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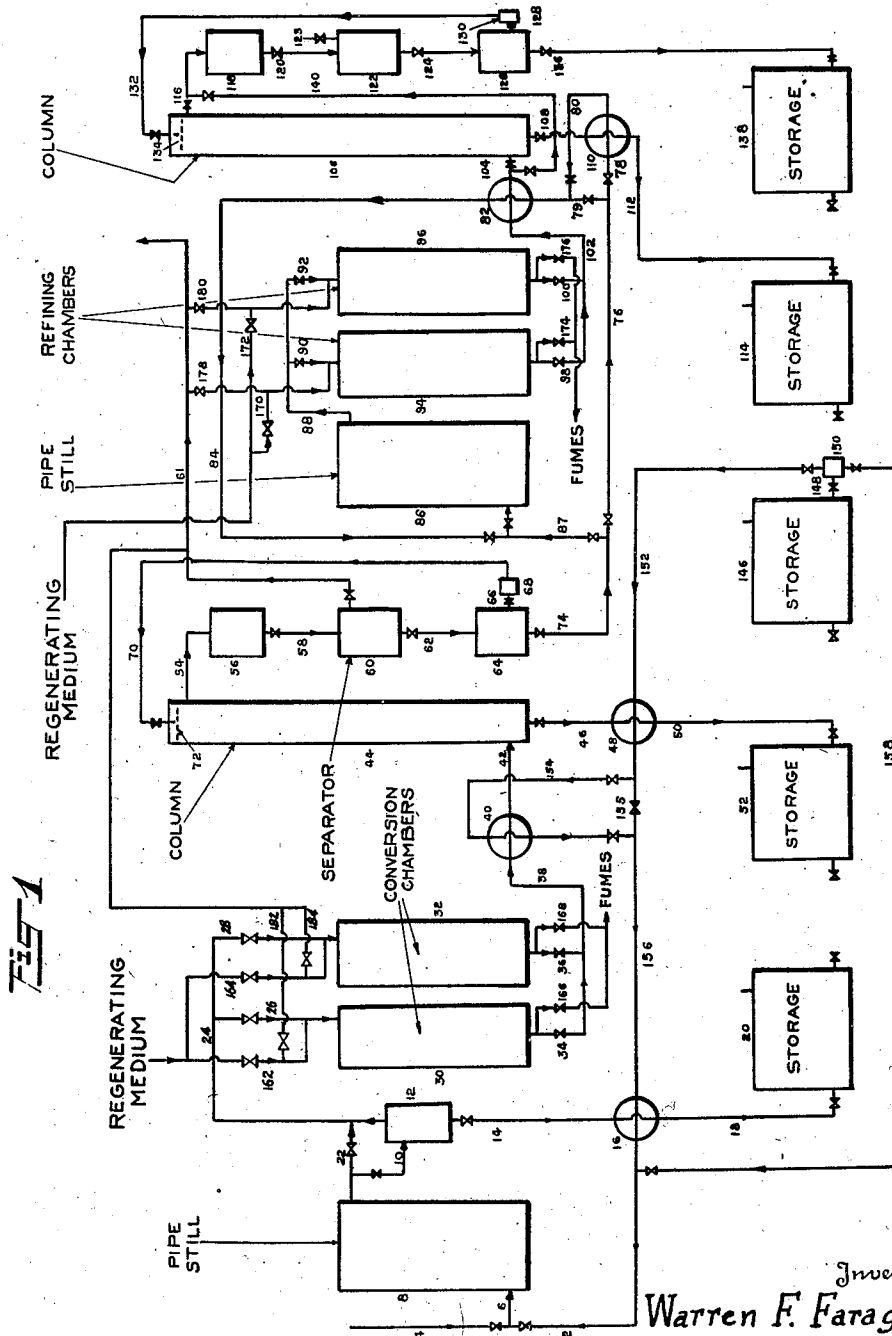
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TREATMENT OF HYDROCARBONS

