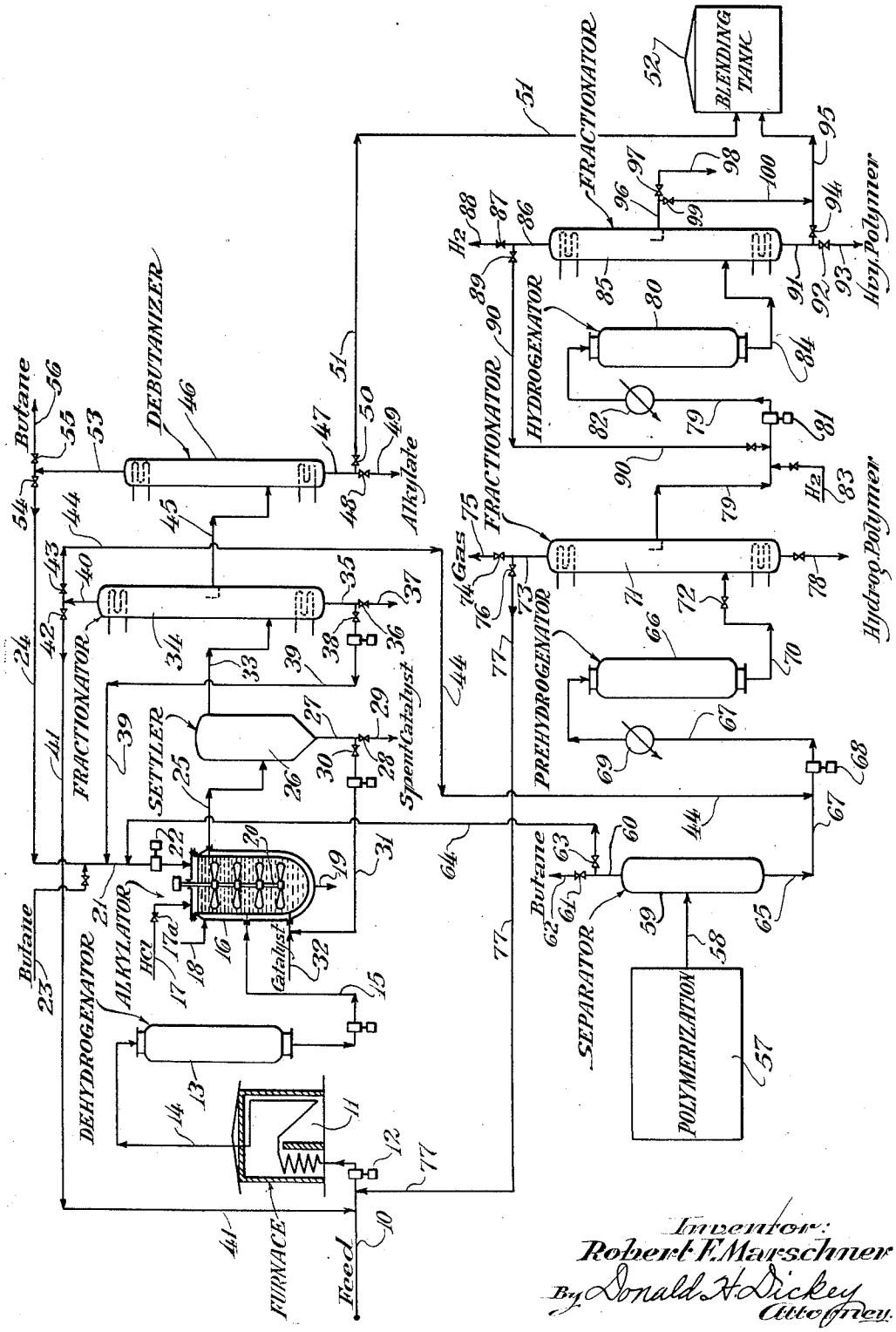
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HYDROCARBON CONVERSION

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Inventor:
Robert F. Marschner
By Donald H. Dickey
Attorney

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HYDROCARBON CONVERSION

Robert F. Marschner, Chicago, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

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This invention relates to the conversion of hydrocarbon materials to valuable motor fuels and relates more particularly to the catalytic dehydrogenation of normally gaseous paraffinic hydrocarbons.

