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CHEMICALS COKING QUENCHING SYSTEM

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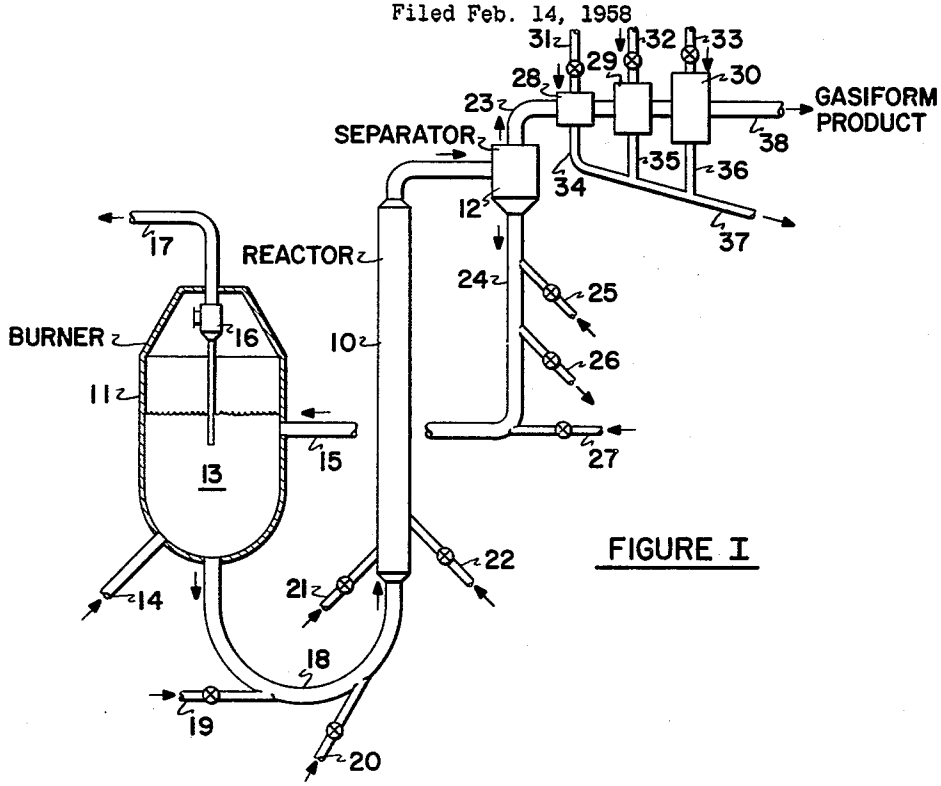


FIGURE I

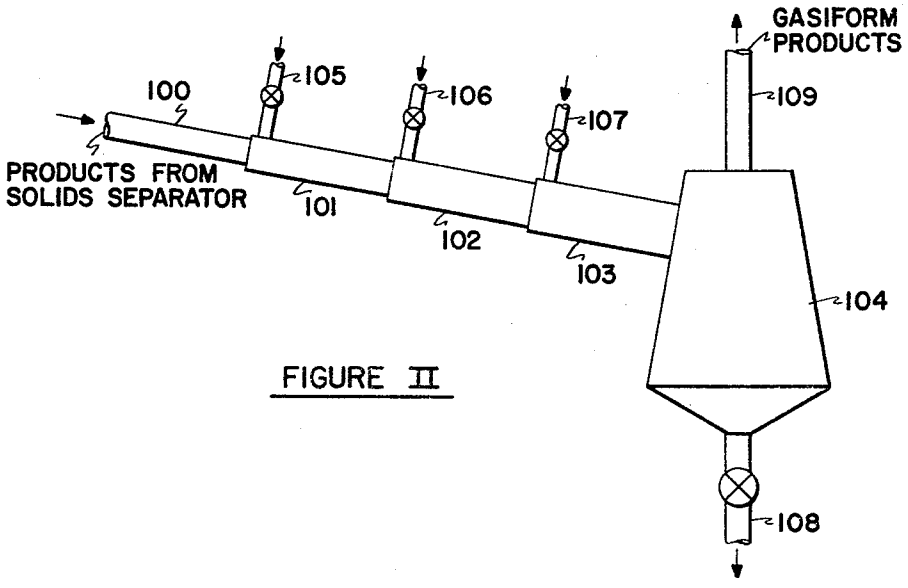


FIGURE II

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CHEMICALS COKING QUENCHING SYSTEM

