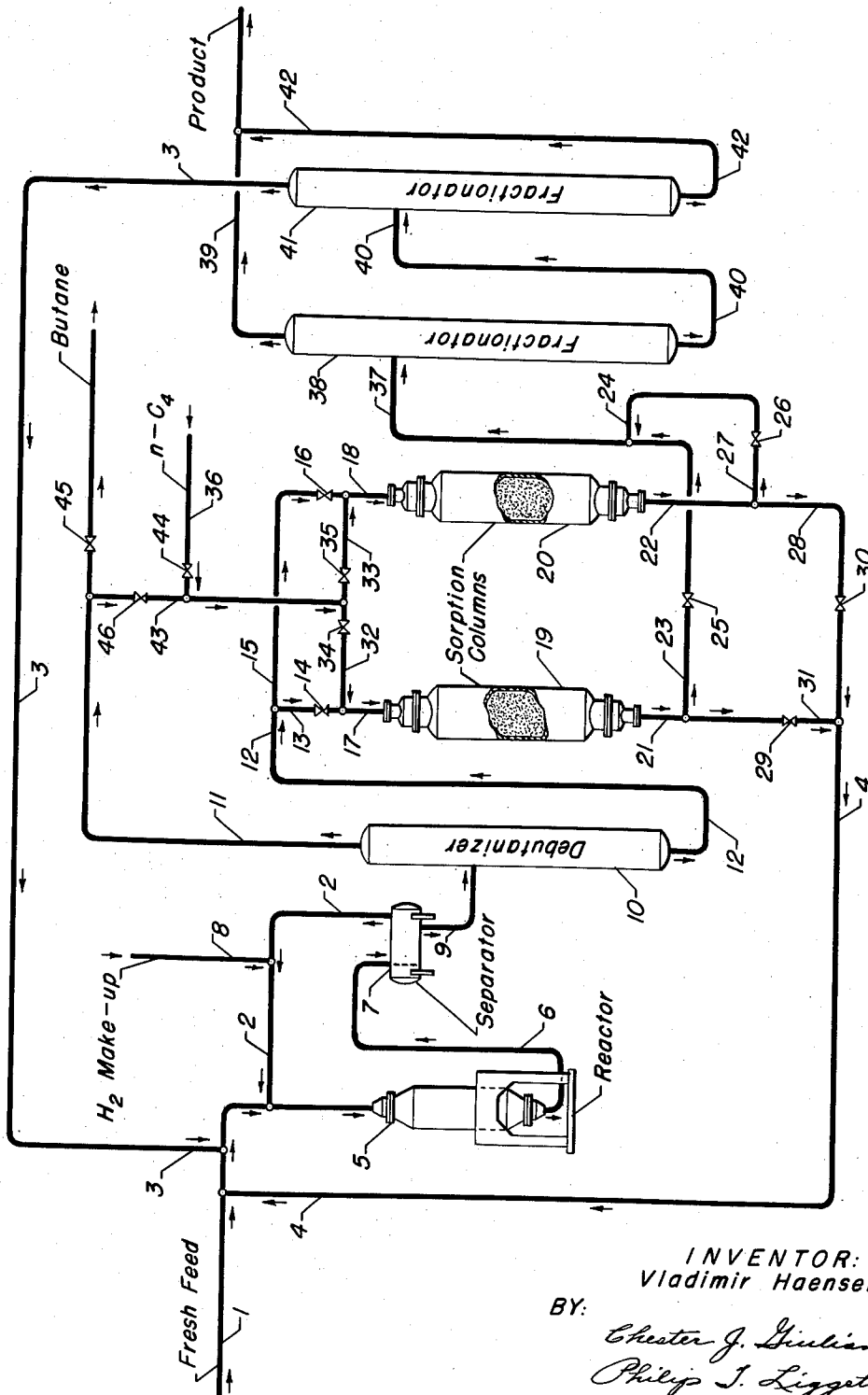


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COMBINATION PROCESS OF ISOMERIZATION AND A SORPTION
PROCESS FOLLOWED BY SELECTIVE FRACTIONATION
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**COMBINATION PROCESS OF ISOMERIZATION
AND A SORPTION PROCESS FOLLOWED BY
SELECTIVE FRACTIONATION**

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This invention relates to a process for producing a hexane having a high octane number from a mixture of C₆ paraffin and naphthene feed stock. More particularly, this invention is concerned with a combination process whereby an isomerization reaction zone effluent is introduced into a sorption process wherein low octane number normal hexane is removed and followed with selective fractionation of the remaining effluent so that the desired high octane number hexanes are obtained.

