CONTACTING LIQUID HYDROCARBONS IN A MOVING BED HYDROCARBON CONVERSION SYSTEM

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Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5.

INVENTOR
William W. Weinrich

BY
Mark Kevit

ATTORNEY
The present invention relates to systems and methods for conversion or other processing of hydrocarbons in contact with a granular contact mass and is particularly directed to contacting of hydrocarbons in liquid state with such granular mass. The invention is especially concerned with those systems and operations wherein the granular contact mass is circulated to and from a reaction zone or treating zone and during such circulation is elevated from a lower to an upper level in the system by a lifting fluid stream.

Various hydrocarbon conversion or treating operations employ systems of the type above designated; for example in catalytic conversion of hydrocarbons using a moving bed of adsorptively granular catalyst as in cracking, desulfurization, reforming, etc. Other operations coming into consideration include those wherein a granular contact mass, having little or no catalytic activity, is employed chiefly as a means of transferring contained sensible heat to an oil to be processed, whether for the purpose of thermally cracking or pre-cooking the oil, or for heating the same to required reaction temperature or to vaporization temperature in the case of previously unvaporized liquid oils. While certain aspects of the present invention are applicable to operations of the various types hereinbefore designated, the invention will be more particularly described in connection with the cracking of normally liquid hydrocarbons in contact with adsorptive catalysts, to products of lower boiling point and lower molecular weight, such as products in the gasoline-boiling range.

Normally liquid hydrocarbons when subjected to certain elevated temperatures, whether or not in the presence of a catalytically active mass, break down to form in part solid carbonaceous or hydrocarbonaceous deposits called "coke." As a general rule higher boiling hydrocarbons at a given cracking severity display a comparatively greater tendency to form coke deposits. Where such coke material is inherently or concomitantly formed as a result of contact of hydrocarbons at elevated temperature with circulating catalyst or other adsorptive contact mass, the cokeable material is deposited in the contact mass, and can be periodically removed therefrom by transporting the thus contaminated mass, in the course of its circulation, to a regeneration zone wherein the mass is contacted at ignition temperature with oxygen-containing gas to effect combustion of the coke and resulting restoration of the mass for further use in the hydrocarbon processing operation.

It is often found desirable in connection with moving bed hydrocarbon conversion and treating operations to contact hydrocarbons in liquid state with the hot catalyst or other hot contact mass for purposes of vaporizing and/or otherwise converting such hydrocarbons to vaporized products. The handling of hydrocarbons in liquid state, for instance, offers important advantages particularly but not exclusively in connection with further cracking of condensed gas oil from a catalytic cracking operation; also in cracking or pre-cooking of high boiling liquid fractions not readily vaporized below coking temperatures, such as fractions obtained as bottoms in flash vaporization of a crude oil or other oil charge; and in other operations generally where it is sought to take advantage of the sensible heat content of hot catalytic or other contact mass from regeneration by directly transferring heat therefrom to relatively cooler hydrocarbons. In practical operation considerable difficulty has been experienced in distributing the liquid oil uniformly in or on the contact mass, and non-uniform distribution of the oil results in deficient conversion or processing of the oil by reason of localized cooling of the granular contact mass and in irregular distribution of coke in the contact mass, resulting in regeneration difficulties, such as the development of localized hot spots during regeneration of the contact mass. In addition, liquid hydrocarbons in or on the intended contact with the granular contact mass, may deposit on metallic or other hot surfaces of the apparatus adjacent to the zone with consequent coking, leading to the undesirable accumulation of interfering quantities of coke on such surfaces. Accumulation of coke on non-circulating contact mass which cannot be subjected to regeneration, or on parts of the apparatus as a result of coke-producing hydrocarbons remaining on the hot walls thereof, in many instances constitutes a severe problem, often to the extent of precluding practical adaptation of a processing technique that would otherwise be highly desirable from the standpoint of efficiency and economy of operation.

