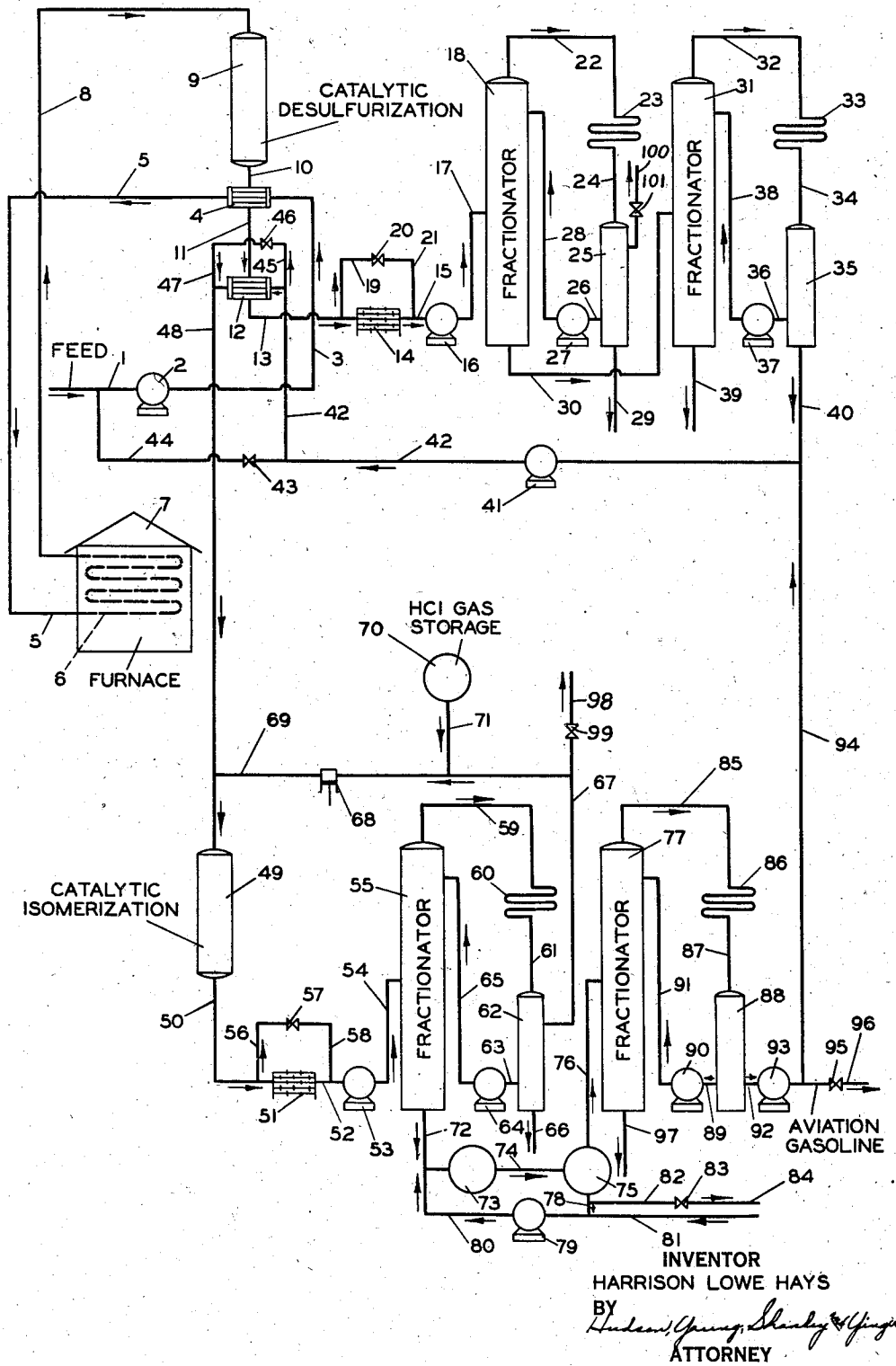
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TREATMENT OF HYDROCARBONS

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TREATMENT OF HYDROCARBONS

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This invention relates to the manufacture of higher octane number hydrocarbons from lower octane number hydrocarbons and more particularly to the manufacture of aviation and/or motor fuels of high octane number from a charge stock which may contain any combination of the hydrocarbons in the natural gasoline range in any concentration whatsoever.

