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E. BUDDRUS ET AL

2,361,008

PROCESS FOR THE TREATMENT OF HYDROCARBONS

Filed May 26, 1941

3 Sheets-Sheet 1

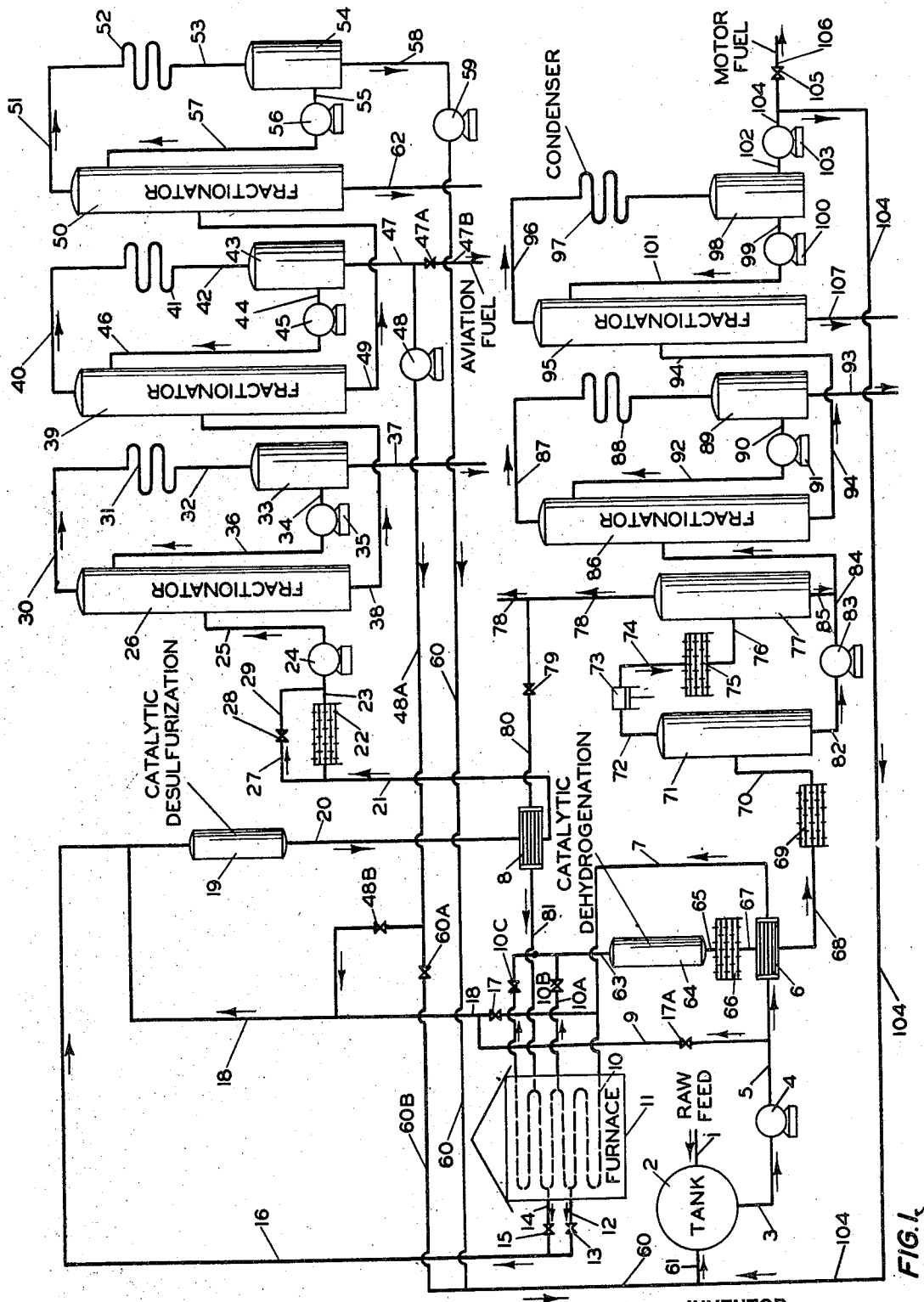


FIG. 1c

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3 Sheets-Sheet 2

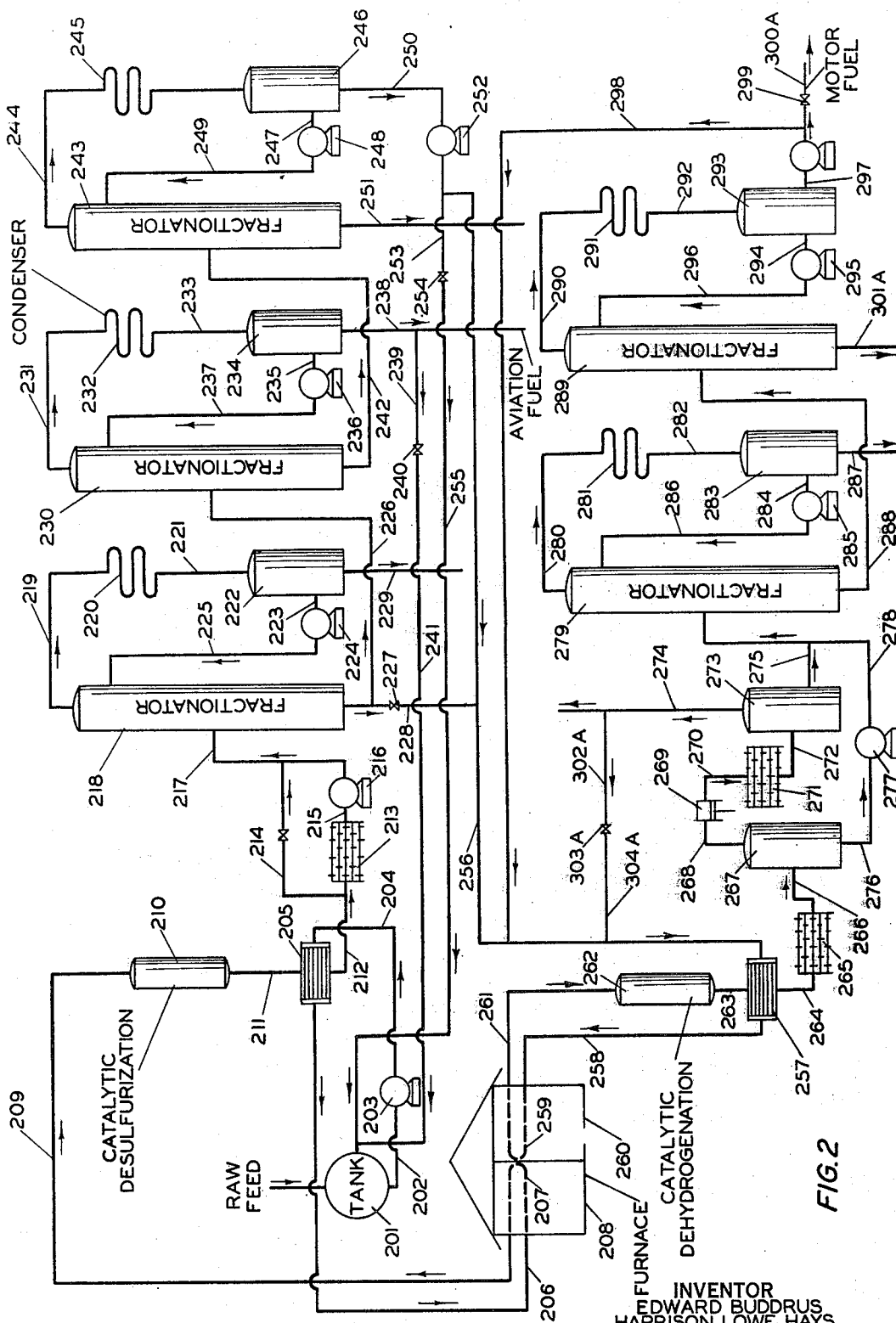


FIG. 2

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3 Sheets-Sheet 3

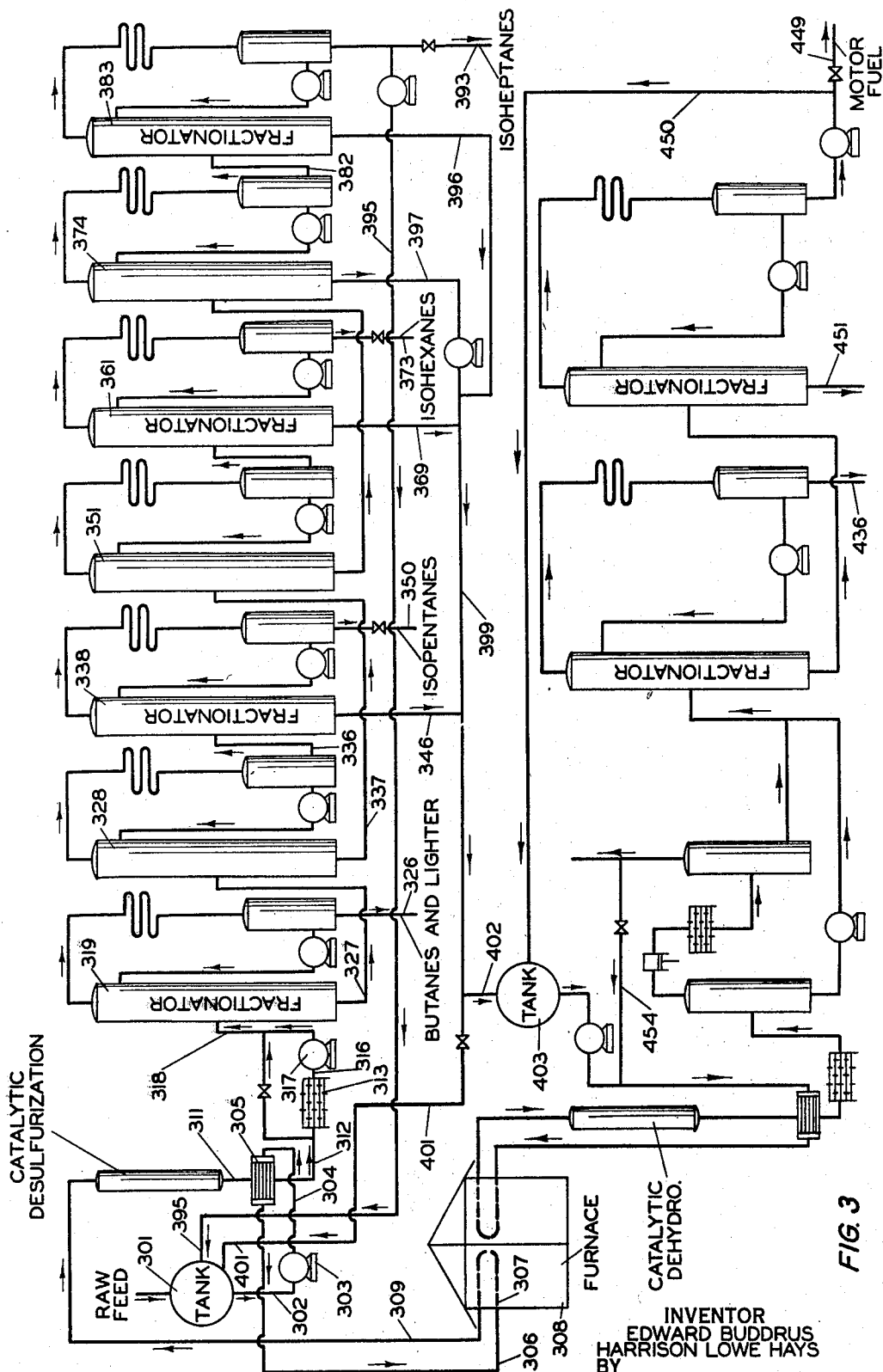


FIG. 3

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2,361,008

PROCESS FOR THE TREATMENT OF
HYDROCARBONS

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Application May 26, 1941, Serial No. 395,266

7 Claims. (Cl. 196—28)

This invention relates to a method for the manufacture of high octane number hydrocarbons from lower octane number hydrocarbons. More specifically, it relates to the production of high octane number aviation and/or high octane number motor fuels through the utilization of a combined catalytic desulfurization and dehydrogenation treatment wherein hydrocarbons in the natural gasoline range comprise the charge stock to the process.

