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HYDROCARBON CONVERSION METHOD

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FIG. 1

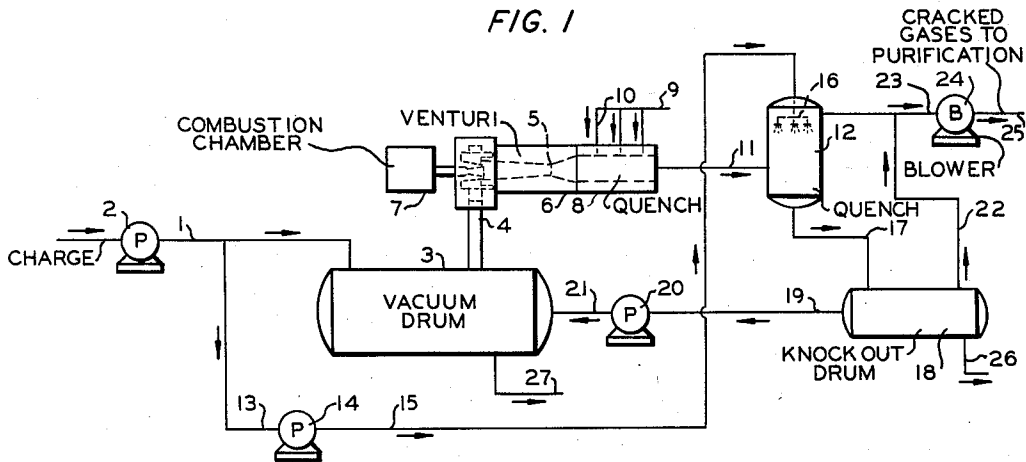
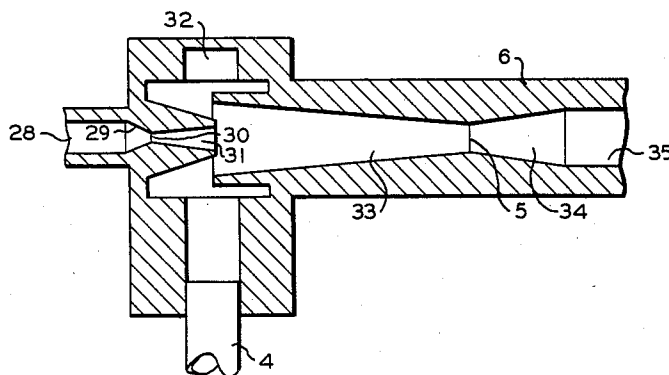


FIG. 2



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HYDROCARBON CONVERSION METHOD

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1 Claim. (Cl. 260—679)

This invention relates to the conversion of hydrocarbons. It also relates to a combination apparatus for effecting conversion of hydrocarbons. In one of its aspects, the invention relates to a method in which hot gases or products of combustion are forced into a venturi in which the gases are admixed with distillate aspirated by said venturi from a distillation zone. In another aspect the invention relates to a combination of a combustion zone, a venturi and a distillation zone so arranged and adapted that combustion gases produced in said combustion zone can be fed to the venturi rendering the same operative to aspirate distillate from the distillation zone into the said venturi for a controlled reaction time at a controlled temperature following which there can be effected a controlled quench. In another of its aspects, the invention relates to apparatus adapted to carry out the various modus operandi set forth and described herein, the said apparatus being so combined and proportioned as to permit flexible, yet simultaneous, conversion of, say, a hydrocarbon gas and a hydrocarbon oil to useful products, the said apparatus in one embodiment consisting essentially of a pressure combustion chamber communicating with a venturi, a vacuum drum communicating with the throat of the venturi and a quench vessel communicating with the discharge of the said venturi.

In the refining of petroleum, a reduced crude or heavy residual oil, that is, a crude oil from which propane, butane, gasoline, kerosene, and light and heavy gas oils have been removed, is vacuum flashed to remove vacuum distillate. This fraction makes a suitable stock for cracking, and if subjected to high temperatures, can be used as a feed for ethylene and acetylene manufacture. In high temperature thermal cracking to form ethylene and, more particularly acetylene, the temperature-reaction time relationship is critical to the attaining of optimum results. To obtain appreciable yields of acetylene temperatures of 2500° F. to 3000° F. are required. However, at these temperatures, a short controlled reaction time is essential, or decomposition of the product will be severe with concomitantly reduced yield.

