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PREPARING ACETYLENE AND ETHYLENE

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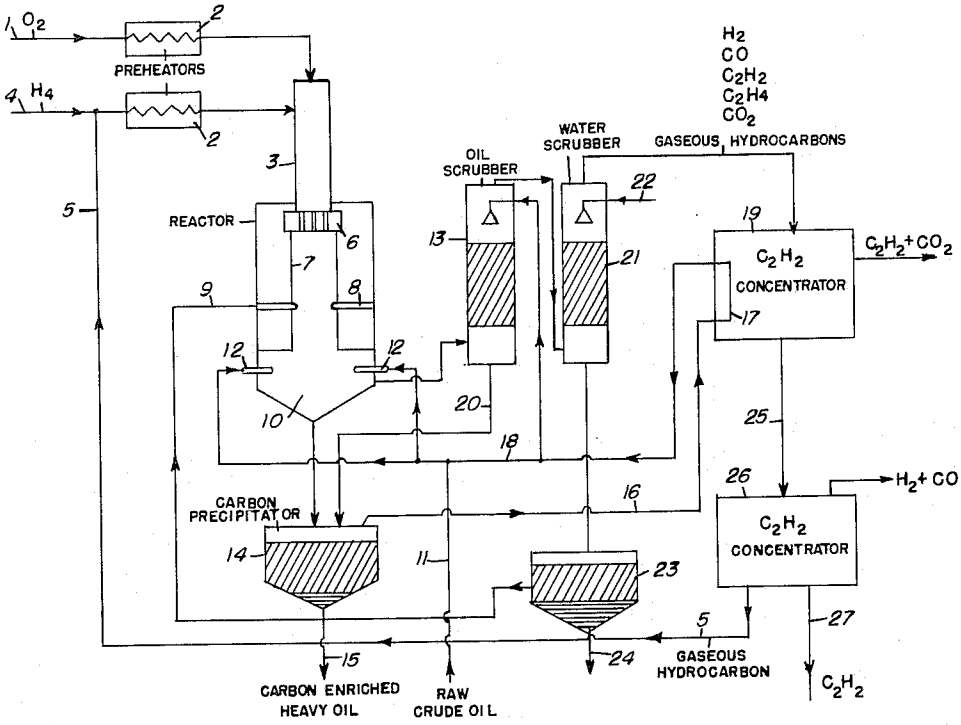


FIG. 1

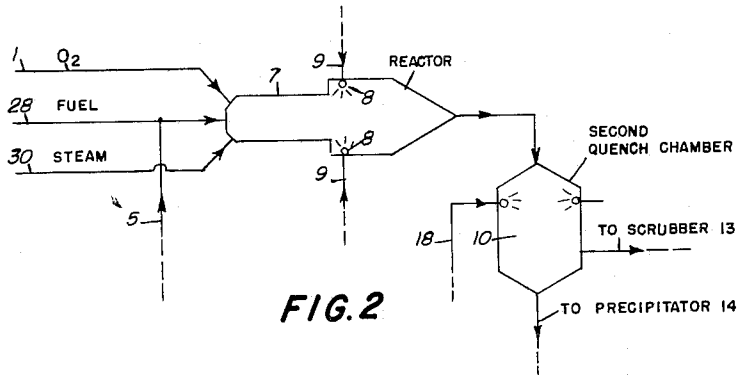


FIG. 2

INVENTORS

EIJI OTSUKA
HIROO WATANABE
MINORU TAKADA

BY Fisher, Christen and Goodson

ATTORNEYS

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PREPARING ACETYLENE AND ETHYLENE

Eiji Otsuka, Hiroo Watanabe, and Minoru Takada, Kanagawa Prefecture, Japan, assignors to Toyo Koatsu Industries, Inc., Tokyo, Japan, a corporation of Japan

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This invention relates to improvements in and relating to methods for preparing acetylene and ethylene by the partial oxidation and pyrolysis of hydrocarbons or by the pyrolysis of light distillate oil.

