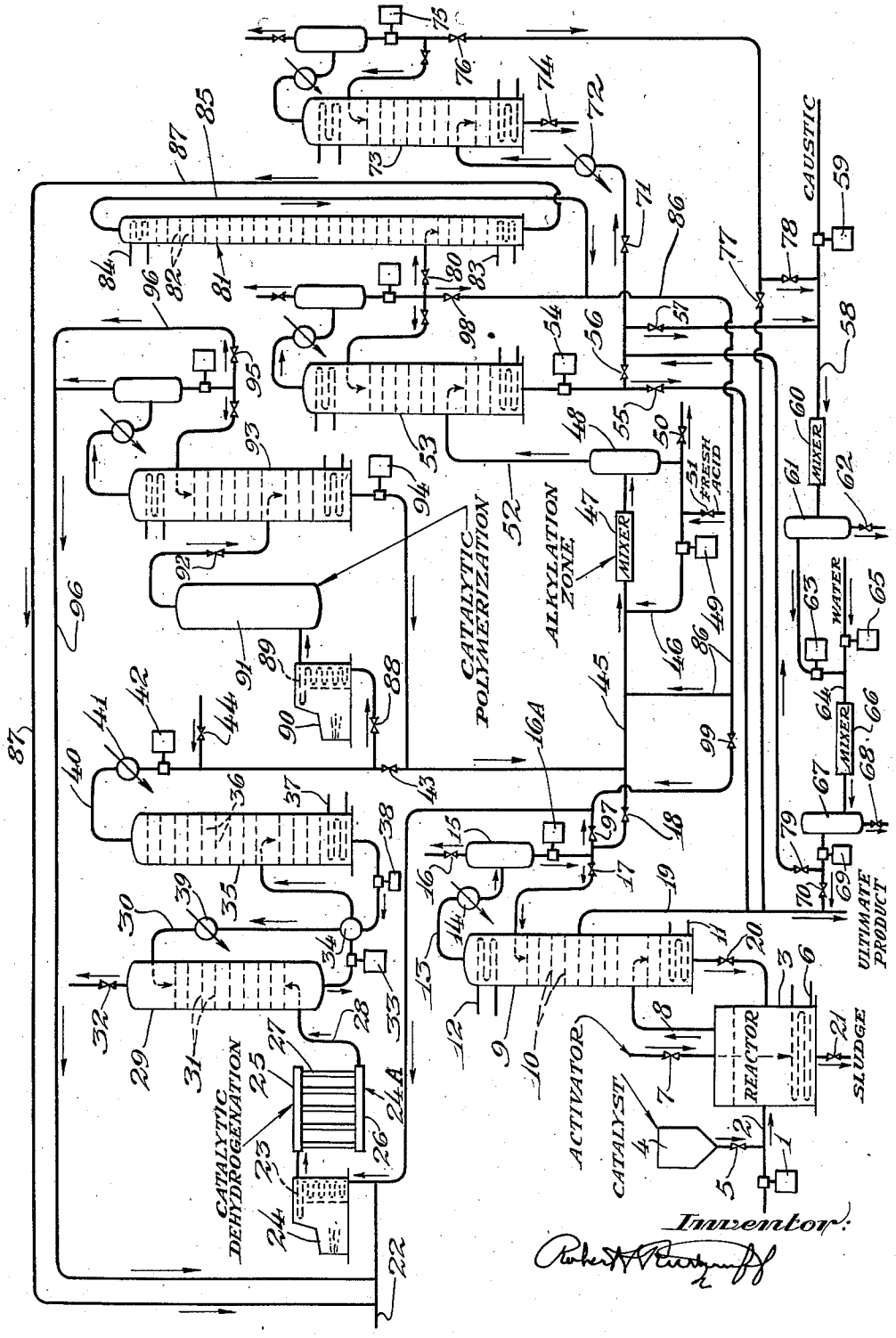
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MOTOR FUEL AND PREPARATION THEREOF

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MOTOR FUEL AND PREPARATION THEREOF

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4 Claims. (Cl. 196—10)

This invention relates to motor fuel and the preparation thereof. More particularly, this invention relates to motor fuel of high octane number and controllable volatility and the preparation thereof.

During the last few years the steady improvement in motor fuel quality as regards octane number, volatility and other characteristics is too well known to those skilled in the art to merit further discussion. While the possible limits to such improvements have not as yet been approached in all probability, nevertheless, in certain directions, additional improvements are becoming increasingly difficult to achieve and all the resources of petroleum technology must be applied to the problem. This is particularly true in the case of high octane motor fuels for aviation use.

