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CRACKING OF HYDROCARBONS

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Fig-1

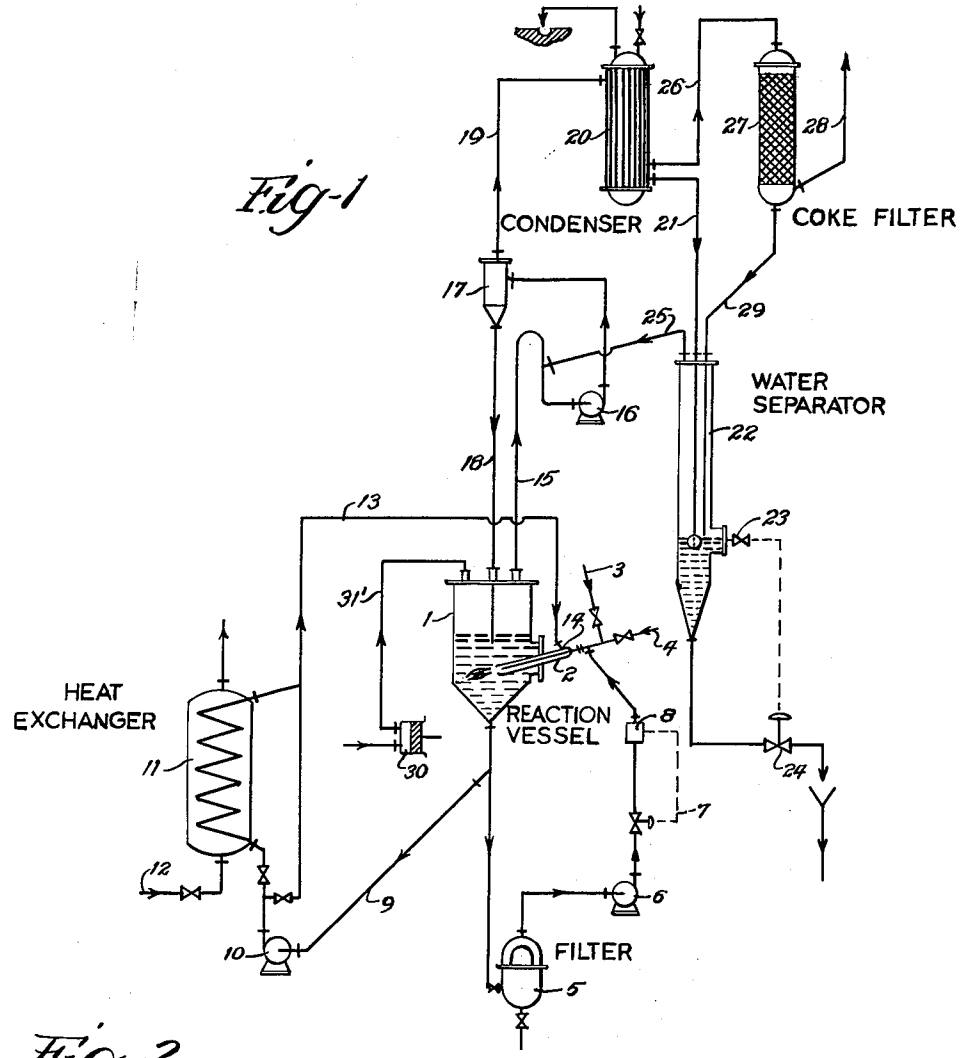
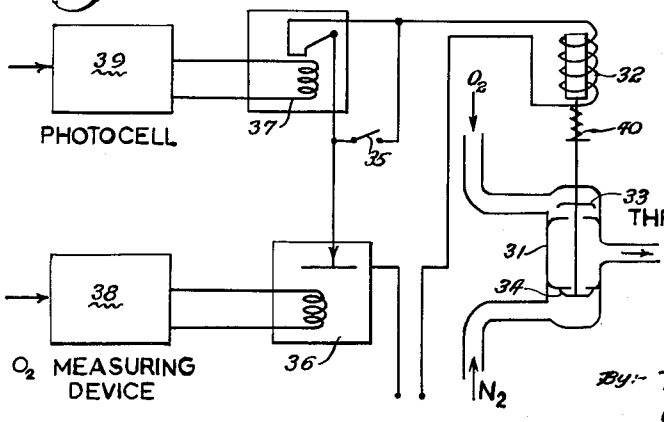