The advantages to be obtained through the utilization of higher octane number fuels over those of lower octane number in internal combustion engines designed for their use are well known to those who have knowledge of the art. It is also well known that olefin hydrocarbons have a higher octane rating, that is, are less likely to cause detonation when used in internal combustion engines than are the corresponding normal paraffin hydrocarbons. It has further been demonstrated that hydrocarbons which belong to the same class and have the same molecular weights exhibit widely different detonation properties. This variation in octane number appears to be a function of the degree of complexity of the structure of the hydrocarbon molecule. For example, hexane, a straight chain paraffin hydrocarbon, has an octane number rating of 59, whereas an isomer, 2,2-dimethylbutane (neohexane), which possesses a highly branched molecular structure, has an octane number rating of 95. Relatively low molecular weight, saturated branch chain hydrocarbons are generally preferred for use in aeroplane fuel. Since the advantages which accrue from the use of higher octane number fuels are well known, many methods and processes have been evolved for their manufacture.

It has been demonstrated recently that desulfurization and dehydrogenation processes have certain advantages when applied to the manufacture of higher octane number hydrocarbons from lower octane number hydrocarbons. For example, Walter A. Schulz et al. (see Oil and Gas Journal, vol. 34, No. 21, p. 22 (1935)) have proved that it is possible to obtain an increase in anti-detonation rating of 2 to 4 octane numbers when catalytic desulfurization is applied to hydrocarbon stocks which contain varying concentrations of the sulfur compounds usually found in natural gasoline hydrocarbons. Another beneficial effect noted by these investigators is the increased response of stock so treated to the addition of lead tetraethyl. They observed that an increase in lead response of the order of 6 to 8 octane

numbers was realized through the addition of one cubic centimeter of lead tetraethyl per gallon to a desulfurized hydrocarbon material. It is also now well-known that there is an improvement in detonation characteristics of the order of 6 to 10 octane numbers in natural gasoline stocks which have been subjected to catalytic dehydrogenation. An appreciable increase in the lead susceptibility of the same natural gasoline has been observed following the dehydrogenation treatment.

The demand for extremely high octane number aviation gasoline has promoted extensive research on this subject and various treatments such as desulfurization, isomerization, and the like have been employed to attain 100 octane rating or better to meet government specifications. Unsaturation requirements, however, are correspondingly rigid and such treatments must be carefully controlled to avoid decomposition reactions. As a general rule, complete desulfurization of motor fuel is not essential and government specifications in this case allow a sulfur content up to about one-tenth of one per cent.

An object of the present invention is generally to produce higher octane number normally liquid hydrocarbons from lower octane number normally liquid hydrocarbons in the natural gasoline range.

A further object is the production of hydrocarbons in aviation and motor fuel ranges by combined catalytic desulfurization and catalytic dehydrogenation means wherein a portion of a hydrocarbon charge stock of any composition whatsoever in the natural gasoline range is subjected to catalytic desulfurization, while the remainder of this hydrocarbon material, combined with a certain portion of the desulfurized product, is subjected to catalytic dehydrogenation.

In a preferred form the invention contemplates thorough desulfurization of hydrocarbons from which aviation fuel is derived, at a temperature regulated to substantially preclude unsaturation, while at the same time subjecting a fraction of the stock to dehydrogenation for the production of an improved octane number motor fuel. The invention also contemplates desulfurization to a desired amount of the motor fuel fraction. More specifically, and in one embodiment of the invention, the processing elements are so arranged that a portion of the charge stock is continuously removed from a single coil furnace or heating means at a temperature high enough for desulfurization to proceed but sufficiently low that splitting or decomposition reactions will not be

appreciable during the desulfurization step. The remainder of the charge stock is preheated to dehydrogenation temperature and the process is so controlled and of such flexibility that the high octane aviation gasoline and high octane motor fuel may be obtained in any desired proportion. The cut withdrawn, following desulfurization, is fractionated to separate aviation and motor fuel fractions either or both of which are combined with fresh charge stock to the preheating coil, thereby regulating sulfur content and character of motor fuel recovered and enabling manufacture of high octane aviation gasoline and high octane motor fuel in any desired proportion whatsoever.

According to this invention, a portion of a feed stock withdrawn at desulfurization temperature, as heretofore described, is subjected in the presence of a suitable catalyst such as bauxite impregnated with sodium hydroxide to desulfurization under reaction pressure and temperature conditions of the order of 0 to 100 or more pounds per square inch and 500 to 800° F., respectively. Preferably desulfurization is carried out at pressures of from 0 to 50 pounds per square inch and within the temperature range of from 600 to 700° F. to maintain conditions such that decomposition or splitting reactions are slight and occur to an extent less than 5% and desirably less than 2% of the charge stock. Under such conditions desulfurization proceeds with its attendant beneficial effect, both with respect to octane number and to lead response as heretofore described.

