

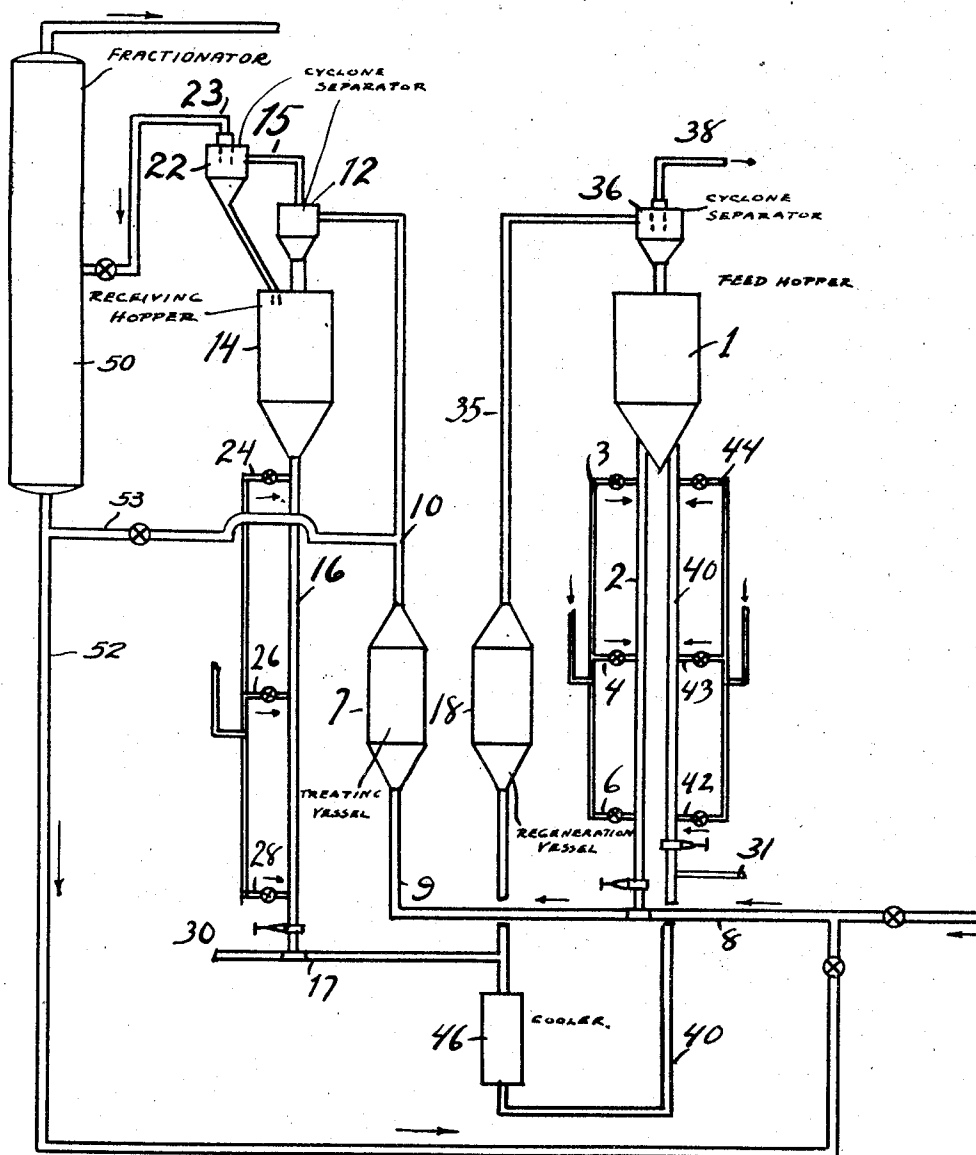
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METHOD OF TREATING HYDROCARBONS

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## UNITED STATES PATENT OFFICE

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## METHOD OF TREATING HYDROCARBONS

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The present invention relates to the art of refining hydrocarbon oil distillates, such as naphtha, gasoline, kerosene, gas oil, and the like, by contacting the said distillates in vapor phase with a solid treating material in finely divided condition, such treating material including substances such as clay, bauxite, and the like. More particularly our present invention relates to improvements in feeding the solid treating material to the treating zone without employing motivating means which involve moving parts, and our invention is fully described in the following specification and claims, reference being had to the accompanying drawing.

Prior to the present invention, it was known to treat a gasiform material with a solid material or to cause the gasiform material to undergo a chemical change in the presence of a finely divided solid material, and in these processes it was common practice to force the solid treating material into the treating zone by means of screws, such as the well-known Fuller-Kinyon pump or star-feeders. Mechanical devices such as screw-feeders have not proved entirely satisfactory as solid feeding means because of excessive wear. Another disadvantage is that screws are expensive and when they are of the compression type, the power consumption necessary to actuate the screw is excessive and impractical for many commercial operations.