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2 Sheets-Sheet 1



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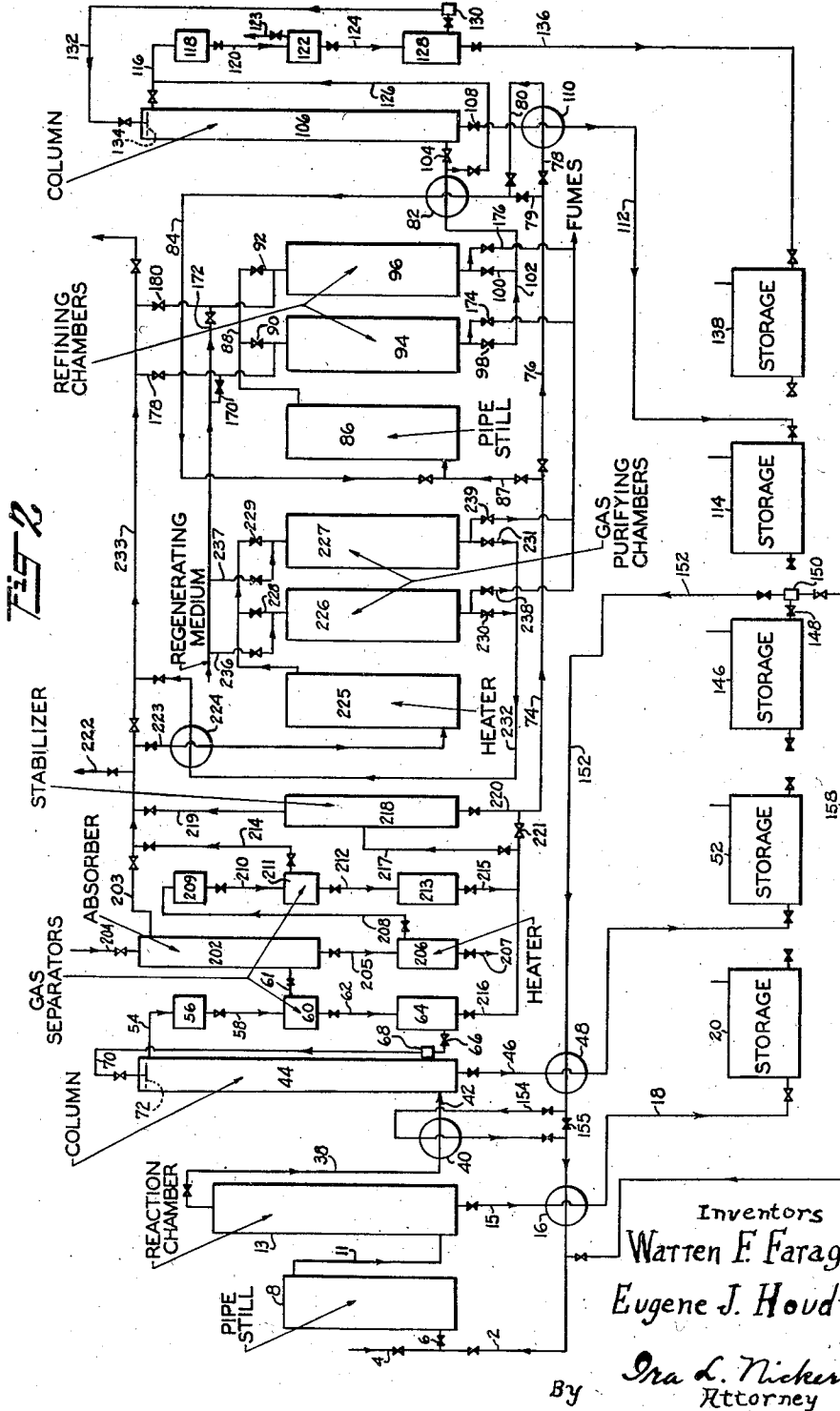
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## UNITED STATES PATENT OFFICE

2,035,467

## TREATMENT OF HYDROCARBONS

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6 Claims. (Cl. 196—52)

This invention relates to processes and apparatus for the treatment of hydrocarbons, especially in the refining of the same through contact with an active mass capable of regeneration in situ. In certain aspects it may be considered as an improvement upon or further development of the processes and apparatus disclosed in the copending application of Eugene J. Houdry, Serial No. 610,567, filed May 11, 1932.

