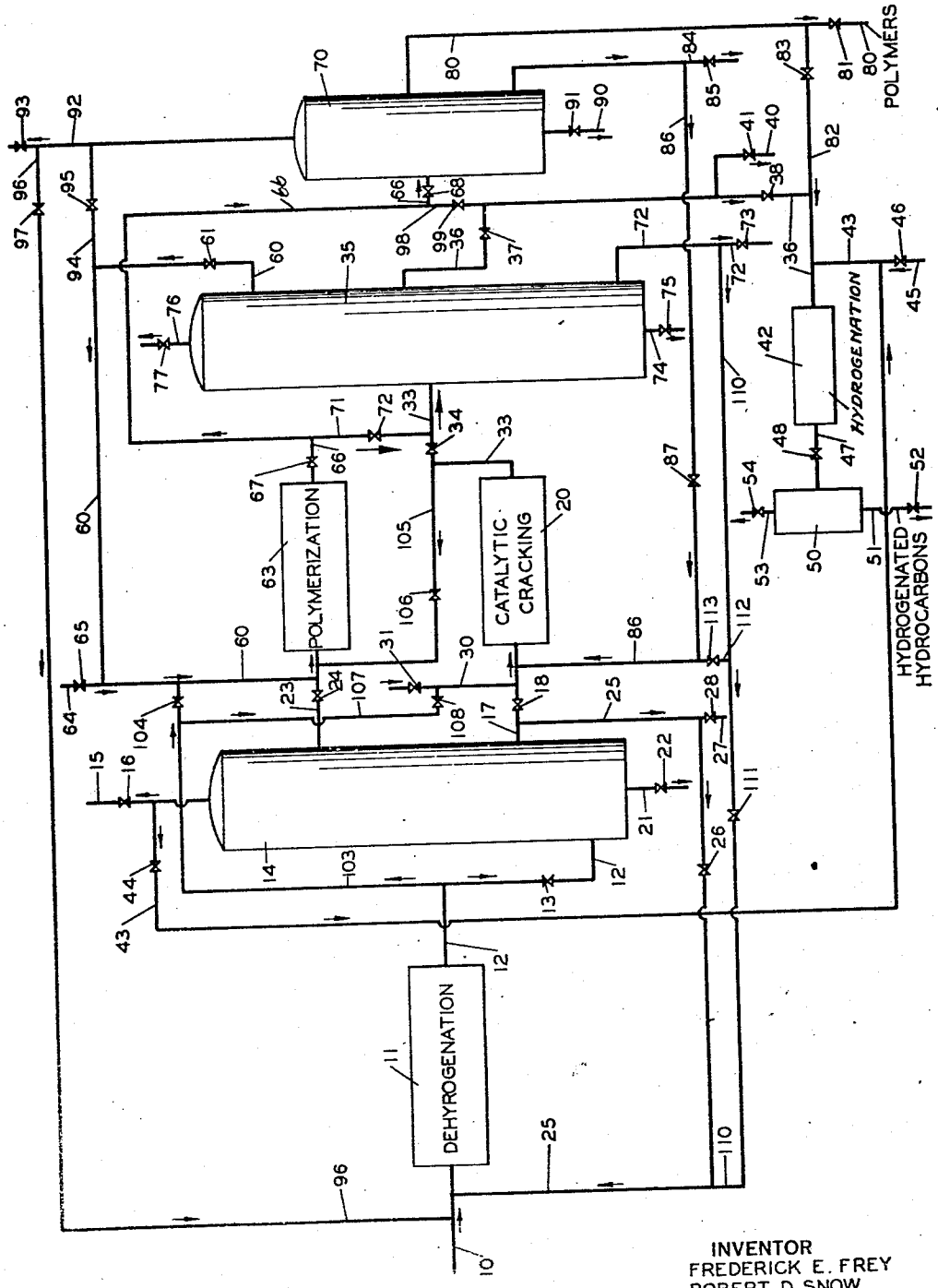
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PROCESS FOR CONVERTING HYDROCARBONS

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PROCESS FOR CONVERTING HYDROCARBONS

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This invention relates to the conversion of simple aliphatic hydrocarbons into volatile, normally liquid hydrocarbons. More specifically it relates to the conversion of paraffins and/or olefins into hydrocarbons boiling in the motor fuel boiling range by a catalytic treatment, and preferably by two or more catalytic treatments. This application is a continuation-in-part of our copending application Serial No. 745,348, filed September 24, 1934, now U. S. Patent 2,227,639, granted Jan. 7, 1941.

Many processes have been proposed in the past for increasing the yield of hydrocarbons in the motor fuel boiling range from hydrocarbon fractions or mixtures which occur naturally, such as natural gas and crude oil, as well as from similar mixtures which are produced artifically, such as by the destructive hydrogenation of heavy tars, lignites, coals, etc., or by the reaction of carbon oxides and hydrogen. While hydrocarbon materials from such sources generally comprise or contain substantial quantities of hydrocarbons in the motor fuel range, the greater proportion of the hydrocarbons in such mixtures are often not in this desirable range.

For quite a number of years there have been increasing demands not only for larger quantities of motor fuel but also for motor fuels with improved antidetonation properties, or fuels with higher octane numbers, as this feature is more often referred to. During the greater part of this period the demands for more motor fuel were met by "cracking" hydrocarbons which boiled above the motor fuel range. Such cracking processes are conducted by heating heavier hydrocarbons to temperatures between about 850 and 1400° F. under low or high superatmospheric pressures. Although these cracking processes permit a considerable increase in the amount of motor fuel which can be obtained from a given amount of crude oil or petroleum, they also result in a production of considerable quantities of light gaseous material and of heavy tars and coke. Both these types of by-products represent valuable carbonaceous material present in the original charge to the cracking process which is not recovered as motor fuel—the desired product.

More recently, the production of motor fuel has been augmented to a small, although appreciable extent by the development of various gas conversion processes, which convert certain light or normally gaseous hydrocarbons to hydrocarbons having higher molecular weights. These processes are readily adaptable to the production of motor fuel from naturally occurring light or gaseous hydrocarbons, or from similar hydrocarbons produced as by-products in the aforementioned cracking processes. Although, comparatively speaking, these gas conversion, or polymerization, processes do not at present produce a large proportion of the total motor fuel produced from all sources, nevertheless the motor fuels produced by such processes generally have premium qualities, and nearly all the so-called "high octane" fuels of the present time are produced by such polymerization processes. We have found that the process which forms the principal subject matter of our hereinbefore mentioned application Serial No. 745,348 is one of the better processes of this type.