The principal object of this invention is to produce high octane number normally liquid hydrocarbons from relatively low octane number normally liquid hydrocarbons, preferably those usually to be found in natural gasoline stock.

Another object is to produce high octane number hydrocarbons suitable for use as aviation and motor fuels, from a charge stock which comprises any combination of the hydrocarbons in the natural gasoline range in any concentration whatsoever.

Numerous other objects of the invention will more fully hereinafter appear.

According to this invention, a natural gasoline feed stock is first subjected to desulfurization, in the presence of a suitable desulfurization catalyst such as bauxite impregnated with sodium hydroxide, under reaction pressure and temperature conditions of the order of from 0 to about 100 pounds per square inch and 500 to 800° F., respectively. Reaction conditions are maintained such that decomposition reactions are slight and that less than 5 per cent and preferably less than 2 per cent of the charge undergoes splitting reactions. The catalytic desulfurization is so conducted that the desulfurization product contains not more than 0.1% and preferably not more than 0.01% of sulfur as determined by the A. S. T. M. lamp method. Actually, pressures and temperatures of the order of 0 to 50 pounds per square inch and 500 to 700° F., respectively, seen to be preferable in promoting the desulfurization reaction in order to suppress more than slight decomposition as described in this invention. Suitable means of separation are now employed, wherein desulfurized hydrocarbons in the aviation or motor fuel range are separated from those which are of both lower and higher volatility. The motor fuel or aviation fuel cut is now subjected to catalytic isomerization. However, a portion of this stream may be recycled to the desulfurization step for process control.

In the catalytic isomerization step, the motor fuel or aviation fuel fraction is subjected, in the presence of a suitable catalyst, such as some one of the metallic halides, aluminum chloride, for example, carried on a satisfactory supporting material and in the presence of hydrogen chloride, to reaction pressure and temperature conditions of the order of 0 to 500 pounds or more per square inch and 0 to 1000° F., respectively. These conditions are maintained such that decomposition reactions are slight, and preferably less than 5 per cent of the charge stock undergoes splitting reactions. The isomerization reaction is favored considerably if the temperatures which are used in conjunction with reasonably high pressures are maintained well below those at which decomposition usually begins. Therefore, pressures and temperatures of the order of 50 to 300 pounds per square inch and 200° to 700° F., respectively, seem to be preferable in promoting the isomerization reaction.

As the isomerization catalyst, there may be used any metallic halide capable, under the reaction conditions employed, of effecting isomerization of normal hydrocarbons of the molecular weight range encountered to branched forms or isomerization of branch chain hydrocarbons to more branched forms. Generally an amphoteric metal halide is employed. It is preferred to use an aluminum halide such as aluminum chloride, aluminum bromide, etc. Generally aluminum chloride is used.

The isomerization is carried out in the presence of appreciable amounts of the hydrogen halide corresponding to the isomerization catalyst. Thus hydrogen chloride is used when aluminum chloride is employed, hydrogen bromide when aluminum bromide is used, etc.

Following isomerization, the isomerization reaction mixture is treated to separate it into various fractions, including a fraction of condensible hydrocarbons (mainly isobutane) lighter than those of aviation or motor fuel grade, a fraction of non-condensible normally gaseous hydrocarbons (propane and lighter) containing gaseous hydrogen chloride, a fraction comprising highly branched chain hydrocarbons of aviation fuel molecular weights, which is suitable for use as, or in the preparation of, aviation gasoline, and at least one fraction of branched chain hydrocarbons of higher molecular weight than the aviation range. The portion of higher molecular weight than aviation grade may, if desired, be resolved into a fraction of hydrocarbons of motor fuel molecular weight and a still heavier fraction which may be withdrawn from the system as a by-product and put to any desired use.