One object of the invention is to devise improved ways and means for the production of a stable motor fuel suitable for use in high compression internal combustion engines. Another object is to extend the operating periods of catalytic contact masses, especially in the refining of converted hydrocarbons, without impairing the quality of the final product. Another object is to secure complete regeneration or reactivation of the contact masses. Still other objects will be apparent from the detailed description which follows.

The treatment of both the gaseous and low boiling liquid products of conversion with a refining catalyst to produce a finished product results in a necessary limitation of the period of operation of the refining catalyst due to the fact that all the gaseous products are refined whether or not it is desirable to utilize them in a refined state. It is desirable to increase the effective period of operation of the refining catalyst in order that a corresponding reduction in the cost of operation may be realized. We have found that a considerable portion of the load may be removed from the refining catalyst by separating the low boiling liquid hydrocarbons from the gaseous hydrocarbons or fixed gases resulting from the conversion of higher boiling hydrocarbons and by refining these lower boiling hydrocarbons apart from the gases. Since the sulphur compounds which rapidly poison the refining catalyst are for the most part in gaseous form as a result of the cracking or transforming operation, the diversion of the so-called fixed gases leaves for removal by the refining catalyst only the small quantity of sulphur remaining in the low boiling hydrocarbons and also relieves it of the polymerizing of certain higher unsaturated hydrocarbons normally present in the fixed gases. The latter may be directed to fuel lines or otherwise used as desired. Inasmuch as the fixed gases contain hydrogen, they may be used in small amount and for a short period as reducing gas to complete the regeneration of the catalyst, especially when it comprises or con-

tains a metallic oxide. If the material undergoing transformation is a "sweet" crude or a distillate of the same, the fixed gases may be taken directly from the line, as the quantity used is too small to produce any appreciable poisoning of the catalyst. On the other hand, if the material is a sulphur or "sour" crude or a distillate of the same, purification of the fixed gases is essential before use as reducing gas. In either case the separated gases may be passed through an absorber to prevent loss of low boiling hydrocarbons. The invention further contemplates a stabilizing step after the separation of gases but in advance of the refining operation, the gases from the stabilizer being directed into the main gas line.

In order to illustrate the invention and the manner of its use, concrete embodiments thereof are shown in the accompanying drawings, in which

Fig. 1 is a somewhat diagrammatic side elevational view of one form of the invention; and

Fig. 2 is a view similar to Fig. 1 of another form, in which provision is made for purifying the fixed gases and for stabilizing the desired product in advance of the refining operation.

Referring to the simpler form of the invention (for the treatment of "sweet" crudes or distillates) disclosed in Fig. 1, the charge of material to be converted, preferably in a partially heated state, is admitted through valved line 2 and passed with or without admixture of water or steam from valved line 4 through line 6 into a heating device such as pipe still 8. The vapors and unvaporized portion of the charge may pass through valved vapor line 10 into a separator 12 where the unvaporized portion is separated from the vapor and passes as a liquid through valved line 14, heat exchanger 16, valved line 18 into a vented storage tank 20. The vapors pass through line 24 into any suitable conversion apparatus as by one of two valved lines 26 or 28 leading to insulated catalyst chambers 30 and 32, respectively, which contain suitable catalytic material for effecting the desired transformation. If vaporization is complete in pipe still 8, the vapors may pass directly through valved line 22 into vapor line 24.

The converted products, substantially in vapor phase, issue either through valved line 34 or valved line 36 into vapor line 38, pass through heat exchanger 40 and discharge through vapor line 42 into the bottom of a fractionating column 44 where separation is effected between lower boiling vapors and higher boiling liquid. The

higher boiling liquid is then withdrawn through valved line 46, heat exchanger 48, and valved line 50 into vented storage tank 52. The vapors of the lower boiling hydrocarbons pass through vapor line 54 into condenser 56 with the resulting mixture of liquid and gaseous hydrocarbons passing through valved line 58 into gas separator 60, whence the separated liquid condensate passes through valved line 62 into receiver 64. The vapors from gas separator 60 are removed through valved line 61. A portion of the liquid condensate may be used to control column 44 by means of valved line 66 leading to pump 68 which discharges through valved line 70 and distributor 72.