Hydrocarbon conversion systems have been in commercial use wherein a granular contact mass, such as catalyst, moves through hydrocarbon conversion zones and through burning or regeneration zones as compact beds and during the course of circulation is raised to elevated position above such zones by mechanical elevators. In more recent installations elevation of the contact mass is effected pneumatically through one or more lift conduits; various kinds of lift gases have been proposed or used for this purpose. Typical systems operating on the gas or vapor lift principle are described in an article entitled, "Houdrillow; new design in catalytic cracking," appearing in the "Oil and Gas Journal," page 78, January 13, 1949. In these systems the contact mass is continuously fed by gravity to a lower transfer zone or lift hopper wherein it is contacted with lift gas which suspended the contact mass and elevates the same into and through an upright lift conduit whose entrance is imbedded in the mass contact material in the hopper.

The contact material under the influence of the introduced lift gas is impelled to enter the entrance of the lift conduit in a state of relatively high concentration and at initially low velocities. During the elevation the contact material is accelerated up to some practical maximum velocity generally at about the discharge region of the lift conduit through pressure changes within the lift conduit the state of relatively high concentration diminishing slowly over a relatively short initial period to a more and more dispersed condition during passage through the lift conduit.

In accordance with the present invention hydrocarbons at least partially in liquid state are discharged into contact material moving generally upward in an unobstructed path below the entrance of the lift conduit and in a region wherein relatively high concentration of contact material exists. In this manner uniform and complete contact or adsorption of the liquid on the contact material is provided. Operating in this manner coke or hydrocarbonaceous material, as it may be formed as a result of subjecting the liquid hydrocarbons to the high temperatures prevailing in the vicinity of the lift entrance, is deposited in or on the contact material that is in positive motion into and ultimately through the lift path and which
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... can be subjected to regeneration as required. Transference of unabsorbed liquid as such in the elevating stream and subsequent discharge into a reaction zone or the like into which the elevated contact material may be discharged for further contacting operations is also prevented.

In operation of the invention sufficient gaseous material is supplied to maintain such elevated contact material in suspension and to effect transportation thereof through the lift path. To provide an unobstructed path below the lift conduit, the liquid hydrocarbons are discharged spirally around the lift path in the form of a liquid ring adjacent to the lift path and directed generally downwardly and inwardly to direct contact with the granular contact mass during the initial flow toward and into the lift path and while still in a state of relatively high concentration. The contact mass being present in comparatively high concentration and moving in its impelled path constantly toward the lift path presents a state wherein the liquid hydrocarbons can be substantially completely and uniformly distributed on contact material in the process of transference from a compact state to a more dispersed state.

In typical procedures directed to the preparation of a charge stock for catalytic cracking, a bottoms fraction of oil or other high boiling fraction containing heavy ends which are not vaporized at the prevailing heating temperature, may be sent from the preheating furnace to a flash distillation zone, providing a vapor effluent and a high boiling liquid fraction. The system and operation of the present invention are advantageously adapted to the handling of both the liquid and vapor product forms from such flash distillation zone. Convenienly such vapor products may be employed as all or part of the lifting fluid for the granular contact mass, while the liquid hydrocarbons are introduced directly at the lift entrance on the moving contact mass as above indicated. The vapor introduced into the lift conduit for lifting or assisting in lifting of the granular solid contact material therein is, of course, not limited to such vaporous effluent from flash distillation, and may be any gas or vapor not incompatible with hydrocarbons, but is preferably hydrocarbon vapor and/or steam. When hydrocarbon vapors are employed as lifting fluid or to assist in lifting the granular catalyst or other contact mass, such vapors may comprise all or a part of the vaporous effluent from a tar separator or other flash distillation apparatus. The liquid hydrocarbons may comprise the non-vaporized fraction from flash distillation, preferably free from tars and other objectionable solids present in tar residues. Alternatively the liquid feed may be composed in whole or part of heavy liquid separated from products of cracking, either recycled from the particular cracking operation or from some other source.

The operation of the novel features of the invention will be understood and other advantages thereof appreciated from the description which follows, read in connection with the accompanying drawings illustrating one form of apparatus that may be employed in practice of the invention, wherein:

Figure 1 is a schematic representation in elevation of the hydrocarbon conversion system employing a lift conduit for elevation of catalyst or other contact material and particularly illustrates the arrangement of the lift conduit and the processing or treating vessels directly associated therewith;

Figure 2 is a partial view in vertical section of the transfer zone and a portion of lift conduit associated therewith;

Figure 3 is a plan view taken along the line 3—3 of Figure 2;

Figure 4 is an enlarged view of a section of the liquid distributing member, of Figure 2, as it appears from underneath, and

Figure 5 is a cross-sectional view of Figure 4 taken along the line 5—5.

