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POLYMERIZATION OF HYDROCARBONS

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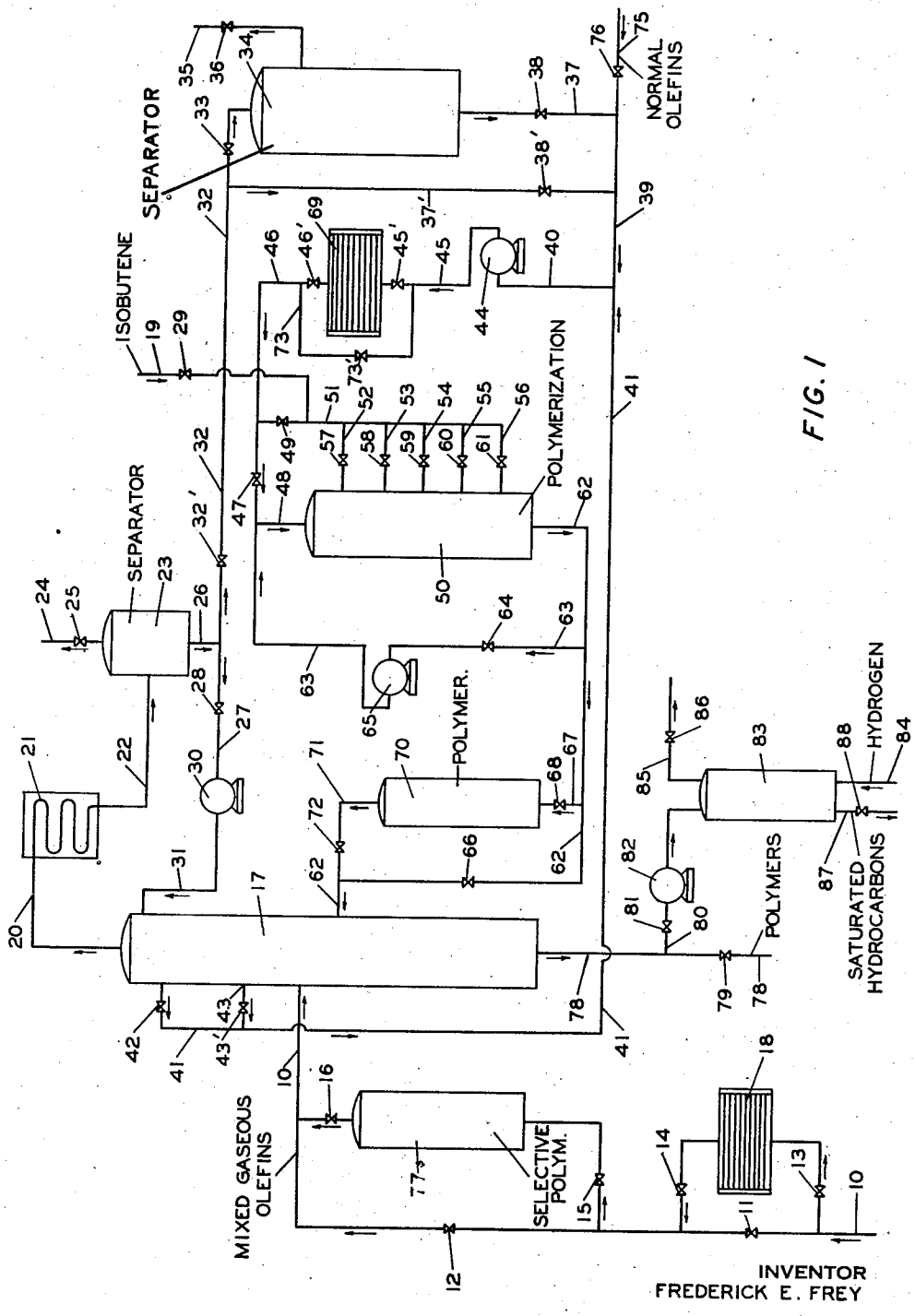


FIG. 1

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POLYMERIZATION OF HYDROCARBONS

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10 Claims. (Cl. 260—683.15)

This invention relates to the formation of higher molecular weight hydrocarbons from olefin hydrocarbons. More particularly it relates to the formation of hydrocarbons in the motor fuel boiling range from olefin hydrocarbons having five or fewer carbon atoms per molecule by catalytic polymerization.

Certain solid, active olefin polymerization catalysts, notably fuller's earth, dried hydrous silica associated with hydrous alumina, "solid phosphoric acids" and the like have been shown to effect the conversion of simple olefins almost exclusively into volatile, normally liquid hydrocarbons having low molecular weights, provided the reactions are conducted at somewhat elevated temperatures while maintaining the olefins at a low pressure and in the gaseous state. Other olefin polymerization catalysts are also known, among which may be mentioned mixtures of aluminum chloride and other Friedel-Crafts type catalysts in combination with sodium chloride and bromide, silver chloride and other metallic halides, and aluminum chloride and other Friedel-Crafts type catalysts with polar organic compounds such as nitro-methane, nitro-benzene, acetophenone and the like. Liquid catalysts such as liquid phosphoric and sulfuric acids have also been used.

It has been shown that, when used as fuel for internal combustion engines, especially those of the spark-ignition type, various hydrocarbons have quite widely different combustion and detonation characteristics. Thus, in general, olefin hydrocarbons are less susceptible to the production of detonation in such engines than are the corresponding paraffins. However, even among one given class of hydrocarbons, such as the paraffins for example, the various individual hydrocarbons differ widely among themselves as to their combustion characteristics. This is exemplified by the detonation characteristics of normal heptane and iso-octane (2,2,4-trimethyl pentane), the well-known standards used for evaluating detonation, the first causing detonation to a great extent and having, by definition, a zero octane number, and the latter causing little if any detonation even in engines of quite high compression ratios and having by definition a rating of 100 octane number. Even hydrocarbons of the same class and molecular weight have widely different detonation characteristics; for instance in one type of test engine various hydrocarbons had widely different ratings in detonation characteristics, as illustrated in Table I.

