April 27, 1965 K. FISCHER ET AL 3,180,904

PROCESS FOR THE MANUFACTURE OF OLEFINS

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Fig. 1.

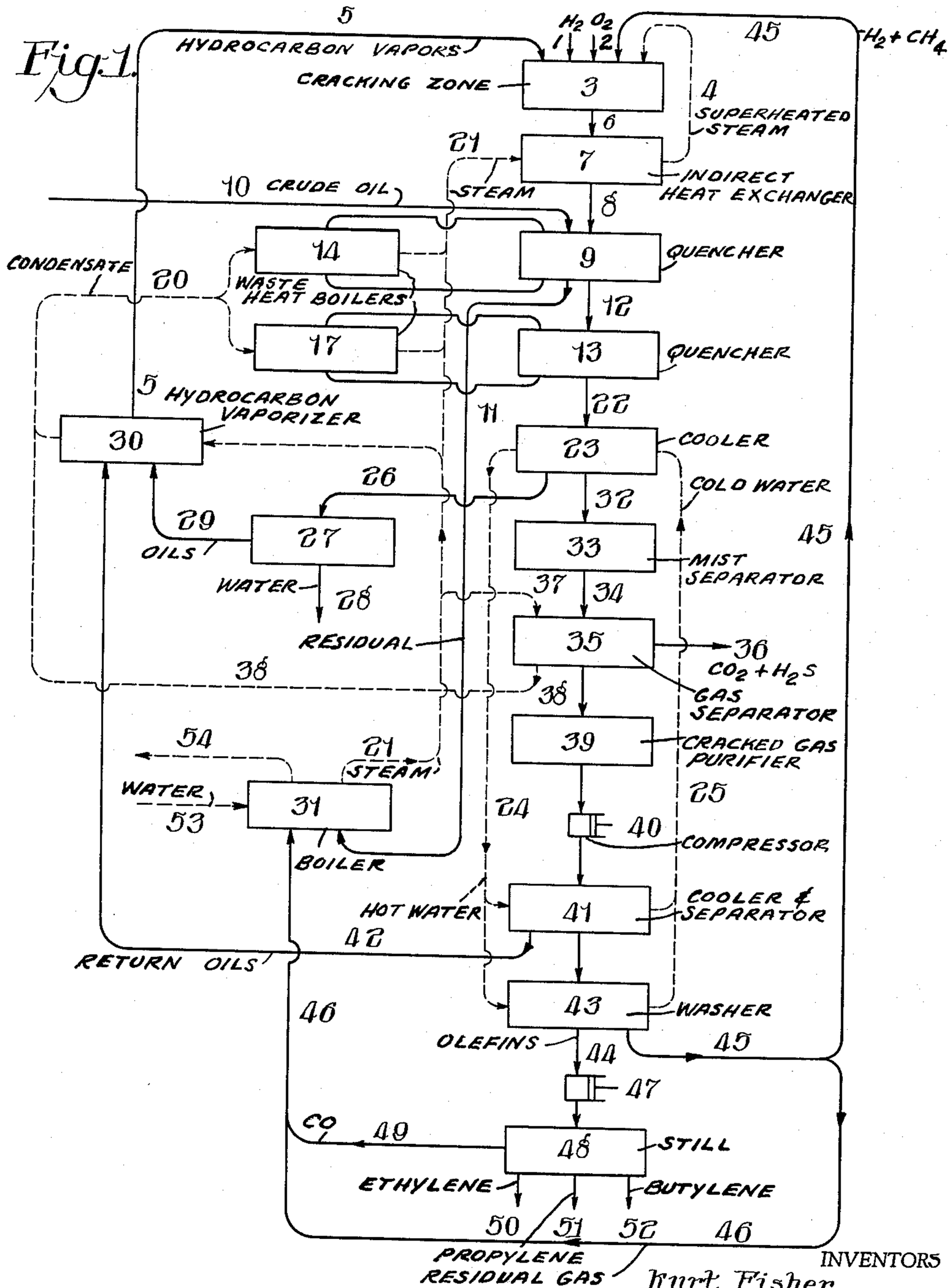


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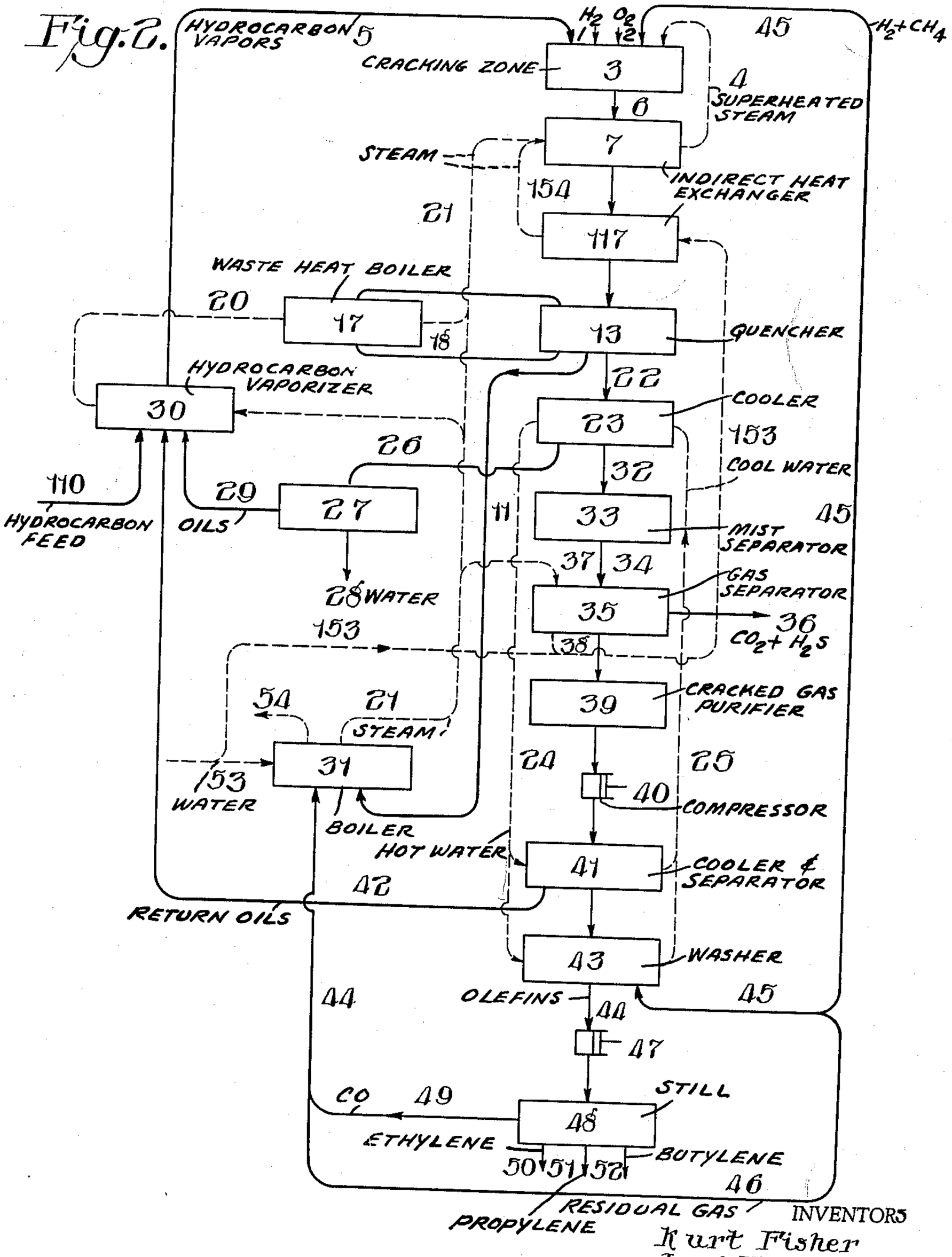
Fig. 2.

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# 3,180,904
# PROCESS FOR THE MANUFACTURE OF OLEFINS

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The present invention relates to a process for the manufacture of olefins of high purity containing 2 to 4 carbon atoms.

Numerous processes have already been proposed for the manufacture of olefins containing 2 to 4 carbon atoms by pyrolyzing hydrocarbons. But only a few of these processes are carried out on an industrial scale since they are uneconomical on account of unsatisfactory yields, disdisturbing carbon separations in continuous operation and the problem to find a suitable material for the apparatus to be operated at high temperatures.

It is known that the pyrolysis of hydrocarbons requires considerable amounts of heat, not only for the endothermal decomposition reaction but also for heating the starting material to the high temperatures necessary in the pyrolysis. Only a small temperature interval can be effectively utilized so that a considerable part of the required heat is obtained as waste heat which must be dissipated since, in general, the reaction products are further processed at lower temperatures. This disadvantage is especially pronounced when the hydrocarbons are cracked in the presence of steam as diluent since in this case the generation of the superheated steam requires large amounts of energy which must be dissipated on cooling the reaction product. This poor utilization, which is intalerable from an economical point of view, of the energy introduced together with the steam is more important than the advantage of the reduction of the carbon separation resulting from the presence of steam.

