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TEMPERATURE CONTROL IN SHOCK-CHILLING PETROLEUM VAPOR PHASE CONVERSION PRODUCTS

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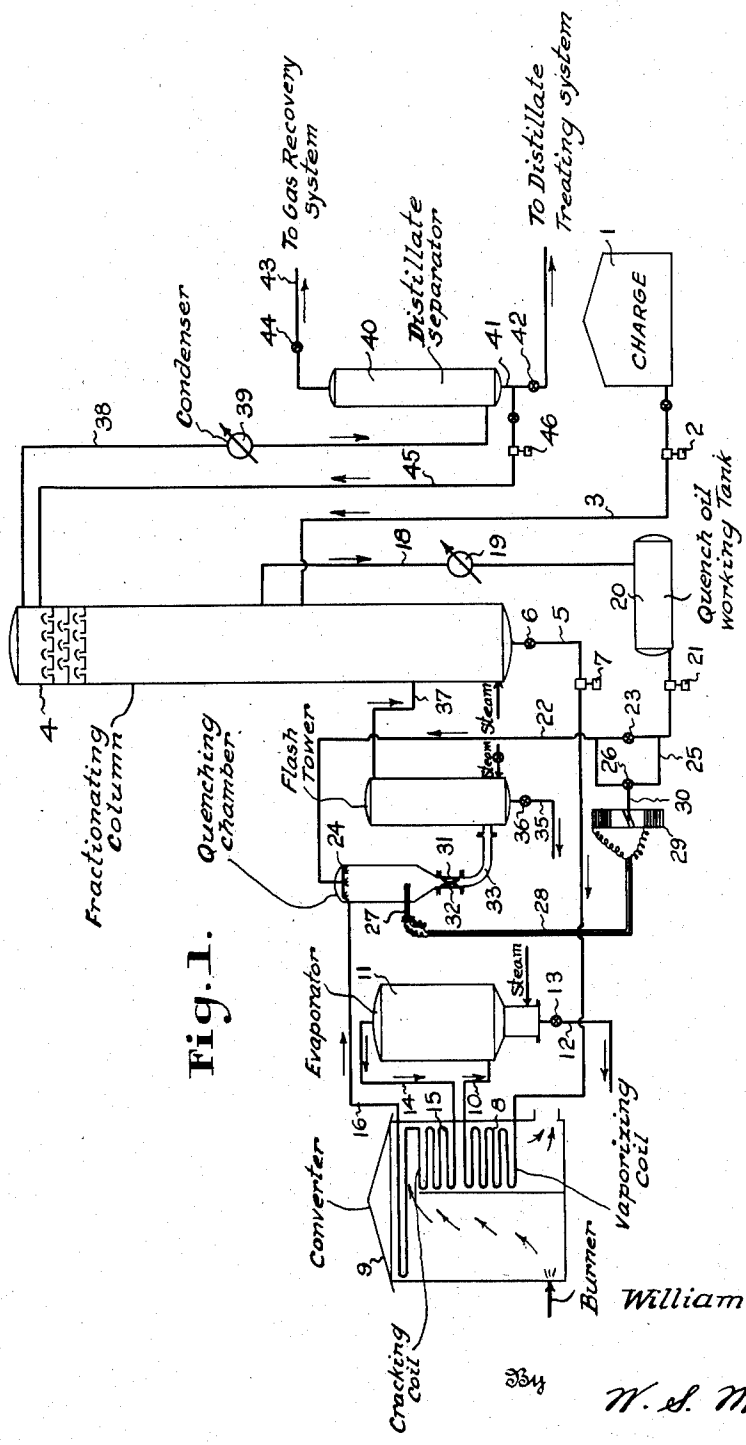


Fig. 1.

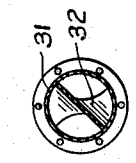


Fig. 3.

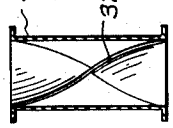


Fig. 2.