TABLE I

Detonation characteristics of some hydrocarbons

Compound	Number of carbon atoms	Blending octane number
Paraffins:		
n-Hexane	6	31
2-methylpentane	6	73
2, 2-dimethylbutane	6	104
2, 3-dimethylbutane	6	127
n-Heptane	7	0
2-methylhexane	7	55
3, 3-dimethylpentane	7	103
2, 2, 3-trimethylbutane	7	120
n-Octane	8	—9
2, 2, 4-trimethylpentane	8	100
2, 2, 3-trimethylpentane	8	109
2, 2, 3, 3-tetramethylbutane	8	133
Olefins:		
1-hexene	6	88
3-methyl-2-pentene	6	112
1-heptene	7	55
2, 3-dimethyl-2-pentene	7	134
2, 2, 3-trimethyl-3-butene	7	139
1-octene	8	29
3-octene	8	74
2, 2, 4-trimethyl-3-pentene	8	150
2, 2, 4-trimethyl-4-pentene	8	156

Most commercial processes today for converting gases to motor fuel, convert or polymerize normally gaseous olefins as a group to higher molecular weight polymers. General exceptions to this treatment are the individual olefins, ethylene and isobutylene. Ethylene is somewhat resistant to catalytic conversion and passes through many processes practically unaffected. However, it may enter into "mixed polymerization," and will react to a certain extent with higher molecular weight olefins, and thus even it is included in general group polymerization. Isobutylene has been recognized by many to be highly reactive, and it has been proposed to isolate it from such group polymerization, or to subject it to selective polymerization. Such selective polymerization of isobutylene is not only desirable in order to remove it from other olefins with which it is associated, but its low-molecular-weight polymers, especially the dimers and trimers, are quite valuable as constituents of premium aviation motor fuels. As can be seen from Table I, its dimers (the 2,2,4-trimethylpentenes) have excellent antidetonating qualities, and when these are non-destructively hydrogenated the product (2,2,4-trimethylpentane) also has excellent antidetonating properties. This is true of any tertiary-base olefin, that is, an olefin containing the $R_2C{=}CR'_2$ structure, where each R is an alkyl group and each R' may be hydrogen or an alkyl group. When the five-carbon-atom olefins are present in hydro-

carbon mixtures which are to be polymerized by my process, the tertiary-base olefins, 2-methyl-1-butene and 2-methyl-2-butene, will react along with the isobutene, while the other pentenes survive for the general group polymerization.

It is also known that not only can dimer and trimer of a single olefin species be thus formed by juncture of two or three molecules through the agency of catalytic polymerization, but also that co-dimer may be formed when two differing species such as isobutylene and n-butene are subjected in admixture to catalytic polymerization, as, for example, by the agency of sulfuric acid as catalyst. Co-dimer or hybrid formation occurs to a degree also by reaction between a simple dimer and a different species of simple olefin by replacement. These two modes of co-dimer formation may be represented thus:

1. Iso-$C_4H_8+C_3H_6=C_7H_{14}$
2. $(Iso\text{-}C_4H_8)_2+C_3H_6=C_7H_{14}+(iso\text{-}C_4H_8)$.

In the production from lighter hydrocarbons of motor fuels, and particularly of aviation fuels, there is desired a maximum yield of one or another individual co-dimer possessing a desired distilling temperature, and also a maximum octane number or non-detonating tendency.

My invention is concerned with means of obtaining an increased yield of co-dimer and of favoring the formation, by primary juncture, rather than by other routes, of co-dimer molecules of higfihly branched structure, which have marked non-detonating tendencies, and it resides essentially in bringing into contact with a solid polymerization catalyst two or more species of olefins in admixture which differ in inherent reactivity and maintaining them in definite and different concentrations to be set forth, the more reactive species being in the lower concentration. The more reactive species furthermore may be supplied in a series of increments to the catalyst whereby the desired concentration is maintained as it is consumed by reaction.

It is an object of this invention to produce higher molecular weight hydrocarbons from olefin hydrocarbons of lower molecular weight.

It is also an object of this invention to produce motor fuels of good antidetonating characteristics.

Another object of this invention is to produce olefin hydrocarbons in the motor fuel boiling range, which may be subjected to non-destructive hydrogenation to produce paraffin hydrocarbons having good antidetonating characteristics.

Still another object of this invention is to subject olefin hydrocarbons having five or fewer carbon atoms per molecule and of two or more species to a controlled polymerization, whereby the juncture of unlike species is favored and polymers other than those formed by simple doubling and trebling of simple molecules of similar species are produced in increased proportions.

It is a further object of the present invention to produce hybrid polymers or copolymers with increased efficiency.

Further objects and advantages of the invention will be apparent from the following disclosure.

As an illustration of the relative reactivities of a few of the normally gaseous olefins, it has been found that in the liquid phase, described in the copending application of Frey, McKinney, and Wood, Serial Number 747,964, filed October 11, 1934, now U. S. Patent 2,198,937, issued April 30, 1940, isobutylene diluted somewhat with paraffins, conveniently butanes, can be polymerized by means of hydrous silica associated with alumina such as the silica-alumina catalyst more completely described hereinafter, at 50 to 100° C.; the straight-chain olefin such as 2-butene, can be polymerized at 100 to 150° C.; and 1-butene and propylene at 150 to 200° C. or more; whereas ethylene is not extensively converted unless a particularly active catalyst is used. The use of both high olefin concentration and high catalyst activity lower the temperatures required, and temperatures somewhat higher or lower than the ranges exemplified will, in some cases, give best results.

I have found that, when a hydrocarbon mixture containing more or less similar quantities of both straight-chain and tertiary-base olefins of low molecular weight is passed in the usual way over an olefin polymerization catalyst, in the initial stage of the reaction the selective polymerization of the more reactive tertiary-base olefin is the predominant reaction. When depletion in the latter has occurred there follows polymerization which involves not only the juncture of like molecules, but also to some extent, a juncture of unlike molecules.

I have further found that it is possible to favor the formation of hybrid polymers by establishing and maintaining, in the hydrocarbon mixture in contact with a polymerization catalyst, a relatively low concentration of the more reactive olefin or olefins, such as the tertiary-base olefins, whereby their union with their own species is discouraged, and at the same time establishing and maintaining a relatively high concentration of the relatively less reactive olefin or olefins—such as the straight-chain olefins. Best results are obtained under superatmospheric pressures of the order of about 200 to 2500 pounds per square inch or more, and generally with pressures of about 750 pounds per square inch or more if liquid-phase operation, or dense-phase operation, is desired. Once a suitable pressure has been established I have found that the reaction conditions to be most controlled are the reaction temperature, the reaction time, and the mode of introduction and concentration control of the more reactive olefin species. The first two factors are closely related, and in general when higher temperatures are used shorter reaction times should be used. When using any particular catalyst, the temperature may be varied over a more or less limited range, with suitable adjustment in the reaction time, without producing a great variation in the polymerization products. As the activity of the polymerization catalyst decreases during use, especially of a solid catalyst such as silica-alumina, it is possible to obtain a substantially constant conversion without too great a change in the characteristics of the product, by gradually raising the reaction temperature through an appreciable range. Since the specific optimum conditions for a particular catalyst are somewhat dependent upon the catalyst, and since several known catalysts can be used in my process, it is more expedient and accurate to state that the time-temperature conditions should be such that the straight-chain olefin would be somewhat slowly polymerized if they were the only olefins present, but experimental exploring must be relied on for specific optimum values. In general, the temperatures will not be appreciably below 25° C., nor above 320° C., and on the whole I have found that successful operation is best carried on between 100 and 260° C. If liquid-

phase or dense-phase operation is desired, the temperatures generally should not be allowed to exceed about 260° C. Even with pressures in excess of about 750 pounds per square inch, in the higher temperature range of around 260° C. and above, there may not be an actual liquid phase existing at the inlet portion of the reaction chamber unless large amounts of heavier hydrocarbons are present as a result of recirculating a part of the polymer-containing effluent of the chamber and/or adding heavier, essentially inert hydrocarbons. However, even if such heavier hydrocarbons are not present to a large extent, the use of these super-critical pressures above 750 pounds, results in the presence of a "dense-phase" condition which provides many of the beneficial effects of liquid-phase operation, although the temperatures are above the critical.