In the past, high octane number motor fuels for aviation use have been prepared by the catalytic polymerization of olefines containing four carbon atoms to the molecule followed by hydrogenation of the polymer formed. Such olefines may be obtained, in admixture with the analogous paraffins, from the gases produced during the cracking of various petroleum fractions or by the catalytic dehydrogenation or the thermal pyrolysis of the butane cut from natural gas. These olefines consist of isobutene and the normal butenes. When such a mixture is passed over a suitable catalyst under suitable conditions as regards to temperature, pressure and time of contact, polymerization occurs. In this reaction the isobutene reacts very rapidly while the normal butenes react at a much slower rate. By the proper selection of operating conditions it is possible to attain almost quantitative conversions of isobutene to polymer with conversions of normal butenes varying from practically zero to practically 100%. The polymer produced consists largely of isomeric octenes and has an octane number of 80 to 82. While an excellent motor fuel for automobile engines, this material is totally unsuited for aviation uses because of its high unsaturate content, low octane number and low lead response. By catalytic hydrogenation the polymer may be converted to isooctanes having an octane number of 90 to 98. The hydrogenated material is completely saturated and exhibits an excellent lead response. The octane number of the hydrogenated product is largely a function of the amount of normal butenes reacting. When the ratio of reacting isobutene to reacting normal butenes is high the octane number of the resulting hydrogenated polymer is high and vice versa.

While hydrogenated catalytic polymer shows considerable promise as a high octane number aviation fuel and has been much used for the purpose, yet the material and the process for preparing the same exhibit numerous disadvantages. For example, the hydrogenated catalytic polymer is not sufficiently volatile for aviation requirements, the unhydrogenated polymer obviously suffering from the same disadvantage. If an attempt is made to increase volatility by the addition of light naphthas the octane number of the blend is considerably lower than that shown by the straight hydrogenated polymer. Furthermore, the possible yield of hydrogenated polymer is quite low. It is obvious that the yield can be no higher than the olefines present in the charge and actually, if a high octane product is desired, is usually much less. If a high octane hydrogenated catalytic polymer is to be made it is well to react not more than one mole of normal butenes per mole of isobutene present. However, as is well known to those skilled in the art, the isobutane-normal butane ratio in natural gas and the isobutene-normal butenes ratio in cracked gas is much less than unity so that if it is desired to make a hydrogenated catalytic polymer of the highest octane number considerable normal butenes must be discarded.

More recently, high octane number aviation gasoline has been made by the alkylation process. In this method, a mixture containing isoparaffins and olefines is contacted with concentrated sulfuric acid at room temperature or below. Under these conditions, paraffins containing a tertiary carbon atom are alkylated by olefines, and when the hydrocarbons concerned contain four carbon atoms, isomeric octanes form. It will be noted that in this process, in contrast to that previously described, no hydrogenation step is required. Obviously, the alkylate does not exhibit the necessary volatility for use alone as an aviation fuel and on fortification with light naphtha the octane number of the blend is considerably lower than that of the straight alkylate. Also, in alkylation, the yield is a function of the isobutane content of the feed.

As has been mentioned previously, the isobutane-normal butane ratio in natural gas is much less than unity so that on catalytic dehydrogenation or thermal pyrolysis of such a cut under commercial conditions, the isobutane content of the resulting gas mixture is less than the content of butenes. Also, the isobutane content of the gas mixture of four carbon atoms obtained in the cracking of petroleum fractions is less than the content of butenes. Accordingly, an excess of butenes remains after reaction is complete. This deficiency of isobutane may be corrected by isomerizing normal butane to isobutane, but the volatility deficiency of the alkylate still remains.

Many attempts have been made to increase the volatility of isooctanes formed by the hydrogenation of catalytic polymer or directly by alkylation. Since isopentane is the only low boiling

liquid isoparaffin readily available, isopentane-isooctane blends have been proposed as aviation fuels. As those skilled in the art are aware, aviation fuels meeting current specifications cannot be prepared in this way. If the blend meets the 10% off specification, the 50% off specification is not satisfied. Likewise if the blend has the proper amount of isopentane to satisfy the 50% off specification, the minimum permissible temperature for 10% off is far exceeded. To correct for these deficiencies, light naphtha has been added to the isopentane-isooctane blend. When this is done the octane number is very much below that shown by the straight isooctane. Very recently, dimethyl butane (2,2) has been suggested as a blending agent for isooctane, with or without isopentane. While the use of this compound as a blending agent results in considerable improvement the fact remains that this hexane is very difficult to obtain. At present this material is made by the thermal alkylation of isobutane with ethene at extremely high pressures. To reduce ethene polymerization, the concentration of this olefine must be kept at an extremely low level. This means that the yield per pass of the desired compound is very low, which in turn necessitates an extremely high recycle ratio and the separation of the small amount of the isomeric hexane from a large amount of unreacted material.

