

Dec. 16, 1941.

F. E. FREY

2,266,019

HYDROCARBON CONVERSION AND POLYMERIZATION

Filed Jan. 27, 1937

2 Sheets-Sheet 1

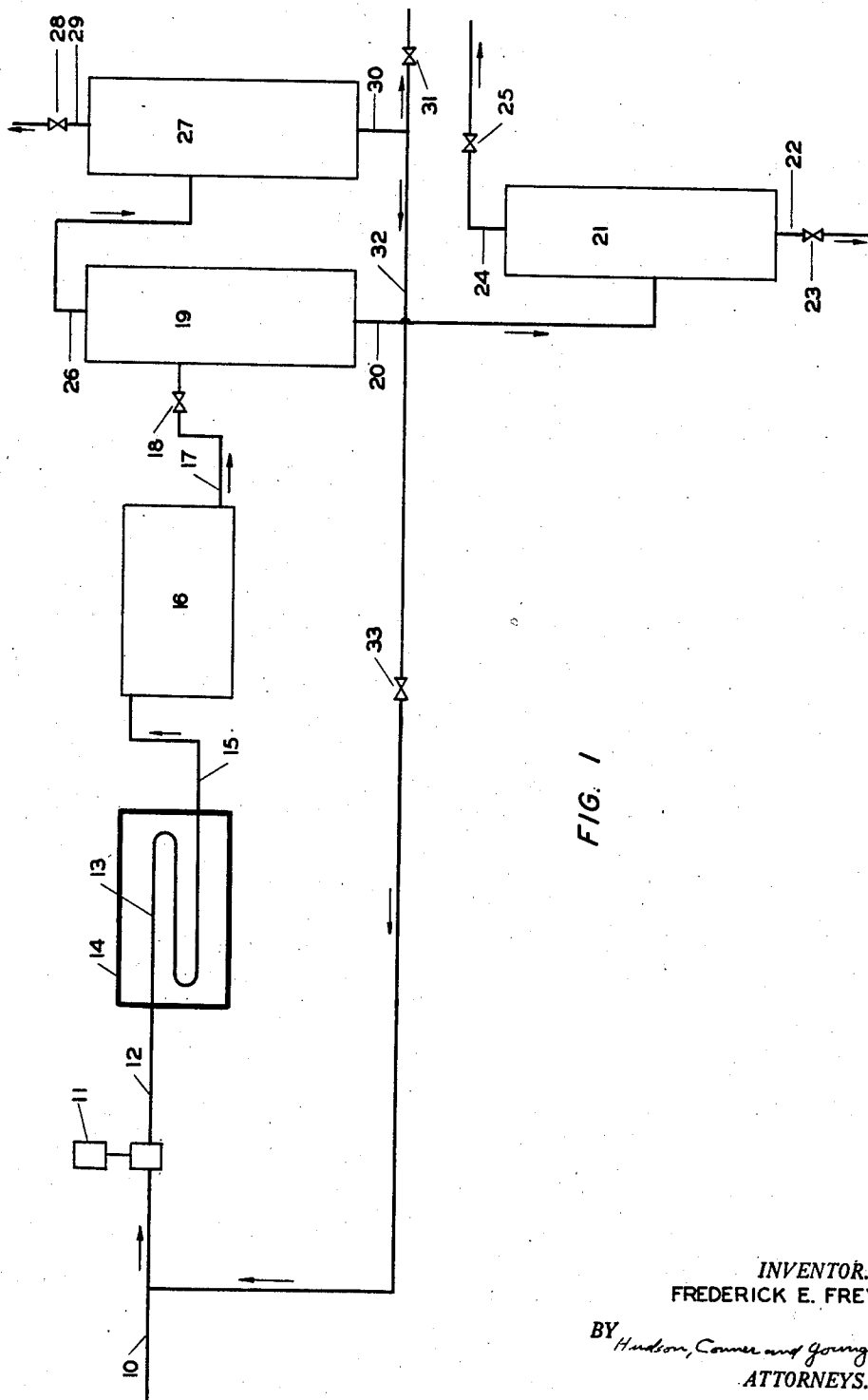


FIG. 1

INVENTOR.
FREDERICK E. FREY

BY *Hudson, Conner and Young*
ATTORNEYS.

Dec. 16, 1941.

F. E. FREY

2,266,019

HYDROCARBON CONVERSION AND POLYMERIZATION

Filed Jan. 27, 1937

2 Sheets-Sheet 2

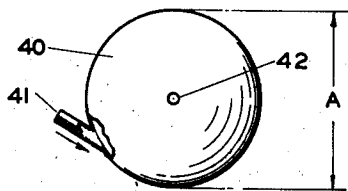


FIG. 2

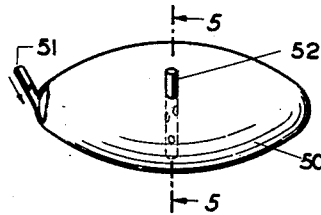


FIG. 4

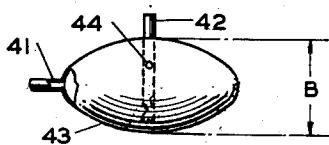


FIG. 3

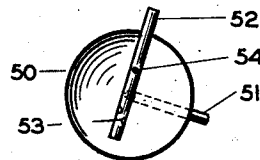


FIG. 5

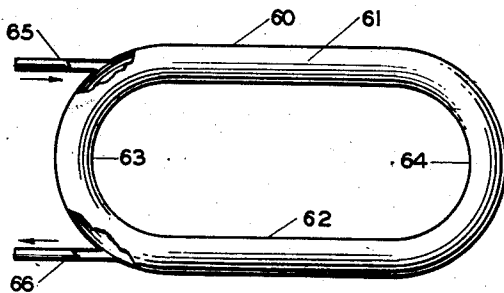


FIG. 6

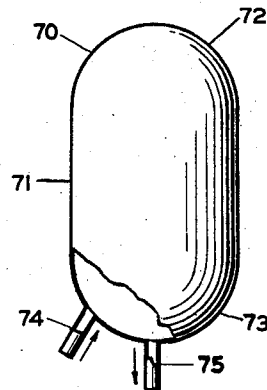


FIG. 7

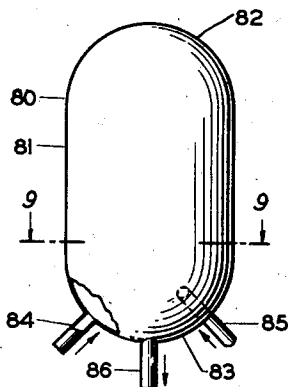


FIG. 8

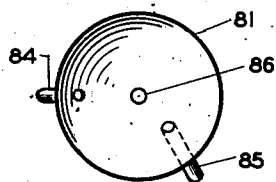


FIG. 9

INVENTOR.
FREDERICK E. FREY
BY *Hudson, Conner and Young*
ATTORNEYS.