With reaction conditions of temperature, time, and pressure established, such as have been just described, I have found that I can produce a polymer product in which hybrid polymers, formed from both straight-chain and tertiary-base olefins, are in outstanding proportion by operating a process so as to establish and maintain certain relative concentrations of straight-chain and tertiary-base olefins in the mixture being polymerized. Under the reaction conditions just discussed, I have found that the process should be operated so that the tertiary-base olefins compose not more than, and usually much less than, about 35 mol per cent of the total olefins to be polymerized and in contact with the polymerization catalyst. In other words, the molecular ratio of unreacted straight-chain to tertiary-base olefins should be at least about 2:1. However, better results can be obtained when the tertiary-base olefins are less than about 16 mol per cent of the unreacted olefins present, although the concentration should be above about 5 mol per cent for efficient operation. That is, with commercial operation of my process, the preferred range in which the ratio of unreacted straight-chain to tertiary-base olefins is to be kept should be between about 5:1 and 19:1, the optimum ratio being determined by adjusting concentration ratio until copolymer formation is found to be optimum or consumption of both olefins is in the desired ratio. The number of addition points should preferably be so great that any one increment produces no more than 25 to 50% momentary increase in concentration above the desired mean value.

The same principles of operation of a process for carrying out my invention, which will be more fully discussed hereinafter, apply also to non-tertiary-base olefins, and in fact all simple olefins, regardless of structural type, providing a suitable difference in reactivity exists. Thus, normal pentenes and normal butenes may be reacted to form hybrid polymers with the less reactive propylene, and other suitable combinations will be evident after determining comparative reactivities.

Olefins having less than six carbon atoms per molecule, are in the following order when listed in accordance with increasing polymerization reactivity: ethylene, propylene, normal butenes, normal pentenes, isobutene, 2-methyl-1-butene, 2-methyl-2-butene. With the exception that ethylene requires a particularly active catalyst, my process can be operated to produce hybrid polymers or copolymers from any of these olefins and a less reactive one of these olefins. However, as previously set forth, hybrid polymers are more readily formed, and are formed in larger amounts, from straight-chain olefins and tertiary-base olefins, because of the greater disparity between the types in respect to reactivity.

The desired concentration relationships of the straight-chain and tertiary-base olefins can be established and maintained in a reaction mixture in one form of my process by adding a mixture which is relatively rich in tertiary-base olefins to a hydrocarbon stream containing straight-chain olefins, flowing over a catalyst, at a number of points arranged progressively down-stream throughout the extent of a reaction zone. In general, I accomplish this in two ways, both of which are a modification of the general process outlined in the foregoing. In the first, it will be assumed for purposes of illustration that both the straight-chain olefin or olefins, and the tertiary-base olefin or olefins, are available mixed together and associated in a single hydrocarbon stream. Such a mixture can be obtained from cracking-still gases, from the dehydrogenation, preferably catalytic, of a mixture of butanes, and from other sources. Also for purposes of illustration, it will be assumed that the reaction takes place in the presence of a solid catalyst which is in a relatively long catalyst chamber. Generally, only a portion of the hydrocarbon mixture is introduced to the chamber through the inlet of the chamber, additional portions being added at a plurality of points along the length of the chamber. If the initial ratio of straight-chain to tertiary-base olefins is in the region of 1:1 at the start of the process, appreciable amounts of tertiary-base olefins will be selectively polymerized, and the ratio will be raised, the temperature and reaction time being such that straight-chain olefins polymerize slowly. A large portion of the straight-chain olefins pass through the reaction chamber unreacted, and I immediately pass a portion of the effluent of the chamber back to the inlet of the chamber. In this manner, after the process has been started and is in steady operation, I pass one half or more of the effluent directly back to the inlet of the chamber, and the unreacted straight-chain olefinic material which is present in this stream serves to maintain the ratio of straight-chain to tertiary-base olefin at a suitably high value and extensive hybrid polymerization is then effected. That portion of the effluent which is not recirculated is passed to separating means directly, or it may first be passed into contact with another polymerization catalyst which polymerizes unreacted olefins.

Another modification of my process may be operated to produce hybrid polymers between straight-chain olefins and tertiary-base olefins which are in separate hydrocarbon mixtures or streams. In this modification the stream containing straight-chain olefins is passed into a catalyst chamber maintained under suitable conditions, and the stream containing the tertiary-base olefins is added to the chamber at a plurality of points, one of which is preferably the inlet of the chamber. By the sequence of additions according to this mode of operation, a limited amount of tertiary-base olefin replaces that consumed between points of addition and a desired high ratio of straight-chain to tertiary-base olefin may thus be maintained throughout the chamber without recirculating a portion of the effluent of the chamber, but such a recirculation may be used if and as desired, or unreacted olefin may be returned. Also if desired, a portion of the stream or mixture containing the straight-chain olefins may be blended with the mixture contain-

ing tertiary-base olefins before the addition of the latter to the polymerization chamber. Instead of adding the stream containing a high concentration of tertiary-base olefins at a plurality of points throughout the length of a single relatively long reaction chamber, a substantially equivalent result may be obviously obtained by using a number of smaller reaction chambers, arranged in series, and adding a portion of such a stream at the inlet of each smaller chamber, the effluent of the first chamber passing to the second, and so throughout the series.

I may also control the temperature of reaction, which tends to rise spontaneously because of the exothermic nature of the reaction, by maintaining the stream introduced at intermediate points to the catalyst-containing passageway at a temperature sufficiently below reaction temperature, to offset the potential temperature rise which will be, in an insulated reaction system, approximately the value computed on the basis of 20,000 to 25,000 calories of heat evolved per gram-mol of polymer formed involving one juncture per average molecule of product polymer. The presence of inert diluent hydrocarbons, such as paraffin hydrocarbons, will tend to reduce the temperature rise caused by the evolution of heat.

In one embodiment of my invention, which may be performed in the arrangement of apparatus shown diagrammatically in the accompanying figure, which forms a part of this specification, the fresh feed stock containing two or more olefins is subjected to polymerization with recirculation as described and that portion of the effluents not returned to the catalyst may then be passed through a second body of polymerization catalyst wherein further polymerization of unreacted olefins takes place and any of the more reactive species which have survived the polymerizing operation in the first-mentioned chamber are polymerized together with any desired part of the less reactive olefin or olefins present. This effects an advantageous increase in total conversion effected while permitting the polymerization step employing recirculation to be conducted under conditions most conducive to hybrid polymer formation, namely, with operating conditions of time and temperature sufficiently mild to permit survival of appreciable concentrations of both the more reactive and the less reactive olefins.