Fig-2



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CRACKING OF HYDROCARBONS

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3 Claims. (Cl. 260—679)

This invention relates to a process for the cracking of liquid hydrocarbons by a flame burning beneath the liquid surface of said hydrocarbons while continuously supplying the hydrocarbons. In particular, the invention relates to a process for the cracking of liquid hydrocarbons by a flame burning beneath the liquid surface of these hydrocarbons with the continuous supply of hydrocarbons and oxygen or oxygen-containing gases in which continuously or periodically a part of the hydrocarbons, together with the carbon which has formed during the reaction, is removed from the reaction vessel.

It is a particular object of the invention to prepare unsaturated hydrocarbons, especially olefines and acetylene.

It is known to crack liquid hydrocarbons in a flame burning below the liquid surface. Such an immersed flame can be produced by burning a combustible gas or a gasified fuel with oxygen or air beneath the surface of the liquid hydrocarbon to be cracked. By working in this way there are formed from the hydrocarbons, for example from petroleum fractions, besides carbon monoxide and hydrogen, a series of lower hydrocarbons, for example methane, ethane, propane, ethylene, propylene and acetylene. The yield of valuable unsaturated hydrocarbons, especially of ethylene and acetylene, is relatively small. Hitherto no success has attended attempts to direct the combustion in such a way that the process can be carried out continuously in a satisfactory manner in order that it should find an entry into industry as a new process for the production of unsaturated hydrocarbons, for example ethylene and acetylene.

The process has the disadvantage that after a short time of operation, the hydrocarbons surrounding the flame become increasingly viscous by reason of the carbon black formed by the combustion. With the increase in viscosity there is a further increase in the formation of carbon black. The strong rise in temperature thereby brought about gives rise to thermal decomposition of the hydrocarbons with the formation of coke-like deposits which bring the reaction to a standstill.

We have now found that in the cracking of liquid hydrocarbons in a flame burning beneath the surface thereof with the continuous supply of hydrocarbons and oxygen or oxygen-containing gases, good yields of unsaturated gaseous hydrocarbons are achieved while avoiding the said disadvantages by continuously or periodically removing from the reaction vessel a part of the hydrocarbons together with the carbon which has formed during the reaction. In this way the carbon cannot become enriched beyond a point at which the hydrocarbons remain a liquid capable of forming drops under the working conditions.

The carbon can be separated from the removed suspension, for example by means of a centrifuge, and freed from adherent hydrocarbons by steam distillation or extraction. The carbon thus obtained is a valuable active carbon black which is suitable for a great variety of purposes, for example for working up rubber or for preparing printing ink.

The purified hydrocarbons may be returned to the reaction vessel, if desired diluted with the condensed light hydrocarbons formed by the cracking. In this way the portion of the cracked product which is not desired as an end product is wholly or partly used as fuel for the cracking. Moreover, the viscosity of the heavier hydrocarbons in the reaction vessel is diminished by the said dilution.

The cracking can also be carried out by supplying the suspension of carbon in the liquid hydrocarbons removed from the reaction vessel, without separation of the carbon, to the oxidizing region of the combustion zone with the aid of a nozzle through which at the same time a current of oxygen is passed. The burner may be constructed as a pressure atomizer. The carbon black finely atomized with the hydrocarbons is burnt in the oxidation zone and thereby yields additional amounts of energy for the endothermic process of cracking.

A specially suitable method of operation is achieved when the oil sump of the cracking vessel is continuously stirred up by mechanical forces, and this may advantageously be effected for example by withdrawing the oil at the lowermost point of the vessel and returning it through a circulatory pump. In this way sedimentation of carbon black in the vessel is avoided and the fluidity of the oil and the heat transfer of the hot gases remain constant. By this measure the acetylene and ethylene content of the cracked gas is kept constant, whereas without the oil circulation it is subject to fluctuations because the residence time of the gases at high temperature is directly proportional to the viscosity of the oil used. By working in this way the amount of carbon black formed is also diminished. The portion of the oil which is supplied to the centrifuge for separation of carbon black may also be branched off from the said oil circulation. The stirring up of the sump oil may also be effected for example by a mechanical stirring device or a vibrator.