The present invention is concerned with a novel process for the manufacture of olefins of high purity and containing 2 to 4 carbon atoms by pyrrolizing higher hydrocarbons and subsequently decomposing the reaction mixture. The process of the invention avoids the disadvantages of the known methods. It is carried out as follows: first a carrier gas mixture consisting essentially of steam is produced, said mixture is then admixed in a cracking zone with the hydrocarbons to be cracked, the reaction mixture leaving the cracking zone is cooled to a temperature in the range from 600 to 150° C. by heat exchange with the carrier gas, the high boiling hydrocarbons that are not suitable for being reconducted into the cracking zone are separated by further cooling, the readily liquefiable hydrocarbons, which are to be reconducted into the cracking zone, are separated by subsequent direct cooling, the cracked gases are freed in known manner from carbon dioxide, sulfur compounds and acetylene hydrocarbons, then compressed at 20–30 atmospheres' gauge in order to separate low boiling hydrocarbons that are still present and are liquid at room temperature, which hydrocarbons are likewise reconducted into the cracking zone, the olefins and carbon monoxide in the cracked gas thus treated are separated by means of solutions containing cuprous salts from hydrogen, methane and homologs thereof, which may be present, an olefin concentrate is obtained from the copper salt solution, and the individual olefins are isolated



from said concentrate in a high degree of purity by distillation.

A characteristic feature of the present invention consists in that the main quantity of the heat set free in the individual cooling phases of the cracked products is used for superheating and generating the steam required in the pyrolysis, while the residual amounts of heat and the main portion of the condensation heat is utilized for covering the heat requirement in the individual stages of the gas purification and decomposition.

The hydrocarbon mixtures to be treated, for example crude oil or crude oil fractions, are introduced either in liquid or vaporous form into the cracking zone where they are mixed with the simultaneously arriving carrier gas.

The amounts of heat required for heating the hydrocarbon mixture to be cracked and for maintaining the cracking reaction are produced by the combustion of hydrogen and oxygen in a steam atmosphere. By dosing the steam there is regulated the temperature level desired in each case as well as the quantitative proportion of carrier steam to the hydrocarbon mixture to be treated. They are adjusted in such a manner that with a high degree of gasification of the starting substances the separation of carbon which accompanies the cracking reaction is largely suppressed. By adding at once the hydrocarbon mixtures to be cracked to the freshly generated carrier steam losses of heat are practically avoided. In the separation of the olefins, described below, by means of cuprous salt solutions there is obtained a residual gas which is free from carbon monoxide and essentially consists of hydrogen, methane and small portions of ethane and propane, which residual gas is well suitable as combustion gas in the cracking unit. Since it is obtained under pressure it can be further decomposed by a subsequent oil wash so that a gas mixture mainly consisting of hydrogen and methane is obtained as combustion gas for the cracking unit. It is likewise possible, of course, to use as combustion gas in the cracking unit a hydrogen-hydrocarbon mixture of another origin, provided that it does not contain essential amounts of carbon monoxide which would lead to an increased content of carbon dioxide in the cracked gas and to undesired and disturbing side reactions in the cracking process.

In addition to the aforesaid advantages the working with relatively high amounts of steam as carrier and diluent presents the further advantage that the apparatus must not be made of highly alloyed, nickel-free chromium steels the processing of which is very difficult as it is known. Materials having a low chromium content, which may also contain nickel, can be used provided that they are stable at a temperature of about 1100° C. The cracking zone is preferably formed by a tube-shaped reaction space made of such a material which is suitably built into a combustion chamber of ceramic construction material and insulated against the said chamber by a ceramic shield.

The process of the invention gives high yields of olefins of high purity containing 2 to 4 carbon atoms and, moreover, it is very economical since the heat required for decomposing the cracked products is taken to a great extent from the waste heat obtained in the cracking process. The heat leaving the cracking zone is completely utilized except for a small amount of condensation heat. The process of the invention can be largely varied with respect to the starting materials and the olefins to be obtained as final products. The olefins cannot only be produced from well defined hydrocarbons and hydrocarbon mixtures but also from crude and waste oils of most different origin.