One method of practicing my process will now be discussed in detail in connection with the arrangement of apparatus diagrammatically shown in the accompanying figure which forms a part of this specification, and which illustrates various methods of practicing my invention.

A mixture of hydrocarbons containing both straight-chain and tertiary-base olefin hydrocarbons of less than six carbon atoms per molecule is introduced to the process under suitable pressure through conduit 10 and passes through valves 11 and 12, valves 13, 14, 15 and 16 being closed, to the fractionating column 17 at an intermediate point thereof. The temperature of this mixture may be controlled, if necessary, by passing all or any part of the mixture through temperature-control means such as heat exchanger 18 with proper and conventional control of valves 11, 13 and 14. A fraction containing any hydrocarbons of lower molecular weight than those most advantageously treated in the process are withdrawn as vapors from the top of the column through conduit 20 and pass through a cooling coil 21, in which any condensible hydrocarbons are liquefied under the existing pressure, the mixture passing through conduit 22 to separator 23. Any undesirable vapor or portion of this light material, is separated and passed from the process through conduit 24, the pressure being controlled with the aid of valve 25. By this means any lighter hydrocarbons in the system are either completely eliminated or withdrawn in controlled amounts. Condensed hydrocarbons are withdrawn from separator 23 through conduit 26 and a portion thereof may be passed to the top of fractionating column 17 as a liquid reflux through conduit 27, valve 28, pump 30 and conduit 31.

If it is desired to subject any part of this light material to further treatment, another portion of this liquid is passed through conduit 32 and valves 32' and 33 to separating means 34. Separating means 34 may include any desirable number and combination of fractionating and other separating units, such as selective solvent extraction units, whereby a separation can be effected between normally gaseous olefin and paraffin hydrocarbons. Light hydrocarbons, essentially paraffinic in nature, are discharged from the process through conduit 35 controlled by valve 36. If the hydrocarbons entering the process come from one or more dehydrogenation processes, the material passing from the process through conduit 35 may be passed or recycled to such process or processes. If more than one stream of paraffinic hydrocarbons are produced by separating means 34, there may be more conduits, not shown, for the discharge of paraffinic material.

The olefins, in a purified or highly concentrated state, pass from the separation effected by separating means 34 through conduit 37, valve 38 and conduit 39 to conduit 40 where they are mixed with a hydrocarbon stream coming from the top part of fractionating tower 17 through conduit 41 controlled by valve 42, and which will, of course, be in the liquid phase. If the material passing through conduit 32 is sufficiently high in olefin content, a part of it may be passed directly to conduit 39 and thence to conduit 40 through conduit 37' and valve 38', valves 33 and 38 being closed, or only partially open. The material passing through conduit 41 will generally contain both paraffin and olefin hydrocarbons and will have a slightly higher average molecular weight than the olefins passing through conduit 37. The olefins will generally be butylenes, both straight-chain and tertiary-base, with some propylene, if that has not all passed through conduits 20 and 32. If there were some amylenes introduced to the process through conduit 10, a quantity of amylenes not substantially exceeding this amount may also be in the stream entering conduit 40 from conduit 41. If amylenes are so present, any portion of them which it is desired to subject to polymerization may be removed from the column 17, along with other hydrocarbons of like and higher boiling point, from a lower point in the fractionating column, such as through conduit 43 controlled by valve 43'. If the hydrocarbon material entering column 17 through conduit 10 does not contain any heavier hydrocarbons, conduit 43 may be placed below conduit 10, as will readily be understood by those skilled in the art.

Hydrocarbons passing through conduit 40 are received and compressed by pump 44 and all or part are passed through conduit 45 and valve 45' to heat exchanger 50, and then through conduit 46 and valve 46' and may be passed through valve 47 and conduit 48 to catalyst chamber 50. As may be desired in connection with temperature

control of the stream being passed by pump 44, all or a part may be passed through conduit 73 and valve 73' to conduit 46, valves 45' and 46' being partially or completely closed as necessary. When desired, and as will generally be practiced, valve 47 will be so controlled that a considerable portion of the material in conduit 46 will enter manifold 51 through valve 49, and will then pass into catalyst chamber 50 at various points through conduits 52 to 56 inclusive, controlled respectively by valves 57 to 61 inclusive. If there is available a hydrocarbon mixture whose olefin content consists largely of tertiary-base olefins, such as would result from dehydrogenation of isobutane, such a stream may be introduced to the process at this point at a suitable temperature and pressure through conduit 19 and valve 29, passing into manifold 51. The heat exchanger 69 is used to aid in the control of the temperature of the material passing through and being treated in the catalyst chamber 50. The extent and direction of this temperature control will not only be dependent upon the conditions existing and desired within the catalyst chamber 50 but also upon the amount and temperature of the material recycled by pump 65 and entering conduit 48 from conduit 63.

The effluent of catalyst chamber 50 passes through conduit 62, and a portion thereof may be diverted through conduit 63 and valve 64 and pump 65 to catalyst chamber 50. As discussed in more detail elsewhere in this specification, the volume of hydrocarbon recycled by pump 65 will generally be equal to from 1 to 10 times the amount of hydrocarbons passed to the catalyst chamber 50 through conduits 46 and 19. If desired, the stream passing through conduit 63 may be cooled somewhat, by means not shown, before it is introduced into the chamber 50. The material not withdrawn from conduit 62 continues on and finally passes into fractionating column 17 at an intermediate point thereof. When the extent of polymerization in chamber 50 has been quite limited, in accordance with prior discussion, there will be an appreciable amount of unpolymerized, low-molecular-weight olefins, which are easily polymerized, in the effluent of chamber 50. For this reason it may at times be desirable to submit that part of the effluent of chamber 50 which is not recycled, to a further polymerization of a portion of this remaining unpolymerized olefinic material. This may be done by closing valve 66 and sending the stream into catalyst chamber 70 through conduit 67 and valve 68, and the effluent of chamber 70 into column 17 through conduit 71 and valve 72 and back into conduit 62, as shown.

If it is desired to operate catalyst chamber 50 under substantially liquid-phase conditions, or supercritical conditions, but at elevated temperatures, it may be found desirable to have a fairly large amount of higher molecular weight hydrocarbons present. This object is attained in part through the recirculation of a portion of the effluent of chamber 50 by means of pump 65. However, additional higher molecular weight material may be desired, and it may be desirable to have this material of a more paraffinic nature. Hydrocarbon material so desired, generally in the gasoline boiling-range and generally paraffinic, may be introduced to the process through conduit 75 controlled by valve 76 and into conduit 39. Such paraffinic material may be a part or portion of the hydrogenated material discharged from the hydrogenating chamber 83 through conduit 87, as is hereinafter described.