It is an object of this invention to convert a hydrocarbon oil to useful products including at least one of acetylene and ethylene. It is another object of this invention to employ hot combustion gases for the controlled time-temperature reaction of a hydrocarbon distillate oil to produce useful products including at least one of acetylene and ethylene.

A further object of this invention is the provision of apparatus so constructed and arranged as to provide for the production of hot gases, preferably under elevated pressure, which can be employed to cause the conversion of a hydrocarbon oil distillate produced with the assistance of the said hot combustion gases.

Other aspects, objects, as well as advantages of the invention are apparent from a study of this disclosure, the drawing, and the appended claim.

The invention is particularly applicable to the cracking of hydrocarbon oil vapors obtained from a distillation

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zone, preferably operated at a reduced pressure, the vapors being cracked by a controlled time-temperature reaction brought about by use of hot combustion gases obtained from a combustion zone, akin to a rocket or jet engine, operated under pressure, by feeding said gases into and through a venturi to which are aspirated by its action the said vapors from the said distillation zone.

Thus, according to the present invention, there is provided a modus operandi for the conversion of a hydrocarbon vapor, produced by distillation of a hydrocarbon oil, preferably under a reduced pressure, which comprises feeding hot gases at a temperature and in quantity sufficient to crack a hydrocarbon oil vapor into a venturi, feeding a hydrocarbon vapor also into said venturi for admixture therein with said hot combustion gases, and in said venturi transferring heat from said hot gases to said hydrocarbon vapor to convert the same to an extent desired by a controlled time-temperature reaction. In the now preferred form of the invention, the reacted gas mixture is immediately quenched to a temperature at which no substantial undesirable degradation or other reaction can occur. Still, in the now preferred form of the invention, the discharge tube of the venturi is so selected or designed that the reaction time, taking into account the nature and quantity of the gases and vapors present therein, is accurately controlled within very close limits.

Also according to the invention, apparatus is provided which in one form comprises a high pressure combustion chamber such as a rocket or jet engine firing into the throat of the venturi, the discharge tube of which is equipped with a quench and the throat of which is connected to a vacuum drum, substantially as set forth and described in connection with the drawing. Figure 1 shows diagrammatically an embodiment of the invention as it is applied to the cracking of a heavy residual oil vacuum distillate employing hot combustion gases. Figure 2 shows details of the venturi apparatus shown in Figure 1.

Referring now to Figure 1, a charge oil is fed by way of conduit 1, by means of pump 2, into vacuum drum 3. Vapors generated in the vacuum drum are aspirated by way of conduit 4 into throat 5 of venturi 6 which is actuated by hot combustion gases discharged into the throat of the venturi from combustion chamber 7. The mixture of reacted hydrocarbon vapors and hot combustion gases is quenched in quench vessel 8 by means of water introduced through manifold 9 and spray heads 10. In quench vessel 8, the temperature is lowered rapidly, almost immediately, to a level at which no undesirable reaction can take place. The quenched products are then passed by way of conduit 11 into a second quench vessel 12 to which is pumped a portion of the charge from conduit 1 by way of conduit 13, pump 14, conduit 15, and spray heads 16. In quench vessel 12, liquid products which are obtained by condensation, admixed with the quench medium, are passed by way of conduit 17 into knockout drum 18 in which a phase separation takes place. The upper hydrocarbon phase is passed by way of conduit 19, pump 20, and conduit 21 into the vacuum drum 3. Vaporized material which is disengaged from the liquid collecting in knockout drum 18 is passed by way of pipe 22 into conduit 23 in which said vaporized material is admixed with the main stream of vapors coming from quench zone 16. The combined vaporized materials are pumped by pump or blower 24 into discharge conduit 25 and from there to gas purification means, not shown. The aqueous phase collected in knockout drum 18 is discarded through conduit 26. The portion of charge 1 unvaporized in vacuum drum 3 is discarded through conduit 27.

Figure 2 is a diagrammatic cross-sectional view showing details of a suitable venturi apparatus 6 for carrying out this invention. Combustion gases from combustion zone

7 pass through conduit 28 to a nozzle, comprising converging section 29, throat 30 and diverging section 31, which communicates with chamber 32 in which vapors from conduit 4 are mixed and entrained with the combustion gases. Downstream of chamber 32 is a diffuser, comprising converging section 33, throat 5 and diverging section 34. The gases pass through conduit 35 to quench zone 8.