Thermal processes for the dehydrogenation of normally gaseous paraffinic hydrocarbons, such as ethane, propane and butane, have been known in the art for some time, and have been practiced commercially. Such thermal processes, however, have various disadvantages, one of which is the degradation of the feed stock to paraffinic and/or olefinic hydrocarbons of fewer carbon atoms per molecule, such as methane, for example, during the production of the corresponding olefin and hydrogen. When catalytic dehydrogenation is employed under carefully controlled conditions, the olefins corresponding to the paraffinic hydrocarbons fed to the process are the only conversion product in addition to hydrogen, but the per cent conversion is small and the amount of unreacted paraffinic hydrocarbon is large. This is probably due to a thermodynamic hydrogenation-dehydrogenation equilibrium which inhibits the further dehydrogenation of paraffinic hydrocarbons at the temperature employed and the concentrations of olefin and/or hydrogen involved. If an attempt is made to increase the conversion by raising the temperature, the same disadvantages are encountered as in the thermal processes, i. e. much of the feed stock is degraded to less useful products such as methane and carbon. Such side reactions lead to short catalyst life due to the deposition of carbonaceous residue.

It is an object of my invention to provide a process for the substantially complete conversion of normally gaseous paraffinic hydrocarbons to olefinic hydrocarbons containing the same number of carbon atoms per molecule. Another object of my invention is to provide an improved process for the production of gasolines of high octane number. My invention also has as its object the provision of a process for the conversion of normally gaseous hydrocarbons to normally liquid hydrocarbons of high antiknock value. A still further object is to provide a combination process for the substantially complete dehydrogenation of a normally gaseous hydrocarbon feed and the use of the dehydrogenation products in the production of gasolines of high octane number gasoline. Further objects and advantages will become apparent as the description of my invention proceeds read in conjunction with the accompanying drawing which represents a flow diagram of apparatus suitable for carrying out one embodiment of my process.

Referring now to the drawing: A feed stock enters through line 10. As a feed stock I may employ a normally gaseous hydrocarbon, such as ethane, propane or butane, or a mixture of any two or all three of these hydrocarbons. A mixture of about two parts ethane and one part propane is particularly suitable. The hydrocarbons are preferably paraffinic in nature but the presence of minor amounts of olefinic materials can be tolerated. Methane and paraffins higher than butane are preferably absent, but small amounts of these are also permissible. The feed gases are directed to heater 11 by pump 12 and are heated to a temperature within the range of from about 800 to 1400° F., the heated gases passing from heater 11 to dehydrogenator 13 via line 14. Dehydrogenation is carried out at pressures near atmospheric, say, within the range of from 0 to 50 pounds per square inch gauge, and at a vapor rate of from 500 to 50,000 liquid volumes per volume of catalyst per hour, depending upon the composition and preparation of the catalyst used. With ethane, a temperature of about 1300° F. and a rate of the order of 1000 liquid volumes per volume of catalyst per hour represent good practice with mild catalysts. More active catalysts permit either lowering the temperature or increasing the rate. A higher yield (based upon ethane reacted) is obtained by lowering the temperature in general and such procedure is preferred. With propane faster rates, for example 3000 liquid volumes per volume of catalyst per hour and lower temperatures, for example, 1000° F. are preferred in the presence of active catalysts such as those containing chromium. Butanes need only about 900° F. at about 5000 liquid volumes per volume of catalyst per hour for satisfactory conversion. Mixed gases in general are dehydrogenated under conditions lying between the preferred conditions for the constituents, but this is not an arithmetical relationship. Higher temperatures and higher rates than the mean values for temperature and rate that would be calculated for the gas composition appear to give less preferential dehydrogenation of the heavier paraffin.