Under the prior art wherein acetylene is prepared by the partial oxidation of hydrocarbon (to be referred to as "partial oxidation method" hereinbelow) there is a disadvantage in respect of recovering and utilizing the heat formed by the reaction. Under the prior art a gaseous hydrocarbon and oxygen in an amount smaller than is necessary for the complete combustion of the hydrocarbon, after having been pre-heated separately to about 500° C., are mixed and the resulting gaseous mixture is conducted via distributors to the combustion zone of a reactor wherein it is incompletely burned. The temperature of the gaseous combustion product in the said zone reaches 1,500–1,600° C. Acetylene is favourably formed by the pyrolysis of the hydrocarbon at such high temperatures, but this atmosphere simultaneously tends to accelerate the decomposition of the acetylene thus formed. To solve this difficulty the gaseous combustion product is usually subjected to rapid quenching. As a means for the said quenching water injection is usually employed. By water injection the sensible and the latent heat of the gaseous combustion product and the water vapour formed in the reaction is transferred to cooling water, and the cooling water elevates in temperature. Inasmuch as the pyrolysis of the hydrocarbon is carried out at ordinary pressures, the temperature of the cooling water cannot rise above about 100° C. since the partial pressure of the water phase then reaches the operating pressure. Thus the temperature of the cooling water must be lower than 100° C., and preferably about 80° C. from an economic point of view. Part of the heat of the gaseous combustion product is utilized in the evaporation of the cooling water and the remaining part is lost with the elevation in temperature of the water up to a temperature not exceeding 100° C. The part of heat content that can be practically recovered for re-use is the latter part used for the elevation of the temperature of the cooling water. But the temperature of 80° C. water is too low to recover the heat content of the water economically.

As a means of solving this difficulty the Montecatini Società have recently proposed partial oxidation under pressure in Belgian Patent 585,928, "Perfectionnement à la Production d'Acètylene et d'Olèfines par Combustion Incomplete d'Hydrocarbures." When partial oxidation is carried out at 3–4 atm. absolute, the temperature of the cooling water may be elevated to 100–110° C. Such a method, however, possesses some drawbacks, for example, it may cause troubles in operation such as an occurrence of back-fire which should result in a lower yield of acetylene. Furthermore, the temperature of 100°–110° C. is still not enough for recovering the heat. Although carbon which is inevitably formed in course of the partial oxidation increases its hydrophile tendency with an increase in temperature of the cooling water, such carbon is not satisfactorily removed by water scrubbing. When an oil, especially a light distillate oil, is employed in the primary quenching of the gaseous combustion

product from 1,500° C. to 800° C., the distillate oil may cause decomposition forming ethylene and a little amount of acetylene. In this case the oil mist adheres to the carbon thereby imparting it with a more hydrophobic property. Accordingly, in carrying out secondary quenching by water injection, the carbon will be intermingled with the water. Furthermore, if such cooling water were to be employed in heat recovery, it would inevitably cause difficulties to heat exchange devices such as clogging of pipes even if the carbon content were very small.

Under the prevailing pyrolysis method, liquid or gaseous hydrocarbon or other gaseous fuel, oxygen and steam are charged into a combustion chamber and the resulting mixture is subjected to complete combustion whereby a high temperature atmosphere at about 2,000° C. is formed. In such atmosphere a light distillate oil is injected into the combustion gas to cause pyrolysis of the distillate oil thereby forming acetylene and ethylene. The temperature of the combustion gas is reduced to about 800° C. by the injection of the light distillate oil, and subsequently water injection is employed for the rapid quenching of the said product to prevent the decomposition of acetylene and ethylene formed, as in the partial oxidation method. Therefore, as far as water is employed as cooling medium, a similar difficulty occurs in the stage of heat recovery and carbon removal as experienced in the partial oxidation.

A principal object of the invention is to provide an improved method for preparing acetylene and ethylene, the method being either the partial oxidation or the pyrolysis method.

Another object is to provide the improved method of the above nature wherein rapid quenching of the high temperature combustion product is carried out in two successive stages; the first stage comprising injecting a light distillate oil into the said product and the second stage comprising injecting a raw crude oil and/or a heavy oil into the said product.

A further object is to provide the improved method of the above nature characterized by recovering the heat quantity which is released in the reaction and utilizing it effectively without substantially increasing the pressure of the reacting system.

Other objects and features of the invention will be understood as the description proceeds in conjunction with flow-diagrams wherein FIGURE 1 and FIGURE 2 are typical flow-diagrams applying the present invention to both partial oxidation and pyrolysis.