One object of this invention is to provide an improved motor fuel and a process for producing the same. A further object of this invention is to provide an improved motor fuel of high octane number and a process for producing the same. An additional object of this invention is to provide an improved motor fuel of controlled volatility and a process for producing the same. Another object of this invention is to provide an improved motor fuel of high octane number and controlled volatility and a process for producing the same. Further objects of this invention will become evident from the following description.

Briefly, the improved motor fuel of the instant invention comprises alkylate blended with a light naphtha of high isoparaffin content obtained by the destructive isomerization of a hydrocarbon fraction. (Destructive isomerization is defined immediately hereinafter.) The alkylate is prepared by the alkylation with olefines of an isoparaffin, for example, isobutane, at least part of which was obtained by the destructive isomerization of a hydrocarbon fraction. The resulting alkylate is blended with a light naphtha of high volatility and high isoparaffin content, and hence high octane number, at least part of which was also obtained by the destructive isomerization of a hydrocarbon fraction. The blend produces a motor fuel of high octane number and of controllable volatility. In the production of this material, the processes of alkylation and destructive isomerization cooperate to produce an unexpected and new result as will become manifest from the following description.

For a description of the process of destructive isomerization reference may be made to my United States application, Serial Number 32,379, filed July 20, 1935, and which has since matured into United States Patent 2,172,146, issued September 5, 1939. In this, it is shown that when a hydrocarbon fraction, for example, a straight run heavy naphtha, is treated at low temperatures, for example, 205–210° F., with a suitable catalyst, for example, aluminum chloride promoted with water, hydrogen chloride, carbon tetrachloride or the like, a large part of the hydrocarbon fraction charged is converted into gaseous products and these consist almost exclusively of isobutane.

To this process the term destructive isomerization is applied. Isomerization is used to designate reactions wherein a compound is converted into a second compound having the same chemical composition and molecular weight but different structure than that of the first. The classical synthesis of urea from ammonium cyanate and the conversion of normal butane to isobutane are examples of isomerization. In the present instance however, in addition to forming a compound of different structure than that of the charge, the new compound also has a different molecular weight. In the example cited, a considerable amount of the heavy naphtha charge, having an average molecular weight of say 142, is converted into isobutane having a molecular weight of 58. In other words, in this reaction, the charge was first decomposed and the resulting fragments were then isomerized—hence the term destructive isomerization.

It might be argued that the above reaction was entirely one of destruction without any isomerization. For example, it might be argued with no little merit that the isobutane resulted from the preferential decomposition of 2-methyl paraffins between carbon atoms 3 and 4. In this way isobutane could be formed without any isomerization. A mass of experimental data shows that this stand is not tenable. For example, in the example cited, Mt. Pleasant heavy naphtha was used as charge. As is well known to those skilled in the art, this material consists largely of straight chain paraffins. In addition, this stock was heavily acid treated before use so as to remove aromatics and similar compounds, so as charged it consisted essentially of a mixture of straight chain paraffins.

Supplementary experiments have also confirmed the fact that straight chain paraffins are destructively isomerized with the production of isobutane. For example, a heavily acid treated Mt. Pleasant heavy naphtha was exhaustively treated with chlorosulfonic acid. This last named reagent removes hydrocarbons having tertiary carbon atoms. Upon subjecting the thus treated material to destructive isomerization as before, large amounts of isobutane formed. Furthermore, synthetic normal heptane and synthetic normal heptane after exhaustive treatment with chlorosulfonic acid as previously described, when subjected to destructive isomerization gave isobutane in greater yields and with greater ease than the Mt. Pleasant heavy naphtha.