UNITED STATES PATENT OFFICE

2,266,019

HYDROCARBON CONVERSION AND
POLYMERIZATIONFrederick E. Frey, Bartlesville, Okla., assignor to
Phillips Petroleum Company, a corporation of
Delaware

Application January 27, 1937, Serial No. 122,658

11 Claims. (Cl. 196—10)

This invention relates to the conversion of low boiling hydrocarbons into higher boiling hydrocarbons, and more particularly to a process wherein a mixture of olefinic and saturated hydrocarbons while under pressure and at a reaction temperature in a gaseous or vaporous state, is subjected in a reaction chamber to conditions of high turbulence while undergoing reaction to produce in high yield hydrocarbons of higher molecular weight suitable for motor fuel.

Another object of this invention is to provide, in a simple form of apparatus, means wherein olefins may be thereby dispersed in paraffins as the olefins are consumed by reaction, thereby augmenting the formation of higher paraffins by paraffin-olefin union.

Another object of this invention is to provide a process for the reaction of an olefin-containing hydrocarbon mixture with a minimum formation of higher boiling hydrocarbons beyond the ordinary gasoline boiling range.

A further object of this invention is to provide a process whereby gaseous reactions involving olefin-containing hydrocarbon mixtures are carried out adiabatically in a reaction chamber, except as the incoming and effluent streams will have a sensible heat content.

Still a further object of my invention is to provide a process wherein a paraffin-olefin hydrocarbon mixture is subjected in a reaction chamber of enlarged cross-sectional area to reaction conditions favorable to the juncture of paraffin and olefin molecules to produce predominantly non-aromatic polymers in particularly high yield, based on olefin consumed.

Still a further object of my invention is to effect thermal conversion of a mixture of simple paraffins and olefins into motor fuel in an enlarged reaction chamber in a new manner whereby an increase in yield and in conversion per thermal treatment is realized.

Further objects and advantages will become apparent as the discussion and disclosure proceed.

When heavier petroleum oils are cracked in the vapor phase to produce a hydrocarbon fraction boiling in the gasoline range there is produced, in addition to oils heavier than the original material, a mixture of normally gaseous hydrocarbons. This mixture may be treated by absorption or compression to recover hydrocarbons containing five or more carbon atoms per molecule, and the residue from such treatment will consist of normally gaseous components with a high content of olefin hydrocarbons and some hydrogen. Such a gas will contain 50-75 per cent by volume of ethane and lighter material, including some hydrogen, and the total mixture will contain about 50 per cent or more by volume of unsaturated hydrocarbons, the content of the

higher gaseous paraffins being relatively low, such as illustrated in the following table, when the cracking pressure is low.

TABLE I

Gas from high temperature oil cracking

Constituent	Volume
	<i>Per cent</i>
CH ₄ and H ₂	35.4
C ₂ H ₄	22.9
C ₂ H ₆	13.3
C ₃ H ₆	18.1
C ₃ H ₈	
C ₄ H ₁₀	5.5
C ₄ H ₁₂	4.8
	100.0

It has been proposed to subject this material, under an elevated pressure and at a suitable temperature, to reaction in an elongated tube coil, surrounded by a gaseous fluid of a temperature lower than the reaction temperature. Such a reaction is highly exothermic in nature, and the surrounding fluid, of a lower temperature than the reactants, will remove some of the heat produced by the reaction so that the reaction will not overheat the reaction coil and become uncontrollable.

It has also been proposed to heat a normally gaseous hydrocarbon mixture containing little if any hydrogen and with about 25 per cent by volume or more of unsaturated hydrocarbons, and pass it into a thermally insulated enlarged reaction chamber where reactions take place to form higher molecular weight hydrocarbons, such reactions involving the olefinic hydrocarbons present. The composition of such a gaseous mixture is given in Table II.

TABLE II

Constituents	Volume
	<i>Per cent</i>
CH ₄	5.0
C ₂ H ₄	7.3
C ₂ H ₆	26.4
C ₃ H ₆	16.3
C ₃ H ₈	32.7
C ₄ H ₁₀	4.1
C ₄ H ₁₂	8.2
	100.0

These reactions are exothermic in nature, and the temperature is prevented from rising excessively by controlling the reactions with respect to the chemical and physical properties of the reactants and of the products desired, and with an appropriate degree of preheat. Gases produced from petroleum oils by familiar pressure cracking processes are among those suitable for conversion, as these gases contain lower volume per-

centages of olefin and higher percentages of the higher gaseous paraffins, such as propane and butane, than gases produced by low pressure vapor phase cracking.

Processes have also been disclosed wherein it is proposed to treat artificially compounded hydrocarbon mixtures of olefin concentrations of 10 per cent or less, operating in such a manner that reactions involving union of paraffins and olefins are predominant, wherein higher molecular weight paraffins formed as the result of such reactions constitute the major products. Such reactions are favored by high pressures and low olefin concentrations, the latter brought about by carefully controlled and proportioned addition of olefins to predominantly paraffinic hydrocarbon streams.

I have disclosed one method of operating these processes in the U. S. Patent 2,002,394, issued to me May 21, 1935, for a Process for converting hydrocarbons. Here the reactions between the olefins and the paraffins are favored and reactions involving olefins only are minimized by the low olefin concentration at any one point.

One of my copending applications, Serial Number 12,981 filed March 25, 1935, for a Process for converting hydrocarbons, which is now U. S. Patent 2,104,296 discloses reactions between paraffins and olefins, wherein paraffinic material is passed through an endless circulatory cycle, while maintained at reaction temperature and pressure, and an olefin-containing hydrocarbon mixture is introduced at one part of the cycle, the concentration of olefins at any part of the cycle being small, and a part of the stream, from which products are to be separated, is withdrawn from another part of the cycle.

In another of my copending applications, namely the application by Frederick E. Frey and Harold J. Hepp, Serial Number 106,482 filed October 19, 1936, for Process for producing hydrocarbons, which is now U. S. Patent 2,209,450 it is proposed to react paraffins and olefins by introducing small amounts of olefins into a paraffinic stream at a single point, and allowing the reaction to proceed in a continuation of the tube coil or by introducing the mixture under pressure and at a reaction temperature into an enlarged chamber where reaction proceeds.

In thermal and catalytic processes for converting lower molecular weight hydrocarbons to higher molecular weight hydrocarbons, now known to the art, especially where use is made of reaction chambers for reacting hydrocarbon mixtures of substantial olefin content, there is a strong tendency for olefinic hydrocarbon molecules to react with other olefinic hydrocarbon molecules, thereby forming progressively higher molecular weight molecules. This is especially true when local concentrations of olefinic molecules are high. Such progressive reactions tend to become quite deleterious in nature, and heavier oils are formed which are out of the gasoline boiling range and which tend to produce tar and coke easily. If a large reaction chamber is used reactions may not take place uniformly throughout the chamber, resulting in a product which has unnecessarily large amounts of heavier reaction products at the expense of more desirable reaction products boiling in the gasoline range.

