March 31, 1942. P. SUBKOW 2,277,938

PROCESS FOR REFORMING AND POLYMERIZING HYDROCARBONS

Original Filed Aug. 12, 1935 2 Sheets-Sheet 1

Fig. 1.

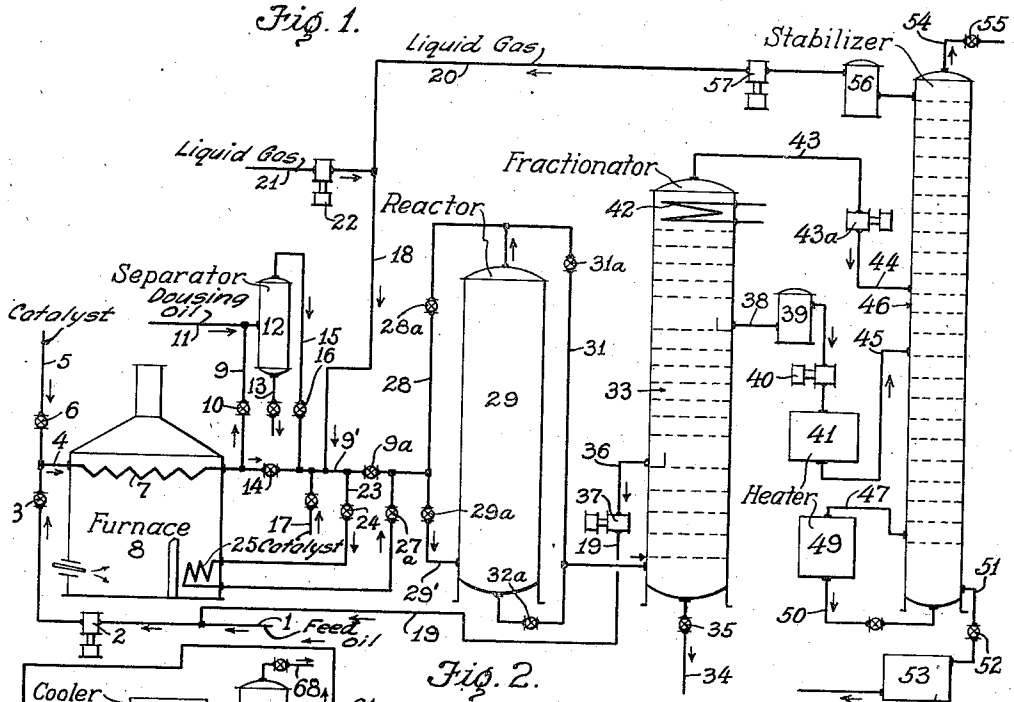
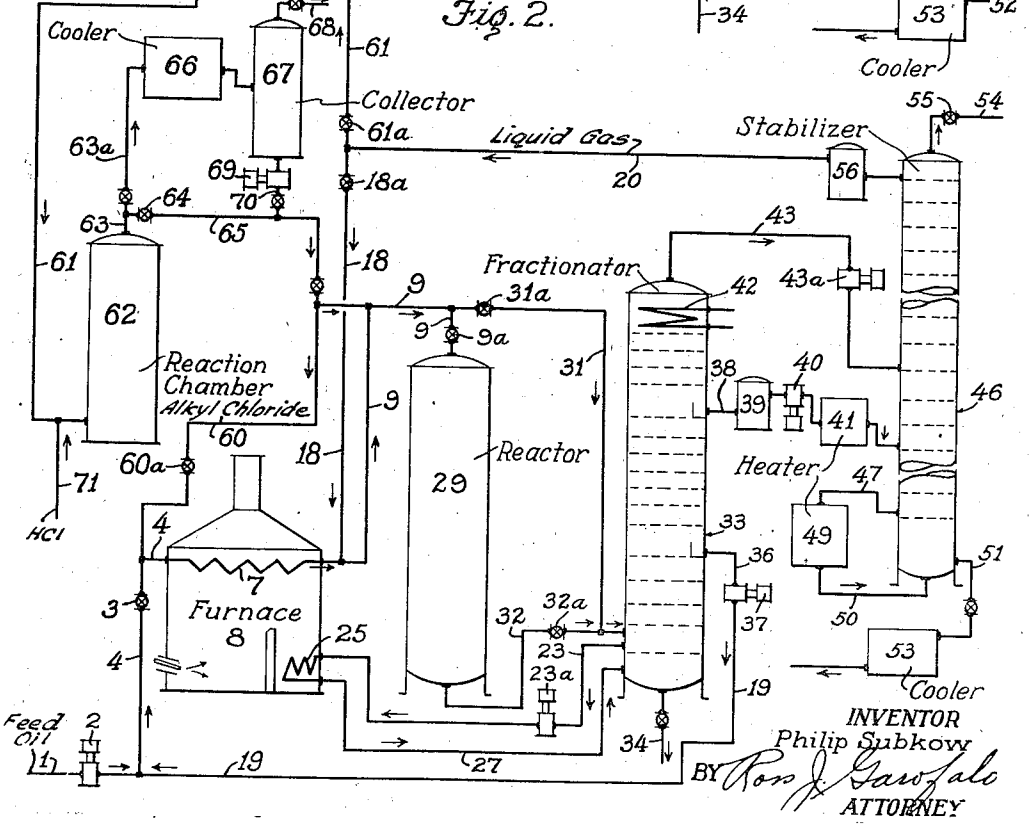


