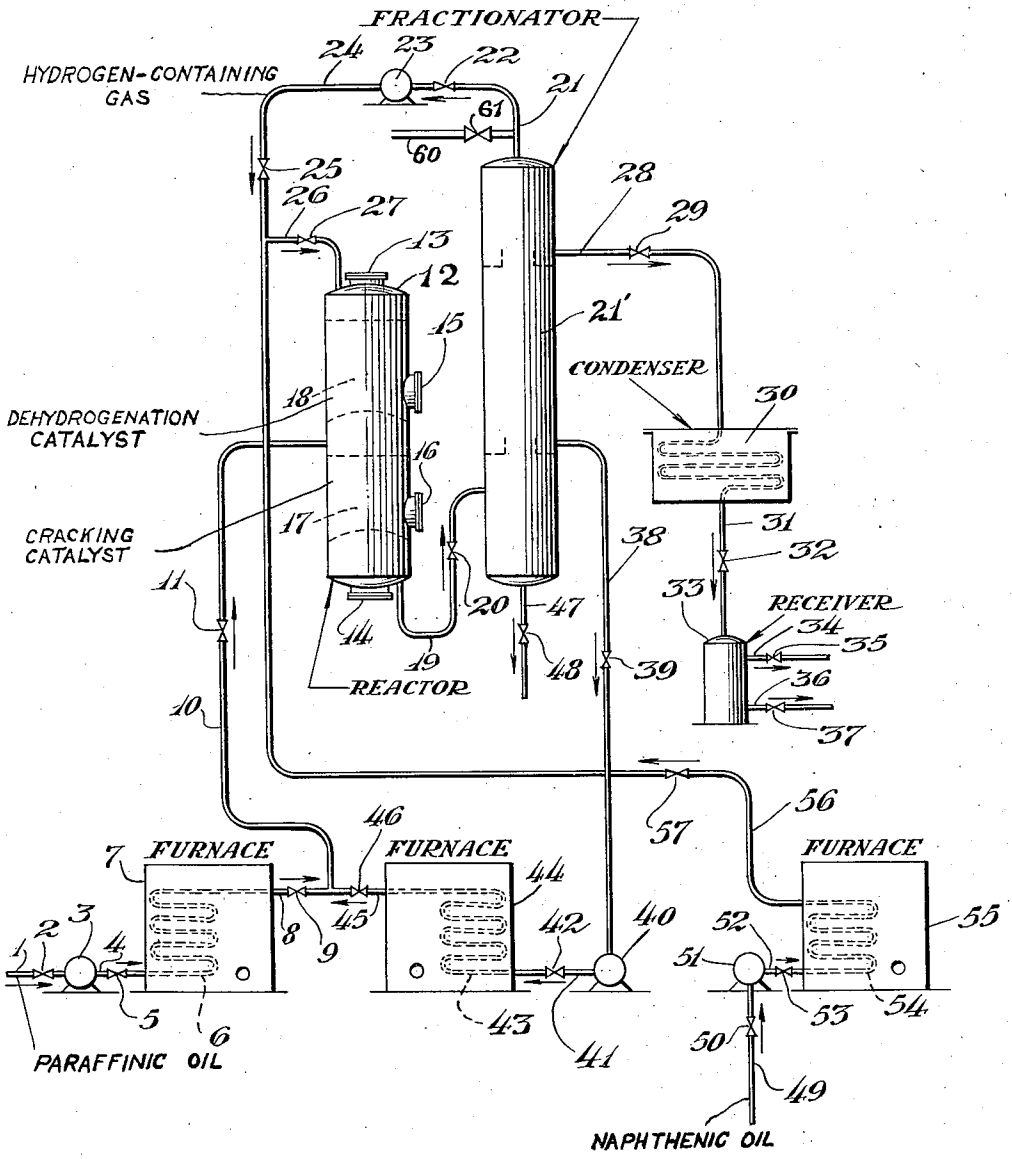
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CONVERSION OF HYDROCARBONS

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CONVERSION OF HYDROCARBONS

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4 Claims. (Cl. 196—49)

This invention relates to the conversion of hydrocarbon fractions obtained from petroleum and containing substantially no gasoline boiling range constituents. It is more specifically concerned with a combination catalytic and thermal treatment which results in the production of improved yields of high antiknock value gasoline. According to the process, stocks having predominantly naphthenic and predominantly paraffinic characteristics are separately treated in the presence of selected catalysts which are useful in effecting the optimum conversion of the individual stocks.

It is customary in most current processes involving the conversion of gas oils into gasoline by thermal and thermal-catalytic methods to consider fractions available for cracking on a basis of boiling range rather than chemical characteristics. Thus while it is recognized that different conditions of operation should be chosen in thermal cracking of different stocks to produce optimum results in the matter of gasoline yields and quality, there is at the present time only a limited art on the catalytic treatment of individual fractions to improve the yields and quality of the gasoline products. The present invention stands as a contribution to the art of catalytic cracking of heavy petroleum fractions to produce gasoline therefrom.