In applying the present invention to a partial oxidation method, main features are classified as follows: (a) a raw crude oil mixed with a heavy oil obtained in the process to be explained hereinbelow, are injected into the high temperature gaseous combustion product for secondary cooling whereby the heat quantity of the said product is employed for the fractional distillation of the raw crude oil and in elevating the temperature of the heavy oil content eventually formed by the said distillation; (b) the volatilized light distillate accompanying the gaseous combustion product is condensed while water scrubbing is applied and it is re-used as a material for the primary quenching of the gaseous combustion product and is subjected to the cracking of the distillate itself; (c) the aforementioned heavy oil content is conducted to any part of the process which requires an external supply of heat (e.g. the acetylene concentrating system to be explained further below); in consequence of the heat exchange the temperature of the heavy oil is lowered and it is re-circulated, together with a raw crude oil newly-fed in a re-circulation system, through step (a) in order to cool the gaseous combustion product; (d) the gaseous com-

bustion product conducted in the heavy oil scrubber exchanges its heat with the heavy oil irrigated for removal of the carbon in the said product; (e) the gaseous hydrocarbon free from acetylene and ethylene which are separated respectively at the acetylene and the ethylene concentrating systems is re-used as a raw material for causing partial combustion. Thus the heat quantity of the combustion product is completely recovered and utilized in several parts of the process.

Another essential feature of the invention is that since carbon which is formed in the combustion zone and which flies out with the combustion product is very oleophile, it is more completely removed from the gaseous combustion product employing heavy oil rather than water as evidenced in Table I.

Moreover the carbon contained in the heavy oil resulting from the fractional distillation of the raw crude oil is well dispersed in the oil, and accordingly no trouble occurs in operation when placed into heat exchange system.

TABLE 1

Comparison in results from removing carbon from the gaseous combustion product by means of heavy oil scrubbing (our invention) and water scrubbing (prior art)

	Scrubbing agent		
	Employing heavy oil maintained at 50° C.	Employing water at—	
		60° C.	80° C.
Carbon concentration in the gaseous combustion product which passes the scrubbing tower:			
At the inlet to the tower (gr./m.^{3})	3.7	4.8	4.1
At the outlet of the tower (gr./m.^{3})	0.02	2.5	2.3
Rate of carbon removal (percent)	99.9	65.8	64.0
Distribution ratio of carbon collected with scrubbing agent:			
Carbon which floats on the agent (percent)	0.00	98.7	96.0
Carbon which suspends in the agent (percent)	100.00	1.3	4.0

NOTE.—Employing heavy oil as a scrubbing agent, the carbon which has been collected suspends substantially completely in the agent.

In applying the present invention to a pyrolysis method, similar features prevail as in the partial oxidation method as are hereinabove explained except that in this case the light distillate oil as primary quenching agent acts as the sole raw material for producing acetylene and ethylene.

In a preferred embodiment of the present invention as applied to the partial oxidation method, firstly a gaseous hydrocarbon is caused to react in a mixture with an amount of oxygen insufficient for the complete combustion of the hydrocarbon. It is known that not only methane but also some higher hydrocarbons having a carbon atom number of 2–5 may be employed. The starting materials, after having been pre-heated to 450–500° C. separately, are completely mixed in the mixing device of a reactor in about 0.1 second. The resulting gaseous mixture is injected at the nozzles of a distributor into the combustion zone of the reactor thereby being ignited to about 1300–1700° C., preferably 1400–1500° C. for 0.01–0.05 sec., preferably 0.02–0.03 sec. in the acetylene forming zone. Acetylene of a concentration of 8–9% by volume is formed in the gaseous mixture in the said zone. The gaseous combustion product is then conducted into a primary quenching zone wherein the light distillate oil recovered in a subsequent scrubber is injected at the oil injection nozzles of the reactor. The light distillate oil may have a 4–10 carbon atom number and a boiling point range of 50–200° C. Thereby the gaseous combustion product is reduced in temperature to 500–1100° C., preferably 750–900° C. and the injected light distillate oil is pyrolysed into a substantial portion of ethylene and a minor portion of acetylene in 0.02–0.1 sec., preferably 0.03–0.05 sec. in the ethylene forming zone. The gaseous combustion product comprises 8–9% of acetylene and 3–4% of ethylene. The gaseous combustion product is then conducted into a secondary quenching zone. A raw crude oil which has been newly fed in the recirculating system and the heavy oil, the heat quantity of which has been recovered in an acetylene concentrator after the heavy oil was recovered in a carbon precipitator, are mixed and the mixture is injected into the second quenching zone. Thereby the temperature of the gaseous combustion product is reduced from 800–900° C. to 150–200° C. in at least 0.001 sec., preferably 0.001–0.003 sec. We have found also that the above secondary quenching increases the yield of ethylene by 1 to 1.5% in volume in the gaseous product.