Furthermore, if an olefin-paraffin mixture is thermally reacted at a temperature below that at which the paraffin hydrocarbons present are appreciably decomposed so that reactions involv-

ing only olefins are predominant, the proportion of normally liquid hydrocarbons then formed is low in processes heretofore known to the art. In such a case the greater part of the paraffin hydrocarbons present will be present essentially as inert material, needlessly overtaxing various pieces of equipment used in the process and thus making operating costs unnecessarily high in consideration of the value of products obtained.

I have found that a normally gaseous hydrocarbon mixture containing both olefins and paraffins can be thermally treated in such a manner that the reaction of olefins with paraffins can be effected to produce high yields of motor fuel, with decreased degradation to heavy tar, in a reaction chamber of large cross-section by injecting the reactants at such a velocity and in such a direction that uniform direct transit through the reaction chamber from inlet to outlet is prevented, but instead a turbulent circulatory motion is maintained within the chamber while the entering reactants are dispersed intimately in large volumes of the partly reacted hydrocarbons and while a reaction temperature preferably of 700° to 1100° F. is maintained. I have also found that if high pressures are maintained during conversion, namely in excess of 1000 pounds per square inch and preferably of 2000 to 4000 pounds per square inch or more, higher yields of hydrocarbons in the gasoline boiling range are obtained, and the higher the pressure the more efficient is the consumption of paraffin hydrocarbons by direct union with olefins. Indeed with proper equipment pressures of 5,000 to 10,000 pounds per square inch or more may be used.

A novel feature of my invention is the use of a reaction chamber which will serve a somewhat different purpose from those previously used in the art of hydrocarbon cracking and polymerization. Its general design and construction, and the design, construction and position of the inlet and outlet connections will be such that the reactants within it will be put into and maintained in a high state of turbulent circulation and mixing. In the familiar cracking of petroleum in an enlarged reaction chamber, such circulation of hydrocarbon material within the chamber is undesirable in many cases, since it leads to the discharge of uncracked hydrocarbons from the chamber and therefore this is at present minimized in practice. However under the conditions peculiar to my process, as will be discussed, the nature of the reactions taking place is markedly and favorably affected by such turbulence. The intimate mixing of incoming reactants with partially reacted and therefore more highly paraffinic hydrocarbon material insures that an appreciable proportion of the reactions taking place in the chamber will involve the juncture of olefins and paraffins to form higher molecular weight paraffins, and progressive reactions which involve only olefin hydrocarbons are limited in extent so that formation of heavy tars and coke is minimized.

Hydrocarbon material suitable for conversion in my process will contain both paraffins and olefins, both of which enter into reaction. Of the paraffins, propane, butane and pentane are particularly suitable since they readily enter into reaction with unsaturated hydrocarbons. Ethane and methane are less reactive and in many cases it will be desirable to limit the quantity thereof present in the conversion stock. Any of the sim-

ple unsaturates, namely ethylene, propylene, butylene, pentene, and acetylene are suitable for this process, with ethylene being somewhat the most reactive of the olefins. These constitute the chief hydrocarbon components of petroleum conversion still gases, natural gases contain the paraffins named, and such gases will also furnish suitable conversion stock. Suitable concentrating operations to provide a mixture of low methane and ethane content is ordinarily desirable because of the low reactivity of these hydrocarbons. Pyrolysis and dehydrogenation may be applied to saturated hydrocarbons to furnish olefin reactants. The gases ordinarily produced by the so-called vapor phase petroleum cracking are not directly very suitable for the process, although the content of the highly desirable ethylene is high, because the amount of paraffins other than methane and ethane is too limited. The gas produced by pressure cracking yields a concentrate containing both suitable paraffins and olefins, usually of suitable composition but with the paraffins in marked predominance. A mixture of methane-low concentrates of vapor phase and pressure cracking gases is accordingly highly suitable because it contains olefins rich in ethylene associated with the desired paraffins.

The paraffin content of conversion stock for my process should preferably consist mainly of paraffins higher than ethane accompanied by unsaturates constituting from 10 to 50 per cent by volume, or somewhat more, of the total conversion stock. The conversion stock may also contain unconverted hydrocarbons separated from the effluents of the process which are usually depleted in olefin. Thus such a predominantly paraffinic recycle stream consisting mainly of unreacted propane and butane, may be mingled with a charge stock of high olefin content to form a very desirable conversion stock.

I use reaction temperatures of 700° to 1100° F., a temperature range wherein olefin hydrocarbons are known to polymerize with themselves under pressure, but wherein paraffin hydrocarbons decompose only slowly, when given an equal reaction time. Nevertheless, the paraffin molecules are in a more or less activated condition, and are capable of reacting with olefin molecules to produce higher molecular weight hydrocarbons, generally paraffinic in nature.

In the practice of my invention the average reaction time or period of residence of the reactants within the reaction chamber will be dependent on the temperature within the chamber, upon the composition of the conversion stock, and upon the design of the reaction chamber. The principal and most desired reactions will tend to reduce the specific volume of the hydrocarbon mixture and increase its paraffinicity, and the extent of these characteristic properties will need to be taken into consideration also. I prefer to operate my process so that at least half of the olefins charged to the process undergo a reaction, and the effluents of the reaction chamber should not contain more than 5 to 10 per cent by volume of unreacted olefin molecules. To fulfill these conditions the average reaction time should be at least 15 seconds and should not be more than 30 minutes, and I have found that the best results are generally obtained with a reaction period of 1.5 to 7.5 minutes. Exact temperatures and reaction periods for any particular case may be readily determined by trial.

In the practice of my process the use of pressures above those heretofore employed, in simple

thermal polymerization of olefin-containing hydrocarbon gases in a reaction chamber, decreases formation of heavy hydrocarbons unsuitable for motor fuel, and with increase in conversion pressure within my disclosed range, the formation of these undesirable heavy products is increasingly suppressed. This is a contrast to the usual result when the active turbulent circulation and dispersal of reactants is not employed, such procedures usually leading to increased formation of heavy products with increase in pressure, which also is the usual effect of pressure increase when petroleum oils are cracked.

I prefer to practice my process in such a manner that reaction takes place in the reaction chamber without substantial addition of heat or abstraction of heat from the chamber. Since the reaction is exothermic the reactants may be heated only to such a degree as will sustain reaction in the chamber at the desired temperature levels. Thus the temperature of the hydrocarbons entering the chamber may be as much as 150° F. or more lower than the temperature of reaction within the chamber, high olefin contents permitting relatively low preheat temperatures. This is of advantage in preventing reaction prior to dispersal in the chamber, since the less desired olefin polymerization tends to set in at lower temperature than the paraffin-consuming reactions in the chamber.

Under the conditions of turbulent circulation and mixing disclosed herein, and treating hydrocarbon gases of the compositions discussed, I have been able to obtain ultimate yields of higher boiling material in the gasoline range of about 1.25 to 2.5 or more times as large by weight as I have at other times obtained under similar temperature and pressure conditions, but using reaction zones such that reactions involving only olefins took place. Furthermore, the products of my present process are considerably more paraffinic in nature. This feature adds greatly to their desirability as motor fuels, as they have very good antidetonating qualities which can be considerably improved with only small additions of tetraethyl lead or other detonation inhibitors, and they are not particularly subject to gum formation and are quite stable during prolonged storage.