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The present invention is concerned with the quenching of hot gasiform products of a transfer line chemicals coker. More particularly, it deals with cooling product vapors so as to arrest after-cracking while minimizing coke deposition in the overhead equipment.

In recent years, there has been an increasing demand for converting heavy end, relatively low valued petroleum hydrocarbons into light unsaturates, such as ethylene and propylene, suitable for use as chemicals raw material. Towards this end, the dispersed solids phase thermal cracking process, more commonly referred to as transfer line chemicals coking, has been developed. Basically, the process comprises introducing a suitable preheated hydrocarbon oil feed into a rapidly moving (greater than 20 ft./sec.), gaseous suspension of hot inert solids. The oil, upon contacting the solids which are at temperatures of at least 1200° F., is converted into light gasiform material and carbonaceous matter which deposits on the solids' surfaces. After, or even before, passing through a solids separation, the gasiform reaction products are quenched to arrest further thermal cracking. Separated solids are normally passed to a combustion zone wherein oxidation of the carbonaceous residue deposited upon them during the reaction serves to heat them to a temperature 50 to 400° F. above that of the reaction zone. If desired, an extraneous fuel may be added to the combustion zone. The thus heated solids are then recirculated to the reaction zone so as to supply requisite thermal energy for conversion.

Among solids suitable for use are sand, coke particles, ceramic or metallic solids, etc. The solids ordinarily range from about 20 to 800 microns in size.

A wide variety of hydrocarbon oil fractions may be utilized as feed. For example, reduced crudes, asphalts, tar, shale oil fractions, gas oils, etc. are readily cracked in the transfer line chemicals coking system. Generally, the feed has an initial boiling point above 600° F., an A.P.I. gravity of about 0 to 20°, and a Conradson carbon content of about 5 to 40 wt. percent.

One of the serious problems encountered in transfer line coking for chemicals is the deposition of carbonaceous matter in the overhead equipment e.g. conduits downstream of the solids separator and the quench point. In addition to light unsaturates, the reaction product stream contains heavy materials such as unconverted feed and high molecular weight unsaturates. In practical operation, it has heretofore been found that upon quenching the reactor products from about 1300° F. to approximately 500° F. by conventional means, a mist or fog of heavy hydrocarbons is formed. Dew point cooling and condensation occur in the high velocity gas stream thus causing formation of the mist of heavy material.

This mist or fog upon contacting the surfaces of the equipment condenses thereon, resulting in deleterious carbonaceous deposits on the structural surfaces. These carbon deposits may continuously build up to such levels as to interfere with the flow of overhead vapors, ultimately causing shutdown of the entire system.

The present invention sets forth means whereby heavy hydrocarbon mist formation is avoided, coke deposition minimized and improved operating realized.

More particularly, in accordance with the present invention the reactor gasiform effluent is passed through a plurality, preferably three or more, quenching stages, each of which reduces the stream temperature by a substantially equal amount. Quenching liquid is introduced into each stage in sufficient amounts to be only partially vaporized while cooling the stream to the desired degree. The normal 800–900° F. temperature drop of reactor vapors is thus broken up into steps of about 200 to 300° F. The temperature drop of 200 to 300° F. in each quenching stage is low enough to prevent the major portion of the main gas stream from reaching its dew point, while condensing enough of the heavy, high boiling material so as to lower the dew point of the gasiform stream leaving the stage to below the temperature the stream will reach in the subsequent stage. Thus heavy material is removed from the reactor effluent in a stepwise manner, diluted and washed away by unvaporized quench liquid without forming the undesirable mist which characterized prior art systems.

