PRODUCTION OF ACETYLENE BY THERMAL CRACKING OF LIQUID HYDROCARBONS

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This invention relates to improvements in a process for the production of acetylene by thermal cracking of liquid hydrocarbons with amounts of oxygen insufficient for complete combustion of the hydrocarbons, and quenching of the reaction products.

More especially, it relates to the introduction of liquid hydrocarbons and their liquid cracked products into the process and to the circulation of liquid cracked products for quenching the reaction mixture.

It is known to crack hydrocarbons into unsaturated gaseous products, especially acetylene, by the supply of energy. On the other hand substantial energy must immediately be withdrawn from the cracked products formed at high temperature in order to prevent further decomposition and side reactions.

The known processes for the cracking of hydrocarbons, to acetylene in particular, therefore differ from each other not only in the particular hydrocarbon used but also especially in the method of supplying energy to the initial material and withdrawing the energy during quenching of the gas produced.

To crack liquid hydrocarbons, the energy necessary may be supplied, for example, by an electric arc or by introducing vaporizable raw materials into the hot combustion products of the same or another vaporizable or gaseous fuel. Processes are also known with a supplementary supply of heat to the liquid hydrocarbons. Other cracking processes produce the heat required for cracking by partial combustion of part of the liquid hydrocarbons with air or oxygen within the liquid hydrocarbons to be cracked. The hydrocarbons present in excess are cracked by the combustion heat developed.

The subsequent rapid quenching of the hot reaction products necessary after each cracking may be effected, for example, by injecting water into the effluent production gas. In this way, however, a very large quantity of the total energy input is lost. In order to make the sensible heat of the production gas utilisable for preheating the input substance, it has also been proposed to use the hydrocarbons to be cracked as the quenching agent instead of water, the said hydrocarbons being atomized into the production gas, or conversely the production gas being led directly through the liquid hydrocarbons to be cracked.

From this further differences arise in carrying out the thermal cracking of liquid hydrocarbons by partial combustion.

It is known to maintain a flame below the surface of liquid hydrocarbons, especially mineral oils. For this purpose the liquid hydrocarbons to be cracked are atomized with oxygen within a submerged bell serving as a flame chamber and ignited therein. The heat reflection of the bricklined bell wall determines the stability of the flame. In the course of the partial combustion, the hydrocarbons supplied in excess to the burner nozzle are cracked. The reaction gas formed passes at the lower edge of the bell into the liquid hydrocarbon phase and is thereby rapidly cooled. The liquid products arising from the cracking and also the carbon black mix with the liquid hydrocarbons present to form oil bottoms the viscosity of which constantly increases. In the stationary state therefore part of the oil bottoms is supplied from the quenching chamber (or the burner nozzle for combustion and cracking. The used hydrocarbons are replaced by supplying liquid initial material either in front of the burner nozzle or directly to the oil bottoms of the quenching chamber.

Another process for cracking liquid hydrocarbons operates without a submerged bell. A submerged flame is therefore directly in the liquid hydrocarbons to be cracked. In one embodiment, the oxygen alone is led beneath the surface of the liquid and allowed to react as a flame. The reaction heat liberated in the boundary surface between the flame and the surrounding liquid phase cracks the hydrocarbons. The oil bottoms to which the hydrocarbons to be cracked are added to replace the oil consumed, serves to quench the reaction products. In order to control the carbon black content of the oil bottoms, for example, part of the suspension of finely divided carbon in the liquid hydrocarbons may be withdrawn periodically or continuously. After separation of the carbon black, the liquid hydrocarbon is returned to the reaction vessel. The procedure may also be that part of the hydrocarbon containing carbon black is withdrawn from the reaction chamber and part thereof returned to the reaction chamber through the burner so that upon entry into and in the flame chamber it surrounds the oxygen. The remaining considerably smaller amount of hydrocarbons containing carbon black, which is 3 to 50 times the amount which could be completely burnt by the whole of the oxygen supplied to the flame chamber, is atomized in the oxygen for partial combustion.

For the thermal cracking of liquid hydrocarbons it has also been proposed to atomize them in a free reaction chamber with amounts of oxygen insufficient for combustion and to allow them to react after ignition. This process makes use of a special direct method of quenching the reaction mixture which consists of the combustion of gases and cracked gases, with the hydrocarbons heat that are used for cracking. This consists in atomizing such an excess of liquid hydrocarbons with the oxygen prior to combustion and cracking that simultaneous quenching of the reaction gas is made possible. In stationary operation, the atomizing nozzle is filled with the products of the bottoms collecting in the reaction vessel with an admixture of initial oil to replace the amount of hydrocarbon used up.

One characteristic common to all the said processes for the thermal cracking of liquid hydrocarbons by partial combustion is, that in carrying them out, the actual liquid raw material to be cracked and the liquid products of the reaction are introduced into the process not separately but mixed with one another. The acetylene of the production gases therefore collects for working up a diluted condition by reason of a considerable content of olefinic gases, especially ethylene. The undesirably large portion of olefinic gases is the result of subsequent cracking reactions which may occur during the quenching process at lower temperatures than that of the original cracking, with hydrocarbons of the quenching liquid.