When such gas conversion processes are used to convert hydrocarbon gases produced in cracking process, the ultimate yield of hydrocarbons in the motor fuel range from a given quantity of heavier hydrocarbons charged to the cracking process is increased several per cent. A further increase in ultimate yield has, at times, been realized by subjecting the aforementioned tars, etc., produced by cracking to a destructive hydrogenation. However, both these expedients involve additional equipment and the like, which represent undesirable increases in plant investments. In addition to this, large proportions of the gases produced by ordinary cracking processes are not readily converted to motor fuel range hydrocarbons, such as ethane and more especially methane, large amounts of valuable carbonaceous materials being lost every day in the form of methane.

As has just been mentioned, there is an increasing demand not only for more motor fuel, but also for motor fuels with improved antidetonation properties. Many hydrocarbons or hydrocarbon fractions in the motor fuel range recovered from natural sources, or recovered from a synthetic hydrogenation process, do not have desirable antidetonating qualities. It has therefore been found necessary in many cases to subject such hydrocarbon fractions to some sort of reforming operation, whereby a fraction in the motor fuel range is recovered with better antidetonating qualities. Most such reforming operations are similar to the aforementioned cracking processes and are accompanied by the production of appreciable amounts of tar and light gases, which represent lost carbonaceous material.

In our hereinbefore mentioned copending ap-

plication we have disclosed that, when low boiling olefins are polymerized to produce hydrocarbons in the motor fuel boiling range, heavier hydrocarbons are, at times, also produced, and we have also disclosed that such heavier hydrocarbons can be depolymerized in the presence of a depolymerization catalyst to form lighter olefins. The lighter olefins so formed may be in the motor fuel boiling range and suitable for inclusion in motor fuels as they are, or after nondestructive hydrogenation, or they may be somewhat lower boiling than the motor fuel range but suitable for subsequent polymerization to form hydrocarbons in the motor fuel range. We have also disclosed that certain solid depolymerization catalysts are especially suitable for use in such depolymerization operations, namely, hydrous aluminum silicates, mixed alumina and silica gels, such as disclosed in McKinney 2,142,324 and 2,147,985 and in the copending application of Frey Serial No. 329,195, filed April 11, 1940, fuller's earth, especially when activated by treatment with a halogen acid, and the like catalysts. We have found that these same catalysts are good catalysts for the polymerization of olefins to form motor fuel range hydrocarbons, and they are often referred to as polymerization catalysts. However, modifications best adapted for depolymerization may not best adapted for polymerization, as may be determined by trial for any particular case.

We have found that not only may heavier polymeric olefin hydrocarbons be treated in the presence of depolymerization catalysts to produce lighter olefins, but also that other heavier unsaturated hydrocarbons which have not been produced through a polymerization step can be treated, or cracked, in the presence of a depolymerization catalyst and will produce lighter olefin hydrocarbons. We have also found that very little material lower boiling than propene is produced by such treatment. Thus we have found that olefin hydrocarbons boiling above, or in the upper part of the motor fuel boiling range and produced by either thermal or catalytic dehydrogenation, may be cracked in the presence of a depolymerization catalyst to produce lighter olefins which are predominantly either in the motor fuel range or which may be readily catalytically polymerized to form hydrocarbons in the motor fuel range. We have further invented a process whereby heavier hydrocarbons can be converted to lighter hydrocarbons in the motor fuel range with very little, if any, loss of carbonaceous material comprising first catalytically dehydrogenating such heavier hydrocarbons and subsequently cracking the unsaturated hydrocarbons so produced in the presence of a depolymerization catalyst.

It is an object of our invention to produce lighter hydrocarbons from heavier hydrocarbons with a minimum loss of carbonaceous material.

A further object of our invention is to produce practically a quantitative yield of hydrocarbons by a process which involves a catalytic cracking step.

It is another object of our invention to submit heavier olefin hydrocarbons from any source to catalytic cracking in the presence of a depolymerization catalyst to produce lighter hydrocarbons which do not comprise substantial amounts of methane or ethane.

Another object of our invention is to obtain motor fuel range hydrocarbons from heavier paraffin hydrocarbons by a process comprising the combination of dehydrogenation of the heavier paraffins to form olefins and a catalytic cracking of the olefins so produced in the presence of a solid depolymerization catalyst.

Still a further object of our invention is to dehydrogenize catalytically paraffins heavier than motor fuel to form heavy olefins and free hydrogen, to crack catalytically heavier olefins so produced to form hydrocarbons in the motor fuel range, and to hydrogenate at least a part of the hydrocarbons so produced in the presence of hydrogen produced by said dehydrogenation.

Further objects and advantages of our invention will be found from the accompanying disclosure and discussion:

Reference is made herein both to cracking and to depolymerization. We consider cracking as being a generic term, having reference to a reaction wherein a hydrocarbon molecule or radical is broken with a scission of carbon-to-carbon bonds, forming at least two smaller hydrocarbon molecules or radicals. Depolymerization is a specific form of cracking, wherein hydrocarbons formed by polymerization are converted to hydrocarbons of lower molecular weights, generally the original monomeric hydrocarbons. Reference is made to cracking in the presence of a depolymerization catalyst, and we have found that, for the purpose of our disclosure a catalyst may be defined as a depolymerization catalyst when it will promote the formation of isobutylene from diisobutylene. For instance, we have depolymerized diisobutylene by passing the vapors over a granular silica-alumina catalyst at a temperature of 392° F. at an absolute pressure of 0.58 pound per square inch and a flow rate of 1.27 volumes of liquid per volume of catalyst granules per hour, with a depolymerization of 58 per cent of the diisobutylene per pass into isobutylene with a formation of heavy polymer of less than one per cent. While we have not found any exceptions to the rule that such a depolymerization catalyst will be effective in our process, we have found that certain depolymerization catalysts are especially efficient in our process. These catalysts are hydrous aluminum silicates, silica-alumina catalysts such as mixed alumina and silica gels and more especially those silica-alumina catalysts disclosed in McKinney 2,142,324 and 2,147,985, and in the copending application of Frey Serial No. 329,195, filed April 11, 1940, fuller's earth, especially fuller's earth, activated with a halogen acid, and the like. In the silica-alumina catalysts as mentioned above there will be a major proportion of silica and a minor proportion of alumina; generally not more than 5 per cent by weight and more often between about 0.5 and 2 per cent.