It has been found to be particularly advantageous to recycle at least a portion of and preferably all of the above-mentioned fraction of

normally gaseous hydrocarbons containing hydrogen chloride to the incoming isomerization feed, supplying only such additional hydrogen chloride as may be necessary to make up system losses. This material is recycled only because of its hydrogen chloride content. The hydrogen chloride serves to activate the aluminum chloride isomerization catalyst.

The fraction of the isomerization products which comprises aviation fuel hydrocarbons, motor fuel hydrocarbons, and heavier, is preferably neutralized, prior to or after formation, by means of an aqueous solution of an alkali capable of neutralizing the hydrogen chloride therein, such as aqueous sodium hydroxide. In this way the traces of hydrogen chloride appearing in this fraction are removed and are prevented from appearing in the final aviation fraction and in any motor fuel fraction which may be prepared.

The process of this invention may be carried forward in equipment such as is shown in the drawing, which is a diagrammatic view of the various processing elements, not drawn to scale, and illustrates one means by which the process may be practiced.

With reference to the drawing, a natural gasoline feed stock, as heretofore described, is introduced through conduit 1 together with insufficiently desulfurized recycle stock from conduit 44. The total feed is compressed to a suitable reaction pressure by means of pump 2. This pressure is between 0 and 100 or more pounds per square inch. The total feed then passes through conduit 3 and thence through heat exchanger 4 and conduit 5 into preheating coil 6 which is suitably housed in a furnace or heating means 7. The preheated hydrocarbons then pass through conduit 8 into a suitable catalyst case 9 where they are subjected to the desulfurizing 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 per cent by weight for contact periods corresponding to flow rates 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 reaction zone, the hot reaction products passing out via conduit 10 exchange heat with the cold feed passing through exchanger 4 as heretofore mentioned. The reaction products then pass via conduit 11, exchanger 12, conduit 13, cooler 14, conduit 15, pump 16 and conduit 17 into fractionator 18 or other suitable separation means. A portion of the reaction products may be by-passed around cooler 14 by means of valve 20 and conduit 21 for the purpose of controlling the temperature of the feed to separating means 18. In separator 18 the hydrocarbons lighter than those desired in aviation or motor fuel fractions are separated therefrom and pass through conduit 22, condenser and cooler 23, and conduit 24 into condensate accumulator 25. Excess light gases, including hydrogen sulfide formed by decomposition of organic sulfur compounds in the desulfurization step, may be removed through conduit 100 controlled by valve 101, or by other suitable means. A portion of the condensate is taken from the accumulator 25 through conduit 26, and compressed by means of pump 27 to a pressure sufficiently high to permit introducing it as a reflux or cooling medium near the top of 18 by means of conduit 28. A quantity in excess of that required for this purpose is removed from the system through conduit 29. The bottom product, which comprises hydrocarbons of aviation and motor fuel molecular weight and heavier, passes through conduit 30 to separation element 31 where the hydrocarbons of aviation and motor fuel molecular weight pass through conduit 32, condenser and cooler 33, and conduit 34 into condensate accumulator 35. As in the preceding step, a portion of this hydrocarbon material is introduced near the top of element 31 by means of conduit 36, pump 37, and conduit 38, to act as a reflux or cooling medium. Hydrocarbons of heavier than aviation and motor fuel grade are removed from the system through conduit 39. Hydrocarbons in accumulator 35 in excess of the amount required for reflux to 31 comprise the feed to the isomerization step.