Referring now particularly to Figure 1 there is shown a transfer zone 1 into which catalyst or other contact material is continuously admitted through the conduit 2 to form a bed within the zone maintained at a substantially constant level as indicated at 3; rising vertically from the transfer hopper 1 is a lift conduit 4 having its inlet end, in the illustrated embodiment, below the maintained level indicated at 3. The lift conduit 4 extends for a substantial distance above the top of the transfer zone 1 and has its upper terminal within a separating or disengaging vessel 5 which is provided with a discharge conduit 6 at or near the bottom thereof.

Conduit 6, in the embodiment shown, discharges into a rector or purging vessel 7 which in turn is connected by means of conduit 6 to a regeneration vessel 9. By the arrangement described, catalyst or other contact mass is continuously circulated from the bed in the transfer zone 1 upwardly through the lift conduit 4 discharging into the vessel 5 and then passes through a downward path comprising conduit 6 and vessel 7, conduit 8 and vessel 9 and conduit 2 and returns to the transfer zone 1.

The discharge line 19 communicates with the upper portion of vessel 5 above or separate from the outlet of conduit 4 therein to carry off vapors separated from the granular mass. The discharge line 19 communicates through a branch line 20 with the reaction vessel 7 through which all or a portion of the vapors in line 19 may be brought into the vessel 7.

In the illustrated embodiment the vapors are brought into the top of vessel 7 and passed concurrently with the solid granular contact mass gravitating therethrough, and vaporous products are withdrawn from the vessel by means of a vapor discharge line 21. It will be understood that the vapors may be passed upwardly through vessel 7, if desired, for countercurrent contact with the descending bed of contact material therein instead of the previously described concurrent operation. In either event, provision is made in the vessel 7 to purge or otherwise remove included and occluded hydrocarbon vapors from the contact material to prevent admixture of incompatible vapors or gases subsequent to the passage of the contact material from vessel 7 through line 8. A suitable amount of inert gas such as steam may be introduced to such a purge region through line 22. The conduit 8 between vessels 7 and 9 operates as a transfer member and also as a seal leg to prevent transference of gases in vessel 7 or 9 and a small amount of inert or seal gas may be flowed into such seal leg to effect such sealing and may be a portion of the gas introduced through line 22, or may be separately introduced to flow in conduit 8 in appropriate direction depending upon the position of the bottom portion of vessel 7 and the top of vessel 9.

The regenerating vessel 9 may be of any known or desired construction. In the illustrated embodiment shown the regenerating gas is supplied through line 23 with countercurrent flow through vessel 9 and removal therefrom through line 24. In order to prevent intermixing of incompatible gases and also if desirable to provide the sealing fluid between the base of vessel 9 and transfer zone 1 a suitable purging and/or sealing medium may be introduced as through line 25. The vapors introduced through line 23 are distributed as desired within vessel 9 and after regeneration of the contact material gravitating therethrough by passing in countercurrent relation thereto, are removed as flue gases as above indicated through line 24. The regenerated catalyst in heated state gravitates from the base of vessel 9 through conduit 2 and provides the continuous liquid supply within transfer zone 1 with an upper level established at 3.

Referring to Figure 2, where there is a showing of the region comprising the transfer zone, the lift conduit 4 is surrounded by a concentric sleeve or housing 10 which terminates at its lower end at or about the level of the lift pipe entrance. There is thereby formed between the outer wall of conduit 4 and the inner wall of sleeve 10...
an annular chamber 11 open at the bottom end 12 and sealed at its top end 13. The top end of sleeve 10 is in communication with a vapor supply line 14. At an upper portion of the transfer zone 11 there also may be provided an additional vapor inlet as indicated at 15 for reasons which will hereinafter appear.

In Figures 2 and 3 it will be seen that the lift conduit 14 is peripherally surrounded at the bottom thereof by a fluid distributing manifold 16, which is provided with suitable perforations, slots or the like, 16a which open generally downwardly and inwardly for communication with that portion of the contact material designated as 17; a liquid supply line 18 communicates with manifold 16 for furnishing liquid hydrocarbons thereto for distribution to the catalyst in the region 17.