We have found that not only olefin polymers, but also nonpolymeric olefins can be cracked in the presence of these catalysts. We have further found that olefins having at least six carbon atoms per molecule are most efficiently treated, and will produce very little material lighter than propene when the cracking conditions are properly controlled. We have found that, in general, the temperature should be between about 300 and 1100° F., and preferably between about 550 and 1050° F. The operating pressure for the hydrocarbons in the cracking step is relatively low and generally should not exceed 250 pounds per square inch. We prefer to operate below 100 pounds per square inch, with the reactants being present in the vapor

phase, and subatmospheric pressures may be employed at times although this is generally not feasible on a commercial scale. Inert gases may be included to facilitate operation in the vapor phase, if it should appear feasible in any particular instance. In many instances the olefins will be accompanied by saturated hydrocarbons, which will be substantially inert under the conditions of cracking. The flow rate should be between 0.25 and 10 liquid volumes of hydrocarbon per volume of catalyst per hour, with the best operation being between 1 and 4 liquid volumes of charge. It is desirable in this operation to avoid excessive deposition of carbonaceous material on the catalyst, and the rate of formation of such material will be a factor to be considered in establishing reaction conditions. For any particular catalyst and/or charge stock, optimum conditions of temperature, pressure, and flow rate can be readily determined by trial by one skilled in the art.

The unsaturated hydrocarbon material charged to our catalytic cracking step is preferably olefinic, and may be derived from substantially any source. As mentioned, hydrocarbons having at least six carbon atoms per molecule are most efficiently treated. In most cases, the catalytic cracking step will be only a part of a complete process which will include a dehydrogenation step, the entire process being conducted to produce a desirable motor fuel. Although in one modification our process may be operated to produce more desirable hydrocarbons in the motor fuel range from less desirable hydrocarbons in the motor fuel range, in which case hydrocarbons of six to eight or nine carbon atoms will be charged, and treated in the cracking step to produce hydrocarbons of similar molecular weight, or molecular weight range, but more desirable molecular structure the most usual operation will be in connection with the production of hydrocarbons in the motor fuel range from hydrocarbons of 10 or more carbon atoms per molecule, generally of 14 to 20 or 22 or more carbon atoms per molecule. Hydrocarbons of 10 to about 14 carbon atoms per molecule are in the motor fuel range, but are definitely in the upper part of it as defined at present and such hydrocarbons will be more often treated than lighter normally liquid hydrocarbons. When heavier hydrocarbons are treated in our process, a substantial proportion of the products of the catalytic cracking step will be in the motor fuel range, while when lighter hydrocarbons are treated, substantial proportions of very light or normally gaseous hydrocarbons are produced which can be readily polymerized to form motor fuel range hydrocarbons, as will be more fully described.

When our complete process includes a dehydrogenation step, we prefer that this should be operated as a catalytic step also. In this way, full advantage is taken of our catalytic cracking step, since catalytic dehydrogenation can be operated to produce olefins with little loss of carbonaceous material, and catalytic dehydrogenation thus combines with catalytic cracking of olefins to produce a lighter hydrocarbon product with little overall loss of carbonaceous material. Furthermore, since olefins can thus be formed by the disjuncture of free hydrogen rather than the disjuncture of a smaller saturated hydrocarbon molecule, hydrocarbons produced by the process may be saturated with free hydrogen produced within the process. For the dehydrogenation catalyst we prefer to use some form of chromium oxide catalyst, especially the chromium oxide gel disclosed in Huppke and Frey 1,905,383, Frey and Huppke, 2,098,959 (Re. 21,911), and other forms of black, unglowed chromium oxide such as disclosed in the copending applications of Morey Serial No. 113,091, now Patent 2,288,320, issued June 30, 1942, and Serial No. 359,295, filed October 1, 1940, of Matuszak and Morey Serial No. 173,708, now Patent 2,294,414, issued September 1, 1942, of Morey and Frey Serial No. 173,709, now Patent 2,312,572, issued March 2, 1943, and Serial No. 359,296, filed October 1, 1940, and Schulze Serial No. 10,697, now Patent 2,183,591, issued December 19, 1939. However, we do not necessarily wish to restrict ourselves to such catalysts, and other catalysts which will promote a clean cut dehydrogenation of paraffin hydrocarbons to form free hydrogen and olefins of the same number of carbon atoms per molecule, with a minimum of concomitant cracking reactions, may be used. In many instances the hydrocarbon fractions to be treated will contain organic sulfur compounds, such as mercaptans, sulfides, disulfides, thiophenes, thiophanes and the like. These compounds will be more or less completely decomposed along with or prior to the dehydrogenation, and in such instances the dehydrogenation catalysts used should be such as will not be poisoned by sulfur compounds, an advantage of the chromium oxide catalysts mentioned. In such cases, the desulfurization and dehydrogenation may be carried out in two or more steps, similar to those disclosed in Schulze 2,151,721. However, this part of our process is primarily a dehydrogenation step rather than one of desulfurization alone. The temperature of the dehydrogenation will generally be between about 750 and 1200° F., and we prefer to use low pressures, not in excess of about 250 pounds per square inch and preferably less than 100 pounds per square inch. The reaction times should be such that the effluent will contain between 10 and 40 per cent by volume of olefins, preferably 15 to 25 per cent, but not long enough to induce appreciable cracking reactions. Actual temperatures, pressures, and reaction times will vary between individual cases since these factors are also dependent upon catalyst activity and characteristics of the charge stock, and optimum conditions for each application of the process may be readily determined by trial by one skilled in the art.