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TEMPERATURE CONTROL IN SHOCK-CHILLING PETROLEUM VAPOR PHASE CONVERSION PRODUCTS

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This invention is directed to the cracking of hydrocarbons in the vapor phase, and particularly to the thermolytic conversion of relatively heavy liquid hydrocarbons into products boiling within the gasoline range. It also relates to the pyrolysis of saturated hydrocarbon gases for the production of unsaturated compounds widely used in the field of chemical synthesis, and is primarily concerned with a method and means of controlling the temperature when shock-chilling the products of such conversion reactions.

In the pyrolytic conversion of hydrocarbons, normally either in the liquid or gaseous state, when conversion is carried out in the vapor phase, the time element is so short because of the high temperatures involved that the reaction will proceed too far or secondary reactions occur unless adequate precautions are taken to check the progress of the reaction suddenly and at precisely the correct point. There is also the ever-present danger of excessive coke formation unless the reaction conditions are under definite and positive control.

The practice of shock-chilling the products of conversion reactions has been followed in some vapor phase cracking processes by directly contacting the hot vapors emerging from the conversion zone with a relatively cool oil in a quenching zone, thus reducing the temperature to a point where the cracking reaction ceases, but the results have been only measurably satisfactory because of the absence of any definite means of exact temperature control at this critical stage of the conversion operation. If the temperature is not substantially instantaneously reduced to the proper degree at this stage, and maintained relatively constant, not only will the cracking reaction continue beyond the desired point but coke will be formed in the quenching zone, causing a premature shut-down of the equipment and the loss of valuable operating time. Also if the temperature is reduced only to a point below that required for cracking or below the critical coking temperature, the chilled products have a marked tendency to deposit granular carbon in the transfer lines between the quenching zone and the after equipment, eventually plugging the lines and necessitating major repairs. On the other hand, if the temperature is reduced to too low a degree, undesirable condensation results and the residual heat in the uncondensed vapors is not sufficient to cause the fractionating column to function properly without the addition of extraneous heat from some source.

It is, therefore, an object of this invention to

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provide efficient and reliable means of controlling the temperature of the vapor phase cracking operation at the critical stage between the period of maximum cracking and that at which cracking has ceased altogether, and to reduce the time element at this stage to the shortest possible interval.

It is also an object of this invention to provide means whereby the deposition of coke in the transfer lines between the quenching zone and the fractionating column is reduced to a minimum, and such granular coke as may be held in suspension in the oil is collected in a confined area and removed from the system without interfering with the continuous operation of the process.

It is a further object of this invention to retain sufficient residual heat in the products of the quenching operation to cause the fractionating column to function properly and efficiently in effecting the desired separation of the light and heavy fractions resulting from the pyrolytic conversion operation.

Other objects of this invention will become apparent as further details of the process are set forth.

In the vapor phase conversion of liquid hydrocarbons for the production of high grade motor fuel, temperatures in excess of 1100° F. are usually required, and for particularly refractory charging stocks, such as cycle stocks produced in previous cracking operations, temperatures of the order of 1250° to 1350° F. are not infrequently required. In the case of gaseous charging stocks, however, such as, for example, the saturated C_2, C_3 and C_4 compounds generally used in the pyrolysis of gases for the production of unsaturated hydrocarbons for chemical synthesis, the conversion temperatures may range from 1350° to 1550° F. But in either case, whether the charge is normally in the liquid or gaseous state, the temperature of the products of the conversion reaction must be reduced as nearly instantaneously as possible, immediately upon emergence from the cracking zone, to a degree where cracking ceases altogether. Several factors may govern the optimum temperature at this point, the most important of which is that it must be below the temperature at which further pyrolytic decomposition can take place or coke can be formed, and it must be below the temperature at which secondary reactions occur. On the other hand, the vapors preferably must retain sufficient residual heat for the required fractionating purposes, which is governed by the degree of separation

desired, which in turn is dependent upon the height of and the number and efficiency of the bubble trays in the fractionating column. Generally speaking, quenching temperatures not substantially in excess of 600° F. are suitable for the purpose, but the exact temperature best suited to an individual operation should be calculated from theoretical considerations or preferably determined by experimental methods.