In the illustrated embodiment thus far described, the lift vapors, such as steam and/or hydrocarbon vapors, are introduced at the required pressure and in required quantity through line 14 into the annular zone 11 between the sleeve and the lift conduit. These vapors flow downwardly in the annular zone 11 and issue through the bottom 12 of that zone as an annular stream which flows to a level somewhat below the lower end of conduit 4. The vapors then reverse their direction of flow and pass upwardly to the lift conduit 4. In doing so the vapors contact granular material from the bed in hopper 1 which lie in the vapor path adjacent the lower ends of sleeve 10 and conduit 4, causing the granular material to pass below the lower periphery of conduit 4 and upwardly into that conduit. The granular material is then impelled upwardly in the conduit 4 by the vapors passing into and through that conduit, and is discharged from the upper end of the conduit into the disengaging vessel 5. Because of the expanded cross-sectional area of the vessel, the vapors discharged therefrom in conduit 4 lose velocity to the extent that the granular material is no longer supported by the vapors and settles out therefrom to accumulate as a bed in the vessel 5.

The illustrated embodiment of Figure 2, hydrocarbons in liquid state are introduced into contact with the inwardly and upwardly moving granular material in the region generally designated as 17. As shown the liquid hydrocarbons are introduced through supply line 18 into the peripheral distributing ring or manifold 16 and are discharged generally downwardly and inwardly through opening 16a to contact the granular material moving therepast. Although opening 16a is represented as a continuous slot discharging the liquid hydrocarbon in a substantially complete circular pattern it will be understood that other suitable means of permitting egress of the liquid hydrocarbon may be employed such as multiple vents, slots, ports or the like preferably discharging in a generally circular pattern more or less uniformly distributed around the radial axis of the granular material.

Liquid hydrocarbons thus introduced through line 18 and peripheral distributing member 16 surrounding the entrance to the lift path of the lift conduit 4 are distributed in and on the moving mass of granular contact material.

In practical operation such granular material will be at an elevated temperature and will transfer heat to the liquid hydrocarbons, thus heating the same to desired temperature and effecting substantial vaporization of the hydrocarbons, which may be accompanied by conversion, to more or less extent, to cracked products, with concomitant deposition of coke.

Liquid thus introduced at the entrance to lift pipe 4 should be made with relatively complete and uniform distribution of the liquid hydrocarbons on the granular contact material so that adsorption thereon is assured in order that no non-absorbed liquid as such may be carried with the rising stream for discharge into separating vessel 5. As long as complete or substantially complete vaporization and/or adsorption of the liquid is obtained by contact with the moving granular material the relative amount of vaporization versus adsorption is, to some degree, of minor importance in that the presence of free liquid which is undesirable in subsequent stages is avoided by the proper contact with the granular material; however, in general since the process is directed to the processing of vapor from hydrocarbons the greater the amount of vaporization the more desirable the process.

To prevent flow of hydrocarbon vapors introduced to transfer zone 1 in any direction other than the intended direction i.e., into and through the lift path, a suitable gas under pressure may be maintained in the regions external to the desired flow path of the introduced lifting vapors, such gas should be maintained at a pressure above the level substantially equal to the pressure of vapors thus introduced specifically as the lifting vapors. For this purpose seal gas which may be steam or other inert gas admitted into the catalyst inlet line 2 such as through line 25 may be introduced at a suitable pressure so that a portion of the gas flows concurrently with the catalyst down conduit 2 and thus furnishes an effective restraining blanket generally insuring flow of liquid gases and admitted liquid in the proper and desired direction; or in addition, seal gas might be introduced directly into transfer zone 1 above the catalyst level 3 by means of the valve controlled inlet line 15. The use of steam for this purpose has the advantage of providing at least a portion of the steam that may be desired as process steam generally added to the hydrocarbon conversion reaction involving higher boiling hydrocarbons including the type introduced as liquid in this system.