The present invention will be best understood by reference to the accompanying drawing which shows diagrammatically, a form and arrangement of apparatus in which the present invention may be carried into effect.

Referring in detail to the drawing, reference numeral 1 represents a feed or supply hopper containing a finely divided solid material, such as bauxite, having a particle size substantially in the range of 1 to 80 microns. This bauxite is discharged from hopper 1 into an elongated pipe 2 where it is uniformly admixed with a quantity of a gaseous material such as carbon dioxide, nitrogen, hydrogen, a normally gaseous hydrocarbon, or the like, through a plurality of branch pipes 3, 4, and 6, to the extent that each cubic foot of gaseous material is admixed with or contains therein 10-40 lbs. of bauxite in pipe 2. From elongated pipe or conduit 2, the bauxite discharges into pipe 9 and thereafter into a treating vessel

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7, which preferably is of a substantially greater diameter than the conduit 2. Before it discharges into treating vessel 7 gasoline vapors at a temperature of about 400-950° F. are discharged through line 8 into the pipe 9 as shown. Treating vessel 7 operates at 0 to 500 lb. pressure and 400-950° F. On entering the upflow treating zone 7 of greater internal diameter than the pipe 9 the upward velocity of the vapors is decreased to ½ to 10 feet per second. Moreover, the upward velocity of the bauxite is lower than that of the vapors due to a slippage or settling effect. As a result of the foregoing, the bauxite remains for a greater period of time in the treating zone 7 than the vapors. A "jiggling" phenomenon thus takes place, with regard to the bauxite, in the treating zone, effecting an intimate contact between the gasoline and the bauxite whereby the content of sulfur, sulfur compounds and other undesirable constituents in the gasoline is substantially reduced and the octane rating is improved. The admixture of gasoline vapors and bauxite is discharged from the treating zone through conduit 10 into a primary cyclone separator 12 in which separator the major portion of the bauxite contained in the vapors is removed. The gasoline vapors which may contain some bauxite which was not removed in cyclone separator 12 are withdrawn overhead through line 15 and thence discharged into a second cyclone separator 22 where substantially the remaining bauxite is removed and passes by gravity into receiving hopper 14. The gasoline vapors substantially completely free from bauxite are withdrawn from cyclone separator 22 through line 23 and may be passed to condensing and stabilizing equipment (not shown). Any catalyst particles remaining in the gasoline vapors may be recovered as a slurry in the bottoms stream 51 from the fractionator 50 and returned to the catalytic system to the feed in line 8 via pipe 52 or through line 53 to line 10.

From hopper 14 the bauxite is discharged into an elongated pipe 16 similar to pipe 2, which pipe 16 is connected through pipe 17 to a regeneration vessel 18, which may be of the same form and construction as treating vessel 7. Pipe 16 is provided with a plurality of branch pipes 24, 26, and 28 corresponding to pipes 3, 4, and 6 carried by pipe 2, and these branch pipes 24, 26, and 28 are employed to deliver a gaseous medium such

as CO<sub>2</sub>, flue gas, steam, and the like into pipe 16 for the purpose of fluidizing the bauxite therein. The amount of gas introduced into the pipe will vary according to many factors, but ordinarily sufficient gas is introduced to cause the material at the bottom of pipe 16 to have a density of from 10-40 lbs. per cu. ft. At a point near the bottom of pipe 16 air is introduced into said pipe 17 through line 30. The air serves to reduce the density of the bauxite as did the hydrocarbon vapors in pipe 9. The suspension or mixture of bauxite and air passes upwardly through vessel 18 which, as shown, has a greater internal diameter than pipe 17 so that a slippage of the bauxite occurs whereby the bauxite remains resident in the regenerating vessel 18 for a longer period of time than do the gases. In the regeneration vessel 18 the oxygen present causes any carbonaceous or sulfurous deposits contained in the bauxite as a result of the treating operation in vessel 7 to be consumed by combustion or oxidation. The temperature during regeneration is prevented from exceeding 1200° F. by the recycling of cooled regenerated catalyst. The recycled catalyst passes from hopper 1 to pipe 40 in which the powdered material is fluidized by introduction of a gaseous medium through pipes 42, 43, and 44. The material flows out of pipe 40, mixes with air entering through pipe 31 and passes through cooler 46. This stream, together with the spent catalyst stream from 17, enters the burning zone 18. The amount of regenerated catalyst recycled may amount to from 1 to 10 parts by weight of regenerated catalyst to 1 part of fouled catalyst. The regenerated catalyst which is mixed with the fouled catalyst is preferably cooled to a temperature of about 500° F. The fouled catalyst ordinarily will be at a temperature of about 600-900° F., particularly if it is obtained directly from the treating zone. The air which is charged into the system through line 30 may be at ordinary atmospheric temperature. The pressure in the burning zone may vary from 0 lbs./sq. in. gauge to say 500 lbs./sq. in. gauge. Under the conditions specified, the regeneration of the catalyst proceeds. The regenerated bauxite, together with the gases, passes upwardly through elongated pipe 35 into a cyclone separator 36 similar in construction to cyclone separators 12 and 22. The bauxite which is separated in cyclone separator 36 from the gases is conveyed by any convenient means (not shown) to hopper 1. A good method of conveying the bauxite from separator 36 to hopper 1 is to elevate the cyclone separator 36 sufficiently so that the bauxite may flow by gravity to hopper 1 or the powder discharge of the cyclone may be connected directly to the top of the hopper 1 so that the separated catalyst falls directly into the hopper. If desired, a second cyclone separator and/or electrical precipitator may be employed to remove still further quantities of bauxite contained in the effluent gases discharged from separator 36 through line 38 and this bauxite may be returned to the hopper 1. The hot gases in line 38 are preferably employed to preheat the gasoline to vaporization temperatures. Furthermore, the system should be operated so as to take advantage of the heat content of the freshly regenerated bauxite; that is to say, the hot regenerated bauxite in separator 36 should be delivered immediately to hopper 1 and then discharged into treater 7 so that advantage may be taken of its heat content.