As catalysts I prefer those having a selective dehydrogenating action for the paraffins employed so that the corresponding olefinic materials are prepared without degradation of the feed stock to hydrocarbons of lower molecular

weight, and particularly those which do not degrade the feed stock to methane. Although certain catalysts are definitely more selective than others, giving a higher yield of the corresponding olefin per unit paraffin dehydrogenated, the selective effect of the catalyst is not as pronounced as that of the extent of conversion. In order to obtain high yields, the unhydrogenated paraffin content of the dehydrogenated gas is preferably maintained above 50%. Other reasons for maintaining a high concentration of unreacted paraffin will be described later. For economic reasons, however, the unreacted paraffin content is ordinarily maintained below 90% and preferably below 80%. The optimum range for average paraffins is of the order of 70% unreacted paraffins in the dehydrogenated gas. With the proper catalysts and conditions, the olefin yields can usually be maintained above about 95%. My preferred catalysts include those containing aluminum, chromium, molybdenum, vanadium and/or tungsten, particularly their oxides. Mixtures of two or more of these compounds can be suitably employed; for example, mixtures of chromia and alumina are very suitable. One such catalyst suitable for the process consists of about four parts of alumina and one part of chromic oxide by weight. These catalysts may be supported catalysts such as, for example, chromic oxide on silica or promoted catalysts such as chromic oxide containing small amounts of zinc, tin or zirconium oxides.

The dehydrogenated products together with the unconverted hydrocarbons and the hydrogen produced during the reaction pass from dehydrogenator 13 through line 15 to alkylator 16. In alkylator 16 the olefins produced in dehydrogenator 13 are contacted with an isoparaffinic hydrocarbon in the presence of a catalyst under such conditions of time, temperature, pressure and contact that the olefinic hydrocarbons present alkylate the isoparaffinic hydrocarbons present to branched-chain paraffinic hydrocarbons of higher molecular weight. Catalysts can suitably be aluminum chloride or preferably an aluminum chloride-hydrocarbon complex, formed by the reaction of anhydrous aluminum chloride with paraffinic or naphthenic hydrocarbons substantially free of aromatic or olefinic hydrocarbons in the presence of a promoter such as hydrogen chloride at temperatures of from about 50 to about 250° F. The complex formed by the isomerization of light virgin naphthas having an end point of, for example, 158° F., or by reaction with hydrogenated polymers such as those of dibutylene or tributylene, using aluminum chloride as the reagent or isomerization agent, are particularly suitable. Aluminum bromide complexes are also suitable for my purpose and in the event that olefins having more than two carbon atoms per molecule are the only products formed during the dehydrogenation, sulfuric acid can be employed. I will further illustrate my process by reference to the use of the previously mentioned aluminum chloride-hydrocarbon complex in a continuous process. It is obvious, however, that batch processes can be employed.

A promoter, such as for example hydrogen chloride or hydrogen bromide, can be added through line 17 and valve 17*a*. Generally speaking, a promoter is desirable, but not always necessary. The temperature within the alkylator 16 can be maintained by a suitable jacket about alkylator 16 through which flows a temperature-control medium which enters at line 18 and is discharged through line 19. Other means for control, such as coils within the alkylator, etc., can be suitably employed. Intimate contact between the reactants and the catalysts is necessary and this may be accomplished by the use of mechanical stirrer 20 as illustrated, or by other suitable means, such as for example by passing the reactants and catalyst through a coil in alkylator 16 where the turbulent flow will cause the proper contact between the reactants and catalyst. Other methods which are suitable include the use of jet injectors, turbo mixers, and in some cases packed towers can be employed.

Alkylator 16 is maintained at a temperature of from about 50 to about 350° F., preferably about 150° F., and under suitable pressures, for example, from about 25 to about 750 pounds, so that the reactants are in the liquid phase, thus assuring more intimate contact. The contact time necessary will depend upon the catalyst activity and the temperature primarily. The isoparaffinic hydrocarbon enters through line 21 having pump 22 therein and is preferably introduced in amounts such that the ratio of isoparaffin to olefin is greater than 1:1 and preferably from about 2:1 to 5:1, although a higher ratio such as 10:1 can be used. Isobutane is a particularly suitable isoparaffinic hydrocarbon for use in my process, although higher molecular weight isoparaffinic hydrocarbons such as isopentane, isohexane, etc., are equally advantageous. Generally speaking, however, isopentane and isohexane form in themselves a desirable constituent of high octane number motor and aviation fuels, and accordingly, unless there is a surplus of such hydrocarbons available or the demand is great for hydrocarbons of higher molecular weight than isopentane and isohexane, these latter hydrocarbons will not be utilized for alkylation.