The process is especially suitable for treating paraffinic oils, but it can likewise be used for other hydrocarbon mixtures containing, in addition to paraffins, also naph-

thenes and aromatic compounds. Oils containing a fairly small portion of aromatic hydrocarbons are preferred since the latter favor the formation of undesired residues unless they are removed by an additional device. When using light benzine fractions and natural gasolines obtained as by-products in the production of benzines suitable as engine fuels very high yields are attained due to the small residue formation.

Starting materials which do not contain unvaporizable residues are advantageously vaporized in a vaporizer preceding the cracking unit and being disposed within the heat conduction of the process, and introduced into the cracking zone in the form of vapor. In many cases it is also possible to introduce liquid starting materials directly into the cracking zone. Crude oils, residue oils and waste oils often contain considerable amounts of portions which are not suitable for the production of the desired olefins and form high boiling residues. It is, therefore, of advantage not to introduce such oils directly into the cracking zone but to inject them into the hot reaction mixture in the direct cooling zone (quenching) following the heat exchange after the cracking zone. This is suitably done in a washing or trickling tower which is charged with the oils to be treated in cocurrent with the reaction mixture while the temperatures are adjusted in a manner such that at the bottom of the tower only the high boiling products are collected as residues and the constituents of the charged oils that can be utilized in the cracking process leave the tower in gaseous or vaporous form together with the reaction mixture. It is thus possible largely to separate by distillation even high boiling oils since, due to the strong dilution with steam and cracked gas, the distillation takes place without additional energy at a very low partial pressure. In a similar second tower the reaction mixture is cooled in countercurrent manner by a treatment with a cycle oil to about 200–250° C. For said second oil cycle there are preferably used high boiling fractions of the starting oil. It is of advantage to branch off part of the oil of the second cycle which is introduced into the first washing tower. Thus the drop in temperature within the two quenching systems can be adjusted to the requirements of the total process. The amounts of heat taken up by the quenching cycles are used in waste heat boilers for the generation of steam, which, after having been superheated in indirect heat exchangers immediately following the cracking zone, is reconducted as heat carrier to the cracking zone.

In the indirect heat exchange taking place immediately after the cracking zone the reaction mixture is cooled to 500–400° C. while the heat carrier steam is simultaneously heated to 600–700° C. Said heat exchange is preferably carried out in single or double cyclones, as described for example in German Patent 1,000551 or Belgian Patents 552,522 and 561,754, by superheating the steam which enters at a temperature of about 100° C. to 600–700° C. while reaching high heat transfer coefficients. According to the invention said heat exchangers or part of them can also be used for generating the heat carrier steam required in the cracking zone from water or preferably steam condensate.

The subsequent final cooling to normal temperature in the indirect heat exchange with cooling water or another liquid presents further technical and economical advantages. It has been found that in the condensation of the steam used as carrier gas the hydrocarbons obtained in the quenching towers from the introduced crude oil, which hydrocarbons can be vaporized and converted into olefins, separate together with the hydrocarbons that do not react on passing through the cracking zone in the form of a layer which can be readily separated from the water. Furthermore, by heating the cooling agent to 80–100° C. a great part of the condensation heat is recovered so that it can be re-used in the process.

The heat balance of the process of the invention is



furthermore improved by the suitable intercalation of known devices for the gas purification and separation, which are arranged so that they utilize, on the one hand, the waste heat still available from the cracking unit and, on the other hand, the desired olefins are obtained in a high degree of purity, independent of the composition and amount of the cracked gases. The combination in accordance with the invention of the gas purification and gas separation is, furthermore, fairly independent of possible variations in the cracking zone, for example by the use of other starting materials or by milder or stronger cracking conditions.

According to the invention the gas is purified and separated in several stages. The cracked gases are first freed in known manner from carbon dioxide, sulfur compounds and acetylene. Then the portions that are liquid at normal temperature and pressure are separated from the gas mixture by compression at 10–30 atmospheres' gauge, for example 25 atmospheres' gauge. Subsequently, the olefins are separated in concentrated form from the residual gas mainly consisting of hydrogen and methane and no longer suitable of being converted into olefins by washing the gas with a solvent having a selective action for olefins, and the latter are decomposed. As selective washing liquids for the separation of the olefins from the cracked gas cuprous salt solutions are preferably used, other washing liquids having a selective action such as solutions of silver nitrate or of a silver-boron fluoride complex compound being likewise suitable. The separation by means of cuprous salts is preferably carried out as described in Belgian Patents 564,888, 565,181 and 569,799. The residual gas that is free from carbon monoxide and essentially consists of hydrogen, methane and small amounts of ethane and propane may serve as mentioned above as combustion gas for the cracking unit where it can be used instead of or in addition to hydrogen.