Fig. 2.



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Fig. 3.

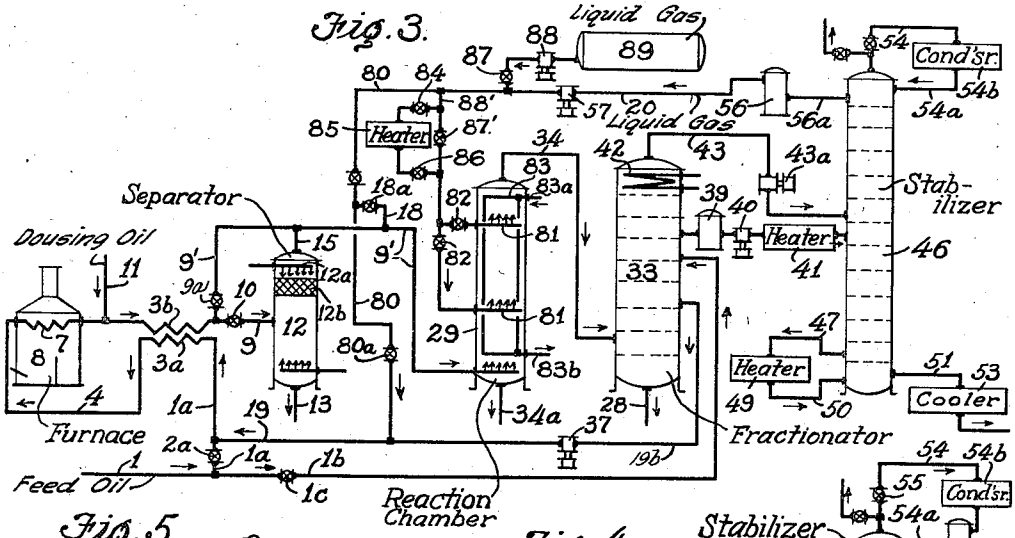


Fig. 5.

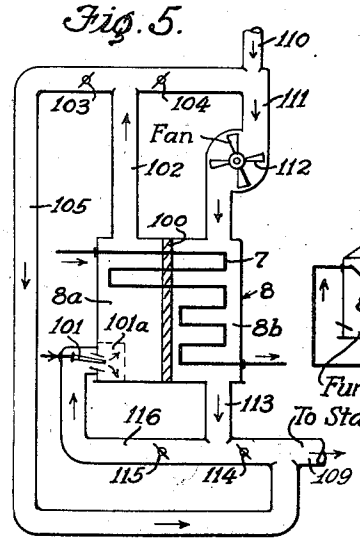


Fig. 4.