The major portion of the liquid condensate is transferred for refining through valved line 74, valved line 76, valved line 78, heat exchanger 110, valved line 80, heat exchanger 82, valved line 84 into a second heating device or pipe still 86. A valved line 79 may be used to control the flow of unrefined low boiling hydrocarbons through or around heat exchanger 110. The extent to which the feed to pipe still 86 is heated may also be controlled by a direct valved line 87. The vaporized mixture from pipe still 86 passes through vapor line 88 into one of two valved lines 90 or 92 leading to insulated catalyst chambers 94 and 96, respectively, which contain suitable catalytic material for effecting the desired refining. The resulting products, substantially in vapor phase, issue either through valved line 98 or 100 into vapor line 102 whence they pass through heat exchanger 82 and vapor line 104 into the bottom of a second fractionating column 106, where separation is effected between the lower boiling vapors and higher boiling liquid. The higher boiling liquid is withdrawn by valved line 108, through heat exchanger 110, and valved line 112, into vented storage tank 114. The vapors of the lower boiling hydrocarbons pass through valved vapor line 116 into condenser 118 with the resulting mixture of liquid and gaseous hydrocarbons passing through valved line 120 into gas separator 122, whence the separated liquid condensate passes through valved line 124 into receiver 126. A portion of this liquid condensate may be used for the control of column 106 by means of valved line 128, pump 130, valved line 132 and distributor 134. Vapors from gas separator 122 are removed through valved line 123. The major portion of the liquid condensate, which is the finished product, is passed by valved line 136 into vented storage tank 138. If final separation of higher boiling liquid hydrocarbons is not required, the refined vapors from line 104 may pass by valved line 140 directly into line 116.

The charging stock, such as a gas oil, may be forced from a storage tank 146 through valved line 148 by means of pump 150 into valved line 152 and thence through heat exchanger 48, valved line 154, heat exchanger 40, line 156, heat exchanger 16 and finally into line 2 as partially heated charging stock. Valved line 155 may be used to control the flow of charging stock through heat exchanger 40. The charging stock may also be forced by pump 150 through valved line 158 directly into valved line 2. After the fresh feed in tank 146 is exhausted, additional runs on recycling stock may be made by connecting tanks 114 and 52 either together or successively to pump 150.

The catalyst chambers 30 and 32 and 94 and 96 are provided in pairs in order that the plant may be in continuous operation with one chamber of each pair on stream while the other is in re-

generation. Thus each chamber alternates in function. The chambers are supplied with catalysts suitable for their respective operations and in such shape and form as to permit regeneration in place. Certain suitable catalytic materials for conversion and refining are disclosed in the copending application of Eugene J. Houdry, Serial No. 600,581, filed March 23, 1932 comprising adsorbent or catalytically active substances such as active or activated hydrosilicate of alumina, without or with additional non-active or active materials including finely divided metals or metallic oxides. The preferred operating temperatures for the conversion or transforming catalyst are from 800° to 1000° F., and for the refining catalyst from 400° to 650° F.

The regeneration of the catalysts in chambers 30 and 32 is effected by passing suitable fluids through valved inlets 162 and 164 and venting the resulting products or fumes through valved outlets 166 and 168. Similarly, the regeneration of the catalysts in chambers 94 and 96 is effected by admitting regenerating fluids through valved inlets 170 and 172, and discharging the resulting gases through valved outlets 174 and 176. If the catalysts comprise or contain metals or reducible metallic oxides, the final stage of regeneration may be accomplished by the use of a small quantity of reducing gas which may be obtained by tapping gas line 61 as by valved lines 178 or 180 to the refining chambers and by valved line 182 or 184 to the conversion chambers. The purpose of this step is the reduction of a part of the metallic oxide in the catalyst to metal to insure the subsequent removal of elementary sulphur. The regeneration of catalysts may be accomplished by the processes disclosed in the copending application of Eugene J. Houdry, Serial No. 604,997, filed April 13, 1932, and the operating temperatures during regeneration will depend to a considerable extent upon the catalysts used. For regeneration by oxidation, the temperature should not fall below 800° F., and if the catalysts comprise or contain hydrosilicate of alumina, the temperature should not be allowed to rise much above 1050° F.