In case a hydrocarbon fraction is available which has the desired composition without further fractionation, it may be introduced directly to the catalyst chamber through conduits 75, 40, 45 and 46, or through conduit 19. If this is done, the conduit 10 will not be used, and the only olefins which will pass through conduit 41 or conduit 32, will be unreacted portions of the olefins initially introduced through conduit 75 or conduit 19, which may be recycled through one or both of these conduits. With this arrangement, one advantageous modification is to introduce a hydrocarbon stream containing both normal butenes and isobutylene as from the catalytic dehydrogenation of a butane fraction, or both propylene and isobutylene such as is produced from the thermal dehydrogenation of isobutane followed by the removal of hydrogen and methane through conduit 19 at a suitable superatmospheric pressure and temperature. In such a case, the tertiary-base olefins and the straight-chain olefins should be present in about equimolecular amounts. In this modification the effluent of chamber 50 will pass to fractionating column 17, the polymers will pass therefrom through conduit 78, and unreacted hydrocarbons will pass therefrom through conduit 20 and conduit 32 to separating means 34. In separating means 34 a separation takes place of paraffins from olefins, the former being passed through conduit 35 and returned to the dehydrogenation, if desired, and a stream containing the latter is passed through conduits 37, 39 and 40, pump 44 and conduits 45, 46 and 48 to chamber 50. These olefins will comprise essentially unreacted straight-chain olefins, and in this case a portion of the stream entering through conduit 19 may be passed from manifold 51 through valve 49 into conduit 46, where it will be mixed with the recycled straight-chain olefins and enter chamber 50 through valve 47 and conduit 48.

The charge stock to the process entering through conduit 10 may contain a larger quantity or proportion of tertiary-base olefins than can be most efficiently converted in catalyst chamber 50 which, if all polymerized there, would lead to the production of too much high molecular weight polymer. By properly controlling valves 12, 15 and 16, any desired portion of such charge stock may be passed through catalyst chamber 77 where some of such tertiary-base olefins are selectively polymerized, under appropriate conditions of temperature, pressure and reaction time.

High molecular weight material introduced into fractionating column 17 through conduit 10 and/or conduit 62 becomes concentrated in the base of this column and is discharged therefrom through conduit 78 controlled by valve 79. It may at times be more desirable to produce an essentially paraffinic product, in which case polymers produced in the process may be subjected to hydrogenation. This can be done by partially or completely closing valve 79 and passing the material it is desired to hydrogenate from conduit 78 through conduit 80 and valve 81, compressing it by pump 82 in conduit 80 to any desired hydrogenating pressure, and passing it to hydrogenating chamber 83 which contains a suitable hydrogenating catalyst such as the one disclosed herein. Hydrogen, or a gas containing free hydrogen, under suitable pressure is introduced into this chamber through conduit 84, and passes

countercurrent to the hydrocarbons being treated therein. Gases containing or consisting of excess hydrogen are withdrawn from chamber 83 through conduit 85 and valve 86. Treated hydrocarbons, now essentially paraffinic, are passed from the chamber 83 through conduit 87 and valve 88. The effluent of the process, passing from conduit 78 and/or conduit 87, may be subjected to further treatment, such as fractional distillation, blending and the like. It may be desirable to hydrogenate only a part or a certain fraction or fractions of the polymer produced, in which case conventional fractionating means, not shown, may be interposed in conduit 80, and only the desired fraction sent to the hydrogenation chamber 83.

The efficient production of hybrid polymer can be secured with conversion stocks of suitable composition without the aid of the recirculation operating or the use of column 17 to produce conversion stock. In such a case a conversion stock containing reactive olefin, such as isobutylene from the catalytic dehydrogenation of isobutane, in a concentration exceeding the desired concentration to be maintained in proximity to the catalyst, is introduced through conduit 19 and manifold 51, and a stream containing the less reactive olefins predominantly, suitably propylene, and/or normal butenes, through conduit 75, and ultimately entering chamber 50 through conduit 48. The hydrocarbon streams pass through catalyst chamber 50, olefins undergoing polymerization, and the reacted material passes therefrom by conduit 62 and valve 66 wholly to fractionator 17 wherein the polymer formed is isolated and discharged through conduit 78 and valve 79, while the unpolymerized part is discharged through conduit 20 and eventually passes from the system through conduit 35 controlled by valve 36. Examples I and III to be presented typify this mode of operation. In such a case, a portion of the material entering the process through conduit 19 may be passed through valve 49 into conduit 48, so that this portion will enter the inlet of the polymerization chamber 50. Although it is possible to employ such a modification without recirculation through conduit 63, such recirculation may, at times, be quite advantageously employed.

The charge stock may result from catalytic dehydrogenation, thermal treatment of gaseous hydrocarbons or may come from oil cracking processes, especially vapor-phase processes. The selection may be made of suitable paraffins corresponding to the olefins desired as conversion stock for catalytic dehydrogenation. Thus, a mixture of substantially equal parts of normal butane and isobutane yields, upon dehydrogenation, isobutylene and butenes, which yield in the polymerization a co-dimer consisting mainly of octylenes that are particularly suitable after hydrogenation as an ingredient of aviation fuel.

The presence of high molecular weight hydrocarbons, in the mixture charged to the process through conduit 10, is not necessarily deleterious; if any such heavier material is present, such as would be present in an unstabilized cracked or reformed gasoline, or in the product of the thermal conversion of gaseous paraffins, it will become mixed with the polymers produced by the process and be discharged from fractionating column 17 through conduit 78. High concentration of light olefins is desirable in the charge stock, and although completely olefinic charge stock may be handled satisfactorily, hydrocarbon mixtures containing 50 to 70 per cent or more of paraffins are more generally available and can also be well taken care of. Excess propane will be discharged in part through conduit 24 and mainly through conduit 35. Excess butanes will generally be discharged through conduit 35, and column 17 may be so operated as to include some butanes in the material passing therefrom through conduit 78. If large amounts of light hydrocarbons are present in the mixture passing through conduit 10, conduit 75 or conduit 19, fractionating column 17 may consist of two or more separate but cooperative units, as will be obvious to those skilled in the art.

It will generally be preferable to use solid polymerization catalysts in the various stages of this process. Such a catalyst will be one such as the silica-alumina type catalysts more fully described herein, activated natural clays, so called "solid" phosphoric acid catalysts, acidic phosphates or pyrophosphates of copper, cadmium, magnesium and other metals, or various metal halides such as ferric chloride and bromide, zinc chloride and bromide. These latter may be deposited on supports such as clay, silica gel, pumice and the like when necessary. Such polymerization catalysts are not considered to be complete equivalents of each other. When I desire to obtain especially high yields of simple, highly branched co-dimers which can be non-destructively hydrogenated to produce paraffin hydrocarbons which have high octane numbers and high response or susceptibility to the addition of tetraethyl lead, I prefer to use a catalyst such as the silica-alumina catalyst described herein. Thus, under conditions wherein polymerization occurs under a pressure which is substantially equal to or greater than the critical pressure of the hydrocarbon mixture and involves appreciably less than the total amount of olefins passing through the reaction chamber, it appears that if catalysts such as "solid" phosphoric acids are used, the combustion characteristics, in internal-combustion engines, of the paraffins produced by non-destructive hydrogenation of the polymers, are not as desirable as those of similar products produced when a catalyst such as silica-alumina is used.