A further study of the products of destructive isomerization has revealed a most important but hitherto unnoticed fact. On fractionating the products obtained by the destructive isomerization of a heavy naphtha for example, one cut may be obtained representing the isobutane produced and a second containing a material boiling from above isobutane up to the endpoint of the heavy naphtha charge. The octane number of this second cut has been found to be materially higher than that of the heavy naphtha charge. As is well known to those skilled in the art, octane number increases as volatility increases. To evaluate the effect of volatility on the octane number increase observed, this second cut was again distilled, taking overhead a fraction boiling from above isobutane up to the initial of the naphtha charge and leaving as bottoms a material having approximately the same boiling range as the heavy naphtha charge. On deter-

mining the octane numbers of the two fractions thus made it was found that the bottoms had an octane number not greatly different than that of the original heavy naphtha charge, while the light naphtha overhead had an extremely high octane number. It is apparent that the reaction is predominantly one of destructive isomerization only, any parts of the original charge escaping destructive isomerization are not affected to any great extent. In a large number of experiments the light naphtha overhead had octane numbers averaging 80 motor, some 15 to 20 units higher than that of an East Texas light naphtha of the same boiling range. Investigation showed that the light naphtha formed during destructive isomerization of hydrocarbon fractions consisted largely of isoparaffins, these accounting for the unusually high octane numbers observed.

To summarize, in the destructive isomerization of heavy naphtha the following major products are obtained:

A. Isobutane.

B. Light naphtha of very high octane number and consisting largely of isoparaffins.

C. Heavy naphtha of the same boiling range and approximately the same octane number as the charge.

D. Material having a higher boiling point than that of the charge.

It will be evident to those skilled in the art that the process of destructive isomerization differs materially from both thermal reforming and catalytic reforming. In thermal reforming, the gas formed contains all gaseous paraffins and olefines together with hydrogen. In destructive isomerization the gas consists essentially of isobutane. In thermal reforming, the light naphtha produced is highly unsaturated. The light naphtha obtained in destructive isomerization operations is completely saturated or nearly so. The product from thermal reforming having the same boiling range as that of the charge is highly olefinic and has a much higher octane number than that of the charge. The same fraction from destructive isomerization contains no olefines or practically none and has an octane number differing little from that of the original charge. In catalytic reforming, the gas produced consists largely of hydrogen, very little light naphtha is produced and the material having the same boiling range as that of the charge consists largely of aromatic hydrocarbons.

For a more complete understanding of the alkylation reaction reference may be made to British Patents 479,345, accepted January 31, 1938, and 479,827, accepted February 11, 1938. In alkylation, a mixture containing isoparaffins and olefines is contacted with a suitable catalyst, usually concentrated sulfuric acid, higher isoparaffins being produced. Usually isobutane is alkylated with olefines containing four carbon atoms, isooctanes being formed as the major products. This material has an octane number from about 91 to 93, exhibits an excellent lead response and is completely saturated. All these factors are much to be desired in aviation fuels. However, as has been mentioned previously, the alkylate is not sufficiently volatile for use as an aviation fuel and when blended with the light naphthas ordinarily available the octane number of the blend is appreciably lower than that of the straight alkylate. Also, the manufacture of alkylated isobutane is not efficient because of the dearth of isobutane. In the ordinary refinery the yield of alkylate could be increased two or more fold were sufficient isobutane available.

The excellent cooperation between destructive isomerization and alkylation for the manufacture of high octane motor fuels, particularly high octane number motor fuels for aviation use should now be evident. For maximum production of alkylate, additional isobutane over that found in the usual refinery is required. Destructive isomerization supplies this isobutane. To confer the proper volatility on the alkylate without at the same time greatly lowering the octane number shown by the alkylate, a light naphtha of high octane number is required. Destructive isomerization furnishes such a light naphtha.

While the specific details of the destructive isomerization process and of the alkylation process, such as temperatures, pressures, contact times and catalysts, form no part of the instant invention, some discussion of these details will be included to aid those skilled in the art to select processes best suited to any particular set of conditions.

With respect to destructive isomerization, a wide variety of hydrocarbon fractions may be used as charging stocks. A particularly suitable charging stock for the purpose comprises a virgin heavy naphtha having a boiling range from about 250° F. to 400° F., more or less. Such naphthas as those from East Texas crudes, Mid-Continent crudes and similar average crudes are well suited to the process as are naphthas having an abnormally high amount of normal paraffins such as Michigan naphthas, Pennsylvania naphthas, liquid hydrocarbons produced by the interaction of carbon monoxide and hydrogen (kogasin), raffinates from the solvent extraction of kerosenes and the like. Preferably, a light naphtha or a straight run gasoline of normal boiling range is not used as charge for in such cases the high octane number light naphtha formed by destructive isomerization would be diluted with uncoverted virgin light naphtha, thus defeating the objects of this invention to a greater or less degree. Also, when aluminum halide type catalysts are employed it is preferable to use an olefine free charge in order to reduce polymer formation to a minimum.