A specially advantageous embodiment of the process in which the carbon black formed in the immersed flame, which is continuously removed from the reaction vessel with a part of the hydrocarbons, can be completely burnt in the process, consists in returning a part thereof, if desired after cooling, to the reaction chamber in such a way that the hydrocarbons upon entry and in the flame space, flow around the oxygen or oxygen-containing gas in which in turn the other part of the carbon-containing hydrocarbon is atomized for partial combustion and which contains 3 to 50 times the amount of carbon which can be burnt completely by the total amount of oxygen supplied to the flame space.

The introduction of carbon black-containing hydrocarbons can for instance be effected by means of 3 concentrically arranged pipes. Carbon black-containing hydrocarbons are fed through the outermost tube, the oxygen or oxygen-containing gases through the middle tube, and the rest of the carbon black-containing hydrocarbons through the inner tube.

Advantageously, a burner nozzle consisting of 2 concentric pipes which are fitted into a jacket pipe, is used.

The reaction vessel is filled partly or completely with the hydrocarbon to be cracked.

Working in this way causes the flame space to be subdivided into smaller sections which are at high temperature. By increasing the amount of hydrocarbon containing carbon black which is atomized in the oxygen up to a multiple of the amount necessary for using up the oxygen, the flame space is subdivided by thick oil layers. In the high temperature zones existing between these oil layers, the finely atomized mixture of oil and carbon black is burnt and cracked, while the oil layers flowing around the flame space, which are formed by the introduction of the other branch stream of the mixture of hydrocarbon

and carbon black, prevent the hot cracked gases from any further reaction by quenching them. The temporary temperature gradient in the direction of the quenching zone is very high.

By working in this way there are formed from the hydrocarbons, for example from petroleum fraction, besides carbon monoxide, dioxide, and hydrogen, acetylene and higher homologues, olefines and diolefines, preferably ethylene, propylene, butylene and butadiene and a number of lower hydrocarbons, for example methane, ethane, propane, and butane.

In carrying out the process it is advantageous to use, for the introduction of the two branch streams of circulating hydrocarbon and oxygen into the reactor, a burner which consists essentially of three supplies arranged one inside another concentrically, one part of the circulating hydrocarbon, which preferably flows through a cooler which may also be constructed as a heat exchanger, being supplied to the outer jacket pipe and flowing around the flame space as an outer cooling zone. Through a burner nozzle arranged centrally in this jacket pipe and which in turn consists of two concentric pipes, oxygen or oxygen-containing gas is introduced through the outer pipe into the reactor and the second branch stream of the hydrocarbon containing carbon black is introduced through the inner pipe.

Figure 1 of the accompanying drawings shows diagrammatically an embodiment of apparatus which is suitable for carrying out the process according to this invention; the way in which it is operated will now be described.

The oil containing carbon black which is to be atomized into the oxygen situated in the flame space through the innermost pipe of the burner should amount to 3 to 50 times the amount which can be completely burnt by the total amount of oxygen supplied. When setting the apparatus in operation, i.e. when filling the reaction chamber with the hydrocarbon to be cracked, it is preferable to work by supplying nitrogen initially and changing the valve over to oxygen only shortly before the ignition which is preferably effected electrically. The hydrocarbons which are led through the two circulations are preferably withdrawn from the reaction vessel at the lowermost point of the sump through a pump. One part of the circulation can be used in an interposed heat exchanger for the production of steam by giving up its heat, while the other part of the circulation, which is to be atomized into the oxygen in the flame space, is preferably returned to the reaction chamber through a filter by means of a centrifugal pump. It is advantageous to use an automatic control. For example a pneumatic valve can be used which keeps the sump oil stream constant by a bulk liquid meter. For the supply of oxygen and the atomization of the oil containing carbon black it is advantageous to use a medium atomizing burner. The initial hydrocarbon can be introduced directly into the reaction chamber by a pump.