The concentrate of olefins obtained in the washing operation with the copper salt solution is decomposed by distillation in known manner. If the olefin mixture leaving the copper salt washing step still contains carbon monoxide formed in the cracking operation the latter is suitably removed by the process described in Belgian Patent 557,538. Alternatively the carbon monoxide can be separated from the olefins in the course of the olefin decomposition by distillation, usually by low temperature distillation. Since in the process of the invention the low boiling constituents of the cracked gas such as hydrogen and methane, the concentration of which in these cracked gases may largely vary, are already removed, the distillative final operation is carried out with mixtures that can be readily separated into the individual constituents. The working up in the process of the invention is also superior from an economical point of view to a total decomposition of the cracked gas by means of a multistage low temperature distillation.

The process of the invention permits, without additional expenditure pertaining to apparatus, to produce either ethylene alone or ethylene+propylene or ethylene+propylene+butylene. For carrying out one or the other working method of the operational conditions must only be varied slightly. By a suitable modification of the pressure and temperature conditions in the separation of the normal hydrocarbons to be carried out after the compression zone butylene and propylene can be wholly or partially separated with the liquid products and reconducted into the cracking zone where they can be converted into ethylene within the extremely short time of about 0.01 second due to the high dilution of the cracked gases by means of steam which is characteristic of the process of the invention.

The invention with its characteristic heat conduction permits to apply in the individual stages of gas purification and gas decomposition processes which entirely utilize with high economy the heat obtained in the crack-

ing stage of the process. Carbon dioxide and hydrogen sulfide can be washed out with hydroxy-alkyl amines or aminofatty acids by the Girbutol or Alkacid process by taking the heat required for the desorption and regeneration from the waste heat of the cracking operation available in the final condensers. The same applies to the separation of the olefins with cuprous salt solutions or other selective solvents. The usual degassing at subatmospheric pressure can then largely be dispensed with.

The accompanying FIGURES 1 and 2 diagrammatically represent flowing schemes illustrating by way of example, the process of the invention, but they are not intended to limit the subject matter of the invention thereto. FIGURE 1 illustrates the processing of a crude oil, whereas FIGURE 2 represents a flowing scheme for the processing of vaporizable hydrocarbons. As far as the latter arrangement is in conformity with the arrangement of FIGURE 1 the same numerals have been chosen.

Through conduit 1 hydrogen and through conduit 2 oxygen are introduced in equivalent amounts into the burner of the reactor where they are burned to steam. Simultaneously, an amount of superheated steam is introduced by way of conduit 4 such that the temperature of the total steam mixture in reactor 3 does not exceed 1400° C. The hydrogen can be wholly or partially replaced by the residual gas obtained in the gas decomposition zone 43 and preferably consisting of hydrogen and methane, which gas is conducted to the burner of the reactor via conduit 45. Corresponding to the higher calorific value of said residual gas smaller amounts suffice for reaching the same temperature and the addition of oxygen through conduit 2 must be dosed, corresponding to the composition of the residual gas, in a manner such that the complete combustion to $H_2O$ and $CO_2$ is warranted.

The heat carrier steam mixture thus generated in reactor 3 is admixed in the cranking zone of reactor 3 designed as reaction tube with the hydrocarbon vapors produced in vaporizer 30 from the crude oil to be cracked, which vapors are introduced into the cracking zone by way of conduit 5. In the cracking zone of reactor 3 the hydrocarbon vapors are cracked to yield a mixture of ethylene, propylene, butylenes, hydrogen, methane and smaller amounts of higher boiling hydrocarbons. Said mixture leaves reactor 3 via conduit 6 and travels into the indirect heat exchanger 7 (preferably designed as described in Belgian Patent 561,754) where it is cooled to about 600–450° C., while steam entering the reactor as heat carrier by way of conduit 4 is simultaneously heated to about 600° C.

After said first cooling step the mixture of the reaction products is passed via conduit 8 into the first quenching device 9 designed as washer in which it is cooled to about 350° C. in a downward cocurrent with the fresh crude oil introduced by way of conduit 10. Simultaneously, the residues which can no longer be used in the cracking operation are discharged through conduit 11 and conducted to a boiler unit 31 where they serve to generate steam from the feed water introduced by way of conduit 53.