In preferred embodiments, the quenching stages are placed immediately after the solids separator and operate at progressively greater residence periods. In this manner, equal temperature change occurs in the several stages without requiring excessively increasing amounts of quenching liquid to offset the decreasing temperature differential between the gasiform stream and the quenching medium.

It should be clearly understood that the present invention does not consist in mere multiple quenching of reactor vapors. Basically, it teaches quenching by the use of a series of stages, each of the stages cooling the stream flowing therethrough to give a substantially equal temperature drop. Heavy materials are thus condensed in a stepwise manner without cooling the major portions of the stream below its dew point.

By way of clarification, the terms "gases" and "vapors" are used synonymously. The phrase "reaction time" denotes the time between the first contact of oil feed and hot solids and the subsequent solids-gas separation.

The various aspects and modifications of the present invention will be made more clearly apparent by reference to the following description, examples and accompanying drawings.

Figure I illustrates a transfer line chemicals coking process employing the present quenching features.

Figure II depicts a preferred type of multi-equal temperature drop quenching stages.

Turning to Fig. I, there is shown a transfer line conversion system comprising essentially reactor **10**, burner **11**, solids separator **12** and multi-quenching units **28**, **29** and **30**.

Reactor **10** is an elongated, conduit-like reaction unit conventionally referred to as a transfer line reactor. Hot solids, e.g. sand, are withdrawn from the heater vessel or burner **11** and passed upwardly through reactor **10** in the form of a dilute gas-solids suspension i.e. density of approximately 5 lbs./ft.^{3}.

Requisite thermal energy for conversion is normally supplied by the combustion of the carbon deposited on the solids during the course of the thermal cracking reaction. As will further be described, contact solids are separated from the reactor gasiform effluent and passed to burner **11** through conduit **15**. As shown, a mass of contact solids is maintained within the burner in the form of a relatively dense fluidized bed **13**. Air, or other oxygen-containing media, passing upwardly through the bed, serves to oxidize the carbonaceous matter on the solids' surfaces while providing fluidization of the solids

mass. Steam may be added for further fluidization. If desired, an extraneous fuel such as the heavy end material separated from the reactor effluent, refinery surplusage and the like may be added to the burner by means, not shown. This type of operation is advantageously employed when insufficient carbon is deposited on the contact solids during the conversion step to supply required fuel needs or when it is desired to recover carbon-containing solids as such. While a fluid bed burner is illustrated, other heating units such as a transfer line burner, fixed bed combustion zone, etc. may alternatively be employed.

Hot combustion gases, after having entrained solids separated therefrom in cyclone **16** and returned to bed **13**, are withdrawn overhead. Their latent heat may then be recovered and utilized for providing heat for the system e.g. preheating of reactor fuel.

Hot solids at a temperature of about 1500° F. are withdrawn from the burner through conduit **18** and passed to reactor **10**. Propelling gases, such as steam, light hydrocarbons or the like, injected by means of taps **19** and **20** serve to carry the solids and form a rapidly moving gas-solids suspension passing through the reactor at about 30 ft./sec.

A hydrocarbon oil feed, such as a South Louisiana reduced crude preheated to a temperature of about 600° F., is injected in overall amount of 100 barrels per day into the hot solids stream by means of inlets **21** and/or **22** disposed about the reactor **10**. The feed injectors are normally disposed circumferentially and longitudinally about the reaction zone so as to ensure good solids-oil contact and provide a convenient means of altering reaction residence times. Residence times of about 0.2 to 1.0 second, e.g. 0.30 sec., are normally employed.

Upon contact with the hot solids stream, thermal cracking of the feed takes place at a temperature of 1350° F. to give light unsaturates (ethylene, propylene, etc.) together with other hydrocarbon fractions while depositing carbonaceous residue upon the surface of the contact solids.

