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METHOD AND APPARATUS FOR CONVERSION OF HYDROCARBONS

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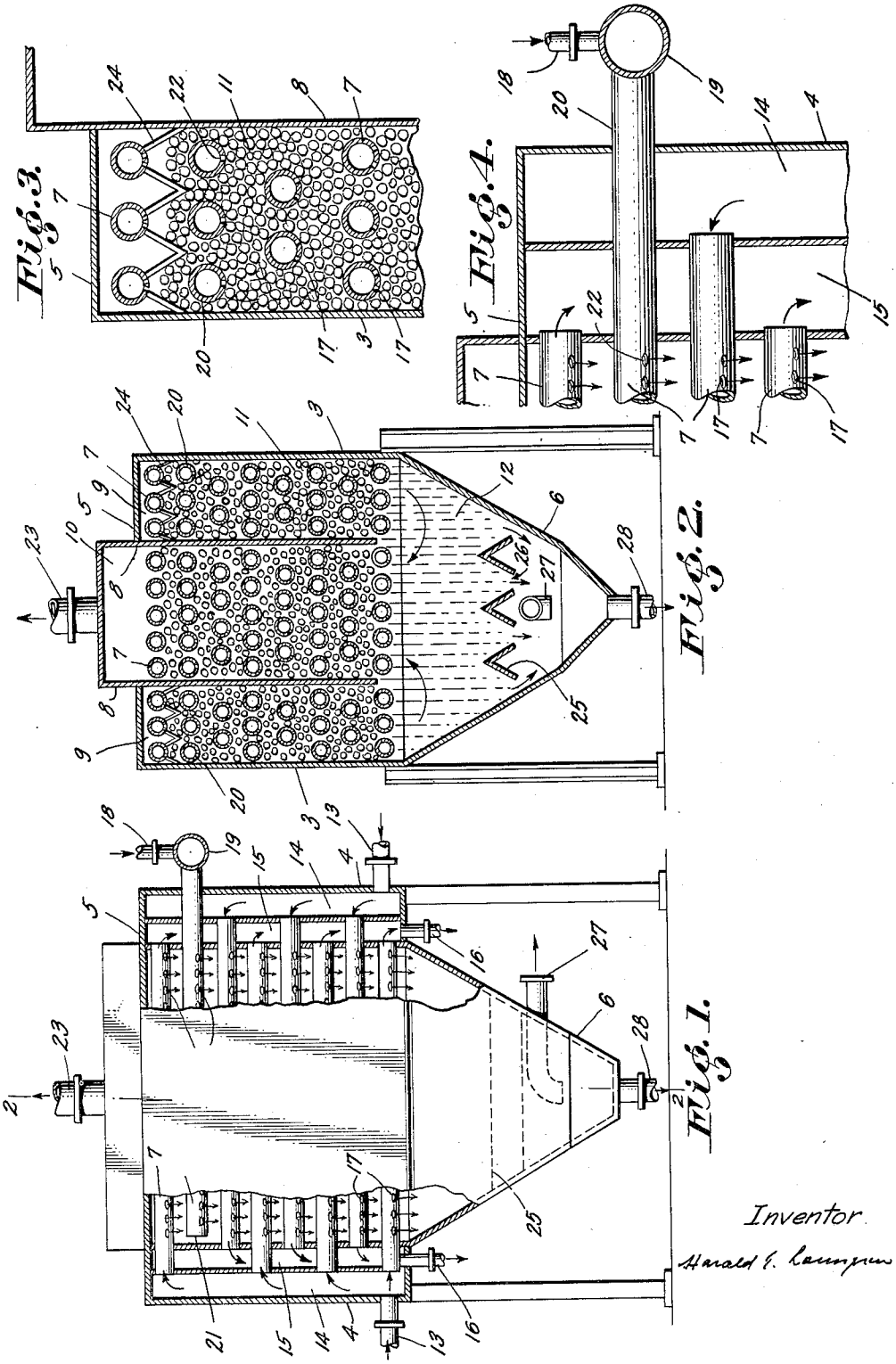


Fig. 3.

Fig. 4.

Fig. 2.

Fig. 1.

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METHOD AND APPARATUS FOR CONVERSION OF HYDROCARBONS

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3 Claims. (Cl. 196—52)

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My invention relates to a method and apparatus for conversion of fluid hydrocarbons and has particular reference to the art of treating hydrocarbons thermally so as to effect distillation and molecular re-arrangements of them. More particularly my invention relates to a continuous endothermic distillation process wherein the coking of high boiling fluid hydrocarbons produces a granular, readily removable pure mass of coke, as said hydrocarbons are heated in one step to a temperature level of about 900–1500 deg. F. without coming in direct contact with metal portions of the process apparatus.