The behaviour of the last-mentioned secondary quenching stage is essential in this invention. A more detailed explanation will follow. The raw crude oil and the heavy oil injected into said quenching zone causes evaporation of the lighter distillate content in the said oil. The boiling point range as well as the amount of light distillate oil to be evaporated depends upon the composition of the cooling oils injected, in more detail, upon the partial pressure of each oil fraction at its subjecting temperature which is determined by the heat quantity to be transferred from the gaseous combustion product, and furthermore upon a running equilibrium based on the contact efficiency of the said oils with the combustion product in the said zone. Subsequent to the evaporation of the light distillate, the heavy oil of 100–150° C., remains at the bottom of the reactor. The said heavy oil is accompanied by a major part of the carbon formed in the reactor as reaction by-product and the gaseous combustion product is accompanied by a small part thereof. The combustion product which goes out from the reactor comprises not only acetylene and ethylene but also the afore-mentioned evaporated low distillate and a small portion of the carbon formed in the reactor.

The gaseous combustion product is then conducted to a heavy oil scrubber and a water scrubber successively. In the former scrubber the gaseous combustion product at 150–200° C. is placed under heat exchange relationship in countercurrent with the irrigating heavy oil (scrubbing agent) whereby the accompanying carbon is completely removed without the light distillate being condensed. In the latter scrubber the light distillate of the gaseous combustion product is condensed and after having been separated from the water in a water separator, it is recirculated through the afore-mentioned primary quenching zone of the reactor. In the meanwhile, the carbon-containing heavy oil present in the secondary zone of the reactor is withdrawn from the bottom of the reactor and it is conducted to a carbon precipitator. Thereby a carbon-enriched heavy oil layer is formed on the bottom of the precipitator and a carbon-impoverished heavy oil layer is superposed thereon. The carbon-enriched heavy oil deposited on the bottom is withdrawn and is used as a fuel in the process. The amount of heavy oil to be withdrawn is adjusted in order to be balanced with the amount of heavy oil in the raw crude oil fed to the system.

On the other hand, the carbon-impoverished heavy oil layer superposed on the carbon-enriched layer is conducted to a suitable device for releasing its heat quantity, e.g. the heating source of an acetylene concentrator and thence a major portion of the rather cooled heavy oil is re-circulated and injected into the secondary quenching zone of the reactor in mixture with the newly-fed raw crude oil; a minor portion thereof is employed as a scrubbing agent in the heavy oil scrubber as hereinabove referred to.

The acetylene-free gaseous mixture taken out of the acetylene concentrator wherein acetylene has been separated comprises hydrogen, carbon monoxide, ethylene, a

small quantity of gaseous matters deriving from the injected raw crude oil such as methane, ethane, propane and butane. In the case where said acetylene-free gas is not conducted to an ethylene concentrator, it may be used as a rich fuel. In the case where is it conducted to the concentrator, wherein ethylene is recovered, a separated gas consisting of low hydrocarbons is obtained and can be employed as a raw material in mixture with other hydrocarbons or without being mixed therewith. The remaining residual gas which has been withdrawn from the concentrator consisting mainly of H_2 and CO is employed as a synthetic gas for the preparation of ammonia or methanol.

In the following will be described some industrial advantages of the present invention. Firstly, cheap raw crude oil can be used as origin of light distillate oil instead of utilizing rather costly naptha. Secondly, such raw crude oil is subjected to spontaneous fractional distillation in the reaction system employing the heat quantity of the combustion product. Thirdly, each fraction of the raw crude oil can be fully used in several suitable parts of the process. The gaseous hydrocarbon as a starting material, the light oil for quenching the combustion product and the heavy oil for removing the accompanying carbon in the gaseous combustion product do not require precise fractional distillation such as is carried out in oil refinery. The simplicity of the fractional distillation makes the present invention more advantageous.

Fourthly, the fact that the heat quantity of the heavy oil content resulting from the evaporation of the light distillate content of the raw crude oil can be used as a source of heat supply in the process is highly valuable. Although such heavy oil, upon contact with high temperature gases subjected to 800–900° C. may partially be decomposed, it is revealed that the decomposition is very small, if at all present, when the amount of recirculating heavy oil is controlled such that the temperature of the heavy oil, immediately after it has been injected into the secondary quenching zone, reaches about 150° C. Moreover, the degradation of the heavy oil is inhibited in the present process since the carbon-enriched oil is continuously withdrawn and a new crude oil is continuously supplied.