The mixture of the reaction products is transported via conduit 12 into the second quenching device 13 where it is cooled to a temperature that is adapted to the boiling range of the crude oil to be processed. For this purpose the mixture is suitably contacted in a countercurrent with a return oil obtained in the process or with another thermostable oil. The heat taken up by the oil in quenching devices 9 and 13 serves in waste heat boilers 14 and 17 to vaporize water, preferably steam condensate obtained in other parts of the unit (30, 35). The steam thus generated is conducted via conduit 21 together with the steam generated in boiler unit 31 into heat exchanger 7 where it is superheated and then passed through conduit 4 into the reactor.



By way of conduit 22 the mixture of the reaction products is conducted to a direct and/or indirect cooling system 23 in which it is cooled to normal temperature while dissipating its heat to a water circuit 24–25 whereby the cold water supplied through conduit 25 is heated to about 90–100° C. The heated water is transported by way of conduit 24 to parts 41 and 43 described below, where it serves as heating agent, and then reconducted as cold water through conduit 25 into the cooling system. By this last cooling the hydrocarbon vapors produced in quenching device 9 from the crude oil, which vapors represent the direct starting material for the cracking operation, and the portions which have not been reacted in the cracking process are separated in liquid form together with the condensing heat carrier steam. They travel via conduit 26 into a separator 27 where the lighter oil layer separates from the water layer. The water is discharged through conduit 28 while the oily hydrocarbons are conducted by way of conduit 29 into vaporizer 30 which is heated via conduit 21 by means of a partial steam current from boiler unit 31 and from which the vaporous hydrocarbons are passed through conduit 5 into the reactor 3.

In general, the current of reaction products leaving the indirect cooling system 23 contains larger or smaller amounts of hydrocarbon mists which may disturb the further processing of the reaction products. Therefore, the reaction mixture is conducted through conduit 32 to the mist dispersion installation 33. The mist is preferably removed by the process described in Belgian Patent 562,894 according to which the mist dispersion is combined with a compression of the reaction mixture at about 1 atmosphere gauge. The gas mixture which is now free from mist is conducted through conduit 34 to the gas purification zone 35 for the removal of $CO_2$ and $H_2S$. It is suitable to purify the gas by washing it with absorbing agents which readily absorb the aforesaid impurities and desorb them by regeneration, for example by a treatment with aqueous solutions of mono- and diethanol amine or salts of amino-acids or amino sulfo acids which are capable of absorbing small amounts, which may be present, of other sulfur compounds. The aforesaid impurities leave the unit by way of conduit 36. It is suitable to connect the washing unit 35 in series with an after wash, not shown, with alkali metal hydroxide solution for the removal of the last traces of $CO_2$. For the regeneration the washing liquid must be heated to about 100° C., the steam required being taken from conduit 21 via conduit 37. The washing liquor to be regenerated is heated in unit 35 by indirect heat exchange. The condensate obtained is passed through conduit 38 to the waste heat boilers 14 and 17, together with the condensate obtained in the hydrocarbon vaporizer 30 which travels through conduit 20, and is then conducted as heat carrier steam again to superheater 7 and reactor 3.

The cracked gas freed from $CO_2$ and sulfur compounds is introduced into the purification unit 39 where it is freed from acetylene hydrocarbons, preferably by selective catalytic hydrogenation (cf. German Patent 612,205 and U.S. Patent 1,836,926) and then compressed by compressor 40 at 10–50 atmospheres' gauge, preferably 20–30 atmospheres' gauge. In this compression the portions that are still present of higher boiling hydrocarbons containing at least 5 carbon atoms separate in liquid form. By suitably selecting the pressure and temperature conditions in the following cooling and separating devices 41 the separation can be realized in a manner such that, in addition to the high molecular hydrocarbons, also the hydrocarbons containing 3 and 4 carbon atoms are wholly or partially separated from the cracked gas. For adjusting the required temperatures said parts of the unit are connected with the hot or cold water circuit 24 and 25 already mentioned. The exact working conditions depend on the partial pressures in the cracked gas mixture and on the desired final products. When, for example, only