The choice of a cooling medium for use in quenching operations or for shock-chilling the cracked vapors issuing from the conversion zone is a matter of convenience rather than exact specifications. Any relatively light distillate that is clean and free from sediment and that will not be completely vaporized when brought into contact with the hot vapors will serve the purpose. However, it should contain no heavy fractions subject to cooking under the temperature conditions prevailing in the quenching zone. It is preferable, of course, to select a distillate fraction produced within the operation itself, rather than from an extraneous source. For this purpose, therefore, a suitable stream of oil may be withdrawn from a tray at an intermediate point in the fractionating column. This material, after cooling, is collected in a working tank from which it is delivered to the top of the temperature arrester or quenching chamber where by suitable mechanical means, such as atomizing spray nozzles, it is intimately mixed in direct contact with the hot vapors issuing from the conversion zone.

The novelty of this invention resides primarily in the design of the quenching chamber and means of controlling the temperature therein, together with its relation to the fractionating column with respect to the disposition of coke during the passage of the products of conversion from one to the other.

Since the temperature maintained in the quenching chamber is dependent upon the quantity of oil delivered thereto from the working tank, it is obviously desirable that the rate of oil flow should be governed by the temperature. It should be stated in this connection that the smoothness of the entire conversion operation, as well as the uniformity in quality of the final products, is more largely dependent upon accurate temperature control throughout the system than any other single factor. Heretofore little importance has been attached to the maintenance of an exact degree of temperature in the quenching zone, a feature which has contributed to the varying character of the final products and inconsistent yields, as well as promoting the formation of coke under fluctuating temperature conditions. It is therefore a primary object of this invention to provide positive means of controlling the temperature at this point and completely checking the rapid pyrolytic decomposition of the hydrocarbon charge at the proper temperature and in the shortest possible interval of time between the point of maximum cracking and that at which cracking ceases altogether.

Temperature control of the conversion elements located in the furnace is precise and exact, as a result of wide experience among oil refiners, extensive experimental work and the careful study of heating problems by designing engineers, but the same attention, so far as I am aware, has never been directed to the simpler yet equally important problem of dealing with the decomposition products of hydrocarbons as they leave the conversion zone.

It is neither practical nor economical to maintain the quenching oil in the working tank at a constant temperature because of its relatively large volume and the varying atmospheric and cooling water temperatures, yet any substantial variation in the temperature of the oil delivered to the quenching chamber is reflected immediately in the character of the cracked products leaving the chamber, as is clearly shown by frequent analyses of the end products. On the other hand, it has been observed that if the quenching chamber is maintained at a reasonably constant temperature, the character of the conversion products is uniform and the yields consistent, and little or no coke is formed in the quenching operation.

To this end a temperature control system is provided, the mechanism of which consists essentially of a thermostatic element inserted through the wall of the quenching chamber, electrically connected with a source of current and means for automatically controlling the delivery of a stream of cool oil from the working tank to the quenching chamber as the thermostatic circuit is established or broken. This arrangement affords ample means of maintaining a constant temperature in the quenching chamber or of regulating the temperature in accordance with any requirements. If the temperature in the chamber rises, a larger quantity of cooling oil is admitted thereto; if the temperature falls, the supply of oil is diminished.

The quenched products of conversion, now reduced in temperature to about 600° F., usually include a small amount of finely divided carbon or soot which should be removed from the system before the other products enter the fractionating tower. This is accomplished by means of a flash drum, acting as a trap for the solid materials which settle to the bottom because of their higher specific gravity and greatly reduced velocity at this point of the operation; while the liquid, vapors and gases are flashed off with the aid of steam under partial pressure conditions, leaving the top of the flash tower and passing directly to the fractionating column. The solid materials, along with a small amount of tar formed in the cracking operation, are withdrawn from the bottom of the flash tower and diverted from the system.