A number of catalysts may be employed to promote the destructive isomerization reaction. Among these may be mentioned aluminum halides, alumina and clays, both natural clays, treated natural clays and synthetic clays. The operating conditions to be employed when operating at atmospheric pressure and when using aluminum chloride as a catalyst have already been outlined and further details may be obtained by consulting the previously mentioned United States Patent 2,172,146. It has been found that aluminum bromide is much more effective in this reaction than aluminum chloride due to the greater solubility of the former in hydrocarbons.

In place of straight aluminum halides, aluminum halides containing various amounts of finely divided metals such as aluminum, magnesium and zinc may be employed. By varying the aluminum halide to metal ratio in the catalyst, the isobutane to light naphtha ratio of the destructively isomerized product may be changed. When large amounts of one of the finely divided metals are incorporated into the halide, isobutane production is largely repressed while light naphtha production is but slightly

repressed. On the other hand, with straight aluminum halides the isobutane to light naphtha ratio is maximum. By varying the composition of the catalyst in this manner, isobutane and light naphtha may be produced in any proportions desired. It should be obvious that in any case, the light naphtha formed may be fractionated to give a fraction of the proper boiling range and volatility for use in the final motor fuel blend and that any excess isobutane over requirements may be discarded.

Destructive isomerization may be conducted batchwise or preferably in a continuous system wherein the charge is passed over any of the various catalysts mentioned or other suitable contacts which may be mounted on supports if desired. Temperature of operation is usually rather low, varying from say 100° F. to 800° F., usually from 200° F. to 700° F. The exact temperature to be employed depends largely upon the catalyst selected. When aluminum halides and similar contacts are used temperatures of from 200° F. to 400° F. may be employed while less active catalysts require higher temperatures, for example in the range 400° F. to 700° F. If desired, the reaction may be conducted under superatmospheric pressure. Actually, because of the rather low velocity of this destructive isomerization reaction, for economy in reactor size and the like it may be desirable to run under high superatmospheric pressure, especially when the less active catalysts are employed.

The destructively isomerized product is separated by fractionation or other suitable means into a low boiling isoparaffin cut, usually comprising isobutane, or isobutane and isopentane depending upon the exact nature of the alkylation run to be carried out subsequently with the material, a higher boiling isoparaffin cut which may boil from the end point of the lower boiling isoparaffinic cut up to the initial of the hydrocarbon charge, a cut having the same boiling range as the hydrocarbon charge and bottoms having a higher boiling point than the hydrocarbon charge. The cut having the same boiling range as the hydrocarbon charge may be recycled if desired. Or, if desired, the hydrocarbon charge may be added continuously to the reaction vessel for destructive isomerization, product boiling lower than the initial boiling point of the hydrocarbon charge may be taken overhead continuously and separated into a low boiling isoparaffinic cut and a higher boiling isoparaffinic cut. From time to time, or continuously, liquid may be withdrawn from the reactor to prevent accumulation of material boiling higher than the hydrocarbon charge, sludge, et cetera. If desired, fresh catalyst may be added with the charge to the reactor.

Before turning to a consideration of the alkylation reaction proper it will be well to devote a few words to the olefines employed. Practically any olefine will alkylate a paraffin containing a tertiary carbon atom. However, ethylene reacts very slowly, propylene at a much higher rate and the butenes and higher olefines at a very satisfactory rate. Gas mixtures containing suitable olefines may be obtained as a by-product from the thermal cracking of petroleum fractions or by the catalytic dehydrogenation or thermal pyrolysis of suitable natural gas fractions. Obviously, suitable olefines from any other source may be employed. If desired, the olefines may be concentrated prior to charging to the alkylation reactor. One ingenious method of doing this is to polymerize the olefines catalytically, thus converting them into liquid olefines easily separable from the gaseous paraffins, these last then being recycled to the dehydrogenation or pyrolysis zone if desired. The liquid olefines are then employed to alkylate isoparaffins. Contrary to expectations, the major product formed by the alkylation of isobutane with diisobutene consists of isooctanes rather than isododecanes.

In the alkylation of isoparaffins with olefines, the mixture of the two, with the isoparaffins preferably in large excess, is contacted with a suitable catalyst, such materials as mercuric aluminum bromide, antimonous aluminum bromide, sodium aluminum chloride, lithium aluminum chloride, boron fluoride plus nickel plus water, aluminum chloride, aluminum chloride-hydrocarbon complexes and concentrated sulfuric acid having been suggested, among others, for the purpose. The reaction products are separated, the alkylate is sent to storage and the excess isoparaffin is added to fresh feed and recycled to the reactor.