Each stage of the polymerization represented by chambers 77, 50 and 70 may consist of two or more similar catalyst chambers, or groups of smaller chambers, which are used one after another, as the catalyst becomes deactivated and it is necessary to provide fresh catalyst. In this manner continuous operation can be obtained for the process as a whole. The same will be true in connection with the hydrogenation step.

EXAMPLE I

The following data are presented as an example of one method of practicing my invention. A catalyst comprising hydrous silica associated with alumina, and which will be spoken of as a silica-alumina catalyst, was prepared from a liquid sodium silicate of 41° Bé. gravity containing 8.9 per cent Na_2O, 28.5 per cent SiO_2 and 62.6 per cent H_2O, and from commercial hydrochloric acid of 18° Bé. gravity. The sodium silicate was diluted by adding 1.5 volumes of water, and the acid was diluted with an equal volume of water. Equal volumes of these two resulting solutions were mixed by rapidly flowing the sodium silicate solution into the acid solution with thorough stirring. The mixture was then allowed to stand overnight, and had set and stiffened to a firm gel about 12 hours after mixing. The gel was broken by forcing it through a coarse screen of

about one-inch mesh, was washed for 12 hours and was then partially dried in hot air to a degree sufficient to shrink the gel only to a point where it attained sufficient rigidity to ring slightly when tumbled. It was again washed and then treated with boiling water containing in solution about 5.5 per cent of aluminum chloride, the treatment continuing for about two hours. The treated material was then thoroughly washed until the wash water just gave a negative test for chlorides, after which it was dried and classified so that it was about 14 to 40 mesh in size. In this manner a limited amount of alumina was thoroughly and intimately incorporated with silica, forming a silica-alumina gel which was suitable as a catalyst for polymerizing olefin hydrocarbons.

A hydrocarbon mixture containing propylene and butane in a molecular ratio of 1:1.86 was passed through a reaction chamber containing such a silica-alumina catlyst under the reaction conditions given in Table II. A hydrocarbon mixture containing isobutylene and butane in a molecular ratio of 1:2.66 was added to the reaction chamber at 14 points throughout the reaction zone, the total amount of this second stream added being about half the first stream. The molecular ratio of propylene to isobutylene in the total charge was 3.7:1, and at no time in the reaction chamber was it less than about 10:1, as a result of the multipoint method of addition. The polymer liquid, after being freed of unreacted hydrocarbons, had the composition given in Table II. Although the average temperature of polymerization was a little higher than I prefer generally to use for such a charge stock, the predominance of polymer produced by the union of propylene and isobutylene is marked.

TABLE II

Hybrid polymerization of propylene and isobutylene

Charge composition:	Mol %
C_3H_6	23.6
Iso-C_4H_8	7.0
C_4H_{10}	69.4
	100.0
Temperature, °C	200–210
Pressure, lbs. per sq. in	1,900
Per cent converted:	
C_3H_6	45
Iso-C_4H_8	54
Gal. charge (liq.)/gal. cat./hr	9
Gal. polymer/gal. cat./hr	0.63
	Weight %
Composition of polymer:	
C_5H_{10}	0.7
C_6H_{12}	17.6
C_7H_{14}	35.6
C_8H_{16}	15.2
C_9+(as $C_{12}H_{24}$)	30.9
	100.0

Only a small proportion of the polymer product was too heavy to be included in the present day, gasoline boiling range. The analysis of the polymer product, which was essentially olefinic, shows that more polymer was formed by union of one molecule of isobutylene with one molecule of propylene (producing heptenes) than was formed either from the union of two molecules of propylene or two molecules of isobutylene.

A hydrogenation catalyst was prepared by forming a concentrated aqueous solution of the nitrates of nickel, aluminum and copper, adding ground pumice stone of 4 to 20 mesh in size and slowly evaporating the water from the mixture while stirring it. For every gallon of ground pumice used, there was used:

	Pounds
$Ni(NO_3)2.6H_2O$	3.05
$Al(NO_3)3.9H_2O$	4.48
$Cu(NO_3)2.3H_2O$	0.36

After the mass of pumice so treated had been dried, it was heated to a temperature of the order of 350—400° C., whereby most of the nitrates were decomposed, forming the oxides. At the end of this treatment, hydrogen was passed over the material at substantially the same temperature, reducing the oxides of nickel and copper. The final material was an excellent catalyst for use in saturating olefin hydrocarbons with hydrogen, forming paraffin hydrocarbons of essentially the same boiling characteristics, and is herein called a nickel-copper-alumina catalyst.

A polymer liquid, produced as described and boiling below 230° C., was non-destructively hydrogenated using a nickel-copper-alumina catalyst, and the olefins in the liquid were converted to the corresponding paraffins, with practically no occurrence of reactions involving any change of carbon skeletons. The hydrogenated material was then fractionated into fractions having narrow boiling ranges, each obviously containing large quantities of highly branched hydrocarbons. The octane numbers of these fractions, as determined by the ASTM method (ASTM—D357—34T), are given in Table III.

TABLE III

Hydrogenated hybrid polymers

	Boiling ranges	Approximate composition	Octane number
1	75–97° C.	C_7H_{16}	92.7
2	97–128° C.	C_8H_{18}	94.3
3	128–180° C.	C_9H_{20}—$C_{12}H_{26}$	89.5
4	180–230° C.	$C_{12}H_{26}$—$C_{15}H_{32}$	86.7
	75–180° C. (1 to 3)	Aviation gasoline	92.7

Example II

On passing a hydrocarbon mixture of the following composition,

	Weight per cent
C_3H_6	7.5
Iso-C_4H_8	19.0
C_4H_{10}	73.5

through a bed of the silica-alumina catalyst of Example I at 180° C. while returning to the inlet continuously a volume of the effluent stream equal to 10 times the fresh hydrocarbon mixture, polymerization is effected incompletely with respect to both propylene and isobutylene, 3.4 per cent of the former and 10.0 per cent of the latter surviving. On passing the non-returned portion of the effluent stream through a second body of the same catalyst in simple once-through fashion, the concentrations are reduced to 9.0 per cent C_3H_6 and 0.5 per cent iso-C_4H_8. After separating it from the effluents, the polymer formed, which is equivalent to the olefin disappearing, contains 33 per cent distilling above the dimer range and 37 per cent of the total consists of branched heptenes. Upon hydrogenation the various fractions of the total hydrogenated polymer liquid

have octane numbers similar to those given for the fractions in Example I.