The cracked gas formed, which entrains with it not only carbon black and vaporized hydrocarbons but also the water formed by the cracking, is preferably freed from carbon black, before being worked up in a suitable gas separation apparatus, for example by leading it through a mechanical washer and separating the carbon black in a cyclone. As the washing liquid there may be used for example the condensate of the vaporous hydrocarbons which have been taken up by the cracked gas according to their vapour pressure. This condensate is obtained for example by cooling the cracking gas freed from carbon black together with the water formed by the cracking, and separated therefrom by simple separation of layers. The washing liquid can be returned to the reaction chamber.

The circulation speed of the hydrocarbon containing carbon black in the sump of the reaction vessel is preferably chosen so that it corresponds to 3 to 50 times the supply speed of the fresh hydrocarbon.

It may be regarded as surprising that by this special embodiment the yield of unsaturated hydrocarbons, to the increase of which the process is directed, is more than doubled. The carbon black contained in the oil circulation is burnt although reducing conditions prevail in the interior of the flame. After operating such a plant (Figure 1) for weeks, no increase in the content of carbon black could be detected in samples taken from the sump. The method of operation of a plant which works according to this method is described in greater detail in the example appearing later in this specification.

As initial materials for the process there come into question in general liquid hydrocarbons, for example those which have a boiling range of 50° to 450° C. at normal pressure, or mixtures thereof, for example petroleums, their distillates, and also distillates of high or low temperature tars. In the case of high boiling point hydrocarbons it is advantageous to add to the flame also more readily combustible substances, such as gases, for example hydrogen, methane or coke oven gas or low boiling point liquid hydrocarbons, so that a readily ignitable mixture is formed. The addition of these substances which increase the ignitability of the mixture can be started after the flame has been ignited. However the flame may also be supported by the continuous supply of cheap gaseous, liquid or solid fuels, which are injected or atomized, so that the hydrocarbons being worked up are used up only for the cracking. Hydrocarbons may also be used however which cannot be distilled without decomposition.

When carrying out the process it is usual to work at flame temperatures of 1,000° to 2,800° C. The temperature to be used when the process is directed mainly to the production of acetylene lies at 1,800° to 2,500° C., especially at 2,000° to 2,300° C. In the production of ethylene it is preferable to work at temperatures of 1,200° to 15,000° C.

The sump temperatures are to be distinguished from the above temperatures; the sump temperature is preferably kept at 150° to 300° C. for example by circulatory cooling or by indirect cooling of the reaction chamber.

The supply of oxygen also depends on the desired end product. When cracking petroleums to ethylene, 0.55 cubic meter of oxygen is used up per kilogram of petroleum to be cracked. On the other hand 0.65 cubic meter of oxygen is necessary for the production of acetylene from the same amount of petroleum.

The composition of the gaseous reaction products of the cracking of liquid hydrocarbons is not only a function of the temperature and the oxygen supply, but in part also of the pressure under which the cracking is carried out. By increasing the pressure the relative proportion of carbon dioxide and carbon monoxide in the cracked gas is especially displaced in favor of carbon dioxide. Since by a complete combustion to carbon dioxide larger amounts of heat are set free, small amounts of hydrocarbon are sufficient in order to yield the heat necessary for cracking by complete combustion. The consequence is an increase in the yield of acetylene and cracked products.

The use of increased pressure in the autothermic cracking of hydrocarbons can also be combined with the feature of the return of the undesired cracked products. In this way it is possible to direct the cracking in such a way that only one desired end product, for example an olefine or acetylene (in addition to carbon dioxide, small amounts of carbon monoxide, water and carbon black) is formed by the process. If it is desired to produce a number of products at the same time, for example acetylene as well as ethylene, then after separating acetylene and carbon dioxide, the ethylene is separated in the usual way, for example by a solvent wash and low temperature distillation, and the residual gas remaining is returned. The ratio of the two cracked products to each other can

be displaced by returning the corresponding excess components to the flame.

After separating the desired end products and the carbon dioxide from the gas to be returned, there may also be added thereto other gaseous fuels, as for example refinery gas, coke oven gas, watergas or gases which are formed in the pressure gasification of coals with oxygen and hydrogen, and also natural gas. The amount of gas added can be chosen so that the liquid hydrocarbons are converted exclusively into the desired products, for example acetylene and ethylene, while the fuel gases yield the necessary cracking energy.

Generally, pressures of 1 to 100, preferably 5 to 40, atmospheres, are used.

