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It is an object of the present invention to provide a process for the catalytic conversion of hy-

It has now been found that, when a hydrocarbon material such as a gas oil, kerosene, and/or naphtha fraction is subjected to catalytic treatment under conditions of high temperature and moderately superatmospheric pressure with the use of a substantially hydrogen-free recycle gas as diluent containing mainly ethylene or ethylene-propylene mixture, increased amounts of valuable light olefinic hydrocarbons are produced along with a normally liquid distillate rich in aromatic hydrocarbons. Additional quantities of this heat-carrying diluent injected toward the outlet end of the catalyst bed promotes further reaction with the formation of substantial quantities of butadiene. Thus in the present process, a large proportion of C₄ and lighter gases is formed in the first or cracking zone of the catalyst bed which is operated at unusually high temperatures and in which relatively long contact times are maintained. Moreover, we have now discovered that the introduction of vapors rich in ethylene or propylene into the stream of reaction gases after these gases have traversed a portion of the catalyst mass serves the threefold purpose of repressing the formation of additional quantities of light gases, encouraging the polymerization of ethylene and promoting the dehy-

drogenation of the butenes for the formation of butadiene.

In order to permit the coexistence of aromatizing and dehydrogenating conditions in the same catalyst bed, so as to obtain both aromatic fractions and olefin- and diolefin-containing fractions, it is necessary to provide relatively long contact time in the aromatizing zone and relatively short contact time in the dehydrogenation zone. This is accomplished by introducing the hydrocarbon diluent, consisting substantially of olefinic hydrocarbon material of two and three carbon atoms, into that point in the catalyst bed at which the treated vapors have been subjected to the desired contact time for the aromatizing reaction to have taken place. At this point sufficient hydrocarbon diluent is introduced to provide the desired effective dehydrogenation contact time in the remaining portion of the bed. The contact time for the cracking-aromatizing portion of the reaction is preferably between about 0.5 and 3 seconds, while the contact time for the dehydrogenation portion of the reaction is between about 0.05 and 0.5 second.

In order to obtain substantial dehydrogenation in the second zone it is necessary to compensate for any endothermic loss of heat occurring in the initial cracking-aromatizing reaction. This may be accomplished by superheating the hydrocarbon diluent to a point sufficiently above the temperature of the reactants at the point in the bed at which the diluent is introduced, to elevate the temperature in the dehydrogenation zone to the desired point. Preferably the cracking-aromatizing reaction is carried out at a temperature between about 1100-1300° F. while the dehydrogenation reaction is also carried out at temperatures within this range.

In the practical operation of the present conversion steps, time-temperature relationships may be relied on to determine the amount and location of the injection of diluent hydrocarbon vapor to the catalyst case. Thus in the cracking section of the catalyst case, the hydrocarbon vapors are permitted a temperature drop of about 100° F. as representing the optimum depth of cracking in this process. Sufficient olefinic hydrocarbon diluent preheated to 1200-1400° F. then enters the chamber in amount sufficient to raise the vapor temperature to about 1150° F. and at the same time to reduce the residence time in the after section of the catalyst bed. In the dehydrogenation section of the catalyst bed, additional diluent vapor is injected at points corresponding to temperature drops of about 50° F., so that the overall temperature in the after section of the catalyst bed is maintained between about 1100-1150° F.

Thus the point in the bed at which cracking has proceeded to an optimum extent is represented by the temperature drop of about 100° F. and at that point and beyond, sufficient diluent is introduced to provide the contact time necessary to give the desired dehydrogenation conditions in the remainder of the bed.

While the theoretical basis for such complex reactions as undoubtedly occur in a process such as that of the present invention is not as yet thoroughly understood and most of the information concerning such reactions is largely empirical, enough evidence has been submitted to permit a few generalizations about the course of the reaction. While not limiting the invention to the theory expressed, the following generalizations may be suggested as aiding in explaining the

mechanism of the reaction. The use of ethylene as diluent and heat carrier after the reaction gases have passed through a portion of the catalyst chamber represses the formation of light gases and at the same time the ethylene itself appears to enter into the reaction with the subsequent production of higher boiling hydrocarbons. The influx of heat carrier maintains a temperature sufficiently high for dehydrogenation of butenes for the production of butadiene. The higher space velocity in the after portion of the catalyst chamber produced by the combined flow of reactants from the anterior portion of the bed and the injected diluent effects a short contact time in the after section of the catalyst chamber and thus reduces the probability of subsequent decomposition or polymerization of the butadiene while at this elevated temperature.