In another embodiment of the invention the heat quantity of the heavy oil transferred from the gaseous combustion product in the reactor is effectively utilized in an acetylene concentrating system as explained hereinbelow.

The gaseous combustion product containing acetylene, higher acetylenes, ethylene, carbon dioxide and other gaseous substances is initially conducted into a higher acetylenes removal tower wherein it is scrubbed with a solvent of selective absorption power which absorbs higher acetylenes and water vapour, whereby higher acetylenes, water vapour and a small amount of acetylene are removed from said product. As an example of the solvent methanol may be used economically.

The combustion product free of higher acetylenes is then conducted into an acetylene removal tower wherein a major portion of the acetylene and CO_2 are absorbed in the same solvent as hereinabove described. The solvent which has absorbed the acetylene and CO_2 is then subjected to desorption by means of reducing the pressure on the solvent and with heating. Thereby, a mixture of acetylene and carbon dioxide is discharged. The acetylene and CO_2 mixture which has been discharged is scrubbed with a basic aqueous solution such as an aqueous monoethanolamine solution to remove the CO_2 whereby pure acetylene is obtained.

In the above system the heat quantity of the heavy oil is utilized for recovering the solvents which have absorbed higher acetylenes, water vapour, acetylene, and CO_2 in the three steps. The three steps are the step for recovering the solvent which has absorbed higher acetylenes and water vapour, the step for desorption of the solvent which has absorbed acetylene and CO_2 and the step for recovering the solvent which has absorbed CO_2. According to practical tests there was almost no need for an external supply of steam.

In a further embodiment, the present invention can be applied to a pyrolysis method, too. Under this method liquid or gaseous hydrocarbon or other gaseous fuel such as coke-oven gas etc., oxygen and steam are reacted at about 1700–2300° C. thereby forming a complete combustion product; a light distillate oil is subsequently injected into the said product and it is pyrolysed into acetylene and ethylene. Since the gaseous combustion product containing C_2H_2 and C_2H_4 is at about 800° C., a raw crude oil and the re-circulating heavy oil are employed to quench the combustion product instead of water as in the prior art. The subsequent treatment and behaviour of the reaction mixture is quite similar to that in the partial oxidation method.

In the accompanying flow diagrams there are described typical embodiments of the present invention as applied to a partial oxidation method and a pyrolysis method. FIGURE 1 refers to a partial oxidation method. As a raw material methane **4**, being mixed with gaseous hydrocarbons **5** recovered in an ethylene separator **26**, is conducted into the reactor **3** via pre-heater **2**. Oxygen **1** in an amount insufficient for the complete combustion of the methane is conducted into reactor **3** via pre-heater **2'** and is mixed with the said gaseous hydrocarbons mixture in the mixing chamber at the upper part of the reactor **3**. Passing through a distributor **6** the gaseous mixture is introduced into a combustion chamber **7** wherein it is reacted to form a gaseous partial combustion product subjected to as high a temperature as about 1,500 C. and wherein acetylene is produced by thermal reaction. A light distillate oil **9** which has been separated from the gaseous combustion product in a water scrubber **21** and from which the water content has been removed in a water separator **23** is injected into the primary cooling zone of the said combustion chamber through oil injection nozzles **8** and cools rapidly the gaseous combustion product from about 1500° C. to 800–900° C. while it is decomposed into a mixture of ethylene, acetylene and other decomposition products. The gaseous combustion product is further rapidly quenched with an injection of a mixture of replenished raw crude oil **11** and recovered heavy oil **18** through injection nozzles **12** from 800–900° C. to 150–200° C. in the secondary cooling zone **10**. The injecting axis of the nozzle is horizontally directed towards the longitudinal axis of the reactor. In order to carry out the most efficient quenching, however, the mixture of raw crude oil and heavy oil is injected conically, at an apex angle of 90° at the exit of each nozzle with a pressure enough to reach the opposite inside wall of the secondary quenching zone **10**. In this manner, the oil mixture is uniformly dispersed in very fine particles over the entire space of the zone and very little, if any, dead space is formed between the adjacent nozzles. For example, in a reactor having a production capacity of 1.0 ton/day acetylene the oil mixture is injected from six nozzles with an inner diameter of 3 m./m. and with a linear velocity of 14–15 m./sec. and an oil pressure of 4 kg./cm.^{2} at the exit of nozzles to obtain the desired effect. The gaseous hydrocarbon and light distillate contents of the injected crude oil are subjected to "topping" and then they are conducted into a heavy oil scrubber **13** together with the gaseous combustion product. The heavy oil content which has absorbed a major portion of the carbon formed is withdrawn from the bottom of the reactor **3** and it is conducted into a carbon precipitator **14** wherein a carbon-enriched heavy oil layer is formed on the bottom thereof. This oil is withdrawn (**15**) and is utilized as a fuel in the pre-heater **2** and **2'** and other devices. The upper layer of carbon impoverished heavy oil, is circulated through heat exchange zone **17** of an acetylene