The remainder of the charge stock is subjected in the presence of a suitable catalyst such as chromium oxide gel, chromic oxide carried on a suitable porous support, or bauxite, to dehydrogenation under pressure and temperature conditions of the order of 0 to 100 or more pounds per square inch and 600 to 1200° F., respectively. Dehydrogenation may be accomplished to some extent with certain catalysts, e. g., chromium oxide gel, at the lower temperatures in this range, i. e., from 600 to 800° F. However, we prefer to operate at temperatures of from 800 to 1200° F. to obtain a substantial degree of dehydrogenation per pass. These conditions are maintained such that not more than 30% of the charge stock is converted per pass through the reaction zone. The suitable exact conditions depend upon the type of feed stock and the catalyst used and are best determined through trial by one who is skilled in the art. Separation steps are employed both here and in the desulfurization step in order to separate and remove the sufficiently reacted products from the system. The insufficiently reacted hydrocarbons are recycled for further treatment.

The process of this invention may be carried forward in equipment such as is shown in Figure I, which is a diagrammatic side elevation of the various processing elements, and illustrates one means by which the process may be practiced.

Referring to Figure I, a natural gasoline feed stock, as heretofore described, is introduced through conduit 1, tank 2 and conduit 3 into pump 4, where it is compressed to a pressure suitable for entry into tubular heating coil 10 via conduit 5, heat exchanger 6 (heat exchange with a portion of the dehydrogenation effluent) and conduit 7. After entering the heating coil, the charge stock is progressively preheated from a relatively low temperature to a higher temperature suitable for catalytic dehydrogenation. At some intermediate point in the preheating coil

10, housed in a suitable furnace or heating means 11, a portion of the charge is withdrawn for desulfurization. Withdrawal of this preheated portion may be made at any number of points such as through conduits 12 and 14 and valves 13 and 15, respectively, for regulative purposes. Precautions are taken that the temperature of the stream entering the desulfurization reaction zone will produce materials in the aviation range which will meet the unsaturated specifications for aviation fuels. In order to aid in the control of this part of the process, valves 17 and 17-A and conduits 18 and 9 respectively are provided in order to shunt material at a lower temperature around the preheating coil to mix with the hydrocarbons being withdrawn directly by means of the valves and conduits previously mentioned. The best method of control can be selected by those who are skilled in the art. The preheated desulfurization feed passes through conduit 16, together with bypassed material entering through conduit 18, into catalyst case 19 where the desulfurization reaction occurs. Here the hydrocarbon material is subjected to the influence of a suitable catalyst such as bauxite impregnated with sodium hydroxide. The reaction temperature is such that the decomposition of the hydrocarbons so treated will not be more than 2% by weight for contact periods which may vary from 1 to 2 liquid volumes of feed per hour per volume of catalyst, the most suitable exact conditions being determined by trial.

Following passage through the desulfurization reaction zone, the hot reaction products exchange heat in exchanger 8 with a portion of the recycled feed to the dehydrogenation step and flowing via lines 20 and 81 into a subsequent portion of the stream being heated in coil 10. The reaction products then pass via conduit 21, cooler 22, conduit 23, pump 24 and conduit 25 into fractionator 26, or other suitable separation means where the hydrocarbons lighter than those desired in the aviation fraction are separated therefrom, pass through conduit 30, condenser and cooler 31, and conduit 32 into condensate accumulator 33. A portion of the condensate is taken from accumulator 33 through conduit 34 and compressed by means of pump 35 to a pressure sufficiently high to permit introduction as a reflux or cooling medium near the top of 26 by means of conduit 36. A quantity in excess of that required for this purpose is removed from the system through conduit 37. The bottom product, which comprises hydrocarbons of aviation fuel molecular weight and heavier, passes through conduit 38 into separation element 39 where the hydrocarbons of aviation fuel molecular weight pass through conduit 40, condenser and cooler 41 and conduit 42, into condensate accumulator 43. As in the preceding step, a portion of hydrocarbon material is introduced near the top of element 39 by means of conduit 44, pump 45, and conduit 46 to act as a reflux or cooling medium. Hydrocarbons of aviation fuel grade, in excess of the amount required for this purpose, are removed from the system through conduit 47, valve 47-A and conduit 47-B. At times, however, it may be necessary, for purposes of control, to recycle a portion of this stream by way of pump 48, conduit 48-A, valve 48-B and conduit 18 directly to the inlet of catalyst case 19, or by way of pump 48, conduit 48-A, valve 60-A, conduit 60-B, conduit 60 and conduit 61 into cold raw feed tank 2. The bottom product, which contains hydrocarbons of motor fuel molecular weight and heavier, passes

through conduit 49 into element 50. The motor fuel hydrocarbons pass into accumulator 54 via conduit 51, condenser and cooler 52 and conduit 53. A portion of these motor fuel hydrocarbons are introduced near the top of 50 as reflux or cooling medium by means of conduit 55, pump 56, and conduit 57. The volume of these in excess of the amount required for this purpose is removed from the accumulator and is transferred through conduit 58, pump 59, conduit 60 and conduit 61, into tank 2, where it comprises a portion of the feed to the process. The bottom product is removed from the system through conduit 62.