Normal paraffins find use as intermediates for raw materials in the production of many petrochemical compounds and these same normal paraffins also find wide use as solvents. While normal paraffins are not particularly desirable as a motor fuel, because of their relatively low octane numbers, they may be isomerized readily to isoparaffins which have substantially higher octane numbers. Since isomerization is an equilibrium reaction, it is preferred that isoparaffins be separated from normal paraffins before subjecting the normal paraffins to isomerization. In this manner, more of the normal hexane can be isomerized than would take place in the presence of isoparaffins. In the present process the normal hexane is removed from the fractionation product thereby increasing the octane number of the combination process hexane product. The normal hexane separated from the fractionation residue is subjected to further treatment in the isomerization reaction zone to convert them to isoparaffins of higher octane number.

It is an object of the present invention to subject a mixture of C₆ paraffins and naphthenes to isomerization, a sorption process whereby normal hexane may be separated from the isomerization reaction zone effluent, and follow this with selective fractionation of the branched chain hexanes and cycloparaffins so that a high octane number product is obtained. It is also an object of the present invention to provide a sorption zone with a means whereby the sorbed normal hexane may be recycled to the isomerization reaction zone for the conversion to higher octane number hexanes.

In one embodiment this invention relates to a process for producing a hexane having a high octane number from a C₆ paraffin hydrocarbon feed stock which comprises subjecting said feed stock to isomerization in the presence of an isomerization catalyst at isomerization conditions within a reaction zone, contacting resulting isomerization reaction zone product with a solid sorbent in a sorption zone to effect the selective sorption of the normal hexane component of the isomerization product and the selective rejection of branched chain hexanes and cycloparaffins, separately withdrawing from the sorption zone a stream comprising a product having an octane number greater than said feed stock, separately contacting spent sorbent with a desorbent stream comprising a normal paraffin of at least 4 but less than 6 carbon atoms per molecule, recovering a desorbed effluent comprising normal hexane and passing the latter to said isomerization reaction zone, passing the rejected hexanes to a first fractional distillation zone, separating therefrom a first

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overhead comprising dimethylbutanes, subjecting the residue of said first fractional distillation to a second fractional distillation zone and therein separating an overhead comprising monomethylpentanes, recycling said last mentioned overhead product to said isomerization reaction zone, and recovering a second distillation residue comprising branched chain and cyclic C₆ hydrocarbons from the bottom of said second fractionation zone.

In another embodiment the present invention relates to a process for producing a hexane having a high octane number from a mixture of C₆ paraffins and naphthenes feed stock which comprises subjecting said feed stock to isomerization in the presence of an isomerization catalyst at isomerization conditions within a reaction zone, passing the resulting isomerization reaction product to a debutanizer column wherein low boiling hydrocarbon gases are passed overhead, contacting the resulting residue of said debutanizer column with a solid sorbent in a sorption zone to effect the selective sorption of the normal hexane and the selective rejection of the branched chain hexanes and cycloparaffins, separately withdrawing from the sorption zone a stream comprising the thus rejected hydrocarbon having an octane number greater than said feed stock, separately contacting spent sorbent with a desorbent stream comprising a normal paraffin of at least 4 but less than 6 carbon atoms per molecule, recovering a desorbed effluent comprising normal hexane and passing the latter to said isomerization reaction zone, passing the rejected hydrocarbon to a first fractional distillation zone, separating therefrom a first overhead comprising dimethylbutanes, subjecting the residue of said first fractional distillation to a second fractional distillation zone and thereby separating an overhead comprising monomethylpentanes, recycling said last mentioned overhead to said isomerization reaction zone, and recovering a second distillation residue comprising branched chain and cyclic C₆ hydrocarbons from the bottom of said second fractionation zone.