The isobutane or other isoparaffinic hydrocarbon can be obtained from any suitable source (not shown) and injected through line 23, or it can be the off-gas from a polymerization process (to be described in more detail later) in which event the isobutane is injected into line 21 from line 64. Dilution with normal butane is by no means prohibited and, generally speaking, isobutane from refinery sources will be found to be mixed with greater or lesser quantities of normal butane, so that as a practical matter the isoparaffinic feed to alkylator 16 will contain varied amounts of unreactive hydrocarbons.

The reaction products including alkylate, unreacted hydrocarbons, hydrogen and catalyst are withdrawn from alkylator 16 through line 25 to settler 26 wherein the separation is made between the catalyst, and the hydrocarbons and normally gaseous constituents, the catalyst being withdrawn through line 27. If its activity for alkylation is spent the catalyst can be discarded by opening valve 28 in line 29, but since, generally speaking, it still is active for alkylation it can be returned by opening valve 30 in line 31 which joins line 32. Alternately, a part of the catalyst can be withdrawn through line 29 for regeneration and the remainder recycled to alkylator 16 through line 31 for use in conjunction with fresh catalyst introduced through line 32.

The hydrocarbon products together with unreacted hydrocarbons, hydrogen and any promoter present pass from settler 26 through line 33 to fractionator 34. Fractionator 34 is maintained under suitable conditions of temperature and pressure so that a fractionation can be obtained

between normally gaseous constituents lower boiling than butane, hydrocarbons of gasoline boiling range including, if desired, the butanes, and a fraction higher boiling than that desired for gasoline or aviation fuels. This latter heavy fraction is withdrawn from fractionator 34 through line 35 and can be discharged from the system by opening valve 36 in line 37, but preferably is recycled to the alkylation reactor 16 by opening valve 38 in line 39 which joins line 21.

In order to obtain further conversion to hydrocarbons of gasoline boiling range or to suppress the formation of hydrocarbons higher boiling than the gasoline range desired, hydrocarbons lower boiling than butane, or if butanes were included in the original feed stock, the hydrocarbons containing at least a portion of the butanes from fractionator 34 pass overhead through line 40 and can be returned to the dehydrogenation system through line 41 by opening valve 42 therein. The hydrogen chloride, of course, together with the hydrogen will also be included with these gases and it is desirable to subject the gases to a caustic washing step or other means for removing or recovering the hydrogen chloride prior to the injection of the light gases and hydrogen into the dehydrogenation system. On the other hand the light gases containing hydrogen can be utilized for hydrogenation as will be described in detail, in which event valve 42 is closed and valve 43 in line 44 is open. Alternately, a part can be recycled through line 41 to line 10 and the remainder directed to the hydrogenation step through line 44.

The hydrocarbons of gasoline boiling range, hereinafter referred to as alkylate, are withdrawn from fractionator 34 through line 45 to debutanizer 46 in which a part or all of the butane can be removed depending upon the volatility desired in the final product. The alkylate of gasoline boiling range with or without butane therein is withdrawn from debutanizer 46 through line 47 and can be taken from the system by opening valve 48 in line 49 or directed to blending tank 52 by opening valve 50 in line 51 leading thereto. Since the isobutane or other isoparaffinic hydrocarbons were present in excess this can be taken overhead from debutanizer 46 through line 53 and recycled to the alkylation system by opening valve 54 in line 24 which joins line 21. Alternately the butane can be discarded by opening valve 55 in line 56, either for use elsewhere or for fractionation of the isoparaffinic hydrocarbons from the paraffinic hydrocarbons. It should also be obvious that in the event that isoparaffinic hydrocarbons having five and/or six carbon atoms per molecule were employed as an isoparaffinic feed to the alkylation reaction these can be taken overhead through line 53 and recycled through line 24, leaving the alkylate of heavier molecular weight to be withdrawn through line 47.