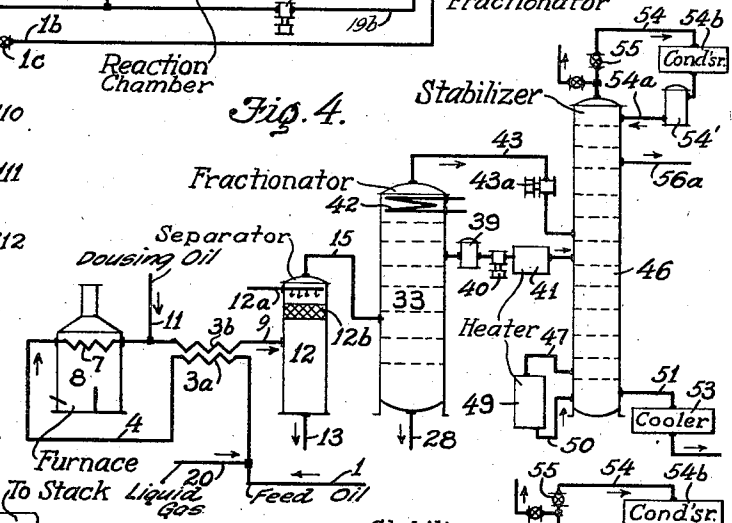
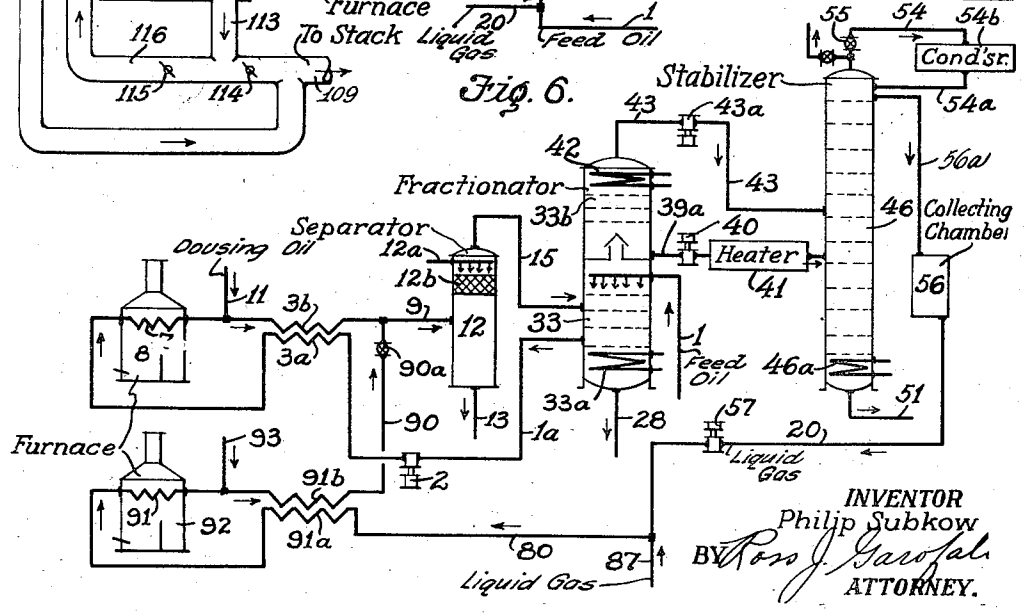


Fig. 6.



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UNITED STATES PATENT OFFICE

2,277,938

PROCESS FOR REFORMING AND POLYMERIZING HYDROCARBONS

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Original application August 12, 1935, Serial No. 35,702. Divided and this application July 12, 1938, Serial No. 218,777

4 Claims. (Cl. 196—9)

This invention relates to a process and apparatus for the formation of high anti-knock gasoline, and particularly to a process for the conversion of low anti-knock gasoline to high anti-knock gasoline by a modification of the process known as "reforming" which utilizes recombining and polymerizing reactions as well as decomposing reactions. The process of this invention combines the processes for the conversion of high molecular weight into lower molecular weight hydrocarbons, known as "cracking," "dehydrogenating" and "reforming," with processes for building hydrocarbons of high anti-knock quality from low molecular weight hydrocarbons, particularly those which are normally gaseous at atmospheric temperatures and pressures, and known as "polymerization" or "synthesis," and processes for obtaining improved anti-knock qualities by molecular rearrangement, known as "isomerization."

The conventional process for reforming gasoline consists in subjecting hydrocarbons in the gasoline range, preferably in vaporous form, to high temperatures, under which conditions the gasoline is converted from one having low anti-knock properties to one having high anti-knock properties. The gasoline is then separated from the fixed gases and normally gaseous hydrocarbons to form a stabilized and reformed gasoline. This process for the formation of high iso-octane number material is visualized as proceeding through cracking, dehydrogenating and isomerizing reactions which yield as an intermediate or by-product, low molecular weight olefinic fractions and chemical radicals with unsatisfied valences called residuals. In conventional reforming operations there is no attempt to control the subsequent polymerization of these materials to retain and conserve those desirable anti-knock characteristics and to polymerize the gaseous residuals to liquid hydrocarbons of high anti-knock value. The process of this invention provides for controlled polymerization and conservation of these residuals and olefins, particularly those of the ethylenic type, in the reaction zones, thus favoring continued decomposition of the petroleum hydrocarbons and increased yield of high octane material over that resulting from a simple reforming operation. A reformed gasoline containing increased percentages of polymer gasoline of high octane value results.

The reactions here generically termed "polymerization" include alkylation reactions wherein saturated hydrocarbons combine with unsaturated hydrocarbons to form high molecular weight branched chain hydrocarbons or alkylation reactions between aromatics and unsaturated low molecular weight hydrocarbons such as ethylene, propene or butene, or straight polymerization reactions wherein olefins such as mono or diolefins are polymerized to higher molecular weight polymers. Isomerization, although not strictly a polymerization reaction in the sense that higher molecular weight bodies are formed, is included within this term since it occurs along with such polymerization reactions. The term "polymerization" as here used is intended to embrace these types of reactions for building higher molecular weight bodies by reaction of lower molecular weight hydrocarbons. The gasoline produced by this process is termed "polymer" gasoline, and when produced as a mixture with reformed gasoline it is here termed "reformed and polymer" gasoline.