In the operation of catalytic reforming processes, it has been observed that the product, usually called reformate, contains a small amount of normal paraffin having a relatively low octane number. The presence of these paraffins is due to the fact that under operating conditions of reforming, equilibrium concentration represents a fair concentration of normal paraffins. The presence of these normal paraffins in the reformate causes a substantial depreciation of the octane number of the reformate.

As reforming processes are operated to obtain a conversion of these normal paraffins into aromatics or into higher octane number branched chain and lower boiling paraffins during the reforming reaction, it has been found that the yield-octane number improvement relationship is such that somewhat more than one yield percent is lost for each octane number gained in the range of octane numbers in the order of 85-95 F-1 clear. This is due to the conversion of normal liquid components into normally gaseous components. However, if the normal paraffins were removed from the reformate the octane number would improve more favorably, for example, a reformate having an octane number of 85 F-1 clear and containing 10% normal paraffin, having an average octane number of 0, would have an octane number improvement of 85 to 94.5 on the strictly arithmetical blending basis. In the present process the octane number of the isomerization reaction zone effluent is increased through the use of a sorption process whereby normal paraffins are sorbed and the branched chain hexanes and cycloparaffins are rejected and said hydrocarbons are then selectively fractionated to produce high octane number branched chain hexanes and cycloparaffins. The normal hexane is subjected to a desorbent

stream comprising a normal paraffin of at least 4 but less than 6 carbon atoms per molecule and said normal hexane is returned to the isomerization reaction zone as recycle to be further isomerized to higher octane number hexanes. The contact of the normal hexane, cycloparaffins and branched chain hexanes in the sorption zone is with a solid sorbent which has a selective sorbing power for normal hexane. The contact is for a time sufficient to sorb a substantial amount of the normal hexane present in the charge to the sorption zone. The sorption tower is maintained at a temperature and pressure so that the charge is maintained in the liquid phase. It is preferred to maintain the temperature in the sorption zone substantially within the range of from about 80° C. to about 152° C. The pressure in the sorption zone is within the range or from about 13.5 to about 68 atmospheres such that the charge is kept in the liquid phase.

Any solid sorbent material which has a high power of selectively sorbing normal paraffins from their mixtures with other hydrocarbons may be used in the present process. Crystalline metal alumino-silicates, such as calcium alumino-silicate, strontium alumino-silicate, barium alumino-silicate, and potassium alumino-silicate are suitable sorbents to be used although they do not necessarily provide quantitatively the same results. Crystalline calcium alumino-silicate, which has been heated to remove the water of hydration, is preferred. These crystalline calcium alumino-silicates which have been heated to remove the water of hydration have pore diameters of about 5.1 A. units; this diameter is slightly larger than the calculated critical diameter but somewhat smaller than the critical diameter of isoparaffins, cycloparaffins and aromatics. Thus, it is possible to sorb normal paraffins from the mixture of branched chain and cyclic paraffins.

The contact of the charge with the solid sorbent is for a time sufficient to sorb substantial quantities of the normal paraffin from the charge. After a substantial quantity of the normal paraffin is sorbed, the sorbed normal paraffin is removed and recovered from the solid sorbent and subsequently returned as recycle to the isomerization reaction zone for further conversion to high octane number isoparaffins.

The usual procedure for the removal of the sorbed normal paraffins from the solid sorbent is heating under vacuum. Such a procedure involves a considerable expenditure with respect to both initial installation and operating cost. The present invention provides for a simple and in its preferred embodiment essential isothermal operation of the sorption cycle. This results in a great saving in operating cost and the equipment necessary for the operation is simple and readily available.

The accompanying drawing illustrates diagrammatically the process flow embodying the present combined process for producing high octane hexane fractions. Also in referring to and describing the drawing, a Skellysolve B was utilized as the charge stock, said charge having an initial boiling point of 150° F. and an end boiling point of 175° F. and containing 48% by weight normal hexane. The charge stock was passed through line 1 and commingled with a monomethylpentane recycle stream 3 and a normal hexane recycle stream 4, the source of these latter two streams will be subsequently described. The charge stock, a monomethylpentane stream and a normal hexane stream are combined with a hydrogen recycle gas stream 2 and then passed to an isomerization reaction zone 5 containing isomerization catalyst.