The accompanying drawing illustrates diagrammatically in conventional side elevation one specific form of apparatus for accomplishing the objects of the invention.

With reference now to the drawing, the feed stock for the operation which may comprise a middle-boiling petroleum distillate such as 37° A. P. I. light gas oil boiling between 450° and 650° F. and which may be obtained either by straight distillation of a crude oil or by the mild cracking of a reduced crude is introduced by line 1 and admixed with a diluent from line 2 which comprises a C₃ and lighter, substantially hydrogen-free, olefinic recycle gas. The mixture of vaporized gas oil charge stock and diluent is conducted through line 3 in the furnace 4 in which it is heated to a temperature of about 1100-1300° F. and conducted through transfer line 6 to the top of the catalyst chamber 8.

The reaction chamber 8 may be any one of various reactors familiar to those versed in the art. Inasmuch as the invention is concerned primarily with a novel and advantageous cracking procedure rather than a particular type of equipment, no attempt will be made to describe in detail the various reaction chambers which may be employed in carrying out the invention. An appropriate reaction vessel for use in this process, however, may be a multiple-bed type of chamber provided with suitable arrangements for the injection of diluents. The reactor may, if desired, comprise a unit with the reaction chamber in two sections, the lower of which is provided with suitable arrangements for the injection of diluents. The reaction chambers herein mentioned, however, are merely optional forms of satisfactory chambers and it is not intended that the invention should be limited to these particular types of reactors.

A stream of recycle gases rich in ethylene or in ethylene and propylene but substantially free of hydrogen passes from line 2 through line 5 in the furnace 4 in which the gases are heated to approximately 1300-1400° F. These hot diluent gases then pass through transfer line 7 and are admitted to the catalyst bed where they raise the temperature of the reactants to 1100-1200° F., increase the vapor velocity and reduce the contact time of the reactants while at this high temperature. Lines are shown for introducing the olefinic diluent at one or more points in the latter portion of the bed, as desired.

From the catalyst chamber the reaction mixture passes through a cooler 9A in line 9 into the fractionator 10 in which the gas oil and higher boiling materials are separated and withdrawn through line 12. The overhead vapors from the

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fractionator pass through line 11 into the stabilizer 13 from which a debutanized end point gasoline is withdrawn as bottoms through line 15. This stabilized gasoline may be subjected to refractionation and further treatment to obtain a high-octane, aromatic gasoline suitable for aviation fuel. The stabilizer overhead passes through line 14, cooling coil 16 and line 17 into the accumulator 18 from whence vapors are withdrawn via line 24, the compressor 25 and the cooler 27 into the high-pressure accumulator 29 from which the non-condensable gases are vented through line 30 to the refinery gas plant. A portion of the heavier material, comprising C₃'s and C₄'s, from the accumulator 18 is suitably withdrawn through line 19 and pump 20 and via line 22 to serve as reflux to the stabilizing column while the remainder is taken through line 23 and added to the material in line 31, comprising the C₃ and C₄ fraction from the high-pressure accumulator 29, and thence through a suitable heat-exchange element 32 and line 33 into the depropanizer 34. The C₄ fraction comprising the bottoms from the depropanizer 34 is taken through line 43 to an appropriate system 44 for effecting the separation of the fraction into such components as butadiene which may then be further utilized and into butylenes and isobutane which may be used directly as feed to alkylation and polymerization processes. Isomerization reactions may be employed to increase the amount of isobutane available for these processes.