Our process may also include a polymerization step and/or a hydrogenation step. As mentioned, in one specific modification our catalytic cracking step may be one of depolymerization, operated primarily in combination with a polymerization step to produce motor fuel from heavier polymers formed in such a step. It is most advantageously combined with a polymerization step such as is disclosed in our copending application of which this is a continuation-in-part. Substantially any polymerization catalyst may be used, either a solid catalyst such as a silica-alumina catalyst, and the like, or "solid" phosphoric acids, or liquid catalysts such as sulfuric and sulfonic acids, or phosphoric acids, or a vaporous catalyst such as boron trifluoride. We find that these polymerization catalysts are not the full equivalents of each other, and most desirable results are obtained with a silica-alumina catalyst, such as disclosed in McKinney, 2,142,324 and 2,147,985, which are most efficiently used under liquid phase conditions as disclosed in the copending application of Frey, McKinney and Wood, Serial No. 747,964, filed October 11, 1934, now U. S. Patent 2,198,937, granted

April 30, 1940. When the process is primarily one involving the catalytic cracking of olefins from a nonpolymeric source, a polymerization step may be included to react lighter olefins formed by the catalytic cracking. Again, any such polymerization step may be employed, and in this latter case it may be a specific modification which involves alkylation, either with paraffins, aromatics, or the like. With such modification, a catalyst such as sodium chloroaluminate, or concentrated sulfuric acid used in conjunction with vigorous agitation and isoparaffins, or concentrated hydrofluoric acid may be used.

Any process for essentially nondestructive hydrogenation may be included, and may be operated with hydrogen produced in this process as being at least a part of the hydrogen used. If only a part of the total product is hydrogenated, such hydrogen may be sufficient in quantity, but if it is desired to effect a complete conversion of heavier paraffinic hydrocarbons into lighter paraffinic hydrocarbons, additional hydrogen will, of course, have to be used. Simple hydrogenation in the presence of a nickel-containing catalyst is to be preferred.

A modification of our invention will now be discussed in connection with the accompanying drawing which forms a part of this disclosure and which shows diagrammatically and in partial elevation one arrangement of apparatus adapted to the practice of our invention.

A paraffinic hydrocarbon material, such as a petroleum fraction in the upper part of the gasoline boiling range, or in the kerosene or gas oil range, is introduced to the process through pipe 10, and is introduced into an apparatus 11 for dehydrogenation and/or desulfurization. The dehydrogenation and/or desulfurization step which is carried out in apparatus 11 is preferably a catalytic operation, and as will be readily appreciated by those skilled in the art the apparatus 11 will comprise a heating unit or furnace, one or more catalyst chambers, with various pumps, valves, temperature indicating and controlling devices, and the like, which are common and usual in such installations. When the reaction is one of dehydrogenation, we prefer to use some form of chromium oxide catalyst, as previously discussed. Ordinary hard bauxite and other mineral ores may also be used, but we prefer to use these for simple desulfurization steps. The chromium oxide catalysts may also be used for desulfurization, either alone or where such a reaction takes place along with dehydrogenation, but such a catalyst is generally more expensive than the mineral ore catalysts which are quite suitable for desulfurization. In any event the reaction pressure should not exceed about 250 pounds per square inch, and is preferably below 100 pounds per square inch. For dehydrogenation the temperature is preferably between about 750 and 1200° F. Desulfurization without extensive dehydrogenation can be effected at temperatures between about 500 and 800° F., and again specific temperatures and contact times will be dependent on catalyst activity and on charge stock. Contact times for desulfurization will be shorter than contact times for dehydrogenation, even with the lower temperatures, and in any event optimum specific values for any specific case can be readily determined by trial by one skilled in the art. When the entire process is primarily one of dehydrogenation-polymerization-hydrogenation, as claimed in our copending application of which this is a continuation-in-part, the charge stock which is introduced through pipe 10 will comprise primarily normally gaseous hydrocarbons, such as propane and/or butane.

The material which has been treated in apparatus 11 is passed through pipe 12 and valve 13 to the fractionating and separating equipment 14. In actual practice the stream which enters the equipment 14 may be at a higher pressure than existed during the previous dehydrogenation step, or other treatment, and will also be at an appreciably lower temperature. Adequate cooling and compressing equipment, and the like, can, of course, be included to accomplish the indicated result. The fractionating and separating equipment 14 will include various fractionating columns, separators, heaters and coolers, and pumps, and the like, necessary to the separation of the effluent from the dehydrogenation step into fractions suitable for treatment in the subsequent steps, as will be more fully discussed.

When the charge stock, which is passed through pipe 10 to the dehydrogenation step, is a petroleum fraction heavier than an ordinary gasoline fraction, and the principal object of the process is to produce valuable hydrocarbons in the gasoline boiling range, and when the initial treatment in apparatus 11 is primarily one of dehydrogenation accompanied by cracking reactions to only a small or negligible extent, the effluent is easily separated into a light gas fraction predominating in free hydrogen which is removed through pipe 15 and valve 16, and an unsaturated hydrocarbon fraction which is removed through pipe 17 and is eventually passed to the catalytic cracking apparatus 20, as through valve 18. Heavier hydrocarbons and tar may be removed from the system through pipe 21 and valve 22. If polymerizable olefins are formed, and it is desired to polymerize them to form gasoline range, or heavier, hydrocarbons, they may be removed through pipe 23 and valve 24 and passed to the polymerization apparatus 63. If these polymerizable olefins are present in only minor amounts, and it is not desired to submit them to polymerization, they may be removed from the system, as by including them with lighter material passing through pipe 15.

As previously discussed, the catalytic cracking operation which is conducted in apparatus 20 takes place at a temperature between about 300 and 1000° F., and at a relatively low pressure, generally not in excess of about 250 pounds per square inch. The most desirable operation is obtained with the reactant present in the vapor phase. The reaction is quite endothermic, and for this reason it may be desirable to conduct the operation with the catalyst mass in a heat-exchange relationship with a heat-supplying medium. However, we have found that the process is successfully operated with a large body of catalyst, the heat being supplied solely by the heat content of the charge stock.