The polymerization of normally gaseous olefinic hydrocarbons to form dimers, trimers and tetramers thereof, as well as the cross polymers and interpolymers, is well known in the art. Polymerizer 57 represents any well known polymerization process, preferably one employing a hydrocarbon fraction desirably of petroleum origin comprising substantially hydrocarbons having four carbon atoms per molecule and containing sufficient quantities of normal and/or isobutylenes therein to form dibutylenes in the process. The polymers together with the unreacted paraffinic hydrocarbons including normal and isobutanes are withdrawn from polymerizer 57 through line 58 to separator 59 wherein a separation is made between the paraffinic hydrocarbons and the polymers. The butane-containing stock passes overhead through line 60 and can be discarded by opening valve 61 in line 62 or if it contains considerable amounts of isobutane can be directed to alkylation reactor 16 by opening valve 63 in line 64 which joins line 21. The dimers with or without heavier polymers which may be present are withdrawn through line 65 and directed to a prehydrogenator 66 through line 67.

The hydrogen containing gas together with the unconverted normally gaseous paraffinic hydrocarbons from fractionator 34 and line 44 joins line 67 prior to prehydrogenator 66. A pump 68 in line 67 aids in compressing the reactants to the desired pressure while heater 69 elevates the temperature to the desired range. Prehydrogenation is carried out at temperatures of from about 200 to about 800° F. and at pressures within the range of from 15 to 5000 pounds per square inch over a suitable hydrogenating catalyst such as a reduced metal, metal oxide or metal sulfide, including such compounds as reduced copper, nickel-nickel oxide, molybdenum sulfide, and sulfided mixed oxides of molybdenum, zinc and magnesium. A throughput of from 1 to 10 liquid volumes per volume of catalyst per hour is suitable with a partially reduced supported nickel catalyst; for example, a temperature of about 425° F., a pressure of about 50 pounds per square inch, and a rate of about three volumes of liquid feed per volume of catalyst per hour, can be suitably used. With a sulfide catalyst containing molybdenum a temperature of about 700° F., a pressure of about 3000 pounds per square inch, and a rate of about four volumes of liquid feed per volume of catalyst per hour is preferred. Although this prehydrogenation step can perhaps be carried out more rapidly in the presence of pure hydrogen than when using hydrogen diluted with normally gaseous paraffins, the latter serves to simplify temperature control of the highly exothermic hydrogenation reaction by serving as a diluent and carrying heat from the reaction vessel. Such dilution of the reaction mixture smoothes out the catalyst temperature and raises the yield of hydrogenated polymer due to elimination of temporary and local hot spots which tend to destructively hydrogenate the feed.

The olefinic hydrocarbons are preferably present in prehydrogenator 66 in excess so that by utilizing all of the hydrogen present from line 44, from about 75 to about 95% of the olefins are hydrogenated in this step. The partially hydrogenated polymers are withdrawn from prehydrogenator 66 via line 70 and directed to fractionator 71, which is maintained at suitable temperatures and pressures to permit the separation of the normally gaseous hydrocarbons from the normally liquid hydrocarbons. A pressure reducing valve 72 may be inserted in line 70 prior to fractionator 71. The normally gaseous hydrocarbons are passed overhead from fractionator 71 through line 73 and may be discarded by opening valve 74 in line 75 or preferably are recycled to the dehydrogenation step by opening valve 76 in line 77 which joins line 10. Commercially, a small part of the gas is discarded, due to imperfections in commercial fractionation equipment, etc., through line 75 and the greater part is recycled through line 77. Since the hydrogen will have been substantially completely removed in prehydrogenator 66, the overhead gas from frac-

tionator 71 will comprise essentially paraffinic hydrocarbons originally in the feed stock and unconverted in the dehydrogenation step.