The term "reforming" is intended to embrace the reactions of cracking or decomposition, dehydrogenation and isomerization by which low octane material of gasoline or higher boiling range is converted into gasoline fractions of high anti-knock properties.

The object of this invention is to reform gasoline under such conditions that along with the cracking, dehydrogenating, and isomerizing operations there is a parallel, subsequent, or conjoint polymerizing reaction where the gases formed or added to a reforming operation are converted into polymerized materials, and a blend of reformed and polymer gasoline is formed directly in the process. Broadly stated, the invention consists in reforming liquid hydrocarbons, and particularly hydrocarbons in the gasoline range, to produce hydrocarbons having boiling points in the gasoline range and vapors containing hydrocarbons of five or less carbon atoms, which vapors are polymerized, separately if desired, but preferably in the presence of the gasoline fractions produced by the reforming operation.

The invention also contemplates the addition of hydrocarbons having five or less carbon atoms to the gasoline being polymerized to increase the concentration of these hydrocarbons.

Normally gaseous hydrocarbons such as propane, butane, propylene or butylene may be polymerized. Instead of using the hydrocarbons having four or less carbon atoms, stabilized natural gasoline containing these fractions may be employed. It is preferred, however, to use hydrocarbons of the unsaturated type. Sources of such gases are processes in which gas oil and/or fuel oil are cracked at temperatures below 1000° F.,—that is, in the neighborhood of 850–950° F.

The reforming operation, which is at least partially a combined cracking, dehydrogenating and isomerizing operation, may be aided by choice of conditions of temperature and pressure and rate of feed and by selection of catalysts. In general, high temperatures, short time, and moderate pressures are desirable. Temperatures may

range from 650–1850° F., but the range from 850–1200° F. is preferred. Pressures ranging from atmospheric to 1500 lbs. may be used, but low pressures, as for instance, in the neighborhood of 5–30 atmospheres, are to be preferred. Reforming catalysts for the above process which have been found useful for this purpose are:

Metals.—Nickel, palladium, platinum, copper, cobalt, iron, zinc, titanium, aluminum, tungsten, molybdenum, thorium;

Sulfides.—Cobalt, iron, zinc, nickel, manganese, tungsten;

Oxides.—Alkali metals such as calcium, magnesium, barium, aluminum, chromium, zinc, manganese, silica;

Hydroxides.—Chromium, alkali metal;

Acids.—Molybdic, tungstic, chromic, phosphoric, arsenious, silica, boric;

Salts.—Aluminates, chromates, tungstates, vanadates, uranates, phosphates, of the alkali earth metals such as calcium; and the phosphates, chromates and vanadates of aluminum, chromium or zinc; phosphates of molybdenum, tungsten; ammonium molybdate, aluminum sulfate; adsorbents like fuller's earth, bentonite;

Adsorbent charcoal or other adsorbent carbons;

Halides such as aluminum chloride, iron chloride, aluminum bromide and iron bromide.

When hydrocarbon fractions having a boiling range up to about 600–650° F. are passed over these catalysts at temperatures from 662–1832° F. a reforming reaction occurs. In producing gasoline containing olefinic materials temperatures of about 850–1050° F. may be employed. Higher temperatures in the neighborhood of 1380–1830° F. favor aromatic formation. The salts and oxides of the difficultly reducible metals, as for instance, the alkali metals such as calcium, magnesium, barium, require in general higher temperatures for the formation of olefins, i. e. temperatures in the neighborhood of 1020–1380° F. The gases resulting may then be reacted in the presence of a polymerizing catalyst.

Catalysts which have been found to aid polymerization are termed "polymerizing catalysts." Such catalysts are fuller's earth, absorbent carbon, phosphorous acids such as orthophosphorous acid, and phosphoric acid such as orthophosphoric acid. In solid form, aluminum oxide, calcium oxide, carbonates of the alkaline metals, the oxides and carbonates of magnesium or beryllium, the acids of boron and antimony, thoria, zinc chloride or aluminum chloride, cadmium phosphate, aluminum sulfate in solid form, adsorbent clays like bentonite, graphite, charcoal, copper alkali metal salts (especially oxygen-containing salts), phosphates, borates, antimonates, boron trifluoride, either alone or as a double compound with ethylene in the form of ethylene fluoboric acid, cadmium phosphate, and siliceous earths, tin, zinc, aluminum, chromium, silicon, lead or alloys of these metals.