One object of my invention is to effect endothermic conversion of fluid hydrocarbons by heating them to suitable conversion temperature levels in such a manner that formed coke can not adhere to metal portions of the process apparatus. This is accomplished by cascading molten lead of a temperature of about 1000–2000 deg. F. externally over tubular heat exchange members and along all interior surfaces of the process apparatus. In this manner the hydrocarbon reactants come in direct contact only with molten masses of previously heated lead onto which the formed coke will adhere. The heating of the reactants for their endothermic conversion is effected by molten lead which is simultaneously passed thru the tubular members.

Another object of my invention is to reduce in a confined space, by simple destructive distillation, high boiling fluid hydrocarbons to lower boiling vaporous fractions in the presence of a moving, previously heated fluidized metal mass, arranged to cascade over tubular heat exchange members in such a manner that the formed coke will solidify as it comes in contact with said fluidized metal mass and can not be carried in suspension by the vapors which thus are obtainable free of entrainment.

Still another object of my invention is to conduct a complete hydrocarbon conversion process —using mobile, fluidized metallic coke removing means in the heating and cracking steps—within the true realm of one and the same process apparatus, the heating step of which process in particular is effected in such a manner that there will be no temperature gradient in the direction of the flow of the hydrocarbons.

A further object of my invention is to effect the supply of heat to the hydrocarbon reactants for their endothermic conversion in such a manner that the control thereof is simple and expeditious.

A specific object of my invention is to provide

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an apparatus for conversion of fluid hydrocarbons which can be quickly and inexpensively heated up from a cold state without undue temperature strains.

Another specific object of my invention is to nullify the well-known detrimental influence from formed coke in an endothermic hydrocarbon conversion process so as to obtain entrainment-free vapors in a continuous once-thru manner of operation. For this purpose I provide within a confined space a great surface area of cascading molten lead to which the formed coke has a great affinity.

Still another object of my invention is to make it possible to use crude oil directly for conversion purposes. This is feasible in my conversion method and apparatus because the formed coke and other mineral impurities can not hamper the conversion steps when their disturbing influence is nullified by cascading masses of molten lead which wash away solidified coke and other solid matter.

Other and further objects of my invention will hereinafter appear from the ensuing description and claims.

The prior art—particularly the so called catalytic cracking phase of it—ascribes the character of catalysis to a foreign substance which is primarily used to convey the required heat to the process mass. I have found that the formed coke is the real catalyst in as much as it retards the chemical conversion of hydrocarbons without itself being chemically involved. That this is so is readily appreciated by the fact that coke-free hydrocarbon reactants do not need a catalytic aid for proper and expeditious interaction. I have discovered that formed coke has great affinity to lead in molten state. By thus allowing it to freely adhere to cascading masses of molten lead, as soon as it is being formed, a granular solidified coke is caused to be formed which lends itself readily for removal by simple means in a continuous manner. This represents an important advance in the art because adherent coke must be burned off in present catalytic conversion methods.

My invention is fully disclosed in this specification and claims, reference being had to the accompanying drawing.

In the accompanying drawing

Fig. I represents an elevational view, partly in section, of an apparatus in which my invention may be performed and comprises essentially a rectangular housing, inlet header and tubes for the oil, inlet and outlet headers and tubes for

the molten lead, packing between the tubes, bottom hopper for collecting lead and precipitated coke, a spray zone, partition baffles and outlet plenum box for the vapors.

Fig. II is a cross-sectional view along line 2—2 of Fig. I showing the tube bundle and other details.

Fig. III is an enlarged cross-sectional view of the oil heating zones, showing the relationship between oil inlet tubes and the lead containing tubes, also roof deflector plates in said zones.

Fig. IV is an enlarged detail of upper right hand corner of Fig. I, showing oil inlet header and tubes, also lead inlet and outlet header compartments and tubes. It will be noted that molten lead is passed thru alternate horizontal rows of tubes in both directions, as indicated with arrows.

My hydrocarbon conversion apparatus is constructed of 18–8 CR–Ni steel plates welded together. This material can readily withstand the called for high process temperature. The apparatus is of a rectangular shape and resembles a large box with long sides 3, 3, end portions 4, 4, top portion 5 and bottom portion 6. A multiplicity of tubes or pipes 7 are spun horizontally between the two end portions 4, 4 which are constructed so as to form headers or plenum boxes into which the tubes are rolled or welded. The thus formed tube bundle is partitioned with vertical baffle plates 8 into three banks or zones, the two outer ones 9, 9 of which serve as oil heating and vaporization zones and the center bank 10 as the reaction zone. The space between the tubes in each bank is filled with small size alloy steel balls 11 of varying diameter. This ball mass forms a so called packing. Directly below the tube bundle there is an unrestricted space or compartment 12 which serves as a scrubbing zone.