In vapor phase cracking operations, there is always the possibility of the deposition of finely divided coke in horizontal transfer lines of any considerable length between the quenching chamber and the fractionating column. This invention is particularly directed to the avoidance of such a condition. To this end, the quenching chamber is provided with a conical bottom constructed on about a sixty degree angle to facilitate the complete and rapid exit of the quenched products from the bottom of the chamber, the turbulence within washing the walls of the cone free of carbon. Immediately below the cone is a pipe fitter's "spool" about twelve inches in length in which a helical vane is placed. Because of the high velocity of the materials passing through the "spool," this vane imparts a rapid spiral or swirling motion to the liquid and vapors which effectively scrub the inner walls of the comparatively short line leading to the flash drum, thus avoiding the deposition of coke before it is trapped at the desired point in the bottom of the flash drum, from which it is withdrawn in the form of a suspension in the liquid residue. The placing of baffles in the flash drum

to obstruct the upward passage of the finely divided coke particles is optional, although experience indicates that the increased velocity resulting therefrom renders the advantage of baffles questionable.

This invention will be clearly understood by reference to the accompanying simplified flow diagram forming a part of these specifications, in which Fig. 1 represents in partial section and side elevation apparatus and equipment adapted to the continuous performance of the functions and operations herein described;

Fig. 2 is an enlarged longitudinal section of the pipe fitter's "spool" containing the helical vane; and

Fig. 3 is a transverse cross section of the "spool."

Referring to the drawing, the numeral 1 represents a tank containing a liquid hydrocarbon charging stock such as crude oil, topped crude, gas oil, kerosene or the like, which is delivered by pump 2 through line 3 to an intermediate point in the fractionating column 4 where it first serves as a reflux for, and is preheated by, the hot ascending cracked products of the conversion operation. The preheating of the charge or feed stock, however, is not limited to this means alone, since it is customary to take advantage of any economical source of heat exchange wherever possible in such systems, especially when charging crude oil, in which event the natural gasoline is usually removed through heat exchange with hot products, such as residuum from the evaporator, before entering the cracking coils in the furnace.

The preheated feed stock, mixed with condensate produced within the fractionating column, is withdrawn from the bottom of the column through line 5, controlled by valve 6, and is delivered by pump 7 to a vaporization coil 8 located preferably in the convection section of a furnace 9 where it is substantially converted into vapor. The vaporized and unvaporized portions of the charge or feed then pass through line 10 into an evaporator 11 where vaporization is effected with the aid of steam under partial pressure conditions, the unvaporized heavy residue being withdrawn from the bottom of the evaporator through line 12, controlled by valve 13, and diverted from the system. This residue may be subjected to a viscosity-breaking operation, run to coke or processed by any suitable means for the production of road oil, bunker C fuel or other desirable products.

The oil vapors leaving the top of the evaporator, commingled with steam, pass through line 14 and enter the cracking coil 15 where the conversion into lighter products is effected. Any suitable arrangement of preheating coils, drying coils or cracking elements may be used for this purpose, depending upon the character of the charging stock and the end products desired. That is to say, whether the charge is normally in the liquid or gaseous state, or whether the final products are to be used primarily for the purpose of motor fuel or as unsaturated hydrocarbons for the synthesis of chemical compounds, or for both purposes.

The process herein described is adapted to the conversion of either liquid or gaseous hydrocarbons, although in the latter case, a somewhat different arrangement of equipment is required and higher conversion temperatures are employed. For example, when charging a liquid hydrocarbon according to Fig. 1 of the accompanying drawing, conversion temperatures of the order of 1000° to 1350° F. may be adequate for the desired conversion; while if the charge is in the gaseous state under normal temperature and pressure conditions, the conversion temperatures may range from 1350° to 1550° F., depending upon the composition of the charge and the end products desired.