In the event that the unsaturate content of the hydrocarbon stream passing through pipe 17 from the fractionating equipment 14 is initially not sufficiently great to give a desirable operation in the catalytic cracking equipment, a portion of the stream may be diverted from pipe 17 through pipe 25 and passed through valve 26 to pipe 10 where it is reintroduced to the dehydrogenation step. In this manner, the unsaturate content of the material leaving the fractionating equipment 14 through pipe 17 is raised, and will remain at a substantially steady state after the starting-up period is passed and an equilibrium within the plant has been reached. If such a modification

of operation does not give a desired result, a part or all of the stream passing through pipe 17 may be removed through pipe 27 and valve 28, and the unsaturated hydrocarbon material separated in a more concentrated form, in apparatus not shown, and this more concentrated fraction can be introduced to the catalytic cracking step through pipe 30 and valve 31, which leads into pipe 17 on the far side of valve 18. In this case, the unreacted saturated hydrocarbon material which remains may be reintroduced to the process through pipe 10, as may be desired. In the event that a suitable unsaturated hydrocarbon material is available as such from an outside source, it may be introduced directly to the process through pipe 30. Such an unsaturated hydrocarbon material may be a fraction from a thermal cracking operation, or a fraction of polymers produced by the well known clay treating and stabilization of cracked gasoline, and the like. Alternatively, if the catalytic cracking step carried out in the apparatus 20 is so adapted as to operate satisfactorily on a saturated charge stock, such a saturated stock may be introduced directly to the catalytic cracking step through pipe 30.

The effluent from the catalytic cracking step passes through pipe 33 and valve 34 to fractionating and separating equipment 35. This equipment comprises various conventional units, as has been discussed in connection with the fractionating equipment 14. A hydrocarbon stream comprising hydrocarbons boiling in the motor fuel range produced by the catalytic cracking is passed from the fractionating equipment 35 through pipe 36 and valve 37, and may be recovered from the process as such through pipe 40 and valve 41. Inasmuch as this fraction will have a high content of unsaturated hydrocarbons, and since it may be desirable in many instances to secure a more or less saturated product, this stream, or at least a part of it, is conveniently hydrogenated. This is accomplished by passing the material to be hydrogenated through valve 38 in pipe 36 to the hydrogenation apparatus 42, where it it treated with free hydrogen in the presence of a suitable hydrogenation catalyst. Appreciable quantities of hydrogen are produced in the dehydrogenation step in apparatus 11, and this hydrogen can be used directly by passing the stream from pipe 15 through pipe 43 and valve 44 to the latter part of pipe 36, where it is mixed with the hydrocarbon material charged to the hydrogenation step. When the hydrogen passing through pipe 15 is too diluted or contaminated with other materials, such as light hydrocarbons and/or hydrogen sulfide and the like, the hydrogen may be removed through valve 16, purified in apparatus not shown and adapted to remove whatever deleterious or undesirable impurities are present, and the concentrated and/or purified hydrogen can be reintroduced into the process through pipe 45 and valve 46, leading into pipes 43 and 36. The hydrogenation effluent passes through pipe 47 and valve 48 to separating means 50, and a hydrogenated hydrocarbon fraction is recovered through pipe 51 and valve 52, while other products such as light gases may be recovered through pipe 53 and valve 54. These light gases may have a high content of free hydrogen, and may be recycled to the hydrogenation step, at least in part, by being introduced through pipe 45. It will, of course, be appreciated that various processes may be practiced in the apparatus 42, although we have found that the simple illustration diagrammatically illustrated will work quite satisfactorily in most cases.

The effluent from the catalytic cracking step will contain other hydrocarbon material than the motor fuel range material which is a principal product and which is removed through pipe 36. In most of the modifications of operation of the catalytic cracking step a certain amount of light polymerizable olefins, often quite substantial in amount, are produced. These can be separated from the effluent and passed from fractionating equipment 35 through pipe 60 and valve 61 to pipe 23 and the polymerization apparatus 63.

Hydrocarbons which are higher boiling than the gasoline range can be removed from the catalytically cracked effluent and from fractionating means 35 through pipe 72 and may be discharged from the process through valve 73. The hydrocarbons in this stream may be predominantly unreacted hydrocarbons, in which case they can be recycled to the dehydrogenation step, and are passed from pipe 72 through pipe 110 and valve 111 to pipes 25 and 10. When the process is so operated that these hydrocarbons are adapted for direct treatment in the catalytic cracking apparatus 20, they can be passed from pipe 72 through pipe 110 and then through pipe 112 and valve 113 to pipe 86 and pipe 17. Hydrocarbon material which is too refractory and high boiling for retreatment in the process is removed through pipe 74 and valve 75, while light material, such as gas containing ethane, methane, and/or hydrogen is removed through pipe 76 and valve 77. When it is not desired to treat lighter olefins which may be produced by the catalytic cracking, these may be discharged from the process, as through pipe 76.

In the polymerization apparatus 63 polymerizable olefins charged through pipe 23 are polymerized to higher molecular weight hydrocarbons, preferably with hydrocarbons in the gasoline boiling range as the predominant product. While the polymerization may be carried out in the absence of a catalyst, preferably in such a case at a temperature between about 750 and 1000° F. and an elevated pressure above about 500 pounds per square inch, preferably 750 to 5000 pounds per square inch or more, we prefer to make this step a catalytic one, as previously discussed. Not only can the operation be carried out under milder conditions of temperature and pressure when a catalyst is used, but also we are generally able to get a higher yield of product and also a product of somewhat different and often more desirable characteristics. The various units included in the polymerization apparatus 63 will vary with each particular mode of application, but will include heaters, coolers, pumps, reaction coils and/or reaction chambers, and the like common to the art, which may be readily adapted by one skilled therein. The olefins charged may be those produced in the catalytic cracking operation, olefins produced directly by dehydrogenation in the apparatus 11, or in some instances may be introduced from an outside source; as through pipe 64 and valve 65. When the principal source of polymerizable olefins is from the catalytic cracking step, these may be in a more highly concentrated form then is feasibly charged to a polymerization unit. Such a charge may be suitably diluted with inert material, preferably of a somewhat higher boiling range.