ethylene or ethylene+propylene or ethylene+part of the producible propylene shall be obtained as final products, the undesired olefins are separated in separator 41 together with the higher boiling hydrocarbons and conducted via conduit 42 to the hydrocarbon vaporizer 30 and from there through conduit 5, together with the other vaporized hydrocarbons, into reactor 3. The portions of the reaction mixture that are to be discharged and the portions that are to be reconducted can likewise be separated from one another by fractionation or by an oil wash. Alternatively, both working methods can be combined by first carrying out a rough fractionation and by removing the other component to be separated in a subsequent oil wash. A variant of said separating process is described, for example, in Belgian Patent 565,181. The still gaseous reaction products travel from separating unit 41 to a washing unit 43 where the olefins and the carbon monoxide are separated in known manner from the residual constituents of the gas by a treatment with cuprous salt solutions. Said washing process is suitably carried out under the pressure under which the gases to be treated are obtained in separator 41 or under a somewhat inferior pressure. The gases are desorbed from the cuprous salt solution in known manner by releasing the pressure of the charged copper solution and heating the solution by means of the heat of the hot water circuit 24 and 25 already mentioned. Since the cracked gas may contain considerable amounts of carbon monoxide, the cuprous salt solution is suitably treated according to the processes of Belgian Patents 564,888 and 569,799.

The residual gas which has been freed from the olefins mainly consists of hydrogen and methane and is conducted, as already mentioned, by way of conduit 45 into the burner of reactor 3. The portions of residual gas that cannot be used in the burner are passed through conduits 45 and 46 into the boiler unit 31 where they serve for the generation of steam.

The olefins which have been separated in washing unit 43 and which contain the carbon monoxide formed in the cracking reaction are conducted via conduit 44 to compressor 47 where they are again compressed at 20–30 atmospheres gauge and then passed to the low temperature distillation device 48 for being finally separated. In this device the olefins are decomposed into ethylene, propylene and butylene of high purity which leave the unit through conduits 50, 51 and 52. The residual gas essentially consisting of carbon monoxide is conducted via conduits 49 and 46 to boiler unit 31 where it is used as combustion gas for the generation of steam. Unless it shall serve as combustion gas the last residual gas essentially consisting of carbon monoxide may be discharged for being used in another process.

As final products the process only yields the desired olefins of high purity. Finally, varying amounts of steam having a pressure of 20–25 atmospheres gauge are obtained from boiler unit 31, which, as far as they are not needed, can be removed through conduit 54.

FIGURE 2 represents a flowing scheme for the processing of vaporizable hydrocarbons, such as light gasolines, natural gasolines, middle oils and the like, which can be directly vaporized without the formation of noteworthy amounts of residue. In this case the arrangement of apparatus must be modified.

On account of the different nature of the starting material it is not necessary to introduce the crude material via conduit 10 into the quenching device 9. The quenching device 13 is sufficient, from which, in this case, the residue is discharged through conduit 11 and conducted to boiler unit 31.

A further modification consists in that the indirect heat exchangers 7 and 117 installed between reactor 3 and quenching device 13 not only serve to superheat the heat carrier steam supplied but also to generate steam.

An advantage of the process of the invention resides in the fact that an arrangement as shown in FIGURE 1 can also be operated as illustrated in FIGURE 2 with vaporizable hydrocarbons.



The hydrocarbons to be treated are conducted via conduit 110 into vaporizer 30 where they are vaporized together with the return oils supplied through conduits 29 and 42, and the vapors are introduced into reactor 3 via conduit 5. The reactor 3 is heated and charged with heat carrier steam as shown in FIGURE 1. The mixture of hydrocarbon vapors and steam leaving the reactor travels through conduit 6 into heat exchanger 7 connected in series with steam generators 117 likewise designed as heat exchangers, which bring about an intensified cooling of the reaction mixture to about 400° C. Said heat exchangers 117 are fed with condensate by way of conduit 153 which is branched off from condensate inlet 53. Said condensate supply is admixed via conduit 38 with the condensate obtained in unit 35 (removal of $CO_2$ and sulfur compounds). The condensate supplied via conduit 153 leaves heat exchangers 117 as steam through conduit 154 and is combined on the way to heat exchanger 7 with the steam introduced into conduit 21 from boiler unit 31 and waste heat boiler 17.

The working method according to FIGURE 2 which corresponds to that illustrated in FIGURE 1, unless otherwise stated, permits an elastic temperature control and heat conduction which can be further improved by treating in one unit a partial current of the hydrocarbon mixture according to FIGURE 1 and another partial current according to FIGURE 2. In each of the partial units different starting materials can be processed while the reaction products are worked up and the gases are purified and separated in a common unit which is connected in the same manner with both reactor units and utilizes the waste heat thereof.

The described combination of many individual steps known as such represents a cracking process of an economy not yet reached.