In one specific embodiment the present invention comprises subjecting a predominantly naphthenic petroleum fraction to contact with a catalyst effective in dehydrogenating the naphthenic content thereof to produce aromatic hydrocarbons, simultaneously subjecting the predominantly paraffinic fraction in admixture with process refluxes to contact with a catalyst effective in promoting cracking and other conversion reactions in admixture with the treated naphthenic products from the catalytic treatments to produce fixed gases which are recycled to the dehydrogenating zone, gasoline which is condensed and collected, light refluxes which are recycled to conversion in admixture with the paraffinic fractions and heavy refluxes which are removed from the process.

To further indicate the features of the present process and indicate its commercial advantages the attached diagrammatic drawing has been provided which shows by the use of conventional figures in general side elevation an arrangement of interconnected elements in which the steps of the process may be carried out. The drawing is not to any absolute or relative scale and is not intended to unduly circumscribe the proper scope of the invention.

Referring to the drawing a gas oil of predominantly paraffinic characteristics is introduced to the plant through a line 1 containing valve 2 to charging pump 3 which discharges through line 4 containing valve 5 into a heating element 6 disposed to receive heat from a furnace 7. The temperature and pressure at the exit of heating element 6 will depend largely upon the nature of the hydrocarbons composing the fraction but it may be stated that temperatures within the range of about 850 to about 1050° F. are usually employed. Pressures will usually be of a relatively low order, say from atmospheric to 100 pounds per square inch. The heated products pass through line 8 containing valve 9 into line 10 containing valve 11 after admixture with heated refluxes from line 45 containing valve 46, the source of which will be later described. The total heated products from line 10 pass into a central portion of catalytic reactor 12 and pass downwardly through a bed of granular cracking catalyst contained in lower space 17, along with dehydrogenated naphthenic stocks from upper catalyst bed 18. Reactor 12 is preferably provided with manheads 13, 14, 15 and 16 to permit the easy charging and removal of the catalysts.

The total products from reactor 12 pass through line 19 containing valve 20 to a fractionating column 21' which is representative of any type of equipment neecssary for the production of desired fractions. For assisting in controlling the selectivity of the dehydrogenation reactions and reducing carbon deposits the fractionating equipment should produce a gaseous fraction relatively high in hydrogen which is indicated as passing through line 21 containing valve 22 to recycle compressor 23 which discharges through line 24 containing valve 25 into line 26 containing valve 27 and thence to the reactor space above the dehydrogenating section 18. Excess gas is withdrawn through line 60 containing valve 61.

Gasoline fractions of desired boiling range are removed as a side-cut through line 28 containing valve 29 along with dissolved gases which may be later removed by stabilization and are cooled and condensed during passage through the condenser 30. The effluent materials from condenser 30 pass through line 31 containing valve 32 to receiver 33 which is shown provided with the conventional gas vent line 34 containing valve 35 and liquid draw-line 36 containing valve 37 for the principal product of the process.

Intermediate refluxes amenable to further conversion pass through line 38 containing valve 39 to a recycle pump 40 which discharges through

line 41 containing valve 42 and through a secondary heating element 43 arranged to be heated by furnace 44. Experience has shown that intermediate refluxes of the character of those produced by catalytic conversion reactions are well adapted to thermal treatment and thus intermediate refluxes from the fractionator are heated and thermally cracked at temperatures of from about 900 to about 1100° F. under moderately superatmospheric pressure during passage through heating element 43. The heated products pass through line 45 containing valve 46 and thence into line 10 as already described. Heavy refluxes of a character unsuitable for further conversion on account of their high coke forming tendencies are removed from the process through lower line 47 containing valve 48.

In accordance with the present invention predominantly naphthenic gas oil fractions are separately and concurrently treated along with the paraffinic fractions whose course through the plant has already been described. Thus line 49 containing valve 50 admits a naphthenic gas oil fraction to a secondary charging pump 51 which discharges through line 52 containing valve 53 to a heating element 54 arranged in a furnace-setting 55. The temperatures which may be employed at the exit of heating element 54 may range from about 850 to 950° F. and the pressures will be of about the same order as those employed at the exit of the other simultaneously operated heating element. The heated products from coil 54 pass through line 56 containing valves 57 to enter the uppermost space of reactor 12 through line 26.