The polymerization effluent passes from the polymerization apparatus 63 through pipe 66 and

valves 67 and 68 to the fractionating or separating means 70, or it may be passed from pipe 66 through pipe 71 and valve 72 to pipe 33 and fractionating equipment 35 in admixture with the effluent of the catalytic cracking step. When the polymerization effluent is passed to fractionator 70, a hydrocarbon fraction containing polymers in the motor fuel range is removed through pipe 80 and valve 81. If it is desired to submit this fraction to hydrogenation, it may be passed, entirely or in part, from pipe 80 through pipe 82 and valve 83 to pipe 36 and hydrogenation apparatus 42. Heavier polymers, boiling below the tar range, can be separated from the polymerization effluent and passed from fractionating means 70 through pipe 84 and may be discharged through valve 85 or may be passed, entirely or in part, through pipe 86 and valve 87 to pipe 17 and the catalytic cracking step, wherein these heavy polymers are depolymerized or cracked. Heavy material such as tar can be separated from the polymerization effluent through pipe 90 and valve 91, and light low boiling material can be separated and removed through pipe 92 and valve 93. When this stream has an appreciable content of unreacted polymerizable olefins, at least a portion of the stream may be passed to the polymerization step from pipe 92 through pipe 94 and valve 95 to pipe 60. When this stream contains paraffins which can be dehydrogenated to produce polymerizable olefins, the material discharged through valve 93 may be dehydrogenated in apparatus not shown, and the olefins so produced may be passed to the polymerization step 63 by being introduced through pipe 64. When the paraffins charged to the dehydrogenation apparatus 11 through pipe 10 are lighter than the final gasoline range products and similar in molecular weight range to paraffins passing through pipe 92, these unreacted paraffins may be passed to the dehydrogenation apparatus 11 from pipe 92 through pipe 96 and valve 97 to pipe 10, and in this manner can be dehydrogenated within the apparatus shown.

When the composition of the polymerization effluent is such that it can conveniently be sent directly to the hydrogenation step, the stream may be passed from pipe 66 through pipe 98 and valve 99 directly to pipe 36 and the hydrogenation apparatus 42. While we prefer to separate hydrogen and any heavy tar-like materials from the dehydrogenation effluent before catalytically cracking the olefins contained therein, it is possible at time to operate the dehydrogenation process with practically no production of tar or the like, and when using a depolymerization catalyst which will operate satisfactorily in the presence of free hydrogen, the entire dehydrogenation effluent may be passed directly to the catalytic cracking step through pipes 12, 103, 107 and valve 108 to pipes 30 and 17, with valves 13 and 104 being closed. As discussed in our hereinbefore mentioned copending application, a motor fuel may be produced directly from propane and/or butane by a straight-through process, which can be carried out by dehydrogenating in apparatus 11, passing the effluent through pipes 12 and 103 and valve 104 to pipes 60 and 23, polymerizing in apparatus 63, passing the effluent through pipes 66, 98, and 36, hydrogenating in apparatus 42, and recovering saturated motor fuel so produced from pipe 51, with no intervening separating steps.

Our process also may be operated to produce premium motor fuel hydrocarbons from less desirable hydrocarbons in the motor fuel range. Thus, more or less straight-chain paraffin hydrocarbons in the motor fuel range, which have relatively low octane number, such as a natural gasoline fraction comprising substantial amounts of normal hexane, heptane and/or octane, can be charged through pipe 10 and subjected to catalytic dehydrogenation in 11. The corresponding normal olefins so produced are cracked in the presence of a depolymerization catalyst in 20, the olefin products so produced being, in general, lower boiling than is a desired motor fuel product and predominantly normally gaseous. In such a case, the effluent can be passed from 20 through pipe 33, pipe 105 and valve 106 to pipe 23 and the polymerization step 63 directly. In 63 the light olefins are polymerized to hydrocarbons in the motor fuel range. The effluent will comprise both unreacted paraffins and olefin polymers and may be recovered as such through pipe 40 or through pipe 80. Since olefins have higher blending octane numbers than straight octane numbers, this effluent which comprises a blend of olefins in paraffins can be used directly. As the polymers are more highly branched than the olefins initially formed by the dehydrogenation, this motor fuel fraction has a higher octane rating than the hydrocarbon effluent from dehydrogenation unit 11. If desired, the light olefins may be separated from the heavier paraffins in 35 before the polymerization operation, as has been discussed, and other adaptions and modifications may be made, as will be obvious. If it is desired to hydrogenate olefins produced by any modification of our process, and produce a saturated product free of any unreacted paraffins of similar boiling range, a stream may be withdrawn from pipe 40 or pipe 80, olefins may be separated from paraffins as by selective solvent extraction or the like, known to the art and concentrated olefins may be hydrogenated by being introduced through pipe 45.

In any modification or adaptation, when low boiling olefins are separated in a relatively concentrated fraction from the effluent of the catalytic cracking step, they may be converted to motor fuel by a modification of catalytic polymerization which involves catalytic reaction with some other type of hydrocarbon to produce a premium motor fuel range product, as by an alkylation reaction with isoparaffins in the presence of concentrated sulfuric acid, or other alkylation catalyst, as previously discussed.

Example I

The following is cited as an example of the operation of our process as adapted to crack heavy polymers produced during the polymerization of normally gaseous olefins to form motor fuel range hydrocarbons.

A normally gaseous hydrocarbon mixture of the following composition was charged to a catalytic polymerization step.

	Per cent by weight
C_3H_6	13.4
i-C_4H_8	8.6
C_4H_{10}	78.0
	100.0

This material was polymerized under a pressure of about 1500 pounds per square inch in the presence of a silica-alumina catalyst prepared by treating a partially dried hydrous silica gel

with a five per cent aluminum sulfate solution at a temperature near the boiling point of the treating solution, washing the treated gel with water, and subsequently drying it. The polymerization temperature was initially 266° F. and 70 per cent of the olefinic material being charged was polymerized. The temperature was gradually raised as the polymerization proceeded to give a constant amount of polymerization, and the flow of the charge stock was such as to give a yield of one volume of polymer per volume of catalyst per hour.