Motor fuel hydrocarbons passing through conduit 60, together with dehydrogenation liquid recycle stock passing through conduit 104 and raw feed entering through conduit 1, comprise the total liquid feed to the dehydrogenation step. This total liquid feed passes from tank 2 through conduit 3 into pump 4 where it is compressed to a suitable reaction pressure. This pressure is between 0 and 100 or more pounds per square inch. Thence, it passes through conduit 5 into heat exchanger 6 where a certain temperature is obtained, as heretofore described, by heat interchange with hot dehydrogenation catalyst chamber effluent products which are passing through conduit 67. At this pressure and temperature the hydrocarbon material passes through conduit 7 into heating coil 10, as heretofore mentioned, where a portion is removed as desulfurization feed. The remainder passes through the coil together with hydrogen and light hydrocarbons which enter the coil through conduit 81 from elsewhere in the dehydrogenation step. The preheated feed stock then passes through conduit 63 controlled by valve 10—C into a suitable catalyst case 64 where it is subjected to the influence of a suitable catalyst such as bauxite, chromium oxide gel, or chromic oxide carried on a porous support. Temperature of the dehydrogenation feed may be controlled by passing a portion thereof through conduit 10—A accurately regulated by valve 10—B. Ordinarily, dehydrogenation is carried out at relatively higher temperatures than desulfurization but in accordance with this invention provision is made whereby dehydrogenation may be accomplished to some extent at the same or even lower temperatures under certain circumstances. See for example U. S. Patents 1,905,383; 2,098,959; and 2,205,141; all of which disclose dehydrogenation at temperatures below 800° F. The dehydrogenation reaction temperature is preferably so regulated (between 600 and 1200° F.) that the decomposition of the charge so treated will not exceed 30% per pass through the reaction zone for contact periods which may range from 1½ to 3 liquid volumes of gasoline feed per hour per volume of catalyst, the most suitable conditions being determined by trial.

Following passage through the reaction zone, the hot reaction products pass through conduit 65 into cooler 66 where they undergo partial cooling, thence, by way of conduit 67 into exchanger 6 where they exchange heat with the cold liquid feed, as heretofore described. The reaction products then pass through conduit 68, cooler 69, and conduit 70 into separation element 71 where a rough separation is obtained between the non-condensable gases and heavier materials. The non-condensables, which may contain a certain percentage of hydrocarbons in the gasoline range, pass through conduit 12 into pump 73 where they are compressed to a pressure which

is sufficient to condense nearly all the hydrocarbons heavier than ethane following passage through conduit 74 and cooler 75. The mixture passes through conduit 76 into separation element 77, where vapors which comprise essentially ethane and lighter, including hydrogen and some propylene and propane, may be removed from the system through conduit 78. A portion of this material, however, may be recycled to the system through valve 79, conduit 80, heat exchanger 8 and conduit 81 for better control over yield and octane number of desirable products. The butanes and heavier pass from 77 through conduit 85 where they mix with the greater bulk of the normally liquid hydrocarbons which have been removed from 71 via conduit 82, pump 83 and conduit 84 for entry into separation element 86. The hydrocarbons lighter than motor fuel pass through conduit 87 and condenser and cooler 88 into condensate accumulator 89. A portion of the condensate is taken from the accumulator 89 through conduit 90 and compressed by means of pump 91 to a pressure sufficiently high to introduce it as a reflux or cooling medium near the top of 86. A quantity in excess of that required for this purpose is removed from the system through conduit 93. The bottom product, which contains the valuable motor fuel fraction and a small amount of heavier material, passes through conduit 94 into element 95 where the motor fuel fraction passes through conduit 96, and condenser and cooler 97 into condensate accumulator 98. As in the preceding step, a portion of this material is introduced near the top of 95 by means of conduit 99, pump 100 and conduit 101, to act as a reflux or cooling medium. A portion of the amount in excess of this requirement is continuously removed from the system through conduit 102, pump 103, conduit 104, valve 105, and conduit 106 for use as a high octane number motor fuel or as one of its ingredients. The remainder of the excess amount is recycled through conduit 104 to tank 2 for control purposes. The bottom product is removed from the system through conduit 107.

By suitable location of conduits 12 and 14 relative to the heating coil and adjustment of valves 13 and 15 the temperature to which the stock is raised for desulfurization may be accurately controlled, and also the relative quantity of aviation and motor fuel respectively recovered may be regulated. Valves 10—B and 10—C provide further means for regulating the relative flow of material to the respective desulfurizing and dehydrogenating units. For instance, by appropriate regulation of these valves the principal portion of the feed stock may be directed through the desulfurization unit and a high proportion of aviation fraction recovered, while at the same time a substantial quantity of the motor fuel is desulfurized, being returned through conduit 80 to the tank 2 and combined therein with raw feed stock. On the other hand by diminishing the flow through branch conduits 12 and 14 and where the demand is low for aviation fuel, the bulk of the charge stock may proceed directly through the heating coil to the dehydrogenation unit for production of motor fuel. Likewise a low sulfur high-octane motor fuel is obtained by desulfurizing the major portion of the raw feed and either cycling a portion of the aviation hydrocarbons therewith through dehydrogenation or separating and blending with dehydrogenated motor fuel. It is generally desirable, however, to obtain as complete a recovery as possible of the

desulfurized aviation fuel fraction. Thus the process is of such flexibility that products having also any desired characteristics may be obtained in any desired proportion.

A modified form of the invention is shown in Figure II of the drawings, in which the processing elements are so arranged that the total feed stock is subjected to catalytic desulfurization in the first step of the process. A desired proportion of the desulfurized products is heated to a suitable dehydrogenating temperature and subjected to catalytic dehydrogenation while the remainder is fractionated for the recovery of high octane aviation fuel. The heavier fraction separated in the last mentioned fractionation step is combined with other desulfurized products in any amount, preheated, and subjected to catalytic dehydrogenation. A particularly advantageous feature resides in the fact that a comparatively small quantity of heat is required to raise the desulfurization effluents to the higher dehydrogenating temperature. In the catalytic dehydrogenation step, operating conditions are maintained at such a level that the effluents contain principally a hydrocarbon material suitable for use as an important ingredient in motor fuels, and of higher octane number than materials in the dehydrogenation feed stock of the same boiling range. In a similar manner to that described with respect to Figure I, the process is characterized by flexibility of control so that desired products can be obtained in any proportion. Specifically, means are provided for by-passing a substantial quantity or all of the desulfurized stock in accordance with the demand directly to dehydrogenation.