Depending upon the hot gases supplied to venturi throat 5 and the character of the oil and the distillation of it which is carried out in vacuum drum 3 as well as upon the conditions which are maintained in discharge 6 of the venturi and in quench zone 8, the products which result and which are discharged by way of conduit 25 will be of varying character as will be understood by one skilled in the art having studied this disclosure. Thus, any fuel can be used to supply the hot combustion gases in engine 7. For example, there can be employed gases resulting from fuels such as hydrogen, natural gas, other hydrocarbons such as butane or even liquid hydrocarbons such as kerosenes; etc. Also, oxidizing agents such as air, enriched air, or even oxygen can be used. Further, liquid oxidizing agents as nitric acid or hydrogen peroxide can also be used in the combustion zone or chamber.

Also, as a specific variation within the scope of the claims to this invention, the high pressure combustion zone can be one in which a desirable oil fraction such as an aromatic oil is burned under carbon black producing conditions to produce carbon black contained in combustion gases under pressure sufficient to operate the venturi.

Thus, the invention is applicable to any combination operation wherein a high temperature, high velocity combustion gas stream is used as a source of heat for a thermal operation such as cracking, the said stream, according to the invention, being also a means for creating a vacuum whereby the stock for conversion or cracking is introduced into the hot gases.

The high pressure combustion zone can be operated at any pressure which is sufficient to provide for aspiration into the venturi throat of the vapors from the distillation zone. Preferably, the pressure in the combustion zone will be above atmospheric. The greater the ratio of the pressure in the chamber to that prevailing in the vacuum drum, the greater will be the cooling in the expansion in the venturi discharge. Further, the greater the pressure ratio, the smaller will be the amount of gas which must be expanded to compress the vapors coming from the vacuum drum to a pressure sufficient to discharge the same through the venturi. It will be understood by one skilled in the art in possession of this disclosure that the high temperature combustion gases are expanded through a converging-diverging nozzle to supersonic speeds. These gases entrain the vapors from the vacuum drum and compress them from drum pressure to discharge pressure in a second, and larger, converging-diverging nozzle.

In one embodiment of the invention, the combustion chamber is a reaction zone in which a high temperature cracking can be effected. For example, methane is partially oxidized with oxygen to acetylene at a high temperature, say, in the range 3000 to 5000 degrees F. The pressure ratio in the expansion through the converging-diverging nozzle is adjusted to lower the temperature, upon expansion, to one in the range of 1500 to 2000 degrees F. which is then suitable for cracking vapors from a vacuum distillation, effected in the vacuum drum, to ethylene. The primary expansion, at which time the gases and oil vapors from the vacuum drum are admixed, will quench the acetylene-forming reaction. This results in a gas containing both ethylene and acetylene.

In another embodiment of the invention, the combustion reaction chamber is one in which a high temperature gas mixture is obtained without necessarily forming valuable by-products. In this embodiment, cracking of the vapors from the vacuum drum is effected.

It is not always necessary to operate the distillation

drum under a vacuum. However, a vacuum is preferred and usually a pressure of from 1 to about 5 pounds per square inch absolute in the vacuum drum is considered satisfactory. Though not shown in the drawing, the feed to the vacuum drum, especially when it is a well-reduced crude, will be heated. Suitable heating means (not shown) are provided in the vacuum drum to bring about the desired distillation therein.

The time taken for the cracking of the oil vapors in the venturi discharge is of the order of a fraction of a second. Thus, cracking is effected with contact times of from about 0.005 to about 0.1 second. The temperature as noted is rather high and a water quench, as shown in the drawing, located immediately downstream of the venturi discharge, reduces the temperature of the mixture and arrests the reaction. The following is an example according to the invention in which a specific high methane content natural gas is burned to produce gases with which a reduced crude is cracked.

Example

A high methane content natural gas with the following analysis is burned with the theoretical amount of air.

Natural gas (mol percent)	
CH ₄	96.0
CO ₂	3.2
N ₂	0.8
	100.0

A flow rate of 100 standard cubic feet of natural gas per minute feeds the combustion chamber at 100 p.s.i. Nine hundred twenty standard cubic feet of air per minute is used. Upon combustion, the mixture attains a temperature of 3650 F.