concentrator **19** via duct **16** and thence via duct **18** to the said secondary cooling zone **10** of the reactor together with the fresh crude oil **11**. Reference numeral **17** indicates the heat supply zone of the concentrator **19** in which takes place heat exchange of the heavy oil which is fed via **16** and thereby the heavy oil is cooled from about 150° C. to about 50° C. Part of the thus cooled heavy oil is diverged from duct **18** and is irrigated into the top of the heavy oil scrubber **13** in countercurrent with the ascending gaseous combustion product from the reactor **3** thereby substantially recovering the heat quantity and further removing the carbon content of said combustion product. The descendent heavy oil elevated to 150° C. is conducted to the carbon precipitator **14** via duct **20**. The combustion product leaving the heavy oil scrubber is conducted into the bottom of water scrubber **21** and it goes up in countercurrent with descending scrubbing water fed via **22**, thereby the light distillate vapour carried with the gaseous combustion product is condensed by the scrubbing water and it is conducted from the bottom of the scrubber into water separator **23**. In the separator, there are formed an upper layer of light distillate oil and a lower layer of water. The water is drained off from the bottom of the separator while the light distillate is conducted via duct **9** into the combustion chamber **7** of the reactor **3** via oil injecting nozzles **8**.

The gaseous combustion product leaving from the top of the water scrubber **21** comprises H_2, CO, C_2H_2, C_2H_4, other gaseous hydrocarbons and CO_2, and it is conducted into an acetylene concentrator **19** for recovery of acetylene. The heat necessary for the recovery is supplied in the heat supply zone **17** by the heavy oil coming from the carbon precipitator **14**. The C_2H_2-free combustion product **25** may be employed as a gaseous fuel in the manufacturing system or it may be conducted into an ethylene concentrator **26**. The ethylene concentrator **26** is operated at −170° C. in the coldest parts thereof whereby the gaseous C_3 and C_4 hydrocarbons are condensed in a heat exchanger therein and they are mixed via duct **5** with methane **4** prior to being fed into the reactor or when their volume is sufficient they are fed directly into the reactor **3** via pre-heater **2** without additional methane. The residual gas from the ethylene concentrator **26** comprises mainly hydrogen and CO, and it may be employed as a raw material in separate ammonia or methanol syntheses.

FIGURE 2 relates to a pyrolysis method. A gaseous or vapourous fuel **28** and oxygen **1** are introduced into reactor **3** to produce a complete combustion gas in the combustion chamber **7**, thereof. When liquid hydrocarbon is used as fuel, it is vaporized through a vaporizer (not shown) prior to injection into the reactor. Together with this gaseous mixture, superheated steam **30** is also introduced therein to control the temperature of the complete combustion gas so as to protect the wall of the combustion chamber from the effects of heat and to prevent the formation of carbon.

Downstream of the reactor **3**, a hydrocarbon, i.e., a light distillate oil which has been separated from the gaseous combustion product as before-mentioned in the partial oxidation method, is injected through oil injection nozzles **8** into the complete combustion gas after having been preheated to about 300° C.–450° C. When the light distillate oil obtained from the system is not enough to be injected as raw material, some amount of hydrocarbon can be supplied externally.

The effluent gas from the reactor is introduced into the secondary quenching chamber **10** wherein a mixture of recovered heavy oil **18** and oil **11** is injected through nozzles **12** into the gaseous combustion product to reduce the temperature to about 150° C. The subsequent treatments and the flow diagram are quite similar as in the previous partial oxidation method.

This invention is illustrated by the following examples.