My invention will be more clearly understood by reference to the accompanying drawings, which form a part of this specification, and wherein,

Fig. 1 is a diagrammatical illustration of one form or arrangement of apparatus for realizing my invention,

Fig. 2 illustrates one type of reaction chamber,

Fig. 3 is a side view of the reaction chamber as illustrated in Fig. 2,

Fig. 4 illustrates in perspective a modified type of reaction chamber,

Fig. 5 is a transverse cross-sectional view of the reaction chamber as illustrated in Fig. 4, and is taken on line 5—5 thereof, looking in the direction of the arrows,

Fig. 6 is a side view illustrating another modified type of reaction chamber,

Fig. 7 is a side view, being broken away in part, illustrating still another type of reaction chamber,

Fig. 8 is a side view, being broken away in part, illustrating a further type of reaction chamber; and

Fig. 9 is a cross-sectional view of the reaction chamber illustrated in Fig. 8, and is taken on line

9—9 thereof looking in the direction of the arrows.

Referring now to Fig. 1, one mode of practicing my invention is as follows:

Hydrocarbon material of suitable composition of the type described, is introduced through pipe 10, compressed to any desired pressure in excess of 1000 pounds per square inch by pump 11, and passed through conduit 12 to the heating coil 13, which may be housed in any suitable furnace 14, or which may be heated by other means. In passing through the coil 13 the hydrocarbon mixture, or stream, is rapidly heated to a more or less elevated temperature, usually less than 1100° F., sufficient to sustain reaction in the reaction chamber to which it passes. It is desirable that this heating take place rapidly, so that no appreciable or extensive reactions will take place in the coil 13.

From coil 13 the stream is passed through conduit 15 directly to a reaction chamber such as will be described hereinafter and which is designated here by the numeral 16, and which is so constructed that a high degree of turbulent circulation and mixing may be maintained therein, and the stream is introduced into chamber 16 in such a manner as to create and maintain this turbulent state, as will also be discussed hereinafter. Effluents from the reaction chamber 16 are passed through conduit 17 and expansion and control valve 18 to separator 19. Separator 19 will preferably be operated at a pressure of about 200 pounds per square inch or more, but appreciably less than the pressure maintained in reaction chamber 16. Heavier products of the reactions will pass through conduit 20 to separating means 21, wherein heavier oils and tar are separated and discharged through conduit 22 and valve 23. A fraction containing the gasoline boiling range hydrocarbons produced is passed out of the process through conduit 24 and valve 25, and may be subjected to further treatment with stabilization of the gasoline.

Effluents from the chamber 16 not passing through conduit 20 will consist of unreacted material and lighter material. These are passed out of the separator 19 by means of conduit 26 to separator 27, wherein a separation is made between unreacted material and lighter material. Lighter material is discharged through conduit 29 and valve 28. Unreacted hydrocarbons are discharged from the separator 27 through line 30, and may be discharged from the system through valve 31. Any part or portion or all of this material may be passed through conduit 32 and valve 33 and into pipe 10 where it is mixed with the incoming hydrocarbons and subjected to further treatment.

It is to be understood that the reaction chambers and all modification thereof herein described are constructed to withstand relatively high pressures and temperatures, and therefore suitably constructed and fabricated from metal.

With reference now to Figs. 2 and 3 wherein are illustrated one form of reaction chamber which may be used in practicing this invention, it is to be noted that Fig. 2 is a plan view of the same, while Fig. 3 is a side view thereof. Such a reaction chamber is of the general configuration of a hollow oblate spheroid, designated by the reference numeral 40, and having the major axis A evidenced in Fig. 2, and the minor axis B as evidenced in Fig. 3. The ratio of A to B may conveniently be between the limits of 5:1 and 1:1, and is preferably about 2:1. The reaction cham-

ber 40 here under consideration may be provided with an inlet conduit 41, through which the effluents from the heating coils, such as the ones described in Fig. 1 enter the interior of the reaction chamber. The axis of the inlet conduit 41 is preferably on a line with the extension of a chord of the largest possible circular cross section of the spheroid constituting the reaction chamber 40. This allows the heated reactants entering chamber 40 by way of conduit 41 to enter therein in such a manner as to set up the desired turbulence and circulation within the chamber.

Reaction chamber 40 is provided with an outlet conduit 42, the axis of which is preferably coincident with the minor axis B of the chamber, and on a line with the center of rotation of the spheroidal reaction chamber. The end of the outlet conduit 42 disposed within the reaction chamber 40 may be provided with apertures at the end thereof as shown at 43, and also provided with an aperture at the top thereof as at 44. The end of the outlet conduit 42 may be closed, if desired, and the contents of the chamber will then pass therefrom through the apertures 43 and 44 above described.

Other types of reaction chambers may be used which will also insure the introduction of the effluents from the heating coils into the chamber in such a manner that the effluents therein undergo turbulence and circulation. For instance a modified type of reaction chamber is illustrated in Figs. 4 and 5, the body of which comprises a prolate spheroid generally designated by the reference numeral 50, having an inlet conduit 51 and an outlet conduit 52, the inlet conduit being positioned with respect to the chamber in relatively the same manner as the inlet conduit of the reaction chamber 40. The portion of the outlet conduit 52 positioned within the reaction chamber is provided with the apertures 53 and 54 as shown.

Fig. 5 is a transverse cross-sectional view of the chamber illustrated in Fig. 4, and is taken on line 5—5 thereof looking in the direction of the arrows, and shows the inlet and outlet conduits 51 and 52 respectively, and their position with respect to the chamber 50.

Still another modification of a reaction chamber suitable for use in practicing this invention is illustrated in Fig. 6. Here the reaction chamber generally designated by the reference numeral 60, comprises a pair of parallelly disposed conduits 61 and 62, which are joined at either end by the curved conduits 63 and 64. To the ends of either of the curved conduits may be fitted the inlet and outlet conduits. As illustrated the inlet conduit 65 is fitted at or near one end of the conduit 63 and so disposed as to be substantially parallel with conduit 61, while the outlet conduit 66 is fitted at or near another end of the curved conduit 63 and is positioned substantially parallel with respect to conduit 62. The diameter of the reaction chamber 60, being the same as the diameter of the respective conduits 61, 62, 63 and 64 is preferably about eight (8) or more times larger than the diameter of the inlet conduit 65, and more preferably up to twenty (20) or thirty (30) times larger, or more.

It should be apparent that such a reaction chamber as the one designated by the reference numeral 60, and illustrated in Fig. 6, will serve to set up turbulence in the effluents from the heating coil when the same effluents are introduced into the reaction chamber by way of the

inlet conduit 55, for the same will be caused to circulate through the chamber 60 in a turbulent manner and cause a circulation of the chamber contents.

Fig. 7 illustrates a still further modified type of reaction chamber which is generally designated by the reference numeral 70, and which consists essentially of a cylindrical portion 71 having the hemispherical ends 72 and 73. A chamber of this type may be provided with one or more inlet conduits arranged in different positions as is desired. If only one inlet is to be used it may be positioned in the manner of the inlet conduit 74 shown in Fig. 7. An outlet conduit is provided at 75.