As concentrated sulfuric acid is the most widely used catalyst for the alkylation reaction, further discussion will relate to this contact agent. An isoparaffin-olefine ratio of three or higher is preferably employed. The acid is added to the reactor in a highly concentrated form, say 98% acid, and is withdrawn from the reactor at such a rate that the concentration of the acid within the reactor remains at about 92–93% more or less. When operating at rather high temperatures (as far as the alkylation reaction is concerned), say 70° F., fresh acid may be added at a rate of 3 to 4 pounds per gallon of alkylate made; at lower temperatures, say 35° F. or below, at a rate of one pound per gallon. The crude alkylate boils within the usual motor fuel range but for aviation use it is usually necessary to distil the product taking about 90% overhead and leaving 10% heavy ends as bottoms.

The blending of either the total alkylate or the aviation stock from the total alkylate with the higher boiling cut from destructive isomerization, or the desired portion of said higher boiling cut to produce a motor fuel of high octane number, high lead response, high and controlled volatility and low unsaturate content is a procedure obvious to those skilled in the art.

It is not absolutely essential to separate the destructively isomerized product into a low boiling fraction for alkylation and a higher boiling blending stock. If desired, the whole material may be employed in the alkylation reaction. However, greatly improved results follow when the destructively isomerized product is separated as described.

For the better understanding of this invention reference may be had to the accompanying figure, forming a part of this specification, which is a diagrammatic representation of one form of apparatus suitable for use in accomplishing the objects of this invention.

Turning now to a more detailed consideration of the figure, suitable liquid charge of a nature previously described is moved by pump 1 through line 2 to destructive isomerization reactor 3. A suitable catalyst, for example, aluminum chloride, is held in hopper 4 and is added to the liquid charge at a suitable rate through valve 5, the addition being accomplished by means of an

eductor or similar device. Reactor 3 is supplied with heating means, for example, coil 6 through which steam, hot oil, heated biphenyl, heated biphenyl-diphenyl oxide mixture or the like may be circulated. An activator such as water, steam, hydrogen chloride, an alkyl chloride, or the like, may be supplied to reactor 3 at a predetermined rate through valved line 7. The reactor 3 may be provided with suitable agitation means (not shown) if desired.

Volatile reaction products leave reactor 3 through conduit 8 and pass to fractionator 9 which is conventional, being provided with means to promote liquid-vapor contact, for example bubble trays 10, with bottom heating means, for example heating coil 11, and upper disposed cooling means, for example, cooling coil 12. The volatile reaction products are fractionated in 9, isobutane being taken overhead through line 13, cooled in exchanger 14 and sent to separator 15. (Usually, when operating in accordance with the very specific scheme being described, tower 9 is at low pressure and hence water will not liquefy isobutane and accordingly a refrigerated exchanger is used at 14.) Uncondensed products leave through valved line 16. Liquid isobutane is moved by pump 16A. Part may be circulated through valved line 17 to tower 9 to provide open reflux therein. Net isobutane passes through valved line 18 to the alkylation zone. Material boiling above isobutane but below the liquid charge is removed from an intermediate point of tower 9 through line 19 to be utilized as will be explained subsequently. Bottoms falling within the boiling range of the liquid charge are removed from tower 9 through valved line 20 and are returned to reactor 3. Sludge and polymer are removed from reactor 3 at a predetermined rate through valved line 21.

Natural gas butanes are passed through line 22 to coil 23 in furnace setting 24. On passage through coil 23 the gas stream is heated to catalytic dehydrogenation temperature and is then passed to reactor 24A, which, if desired, may take the form of an upper manifold 25, a lower manifold 26 and a plurality of connecting tubes 27. These tubes are filled with a suitable hydrogenation catalyst, for example, chromium oxide on alumina, and are preferably placed in a furnace setting to supply the endothermic reaction heat. Reaction products pass via 28 and through a suitable cooler (not shown) to the bottom of absorber 29 wherein they are contacted with a descending stream of absorber oil introduced through 30. Absorber 29 is provided with means to promote liquid-vapor contact, for example, bubble trays 31. Hydrogen and any small amounts of lower gaseous hydrocarbons, e. g., methane, ethane and ethylene, are eliminated through valved line 32. Rich absorber oil is moved by pump 33 through exchanger 34 to stripper 35. Stripper 35 is provided with means to promote liquid-vapor contact, for example bubble trays 36, and with bottom heating means, for example, coil 37. Stripped absorber oil is moved by pump 38 through exchanger 34, cooler 39 and line 30 back to absorber 29. Dehydrogenated butanes, comprising butane, isobutane, isobutene and the butenes, are discharged from stripper 35 through line 40, are liquefied in cooler 41 (refrigerated if necessary) and are moved by pump 42 into valved line 43. If available, C_4 hydrocarbons from cracking still gas may be introduced through valved line 44. Obviously, if desired, these may constitute the whole gaseous charge to the unit.