In using the reforming and polymerizing catalysts, one skilled in the art will understand that the conventional methods of preparing catalysts of this nature are to be followed. Thus, the metals are best used when in finely divided form, and better when supported on carriers. For example, the metal might be formed by reducing the oxide of metal absorbed upon a carrier such as charcoal or silica gel in a stream of hydrogen. These methods are well known and conventional in the catalytic art. The salts or acids are best formed when precipitated on a carrier or fused with a carrier and ground into a fine state. The clays such as bentonite and fuller's earth are best used in their activated states, thus fuller's earth is used in the acid treated state, in which state their adsorptive activity is best brought out. Methods of increasing the adsorptive activity of clays and adsorbent carbon are well known in the adsorption art.

In using catalysts to be carried in the stream of gases, the catalyst, if it is boron fluoride, may be fed as a gas to this stream or mixed in the liquid state at low temperature. If the catalysts are solid they are best ground fine and carried in suspension by mixing with the liquid feed and carried along by the high velocity of the vapors. The solid catalyst may also be positioned as a contact mass in the reaction zone and the vapors passed through the body of catalyst.

The reactions which have been termed "polymerization reaction," and "reforming reaction" are parallel reactions. These reactions are generally reversible, the reaction in one direction being a polymerization reaction, and the reaction in the other direction being a reforming reaction. Consequently, in the polymerization operation and in the reforming operation, all reactions may occur. In general, the polymerization reactions are favored by lower temperatures, while the reforming reactions are favored by higher temperatures, the temperatures chosen should be those at which the desired reaction predominates. The temperature will also vary with the feed stock, particularly upon its boiling range and the chemical type of the feed stock and with the pressure. An additional factor is time. The polymerization reactions and decomposition reactions may proceed further by allowing a longer time of contact with the catalyst. Care must be taken to prevent the reforming reaction from going too far, thus forming light, undesirable fractions, or from allowing the polymerization reaction to form undesirable heavy bodies by too long a polymerization contact time.

Various catalysts promote one or the other reactions favorably, under certain temperature conditions. The temperatures and pressures herein disclosed are merely illustrative and are those at which the various reactions predominate, but the opposite reaction, whether it be reforming or polymerization, also occurs. The temperatures are merely illustrative and are for feed stocks as herein described, and for pressures from atmospheric to 5000 lbs.

Thus, with metal catalysts, tin, zinc, copper, aluminum, chromium, silicon, lead and nickel favor polymerization reactions in the temperature range between 350 and 700° F. Nickel favors the reaction in the lower of the said range, that is, around 350–355° F. These materials favor the reforming operation at higher temperatures. Iron and nickel favor the reforming operation above about 390° F. and in general, iron, nickel, copper, cobalt, zinc, aluminum, chromium favor the reforming operation at temperature ranges above 932° F.

It will be seen that certain of the materials here recited, for example, both zinc and nickel catalyze both reactions, but at lower temperatures, zinc in the range between 350–700° F., and nickel in the range between 355–390° F. favor the polymerization reaction, while the reforming reaction is favored at temperatures above 930° F. In choosing temperatures for polymerization and reforming, using metal catalysts of the nature

shown above, it is preferable that polymerization reactions be carried out at lower temperatures here indicated, and the reforming operations at the higher temperatures, however, by applying higher pressures as hereinafter described, the reaction temperatures are brought closer together and polymerization and reforming may occur together at the same temperature.

Catalytic oxides used for these reactions, such as aluminum oxide either alone or combined with silica in the form of aluminum silicates, for instance, floridin or fuller's earth, favor polymerization in the temperature range between 570 and 750° F. Preferably, aluminum oxide should be used in the neighborhood of from 640 to 700° F. Lime and other alkali earths or oxides or carbonates favor polymerization in the range between 660° F. and 840° F. Magnesium and beryllium oxides favor polymerization reactions in the upper part of said range around 840° F. to 930° F. Aluminum chloride and boron trifluoride are very active at temperatures from 32° F. to 300 or 390° F. Magnesium oxide, lime and silica, such as silica gel, can be used in reforming reactions in temperature ranges above 930–1290° F. Aluminum oxide or aluminum silicate such as fuller's earth or floridin or other forms will favor reforming above 750° F. Thus in using aluminum oxide, either alone or in the form of silicate, the temperature ranges should be adjusted depending on the form of the reaction which is to be favored. In operating in the upper ranges around 750° F. aluminum oxide will have a favorable influence on both reactions, aiding in the decomposition in the higher molecular weight liquid hydrocarbons, and aiding in the lower molecular weight gaseous hydrocarbons. The temperature range should be chosen to form a balance between the two.