The higher utilization of energy by the conversion of sensible heat into chemical energy of the olefinic cracked products is counteracted, however, by the separation of acetylene from the production gas which is more strongly troubled by the increased content of olefines. Moreover, a lean gas is obtained in the acetylene separation which is still considerably enriched in olefines and must be separated from the olefines in a further step.

A process for the cracking of liquid hydrocarbons which yielded a production gas rich in acetylene but poor in ole-
finesses would therefore offer advantages over the known processes. A further disadvantage, for example of submerged flame cracking, lies in the high expenditure for protective measures. Thus the large reaction chamber filled with the liquid hydrocarbon in which the submerged flame burners must be placed in an appropriately large concrete chamber because, lasting spontaneous ignition of the flame in a liquid system cannot be assured. The throughput itself is limited by the violence of the gas evolution which carries up the liquid from the reaction vessel. These disadvantages interfere with every enlargement of the scale on which the process is to be carried out. Since, because of their ash content, the combustion of cracked oils in combustion chambers leads, in the long run, to total destruction of the walls the known processes which supply the necessary cracking energy in the form of hot fuel gas, make use of the combustion of gaseous or readily vaporizable hydrocarbons. On account of the technical difficulties which interfere with a return of residues from petroleum cracking for combustion in combustion chambers, only gaseous or vaporized hydrocarbons of light to medium petroleum fractions are used for cracking in the reactor which is arranged after the combustion chamber. The exclusion of crude oils from cracking is a disadvantage of this process.

We have now found for the production of acetylene by thermal cracking of liquid hydrocarbons, especially hydrocarbon mixtures containing unvaporizable constituents, for example crude oils, which avoids the said disadvantages and, in contrast to the known processes, yields a production gas which by reason of its lower olefine content permits a more ready separation of the acetylene from the production gas. Moreover, the residual gas poor in olefines, since it is not subjected to any further separation, can be employed in a simple way, for example by flameless cracking with oxygen, into synthesis gas.

The process according to this invention comprises introducing the hydrocarbons, especially petroleum, to be cracked and their liquid cracked products separately into the process, by cracking the more liquid products containing carbon black which are formed by the cracking and are returned with oxygen in a common free space by means of a burner and supplying to the stream of the hot reaction products thus formed laterally first or more jets of the hydrocarbon to be cracked and then, to quench the reaction mixture, one or more jets of circulated liquid cracked products containing carbon black, the laterally introduced jets having such an impact pressure that they penetrate into the stream of the reaction products and are substantially mixed therein, the amount of the hydrocarbon to be cracked being so measured that 3.0 to 1.0 kg, preferably 2.5 to 1.5 kg, of the hydrocarbon to be cracked is used for every cubic meter (S.T.P.) of oxygen, and the amount of cracked product circulated and used for quenching the reaction mixture being sufficient to decrease the temperature of the reaction mixture to below 500 °C. It has been found that for a rapid mixing of the jets by intersection of the jets the product of the ratio of the impact pressure of the lateral jets to the impact pressure of the reaction products, both measured at the point of penetration, and the corresponding ratio of the jet diameters must lie within the range of 0.01 to 3, especially at 0.02 to 1.

In order that the liquid cracked products boiling above 85 °C. formed by the cracking may be completely reacted with oxygen, they are advantageously returned to the burner in an amount of 30 to 150% of the hydrocarbons to be cracked.

The stream of hot reaction product formed has, prior to mixing with the hydrocarbons to be cracked, a temperature of 1200° to 2800 °C, especially 1800° to 2200 °C. After mixing with the hydrocarbons to be cracked, a temperature of 800° to 1600 °C, especially 1000° to 1400° C., prevails. This temperature is lowered to about 100° to 500° C. by quenching with the liquid cracked products circulated.

The process according to this invention can be carried out at normal or increased pressure, for example 3 to 20 atmospheres. The process is not limited to pure oxygen. Diluents such as nitrogen, carbon dioxide and especially steam, may also be added to the oxygen.

It is also possible to supply carbon dioxide or steam to the reaction chamber together with or separately from the hydrocarbons to be cracked and/or the cracked products used for quenching, mixing with the reaction products or reaction mixture being effected by intersection of streams.

This cracking process was first carried out on a laboratory scale with model substances in order to investigate the stable relationships of flame formation under the conditions of the reaction according to this invention. As model substance of the hydrocarbon to be cracked was used made of light gasoline and as model substance for the liquid cracked product, benzene.

The hydrocarbon to be cracked was supplied as gasoline vapour, for example, from two nozzles arranged directly opposite each other into a cold jet of oxygen, which issued from a burner into a free space at a speed of between 50 and 125 meters per second in deficiency to the methane surrounding it after ignition. The ratio of cubic meters (S.T.P.) of oxygen to kilograms of injected oxygen between 0.5 and 0.8, the outlet speed of the gasoline jets was between 5 and 25 meters per second. The production gas at 1000° to 1300° C. was quenched to about 300° C. by benzene vapour slightly above the visible reaction zone.