A survey of the displacement of the composition of the cracked gas, such as can be achieved for example by the use of increased pressure, is given in the following table:

	100 kilograms of gas oil (boiling limits 180° to 300° C.) yield at—	
	30 atmospheres	normal pressure
	Kilograms	*Kilograms*
carbon dioxide	58.3	22.9
carbon monoxide	25.95	91.7
water	21.95	20.3
hydrogen	3.98	4.99
acetylene	20.70	15.21
ethylene	22.30	16.20
propylene	13.92	6.36
methylene	7.44	7.66
carbon black	2.20	2.00

The oxygen consumption for the cracking of 100 kilograms of gas oil amounts to about 87 kilograms at normal pressure as compared with about 77 kilograms at 30 atmospheres.

Deposits of carbon occur especially readily at the mouth of the oxygen nozzle. At this point, tubular coke deposits may form which when they reach a certain size break off and gradually fill the reaction chamber and cause stoppage in the oil pipe. This trouble can be avoided by using a burner nozzle of which the mouthpiece is formed not as a round surface but as a sharp edge which offers no place for the carbon deposit to form. The mouth may proceed to a sharp edge from the inside to the outside or from the outside to the inside.

In carrying out the process technically it is of great importance to carry out the ignition of the flame free from trouble and free from risk. The risk of explosive decomposition is always present when large amounts of inflowing gas collect owing to delay in ignition. The collection of large amounts of an ignitable gas mixture in the free spaces of the reaction vessel, i.e. above the surface of the liquid of the hydrocarbon to be cracked, must therefore be avoided.

This difficulty can be overcome by carrying out the ignition simultaneously with the commencement of the supply of gas and in the immediate neighbourhood of the point of entry of the oxygen into the liquid hydrocarbon.

By way of example, we give three different methods of ignition by which the ignition can be effected with complete certainty of operation. For example simultaneously with the beginning of the supply of gas it is possible to effect ignition by initiating a high voltage discharge in the immediate neighbourhood of the oxygen and fuel gas supply in the gas bubble forming underneath the liquid surface, the high voltage discharge being effected by means of one or two insulated leads. When using only one electrode, the spark path forms to the oxygen nozzle. When using two electrodes, the spark path forms between the same. It is necessary to arrange the electrodes above the point of outlet of the oxygen at a distance of 0.5 to 10 millimeters in such a way that the ignition sparks penetrate into the ascending gas bubbles. The leads lie beneath the surface of the hydrocarbon in the reaction vessel. They must be so well insulated that the spark discharge or the electric spray discharge can only take place at the place provided, i.e. at the mouth of the nozzle. The high specific resistance of the liquid hydrocarbon prevents a penetration of the sparks into the gas space above the liquid surface in this arrangement. In a retarded ignition, an electric spark which struck through the liquid layer of hydrocarbon could ignite the fuel gas-oxygen mixture above the liquid surface.

The gas mixture can also be ignited by preheating the oxygen to a temperature which lies above the ignition temperature of the fuel gas or the liquid hydrocarbon, for example to 60° C. In this case the ignition is initiated at the point of contact of the oxygen with the hydrocarbon.

Moreover the ignition process may also be effected by chemical reactions which proceed with the formation of a flame. A special embodiment consists in introducing with the oxygen substances which react with the fuel gas or the liquid hydrocarbon with fire phenomena, for example fluorine and manganese heptoxide. It is also possible however to add to the fuel gas or the liquid hydrocarbon compounds, for example metal compounds such as zinc diethyl and aluminium triethyl, which then react with oxygen with fire phenomena.

Temporary fluctuations in pressure of the oxygen supply also constitute sources of danger. The flame becomes extinguished and the oxygen passes without a fresh ignition into the gas space situated above the liquid where it forms with the cracked gases present an explosive mixture.

We have found that it is possible to work with complete certainty of operation by regulating the supply of oxygen to the reaction vessel by a valve which is coupled with the inverse function of an inert gas valve.

The oxygen supply can be regulated, preferably automatically, in dependence on the flame and on the gas composition in the space above the hydrocarbon to be cracked so that a large accumulation of oxygen in the gas space above the liquid hydrocarbons, in which the cracked gas is situated, is avoided, by closing the oxygen valve and opening an inert gas valve upon the extinction of the flame. The formation of explosive mixtures is thereby avoided. For example the extinction of the flame can operate photoelectrically on the oxygen and inert gas valves. The same action can be produced automatically when the oxygen content in the gas space situated above the surface of the liquid exceeds a certain limit.