Hydrocarbons from accumulator 35 pass through conduit 40 into pump 41 where they are compressed to isomerization reaction pressure and pass thence via conduit 42 into heat exchanger 12 where they are heated to reaction temperature. Temperature control is maintained through by-passing the heat exchanger with a portion of the stream by means of conduit 45, valve 46, and conduit 47. By means of valve 43 and conduit 44 a portion of this hydrocarbon stream may be recycled to the desulfurization system for the purpose of process control. The preheated isomerization feed passes from heat exchanger 12 through conduit 48 into catalyst case 49 together with light hydrocarbon vapors and hydrogen chloride which join this stream through conduit 69. In the catalyst case the natural gasoline hydrocarbons are subjected to the influence of a suitable catalyst such as one of the metallic halides. The reaction temperature is such that decomposition of the hydrocarbons so treated will be less than 5 per cent by weight for reaction periods which may vary from about 5 to about 30 minutes, the most suitable exact conditions being determined by trial. Conditions may be maintained to vary the composition of the equilibrium mixture of reaction products in accordance with the type of product desired.

Following passage through the reaction zone, the hot reaction products pass via conduit 50 into exchanger 51 where they are cooled by suitable means prior to entry into separation element 55 through conduit 52, pump 53, and conduit 54. Conduit 56, valve 57, and conduit 58 comprise a by-pass through which a portion of the reaction products may be passed for temperature control. Hydrocarbons lighter than those desired in the finished product together with hydrogen chloride pass through conduit 59, condenser and cooler 60, and conduit 61 into condensate accumulator 62. A portion of the condensate is taken from accumulator 62 through conduit 63 and compressed by means of pump 64 to a pressure sufficiently high to permit its introduction as a reflux or cooling medium near the top of 55 via conduit 65. The condensed portion in excess of that required for this purpose is continuously removed from the system through conduit 66. An uncondensed portion (propane and lighter) which contains an appreciable quantity of hydrogen chloride is removed near the top of 62 and passes through conduit 67, compressor pump 68, and conduit 69 to its point of junction with the hot catalyst chamber feed. If operations render it desirable, a portion of this uncondensed material may be vented from conduit 67 by suitable venting means, such as conduit 98 controlled by valve 99. Pump

68 may or may not be needed depending upon the desired operation pressure of catalyst case 49. Fresh hydrogen chloride make-up is provided by means of tank 70 and conduit 71. The bottom product from 55 which contains the valuable constituents, together with insufficiently reacted materials and some heavier hydrocarbons which were formed in the reaction zone, passes through conduit 72 into a neutralization contactor 73 where a material such as caustic soda is employed for the purpose of neutralizing or removing a small quantity of hydrogen chloride. Thence the hydrocarbons and neutralizing solution pass through conduit 74 into a settling tank 75 where the hydrocarbons are separated from the neutralizing solution and pass through conduit 76 into separation element 77. Conduit 78, pump 79, and conduit 80 permit recirculation of the partially used neutralizing solution. Fresh solution is introduced through conduit 81, and spent solution is removed from the system through conduit 82, valve 83, and conduit 84. The valuable hydrocarbon constituent passes through conduit 85, condenser and cooler 86, and conduit 87 into condensate accumulator 88. As in the preceding step, a portion of this material is introduced near the top of 77 by means of conduit 89, pump 90, and conduit 91 to act as a reflux or cooling medium. The valuable constituent in excess of that required for this purpose is removed from the system through conduit 92, pump 93, valve 95, and conduit 96. A portion of this material, however, is recycled to the isomerization system through conduit 94 for the purpose of process control, particularly to increase the efficiency of the system. The bottom product from 91 which comprises hydrocarbons of higher molecular weight is removed from the system through conduit 97.

The process of the present invention presents numerous advantages. The employment of the catalytic desulfurization step prior to the catalytic isomerization step enables the production of a higher octane product displaying superior lead response. It has been found that the presence of sulfur in appreciable amounts in the isomerization feed interferes seriously with the progress of isomerization and prevents the attainment of the desired degree of isomerization and that this difficulty is overcome by catalytic desulfurization of the material undergoing catalytic isomerization. In addition, catalytic desulfurization of the isomerization feed stock is beneficial from the standpoint of the adverse poisoning effect of sulfur even in concentrations as low as 0.004% upon the isomerization catalyst. With the present invention it is readily possible to maintain the sulfur content of the isomerization feed at a value which is sufficiently low to insure an economically long catalyst life and satisfactory operation.