The composite polymer produced after 289 hours of operation had the following composition:

	Per cent by weight
C_5	8.9
C_6	10.9
C_7	27.0
C_8	19.5
B. P. 266–365° F.	16.7
B. P. 365–400° F.	5.3
B. P. >400° F.	11.7
	100.0

A portion of the material boiling above 365° F. was catalytically cracked by being passed over a silica-alumina depolymerization catalyst at a temperature of 710° F. and approximately atmospheric pressure at a rate of 1.63 volumes of liquid per volume of catalyst per hour. Another portion of the same material was subjected to noncatalytic cracking at approximately atmospheric pressure, a temperature of 1022° F. and a contact time of 4.6 seconds in the cracking chamber. The results of these two cracking runs were as follows:

Yields (per cent by weight)	Thermal	Catalytic
Gas	17	27
Light liquid	20	36
Heavy liquid	59	29
Loss	4	8
	100	100

Composition of gas (per cent by volume)	Thermal	Catalytic
CH_4	[1] 35.1	[2] 1.1
C_2H_4	10.0	1.8
C_2H_6	11.8	
C_3H_6	16.8	24.6
C_3H_8	8.4	2.8
i-C_4H_8	9.7	37.0
n-C_4H_8	3.6	13.5
C_4H_{10}	4.6	19.2
	100.0	100.0

[1] Not including 4 out of the 17 per cent which was C_4 dissolved in light liquid.
[2] Not including 15 out of the 27 per cent which was C_4 dissoved in light liquid.

The fact that much more gaseous material was produced by the catalytic cracking, at an appreciably lower temperature, and that this gaseous material contains very little material lighter than propene and very little saturated material is quite striking, and brings out a distinct advantage of our invention.

Example II

The following is cited as an example of the operation of our process as adapted to crack nonpolymeric olefins. Normal heptene such as is obtained by catalytic dehydrogenation of the normal heptane in natural gasoline, was passed over a silica-alumina catalyst maintained at a temperature just under 400° F. The flow rate was 0.72 volume of liquid normal heptene per volume of catalyst per hour, and the absolute pressure was about atmospheric. The effluent had the following composition.

	Mol per cent
C_2 and lighter	0.0
C_3	11.8
C_4	1.2
C_5	1.2
C_6 + (Predominantly C_7H_{14})	85.8
	100.0

Over 98 per cent of the C_3 fraction was propylene, and over 30 per cent of the C_4 fraction was butylenes. These light gases are readily catalytically polymerized to produce a motor fuel superior as to antiknock characteristics as compared with the normal heptane corresponding to the original normal heptene.

Example III

A paraffinic-base crude oil had the following analysis, derived from a simple distillation test.

Fraction	Per cent by volume
Gasoline (distil. up to 392° F.)	20.0
Kerosene (distil. 392-527° F.)	21.1
Gas-oil	13.3
Lubricating oil	17.7
Residue	25.9
Loss	2.0
	100.0

The straight run gasoline fraction had an octane number of 45.6, a gravity of 57.5° A. P. I., and a Reid vapor pressure of 4.15 pounds. The kerosene fraction may be dehydrogenated by being passed at a temperature between 950 and 1000° F. over a granular catalyst comprising unglowed chromium oxide at a pressure of about 25 pounds per square inch gauge and at a flow-rate of about two liquid volumes per volume of granular catalyst per hour. The light gases contain only about 10 per cent methane and other light hydrocarbons, being predominantly free hydrogen. The liquid hydrocarbons have substantially the same boiling range as the initial charge stock and contain about 16 per cent olefins. This olefin-containing material is passed over fuller's earth, which has been activated by treatment with hydrogen chloride, at a temperature of about 775° F. and a pressure of about 20 pounds per square inch and a flow rate of 1.3 liquid volumes per volume of catalyst per hour. The effluent is fractionated into a gaseous fraction comprising propylene and butylene, a fraction comprising normally liquid hydrocarbons boiling below 400° F., and a heavier fraction. The heavier fraction is returned to the dehydrogenation step. A blend comprising 80 per cent of the original straight run gasoline and 20 per cent of the gasoline produced by the catalytic cracking has an octane number of 58. The gaseous fraction is polymerized in the presence of a silica-alumina catalyst to produce a motor fuel which, after hydrogenation, has an octane number of 88, and has an octane number of 100 by the Army method upon the addition of 1.3 cc. of tetraethyl lead fluid.

Many modifications and variations of this invention may obviously be used, and can be adapted by one skilled in the art without departing

from the spirit of the disclosure. The restrictions used in the examples, and in connection with the drawing, need not necessarily be used as limits for any particular operation or set of conditions, as they are presented primarily as illustrative examples. While it will generally be desirable to practice our invention as a continuous process, it may be practiced in an interrupted manner, or otherwise, as conditions or circumstances may warrant or indicate. It will be understood that the flow diagram presented and described as a part of the disclosure is schematic only, and that many additional conventional pieces of equipment, such as pressure gauges, valves, pumps, heat exchangers, reflux lines and accumulators, heaters and coolers, and the like, will be necessary for any particular installation, and can be supplied to meet the requirements for any particular case by anyone skilled in the art. However, the essential equipment and conditions have been described and the modifications discussed in sufficient detail to serve as efficient guides.

We claim:

1. A process for converting paraffinic hydrocarbons boiling above the lower part of the gasoline boiling range into hydrocarbons of a smaller number of carbon atoms per molecule and in the gasoline boiling range, which comprises subjecting such a paraffinic hydrocarbon material to dehydrogenation in the presence of a solid dehydrogenation catalyst to produce olefins and free hydrogen without substantial cracking, subjecting a fraction comprising olefins so produced in the presence of a solid depolymerization catalyst to conditions of time, temperature and pressure adapted to crack said olefins to produce a substantial portion of hydrocarbons of a smaller number of carbon atoms per molecule and in the gasoline boiling range along with lighter olefins having at least three carbon atoms per molecule, passing the effluent to a separating zone, removing from said separating zone a fraction comprising said lighter olefins having at least three carbon atoms per molecule, subjecting said lighter olefins to catalytic polymerization to form hydrocarbons in the gasoline boiling range and passing the effluent to said separating zone, and removing from said separating zone a hydrocarbon fraction comprising hydrocarbons in the gasoline boiling range produced by said cracking and by said polymerization.