Of the salts or adsorbents which accelerate polymerization reaction, the alkli metal carbonates, phosphates and borates are active in the neighborhood of 750–930° F.; bentonite is active from 660–840° F.; phosphoric acid is active from 350–475° F. Absorbent charcoals and carbons favor the polymerization reaction at around 750° F. Above these temperatures, and particularly at substantially higher temperatures reforming is favored by these catalysts. Calcium aluminate, ammonium molybdate favor the reforming operations at temperatures of 930–1290° F. and higher. Aluminum sulfate and phosphoric acid are active in reforming reactions above 660° F. and very active above 930° F.

Mixed catalysts composed of mixtures of any one or more of the above reforming catalysts, and any one or more of the above polymerizing catalysts, which are active, i. e. promote and accelerate the reforming and polymerizing operation in the neighborhood of 700–930° F. will permit of the joint and favorable reactions of reforming and polymerization when operated at temperatures between about 700–930° F. at pressures of about 75–1500 lbs.

Higher pressures favor the polymerization reaction and therefore, by the amplification of pressure, the tolerable temperature for polymerization is increased. At the same time pressure tends to decrease the reforming operation, and the two operations may be brought closer together by the application of pressure. By choosing a temperature intermediate the preferred reforming and polymerization reaction temperature at atmospheric pressure, and applying high pressure in the neighborhood of 1000–5000 lbs. the same catalyst may be used for both reactions. It may be chosen to use a catalyst or catalyst mixtures whose temperature at which they accelerate the reforming operation, and the temperature at which they accelerate the polymerization operation, do not lie far apart. Thus, for instance, one may choose catalysts which are active, i. e. promote or accelerate, in reforming at temperatures in the neighborhood of 840–1060° F., and choose catalysts which are active in, i. e. promote or accelerate, the polymerizing reaction at temperatures ranging from about 570–840° F. at pressures ranging as low as atmospheric.

The liquid gases may be washed with alkali to free them of hydrogen sulfide and they can then be charged. The charging stocks to the reforming operation may contain organic sulfur bodies which will poison the catalyst. One may either remove these bodies or use a catalyst which will not be poisoned in these bodies.

The following of the above referred to catalysts are not easily poisoned by the sulfur and sulfur bodies present in the charging stocks here used. Metals: cobalt, iron, zinc; sulfides of cobalt, iron, zinc, nickel, manganese, tungsten; oxides of chromium, zinc, manganese, aluminium; chromium hydroxide; molybdic, tungstic, chromic, phosphoric, arsenious, silicic, boric acids; phosphates of alkali metals, molybdenum, tungsten; ammonium molybdate, aluminum silicate, fuller's earth.

Water and oxygen and traces of alkali poison aluminum oxide and fuller's earth catalysts. Small percentages of moisture in such catalysts as hereinafter described may be tolerated. Oxygen also poisons aluminum oxide, fuller's earth, and the metal catalysts. Air should be excluded.

A good catalyst for the polymerization reaction is aluminum oxide preferably in the form of fuller's earth or artificial fuller's earth formed by co-precipitating silica and aluminum oxide from a mixture of sodium silicate and aluminum sulfate. The aluminum silicate is washed neutral and dehydrated. It is preferred that the mixture be neutral or acid, and free of alkaline material. It is best that the catalyst be substantially free from water, dehydrated by heating, although a small percentage, up to 5 or 6% of moisture is not detrimental. In using this catalyst it has been found that a small amount of hydrochloric acid introduced as alkyl chloride, as for instance, isopropyl chloride may be introduced to aid the polymerization reaction. Apparently, the isopropyl chloride is decomposed in the reaction zone and forms free hydrochloric acid.

It has been found that the alkyl chlorides are conveniently formed by passing a mixture of unsaturated hydrocarbons such as butylene and propylene over the above fuller's earth type catalysts as previously disclosed at ordinary temperatures from about 200–400° F. the alkyl chloride may be introduced either in vapor form as produced by the chlorinating reaction, or first condensed, and then introduced in liquid form. The amount of alkyl chloride required varies from one-tenth to one percent, preferably to about one-half percent of the reaction vapors.

The catalysts here employed may be used in the reforming or polymerizing processes either as a catalyst body or as a mixture with incoming feed. In using the catalyst as a catalyst body, the reaction zone in the tube or chamber is charged with the solid catalyst and the reaction vapors are passed through the body of the cata-

lyst. It is possible, however, to use the catalyst as a slurry with the incoming feed, in which case the reaction zones are empty except for the reaction mixture. When the vaporized hydrocarbons carrying the catalyst ground fine in suspension pass through the reaction zone, the high velocity of the vapors and the fine particle size of the catalyst prevent sedimentation of the catalyst in the tubes or chambers.