Example III

Normal butenes and isobutene may be copolymerized to form hydrocarbons in the motor fuel boiling range, and containing predominant proportions of highly branched octanes, in the following manner. A hydrocarbon stream containing about 30 per cent olefin hydrocarbons which are predominantly normal butenes is passed to a reaction chamber containing a silica-alumina catalyst and maintained at a temperature level between about 140 and 180° C., under a pressure of about 1500 pounds per square inch. A second hydrocarbon stream containing isobutylene in an amount substantially equivalent to 50% of the normal butenes in the first stream, is divided into five substantially equal portions which are passed to the reaction chamber, one portion being mixed with the stream containing normal butenes immediately prior to its introduction to the catalyst chamber. The effluent of the reaction chamber is cooled and passed to separating means wherein hydrocarbon polymers are separated from unreacted hydrocarbons. The octene fraction of this liquid is predominant in highly branched olefins and is readily separated by fractional distillation.

The octanes produced therefrom by non-destructive hydrogenation have an octane number (A. S. T. M. D357—37T) of about 90—95, and after the addition of 1 cc. of tetraethyl lead per gallon, the octane number is approximately 100 or higher.

The hydrocarbon mixtures which are suitable for charge stocks are usually relatively simple in composition, and the olefins which are to be polymerized are readily identified by modern analytical methods such as low-temperature fractional distillation combined with controlled acid absorption, both as to actual identities and as to concentrations. Likewise, the polymerization conditions are such that side reactions are at a minimum, and polymers formed can be readily analyzed by combinations of fractional distillation, both of the polymers and of the corresponding saturated compounds produced by nondestructive hydrogenation, determination of physical properties, and by determination of combustion characteristics in well-known test engines. With such accurate testing methods possible for the simple materials involved, one skilled in the art may readily control the process to produce optimum results for a given charge stock and polymerization catalyst, and establish suitable conditions for operation by simple trial. Likewise, when charge stocks come from known dehydrogenation processes wherein hydrocarbon mixtures of simple compositions are dehydrogenated, the most desirable recycling of unreacted paraffins which are separated from the effluent of the polymerization, in appropriate amounts and composition, to such a dehydrogenation, is easily and readily determined.

This invention is not necessarily restricted to any narrowly defined catalyst or set of operation conditions. The general rules have been given relative to these matters so that optimum results may be obtained, and when dealing with a particular charging stock or mixture of hydrocarbons, anyone skilled in the art may follow the directions given herein and obtain results as shown.

I claim:

1. A process for producing a hydrocarbon polymeric product having a boiling range within the motor-fuel boiling range from two separate and different olefin hydrocarbon fractions, one of which contains olefins that have generally more-highly-branched structures than those contained in the other fraction, which comprises passing the fraction containing the generally less-highly-branched olefins under reaction conditions such that copolymerization between the more-highly-branched olefins and less-highly-branched olefins takes place readily but reaction between the less-highly-branched olefins takes place only to a minor extent over a solid polymerization catalyst in a catalyst chamber and adding the other fraction containing the generally more-highly-branched olefins to said catalyst chamber at a plurality of successive points in said catalyst chamber to react olefins of the one fraction with olefins of the other fraction to form copolymers, maintaining a reaction time sufficient to effect reaction of substantially all said more-highly-branched olefins charged, and separating a polymer fraction having a boiling range within the motor-fuel boiling range from the effluent of said catalyst chamber.

2. A process for producing a hydrocarbon polymeric product from two different olefin hydrocarbons having low molecular weights, which comprises passing the less-reactive olefin into contact with a solid polymerization catalyst under reaction conditions such that said olefin would polymerize with itself at only a relatively low rate and to a relatively small extent and such that the more reactive of the two olefins would polymerize with itself at a relatively high rate and to a substantial extent, adding at a plurality of successive points to the mixture in contact with said catalyst the second more-reactive olefin in such amounts at the respective points that the molecular ratio of the first less-reactive olefin to the second more-reactive olefin throughout a substantial portion of the reaction mixture that is in contact with the catalyst is greater than approximately 5 to 1, whereby copolymerization between said olefins takes place forming higher-molecular-weight polymers, and subsequently separating a polymer fraction from at least a portion of the mixture which has been in contact with said catalyst.

3. A process for producing a hydrocarbon polymeric product from two separate olefin-containing hydrocarbon mixtures, the olefins contained in the one mixture being generally more highly reactive than those contained in the other mixture, which comprises passing the first mixture containing the less-reactive olefins into contact with a solid polymerization catalyst under reaction conditions such that a substantial portion of the individual olefins contained therein would polymerize with themselves at only a relatively low rate and to a relatively small extent and such that a substantial portion of the individual more-reactive olefins contained in the second mixture would polymerize with themselves at a relatively high rate and to a substantial extent, adding at a plurality of successive points to the mixture in contact with said catalyst the second fraction containing the more-reactive olefins in such amounts at the respective points that the molecular ratio of the less-reactive olefins contained in the first mixture to the more-reactive olefins contained in the second mixture throughout a substantial portion of the reaction mixture that is in contact with the catalyst is greater than approximately 5 to

1, whereby copolymerization between the olefins in the two mixtures takes place forming higher-molecular-weight polymers, and subsequently separating a hydrocarbon fraction containing the polymers from at least a portion of the mixture which has been in contact with said catalyst.

4. A process for producing hydrocarbons having boiling points within the motor-fuel boiling range from olefin hydrocarbons having low molecular weights, which comprises passing a first hydrocarbon mixture comprising essentially straight-chain olefins having not less than three nor more than five carbon atoms per molecule under a pressure between approximately 200 and approximately 2500 pounds per square inch into a polymerization chamber containing a solid olefin-polymerization catalyst, maintaining reaction conditions in said chamber such that said straight-chain olefins are not rapidly nor extensively polymerized with themselves, passing to said polymerization chamber a second hydrocarbon mixture comprising essentially tertiary-base olefins having not more than five carbon atoms per molecule, and adding said second hydrocarbon mixture to the reaction mixture in contact with said catalyst at a plurality of successive points in said polymerization chamber in such amounts at the respective points that the molecular ratio of unreacted straight-chain olefins to unreacted tertiary-base olefins throughout a substantial portion of the reaction mixture in said polymerization chamber is at least approximately 5 to 1, whereby a copolymerization takes place between straight-chain and tertiary-base olefins to form hydrocarbons having boiling points within the motor-fuel boiling range, and separating from at least a portion of the effluent of said chamber a fraction containing hydrocarbons having boiling points within the motor-fuel boiling range so produced.