2. A process for producing lower boiling hydrocarbons boiling in the motor fuel range from higher boiling nonpolymeric olefin hydrocarbons, which comprises subjecting a hydrocarbon material comprising a substantial proportion of heavy nonpolymeric olefin hydrocarbons to the action of a granular silica-alumina catalyst, prepared by activating a hydrous silica gel with an aluminum salt solution, at a temperature between 400 and 750° F. under a pressure not in excess of about 100 pounds per square inch and at a flow rate between 0.25 and 4 liquid volumes of hydrocarbon material per volume of catalyst per hour, and subsequently separating a hydrocarbon fraction containing lower boiling hydrocarbons in the motor fuel range so produced.

3. In a process for producing lower molecular weight hydrocarbons from hydrocarbons of higher molecular weight, the step which comprises contacting a normally liquid, nonpolymeric olefin hydrocarbon with a solid silica-alumina depolymerization catalyst at a pressure less than 100 pounds per square inch and a temperature between 400 and 1050° F. and adequate to produce lower boiling olefins therefrom and at a flow rate between 0.25 and 10 liquid volumes of said hydrocarbon per volume of catalyst per hour and such that corresponding saturated hydrocarbons are substantially inert at said pressure and temperature.

4. In a process for producing lower molecular weight hydrocarbons from hydrocarbons of higher molecular weight, the step which comprises contacting a normally liquid, nonpolymeric normal olefin hydrocarbon with a solid silica-alumina depolymerization catalyst at a pressure less than 100 pounds per square inch and a temperature between 400 and 1050° F. and adequate to produce lower boiling olefins therefrom and at a flow rate between 0.25 and 10 liquid volumes of said hydrocarbon per volume of catalyst per hour and such that corresponding saturated hydrocarbons are substantially inert at said pressure and temperature.

5. A process for converting paraffinic hydrocarbons boiling above the lower part of the gasoline boiling range into hydrocarbons of a smaller number of carbon atoms per molecule and in the gasoline boiling range, which comprises subjecting such a paraffinic hydrocarbon material to dehydrogenation in the presence of a solid dehydrogenation catalyst to produce olefins and free hydrogen without substantial cracking, subjecting a fraction comprising olefins so produced in the presence of a solid depolymerization catalyst to conditions of time, temperature and pressure adapted to crack said olefins to produce a substantial portion of hydrocarbons of a smaller number of carbon atoms per molecule and in the gasoline boiling range along with lighter olefins having at least three carbon atoms per molecule, passing the effluent to a separating zone, removing from said separating zone a fraction comprising said lighter olefins having at least three carbon atoms per molecule, subjecting said lighter olefins to catalytic polymerization to form hydrocarbons in the gasoline boiling range and above the gasoline boiling range, passing effluents of said polymerization to said separating zone, removing from said separating zone an olefinic fraction above the gasoline boiling range comprising olefin polymers produced in said polymerization and subjecting said fraction to said depolymerization catalyst in admixture together with said olefin fraction resulting from dehydrogenation, and removing also from said separating zone an olefinic hydrocarbon fraction comprising hydrocarbons in the gasoline boiling range resulting from said cracking of olefins and from said polymerization.

6. A process for converting paraffinic hydrocarbons boiling above the lower part of the gasoline boiling range into hydrocarbons of a smaller number of carbon atoms per molecule and in the gasoline boiling range which comprises subjecting such a paraffinic hydrocarbon material to dehydrogenation in the present of a solid dehydrogenation catalyst to produce olefins and free hydrogen without substantial cracking, subjecting a fraction comprising olefins so produced in the presence of a solid depolymerization catalyst to conditions of time, temperature and pressure adapted to crack said olefins to produce a substantial portion of hydrocarbons of a smaller number of carbon atoms per molecule and in the gasoline boiling range along with lighter olefins having at least three carbon atoms per molecule, passing the effluent

to a separating zone, removing from said separating zone a fraction comprising said light olefins having at least three carbon atoms per molecule, subjecting said lighter olefins to catalytic polymerization to form hydrocarbons in the gasoline boiling range and above the gasoline boiling range, passing effluents of said polymerization to said separating zone, removing from said separating zone an olefinic fraction above the gasoline boiling range comprising olefin polymers produced in said polymerization and subjecting said fraction to said depolymerization catalyst in admixture together with said olefin fraction resulting from dehydrogenation, removing also from said separating zone an olefinic hydrocarbon fraction comprising hydrocarbons in the gasoline boiling range resulting from said cracking of olefins and from said polymerization, and hydrogenating the last said olefinic fraction with hydrogen produced by said dehydrogenation to saturate olefinic hydrocarbons contained therein.

7. The process of claim 3 in which said solid silica-alumina depolymerization catalyst has been prepared by treating a hydrous silica gel with an aluminum salt solution and subsequently washing and drying the resultant material, and contains not more than above five per cent alumina.

8. A process for the production of hydrocarbons predominantly in the boiling range of gasoline from olefin hydrocarbons of lower molecular weight, which comprises subjecting said olefin hydrocarbons to catalytic polymerization separating from the effluent of the polymerization step polymers boiling in the gasoline range and polymers boiling above the gasoline range, passing at least a portion of the polymers boiling above the gasoline range in contact with a solid depolymerization catalyst comprising mixed alumina and silica gels under such conditions of time, temperature and pressure that the depolymerization reaction produces a substantial proportion of gasoline boiling range hydrocarbons and olefinic gases, and recycling the olefinic gases to the polymerization step.

9. A process for the production of hydrocarbons predominantly in the boiling range of gasoline from olefin hydrocarbons of lower molecular weight, which comprises subjecting said olefin hydrocarbons to catalytic polymerization, separating from the effluent of the polymerization step polymers boiling in the gasoline range and polymers boiling above the gasoline range, passing at least a portion of the polymers boiling above the gasoline range in contact with mixed alumina and silica gels under such conditions of time, temperature and pressure that a depolymerization reaction produces a substantial proportion of gasoline boiling range hydrocarbons and olefinic gases, and recycling the olefinic gases to the polymerization step.

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CERTIFICATE OF CORRECTION.

Patent No. 2,349,160. May 16, 1944.

FREDERICK E. FREY, ET AL.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 2, first column, line 30, before the word "best" insert --be--; and second column, line 6, for "dehydrogenize" read --dehydrogenate--; page 3, second column, line 13, for "No. 10,697" read --No. 106,697--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of September, A. D. 1944.

Leslie Frazer

(Seal) Acting Commissioner of Patents.