A further fractionation can be made in fractionator 71 between polymers heavier than that desired for gasoline and those of gasoline boiling range or the entire partially hydrogenated polymers can be directed to a further hydrogenation step. In the event that the heavier polymer is to be separated, it can be withdrawn tnrough line 78 either for cracking and conversion to polymers of lower molecular weight or for use elsewhere, while the partially hydrogenated polymers of gasoline boiling range are withdrawn through line 79 and directed to hydrogenator 80. A pump 81 in line 79 and a heater 82 therein serve to elevate the pressure and temperature of the partially hydrogenated polymers together with pure hydrogen from an outside source which is injected through line 83 to the point desirable for carrying out a final hydrogenation of the polymer. Hydrogenator 80 can be maintained at a temperature within the range of from 250 to 500° F. and pressures of from 0 to 250 pounds per square inch gage and a throughput of 2 to 10 volumes of liquid hydrocarbon per volume of catalyst per hour. As suitable catalysts we can employ reduced copper oxide, partially reduced supported nickel oxide or sulfided catalysts similar to those previously described. The preferred conditions are 425° F., about 50 pounds per square inch pressure, and a rate of about six volumes of liquid feed per volume of catalyst per hour. The use of considerable excess hydrogen is desirable to saturate completely the polymer and to secure a high reaction rate. I somewhat prefer a low-temperature reduced metal catalyst to a high-temperature sulfide catalyst because of the practically quantitative yields obtained.

Hydrogenated polymer is withdrawn from hydrogenator 80 through line 84 and directed to fractionator 85. Excess hydrogen passes overhead through line 86 from fractionator 85 and can be discarded by opening valve 87 in line 88, but since its purity remains high it is preferably recycled by opening valve 89 in line 90 which joins line 79. All of the hydrogenated polymers can be withdrawn through line 91 and discharged from the system by opening valve 92 in line 93 or directed to blending tank 52 by opening valve 94 in line 95 which joins line 91. It is also possible, in the event that both heavy and light polymers were directed to hydrogenator 80, to separate these into a fraction of aviation gasoline boiling range and a fraction of heavier polymer, the aviation gasoline fraction being withdrawn through line 96 and discharged by opening valve 97 in line 98 or directed to blending tank 52 by opening valve 99 in line 100, while the heavier polymer is withdrawn from the base of fractionator 85 through line 93.

An alternate method is to fractionate the polymers from polymerizer 57 so as to obtain a fraction boiling within the gasoline boiling range, and to subject only these polymers to hydrogenation. In this event, separator 59 and fractionator 71 can be intercharged, it being necessary only to separate the gases from the prehydrogenated polymers before directing the latter to final hydrogenator 80. In such a case, fractionator 85 can be replaced by a separator, since there will be no necessity for separating heavy hydrogenated polymers from gasoline-like material, but only for the elimination and/or recycle of unconsumed hydrogen.

By my process it is thus possible to convert substantially all of the normally gaseous paraffinic feed stock to the corresponding olefins and to use the olefins in the production of highly branched-chain normally liquid paraffinic hydrocarbons while the hydrogen from the process, without separation or purification, can be employed for the hydrogenation of unsaturated, gasoline-like polymers to saturated hydrocarbons suitable for premium fuels. For example, in dehydrogenating ethane within the range of conditions described, a mixture of approximately 60% ethane, 20% ethylene and 20% hydrogen results. In catalytic alkylation of isobutane with ethylene, using an aluminum chloride-hydrocarbon complex as a catalyst, feed streams containing as little as 7% ethylene can be used and the ethylene completely removed. There is also a benefit to the catalyst life due to the presence of appreciable amounts of hydrogen. Using the above dehydrogenated stock, therefore, in alkylation a residual gas having a composition of approximately 75% ethane and 25% hydrogen is obtained. By recycling this to the dehydrogenation step, a gas approaching the approximate composition 40% ethane, 40% hydrogen and 20% ethylene can be obtained, thus yielding further quantities of ethylene for alkylation. Either the once-through or the recycle gas can be sent to the prehydrogenation step, preferably the latter due to its higher hydrogen content. By thus using the diluted hydrogen for first hydrogenating an olefinic polymer to about 75–95%, all of the hydrogen is removed from the stream, while at the same time the synthetic pure hydrogen requirements for hydrogenation of the polymers are greatly reduced. The ethane separated from the partially hydrogenated olefinic material can be returned to the dehydrogenation step and the process thus repeated. Other normally gaseous paraffinic hydrocarbons can be employed in place of or in admixture with ethane, with equally valuable results.