The entire reactor effluent, e.g. solids, conversion products, unconverted feed, propelling steam, etc., are withdrawn overhead and rapidly subjected to a solids separation step in separator **12**. This separation unit normally consists of one or more cyclones, although vane separators or the like may alternatively be employed. Separated solids are recirculated back to burner **11** by conduits **24** and **15**. Stripping gas is advantageously introduced countercurrent to the separated solids by inlet **25**, occluded hydrocarbon thus being removed from the solids' surfaces and recovered overhead with the reactor gasiform products. In order to maintain a constant mass inventory within the system, solids may be withdrawn through outlet **26** positioned in line **24**. Solids may, of course, be withdrawn from other parts of their circulation path. Aeration tap **27** serves to smoothly convey the solids back to burner **11**.

Up to this point, the description has dealt largely with features well known in the art.

In accordance with the present invention, the hot (1275° F.) separated reactor vapors are thereafter subjected to a plurality of quenching steps, each of which reduces the temperature of the vapor stream by a substantially equal amount, e.g. 200 to 300° F. As shown, successive quenching units **28**, **29** and **30** are positioned immediately after separator **12**. The quench units preferably have successive increasing vapor residence times therein. While a series of individual chambers of increasing volume is illustrated, varying length of a constant diameter conduit may be employed for this purpose.

Referring to unit **28**, a quench liquid such as a recycle product fraction boiling in the range of 380 to 710° F. is introduced by the line **31** at a rate of 20 lbs./hr./barrel per day of feed so as to cool the reaction vapors from a temperature of 1275° F. to 1025° F. The quench liquid may be supplied, in part or in total, by fractionation of the transfer line effluent. Alternatively an extraneous gas oil having the desired boiling point characteristics may be used, either independently or in conjunction with a recycle fraction. The quench liquid consists of low boiling material for cooling the flowing stream together with high boiling material which is unvaporized during the quench operation. A portion of the heavy material in the reactor effluent condenses and is diluted with the higher boiling constituents of the quench liquid, thus providing against coke deposition. The major portion of the reactor vapiform stream is maintained above its dew point and leaves quench unit **28** after a residence interval of 0.018 second therein in the gaseous state. The stream then flows into quench unit **29**.

The unvaporized quench liquid, which serves to wash the equipment surfaces and protect them against carbon deposit, together with the condensed heavy material from the reactor effluent stream are withdrawn by outlet **34**. While individual exit systems for the various quench stages may be employed, it is advantageous to utilize a common exit conduit **37** into which each of the quench units discharge their liquid material by lines **34**, **35** and **36** respectively.

Units **29** and **30** operate in a similar manner to that described in reference to quench stage **28**. Quench liquid introduced through inlets **32** and **33** respectively are only partially vaporized as they cool the flowing gasiform stream, condensed heavy ends and unvaporized quench medium being withdrawn through outlet **35** and **36**.

The gaseous effluent of unit **28** enters unit **29** at a temperature of about 1025° F. and leaves it at a temperature of approximately 775° F., heavy material being condensed therein. The condensation of heavy ends in the first stage serves to lower the dew point of the material passing into the second stage by some 300° F., and so the major portion of the reaction product stream remains uncondensed. In an analogous manner, the gaseous effluent of unit **29** is thereafter quenched to a temperature of 525° F., in unit **33**, the thus cooled gasiform reactor products being withdrawn therefrom through line **38**. The gaseous stream may then be further cooled, sent to fractionation, or processed in other manners as desired.

Vapor residence of approximately 0.037 and 0.079 seconds are employed in the second and third stages respectively, the rate at which quench liquid is introduced thereto being substantially the same as that employed in unit **28**. The overall residence period in the plurality of quench stages described is less than 0.2 second.

While three stages are shown in the drawings, additional quench stages may be desired, as for example when very high temperature reaction products, e.g. 1500° F., are to be cooled to relatively low temperatures, e.g. 300° F.