The vapors entering the lift path 4 together with such vapors formed from vaporization and conversion of the liquid feed which is introduced through peripheral member 16 are discharged together with catalyst into the disengager vessel 5. Any liquid hydrocarbons that are not vaporized in the lift conduit are completely adsorbed by the catalyst and will be largely vaporized or converted by remaining in contact with the catalyst in vessel 5, in gravitation of the catalyst therein and discharge through conduit 6, and subsequently during passage through reaction vessel 7. A portion of the vapor products desengaged from the catalyst from the top of the lift may pass downwardly with the gravitating catalyst in vessel 5 and be discharged into the vessel 7 by means of conduit 6. All or part of the hydrocarbon vapors discharged from vessel 5 through line 19 are brought into the reactor 7 by means of branch line 20, and are subjected to further conversion in contact with the catalyst in that vessel. Unvaporized liquid hydrocarbons, if any, carried by the catalyst into vessel 7 in adsorbed state will be vaporized and/or converted in the reactor as hereinabove described and the total vapor conversion products and unconverted vapors are withdrawn from reactor 7 through line 21 through which they flow to suitable apparatus, not shown, for separation into desired fractions or other processing as desired.

The catalyst, continuing its descent in vessel 7, is subjected to purging to remove adsorbed or occluded vapors by means of steam or other inert gas admitted through line 22 and the purged catalyst is then discharged through conduit 6 into the regeneration vessel 9 and in that vessel or kiln the catalyst is contacted with an oxygen-containing gas to effect combustion of coke in the catalyst, which reaction raises the catalyst in temperature and stores sensible heat therein to be subsequently employed for vaporization of liquid hydrocarbons, heating of hydrocarbon vapors to reaction temperature, and providing sufficient heat to continue the desired reaction in spite of the endothermic nature of the reaction involved in the cracking of hydrocarbons.

In the illustrated embodiment illustrated in Figure 2 a vapor inlet line 26 is shown, operatively to introduce vapors upwardly through the catalyst bed. In employing this arrangement vapors admitted through line 26 at a comparatively low velocity merely serve to reduce resistance in the catalyst bed below the lift path 4 so that the catalyst is more
readily picked up by the annular stream discharged into the bed through sleeve 10. The vapors admitted through line 26 mingle with the vapors discharged from the annular chamber 11 passing together upwardly into the lift path 4 and initiating movement and elevating the granular contact material engaged by these vapors. By regulating the rate and quantity of vapors admitted respectively through lines 14 and 26 efficient control of the circulation rate of the contacting material can be maintained. Vapors introduced through lines 14 and 26 may be of the same or different compositions; for instance steam may be admitted through one of these lines and hydrocarbon vapors through the other. The line 26 may be an open ended pipe or may be associated with a diffuser head of suitable design. As shown at 27 the discharge outlet of line 26 may be provided with a suitable baffle or screen to prevent granular material from falling into the pipe and at the same time assisting in the diffusion and distribution of the gas introduced through line 26.

The amount of liquid in such practical operations generally should not exceed about ½ of the catalytic volume and preferably should not be in excess of ¼ of the catalyst volume. The quantity of vaporized hydrocarbons charged in addition to the liquid hydrocarbons will depend upon the operating conditions established for the principal reaction zone (compact moving bed reactor), including the selected catalyst to total hydrocarbon ratio as one of these conditions. Such additional vaporization of hydrocarbons has been introduced entirely or only in part into the lift conduit as previously described to serve as lifting vapors and additional hydrocarbon may be brought into the contact reactor as by means of line 28, designed to make up the required hydrocarbon to catalyst to oil ratio.

The chamber 5 should be maintained at a sufficient pressure above atmospheric so that the vapor product discharged through line 19 can be sent into the process vessel 7 and through that vessel with accompanying pressure drop to be discharged through line 21 at a pressure such that the vapor effluent can be sent to further processing without necessitating pressure boosting. Generally the pressure at the discharge line 21 should be in the order of at least about 6 p. s. i. g. Efficient and smooth operation of the lift with adequate mass flow rate of solids to obtain adsorption of the liquid hydrocarbons contacted therewith, can be obtained under lift operating conditions prevailing with a pressure drop of above 1 to about 12 p. s. i. g. in the lift conduit 4, so that the pressure in transfer vessel 1 immediately below the lift path 4 must be sufficient to take care of the pressure drop in the lift path, in lines 19 and 20, through the bed in vessel 7 and to provide the desired discharge pressure at line 22. The required pressure in transfer vessel 1 will determine the pressure of introduction of vapors through line 14 or through that line and line 26, if the latter is employed.