A method of operation in which the regulation of the oxygen supply is carried out by both measures will now be described.

The light of the flame is controlled by a photocell and the photo-current of varying strength thereby produced is used to actuate the oxygen valve magnetically or, after suitable conversion, pneumatically or hydraulically. When the flame is extinguished, the photo-current is interrupted, so that the oxygen valve is immediately closed and at the same time a gas valve for the admission of inert gas, as for example carbon dioxide, nitrogen or steam, is opened.

After the apparatus has been put into operation, with the oxygen valve open and the inert gas valve closed, the oxygen content of the gas in the space above the hydrocarbon to be cracked is continuously determined analytically. This can be effected with the aid of a device which responds selectively to oxygen, as for example by measuring the paramagnetism of the oxygen. If the oxygen content exceeds 2.5% by volume, the inert gas valve remains opens until the oxygen has fallen below this maximum value again. By suitable amplification of

the measuring effect and transferring it to a switch member, the opening or closing of the valves is effected.

After ignition has taken place, the photocell immediately takes over the control, while the switching via the automatic oxygen determination functions with a slight delay. The fact that the two devices function independently of each other ensures a high certainty of operation for both devices. The two valves are preferably so arranged that upon failure of the controlling force, the inert gas valve is immediately opened and the oxygen valve closed. When the inert gas is open, the gas mixture escapes to the atmosphere.

A circuit diagram for a control plant in which the operation of the valves is supervised by both measures, i.e. both by photo-electric supervision of the flame and by oxygen determination in the gas space, is given in Figure 2 of the accompanying drawings. In principle it is also possible however to carry out the supervision of the plant by only one of the two measures.

When the cracking plant is put into operation, it is rinsed with nitrogen until the oxygen measuring device indicates less than 2.5% by volume of oxygen in the gas whereupon the rest relay **36** closes the contact for the supply of electric current to the electromagnet **32**. If then the switch **35** is closed, there is an electrical connection and the electromagnet **32** actuates a three-way valve **31** in such a way that the oxygen valve **33** is opened and the nitrogen valve **34** is closed. After ignition has taken place, the light formed by the flame reaction falls on a photocell **39**. An electric working relay **37** is actuated through an electronic amplifier (not shown) and the current circuit parallel to the switch **35** is closed. If the switch **35** is then opened, this device supervises continuously the flame and the oxygen content of the cracked gas in such a way that when the flame is extinguished, light impulse no longer falls on the photocell **39**, so that the working relay **37** is without current and the current circuit for operating the magnetic valve **32** is interrupted. Exactly the same procedure is also initiated if the oxygen measuring device **38** detects an oxygen content in the cracked gas which has risen above the maximum value. The rest relay **36** thereby interrupts the exciter circuit for the electromagnet **32**. In both cases the oxgen valve **33** is automatically closed and the nitrogen valve **34** for rinsing explosive mixtures from the plant is automatically opened with the aid of a return spring **40**.

By the process according to this invention it is possible to carry out the cracking of hydrocarbons in so-called immersed flames continuously, and for the first time a process is made available which is useful technically. It is possible to gasify the hydrocarbons used completely even without separation of the more difficulty combustible constituents. By the increase in the proportion of unsaturated hydrocarbons in the cracked gas, the separation of these unsaturated hydrocarbons from the cracked gases is also considerably simplified, because it is well known that the separating effect is considerably improved even by a trivial increase in the content of unsaturated hydrocarbons in the solvent extractions, low temperature condensation or distillation usually employed technically.

The following example, given with respect to Figure 1 of the accompanying drawings, will further illustrate this invention but the invention is not restricted to this example.