In effecting the desired dehydrogenation of the naphthenic charge a temperature of from about 750 to about 850° F., and several types of catalysts may be employed depending upon the proportion of naphthenes in the charging stock. For a highly naphthenic stock reduced nickel preferably in relatively inactive supports is utilizable while if the percentage of naphthenes is lower and some cyclization reactions may be expected, certain metal oxide catalysts are better utilizable which may consist of oxides of such metals as chromium, molybdenum, tungsten, vanadium and cerium which are also preferably on supports, the active oxides being in minor proportions. Products from the upper dehydrogenation section of reactor 12 which contains granular catalyst in section 18 will be aromatic in character and will contain varying proportions of unsaturated aliphatic hydrocarbons. A higher proportion of aromatics will be produced when the naphthenic stock contains high percentages of 6 carbon atom naphthenes since these are more readily dehydrogenated. The olefinic products will result from the dehydrogenation of straight-chain compounds of a paraffinic character. Some aromatics will be produced by the dehydrocyclization of the aliphatic constituents of this charge. The types of catalysts employed in lower catalytic section 17 which acts upon the mixture of products from the dehydrogenation zone and the preheated paraffinic charging stock and refluxes are preferably of a silicate character and may comprise not only natural siliceous materials usch as fuller's earths and clays of the montmorillonite and bentonite types, but may also comprise specially prepared silica-alumina or silica-alumina-zirconia complexes which have outstanding activity as catalysts for the promotion of hydrocarbon conversion reactions. The overall result of subjecting the various fractions to contact with these types of cracking catalysts is the production of high yields of high antiknock value gasoline by a number of types of reactions involving carbon-to-carbon splitting, dehydrogenation, polymerization and to some extent alkylation of aromatic hydrocarbons by olefins.

The following example is introduced to indicate the type of results obtainable in the operation of the process of the invention.

The charging stocks employed consists of a gas oil fraction from the Michigan field of a predominantly paraffinic character and a naphthenic charging stock from the Gulf Coastal field of similar boiling range of approximately 400 to 650° F. The naphthenic stock is heated to a temperature of 750° F. and passed over a bed of catalyst consisting of reduced nickel on granular alumina, while the paraffinic stock, mixed with intermediate boiling range reflux, is passed over a prepared silica-alumina catalyst in admixture with the dehydrogenated naphthenic gas oil at a temperature of 900° F., both operations being conducted at a slight superatmospheric pressure to insure flow through the apparatus.

As a result of the above treatment, a yield of 68% by volume of 75 octane number gasoline is obtained based on the total volumes of the two gas oils which are charged in approximately equal amounts.

I claim as my invention:

1. A process for producing gasoline from naphthenic and paraffinic oils heavier than gasoline which comprises subjecting the naphthenic charging oil to catalytic dehydrogenation to convert naphthenes to aromatics, commingling the paraffinic charging oil with the heated products of the dehydrogenation, contacting the resultant mixture with a cracking catalyst under catalytic cracking conditions, fractionating the conversion products of the last-mentioned step to form gasoline distillate and reflux condensate, heating at least a portion of said reflux condensate to a temperature of from about 900° F. to about 1100° F. and supplying the thus heated material to the catalytic cracking step.

2. A process for producing gasoline from naphthenic and paraffinic oils heavier than gasoline which comprises subjecting the naphthenic charging oil to catalytic dehydrogenation to convert naphthenes to aromatics, commingling the paraffinic charging oil with the heated products of the dehydrogenation, contacting the resultant mixture with a cracking catalyst under catalytic cracking conditions, fractionating the conversion products of the last-mentioned step to form gasoline distillate and reflux condensate, thermally cracking at least a portion of said reflux condensate and supplying resultant cracked products to the catalytic cracking step.

3. A process for producing gasoline from naphthenic and paraffinic oils heavier than gasoline which comprises subjecting the naphthenic charging oil to catalytic dehydrogenation to convert naphthenes to aromatics, commingling the paraffinic charging oil with the heated products of the dehydrogenation, contacting the resultant mixture with a cracking catalyst under catalytic cracking conditions, fractionating the conversion products of the last-mentioned step to form reflux condensate, gasoline distillate and hydrogen-containing gas, supplying hydrogen-containing gas thus separated to the catalytic dehydrogenation step, heating at least a por-

tion of said reflux condensate to a temperature of from about 900° F. to about 1100° F. and supplying the thus heated material to the catalytic cracking step.

4. A process for producing gasoline from naphthenic and paraffinic oils heavier than gasoline which comprises subjecting the naphthenic charging oil to catalytic dehydrogenation to convert naphthenes to aromatics, commingling the paraffinic charging oil with the heated products of the dehydrogenation, contacting the resultant mixture with a cracking catalyst under catalytic cracking conditions, fractionating the conversion products of the last-mentioned step to form reflux condensate, gasoline distillate and hydrogen-containing gas, supplying hydrogen-containing gas thus separated to the catalytic dehydrogenation step, thermally cracking at least a portion of said reflux condensate and supplying resultant cracked products to the catalytic cracking step.

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