With reference to Figure II, a raw natural gasoline feed stock as heretofore described is introduced from feed tank 201 through conduit 202 and compressed to a suitable reaction pressure by means of pump 203 together with any insufficiently desulfurized material which it may be found to be necessary to recycle (by one who is skilled in the art) which joins 202 through the medium of conduits 241 and 255 which discharge into tank 201. This pressure is between 0 and 100 or more pounds per square inch. The total feed then passes through conduit 204 and thence through heat exchanger 205 where a certain temperature is obtained by heat interchange with hot catalyst chamber effluent products which are passing through conduit 211. At this pressure and temperature, the natural gasoline feed passes through conduit 206 into preheating coil 207 which is suitably housed in a furnace or heating means 208 and wherein the temperature of the feed is raised to from 500 to 800° F. and, as previously stated, preferably from 600 to 700° F. The preheated hydrocarbons then pass through conduit 209 into a suitable catalyst case 210 where they are subjected to the influence of a suitable catalyst such as bauxite impregnated with sodium hydroxide. The reaction temperature is such that the decomposition of the hydrocarbons so treated will be not more than 2% by weight for contact periods which may vary from 1 to 2 liquid volumes of feed per hour per volume of catalyst, the most suitable exact conditions being determined by trial. Actually pressures and temperature of the order of 0 to 50 pounds per square inch and 600 to 700° F., respectively, seem preferable in promoting the desulfurization in order to suppress more than slight decomposition.

Following passage through the desulfurization

reaction zone, the hot reaction products exchange heat with the cold feed in exchanger 205 as heretofore mentioned. The reaction products then pass via conduit 212, cooler 213, conduit 215, pump 216 and conduit 217 into fractionator 218, or other suitable separation means where the hydrocarbons lighter than those desired in the aviation hydrocarbon fraction are separated therefrom, pass through conduit 219, condenser and cooler 220, and conduit 221 into condensate accumulator 222. A portion of the condensate is taken from accumulator 222 through conduit 223, and compressed by means of pump 224 to a pressure sufficiently high to permit introducing it as a reflux or cooling medium near the top of 218 by means of conduit 225. A quantity in excess of that required for this purpose is removed from the system through conduit 229. The bottom product which comprises hydrocarbons of aviation fuel molecular weight and heavier, passes through conduit 228 to separation element 230 where the hydrocarbons of aviation fuel molecular weight pass through conduit 231, condenser and cooler 232, and conduit 233, into accumulator 234. As in the preceding step, a portion of this hydrocarbon material is introduced near the top of element 230 by means of conduit 235, pump 236, and conduit 237, to act as a reflux or cooling medium. Hydrocarbons of aviation fuel grade in excess of the amount required for this purpose are removed from the system through conduit 238. At times, however, it may be considered necessary for purposes of control to recycle a portion of this stream by way of conduit 239, valve 240 and conduit 241. The bottom product, which contains hydrocarbons of motor fuel molecular weight and heavier, passes through conduit 242 into element 243. The motor fuel hydrocarbons pass into accumulator 244 via conduit 244, and condenser and cooler 245. A portion of these motor fuel hydrocarbons are introduced near the top of 243 as reflux, or cooling medium, by means of conduit 247, pump 248, and conduit 249. The volume of these in excess of the amount required for this purpose are removed from the accumulator as the primary raw feed stock to the dehydrogenation step. Provided, however, that if it may be considered to be necessary for control, a portion of this stream may be recycled to the desulfurization step via conduit 253, valve 254, and conduit 255. Means have also been provided, whereby a portion of the bottom product from 218 may be fed directly to the dehydrogenation step by way of valve 227 and conduit 228. Determination of the amount to be diverted directly to the dehydrogenation step will be in accordance with relative demands for aviation and motor fuels.

The net overhead product from 243, which comprises the motor fuel feed stock to the dehydrogenation step, passes from accumulator 244 through conduit 250 and into pump 252 where it is compressed to a suitable reaction pressure. This pressure is between 0 and 100 or more pounds per square inch. Thence it passes, together with recycle stock from conduit 208, through conduit 256 into heat exchange 257 where a certain temperature is obtained by heat interchange with hot catalyst chamber effluent products which are passing through conduit 203. At this pressure and temperature the hydrocarbon material passes through conduit 258 into a preheating coil 259 which is suitably housed in a furnace or heating means 260 and wherein the

temperature of the feed is raised to 600 to 1200° F. or as indicated above, preferably from 800 to 1200° F. This may be a portion of furnace coil housing 208 for economy reasons. The preheated feed stock then passes through conduit 261 into a suitable catalyst case 262 where it is subjected to the influence of a suitable catalyst such as bauxite, chromic oxide gel, or chromic oxide supported on a porous carrier. The reaction temperature is such that the decomposition of the charge so treated will not exceed 30% per pass through the reaction zone for contact periods which may range from 1½ to 3 liquid volumes of gasoline feed per hour per volume of catalyst, the most suitable conditions being determined by trial.

Following passage through the dehydrogenation reaction zone, the hot reaction products exchange heat with the cold feed in exchanger 263 as heretofore described. The reaction products then pass through conduit 264, cooler 265, and conduit 266 into separation element 267 where a rough separation is obtained between the non-condensable gases and heavier materials. The non-condensables, which may contain a certain percentage of hydrocarbons in the gasoline range, pass through conduit 268 into pump 269 where they are compressed to a pressure which is sufficient to condense nearly all the hydrocarbons heavier than ethane following passage through conduit 270 and cooler 271. The mixture passes through conduit 272 into separation element 273, where vapors which comprise essentially ethane and lighter including hydrogen may be removed from the system through conduit 274. It is considered to be beneficial from the point of view both of increased yields and octane number to recycle a portion of the hydrogen stream through the process together with the liquid feed. This may be done by way of conduit 302—A, valve 303—A, and conduit 304—A. The butane and heavier pass from 273 through conduit 275 where they join the greater bulk of the normally liquid hydrocarbons which have been removed from 267 via conduit 276, pump 277 and conduit 278 for entry into separation element 279. The hydrocarbons lighter than motor fuel pass through conduit 280, condenser and cooler 281, and conduit 282 into accumulator 283. A portion of the condensate is taken from accumulator 283 through conduit 284 and compressed by means of pump 285 to a pressure sufficiently high to introduce it as a reflux or cooling medium near the top of 279. A quantity in excess of that required for this purpose is removed from the system through conduit 287. The bottom product, which contains the valuable motor fuel fraction and a small amount of heavier material, passes through conduit 288 into element 289 where the motor fuel fraction passes through conduit 290, condenser and cooler 291, and conduit 292 into accumulator 293. As in the preceding step, a portion of this material is introduced near the top of 289 by means of conduit 294, pump 295, and conduit 296, to act as a reflux or cooling medium. A portion of the amount in excess of this requirement is continuously removed from the system through valve 299 and conduit 300—A for use as a high octane number motor fuel or as one of its ingredients. The remainder of the excess amount is recycled through conduit 298 to the dehydrogenation step for control purposes. The bottom product is removed from the system through conduit 301—A.