Example I

Referring to FIGURE 1, 24.6 m.³/hr. of methane and 15.2 m.³/hr. of oxygen, preheated in the preheaters **2**, **2'** to 560° C. and 480° C. respectively at ordinary pressure were conducted to a reactor having a production capacity of 4.18 kg./hr. acetylene. The methane and oxygen were subjected to 1,470° C. for 0.02 sec. in the combustion zone **7** of the reactor. The light distillate oil **9** subsequently recovered in the water scrubber **21** was preheated in a preheater (not shown) to 100° C. and it was injected through nozzles **8** into the primary quenching zone of the reactor at a rate of 5.4 litres/hr. The specification of the said light distillate is shown under (A) in Table II below. The re-circulating heavy oil **18** was injected to the secondary quenching zone **10** of the reactor together with a replenishment of Iranian raw crude oil **11** at a rate of 14.8 litres/hour in the re-circulating system. The total amount of re-circulating oil was 240 litres/hour, and the ratio by volume between the heavy oil and the raw crude oil was about 16:1. The specification of the Iranian raw crude oil employed is shown under (B) in Table II. The reaction mixture after the primary and secondary quenchings was at 830–880° C. and 180–195° C. respectively and the respective contact times for primary and secondary quenchings are each 0.03 sec. and 0.001 sec., while the temperature of the oil mixture **18** upon injection into and upon withdrawal from the reactor was 43° C. and 142° C. respectively. A slight amount of gaseous combustion product stream emerging from the reactor was taken out for sampling purpose, and the light distillate content thereof was condensed by water cooling to room temperature, of which results of analysis are shown under (C) in Table II. The cooled gaseous combustion product was conducted from the reactor **3** to the lower section of a heavy oil scrubber **13** wherein it ascended and was brought into countercurrent contact with the descending heavy oil at 48° C. fed to the top of the said scrubber at a rate of 80 litres/hour, whereby the accompanying carbon of said product was substantially removed, that is, the carbon content decreased from 3.7 gr./m.³ at the entrance to the said scrubber to 0.02 gr./m.³ at the exit thereof. The temperature of heavy oil on the bottom of the said scrubber was 118–122° C. Analysis of the light distillate content of the combustion product at the entrance and exit of the said scrubber was; at the entrance an initial boiling point of 56° C. and a dry point of 253° C., at the exit 52° C. and 208° C. respectively. This is proof that rectification was carried out in a high degree in the heavy oil scrubber **13**.

The gaseous combustion product emerging from the scrubber **13** was at 90–100° C., and it was then conducted to a water scrubber **21**. In the water scrubber **21** the irrigating water was fed to the top at a rate of 500 litres/hour, and the combustion product after having been scrubbed with water has a temperature of 35° C. The temperatures of the irrigating water at the inlet and exit of the scrubber were 24° C. and 28° C. respectively. By the water scrubbing the light distillate content of the combustion product was condensed and removed with the water to a water separator **23**.

The condensate, after having been separated as upper layer accompanying water in the water separator **23**, was recovered at a rate of 5.4 litres/hour. Its specification is shown under (A) in Table II. It had a trace of carbon flotation and has a light brownish colour. It was re-used for quenching and cracking the reaction product in the reactor. The specification of the combustion product which emerged from the water scrubber is shown under (D) in Table II.

In this example the heavy oil which emerged from the bottom of the oil scrubber **13** and from the bottom of the reactor **3** was collected in a carbon precipitator **14**. The carbon-enriched heavy oil withdrawn from the bottom of the precipitator had a carbon content of 18.9

gr./litre which corresponds to 168 grammes/hours. It was employed as a fuel in the methane and oxygen pre-heaters. The carbon impoverished heavy oil was cooled to 48° C. with water and it was recirculated through the manufacturing system via lines **16**, **17**, and **18**.

170 litres/hour. The gaseous reaction product upon injection of the light distillate oil contained carbon by 19.1 gr./metre^3. However, the re-circulating heavy oil contained only about 1% by weight of carbon and no trouble occurred in the re-circulation.

TABLE II

	Light distillate (A)	Raw crude oil (B)	Light distillate (C)	Composition of combustion product (D)
Specific gravity (at 60° F.)	0.724	0.854	0.726	C_2H_2, 8.3.
Initial boiling point	57° C.	44° C.	53° C.	C_2H_4, 3.6; CO, 24.2.
50% distillation point	96° C.	313° C.	102° C.	H_2, 53.6; CO_2, 3.7; C_nH_m,[1] 1.8.
Dry point	212° C.		255° C.	H.A.,[2] 0.2; CH_4, 3.1.
Colour	Light brownish.	Black.	Brownish black.	N_2, 1.4; O_2, 0.1
Remarks	Flotation of a trace of carbon.		Contains some carbon.	
Pour point		−20° C.		

[1] Indicates gaseous hydrocarbons exclusive of acetylene, methane and ethylene.
[2] Indicates higher acetylenes.