The conditions utilized in reaction zone 5 will depend upon the particular isomerization catalyst utilized therein. The preferred catalyst in the process of this invention is one comprising a platinum group metal, particularly platinum, combined halogen, and alumina. With such a catalyst, the pressure utilized in the reaction zone

will range from about 100 to about 1000 pounds per square inch, the temperature will range from about 100° C. to about 450° C. and the liquid hourly space velocity will range from about 0.1 to about 10. The hydrogen to hydrocarbon ratio in the reaction zone will range from about 0.25 to about 5 mols of hydrogen per mol of hydrocarbon. When the catalyst utilized comprises platinum, alumina, and combined chlorine in an amount of from about 2.5 to about 8.0 weight percent of the latter, the reaction zone temperature will be lower than the higher part of the above set forth range, for example, from about 150° C. to about 250° C. In some instances it is desirable and/or advisable to utilize hydrogen halide along with these catalysts and thus the use of hydrogen chloride, for example, is within the generally broad scope of the present invention.

The isomerization reaction zone 5, when being charged with the above mentioned Skellysolve B charge stock is operated at a pressure in the order of 900 p.s.i.g. and a temperature of about 150° C. with a liquid hourly space velocity of 0.5 and a hydrogen to hydrocarbon ratio in the reaction zone of the order of 6.0. The isomerization catalyst contained in said isomerization reaction zone 5 comprises platinum, alumina, and combined chlorine, in an amount of the order of 5.5 weight percent of the latter along with a continuous addition of hydrogen chloride to said isomerization reaction zone 5.

An isomerization reaction zone effluent is withdrawn from said isomerization reaction zone 5 by means of line 6 and passed to a separation zone 7 wherein a separation of hydrogen from hydrocarbons is effected. A relatively high purity hydrogen recycle gas stream is withdrawn from the top of said separation zone 7 by means of line 2 and is joined with a hydrogen gas makeup stream 8 and said total recycle hydrogen gas is passed to isomerization reaction zone 5 as hereinbefore described. A hydrocarbon effluent stream containing of the order of 12% by weight normal hexane is withdrawn from the bottom of separation zone 7 by means of line 9 and passed to a conventional debutanizer column 10 wherein low boiling hydrocarbon gases, in particular isobutane and normal butane, are passed overhead by means of line 11 for subsequent use in a sorption zone herein-after described. A residue product is withdrawn from the bottom of debutanizer column 10 by means of line 12 and passed to a sorption zone. The normal hexane, branched chain hexanes and cycloparaffins in line 12 are passed through either sorption zone 19 or sorption zone 20. In this illustration it will be considered that the charge from line 12 was previously directed to sorption zone 20 and now the charge is being passed into sorption zone 19. Valve 16 in line 15 is closed and valve 14 in line 13 is open. The hexane mixture from line 12 continues through line 13, valve 14, and line 17 to sorption zone 19. In sorption zone 19 the hexane mixture is contacted with a crystalline calcium alumino-silicate which had previously been heated to remove the water of hydration. This sorption zone material sorbs normal hexane from the hexane mixture and allows the branched chain hexanes and cycloparaffins to pass from the sorption zone 19 through line 21. This sorption zone is maintained at a temperature of the order of 156° C. and at a pressure of the order of 37.5 atmospheres. The liquid hourly space velocity is of the order of 1.0, that is, the volume of liquid hydrocarbon charged per volume of sorption material per hour. The effluent from sorption zone 19 when withdrawn through line 21 has a decreased normal hexane content when compared with the charge in line 12. The material in line 21 continues through line 23 containing open valve 25 and then through line 37.

The material in line 37 consists predominately of the branched chain and cyclic hexanes and is passed to a first fractionation zone 33 for further fractionation so that the high octane number hexanes are obtained.