In Figs. 8 and 9 there is illustrated a still further modification of a reaction chamber, which is based on the modified type illustrated in Fig. 7, but which is provided with several inlet conduits. The reaction chamber is generally designated by the reference numeral 80, and essentially comprises a cylindrical portion 81 provided with the end portions 82 and 83. Inlet conduits 84 and 85 are provided as illustrated, and are disposed at an angle, but not necessarily the same, with respect to the transverse axis of the cylindrical portion 81 of the reaction chamber 80. It is preferable that the axis of one of the inlet conduits form a plane with the axis of the outlet conduit, and that at least one of the other inlets, or the other inlet, have an axis which is not in this plane and which does not intersect either of the aforementioned axes. Where a plurality of inlets are used, the combined cross-sectional area of each may be such that the linear velocity of the incoming jet of reactants, or effluents, from each inlet will be the same as if only one inlet conduit was normally used. That is, the cross-sectional area of any one inlet conduit will be in an inverse relationship to the number of inlet conduits, or in lieu of such an arrangement greater inlet velocities may be used. The use of a plurality of inlet conduits in a reaction chamber of this design will help eliminate any dead spaces therein, and provide a positive turbulence and circulation of the effluents of the heating zone entering the chamber resulting in a more uniform reaction.

The relative dimensions of the reaction chambers are such that conversion stock injected at high velocity thereinto will maintain in circulatory motion and in a turbulent state the greater part of the contents of the chamber. Many forms of reaction chambers will meet this requirement, including a simple cylindrical form of large cross-sectional area the length being preferably less than 5 times the diameter. The injection of reactants into the chamber must take place at a linear velocity sufficiently high to circulate the contents within the chamber at least 3 and preferably 10 or more times on the average past the point of injection, the more vigorous circulation being required with conversion stocks of high olefin content. For a reaction chamber of given size it is possible by hydrodynamic calculation to determine the inlet velocity required and the extent to which the cross-section of the inlet orifice must be restricted to obtain the desired degree of turbulent circulatory motion. The inlet orifice may be merely a prolongation of the heating coil of suitably restricted cross-sectional area. The dispersal of the incoming reactants into the circulating contents of the chamber should be sufficiently rapid and complete to minimize premature polymeri-

zation of concentrated and undispersed olefins as they emerge from the inlet into the chamber. At high inlet velocities dispersal is more efficient than at lower ones, although the lower velocities may be adequate for sustaining circulation. Dispersal may be assisted by baffles or equivalent scattering devices upon which the stream impinges, or a Venturi throat or a series of Venturi throats of increasing diameter, the smaller discharging into the larger, surrounding the incoming stream, the use of multiple jets, and other expedients which will be obvious for such use.

This turbulent circulation and mixing within the reaction chamber of my process, designated by the numeral 16 in Fig. 1, is different from the turbulence which exists in the conduit 15 immediately prior to its discharge into the chamber. The linear velocity of the hydrocarbon material being heated in the tube coil 13 will generally vary from 20 to 40 feet per second when this heating section is designed along conventional lines, and this is in the range of turbulent flow within the tube coil under the conditions which exist. The restricted cross-sectional area of the coil and the linear velocity of flow through it permits of local mixing only. Introducing such a stream into reaction chambers as disclosed insures a different effect, namely a rapid and thorough mixing of heated and activated reactants with other and partially reacted hydrocarbon material which is turbulently circulating within the chamber. This circulating hydrocarbon material is in violent agitation, so that extensive over-reacting of localized portions does not take place, and adequate opportunity is given for olefins to react with paraffins while thinly dispersed in their presence.

While my operations have shown that with chambers designed as those previously discussed, or in any variation of these designs which would be readily conceived by one skilled in the art, a linear velocity of the incoming mixture of 10 or 15 feet per second is enough to set up and maintain some turbulence within the reaction chamber, velocities of 20 to 40 feet per second through the heating coil are generally available and more desirable. Still higher velocities are usually preferable, and to obtain them the heating coil 13 and the inlet conduit 15 may be of smaller cross section than is usual in gas conversion heating coils, or the end of the conduit 15, discharging into the reaction chamber, may be of restricted cross section, without prohibitive friction losses, so that the jet of reactants entering the chamber will have a velocity of 50 to 200 feet per second or more, and I may use such velocities in my process. A pressure drop equivalent to the velocity imparted will be experienced at such a constriction. Such discussion as given here is understood to pertain to any particular reaction chamber which may be used in this process.

In general, in this process it is desirable to maintain, (1) the reactants and products in circulatory motion in a large portion of the reaction zone, (2) efficient dispersal of olefin-bearing conversion stock entering the reaction chamber, (3) a minimum of stagnant space, other than in proximity to the outlet and in transit to said outlet, (4) and a characteristic flow which minimizes the residence of hydrocarbons for periods much exceeding the average time of residence in the reaction zone. The familiar principles of hydrodynamics can be applied in many obvious ways to achieve the conditions of reaction which have been stipulated.

EXAMPLE I

As an example of the successful operation of this invention, a hydrocarbon mixture containing 7.3 per cent by weight of ethylene and 92.2 per cent of isobutane was rapidly heated to a temperature of about 915° F. and injected from a small orifice at a velocity of about 40 feet per second into a cylindrical reaction chamber having a length about four times the diameter in such a manner that extensive circulation and turbulent mixing took place. The chamber was insulated so as to be practically without any heat loss, and the temperature of the effluents was about 940° F., the rise in temperature being due to the exothermic reactions taking place. The average period of reaction within the chamber was about 4 minutes, and the pressure was maintained at 4500 pounds per square inch. The effluents contained 9.0 per cent by weight of gasoline, of the composition shown in Table III, run A.

The hexane fraction from this run was isolated from the liquid products and found to consist of ethylated isobutane, chiefly 2,2-dimethylbutane. The total gasoline was subjected to routine motor fuel tests. The olefin content was small, and the gasoline was predominantly paraffinic, being very low in aromatics content. It had a Reid vapor pressure of only 8.3 pounds per square inch, and an octane number of 85. The addition of one cc. of lead tetraethyl per gallon increased this octane rating about ten units, an increase which is unusually high for a motor fuel with such a high initial octane number, and especially for a motor fuel produced by thermal conversion of an olefin-containing normally gaseous hydrocarbon mixture.

EXAMPLE II

As an example of the operation of this invention at considerably less pressure, a hydrocarbon mixture containing 9.8 per cent by weight of ethylene and 90.2 per cent by weight of isobutane was converted according to the process of Example I, except that the reaction pressure was only 2500 pounds per square inch, the temperature of the effluents of the chamber was 968° F., and the time of reaction was 4.3 minutes. The pertinent data of this run are given in Table III, run B. The hexane fraction had practically the same characteristics as the hexane fraction from run A.