By my process normally gaseous paraffinic hydrocarbons are converted substantially completely to more valuable products in an economic and advantageous manner. Although I have illustrated one preferred embodiment of my invention, I do not intend to be limited thereto, since it is by way of example and not by way of limitation. Moreover, I have omitted various details in apparatus and flow, such as pumps, heat exchangers, valves, control means, reboilers, etc. all of which are well known to those skilled in the art, and which would obviously be employed in the commercial utilization of my process.

I claim:

1. A process for producing a blended high octane number gasoline which comprises the steps dehydrogenating at least a portion of normally gaseous paraffinic hydrocarbons having at least two carbon atoms per molecule to the corresponding olefin with the production of hydrogen, subjecting to polymerization gases comprising substantially iso and normal paraffinic and olefinic hydrocarbons having four carbon atoms per molecule, separating a normally liquid polymerization product and unconverted paraffinic hydrocarbons, contacting products from said dehydrogenation with the unconverted paraffinic hydrocarbons including isoparaffinic hydrocarbons separated from the normally liquid polymerization product, said contacting being in the presence of a catalyst under conditions adapted

to promote the alkylation of isoparaffinic hydrocarbons with said olefinic hydrocarbons, recovering from the total alkylation product a high octane number alkylate within the gasoline boiling range, recovering a gaseous fraction from said total alkylation product comprising hydrogen diluted with normally gaseous paraffins, catalytically hydrogenating a fraction of the normally liquid olefin polymer boiling within the gasoline range in the presence of the recovered hydrogen diluted with normally gaseous paraffins adapted to promote the hydrogenation of said polymer to the extent of between about 75% and about 95%, recovering the partially hydrogenated polymer, subjecting the partially hydrogenated normally liquid polymer boiling within the gasoline range to a second hydrogenation in the presence of an excess of substantially pure hydrogen, and blending the completely hydrogenated normally liquid polymer and the said alkylate to produce a high octane number blended gasoline.

2. A process for the production of a blended high octane number fuel which comprises the steps of heating at least one normally gaseous paraffinic hydrocarbon having at least two carbon atoms per molecule at a temperature and pressure adapted to promote the dehydrogenation of at least a portion of said paraffinic hydrocarbon to the corresponding olefin with the production of hydrogen, subjecting to polymerization a stream comprising substantially iso and normal paraffinic and olefinic hydrocarbons having four carbon atoms per molecule, separating the paraffinic hydrocarbons and a normally liquid polymerization product, contacting the products from said dehydrogenation including unconverted paraffinic hydrocarbons, olefinic hydrocarbons and hydrogen with the paraffinic hydrocarbons including isoparaffinic hydrocarbons recovered from the normally liquid polymerization product in the presence of a catalyst under conditions adapted to promote the alkylation of said isoparaffinic hydrocarbon with said olefinic hydrocarbon, recovering from the total alkylation product a high octane number alkylate boiling within the gasoline boiling range, recovering a gaseous fraction from said total alkylation product comprising hydrogen diluted with normally gaseous paraffins, catalytically hydrogenating a fraction of the normally liquid olefin polymer boiling within the gasoline boiling range in the presence of the said hydrogen diluted with normally gaseous paraffins whereby the degree of hydrogenation and the temperature of the highly exothermic hydrogenation reaction are controlled and destructive hydrogenation of the polymer is avoided, recovering the normally gaseous paraffins from the hydrogenation product, recycling the recovered paraffins to the said dehydrogenation step, hydrogenating the partially hydrogenated normally liquid polymer boiling within the gasoline range with an excess of substantially pure hydrogen in a separate hydrogenation zone and blending the hydrogenated normally liquid polymer and alkylate boiling within the gasoline range to form a high octane number fuel.

3. A process according to claim 1 wherein said isoparaffinic hydrocarbons predominate in isobutane.

4. A process according to claim 1 wherein the normally liquid polymerization product comprises substantially dimers of olefins having four carbon atoms per olefin molecule.

ROBERT F. MARSCHNER.