5. A process for producing a hydrocarbon polymeric product having a boiling range within the motor-fuel boiling range from two separate and different butene fractions, one of which contains more isobutene than the other, which comprises passing the fraction containing the smaller proportion of isobutene under reaction conditions such that copolymerization between normal butenes and isobutene takes place readily but reaction between normal butenes takes place only to a minor extent over a solid polymerization catalyst in a catalyst chamber and adding the other fraction containing the greater proportion of isobutene to said catalyst chamber at a plurality of successive points in said catalyst chamber to react isobutene with normal butenes to form copolymers, maintaining a reaction time sufficient to effect reaction of substantially all said isobutene, and separating a polymer fraction having a boiling range within the motor-fuel boiling range from the effluent of said catalyst chamber.

6. A process for producing a predominantly paraffinic premium motor fuel from two separate and different olefin hydrocarbon fractions, one of which contains olefins that have generally more-highly-branched structures than those contained in the other fraction, which comprises passing the fraction containing the generally less-highly-branched olefins under reaction conditions such that copolymerization between the more-highly-branched and less-highly-branched olefins takes place readily but reaction between the less-highly-branched olefins takes place only to a minor extent over a solid polymerization catalyst in a catalyst chamber and adding the other fraction containing the generally more-highly-branched olefins to said catalyst chamber at a plurality of successive points in said catalyst chamber to react olefins of the one fraction with olefins of the other fraction to form copolymers, maintaining a reaction time sufficient to effect reaction of substantially all said more-highly-branched olefins charged, separating a polymer fraction having a boiling range within the motor-fuel boiling range from the effluent of said catalyst chamber and subjecting said polymer fraction to nondestructive hydrogenation.

7. A process for producing hydrocarbons having boiling points within the motor-fuel boiling range from olefin hydrocarbons having low molecular weights, which comprises passing a first hydrocarbon mixture comprising essentially straight-chain olefins having not less than three nor more than five carbon atoms per molecule under a pressure between approximately 200 and approximately 2500 pounds per square inch into a polymerization chamber containing a solid granular silica-alumina catalyst, maintaining reaction conditions in said chamber such that said straight-chain olefins are not rapidly nor extensively polymerized with themselves, passing to said polymerization chamber a second hydrocarbon mixture comprising essentially tertiary-base olefins having not more than five carbon atoms per molecule, and adding said second hydrocarbon mixture to the reaction mixture in contact with said catalyst at a plurality of successive points in said polymerization chamber in such amounts at the respective points that the molecular ratio of unreacted straight-chain olefins to unreacted tertiary-base olefins throughout a substantial portion of the reaction mixture in said polymerization chamber is at least approximately 5 to 1, whereby a copolymerization takes place between straight-chain and tertiary-base olefins to form hydrocarbons having boiling points within the motor-fuel boiling range, and separating from at least a portion of the effluent of said chamber a fraction containing hydrocarbons having boiling points within the motor-fuel boiling range so produced and subjecting said hydrocarbons to nondestructive hydrogenation.

8. A process for producing a predominantly paraffinic premium motor fuel from two separate and different butene fractions, one of which contains more isobutene than the other, which comprises passing the fraction containing the smaller proportion of isobutene under reaction conditions such that copolymerization between normal butenes and isobutene takes place readily but reaction between normal butenes takes place only to a minor extent over a solid polymerization catalyst in a catalyst chamber and adding the other fraction containing the greater proportion of isobutene to said catalyst chamber at a plurality of successive points in said catalyst chamber to react isobutene with normal butenes to form copolymers, maintaining a reaction time sufficient to effect reaction of substantially all said isobutene, separating a polymer fraction having a boiling range within the motor-fuel boiling range from the effluent of said catalyst chamber and subjecting said polymer fraction to nondestructive hydrogenation.

9. A process for the production of hydrocarbons having highly-branched structures and having boiling points within the motor-fuel boiling

range, which comprises passing a hydrocarbon mixture containing straight-chain and tertiary-base olefins having not more than five carbon atoms per molecule to a fractionating means, withdrawing from said fractionating means a stream of hydrocarbons comprising straight-chain and tertiary-base olefins having not more than five carbon atoms per molecule, circulating an endless cycle of hydrocarbons into and out of contact with a solid polymerization catalyst contained in a reaction chamber, maintaining reaction conditions in said chamber such that straight-chain olefins are not rapidly nor extensively polymerized with themselves and such that tertiary-base olefins having not more than five carbon atoms per molecule would be substantially polymerized with themselves, the pressure being between approximately 200 and approximately 2500 pounds per square inch and the temperature between approximately 25° and approximately 320° C., adding said stream of hydrocarbons to said endless cycle of hydrocarbons in such proportions that the molecular ratio of straight-chain olefins to tertiary-base olefins in said endless cycle exceeds approximately 5 to 1, withdrawing from said endless cycle a portion thereof, contacting said portion with a second polymerization catalyst under reaction conditions such that substantially all the olefins having less than six carbon atoms per molecule are polymerized, passing the effluent from said second polymerization catalyst to said fractionating means, and withdrawing from said fractionating means a hydrocarbon fraction containing polymers so produced.

10. A process for the production of hydrocarbons having highly branched structures and having boiling points within the motor-fuel boiling range, which comprises passing a hydrocarbon mixture containing straight-chain and tertiary-base olefins having less than six carbon atoms per molecule and other hydrocarbons to a fractionating column, withdrawing from said fractionating column a stream of hydrocarbons comprising straight-chain and tertiary-base olefins having less than six carbon atoms per molecule and in a molecular ratio of staright-chain to tertiary-base olefins of approximately 1 to 1, circulating an endless cycle of a mixture of hydrocarbons substantially entirely in liquid phase into and out of contact with a solid polymerization catalyst situated within a reaction chamber, maintaining within said reaction chamber a reaction temperature not in excess of approximately 260° C. and a reaction time such that tertiary-base olefins having less than six carbon atoms per molecule would be substantially polymerized with themselves, adding said stream of hydrocarbons to said endless cycle of hydrocarbons in such proportions that the ratio of straight-chain olefins to tertiary-base olefins having less than six carbon atoms per molecule is maintained between approximately 5 to 1 and approximately 19 to 1, adding normally liquid hydrocarbons in an amount such that a liquid phase is maintained in said reaction chamber, withdrawing from said endless cycle a portion thereof, contacting said portion with a second polymerization catalyst under reaction conditions such that substantially all of the original olefins having less than six carbon atoms per molecule are polymerized, passing the effluent from said second polymerization catalyst to said fractionating column and withdrawing from said column a hydrocarbon fraction containing olefin polymers so produced.

FREDERICK E. FREY.

CERTIFICATE OF CORRECTION.

Patent No. 2,377,411. June 5, 1945.

FREDERICK E. FREY.

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 32, for "higfihly" read --highly--; page 3, second column, line 72, for "elefin" read --olefin--; page 4, first column, line 12, after the word "so" insert --on--; page 10, first column, line 29, before "olefins" insert --original--; 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 2nd day of October, A. D. 1945.

Leslie Frazer

(Seal) First Assistant Commissioner of Patents.