EXAMPLE III

In order to bring out more completely the advantages of this invention, a third example is presented for contrast. A hydrocarbon mixture containing 16.5 per cent by weight of ethylene and 83.5 per cent of isobutane was rapidly heated to a reaction temperature of 941° F. under a pressure of 4700 pounds per square inch and allowed to react in an extension of the heating coil for a period of 5.1 minutes, wherein no turbulent mixing into recirculating hydrocarbon could take place. The effluents contained 20.4 per cent by weight of gasoline, of a composition shown in Table III, run C. It is to be noted that the normally liquid products of this run are not predominant in hexanes, that a large amount of heavier liquids were formed, and that a large amount of unsaturated hydrocarbons are present. The liquids corresponding to octane and higher were rich in aromatics.

TABLE III

Gasoline from normally gaseous hydrocarbons

	Run number		
	A	B	C
Temperature (° F.)	940	968	941
Pressure (lb. per sq. in.)	4,500	2,500	4,700
Average reaction time (minutes)	3.2	4.3	5.1
Charge composition, weight per cent (per cent by volume):			
C ₂ H ₄	7.3(15)	9.8(18.4)	16.5(29.1)
Iso-C ₄ H ₁₀	92.2(85)	90.2(81.6)	83.5(70.9)
C ₂ H ₄ in effluent stream	1.6	1.0	0.1
C ₂ H ₄ in charge which reacted	6.2	8.8	16.4
Weight per cent gasoline per pass	9.0	12.8	20.4
Pounds of product per pound of reacted olefin	1.45	1.45	1.24
Products (weight per cent):			
Pentenes	3.5	5.7	4.4
Pentanes	6.2	17.2	23.8
Hexenes	2.9	4.5	2.7
Hexanes	46.0	39.9	17.5
Heptenes	2.7	2.5	1.1
Heptanes	9.3	7.9	5.6
Octenes	2.9	3.9	3.4
Octanes	11.0	8.0	17.2
Heavier gasoline	13.7	7.9	20.5
Tar	1.8	2.5	3.8
Paraffinic products octanes and lighter	100.0	100.0	100.0
	72.5	73.0	64.1

These three examples have all shown the thermal treatment of a normally gaseous hydrocarbon mixture composed of ethylene and isobutane. The invention is not to be considered to be limited to the use of such a mixture, as these hydrocarbons have no special properties or characteristics which would tend to make them specifically different from any of their analogues, nor should any restriction be made to such a low olefin content. These conditions were chosen only because the product of their interreaction would be easily identified in the effluents, and the results of different experiments would bring out the differences due to different conditions of operation, without being obscured by results of other variables. Any olefin containing normally gaseous hydrocarbon mixture, containing up to 50 per cent by volume of olefins when treated under conditions most suitable for that particular mixture, will react in an analogous manner.

A consideration of the analyses of the normally liquid products of these three examples brings out three very important and pertinent points.

1. The hexanes produced in run A were 46.0 per cent by weight of the products, in run B they were 39.9 per cent, while in run C they were only 17.5 per cent. This illustrates forcibly the increased extent of reactions between olefins and paraffins which result from practicing my invention.

2. A consideration of the weight per cent of normally liquid hydrocarbons produced per pass in comparison with the olefin content of the charge stock is very interesting. Although the charge in run C contained 16.4 per cent of olefin which reacted, 2.65 times as much as the charge to run A, only 1.24 pounds of liquid products per pound of olefin resulted in run C while 1.45 pound of liquid products resulted in run A, an increase of 17 per cent in run A.

3. Both runs A and B produced liquid products containing about 73 per cent by weight of saturated hydrocarbons of eight or fewer carbon atoms per molecule, while the products from run C contained only about 64 per cent of equivalent material, as well as a considerably larger propor-

tion of heavier liquids and tar. This again is a direct and valuable result of using my invention, which is not demonstrated or hinted at by the workers in the prior art.

As previously discussed herein, I have found that when olefin molecules react with paraffin molecules to form higher molecular weight paraffins, the reactions are greatly influenced by the total pressure on the system, among other variables. If the total pressure is high, a lower temperature may be used and the paraffinicly of the normally liquid products is considerably increased, and as a concomitant result the ultimate yield of higher molecular weight material within the motor fuel range is also increased, based on a unit weight of charge stock and any given olefin content. Thus under conditions wherein only olefin molecules react with each other only a limited amount of higher molecular weight material may be formed. But when conditions are such that paraffin molecules also enter into the reaction, the yield is increased by an amount corresponding more or less to the amount of paraffinic material entering into the reaction. Since, however, the mode of operation also exerts a considerable influence on the products, a more paraffinic material may be produced by practicing my invention at lower pressures than by a less favorable mode of higher pressures, despite the less favorable condition of lower pressure for efficient participation of paraffins.

In the examples given, run B at 2500 pounds per square inch produced much more paraffinic material in the desirable gasoline boiling range than was produced in run C, although the latter was carried out at a much higher pressure and a somewhat lower temperature. Thus by practicing my invention at 2500 pounds per square inch pressure, very desirable and beneficial results are produced over conventional once-through processes at equal or even higher pressures.

Considerable discussion has been presented herein concerning the theory of the molecular mechanisms involved in my process. I have observed an unusually high content of paraffin hydrocarbons in the products of my process, and have advanced this discussion only as a possible explanation, and I do not wish to give the impression that I am attempting to claim herein any new and novel theories or mechanisms of reaction, however such theories should not be so construed as to limit the scope of this invention as set forth.

Although preferred methods of operation have been discussed, it is to be understood that my invention is not limited by such discussions or the examples given, but only by the claims hereto appended.

What I claim and desire to secure by Letters Patent is:

1. In a continuous process for producing normally liquid motor fuel hydrocarbons from a normally gaseous hydrocarbon mixture containing not less than 10 per cent by volume of olefinic hydrocarbons predominantly ethylene and 50 per cent by volume or more of paraffinic hydrocarbons of three or more carbon atoms per molecule, the steps which comprise heating said hydrocarbon mixture to a reaction-sustaining temperature in a heating zone and introducing the same into a reaction zone which does not include said heating zone as a part thereof, circulating reactants in an endless circulatory flow only within said reaction zone which is so dimensioned as to permit endless circulatory flow and mixing

therein, introducing the mixture at a linear velocity and in a manner such as to establish and maintain such circulatory flow to effect a rapid mixing and dilution of the incoming charge with the circulating more paraffinic reacting mixture, maintaining the mixture in said reaction zone under a pressure in excess of 2000 pounds per square inch and a temperature of 700° to 1100° F. for an average time sufficient to cause the greater part of the olefins to react thereby producing normally liquid motor fuel hydrocarbons, withdrawing from the reaction zone a reacted hydrocarbon mixture and separating therefrom the last mentioned hydrocarbons.