In the conversion of normally gaseous hydrocarbons, an evaporator is not required, the gaseous feed, preheated by any convenient heat exchange means (including that with the hot flue gases leaving the furnace), entering the heating elements directly. In either case, however, whether the charge is in the liquid or gaseous state, the products of conversion leaving the heating elements pass through line 16 into a quenching chamber 17 where by direct and intimate contact with relatively cool atomized oil, the temperature of the highly heated vapors is substantially instantaneously reduced to a degree below that at which further decomposition can take place, secondary reactions occur or coke be formed. Yet the vapors must retain sufficient residual heat to cause the fractionating column to function properly. These requisite conditions can be met only by accurate temperature control of the quenching chamber, upon which the ultimate yields and quality of the finished products largely depend.

The fractionating column, which is preferably of the bubble tower design, provides a suitable source of oil for the quenching operation, a selected stream being withdrawn from an intemediate bubble tray for this purpose, leaving the tower through line 18 and passing through a water cooler 19 into the working tank 20, from which it is delivered by pump 21 through line 22, controlled by valve 23, into the top of the quenching chamber 17 where it is atomized by nozzles 24, contacting the heated vapors at this point as previously stated.

Somewhat less cooling oil is supplied through valve 23 than the total amount required for the complete quenching operation, the remainder being routed through a by-pass 25, around valve 23. It is this portion of the cooling oil that is used for regulating the temperature in the quenching chamber, its rate of flow being governed automatically by thermostatic control of a quick-opening-and-closing valve 26, or any other means designed for the accomplishment of the same purpose. The by-pass provides more delicate and accurate temperature adjustment than if the entire volume of cooling oil were placed under thermostatic control. It also insures a sufficient quantity of oil reaching the quenching chamber at all times, since the major portion of the oil flowing continuously through valve 23 may be manually controlled in the event of failure of the automatic system through mechanical defects or otherwise.

Various mechanical devices involving the use of motors, pumps, valves and the like are available for automatic temperature control under thermostatic conditions, any of which may be used for the purpose at hand; but for reasons of simplicity and reliability, with no intention of limiting the scope of this invention, I prefer the quick-opening-and-closing valve in the by-pass 25 to supply the regulatory quantity of cooling oil, in addition to that passing continuously through valve 23, for the complete quenching of the hot vapor issuing from the cracking coil 15.

Valve 26 may be magnetically actuated to the open or closed position as the thermostatic cir-

cuit is established or broken by the rise or fall of the temperature in the quenching chamber. The thermostatic element 27 inserted through the wall of the chamber is electrically connected with the magnets 29 through conduit 28 and with a source of current (not shown) in such a manner as to control the movement of the valve mechanism 30 to the open or closed position in response to the fluctuation of temperature in the chamber. When the temperature rises above the desired point, valve 26 is opened automatically, admitting more oil to the chamber; when the temperature falls, the valve is closed, diminishing the flow of oil, thus maintaining an even temperature in the quenching chamber.

The bottom of the quenching chamber is constructed in the form of a cone 30, the walls of which are built on an angle of approximately sixty degrees to facilitate the ready exit of the materials from the bottom of the chamber, especially any coke particles held in suspension in the oil. Immediately below the cone, and flanged thereto, is a pipe fitter's "spool" 31, in which is placed a helical vane 32, more clearly shown in the enlarged sectional drawings, Figs. 2 and 3, which imparts a rapid spiral or swirling motion to the oil and vapors as they enter the comparatively short pipe 33 leading to the flash tower 34, scrubbing the inner walls of the pipe free of carbon in transit.