The quenched production gas was free from oxygen even when the oxygen exceeded 2.5 times the amount necessary for complete combustion of the methane.

The safety in operation of the process as compared with those in which accumulations of oxygen can occur in the production gas becomes obvious in the extreme case when the oxygen flows into the reaction chamber without methane. Even under such conditions, the cold oxygen may be completely reacted with the injected hydrocarbons in a short flame. During this experiment, to maintain the flame, a small pilot flame burned in the direction of the mixing point of the oxygen and gasoline vapour. The product of the ratio of the impact pressure of the gasoline vapour jet to that of the oxygen jet and the corresponding ratio of the jet diameters lies between 0.004 and 0.4 at the point of mixing. The production gas also remained free from oxygen when the supply of benzene or gasoline vapour to the reaction vessel was interrupted at will.

The production gas obtained by quenching with benzene shows for example for a value of 0.8 cubic meter (S.T.P.) of oxygen per kilogram of injected gasoline, a percentage mole ratio of acetylene/acycenes plus ethylene of 69.5 and a volumetric ratio of acetylenes to ethylene of 2.29 or a volumetric ratio of acetylene/ethylene plus higher C_nH_2n- olefines of 1.65. Quenching with gasoline instead of benzene gives by comparison the values 54.0, 1.18 and 0.9. A similar displacement toward a gas composition richer in olefines occurs when quenching with benzene-gasoline mixtures.

An apparatus suitable for carrying out the process according to this invention is illustrated by way of example in the accompanying diagrammatic drawing. A burner 1, the opening of which projects upwardly into a free reaction space 2 is fed with the liquid products containing carbon black originating from the cracking. The necessary oxygen is supplied at 4. After the mixture has been ignited by one or more pilot flames 5, one or more jets of the liquid hydrocarbon to be cracked are injected into the stream of hot reaction products laterally through a ring of nozzles 6. To quench the hot reaction products, the stream of the reaction products, after a short reaction period, is substantially dis-
ruptured by one or more jets of circulated liquid cracked products containing carbon black which are emitted from a ring of orifices 7. The inner walls of reaction chamber 2 are rinsed with liquid cracked products from the top through a hollow cone nozzle 8.

The cooled production gas leaves the reaction chamber at 9 together with the liquid products and flows through a pipe 10 to a washing and cooling zone 11 into the top of which phlegm gasoline is pumped through a pipe 12 for evaporation cooling. In many cases it is advantageous to supply the cooled production gas and vapour to the column separately from the liquid products. The liquid products then flow through pipe 10 which is provided with a dip leg into bottom 14 of column 11 and the gaseous and vaporous products leave the reaction chamber above the quenching jets 7 through a pipe (not shown) which opens into bottom 14 above the level of the liquid therein. Additional heat may be withdrawn from the column 11 by a waste heat boiler 13 attached to bottom 14. The column is so operated that the level of the bottoms circulated through the pipes 15, 16, 17, 18, 9 and 10 and container 14 remains constant.

The cooled production gas, freed for the most part from carbon black, leaves the apparatus at 20 for further working up in an attached apparatus 19.

Boms oil is withdrawn through a pipe 21 for the removal of ash.

This invention is illustrated by, but not limited to, the following example, given with reference to the drawing.

**Example**

17 kg. per hour of liquid cracked product containing carbon black is supplied to burner 1 from container 14 and at the same time, for intimate mixing, 15 cubic meters (S.T.P.) of oxygen per hour is supplied to the burner. As the mixture enters the reaction chamber 2 it is ignited by pilot flames 5 fed with fuel gas and oxygen. 25 kg. of crude oil per hour is injected through jets 6 into the stream of hot reaction products formed, for the purpose of cracking. After a cracking period of about 0.003 second, the reaction products are quenched by circulated liquid cracked products containing carbon black to 250° C., by supplying about 1000 kg. of bottoms per hour from container 14 through pipes 15 and 17 to the quenching jets 7. To avoid deposits of carbon black in the reaction chamber, the vessel walls are rinsed with 100 kg. of bottoms (per hour) atomized by means of the hollow cone nozzle 8. The quenched gas and vapour pass together with liquid products through pipe 10 into column 11. 1 kg. of bottoms is withdrawn per hour from 14 through the pipe 21.

By cracking 25 kg. of crude oil, 43 cubic meters (S.T.P.) of cracked gas is obtained which contains 11.0% by volume of acetylene and 4.5% by volume of olefinic hydrocarbons. The remaining gas consists mainly of carbon monoxide and hydrogen.

What we claim is:

1. A process for the production of acetylene by thermal cracking of liquid hydrocarbons with amounts of oxygen insufficient for complete combustion and quenching of the reaction products, wherein part of the liquid product containing carbon black formed by the cracking and re-

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