In carrying out the process of this invention the following principles may act as a guide. The feed of liquid fractions is one preferably having an end point not in excess of 650° F. Usually a heavy gasoline fraction boiling between 300–500° F. will prove satisfactory. The reforming, cracking or dehydrogenation is best carried out at a temperature plane higher than that at which the polymerization reaction is carried out. It is desirable also to control these reactions so that they do not proceed to the ultimate stage of carbon, hydrogen and methane formation or to the production of high boiling fractions in the fuel oil range. It therefore will be desirable in one form of this invention to use relatively high temperatures and short times of contact in the reforming zone, and to cool the reaction products produced by the dehydrogenating and cracking reactions before passing them to the polymerization reaction zone. The yield of polymerization products may be increased by adding to the reaction mixture from an extraneous source hydrocarbon materials of five or less carbon atoms. The polymerizing reaction including addition of unsaturates to unsaturates and alkylation in poly-molecular reaction is favorably influenced by increasing the concentration of the reactants. This may be accomplished by increasing the pressure, and also by adding materials undergoing polymerizing reaction to the reformed vapors. These may be cracking still gases, or liquid gas from a gasoline stabilizer tower.

It is desirable to have present unsaturated hydrocarbons such as butenes, propenes and ethylene, the gases may be obtained from the cracking of gas oil or fuel oil at temperatures from 850–1000° F. and preferably, from 900–950° F. The gases are those produced after the cracked gasoline has been removed. Other processes for producing these unsaturates may be employed to produce the unsaturated normally gaseous hydrocarbons here added to the polymerization and reforming operations, as herein described. The saturated normally gaseous hydrocarbons undergo dehydrogenation and polymerization during the reforming operation. The decomposing reactions occur best at low pressures, the polymerization at higher pressures. It therefore may be desirable to increase the pressure in passing through the polymerization stage. The difficulty of compressing hot vapors makes this step practically difficult. It is, therefore, desirable to compress only the cold feed and to operate the whole system under the desired high pressure for the polymerizing reaction. The use of catalysts permits the use of lower pressures for the polymerizing reaction and lower temperatures for the reforming reaction than would be possible without the catalyst.

While the processes of reforming and polymerization are two distinct processes which may be separated the one from the other by careful choice of conditions and catalysts by control of conditions, as previously described, the two processes may be interwoven.

In operating a combination of reforming and polymerization such as, for example, those shown in Figures 1, 2, 3, and 5, where saturated normally gaseous hydrocarbons are introduced into the reforming zone, this reforming may be operated at a relatively high temperature to form larger amounts of unsaturated normally gaseous hydrocarbons in the vapor mixture passing to the polymerization stage. In such a process an active dehydrogenating or reforming catalyst may be employed. The temperatures to be employed may be in the upper portion of the range suggested for the reforming catalyst. Another procedure to be followed in this connection is to carry the reforming on at relatively high temperatures to produce large amounts of gas by extensive cracking of the feed stock. Thus, for instance, in operating on a charging stock composed of crude gasoline of from 450–500° F. end point, the cracking may be carried on to produce large gas yields in excess of 400–500 cu. ft. per barrel of charging stock. These gases, together with any added gas may be passed to the polymerization stage. In this connection the gasoline fractions may be first removed and the lighter gases polymerized or the polymerization may be carried on in the presence of the reformed gasoline fractions.

The cracking and dehydrogenating processes of reforming are reversible reactions, and concomitant with them occur polymerizing and hydrogenating reactions. The unsaturated bodies formed as a result of the cracking and dehydrogenation are extremely active and tend to combine with each other. The light unsaturated gases tend to polymerize with themselves and with the unsaturated higher molecular weight bodies present in the reaction zone. It is therefore possible to combine the reforming and polymerizing processes and to carry on the polymerization of the lighter fractions (five carbon, and particularly four carbon and lower) in the presence of the hydrocarbons within the gasoline range formed as a result of the reforming operation. By such a combined process, the low molecular weight olefinic products of the reforming processes are continuously and progressively removed by polymerization from the reaction zone as they are formed, thus favoring continued reforming of the petroleum hydrocarbons and an increased yield of high octane material over that resulting from a simple reforming operation. The lower molecular weight unsaturated hydrocarbons, particularly those of five carbon atoms and less are polymerized with themselves and are also polymerized by addition of the higher molecular weight liquid hydrocarbons of six carbon atoms and more formed in the reforming reaction, or present in the hydrocarbon material forming the charge to the operation.