In my method of effecting conversion of fluid hydrocarbons the required heat is transmitted to the oil mass from previously heated lead which is pumped thru the apparatus in molten state. The molten lead—heated in a separate apparatus (not shown)—is conducted thru lines 13, 13 into the inlet header compartments 14, 14 of the end portions 4, 4 of the housing proper. From these compartments it then flows thru therewith connected tubes 7 to the outlet header compartments 15, 15 of said end portions 4, 4 as indicated with arrows. It will be seen that the molten lead masses flow in one direction thru every other horizontal row of tubes and in the opposite direction thru the intermediate rows. The lead mass is re-circulated to the source of heating thru lines 16, 16 in the outlet header compartments. A certain portion of the thus circulated lead mass is caused to cascade over the external surfaces of the tubes 7 and over the packing by diversion thru a multiplicity of apertures or holes 17 in the tubes. The entire tube bundle with the packing can thus be readily visualized as a fixed, porous hot bed thru which molten lead flows in the downward direction. Thru this bed the oil feed and the ensuing hydrocarbon vapors are passed simultaneously with the lead.

The oil is pumped thru line 18 into a header 19 wherefrom it passes into oil distributing tubes 20, 20. These tubes are blanked-off with caps 21 at the free end and the oil feed emerges thru a multiplicity of apertures or holes 22, 22 in said oil distributing tubes. The thus fed oil mass is heated and vaporized as it comes in contact with the cascading hot lead which is kept at a high temperature level thruout the contact with the

oil feed by heat in the lead mass within the tubes which heat passes thru the tube wall to the cascading lead.

The oil feed and the ensuing vapors pass thru the oil heating zones 9, 9 in the downward direction with the cascading lead. Formed coke solidifies and adheres to the cascading lead masses and is washed away with them; deposition upon the tubes or upon the small metal balls is impossible because the cascading lead forms a film on these surfaces which can not be penetrated by the coke. Cascading lead and precipitated coke drop down into the bottom portion 6.

Vaporized hydrocarbons sweep around baffle plates 8 and pass thru the reaction zone 10 in the upward direction, counter currently to the cascading lead in this zone. These vapors are thoroughly scrubbed in zone 12 by the thereinto dropping lead. Coke-free, that is, clean unstable vaporous fractions are brought into intimate contact with each other in the reaction zone. The resulting natural chemical interaction causes molecular re-arrangements of the unstable fractions and a gasoline of high quality and high octane number is thus caused to be formed. Vaporous hydrocarbons are withdrawn thru line 23 in the top portion of the reaction zone.

The top portion of each heating zone 9, 9 is provided with sloping splash plates 24, 24 against which molten lead is ejected so as to prevent coke from adhering to these plates. At the lower portion of the scrubbing zone 12 there are inverted V-shaped deflector plates 25 spun across the housing proper. These plates are so spaced that the deflected dropping lead together with the coke is discharged into the bottom, hopper-like portion 6 thru narrow passageways 26. The entrained granular coke will float upon the lead surface which is maintained at a certain constant level. Plates 25 also prevent the thus accumulated coke from being carried away by the vapors. Accumulated coke is blown out from the apparatus thru line 27 and may readily be used for heating the used lead mass in a separate apparatus (not shown). Used lead is re-circulated to the separate source of heating thru line 28.

Good results are also obtainable when the lead is substituted with zinc, tin, cadmium or bismuth or with alloys of these metals.

My method and apparatus can, of course, also be used for exothermic hydrocarbon reactions. In the polymerization or hydrogenation of hydrocarbons the exothermic heat of reaction is absorbed by the lead mass which then is circulated and cascaded at a temperature substantially below the conversion temperature.

An outstanding feature of my invention in addition to continuity of operation with entrainment-free vapors resides in the feasibility of effecting conversion of hydrocarbons with low pressures. Actually it is only necessary to use a pressure high enough to overcome the resistances to the flow of vapors thru the apparatus and the therewith communicating fractionating tower. An internal pressure of about 1–5 lbs. per sq. in. is sufficient.

The real substance of my invention is thus readily found to reside in the novel method of using molten lead, zinc, tin, bismuth or cadmium or alloys of these metals as a means of supplying the required energy (heat) for the endothermic conversion of fluid hydrocarbons at temperatures ranging from 900–1500 deg. F. and at pressures ranging from 1–5 lbs. per sq. in. and as a means of attracting and removing coke at the very in-

stant at which it is being formed in the progress of said conversion process so as to prevent said coke from ever coming in direct contact with metal portions of the process apparatus.