Turning to Figure II, there is shown a particularly desirable apparatus configuration for quenching in accordance with the present invention. Basically, it illustrates the use of a plurality of pipe sections integrally connected to each other and having a common longitudinal central axis. The diameters of the quench-conduit sections are of increasingly greater value. For example, when solid separator exit conduit **100** is 3 inches in diameter, the diameters of sections **101**, **102**, and **103** are 4, 5, and 6 inches, respectively. The lengths of the individual sections may be approximately the same, e.g. 1.5 ft., or may vary so as to give a further vapor residence differential among the several quenching stages.

Hot reaction vapors flow into the succesive quenching stages through conduit **100**, and are quenched by stepwise reduction of temperature of about 200–300° F. in each quench section. As described in Fig. I, quench oil inlets **105**, **106**, and **107** are provided near the entrance sections of the successive quenching sections. The "quench-conduits" preferably slope downwards, thus promoting drainage of condensed heavy materials and un-

vaporized quench liquid into liquid-gas separator **104**. Cooled gases, e.g. at temperature of about 300–600° F., are withdrawn from the separator by line **109**, while heavy liquid hydrocarbons are removed by exit **108**. The system of Figure II provides for effective stepwise quenching by means of a simple and cheap configuration of pipes of varying diameters.

The following table sets forth a compilation of data applicable to the systems heretofore described:

Table I

	Broad Range	Preferred Range
Reaction Conditions:		
Average Size of Solids, microns	20–800	50–500
Density of Solids—Gas Suspension, Lbs./Cu. Ft.	0.5–15	1.0–5.0
Velocity of Solids—Gas Suspension Ft./Sec.	20–100	25–60
Reaction Temperature, ° F.	1,200–1,600	1,200–1,400
Reaction Time, Sec.	0.1–2.0	0.20–1.0
Quenching Conditions:		
Average Temperature of Reactor Vapors Prior to Quenching, ° F.	1,200–1,600	1,200–1,400
Temperature Drop across Each Quenching Stage, ° F.	100–400	200–300
Quantity of Quench Liquid Introduced into Each Quenching Stage (base on feed).	18#/hr./b./d. feed to 30#/hr./b./d. feed.	20 to 25
Volumetric Ratio of First Three Quenching Stages.	1:2:3	1:1.6:2.3
Overall Temperature Drop across Quenching Stages, ° F.	600–1,200	700–1,000
Final Vapor Temperature after Passing through Stages, ° F.	200–700	300–600

By operating in accordance with the present invention, numerous advantages are secured. Heavy materials are removed from reactor gasiform effluent without formation of a heavy end mist which would deposit carbonaceous matter on structural surfaces. Reaction vapors are cooled and efficiently separated from less desirable heavier hydrocarbons. Since the temperature differential across each section of the overhead vapor passageway is relatively small, there is a decreased tendency of cooling and condensation of vapors on upstream pipe walls. The use of a multi-stage arrangement allows equilibrium, and hence fractionation of vapors, to be more nearly approached as compared with a single large temperature drop quench operation.

What is claimed is:

1. In the coking of hydrocarbons wherein a gas-solids rapidly moving gaseous suspension of inert solids at a temperature above 1200° F. is passed through an elongated, conduit-like reaction zone at a velocity greater than 20 ft./sec., wherein a hydrocarbon oil feed is introduced into said solids suspension and upon contact with said solids is converted into lighter gasiform material and carbonaceous residue which deposits on said solids, and wherein said gasiform materials and said hot solids are separated in a gas-solids separation zone, the improvement which comprises subjecting separated gasiform material leaving said separation zone to a plurality of quenching stages in succession, injecting quenching liquid into each of said stages in sufficient amounts to be only partially vaporized while lowering the temperature of the gasiform material passing through each of the said stages by substantially equal amounts of about 200 to 300° F., said quenching liquid thus condensing out only high boiling material in said stream and diluting and washing away the condensed high boiling material while maintaining the major portion of said gasiform material above its dew point.

2. The process of claim 1 wherein said separated gasiform materials are at a temperature of about 1200 to 1400° F. prior to quenching, and are ultimately quenched to a temperature in the range of 300–600° F. in at least three stages of substantially equal temperature drops.