The C₂-C₃ stream passes overhead from depropanizer 34 through line 35 into the reflux accumulator 36. The liquid condensate in accumulator 36, which is predominantly propane is removed through line 37 and pump 38. A portion of this liquid is returned by line 39 to the head of column 34 as reflux liquid while the excess portion is removed through line 40. The portion passing through line 40 may then be vented to the gas plant through lines 42 and 47 or may be recombined with the vapor stream leaving accumulator 36 through line 41. The composition of this vapor stream in line 41 is predominantly ethylene and ethane with some propylene and propane. The relative proportion of C₂ and C₃ hydrocarbons may be regulated by selection of suitable operating temperature and pressure of column 34. The gas stream from line 41 is particularly suited for use as a diluent and heat carrier in the reaction and the necessary quantity is returned for such use through line 2. The excess is vented to the gas plant through line 47.

Typical operating conditions which may be employed to carry out the process are approximately as follows:

The gas oil charge stock is vaporized in the furnace coils and passed into the top catalyst bed at a temperature of approximately 1100 to 1300° F. Naturally-occurring materials such as bauxite are generally preferred as catalysts. In some instances, however, certain activated adsorbent clays may be suitable as catalysts as may various synthetic materials such as alumina alone or admixed with relatively minor proportions of certain activating agents. Certain synthetic materials such as various silica gel compositions may be used in some cases and may, if desired, be activated by the addition of relatively minor proportions of metal oxides such as alumina and/or zirconia.

In order to increase the velocity of the reaction gases through the furnace tubes and to increase the yield of butadiene, a diluent gas comprising

a C₃ and lighter, substantially hydrogen-free, mainly olefinic recycle gas is added to the charge stock in amount equivalent to 0.5 to 5 mols per mol of feed before or shortly after it enters the preheating furnace. In order to raise the temperature of the reactants to 1100-1200° F. and to reduce the contact time, this diluent vapor stream consisting predominantly of ethylene or ethylene and propylene recycle gas which is substantially hydrogen-free is heated to 1300-1400° F. and admitted to the catalyst chamber at a point or points below the top of the catalyst mass. A ratio of 10 to 25 mols of diluent per mol of charge is utilized for this purpose. The outstanding feature of this process is that a large proportion of C₄ and lighter gases is obtained with the relatively long contact time and high temperatures in the upper zone of the catalyst bed and by the addition of the recycle vapors, rich in unsaturates, the formation of additional light gases is repressed, polymerization of ethylene is promoted, and, by the influx of heat carrier, a temperature sufficiently high for dehydrogenation of butenes is obtained. The short contact time in the second part of the catalyst case reduces the probability of subsequent decomposition or polymerization of the butadiene while at this elevated temperature.

The designation of the reaction zones of the catalyst bed are necessarily arbitrary since the proportion of the bed requiring the heat-carrying diluent will depend on the characteristics of the feed as well as on the type of products desired. However when operating with feed stock such as naphtha, kerosene or gas-oil to produce maximum yields of light unsaturates along with an aromatic distillate, the injection of diluent ordinarily occurs after the original feed has traversed about one-third of the length of the bed. Additional diluent injection points may be spaced at suitable intervals along the latter two-thirds of the length of the bed.

The operation may be carried out under moderately superatmospheric pressures which may vary from atmospheric to about 250 pounds per square inch gage, so selected that the desired contact time may be obtained for a given diluent ratio. In many applications near-atmospheric pressures of zero to 50 pounds gage are preferred.

In order to indicate the novelty and utility of the invention, the following example is given of one specific method of operation of the process which employs the preferred conditions of temperature and pressure and flow rate as well as the preferred feed stock and catalyst. This example is merely illustrative of results normally obtained and should not be construed as a limiting feature of the invention as various changes apparent to those in the art may be made in the catalyst and catalyst chamber design and in the reaction conditions.