2. A process for producing predominantly paraffinic normally liquid hydrocarbons, a major portion of which boil in the motor fuel range, from a normally gaseous hydrocarbon mixture, which comprises substantially continuously passing a normally gaseous hydrocarbon mixture containing at least 10% by volume of simple unsaturated hydrocarbons and at least 50% by volume of paraffin hydrocarbons having at least three carbon atoms per molecule under a pressure in excess of 2000 pounds per square inch through a heating zone of restricted cross sectional area and rapidly heating the said mixture to a temperature below reaction temperature but sufficient to sustain the reaction temperature in subsequent exothermic reaction, passing the heated mixture through a passageway sufficiently restricted as to cross sectional area to impart thereto a linear velocity in excess of 40 feet per second and introducing the mixture at said velocity into an enlarged reaction chamber in such manner as to maintain therein a high degree of circulation and turbulent mixing, maintaining a reaction temperature between 700 and 1100° F. within said reaction chamber without substantial addition of heat to said reaction chamber and detaining the reactants in said chamber for an average period of time between 1.5 and 7.5 minutes, said temperature and time being so chosen as to consume the greater part of the simple unsaturated hydrocarbons and produce normally liquid hydrocarbons predominantly paraffinic in structure, substantially continuously withdrawing a portion of the contents of said reaction chamber and separating therefrom a fraction comprising hydrocarbons in the motor fuel boiling range.

3. A substantially continuous process for producing normally liquid hydrocarbons predominantly in the motor fuel boiling range from lighter hydrocarbons, which comprises substantially continuously passing a normally gaseous hydrocarbon mixture containing at least 10 per cent by volume of simple unsaturated hydrocarbons and at least 50 per cent by volume of paraffin hydrocarbons having three and four carbon atoms per molecule under a pressure of at least 2000 pounds per square inch to a heating zone, passing the heated mixture without substantial reduction in pressure to an enlarged reaction zone of such a shape that the contents thereof can be maintained in a constant circulation therein and so insulated that there is substantially no gain or loss of heat through the walls thereof during a period of reaction, introducing said heated mixture at a linear velocity between about 10 and 40 feet per second into said chamber in a direction and manner to establish and maintain said circulation to effect a rapid mixing and dilution of the incoming charge with the circulating, more paraffinic reacting

mixture, maintaining a reaction temperature in said chamber between about 700° F. and 1100° F. and an average reaction time such that at least half of the originally charged simple unsaturated hydrocarbons undergo reaction, substantially continuously withdrawing a portion of the contents of said reaction chamber and separating therefrom a fraction comprising hydrocarbons in the motor fuel boiling range so produced.

4. A substantially continuous process for producing normally liquid hydrocarbons predominantly in the motor fuel boiling range from lighter hydrocarbons, which comprises substantially continuously passing a hydrocarbon mixture comprising such lighter hydrocarbons and containing at least 10 per cent by volume of simple unsaturated hydrocarbons and at least 50 per cent by volume of paraffin hydrocarbons having three and more carbon atoms per molecule under a pressure of at least 1000 pounds per square inch to a heating zone, passing the heated mixture without substantial reduction in pressure to an enlarged reaction zone of such a shape that the contents thereof can be maintained in a constant circulation therein and so insulated that there is substantially no gain or loss of heat through the walls thereof during a period of reaction, introducing said heated mixture at a linear velocity between about 10 and 40 feet per second into said chamber in a direction and manner to establish and maintain said circulation to effect a rapid mixing and dilution of the incoming charge with the circulating, more paraffinic reacting mixture, maintaining a reaction temperature in said chamber between about 700 and 1100° F. and an average reaction time such that at least half of the charged simple unsaturated hydrocarbons undergo reaction, substantially continuously withdrawing a portion of the contents of said reaction chamber and separating therefrom a fraction comprising normally liquid hydrocarbons in the motor fuel boiling range so produced.

5. A substantially continuous process for producing normally liquid hydrocarbons predominantly in the motor fuel boiling range from lighter hydrocarbons, which comprises substantially continuously passing a hydrocarbon mixture comprising such lighter hydrocarbons and containing at least 10 per cent by volume of low boiling olefin hydrocarbons and at least 50 per cent by volume of paraffin hydrocarbons having three and more carbon atoms per molecule and lighter than said products in the motor fuel boiling range under a pressure of at least 1000 pounds per square inch to a heating zone, heating said mixture in a heating zone to a temperature sufficient to maintain a reaction temperature favoring paraffin-olefin union under the conditions hereinafter set forth, passing the heated mixture without substantial reduction in pressure to an enlarged reaction zone which does not include said heating zone as a part thereof and of such a shape that the contents thereof can be maintained in a constant circulation therein and so insulated that there is substantially no gain or loss of heat through the walls thereof during a period of reaction, circulating reactants in an endless circulatory flow only within said reaction zone, introducing a stream of said heated mixture into said zone in such a direction and manner and at such a linear velocity as to establish and maintain said circulation to effect a rapid mixing and dilution of said incoming heated mixture with the circulat-

ing more paraffinic reacting mixture, maintaining a reaction temperature in said zone between about 700 and 1100° F. and an average reaction time such that at least half of the charged low boiling olefin hydrocarbons undergo reaction, substantially continuously withdrawing a portion of the contents of said reaction zone and separating therefrom a fraction comprising normally liquid hydrocarbons in the motor fuel boiling range so produced.

6. A continuous process for producing higher molecular weight hydrocarbons from an olefin-containing normally gaseous hydrocarbon mixture, which comprises rapidly heating in a heating zone a normally gaseous hydrocarbon mixture of essentially paraffinic hydrocarbons of three and four carbon atoms per molecule and 15 to 30 per cent by volume of normally gaseous olefins to a reaction-sustaining temperature equal to or less than the reaction temperature maintained in a reaction chamber, introducing the heated mixture under a pressure in excess of 1000 pounds per square inch into a reaction zone which does not include said heating zone as a part thereof, circulating reactants in an endless circulatory flow only within said reaction zone which is so dimensioned as to permit endless circulatory flow and mixing therein, introducing said heated mixture in such a manner and at such a velocity that a high degree of circulation and mixing is established and maintained within the zone to effect rapid mixing and dilution of the incoming charge with the circulating more paraffinic reacting mixture, maintaining a reaction temperature within the zone between 700 and 1000° F. for a period of time sufficient to react a major portion of the olefins present in the reaction mixture to produce higher boiling hydrocarbons predominantly paraffinic in structure, continuously withdrawing a reacted hydrocarbon mixture from the reaction mixture, separating the higher molecular weight hydrocarbons produced and discharging them from the process, and also separating essentially paraffinic unreacted hydrocarbons of three and four carbon atoms per molecule and returning at least a portion of these unreacted hydrocarbons to the process.