We claim:

1. A process for the manufacture of olefins of high purity containing 2 to 4 carbon atoms by pyrolyzing hydrocarbons and subsequently decomposing the reaction mixture, which comprises superheating by means described below a carrier gas mixture consisting essentially of steam, admixing said carrier gas mixture in a cracking zone with the hydrocarbons to be cracked, cooling the reaction mixture leaving the cracking zone to a temperature in the range from 600 to 150° C. by heat exchange with said carrier gas, cooling the affluent from the cracking zone to separate therefrom the high boiling hydrocarbons that are not suitable for return to the cracking zone, separating the readily liquefiable hydrocarbons from the cracking affluent by a subsequent further cooling and returning them to the cracking zone, freeing the remaining cracked gases from carbon dioxide, sulfur compounds and acetylene hydrocarbons, separating the low boiling hydrocarbons that are liquid under normal conditions by compression at 20–30 atmospheres' gauge and reconducting them into the cracking zone, separating the olefins and carbon monoxide from hydrogen, methane and homologs of methane that may be present in the cracked gas thus treated by washing with a cuprous salt solution, and isolating the individual olefins from said concentrate by distillation, the amounts of heat required in the various operations being taken from the waste heat of the cracking reaction.

2. A process as claimed in claim 1, wherein the carrier steam is superheated by burning therein hydrogen with oxygen.

3. A process as claimed in claim 1 wherein the carrier steam is superheated by burning residual gas consisting essentially of hydrogen and methane which is obtained in the processing of the reaction mixture with oxygen.

4. A process as claimed in claim 1, wherein high boiling hydrocarbons that are not suitable in the cracking reaction are removed from the crude oil mixtures by contacting the latter in cocurrent manner in a quenching de-

vice desired as washer with the reaction mixture supplied from the cracking zone and the distillate obtained is reconducted into the cracking zone.

5. A process as claimed in claim 1, wherein the reaction mixture leaving the cracking zone is cooled to 600–300° C. in single or double cyclones while the outer jacket of the cyclones the heat carrier gas mixture is superheated.

6. A process as claimed in claim 1, wherein the temperature of the reaction mixture is reduced to less than 80° C. by further cooling operations and the heat thus obtained by heat exchange is used for heating the devices for the gas separation.

7. A process as claimed in claim 1, wherein the hydrocarbons contained in the reaction mixture which shall not be isolated are reconducted into the cracking zone.

8. A process as claimed in claim 7, wherein the hydrocarbons to be reconducted into the cracking zone are separated from the compressed cracked gas by cooling.

9. A process as claimed in claim 7, wherein the hydrocarbons to be reconducted into the cracking zone are separated from the compressed cracked gas by washing with oil.

10. A process as claimed in claim 1, wherein in separate cracking units different hydrocarbon mixtures are simultaneously cracked and the cracked products are further treated in a common processing unit.

11. The process of claim 1 wherein the olefins higher than ethylene in the homologous series are recycled to the cracking zone after they have been liquified by the compression step, thereby producing a high yield of ethylene.

12. A process for the manufacture of olefins of high purity containing 2–4 carbon atoms by cracking hydrocarbons and subsequently decomposing the reaction mixture which comprises the steps of generating the heat required for heating the hydrocarbon mixture to be cracked and the heat required for maintaining the cracking reaction by combusting hydrogen and oxygen in a super-heated steam atmosphere, adding the hydrocarbon feedstock to the cracking zone, the latter zone being heated in the manner described hereafter, cooling the reaction mixture leaving the cracking zone to a temperature of 150–600° C. by heat exchange with a carrier gas mixture consisting essentially of steam, passing the aforesaid carrier gas mixture to the cracking zone and there adding $H_2$ and $O_2$ to the carrier gas mixture for combustion therein, separating from the reaction mixture via a cooling step the high-boiling hydrocarbons which are unsuitable for recycle to the cracking zone, separating the readily liquifiable hydrocarbons by a subsequent further cooling and recycling them to the cracking zone, freeing the remaining cracked gases from $CO_2$, sulfur compounds, and acetylene hydrocarbons, separating the low-boiling normally liquid hydrocarbons by compression at 20–30 atmospheres' pressure and recycling them to the cracking zone, washing the cracked gas with a cuprous salt solution to separate the olefins and carbon monoxide from the hydrogen, methane, and homologs of methane that may be present in the cracked gas, and then distilling from the resulting concentrate the individual olefins present therein, the heat required in the various steps being supplied from the waste heat of the cracking reaction, so that the cracking process is adiabatic.

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