Reaching the flash tower at reduced pressure, the vaporous fractions are flashed off, preferably with the aid of steam injected into the lower section of the tower, while the residue holding the carbon in suspension is diverted from the system through line 35, controlled by valve 36. The flashed vapors leaving the top of the tower through line 37 enter the fractionating column 4 where separation of the light and heavy fractions is effected, also, if desired, with the aid of steam injected into the bottom of the column. The overhead vapors and gases leaving the fractionating column through line 38 are conducted through a condenser 39 and collected in a receiver or separator 40, from the bottom of which the cracked distillate is withdrawn through line 41, controlled by valve 42, and sent to the treating system; while the uncondensed gases leaving the top of the receiver through line 43, controlled by valve 44, go to the gas recovery system.

The temperature of the top tray in the fractionating column, which governs the end point of the distillate produced, is controlled by the quantity of distillate returned to the top of the column through line 45 by means of pump 46.

I claim:

1. In a vapor phase cracking apparatus for the conversion of hydrocarbons, a conversion arrester comprising a quenching chamber, means in the upper part of said chamber for introducing therein a quenching agent in a finely divided form, means for introducing converted hydrocarbons into said chamber for contact with said quenching agent, the chamber being formed with a conical bottom, a flash tower, a transfer line leading from the conical bottom of said quenching chamber to the lower part of said flash tower, helical means disposed in said transfer line to impart a rapid swirling motion to the materials passing therethrough, a vapor line leading from the top of said flash tower, and means for diverting from the system liquid residues and suspended carbon trapped in the bottom of the flash tower.

2. In a vapor phase cracking apparatus for hydrocarbon products, a converter for converting hydrocarbons therein, a conversion arrester comprising a hollow body defining an internal quenching chamber, means for transferring converted hydrocarbons from said converter to said chamber, means in said chamber for contacting the converted products introduced therein with a quenching agent in a finely divided form, a flash tower, a transfer line leading from the bottom of the quenching chamber of said arrester to said tower, means in said transfer line for imparting a rapid swirling motion to the materials passing therethrough, vapor outlet means leading from the top of said flash tower, and means for withdrawing from the bottom of said tower liquids and solids present therein.

3. In a vapor phase cracking apparatus for the conversion of hydrocarbons as defined in claim 2, wherein the bottom of the flash tower is provided with means for introducing steam therein.

4. A conversion arrester for use in vapor phase cracking systems for the molecular conversion of hydrocarbons, said arrester comprising a receptacle formed with an internal quenching chamber, means for introducing converted hydrocarbons into the upper part of said chamber, spray means arranged in the upper part of said chamber for bringing a quenching agent in a finely divided form into direct and intimate contact with the converted hydrocarbons to reduce the temperature of the latter sufficiently to substantially arrest conversion reactions, said quenching chamber being formed with a substantially conical bottom terminating in a flanged outlet, a flanged spool secured to said flanged outlet to form a continuation thereof, and a helical vane means disposed in said spool and operative to impart a rapid swirling motion to materials passing therethrough from said quenching chamber.

5. In a vapor phase cracking system for the conversion of hydrocarbons, means for heating hydrocarbons, a conversion arrester having an internal quenching chamber into which the converted hydrocarbons are introduced, spray devices in said chamber, means for forcing a relatively cool hydrocarbon distillate through said spray devices to bring the distillate in a finely divided form into direct and intimate contact with said hydrocarbon vapors, means constituting a flash chamber, transfer conduit means of reduced cross-sectional area in relation to that of said chambers for transferring hydrocarbons from the bottom of said quenching chamber to said flash chamber, helical vane means arranged in said conduit means for imparting a rapid swirling motion to the hydrocarbons passing therethrough, vapor outlet means leading from the upper part of said flash chamber, and means diverting from the system residual hydrocarbons contained in the bottom of the flash tower.