7. A substantially continuous process for producing normally liquid hydrocarbons predominantly in the motor fuel boiling range from lighter hydrocarbons which comprises substantially continuously passing a hydrocarbon mixture comprising such lighter hydrocarbons and containing 15 to 30 per cent by volume of simple unsaturated hydrocarbons and at least 70 per cent of paraffin hydrocarbons having three or more carbon atoms per molecule under a pressure of at least 2000 pounds per square inch to a heating zone, passing the heated mixture without substantial reduction in pressure to an enlarged reaction zone of such a shape that the contents thereof can be maintained in a constant circulation therein and so insulated that there is substantially no gain or loss through the walls thereof during the period of reaction, introducing said heated mixture at a linear velocity between about 10 and 40 feet per second into said chamber in a direction and manner to establish and maintain said circulation to effect a rapid mixing and dilution of the incoming charge with the circulating, more paraffinic reacting mixture, maintaining a reaction temperature in said chamber between about 700 and 1100° F. and an average reaction time such that at least half of the charged simple unsaturated hydro-

carbons undergo reaction, substantially continuously withdrawing a portion of the contents of said reaction chamber and separating therefrom a fraction comprising normally liquid hydrocarbons in the motor fuel boiling range so produced.

8. In a continuous process for reacting low boiling paraffin hydrocarbons of at least three carbon atoms per molecule with olefin hydrocarbons to produce predominantly paraffinic products of higher molecular weight and predominantly in the motor fuel boiling range, the steps which comprise continuously passing a mixture containing such low boiling hydrocarbons, and comprising between about 10 and 50 per cent by volume of olefin hydrocarbons and more than 50 per cent by volume of such low boiling paraffin hydrocarbons, at a temperature sufficient to maintain a reaction temperature favoring paraffin-olefin union under conditions hereinafter set forth, to a reaction zone of large cross-sectional area which does not include a heating zone as a part thereof and which is so shaped that the reacting contents thereof may be maintained in a constant circulation therein and so insulated that there is substantially no gain or loss of heat through the walls thereof during a reaction period, circulating reactants in an endless circulatory flow only within said reaction zone maintaining a reaction temperature and pressure within said zone favorable to the union of paraffin and olefin hydrocarbons to form paraffin hydrocarbons of higher molecular weight, introducing said mixture into said zone at a linear velocity and in a direction and manner such that said circulation of the contents of said zone is established and maintained to effect a rapid mixing dilution of the incoming mixture with the circulating and reacting contents, maintaining said reactants in said zone for an average period of time such that a major portion of the olefins charged undergo reaction, substantially continuously withdrawing a portion of the contents of said reaction zone, and separating therefrom a fraction comprising normally liquid predominantly paraffinic hydrocarbons in the motor fuel boiling range so produced.

9. A process for producing predominantly paraffinic normally liquid hydrocarbons predominantly in the motor fuel boiling range from lower boiling hydrocarbons, which comprises substantially continuously passing a hydrocarbon mixture containing at least 10% by volume of such lower boiling olefin hydrocarbons and at least 50% by volume of such lower boiling paraffin hydrocarbons having at least three carbon atoms per molecule under a suitable elevated super-atmospheric reaction pressure through a heating zone of restricted cross sectional area and rapidly heating said mixture to a temperature below a subsequent reaction temperature but sufficient to sustain the reaction temperature in subsequent exothermic reaction, passing the heated mixture through a passageway sufficiently restricted as to cross sectional area to impart thereto a linear velocity between about 40 and 200 feet per second and introducing the mixture at such a velocity into an enlarged reaction chamber in such a manner as to maintain therein a high degree of circulation and turbulent mixing, maintaining a reaction temperature between about 700 and 1100° F. within said reaction chamber without substantial addition of heat to said reaction chamber, and detaining the reactants in said chamber for an average period of time between 1.5 and 7.5 minutes, said temperature and time

being so chosen as to consume the greater part of the simple olefinic hydrocarbons and produce normally liquid hydrocarbons predominantly paraffinic in structure, substantially continuously withdrawing a portion of the contents of said reaction chamber and separating therefrom a fraction comprising hydrocarbons in the motor fuel boiling range.

10. In a continuous process for reacting low boiling paraffin hydrocarbons of at least three carbon atoms per molecule with olefin hydrocarbons to produce predominantly paraffinic products of higher molecular weight and predominantly in the motor fuel boiling range, the steps which comprise continuously passing a mixture containing such low boiling hydrocarbons, and comprising a substantial amount of olefin hydrocarbons and more than 50 per cent by volume of the hydrocarbons as such low boiling paraffin hydrocarbons, at a temperature sufficient to maintain a reaction temperature favoring paraffin-olefin union under conditions hereinafter set forth, to a reaction zone of large cross-sectional area which does not include a heating zone as a part thereof and which is so shaped that the reacting contents thereof may be maintained in a constant circulation therein and so insulated that there is substantially no gain or loss of heat through the walls thereof during a reaction period, circulating reactants in an endless circulatory flow only within said reaction zone, maintaining a reaction temperature and pressure within said zone favorable to the union of paraffin and olefin hydrocarbons to form paraffin hydrocarbons of higher molecular weight, introducing said mixture into said zone at a linear velocity and in a direction and manner such that said circulation of the contents of said zone is established and maintained to effect a rapid mixing and dilution of the incoming mixture with the circulating and reacting contents, maintaining said reactants in said zone for an average period of time such that a major portion of the olefins charged undergo reaction, substantially continuously withdrawing a portion of the contents of said reaction zone, and separating therefrom a fraction comprising normally liquid predominantly paraffinic hydrocarbons in the motor fuel boiling range so produced.

11. In a continuous process for reacting low boiling paraffin hydrocarbons of at least three carbon atoms per molecule with olefin hydrocarbons to produce predominantly paraffinic products of higher molecular weight and predominantly in the motor fuel boiling range, the steps which comprise continuously passing a mixture containing such low boiling hydrocarbons, and comprising a substantial amount of olefin hydrocarbons and more than 50 per cent by volume of the hydrocarbons as such low boiling paraffin hydrocarbons, at a temperature sufficient to maintain a reaction temperature favoring paraffin-olefin union under conditions hereinafter set forth, to a reaction zone of large cross-sectional area which does not include a heating zone as a part thereof and which is so shaped that the reacting contents thereof may be maintained in a constant circulation therein and so insulated that there is substantially no gain or loss of heat through the walls thereof during a reaction period, circulating reactants in an endless circulatory flow only within said reaction zone, maintaining a reaction temperature and pressure within said zone favorable to the union of paraffin and olefin hydrocarbons to

form paraffin hydrocarbons of higher molecular weight, establishing and maintaining a circulation of the contents of said reaction zone only within said reaction zone to effect a rapid mixing and diluting of the incoming mixture with the circulating and reacting contents, maintaining said reactants in said zone for an average period of time such that a major portion of the olefins

5 charged undergo reaction, substantially continuously withdrawing a portion of the contents of said reaction zone, and separating therefrom a fraction comprising normally liquid predominantly paraffinic hydrocarbons in the motor fuel boiling range so produced.

FREDERICK E. FREY.

CERTIFICATE OF CORRECTION.

Patent No. 2,266,019.

December 16, 1941.

FREDERICK E. FREY.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 11, beginning with the words "Another object" strike out all to and including "union." in line 16, and insert instead the following paragraph -

It is an object of this invention to provide a process wherein chemical reactions between reactants in the vapor phase may take place in an enlarged reaction chamber while a high degree of turbulent circulation and mixing is maintained.

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 10th day of February, A. D. 1942.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.