Dehydrogenated butanes from valved line 43 and isobutane from valved line 18 are joined in line 45 wherein they are mixed with concentrated sulfuric acid introduced through line 46. This mixture is passed through mixer 47 which may be a cone mixer, an orifice mixer, an impeller mixer or the like. Olefines alkylate isobutane in the presence of concentrated sulfuric acid and the reaction products are sent to settler 48. Sulfuric acid is withdrawn from the bottom of settler 48 by pump 49 and is recycled via 46. A portion of this acid is withdrawn through valved line 50 and an equivalent amount of fresh acid is added through valved line 51.

Hydrocarbons are withdrawn from the top of separator 48 and pass by line 52 to fractionator 53 which is similar to tower 9 with the exception that an intermediate withdrawal point is not necessary. Alkylate bottoms from tower 53 are moved by pump 54 through valved line 55 to line 19 where they mix with light isoparaffinic naphtha to form the ultimate product. Conventionally, alkylate bottoms are caustic washed before use. To accomplish this, valve 55 is closed and the bottoms pass through valved lines 56 and 57 to line 58 wherein they are blended with caustic solution introduced by pump 59. The blend is intimately mixed in mixer 60 and is settled in 61, the aqueous layer being withdrawn through valved line 62. The hydrocarbons are moved by pump 63 to line 64 wherein they meet water introduced by pump 65. The blend is intimately contacted in mixer 66, is settled in 67 and water is withdrawn through valved line 68. Washed alkylate is moved by pump 69 through valved line 70 to line 19 to form the ultimate blend.

If desired, alkylate may be fractionated to give a cut of more desirable boiling range prior to incorporation with light isoparaffinic naphtha. To accomplish this, crude alkylate is moved by pump 54 via valves 56 and 71, through heater 72 to fractionator 73, which is similar to tower 9 except that an intermediate withdrawal point is not essential. Unwanted, high boiling alkylate bottoms are removed through valved line 74 while overhead of the desired boiling range is moved by pump 75 through valves 76 and 77 to line 19. By closing valve 77 and opening valve 78, the fractionated alkylate may be caustic washed prior to entering line 19. If desired, crude alkylate may be caustic washed (as previously described) and then fractionated simply by proceeding as before described with the caustic washing of the crude alkylate but closing valve 76 and opening valve 79 which leads eventually to tower 73 via valved line 71.

Returning now to fractionator 53: Overhead consisting essentially of isobutane and normal butane passes by valved line 80 to tower 81. Tower 81 is highly efficient and is provided with means to promote liquid-vapor contact, for example, a large number of bubble trays 82, and with bottom heating means 83 and top cooling means 84. Isobutane is taken overhead and passed by lines 85 and 86 to line 45. Normal butane is removed as bottoms and passed by line 87 to line 22.

By a very convenient modification, separation of normal butane from isobutane may be avoided but this modification requires a catalytic polymerization unit, which is however frequently available. Valve 43 is closed and 88 is opened, the catalytically dehydrogenated butanes thereby

passing through coil 89 in furnace setting 90 wherein they are heated to a catalytic polymerization temperature. The heated mixture passes to reactor 91 wherein it is contacted with a polymerization catalyst, for example, copper pyrophosphate. Products pass via valve 92 (where some pressure reduction is accomplished) to fractionator 93 which is similar to tower 9 except that an intermediate withdrawal line is not necessary. Olefine polymerization products are moved by pump 94 to line 45 while overhead from tower 93 passes through valve 95 and line 96 to line 22 for recycling. Conditions are so regulated in the catalytic polymerization zone so as to achieve as nearly complete olefine conversion as is conveniently possible.