In Figure III is shown apparatus for carrying out a further modified procedure where individual branch chain isomers are separated which may be used individually or as aviation blending stocks from corresponding normal hydrocarbons which preferably constitute dehydrogenation feed stock. Saturated branch chain hydrocarbons are of optimum octane number and lead susceptibility while unsaturated forms of normal hydrocarbons are of increased octane number over corresponding normal saturated forms. Therefore by means of the herein described integrated process, maximum efficiency is obtained from charge stock of any constitution whatever in the natural gasoline range.

A raw natural gasoline feed stock is introduced from feed tank 301 through conduit 302 and compressed to a suitable desulfurization reaction feed pressure by means of pump 303 together with any insufficiently desulfurized material which it may be found to be necessary to recycle (by one who is skilled in the art) which has entered 301 through conduits 395 and 401. The pressure is between 0 and 100 or more pounds per square inch. The total feed then passes through conduit 304 and thence through heat exchanger 305 where a certain temperature is obtained by heat interchange with hot catalyst chamber effluent products which are passing through conduit 311. At this pressure and temperature, the natural gasoline feed passes through conduit 306 into preheating coil 307, which is suitably housed in a furnace or heating means 308. The preheated hydrocarbons then pass through conduit 309 into a suitable catalyst case where they are subjected to the influence of a suitable catalyst such as bauxite impregnated with sodium hydroxide. The reaction temperature is such that the decomposition of the hydrocarbons so treated will not be more than 2% by weight for contact periods which may vary from 1 to 2 liquid volumes of feed per hour per volume of catalyst, the most suitable exact conditions being determined by trial.

Following passage through the desulfurization reaction zone, the hot reaction products exchange heat with the cold feed in exchanger 305 as heretofore mentioned. The reaction products then pass via conduit 312, cooler 313, conduit 316, pump 317 and conduit 318 into fractionator 319 or other suitable means of separation where hydrocarbons comprising butanes and lighter than those desired as aviation gasoline hydrocarbons are separated therefrom. These pass from the system through conduit 326. Heavier hydrocarbons which may consist of any saturated, straight chain and branched chain hydrocarbons comprise the feed to separation element 328 via conduit 327. There normal and branched chain isomeric pentanes are removed as an overhead product for feed to separation element 338 through conduit 336. The hexanes and heavier comprise the bottom product which are used as feed to separation element 351 via conduit 337. In separation element 338 isopentanes are removed as an overhead product and leave the system through conduit 350. Normal pentane is removed as a bottom product via conduit 346 which joins dehydrogenation feed conduit 399. The various isomeric hexanes may comprise the overhead product of 351 and serve as feed to separation element 361. Heptanes and heavier comprise the bottom product of 351 and serve as feed to separation element 374. Branched

chain hexanes comprise the overhead of 361 and are removed from the system through conduit 373. Normal hexane comprises the bottom product from 361 and serves as one component of the dehydrogenation feed via conduit 369. Isomeric heptanes comprise the overhead product of 374 which feeds separation element 383 via conduit 382. The bottom product of 374 which comprises octanes and heavier hydrocarbons is fed directly to the dehydrogenation step together with other hydrocarbons previously mentioned. Isoheptanes are the overhead product from element 383 and are removed from the system via conduit 393 except for a quantity which it may be found necessary for control to recycle to the desulfurization system through conduit 395. Normal heptane is removed in the bottom product from 383 and comprises another component in the feed to the dehydrogenation step via conduit 396.

The raw feed to the dehydrogenation step which comprises hydrocarbons passing through conduits 346, 369, 396 and 397 passes into feed tank 403 via conduits 399 and 402, except for a portion which may be recycled to the desulfurization system through conduit 401. Following thorough mixing in 403, together with recycle stock which enters through conduit 450, the feed follows the same path as that shown in the dehydrogenation step of Figure II. Hydrogen is recycled to the system through conduit 454 for reaction control, butanes and lighter are removed from the system through conduit 436, and hydrocarbons in the motor fuel range are removed through conduit 449. A portion of the motor fuel hydrocarbons constitutes liquid recycle stock to the reaction zone via conduit 450. Hydrocarbons heavier than motor fuel are removed from the system via conduit 451.

In the interest of simplicity, elements of similar function to corresponding elements in Figure II have not been specifically delineated or described. The operation of these elements however is readily understood from the foregoing description with respect to Figure II.

The separation steps may be extended, if desired, to separate normal octane from its branched chain isomers. The latter is preferably blended with other branched chain and low molecular weight normal hydrocarbons for blending aviation fuel. The normal octane with other straight chain hydrocarbons will constitute dehydrogenation feed stock.