After a period of operation on this sorption cycle, the

sorption material in sorption zone 19 has picked up a substantial amount of normal hexane. For the purposes of this illustration it will be considered that the charge in line 12 was passed through sorption zone 20 previously and that, therefore, the solid sorption material in zone 20 has a substantial amount of normal hexane sorbed thereon.

A normal liquid butane stream from a source other than the process itself will be used in illustrating the desorbing step of the process. Valve 46, line 43 is maintained closed while valve 45 in line 11 is opened so that the overhead product from the conventional debutanizing zone 10 is discharged from the process as a product stream of said process. The liquid normal butane stream is introduced into line 36 containing open valve 44 where said liquid normal butane stream flows through line 43. Valve 26 in line 27 and valve 16 in line 15 are maintained in a closed position and the normal butane stream flows from line 43 through valve 35 in line 33 and then through line 18 into sorption zone 20. Valve 34 in line 32 is maintained closed during the desorption cycle of sorption zone 20 so that the normal butane stream does not flow into sorption zone 19. This liquid normal butane displaces the normal hexane sorbed on the crystalline calcium aluminosilicate. During this desorbing operation chamber 20 is maintained at a temperature of the order of 156° C. and at a pressure of the order of 37.5 atmospheres. The effluent from chamber 20 which is withdrawn through line 22 during this desorbing operation contains predominately normal hexane hydrocarbons. The flow of liquid normal butane into chamber 20 through line 18 is continued until substantially all of the normal hexanes are displaced from the solid sorbent. The normal hexanes continue through line 28 containing open valve 30, and then into line 4 which returns the normal hexane as recycle to the isomerization reaction zone hereinabove described. Normal hexane is subsequently isomerized to the higher octane number isohexanes in the isomerization reaction zone 5. When the normal hexane has been subsequently displaced from the solid sorbent in chamber 20 by the liquid normal butane, the pressure on chamber 20 is reduced to 20.4 atmospheres, thereby vaporizing the liquid normal butane in this chamber.

A convenient source for the liquid normal butane used in the desorbing step of the sorption zone is overhead product 11 from the conventional debutanizer 10. When the overhead product 11 is to be used in the desorbing step, valve 45 in line 11 and valve 44 in line 36 are closed while valve 46 in line 43 is maintained open. The liquid butane stream from column 10 passes through line 11 and open valve 46 in line 43 and then into the sorption zone of the process. Any other source of the liquid normal butane which may be readily available can also be used in the desorption step.

After this desorbing operation the charge in line 12 may be introduced into chamber 20 and a desorbing operation started on chamber 19. This may be accomplished by closing valve 35 in line 33 and closing valves 14 and 25 and opening valves 16 and 26. In this operation the charge passes through line 15, open valve 16, and line 18 into sorption zone 20. The effluent from sorption zone 20 continues through line 22 containing open valve 26 and then into line 24 which allows the rejected branched chain hexanes and cycloparaffins to flow into line 37 and then into a first fractionation zone 38. Further fractionation of the rejected hexanes is accomplished in a first fractionation zone 38 to produce high octane number hexanes, the steps involved in this further fractionation will be hereinafter described.

Sorption zone 19 is now ready for the desorption cycle. Chamber 19 is placed on the desorption cycle by closing valves 14, 35, 30, and 25 and opening valves 34 and 29. In this desorption cycle valve 46 in line 43 is closed while valve 45 in line 11 is open so that the overhead

product from the conventional debutanizer 10 is discharged from the process as a product stream. The liquid normal butane stream is introduced into line 36 containing open valve 44 from where said liquid normal butane stream flows to line 43. The liquid normal butane in line 43 is passed to open valve 34 in line 32 and then into line 17 which introduces said liquid normal butane into sorption zone 19. The effluent which comprises chiefly normal hexane during the desorption cycle, is withdrawn through line 21, continues through line 31 containing open valve 29 and then into line 4. The normal hexane in line 4 is subsequently recycled to isomerization reaction zone 5 for further isomerization to the higher octane number hexanes. After the pressure is reduced on zone 19 so as to vaporize the liquid normal butane, zone 19 is again ready for a sorption cycle.