As has been mentioned heretofore, olefines from any convenient source may be used as one component of the alkylation pair and the preparation of olefines by the catalytic dehydrogenation of gases containing isobutane has been mentioned. Obviously, olefines may be prepared by dehydrogenating pure isobutane and by so doing many apparatus simplifications are possible. Valve 18 is closed and the isobutane is passed via valved line 97 to the catalytic dehydrogenation zone, this gas representing the sole charge to this zone. After absorption and stripping, the resulting isobutane-isobutene mixture passes through valved line 43 to line 45 where alkylation occurs as usual. Overhead from tower 53, consisting essentially of isobutane, passes through valved line 98 and line 86 back to line 45 for recycling. Part or all of this isobutane may be recycled to the catalytic dehydrogenation zone via valved line 99. It will be noted that by this method of operation both the catalytic polymerization zone and the tower to separate butane and isobutane may be eliminated.

For the better understanding of the instant invention a single example illustrating the same is given. It is to be understood that this example is illustrative only and in no way limits the scope of the instant invention.

Example 1

A heavy naphtha obtained from East Texas crude and having a boiling range of from 250° F. to 400° F. and a motor octane number of about 45 was mixed with about 1% aluminum bromide and the resulting material was passed continuously to a liquid phase reactor operating at about 210° F. Overhead from the reactor was partially condensed to produce a gaseous fraction comprising essentially isobutane and a liquid containing large amounts of isoparaffins and having a motor octane number of about 80. From time to time a very small amount of steam was added to the reactor to activate the catalyst. From time to time sludge was withdrawn from the reactor. A butane cut from natural gas, consisting of 80% normal butane and 20% isobutane, was passed through a second reactor containing a highly active chromium oxide on alumina catalyst heated to approximately 1100° F. Considerable conversion of the paraffins present to isobutene and normal butenes was attained. The resulting gas mixture was subjected to orthodox absorption-fractionation to eliminate most of the hydrogen formed during dehydrogenation and the residue, consisting largely of hydrocarbons of four carbon atoms, was mixed with the isobutane produced in destructive isomerization and the whole was passed to an alkylation reactor containing concentrated sulfuric acid and operating at 35° F. Hydrocarbon reaction products were fractionated to produce a cut consisting largely of isobutane, a cut consisting largely of normal butane, and alkylate of an endpoint of 275° F. and bottoms. The isobutane rich cut was recycled to the alkylation reactor after being mixed with fresh feed to the same zone, the normal butane rich cut was recycled to the catalytic dehydrogenating zone, the bottoms were diverted to premium automobile motor fuel while the major alkylate fraction was blended with a sufficient amount of the liquid, highly isoparaffinic material produced in the destructive isomerization step to give an aviation fuel of high octane number, high lead response, high and proper volatility and low unsaturate content. By adding tetraethyl lead to this blend it was easily possible to achieve 100 octane number with less than 3 cc. per gallon and well over 100 octane number with 6 cc. per gallon, this larger quantity of lead tetraethyl being permissible in some aviation fuels for military purposes.

The foregoing description and example serve to outline the scope and spirit of the present invention and manifest its advantages to those skilled in the art to which it pertains but it is not intended that these shall be regarded as limitations upon the scope of the invention except insofar as included in the accompanying claims.

I claim:

1. In the preparation of motor fuel, the steps comprising subjecting a heavy naphtha to destructive isomerization, separating the destructively isomerized product into a relatively low boiling fraction and a relatively high boiling fraction having a maximum boiling point lower than the initial boiling point of said heavy naphtha, alkylating said relatively low boiling fraction with olefines, and blending the resulting alkylate with said relatively high boiling fraction.

2. In the preparation of motor fuel, the steps comprising subjecting a heavy naphtha to destructive isomerization, separating the destructively isomerized product into a relatively low boiling fraction and a relatively high boiling fraction having a maximum boiling point lower than the initial boiling point of said heavy naphtha, alkylating said relatively low boiling fraction with butenes and blending the resulting alkylate with said relatively high boiling fraction.

3. In the preparation of motor fuel, the steps comprising subjecting a heavy naphtha to destructive isomerization, separating the destructively isomerized product into a fraction comprising isobutane and a higher boiling fraction having a maximum boiling point lower than the initial boiling point of said heavy naphtha, alkylating said fraction comprising isobutane with olefines and blending the resulting alkylate with said higher boiling fraction.

4. In the preparation of motor fuel, the steps comprising subjecting heavy naphtha to destructive isomerization, separating the destructively isomerized product into a fraction comprising isobutane and a higher boiling fraction having a maximum boiling point lower than the initial boiling point of said heavy naphtha, alkylating said fraction comprising isobutane with butenes and blending the resulting alkylate with said higher boiling fraction.

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