effluent gases are cooled in drum 27 is above the dew point so that water introduced in the primary quench is not condensed in drum 27. This eliminates the need for an oil-water separator. However, the gas is cooled initially so that the amount of additional oil cooling required is minimized. The step of quenching the furnace effluent to 900° F. by the water quench minimizes the amount of

equipment required, stops the pyrolysis reaction before valuable products are destroyed by side reactions and prevents the deposition of tars and coke in the transfer conduits. The further quenching from 900° F. to 180° F. by the oil results in effective scrubbing of coke and tars from the gas and makes possible substantial heat recovery by heat exchange in the absorber reboiler and the butane vaporizer.

The quench oil employed can be any heavy oil, paraffin or aromatic, which will flow and can be sprayed at the coolest temperatures involved. A present preferred oil is a heavy aromatic oil which is produced in the cracking operation and is permitted to accumulate. The following data are characteristic of such an oil:

Specific gravity at 60/60° F.=1.0655
Kinematic viscosity at 100° F.=14.38 centistokes
Kinematic viscosity at 210° F.=2.86 centistokes
Bureau of Mines Correlation Index=133
ASTM Distillation, corrected to 760 mm.

Percent:	°F.
5	413
10	428
20	450
30	479
40	515
50	558

While the invention has been described in conjunction with a present preferred embodiment, it should be evident that are designated compositions, temperatures and pressures are merely illustrative of the operation of the invention and that the invention is not limited thereto. In addition to butane, the feedstream can comprise ethane, propane, refinery gases or mixtures of these various materials. In general, butane is more economical than propane because greater amounts of valuable olefin and aromatic by-products are produced from the cracking of butane. Obviously, these temperatures and pressures can be varied over considerable ranges depending upon the gases to be cracked, the desired products and various economic factors.

What is claimed is:

1. A process for producing low molecular weight gases which comprises heating a hydrocarbon feed stream to vaporize at least a portion of the stream, further heating the stream to effect thermal cracking of a substantial portion of the stream, adding water to the cracked stream to effect cooling, then directly passing the cooled cracked stream in contact with a cooled quench oil and thereby scrubbing tars from said cracked stream and further cooling said cracked stream, passing the resulting cooled cracked stream to a heated absorbing zone, contacting the cooled cracked stream in the absorbing zone with a lean absorbing medium, passing the resulting heated quench oil in heat exchange relationship with fluid in the absorbing zone to heat the absorbing zone, thereafter passing the quench oil in heat exchange relationship with the hydrocarbon feed stream to effect the first-mentioned heating thereof, and recycling the quench oil to contact additional cracked products.

2. A process for producing ethylene which comprises heating a hydrocarbon feed stream to vaporize at least a portion of the stream, further heating the stream to effect thermal cracking of a substantial portion of the stream, to produce a substantial quantity of ethylene, adding water to the cracked stream to cool same to about 900° F., then directly passing the resulting cooled cracked stream in contact with a cooled hydrocarbon quench oil and thereby scrubbing tars from said cracked stream while also cooling said stream to about 180° F., said temperature being above the dew point so that water is not condensed passing the resulting cooled cracked stream to a heated absorbing zone, contacting the cooled cracked stream in the absorbing zone with a lean absorbing

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medium, passing the resulting heated quench oil in heat exchange relationship with fluid in the absorbing zone to heat the absorbing zone, thereafter passing the quench oil in heat exchange relationship with the hydrocarbon feed stream to effect the first-mentioned heating thereof, and recycling the quench oil to contact additional cracked products.

3. The process in accordance with claim 2 wherein the feed stream comprises paraffins having four carbon atoms per molecule, and wherein said thermal cracking is provided by heating the feed stream to a temperature of about 1500° F. in a period of about 11 seconds.

4. A process for producing low molecular weight gases which comprises heating a hydrocarbon feed stream to vaporize at least a portion of the stream, further heating the stream to effect thermal cracking of a substantial portion of the stream, adding water to the cracked stream to effect cooling, then directly passing the cooled cracked stream in contact with a quench oil and thereby scrubbing tars from said cracked stream and further cooling said cracked stream, said contact being effected under conditions such that water is not condensed and separating

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the resulting water-free quench oil stream, passing the resulting cooled cracked stream to a heated absorbing zone, contacting the cooled cracked stream in the absorbing zone with a lean absorbing medium, passing the hot water-free quench oil in heat exchange relationship with fluid in the absorbing zone to heat the absorbing zone, thereafter passing the quench oil in heat exchange relationship with the hydrocarbon feed stream to effect the first-mentioned heating thereof and recycling the quench oil to contact additional cracked products.

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