3. The process of claim 1 wherein the residence times of the gasiform materials is progressively greater in said plurality of quenching stages, the overall residence time

in said plurality of quenching stages being less than 0.2 second.

4. The process of claim 1 wherein the quantity of quenching liquid used in each stage ranges between 18 to 30 lbs./hr. per barrel per day of feed.

5. In a transfer line chemicals coking process wherein a suitably preheated oil feed is introduced into a disperse phase, rapidly flowing, inert solids stream maintained at a temperature of about 1200–1600° F., said oil feed thus being converted to a gasiform product stream and carbonaceous material which deposits on said solids, and wherein said gasiform product stream after being separated from said inert solids is at a temperature of about 1200 to 1400° F., the improvement which comprises passing said separated gasiform product stream through three quenching stages of successively increased residence periods, injecting quenching liquid into each of said quenching stages in amounts sufficient to be only partially vaporized while cooling said product stream by about 200 to 300° F. in each of said stages, the heavier ends of said gasiform product stream being thus condensed while maintaining the major portion of said gasiform product stream above its dew point and said unvaporized quenching liquid acting to dilute and wash away condensed high boiling hydrocarbons in each stage.

6. The apparatus of claim 7 wherein said plurality of quenching chambers comprising several successive conduits integrally connected to each other, said conduits having a common longitudinal central axis, and wherein the diameters of said conduits are of successively greater size.

7. An apparatus adapted for carrying out hydrocarbon conversion operations, which includes in combination, a vertically arranged reaction vessel having an inlet and an outlet, a gas-solids separating unit, a pipe connecting said reaction vessel outlet with said gas-solids separating unit for passing reaction product effluent from said reaction vessel to said separating unit, a plurality of separate quenching chambers arranged in succession and in spaced relation and spaced from said separating unit, a pipe for conducting separated gasiform reaction products from said separation unit to the first of said quenching chambers, tubular means for connecting said quenching chambers in succession whereby gasiform products to be cooled are passed through said quenching chambers in series, said quenching chambers being of successively larger volume in the direction of flow of gasiform products therethrough, inlet means opening into the top of each of said quenching chambers for introducing a quenching medium into each of said quenching chambers and outlet means communicating with the bottom portions of said quenching chambers for withdrawing liquid collecting in said quenching chambers.

8. An apparatus adapted for carrying out hydrocarbon conversion operations, which includes in combination, a vertically arranged reaction vessel having an inlet and an outlet, a gas-solids separating unit, a pipe connecting said reaction vessel outlet with said gas-solids separating unit for passing reaction products effluent from said reaction vessel to said separating unit, a plurality of quenching chambers arranged in succession and spaced from said separating unit, a pipe for conducting separated gasiform reaction products from said separation unit to the first of said quenching chambers, tubular means for connecting said quenching chambers in succession whereby gasiform products to be cooled are passed through said quenching chambers in series, inlet means for introducing a quenching medium into the top of each of said quenching chambers and outlet means communicating with the bottom portions of said quenching chambers for withdrawing liquid collecting in said quenching chambers.

9. An apparatus according to claim 7 wherein said tubular means includes pipes for spacing and connecting said quenching chambers, and said outlet means in-

cludes a pipe leading from each quenching chamber for withdrawing liquid from each of said quenching chambers.

10. A process according to claim 1 wherein the separated gasiform material is passed through a confined passageway leading from said gas-solids separation zone to said first quenching stage spaced laterally from said separation zone and liquid is withdrawn from the bottom of said quenching stages.

11. A process according to claim 1 wherein the separated gasiform material is passed through a confined passageway leading from said gas-solids separation zone to said first quenching stage spaced laterally from said separation zone and liquid is separately withdrawn from the bottom of each quenching stage.

12. A process according to claim 5 wherein condensed heavy ends are withdrawn from the bottom of said quenching stages.

13. A process according to claim 5 wherein condensed heavy ends are withdrawn separately from the bottom of each quenching stage.

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