The hot combustion gases expand through a converging-diverging nozzle to a pressure of 4 p.s.i.a., the pressure maintained in the vacuum drum. The nozzle is constructed with a 50° angle of convergence to a throat of about 2 inches in diameter with a 15° angle of divergence downstream. A ratio of nozzle discharge area to nozzle throat area of about 4 to 1 exists. The nozzle discharge velocity is about 5700 feet per second. The combustion chamber exhaust gas composition is approximately as follows:

Mol percent	
CO ₂	18.9
H ₂ O	9.6
N ₂	71.5
	100.0

Reduced crude with an API gravity of 25.0 and an ASTM Initial Boiling Point of 320 F. is fed to the vacuum drum after being used as secondary quench for the process off-gases. The vacuum drum is maintained at a pressure of 4 p.s.i.a. and a temperature of about 525 F. Coil heaters are used to maintain the drum temperature. External heaters can also be used for this purpose. Vapors from the vacuum drum are entrained by the high velocity combustion gases and cracked. The vacuum drum vapors have the following characteristics (liquid):

Gravity, API	38.1
Sulfur, weight percent	0.266
Refractive index	1.4633

ASTM distillation:

IBP	280
20%	526
40%	562
60%	606
80%	662
E.P.	672

Cracking is carried out at about 1800 F. and the mixture of gases passes to the converging-diverging diffuser

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where it is compressed from drum pressure (4 p.s.i.a.) to discharge pressure, 16 p.s.i.a. A reaction time of 0.069 second (i.e., of the order of less than $\frac{1}{10}$ second) is maintained by proper sizing of the diffuser and the soaking chamber downstream. A water quench cools the gases to a temperature below that at which any reaction can take place and final cooling is brought about by using the reduced crude feed to the vacuum drum.

Using the quantity of natural gas specified at the beginning of the example (100 SCFM), 1500 pounds per hour of vapors are withdrawn from the vacuum drum.

In the diffuser, the ratio of inlet area to throat area is about 1.4 to 1. A diffuser throat diameter of about 4 inches is required for the flow rates specified in this example.

After the secondary quench, the condensate separates into two layers, a water layer and an organic layer. The water layer amounting to about 750 pounds per hour is discarded and the organic layer is fed to the vacuum drum. In the secondary quench, 250 pounds per hour of heavy oil and tars are removed from the gases for discard with the residual oil from the vacuum drum. The gases from the secondary quench have the following composition.

	Pounds/hour	Mol per cent
H ₂	47	11.6
N ₂	3,270	57.4
CO ₂	690	7.7
CH ₄	270	8.3
C ₂ H ₄	748	13.2
C ₂ H ₆	37	0.6
C ₃	21	0.3
C ₄	72	0.6
C ₅	2	0.3
Benzene.....	45	0.3
	5,202	100.0

These gases are compressed for processing in suitable recovery zones downstream.

In the foregoing example, the cracking to ethylene was carried out in a comparatively long time, that is, approximately 0.07 second. This requires some soaking volume downstream of the diffuser. When higher temperature cracking to acetylene is carried out, a very short reaction time, as low as 0.005 second, is required and the diffuser downstream section is altered accordingly. Or, as an

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alternative, the volume of materials passing through the diffuser section is sufficiently great to reduce the contact time.

It will be noted from the foregoing example that there is present a large percentage of nitrogen in the off-gases. Use of oxygen or an oxygen-enriched air in the combustion chamber will, of course, reduce the nitrogen in the off-gases as well as produce a higher temperature in the combustion chamber.

Reasonable variation and modification are possible within the scope of the foregoing disclosure, drawing, and the appended claim to the invention, the essence of which is that a venturi actuated by hot gases, as described, is used to aspirate vapors from a distillation or other zone for conversion of the said vapors using the heat of the said gases upon admixture with said vapors in the venturi to carry out a time-temperature controlled reaction to produce useful products. When desirable, the products are quenched also as described.

I claim:

A method for converting a hydrocarbon oil to produce ethylene, acetylene, aromatics, and the like which comprises introducing said oil into a distillation zone maintained under high vacuum of the order of 4 p.s.i.a. and at a temperature of the order of 525° F., operating a venturi, the low pressure zone of which communicates directly with said distillation zone by burning a fuel in a jet engine under elevated pressure, forcing combustion gases at said elevated pressure from said jet engine into said venturi at a velocity such that said venturi will by itself maintain said high vacuum of the order of 4 p.s.i.a. in said distillation zone, and sucking vapors immediately as formed, and without any further step, from said distillation zone directly into said venturi, therein cracking said vapors and then quenching and recovering products of reaction from said venturi.

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