Within the spirit of my invention it is, of course, understood that the described apparatus for carrying out my process is not limited to the precise details given hereinbefore. For certain feed stocks the called for packing, for instance, may be eliminated, in which case the tubes are spaced closely to each other. Good results are also obtainable when the tubes have closely spaced fins or gills welded onto them.

What I claim is:

1. The method of continuously reducing a petroleum oil and derivatives thereof to vaporous hydrocarbon fractions and solid formations of coke which comprises passing the oil to be treated through a heating and vaporization zone, a scrubbing zone and a reaction zone within the realm of one and the same process vessel; causing molten masses of a metal selected from the group consisting of lead, zinc, tin, bismuth, cadmium and alloys of the metals to flow in said zones at a temperature of about 1000–2000 deg. F. in a downward direction so as to come in direct contact with the oil to be treated while a pressure of about 1–5 lbs. per sq. in. is maintained in said zones; subjecting the fluid oil in the heating zone to intimate contact with said molten metal masses whereby it is heated and vaporized; causing ensuing vapors to travel downward with said molten metal masses in the heating zone and to pass into the scrubbing zone; causing scrubbed vapors to flow upward through the reaction zone countercurrently to cascading molten metal masses therein; withdrawing clean vapors from the reaction zone and a granular coke from the lower portion of the scrubbing zone.

2. The method of continuously cracking petroleum oil which comprises conducting the fluid oil feed in the form of a multiplicity of downward directed jets through a heating and vaporization zone which consists of loosely arranged packing elements between a multiplicity of horizontal alloy steel tubes through which and externally over which and over said packing elements are passed molten masses of a previously heated metal selected from the group consisting of lead, zinc, tin, bismuth cadmium and alloys of these metals whereby said oil feed is vaporized upon contacting said molten metal masses and further heated in vaporous state as the ensuing vapors and the molten metal masses travel in the same downward direction in close contact with each other through said zone; causing said molten metal masses to drop downward and to form a shower zone wherein the ensuing hydrocarbon vapors are scrubbed when they are passed through said zone; supplying additional heat to the vaporous reactant mass in a separate reaction zone while the chemical reactions take place therein by means of conduction from previously heated molten masses of a metal selected from the group consisting of lead, zinc, tin, bismuth, cadmium and alloys of these metals which are introduced thereinto horizontally through a multiplicity of alloy steel tubes and emanate thereof through a multiplicity of small apertures in the walls of said tubes so as to cascade over said tubes and the said loosely arranged packing elements between said tubes in said zone; causing inherently formed coke to adhere to the cascading molten metal masses whereby this coke

can not hinder the transmittal of heat nor prevent the reactants from coming in good contact with each other; separating solidified granular coke from the molten metal masses; withdrawing clean vapors from the reaction zone and a granular coke from the lower portion of the scrubbing zone.

3. An apparatus for continuous conversion of fluid hydrocarbons into lower boiling hydrocarbons which comprises a rectangular housing with closed top and bottom portions so as to form a confined space within which the conversion is carried out the bottom portion of which housing is sloped so as to hold and contain a molten mass of lead and the end portions of which housing are constructed so as to form plenum boxes for molten lead which is passed thereinto and therethrough into a multiplicity of therewith communicating horizontal tubes, vertical partition plates in the housing which divide the confined space into communicating compartments and also direct the flow of vapors through said compartments said horizontal tubes being arranged one above another in several rows in a staggered relationship between said headers so as to permit molten lead to flow through them in both directions between said headers, a multiplicity of narrow apertures in the lower half of said tubes through which said molten lead can and will emerge substantially in a downward direction so as to cascade over other tubes in the path, a packing between said tubes comprising loosely arranged alloy steel elements, fluid hydrocarbon inlet headers together with thereinto rolled horizontal tubes which have a multiplicity of narrow apertures cut into their lower half through which the oil feed emerges substantially in a downward direction so as to cascade over the molten lead containing tubes in its path and also over the packing elements between said tubes without coming in direct contact with the metal of said tubes and said packing elements, sloping splash plates attached to the uppermost row of the lead containing tubes against which plates molten lead is splashed so as to sweep over the oil containing tubes directly thereunder, inverted V-shaped deflector plates running horizontally at a distance from the lowermost row of tubes and spaced so as to form narrow passageways for dropping lead masses and coke and so as to constitute a sealing member for the coke mass which accumulates on top of the lead surface in the bottom portion of the housing, withdrawal pipe for the coke, inlet and outlet nozzles in the end headers for molten lead, inlet nozzle in the oil header, outlet nozzle in the bottom portion of the housing for lead and outlet nozzle for hydrocarbon vapors in the top portion of the housing.

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