Another advantage which accrues from the use of the desulfurization step prior to isomerization is the economy which can be secured through the use of carbon steel in equipment fabrication, particularly in that portion of the equipment employed after the desulfurization step, except in operating zones where temperatures of 1000° F. or higher compel the use of alloy steels of adequate creep stress characteristics. The presence of sulfur compounds in appreciable concentrations causes severe corrosion of ordinary steel equipment and forces the use of expensive, difficultly obtainable chromium-containing corrosion-resistant steels.

Another advantage is that the process enables the ready and economical production of aviation fuel which is superior from the standpoint of octane number, volatility, lead response and content of highly branched hydrocarbons from relatively low grade natural gasoline stock, of which an excess is available. Thus the invention enables the conversion of low grade, relatively abundant material for which there is little demand into aviation gasoline or aviation blending stock which may be used to prepare aviation fuel of superior anti-knock qualities, to thereby meet the increasing demands for high octane aviation gasoline and to more easily meet the increasingly stringent aviation fuel specifications.

Still another advantage is that the process allows the production of a fraction of relatively high octane motor fuel material comprising hydrocarbons which, while above the molecular weight range for aviation fuel, are highly branched and are eminently satisfactory for, or in the blending of, automotive gasoline.

While the foregoing description refers to that specific embodiment of the invention which is now preferred by me, it is to be understood that numerous changes and modifications may be made therein without departing from the inventive thought, and that the invention is to be limited only by the spirit and the terms of the appended claims.

I claim:

1. In a process of producing high octane number highly branched chain hydrocarbons in the aviation fuel range by catalytic isomerization, with a metal halide isomerization catalyst, of a low octane number natural gasoline charge stock containing substantial amounts of sulfur, wherein said charge stock is subjected to treatment prior to isomerization to reduce the sulfur content thereof, the improvement which comprises: subjecting such a charge stock to catalytic desulfurization with a solid desulfurization catalyst consisting of bauxite impregnated with sodium hydroxide, under a pressure of from about 0 to about 50 pounds per square inch, at a temperature of from about 500 to about 700° F., and under conditions such that less than 2% of the hydrocarbons charged undergo splitting reactions, to produce an effluent comprising a fraction of desulfurized hydrocarbons in the aviation and motor fuel range, said fraction containing not more than 0.01% of sulfur; fractionating said effluent to separate said fraction from lower and higher boiling material; recycling a portion of the so-separated fraction to said catalytic desulfurization step; and subjecting the remainder of the so-separated fraction directly to said catalytic isomerization.

2. In a process of producing high octane number highly branched chain hydrocarbons in the aviation fuel range by catalytic isomerization, with a metal halide isomerization catalyst, of a low octane number natural gasoline charge stock containing substantial amounts of sulfur, wherein said charge stock is subjected to treatment prior to isomerization to reduce the sulfur content thereof, the improvement which comprises: subjecting such a charge stock to catalytic desulfurization with a solid desulfurization catalyst consisting of bauxite impregnated with sodium hydroxide, under a pressure of from about 0 to about 50 pounds per square inch, at a temperature of from about 500 to about 700° F., and under conditions such that less than 2% of the hydrocarbons charged undergo splitting reactions, to produce a hot effluent comprising a fraction of desulfurized hydrocarbons in the aviation

and motor fuel range, said fraction containing not more than 0.01% of sulfur; cooling said hot effluent by heat exchange as hereinafter described; fractionating the so-cooled effluent to separate said fraction of desulfurized hydrocarbons from lower and higher boiling material; recycling a portion of the so-separated fraction to said catalytic desulfurization step; heating the remainder of the so-separated fraction to an isomerization temperature of from about 200 to about 700° F. solely by heat exchange with said hot effluent; and subjecting the thus-heated material directly to said catalytic isomerization.

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