Fig. 2 is a diagrammatic lay-out of a complete treating plant for handling any type of petroleum product, either a crude or a distillate, and either "sweet" or "sour". While somewhat more expensive in first cost, due to the inclusion of apparatus additional to that disclosed in Fig. 1, it has such flexibility of control that it may be operated substantially like the plant shown in Fig. 1, but has many advantages thereover. For example, it provides for the removal of low boiling vapors which may be entrained with the fixed gases issuing from the separator which follows the first fractionating column. These vapors are condensed and the condensate, after a second gas separation, is directed into the line of raw low boiling hydrocarbons which pass to the refining section. The vapor pressure of this raw product may be reduced by stabilizing the same prior to refining. All of the fixed gases resulting from absorption, from the second separating step, and from the stabilizing step, may then be subjected to a purifying treatment, which includes the removal of all sulphur compounds. A portion of this purified gas may be used as a reducing gas to complete the regeneration of the refining catalyst, as described in connection with the plant shown in Fig. 1, with the advantage that complete removal of sulphur compounds from the gas avoids any poisoning whatever of the catalyst through the

forming of sulphates. In addition, purified gas over and above that required for reducing purposes is available as fuel for special purposes and for other uses which would otherwise be barred to gas containing even a small or moderate amount of sulphur compounds.

Much of the apparatus and many of the connections disclosed in Fig. 2 conform to those shown in Fig. 1, and, as such, bear the same reference characters. The major difference between the two figures resides in the apparatus for treatment of the converted products after primary condensation following the first fractionation and prior to the refining operation, and the new features appearing in Fig. 2 are made readily distinguishable by bearing reference characters above 200. Since, for the most part, the invention concerns itself with the refining of hydrocarbons, it is, in certain respects, immaterial what apparatus is used to begin the treatment of the starting material. In order to emphasize the fact that the primary conversion may be by any known, or suitable, or desired apparatus, a conventional reaction, soaking, or vaporizing chamber is indicated at 13 (Fig. 2) to receive the starting material, at conversion or cracking temperature, from pipe still 8 by line 11, the cracked or converted vapors leaving reaction chamber 13 through valved line 38 to be fractionated, and the liquid residue leaving through valved line 15 for storage tank 20.

Beginning now at gas separator 60, the gases leaving by valved line 61 enter an absorber 202 of any desired type, and leave by valved line 203. The absorber shown uses a low boiling liquid condensate which enters through valved line 204 to scrub the gases, the enriched condensate or absorbent leaving by valved line 205 which discharges into a heater or still 206, where the absorbed vapors are stripped from the low boiling condensate which leaves as lean absorbent through valved line 207. The stripped vapors pass by valved line 208 into condenser 209, thence by valved line 210 into a second gas separator 211, from which the liquid condensate passes by valved line 212 into receiver 213, while the gases from separator 211 pass by valved line 214 into main gas line 203.

The raw liquid product of the desired boiling range in receiver 213 is drained by valved line 215 into the valved line 216 from receiver 64. Before passing the raw liquid product from these two sources to liquid line 74 which leads to the refining section of the apparatus, it is preferable, in most instances, to effect stabilization of the same by removing the gases and very light vapors which are dissolved in the liquid and which increase its vapor pressure to an undesirable extent. This is effected by conducting the raw liquid by valved line 217 into a stabilizer 218 of any known or desired type from which the vapors escape through valved line 219 into main gas line 203, while the stabilized raw liquid is discharged by valved line 220 into liquid line 74. A valved connection 221 between line 217 and line 74 permits the stabilizing step to be omitted when desired.

Coming back now to main gas line 203, the gas in its raw and unpurified state may be withdrawn for fuel and other purposes through valved connection 222. For purification, it is withdrawn through valved line 223, passed through heat exchanger 224 and into an additional heater 225 of any suitable or desired type, where its temperature is raised sufficiently to pro-

mote the desired purifying reaction in a battery of purifying chambers 226 and 227, the raw heated gases passing into the same through valved lines 228 and 229 respectively, and leaving by valved outlets 230 and 231, respectively, which discharge into line 232. The latter passes back through heat exchanger 224 (where the purified gases give up a portion of their heat to the unpurified gases in line 223) and line 232, into purified gas line 233, from which valved connections 178 and 180 lead to refining cases 94 and 96. The valved connection 234 beyond line 180 permits the withdrawal of purified gas for use as fuel or for other special purposes requiring a sulphur-free gas.