6. In apparatus for the molecular conversion of hydrocarbons in the vapor or gaseous phase, a converter through which vaporous hydrocarbons are passed and heated to reaction temperatures, drum structures providing separated quenching, flashing and fractionation chambers, means for passing the heated products of said converter to said quenching chamber, means for introducing into the top of said chamber a liquid hydrocarbon distillate in a finely divided form for direct and intimate contact with said converted products to effect a substantially instantaneous reduction in temperature of the con-

verted products to non-reacting temperatures, means for transferring the quenched products from the bottom of said quenching chamber to the lower part of said flash chamber, vapor outlet means leading from the top of said flash chamber to the lower part of said fractionating chamber, liquid outlet means for the withdrawal of a heavy residual from the bottom of said flash chamber, fractionating trays provided in said fractionating chamber in vertically superposed order, vapor outlet means in the top of said fractionating column, vapor liquid outlet means leading from the top of said fractionating chamber above said trays, liquid outlet means leading from said fractionating chamber intermediately of the height thereof for advancing the same as the cooling distillate into the top of said quenching chamber, thermostat means associated with said quenching chamber, and means governed automatically by said thermostat means and the operating temperatures within said quenching chamber for increasing or diminishing the flow of the cooling distillate to said quenching chamber, whereby to maintain a constant temperature in the quenching chamber.

7. In apparatus for the molecular conversion of hydrocarbons in the vapor or gaseous phase as specified in claim 6 in combination with means for introducing steam under regulated flow into the bottoms of said flash and fractionating chambers.

8. In a vapor phase system for the molecular conversion of hydrocarbons, a conversion arrester defining an enclosed quenching chamber, means for introducing converted hydrocarbons into said chamber, spray means in said chamber for bringing a relatively cool hydrocarbon distillate in a finely divided form into intimate and direct contact with the converted hydrocarbons, vapor fractionating means, a transfer conduit leading from the bottom of said quenching chamber to said fractionating means, means for withdrawing at an intermediate point from said fractionating means a quenching distillate, pipe means for advancing said quenching distillate to the spray means in said quenching chamber, an electro-responsive valve in said pipe means for increasing and decreasing the rate of flow of the distillate through said pipe means, an operating circuit for said valve, and a switch in said circuit responsive to the internal temperatures of said quenching chamber to open and close said valve.

9. In a process of converting hydrocarbons in the vapor phase, the steps of converting hydrocarbons at temperatures between 1000° F. and 1550° F., introducing the converted hydrocarbons into a conversion arrester, spraying the converted hydrocarbons with a cool hydrocarbon distillate in said arrester to substantially instantaneously reduce the temperature of said hydrocarbons to reaction-arresting temperatures of the order of 600° F., and maintaining the arrester at a constant temperature, by regulating the rate of flow of hydrocarbon distillate thereto in response to valve means thermostatically controlled by the temperature in said arrester.

10. In a process of converting hydrocarbons in the vapor phase, the steps of converting hydrocarbons at temperatures between 1000° F. and 1550° F., introducing the converted hydrocarbons into a conversion arrester, spraying the converted hydrocarbons with a cool hydrocarbon quenching medium in said arrester to substantially instantaneously reduce the temperature of said hydrocarbons to reaction-arresting temperatures of the order of 600° F., and continuously controlling the quantity of quenching medium to be sprayed and maintaining the temperature in the arrester constant by bypassing a quantity of the said quenching medium in response to thermostatic control by the temperature in the arrester.

11. In a process of converting hydrocarbons in the vapor phase, the steps of arresting the conversion reactions with a quenching medium in a quenching zone maintained at a constant temperature, transferring the arrested reaction products to a flashing zone, and imparting a rapidly swirling motion to the arrested reaction products during such transfer.

12. In a vapor phase cracking system for the conversion of hydrocarbons, the combination including a quenching chamber, said chamber being provided with a conical bottom, a spool flanged to the lower end of said conical bottom, a helical vane disposed in said spool, a tower, a conduit connecting said spool to said tower, a thermostat associated with said quenching chamber, a conduit entering said quenching chamber for providing a fluid quenching medium thereto, valve means associated with said last named conduit for controlling the flow of fluid quenching medium to said chamber, and means controlled by said thermostat operable to increase or decrease the flow of fluid quenching medium through said valve means to the quenching chamber, whereby the temperature in said chamber is maintained constant by automatic control.

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