Example

Figure 1 shows a scheme for a plant in which, for example, crude Kuwait petroleum can be cracked by the process according to the invention. The reaction vessel **1** (a vessel about 0.5 meter in diameter and 2 meters high) is half filled with petroleum. About 40 centimeters beneath the surface of the oil is the end of an inclined, downwardly directed medium atomizing burner **2**. Before and during the filling of the vessel, nitrogen is blown through the burner **2** from a pipe **3** so that no oil penetrates into the oxygen-conveying part of the burner. After reversing the gas valve, the oxygen flowing in from the pipe **4** is ignited by electrical ignition. At the same time there are supplied through the inflowing oxygen (18 cubic meters per hour) 200 liters per hour of sump oil through a filter **5** by means of a centrifugal pump **6** through a pneumatic valve **7** to the medium atomizing burner **2**. The control of this valve takes place through a mass flow meter **8** to keep the stream of sump oil constant. At the lowermost point of the vessel **1**, 10 cubic meters per hour of sump oil are withdrawn through a pipe **9** by means of a pump **10** and passed through a heat exchanger **11** in which the sensible heat is utilized for the production of steam from water introduced through a pipe **12**. The sump oil temperature is thereby kept constant at 160° to 200° C. The cooled oil is returned to the reaction vessel through pipes **13** and **14**, the burner **2** being centrally arranged within the inner space of the pipe **14**. The cracked gas leaves the reaction vessel through a pipe **15**, is freed from entrained carbon black in a mechanical washer **16** (shown as a pump in the drawing) and flows to a cyclone separator **17** from which the washing liquid containing carbon black is supplied to the reaction vessel **1** through a dip tube **18**. The hot vapor-laden gas passes from the cyclone through a pipe **19** to a condenser **20**. The water formed by the cracking of the hydrocarbons and the co-vaporized hydrocarbons are condensed out from the cracked gas in the condenser **20**. The condensate flows through a pipe **21** to a water separator **22** in which the specifically heavier water forms the lower layer. The separate withdrawal of the two liquids is controlled by a separating layer separator **23**. The water is run off through a valve **24**, while the hydrocarbons (light oils) contained in the condensate are used as a washing liquid and supplied through a pipe **25** to the mechanical gas purifier **16**.

The cooled cracked gas on the other hand passes from the condenser **20** through a pipe **26** into a coke filter **27** before being led off through a pipe **28** into a gas separation plant. In the coke filter **27**, the cracked gas is separated from suspended light oil particles which as a condensate are supplied through a pipe **29** to the water separator **22**. The fresh oil is supplied by means of a pump **30** through a pipe **31'** direct to the reaction vessel **1**.

With an hourly throughput of 32 kilograms of crude oil, there are obtained 48 normal cubic meters of cracked gas which has the following composition:

10.5% by volume of acetylene and higher homologues,
10.2% by volume of ethylene and higher olefines,
8.2% by volume of carbon dioxide,
40.0% by volume of carbon monoxide,
28.0% by volume of hydrogen and
3.1% by volume of methane and higher paraffins.

The crude petroleum is completely gasified and there are no liquid or solid byproducts.

We claim:

1. A process for the production of an unsaturated hydrocarbon selected from the group consisting of acetylene, ethylene, propylene, butylene and butadiene which comprises cracking a liquid hydrocarbon in an oxygen-supported flame which burns in a reaction zone beneath the surface of a body of said liquid hydrocarbon, continuously supplying fresh liquid hydrocarbon to said body, continuously removing a portion of said liquid hydrocarbon from said body and returning a portion thereof to the reaction zone in an atomized condition, returning the remaining portion of the recycled hydrocarbon to the reaction zone as an annular stream which substantially surrounds said atomized hydrocarbon, passing oxygen into said reaction zone to support said flame, said atomized portion of said hydrocarbon being partly utilized as a fuel for said flame, said annular stream providing a quench zone around said atomized hydrocarbon and said

flame, the atomized liquid amounting to 3 to 50 times the amount which could be completely burnt by the oxygen supplied to the reaction zone.

2. A process as in claim 1 wherein the portion of the hydrocarbon formed into an annular stream is cooled before it is returned to the reaction zone.

3. A process as in claim 1 wherein the hydrocarbon which is removed from the body of liquid hydrocarbon is filtered to eliminate carbon black before it is returned to the reaction zone.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

May 23, 1961

Patent No. 2,985,695

Rolf Platz et al.

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

Column 4, line 37, for "15,000° C." read -- 1,500° C. --; column 6, line 17, for "60° C." read -- 600° C. --.

Signed and sealed this 5th day of December 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents

USCOMM-DC