Gas purifying chambers 226 and 227 contain any suitable or desired material for removing sulphur and/or other objectionable compounds or for otherwise purifying the gases directed thereto from heater 225. For example, there may be used finely divided metals or metallic oxides supported by carriers of the type disclosed in United States patents of Alfred Joseph, Nos. 1,775,366 and 1,818,403, dated September 9, 1930 and August 11, 1931, respectively, which permit regeneration of the contact masses by oxidation in situ. The chambers are arranged and intended for alternate operation and regeneration, and to alternate in function, so that there may be continuous operation of the entire plant. To restore the purifying material to active condition, a regenerating medium of the same or different type as that used for catalyst refining chambers 94 and 96 may be admitted by valved lines 236 and 237 to chambers 226 and 227, respectively, while the heat and fumes may be discharged through valved lines 238 and 239, respectively. No separate reducing step to complete the regeneration of the gas purifying material will be required. The operating temperatures for gas purifying chambers 226 and 227 may range from 350° to 700° F.

The regenerating connections to the gas purifying chambers and to the refining chambers are such that each chamber may be regenerated independently of the others. The length of time that any of the chambers may be continued on stream will depend upon a number of factors, the principal ones being the amount of poison in the material acted upon, the quantity of material fed, and the quantity of purifying or catalytic material within the chamber.

We claim as our invention:

1. In the production of low boiling hydrocarbons in the gasoline boiling range stable against oxidation from complex hydrocarbon vapors which include fixed gases, the process steps which comprise separating the fixed gases and the desired low boiling material from the complex vapors, stabilizing the desired low boiling material by removing entrained gases therefrom, subjecting the thus stabilized material alone without any fixed gas to the action of a catalyst capable of inducing a refining reaction to stabilize the gasoline against oxidation and of regeneration in situ, and utilizing the gases including those resulting from the stabilizing step in the regeneration of the catalyst after a refining run.

2. In the production of low boiling hydrocarbons, that process comprising the steps recited in claim 1 and in which the action of the catalyst on the stabilized material is effected in a single treatment in the temperature range of 400° to 650° F.

3. In the production of low boiling hydrocarbons in the gasoline boiling range stable against oxidation from complex hydrocarbon vapors, the process steps which comprise separating the fixed gases and the desired low boiling material from the complex vapors, stabilizing the desired low boiling material by removal of entrained gases, subjecting the thus stabilized material alone without any fixed gas to the action of a catalyst capable of inducing a refining reaction to stabilize the gasoline against oxidation and of regeneration in situ, purifying the separated fixed and uncondensed gases including those resulting from the stabilizing step of impurities including sulphur compounds, and utilizing the purified gases in the regeneration of the catalyst.

4. The process of producing low boiling hydrocarbons according to the steps recited in claim 3 and in which the refining and stabilizing reaction against oxidation is effected in vapor phase in the temperature range of 400° to 650° F.

5. In the catalytic conversion of high boiling hydrocarbons into low boiling hydrocarbons stable against oxidation by subjecting the high boiling hydrocarbons to successive treatment by two catalysts capable of regeneration in situ, the process steps which comprise subjecting the high boiling hydrocarbons to conversion into low boiling hydrocarbons with the aid of the first catalyst, separating the high boiling products and the fixed

gaseous products from the low boiling condensible products, subjecting the low boiling condensible products alone and without fixed gases to treatment by the second catalyst for refining and stabilization against oxidation, and utilizing said fixed gaseous products in the regeneration of the catalysts following the conversion and refining runs.

6. In the treatment of high boiling hydrocarbons to produce low boiling hydrocarbons in the gasoline boiling range stable against oxidation by subjecting the former to conversion, to fractionation, and the resulting condensible vapor products to the action of a refining catalyst, the latter being capable of regeneration in situ and disposed in at least two chambers for alternate operation on stream and in regeneration, the process steps which comprise subjecting the low boiling products after conversion and fractionation to condensation, removing the uncondensed gases from the low boiling condensate, revaporizing the said condensate and subjecting it alone without fixed gases to treatment by the refining catalyst in one chamber, and utilizing the uncondensed gases in the regeneration of the refining catalyst in another chamber then off stream as to said condensate.

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