We claim:

1. A process for the manufacture of high octane aviation gasoline and high octane motor fuel which comprises passing hydrocarbon charge stock in the gasoline range through an elongated heated passageway, withdrawing at an intermediate point in said passageway a portion of said charge stock at a temperature high enough for catalytic desulfurization but sufficiently low to prevent decomposition reactions, subjecting said withdrawn portion to catalytic desulfurization, recovering from the effluent a relatively low molecular weight hydrocarbon fraction suitable as high octane aviation gasoline, separating from the effluent another fraction containing relatively high molecular weight hydrocarbons heavier than the aviation gasoline range, and combining the same with new charge stock, passing the remainder of said charge stock through said heated passageway to attain a higher temperature suitable for catalytic dehydrogenation, and subjecting said remaining portion to catalytic dehydro-

genation for the production of high octane motor fuel.

2. A process for the manufacture of high octane aviation gasoline and high octane motor fuel which comprises passing hydrocarbon charge stock in the natural gasoline range through an elongated heated passageway, withdrawing at an intermediate point in said passageway a portion of said charge stock at a temperature high enough for catalytic desulfurization but sufficiently low to prevent decomposition reactions, subjecting said withdrawn portion to catalytic desulfurization and recovering from the effluent a relatively low molecular weight hydrocarbon fraction suitable as high octane aviation gasoline, separating from the effluent another fraction containing relatively high molecular weight hydrocarbons heavier than the aviation gasoline range, and combining said fraction with said original charge stock, passing the remainder of said charge stock through said heated passageway to attain a higher temperature suitable for catalytic dehydrogenation, and subjecting said remaining portion to catalytic dehydrogenation for the production of high octane motor fuel.

3. A process for the manufacture of high octane aviation gasoline and high octane motor fuel in the desired proportion, which comprises passing hydrocarbon charge stock in the gasoline range through an elongated heated passageway, withdrawing at an intermediate point in said passageway a portion of said charge stock at a temperature of between 500 to 800° F. and pressure from 0 to 100 pounds per square inch, catalytically desulfurizing said portion and recovering a relatively low molecular weight fraction therefrom suitable as high octane aviation gasoline, separating from the desulfurization effluent another relatively higher molecular weight hydrocarbon fraction heavier than the aviation gasoline range and combining the same with fresh charge stock, passing the remainder of the charge stock through said heated passageway to attain a materially higher temperature suitable for catalytic dehydrogenation, subjecting said remaining portion to catalytic dehydrogenation, and recovering high octane motor fuel from the effluent.

4. A process for the manufacture of high octane aviation gasoline and high octane motor fuel in the desired proportion, which comprises passing hydrocarbon charge stock in the gasoline range through an elongated heated passageway, withdrawing at an intermediate point in said passageway a portion of said charge stock at a desulfurization temperature of between 600 to 700° F. and pressure from 0 to 100 pounds per square inch, catalytically desulfurizing said portion and recovering a relatively low molecular weight fraction therefrom suitable as high octane aviation gasoline, separating from the desulfurization effluent another relatively higher molecular weight hydrocarbon fraction and combining the same with fresh charge stock, passing the remainder of the charge stock through said heated passageway to attain a dehydrogenation temperature of from 800 to 1200° F., subjecting said remaining portion to catalytic dehydrogenation, and recovering high octane motor fuel from the effluent.

5. A method for the treatment of hydrocarbons for the production of separate fractions of desulfurized hydrocarbons and dehydrogenated hydrocarbons which comprises passing hydrocarbon charge stock in the gasoline range through a tubular heating coil and progressively preheating said hydrocarbons from a relatively low tempera-

ture to a higher temperature of at least 800° F. suitable for catalytic dehydrogenation, withdrawing a portion of said charge stock at an intermediate temperature substantially below 800° F. and subjecting said portion to catalytic desulfurization at said intermediate temperature, recovering from the effluent a fraction in the aviation gasoline range and a heavier fraction in the motor fuel range, combining said heavier fraction with said original charge stock, and subjecting the remaining portion of said charge stock at said higher temperature to catalytic dehydrogenation.

6. A process for the manufacture of high octane aviation gasoline and high octane motor fuel which comprises passing hydrocarbon charge stock in the gasoline range through an elongated heated passageway, withdrawing at an intermediate point in said passageway a portion of said charge stock at a temperature high enough for catalytic desulfurization but sufficiently low to prevent decomposition reactions, subjecting said withdrawn portion to catalytic desulfurization, recovering from the effluent a relatively low molecular weight hydrocarbon fraction suitable as high octane aviation gasoline, separating from the effluent another fraction containing relatively high molecular weight hydrocarbons heavier than the aviation gasoline range, and combining the same with new charge stock, passing the remainder of said charge stock through said heated passageway to attain a higher temperature suitable for catalytic dehydrogenation, and subjecting said remaining portion to catalytic dehydro-

genation, recovering from the catalytic dehydrogenation effluent a fraction suitable as high octane motor fuel, and recycling a portion of said high octane motor fuel with the aforesaid new charge stock.

7. A process for the manufacture of high octane aviation gasoline and high octane motor fuel which comprises passing hydrocarbon charge stock in the natural gasoline range through an elongated heated passageway, withdrawing at an intermediate point in said passageway a portion of said charge stock at a temperature high enough for catalytic desulfurization but sufficiently low to prevent decomposition reactions, subjecting said withdrawn portion to catalytic desulfurization and recovering from the effluent a relatively low molecular weight hydrocarbon fraction suitable as high octane aviation gasoline, separating from the effluent another fraction containing relatively high molecular weight hydrocarbons heavier than the aviation gasoline range, and combining said fraction with said original charge stock, passing the remainder of said charge stock through said heated passageway to attain a higher temperature suitable for catalytic dehydrogenation, and subjecting said remaining portion to catalytic dehydrogenation, recovering from the catalytic dehydrogenation effluent a fraction suitable as high octane motor fuel, and recycling a portion of said high octane motor fuel with said original charge stock.

EDWARD BUDDRUS.
HARRISON L. HAYS.