As a general rule, practice of the invention does not necessitate a departure from the usual processing conditions used in conventional systems for carrying out hydrocarbon conversion reactions, for instance those employing gravitating compact beds of catalyst or other contact mass, as in catalytic cracking of hydrocarbons to gasoline, catalytic reforming of naphthas to products of improved quality, or corresponding non-catalytic operations wherein the granular contact mass is relied upon chiefly as a heat source.

As catalysts for hydrocarbon cracking operations there may be employed the known silica-alumina and other cracking catalysts including acid-activated clay pellets or synthetic silica-alumina in the form of cylindrical or spherical pellets (beads), of a size range designated as granular as distinguished from finely divided powders of up to 100-200 mesh size. Such granular catalyst or other solid contact mass is characterized by the property of forming compact beds through which gases and vapors can be passed upwardly at practical operating velocity without significantly disturbing the bed, as distinguished from finely divided powders which are impelled or form “fluidized” beds by passage of gases or vapors throughput at considerably lower velocity. The granular catalyst or other contact mass employed in practice of the present invention should generally be of a size greater than about .05 inch in major dimension, and up to about .15 inch.

Obviously, many modifications and variations of the invention as hereinafter set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

1. The method for contacting hot granular contact material with liquid hydrocarbons and effecting concomitantly transportation of said granular contact material and vaporization of said liquid hydrocarbons, which comprises continuously supplying said hot granular contact material to a transfer zone to form a compact bed of said granular contact material in said zone, introducing gaseous material compatible with hydrocarbons into said bed and under pressure to initiate elevation of a portion of said contact material and suspension in said gaseous material, directing said gaseous material and said contact material in a state of relatively high concentration through an unobstructed path into a laterally confined lift path, the entrance to which confined path is circular in cross-section, and lies below the top level of said compact bed, and said unobstructed path has a cross-sectional area at least equal to that of said entrance, discharging liquid hydrocarbons peripherally around the entrance to the lift path and in a direction generally downwardly and inwardly from about the level of said entrance to directly engage said contact material moving in said unobstructed path toward and into said confined lift path but prior to its entry into said confined path and while said contact material is in a state of relatively high concentration, and transporting said contact material through said confined path under the influence of said introduced gaseous material and of gas produced by contact of said liquid hydrocarbons with the hot contact material.

2. The method of converting higher boiling liquid hydrocarbons to products of lower boiling points in contact with granular adsorptive catalyst, which comprises heating and partially vaporizing such liquid hydrocarbons by contacting the same in liquid state with heated solid of a temperature capable of causing coking of said liquid hydrocarbons, said contacting being effected by engaging said hot catalyst while in a state of relatively high concentration and while being impelled and elevated through an unobstructed path into a laterally confined lift path but prior to entrance into said confined lift path with a peripherally introduced stream of said liquid hydrocarbons directed generally downwardly and inwardly from a level approximately the entrance to said confined lift path, said hot catalyst being so impelled and elevated by a flowing gas stream compatible with hydrocarbons, discharging said catalyst from said confined lift path to terminate upward movement of said catalyst, thereafter passing said catalyst by gravity as a compact bed through a conversion zone, and contacting said bed of catalyst in said conversion zone with at least a portion of the hydrocarbon vapors formed from said liquid hydrocarbons to effect desired conversion of hydrocarbon vapors under catalytic conversion conditions.

3. The method in accordance with claim 1 wherein said gaseous material comprises hydrocarbon vapors.

4. The method in accordance with claim 1 wherein said contact material is catalyst having cracking activity.

5. In apparatus for contacting fluids with contacting solids circulating through an upward path comprising a gas lift and a downflow path comprising at least one zone of relatively large cross-sectional area in which said solids grav-
tate as a compact bed and a lower transfer zone comprising a lift hopper, means associated with said hopper adapted to admit thereto supply of said solids, a lift conduit adapted to continuously remove said solids from said hopper under the influence of lift gas introduced through an annular member adjacent said lift conduit, the improvement in apparatus for the introduction of liquid into uniform distribution on said contact solids in the region immediately below the entrance to said lift conduit which improvement comprises a circular tubular member surrounding the lower outer periphery of said lift conduit, said tubular member having liquid introduction means, and liquid discharge passage-forming means disposed around the inner periphery of said tubular member, said discharge passage-forming means being directed inwardly and downwardly for effecting distribution of liquid on the contact solids therebelow.

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