Example

A light gas oil of 37° A. P. I. gravity boiling in the range of 450-630° F. was introduced into a catalyst chamber containing regenerated 10-20 mesh bauxite catalyst at a charge rate of about 1 liquid volume of gas oil per volume of catalyst per hour, with recycle C₂-C₃ gas at the inlet in the proportion of 1 mol of gas oil per 3 mols of recycle gas per hour. The temperature of the mixture at the inlet was maintained at 1220-1230° F. and the pressure was maintained at 6 pounds per square inch gage. After the mixture had traversed about one-third the length of the cat-

alyst bed the temperature was found to have dropped about 100° F. At this point additional C₂-C₃ diluent preheated to about 1400° F. was introduced at a rate of 7 mols per mol of hydrocarbon feed per hour, raising the temperature to 1200° F. After this mixture had traversed approximately another third of the bed the temperature was found to be about 1150° and at this point additional C₂-C₃ diluent at 1400° F. was added at the rate of 10 mols of diluent per mol of hydrocarbon feed per hour. The effluent left the chamber at about 1200° F. Fractionation of the depropanized effluent yielded a C₄ fraction amounting to 12.3 per cent of charge. On a volume basis 9 per cent of this fraction consisted of butanes and 65 per cent was butylenes. Butadiene amounted to 26 per cent of the C₄ fraction, corresponding to 3.2 per cent by volume of the charge. A butane-free gasoline was separated in a yield of 16.5 per cent of charge. The gasoline was refracted and this 150-400° F. gasoline had an A. P. I. gravity of 32.0 and a Reid vapor pressure of 3.0. The clear A. S. T. M. octane number was 90.8 and the Research octane rating was 100.1. A high aromatic content is indicated by the low A. P. I. gravity of the gasoline and by the refractive index of 1.4965.

Another portion of the same feed was treated under identical conditions with diluent supplied at the inlet and without further addition of diluent throughout the reaction zone. Fractionation yielded a C₄ fraction amounting to 11.5 per cent of the charge and containing 67.8 per cent butylenes and 19.1 per cent butadiene, the butadiene content representing 2.2 volume per cent of the charge. The butane-free gasoline amounted to 17.3 per cent of the charge and had an A. P. I. gravity of 33.2 degrees and a refractive index of 1.4939. The ASTM octane number of this gasoline was 89.2 and the Research octane rating was 99.6.

A comparison of the results obtained by the two methods shows an all over increase in the olefin and diolefin production when using the former method of introducing substantial quantities of C₂ and C₃ olefinic hydrocarbons after the feed stock has traversed a substantial length of catalyst bed. Although the yield of butane-free gasoline is slightly less, the octane value and the aromatic content are somewhat higher as shown by comparing the A. P. I. gravities and the refractive indices.

We claim:

1. A process for the conversion of a normally liquid hydrocarbon distillate to an aromatic

fraction and normally gaseous unsaturated hydrocarbons which comprises vaporizing and heating the said distillate to a temperature of 1100-1300° F., passing said vaporized distillate in contact with a solid cracking and dehydrogenation catalyst for a contact time of 0.5 to 3 seconds for an endothermic temperature drop of about 100° F., injecting sufficient substantially olefinic hydrocarbons of two to three carbon atoms preheated to 1200-1400° F. at a plurality of points spaced along the length of the catalyst bed in the direction of vapor flow after the initial contact period to allow the distillate a further contact time of 0.05 to 0.5 seconds with the catalyst, and separating butadiene, normally gaseous olefins and an aromatic fraction from the effluent.

2. The process of claim 1 in which the preheated olefinic hydrocarbons are introduced at said points in catalyst bed in a volume and at a temperature sufficient to raise the temperature to 1100-1200° F. in the dehydrogenation zone and maintain the temperature in a range of 50° F.

3. The process of claim 1 in which the cracking and dehydrogenation catalyst is bauxite.

4. A process for the production of an aromatic gasoline and normally gaseous olefins and diolefins which comprises cracking and aromatizing a vaporized normally liquid hydrocarbon in the presence of a mass of solid cracking and dehydrogenating catalyst for a contact time of 0.5 to 3 seconds in an anterior portion of said catalyst mass and immediately dehydrogenating the hydrocarbon products from the anterior portion under dehydrogenating conditions for a contact time of 0.05 to 0.5 second in a posterior portion of said catalyst mass and in the presence of substantially olefinic gases of two and three carbon atoms added multipointwise in said posterior portion of the catalyst mass.

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