Example II

This example is illustrative of applying the invention to a pyrolysis method, referring to FIGURE 2.

39 m.^{3}/hour of a residual gas resulting from recovering acetylene (ethylene not recovered) from the combustion product, 36 m.^{3}/hour of oxygen and 35 kg./hour of steam were conducted into the combustion chamber of the reactor **3** wherein complete combustion was caused. The reactor was jacketed with zirconium refractory brick and the combustion zone reached 1,850° C. The combustion product was then quenched to 750° C.–800° C. by means of an injection at a rate of 60 litres/hour of a low distillate oil preheated in a preheater (not shown) to 450° C. through nozzles **8** around which a cooling water jacket is provided and the pyrolysis reaction time was about 0.05 sec. Then a mixture of a raw crude oil replenished in the re-circulation system and the re-circulating heavy oil **18** was injected through nozzles **12** into the second quench chamber **10** as in the preceding example at a contact time of 0.003 sec., whereby the temperature of the reaction mixture was reduced to 200° C. From the bottom of the chamber **10** heavy oil content at 150° C. was withdrawn and it was conducted to the carbon precipitator **14**. The carbon-enriched heavy oil was withdrawn from the bottom of the precipitator at a rate of 140 litres/hour and it was employed as fuel in pre-heating the aforementioned light distillate oil, etc. The carbon-impoverished oil withdrawn from the upper layer of the precipitator **14** was cooled to 50° C. in the acetylene concentrator and it was re-circulated to the reactor via lines **16**, **17**, and **18**. The gaseous combustion product, after having been successively passed through the heavy oil scrubber **13** and the water scrubber **21**, was compressed to 13 atm. absolute and it was conducted to the acetylene concentrator **19** for recovering the acetylene content. Part of the residual gas from said concentrator was employed as a starting material. The composition of the residual gas employed as fuel, resulting from removal of aectylene from the gaseous reaction product and the gaseous reaction product collected upon passage through the water scrubber **21** are shown under (A) and (B) in Table III respectively. As a feed material similar Iranian raw crude oil was replenished in the re-circulating system at a rate of

TABLE III

Composition of gases sampled (percent by volume)

Component	Gas-(A) [1]	Gas-(B) [2]
C_2H_2	0.4	8.3
C_2H_4	9.1	7.9
CO	27.0	23.5
H_2	45.9	39.9
CO_2	0.0	4.9
C_nH_m	2.1	2.0
H.A.	0.8	0.8
CH_4	10.5	9.1
N_2	3.9	3.4
O_2	0.3	0.2

[1] Gas-(A) indicates the residual gas from C_2H_2 concentrator 19 employed as fuel, which results after removing acetylene from the gaseous reaction product from the water scrubber 21.
[2] Gas-(B) indicates the gaseous reaction product collected upon passage through the water scrubber 21.

As seen from the foregoing two examples, the dry point of the light distillate oil in the reactor **3** is much higher than the temperature of the heavy oil withdrawn at the bottom of the reactor **3** or chamber **10**. This is explained by the presence of neutral gases such as H_2 and CO in the gaseous combustion product causing a lowering of the partial pressure of said distillate oil and accordingly bringing about a similar effect as vacuum distillation in the fractional distillation that takes place in the reactor.

What is claimed is:

1. In a method for producing acetylene and ethylene wherein a hydrocarbon having from one to five carbon atoms is partially oxidized at a temperature above about 1300° C. to provide a gaseous product, the improvement which comprises subjecting said gaseous product to a primary quenching step utilizing a light distillate oil wherein the temperature of said gaseous product is reduced to between about 500° and 1100° C. and said light oil is pyrolyzed, subjecting said gaseous product to a secondary quenching step utilizing a raw crude oil wherein the temperature of said gaseous product is further reduced to between about 150° and 200° C. and said crude oil is fractionated to provide a gaseous light distillate oil and a heavy oil residue, condensing said gaseous light distillate oil by scrubbing with water and recycling the condensate for use in the primary quenching step.

2. The method of claim 1 wherein said heavy oil residue is separated from said gaseous combustion product and any entrained carbon particles are removed therefrom to provide a carbon enriched heavy oil and a carbon impoverished heavy oil and wherein said carbon impoverished heavy oil is recycled and mixed with the raw crude oil used in said secondary quenching step.

3. The method of claim 2 wherein the gaseous product from the secondary quenching step is scrubbed with the carbon impoverished heavy oil to remove additional entrained carbon.

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ALPHONSO D. SULLIVAN, *Primary Examiner.*