This process allows the catalyst to be used for

long periods before regeneration becomes necessary; part of the spent catalyst can be recycled to the reactor by means not shown. This recycle catalyst can be heated so as to furnish the heat absorbed by the reaction.

The operation just now described in connection with the apparatus is merely one form or embodiment of the present invention and the process is applicable to clay treating of hydrocarbon oils in vapor phase, to hydrofining and similar processes in which a solid treating material contacts gaseous material in vapor phase.

With respect to the successful operation of the device, it will be understood that the mechanical energy used to transport the materials results from the difference between the density in the fluidized catalyst pipe 2 and the density in the reactor and pipes 9 and 10; that is to say, the product of the density times the height of the material in pipe 2 must obviously be greater than the sum of the products of density times the height for vessel 7 plus the density times the height of pipes 9 and 10. In a process of the type just now described, that is to say, the bauxite treating of gasoline in vapor phase, pipe 2 may have an internal diameter of about 4 ft. and a length of about 120 ft. Pipe 9 may be of similar diameter and the internal diameter of treating zone 7 is substantially greater than that of pipe 9, as indicated in the drawing and may, for example, amount to 12 ft.

Our process is not limited to the precise details hereinbefore set forth and numerous modifications thereof will readily occur to those skilled in this particular art.

The term "refining of hydrocarbon distillates" as employed herein is intended to mean the purification of such distillates by the removal of objectionable impurities therefrom and is not intended to include cracking, reforming, hydrogenation, dehydrogenation, alkylation, isomerization, or other types of treatments in which the oil undergoes a definite change in chemical composition. The refining of oils as herein employed involves the removal of sulfur and nitrogen compounds, color and gum-forming constituents, and other objectionable impurities.

We claim:

1. A process of refining low-boiling hydrocarbon distillates which comprises passing a stream of said hydrocarbon distillates in vapor form upwardly through a refining zone, maintaining a vertical column of solid refining agent in finely divided form, maintaining a fluidizing gas in admixture with said refining agent within said column to maintain said refining agent in a freely flowing, fluidized state throughout the full length of said column, discharging the finely divided refining agent from the base of said column into said first-named hydrocarbon stream, controlling the velocity of the vapors passing upwardly through said refining zone to maintain a relatively dense, turbulent mixture of vapors and refining agent within said refining zone, maintaining said vapors in contact with the refining agent within the refining zone at a temperature and for a period sufficient to obtain a substantial purification of said vapors, thereafter separating the refining agent from the hydrocarbon vapors, maintaining a second vertical column of said finely divided refining agent, conducting refining agent separated from said hydrocarbon vapors to the top of said second-named column, maintaining a fluidizing gas in admixture with the

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refining agent within said second-named column to maintain said refining agent in a freely flowing, fluidized condition, discharging the refining agent from the base of said second-named column into a stream of gases separate and independent from said hydrocarbon vapors, passing said stream of gases containing said refining agent through a regenerating zone, regenerating the finely divided refining agent during passage through said regenerating zone, thereafter separating the regenerated refining agent from the gases and conducting the regenerated refining agent to the top of said first-named column.

2. The process defined by claim 1 wherein the temperature of a portion of the refining agent is modified and said portion then returned to the regenerating zone to control the temperature therein.

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