The rejected branched chain hexanes and cycloparaffins in line 37 are passed to a first fractionation zone 38. A high octane number product containing dimethylbutanes is passed overhead from said first fractionation zone 38 by means of line 39, while a residue product is withdrawn from the bottom of said first fractionation zone 38 by means of line 40 and passed to a second fractionation zone 41. A low octane number monomethylpentane fraction is removed in said second fractionation zone 41 and passed overhead by means of line 3 and then recycled to said isomerization reaction zone 5 as hereinbefore described for further isomerization to higher octane number hexanes. A residue product containing methylcyclopentane and cyclohexane is withdrawn from the bottom of said second fractionation zone 41 by means of line 42 and combined with the dimethylbutanes contained in line 39 to form a high octane number hexane product.

In the above illustration the combination process of this invention has been set forth. As stated hereinabove the combination of isomerization, a sorption process and selective fractionation are combined to produce a high octane number hexane product by the removal of normal hexane from the product stream. It is also illustrated that the normal hexane, when withdrawn from the product stream, is returned for further isomerization along with monomethylpentanes to an isomerization reaction zone containing an isomerization catalyst.

I claim as my invention:

1. A process for producing a hexane having a high octane number from a feed stock mixture of C₆ paraffins and naphthenes which comprises subjecting said feed stock mixture of C₆ paraffins and naphthenes to isomerization in the presence of an isomerization catalyst at isomerization conditions within a reaction zone, debutanizing the resulting isomerization reaction zone product and thereafter contacting the latter with a solid sorbent in a sorption zone to effect the selective sorption of the normal hexane component of the isomerization product and the selective rejection of branched chain hexanes and cycloparaffins, separately withdrawing from the sorption zone a stream comprising the thus rejected hydrocarbon stream having an octane number greater than said feed stock, separately contacting spent sorbent with liquid butane from the debutanizing step to remove said normal hexane component from the spent sorbent, recovering a desorbed effluent comprising normal hexane and passing the latter to said isomerization reaction zone for isomerization treatment therein together with said feed stock mixture, passing the rejected hydrocarbon stream to a first fractional distillation zone, separating therefrom a first overhead comprising dimethylbutanes, subjecting the residue of said first fractional distillation to a second fractional distillation zone and thereby separating an overhead comprising monomethylpentanes, recycling said last mentioned overhead to said isomerization reaction zone, and recovering a second distillation residue comprising branched chain and cyclic C₆ hydrocarbons from the bottom of said second fractionation zone.

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2. The process of claim 1 further characterized in that the overhead product from the first fractional distillation zone is combined with the rejected branched chain hexanes and cycloparaffins from the sorption zone to form a high octane number hydrocarbon product.

3. A process for producing a hexane having a high octane number from a feed stock mixture of C₆ paraffins and naphthenes which comprises subjecting said feed stock mixture of C₆ paraffins and naphthenes to isomerization in the presence of an isomerization catalyst at isomerization conditions within a reaction zone, passing the resulting isomerization reaction zone product to a debutanizer column and therein separating butane from said product, contacting the resulting residue of said debutanizer column with a solid sorbent in a sorption zone to effect the selective sorption of the normal hexane component and the selective rejection of the branched chain hexanes and cycloparaffins, separately withdrawing from the sorption zone a stream comprising the thus rejected hydrocarbon stream having an octane number greater than said feed stock, separately contacting spent sorbent with liquid butane from said debutanizer column to remove said normal hexane component from the spent sorbent, recovering a desorbed effluent comprising normal hexane and passing the latter to said isomerization

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reaction zone for isomerization treatment therein together with said feed stock mixture, passing the rejected hydrocarbon stream to a first fractional distillation zone, separating therefrom a first overhead comprising dimethylbutanes, subjecting the residue of said first fractional distillation to a second fractional distillation zone and thereby separating an overhead comprising monomethylpentane, recycling said last mentioned overhead to said isomerization reaction zone, and recovering a second distillation residue comprising branched chain hexanes and cycloparaffins from the bottom of said second fractionation zone.

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