If desired, instead of using a mixture of catalysts, the catalytic zones may be separated and the reaction mixture passed separately or alternately over a dehydrogenation and polymerization catalyst. This may be accomplished by passing the mixture through a series of tubes of the nature of cracking tubes connected together by return bends and the tubes filled alternately with a dehydrogenation and a polymerization catalyst in a number of runs so that the mixture is reformed and polymerized in repeated passages over the catalyst. The tubes may be placed in a furnace and the temperature and pressure may be uniform throughout the tubes or the tubes may be placed in reaction zones of different temperatures, the reforming tubes being at higher temperatures than the polymerization tubes. The

reaction mixture is then heated and cooled, first heated to the reforming temperature in the reforming tubes, then cooled to a lower polymerizing temperature in the polymerization zone. If desired, temperature alone may be used to produce the desired reforming and polymerization without using catalysts in the tubes.

While catalytic operations are preferred, certain of the advantages of this operation are preserved in non-catalytic processes thus either the reforming or polymerizing reaction or both may be operated without the aid of catalysts to obtain a great number of the advantages of the operation.

Another arrangement which may be used is to carry out the process in a heated chamber through which are passed cooling tubes. Cracking and dehydrogenating catalysts may be deposited on the warm walls of the chamber, and polymerizing catalysts on the cooler tubes.

If desired, air may be passed with the vapors through the cracking and dehydrogenating zone in such cases where the oxygen or water vapors will not have a poisoning action on the catalyst such as zinc phosphate, in order to remove undesirable gum-forming constituents such as diolefine. Olefins other than those that react readily with free oxygen are not objectionable constituents in gasoline, and their conservation is desirable. Retention of these desirable unsaturated compounds may be accomplished by a controlled polymerizing action which only affects those unsaturates which are most readily polymerized and leaves the others to contribute their high antidetonating characteristics to the fuel.

The process of polymerization and also of reforming results in a product which is composed of a polymer and reformed gasoline fraction of high octane and having an end point of from 300–400° F. depending on operations, a heavy gasoline-kerosene fraction having an end point of about 500–550° F. and a heavy portion. The heavier fractions called "heavy gasoline-kerosene" is recycled. While the figures describe the total return, it will be understood that only a portion may be returned and the remaining portion sent to storage or re-run on blending stock with the polymer and reformed gasoline.

It is therefore an object of this invention to subject kerosene and gasoline and heavier petroleum fractions to a reforming operation in the presence of a reforming catalyst.

It is a further object of this invention to form a reformed and polymer gasoline by subjecting gasoline, kerosene and heavier hydrocarbons to a reforming process and to subject light hydrocarbons to a polymerizing reaction to form a polymer gasoline, and to combine and rectify the two to produce a reformed and polymer gasoline.

It is another object of this invention to subject gasoline and kerosene and heavier petroleum fractions to a reforming operation in the presence of a catalyst which will aid the polymerization of the lighter hydrocarbon fractions, and particularly, those which are normally gaseous in the reforming operation.

It is a further object of this invention to subject gasoline and kerosene and heavier petroleum fractions in the presence of a normally gaseous hydrocarbon to a reforming and polymerization reaction, preferably in the presence of catalysts which will accelerate and aid the reforming and polymerization reactions.

It is a further object of this invention to subject gasoline and kerosene and heavier petroleum fractions to a reforming operation and then to subject the product of the reforming operation to a polymerizing reaction, preferably in the presence of a polymerization catalyst.

It is a further object of this invention to subject gasoline and kerosene and heavier petroleum fractions to a reforming operation, and then to subject the product of the reforming operation in the presence of added normally gaseous hydrocarbons to a polymerization reaction, preferably in the presence of a polymerization catalyst.

It is a further object of this invention to subject gasoline and kerosene and heavier petroleum fractions to a reforming and polymerization reaction in the presence of a reforming and polymerization catalyst under such high pressure conditions and such conditions of temperature that the polymerization and reforming operations are both aided by the presence of the polymerization and reforming catalysts.

It is a further object of this invention to subject gasoline and kerosene and heavier petroleum fractions to a reforming operation and subsequently to a polymerization operation under such conditions of temperature and pressure that the reforming operation is carried out at a higher temperature than the polymerization operation wherein the reformed gasoline composed of gasoline and kerosene fractions, and containing normally gaseous hydrocarbons are subject to a lower temperature for polymerization of the polymerizable hydrocarbons at that temperature and pressure.

This invention will be better understood by reference to the subjoined figures in which:

Figure 1 is a flow sheet showing the polymerization and reforming reactions and providing for withdrawal and the addition of a catalyst at an intermediate point in the reaction;

Figure 2 shows a stage reforming and polymerization reaction in which a promoter is added to the reaction undergoing polymerization;

Figure 3 shows a stage polymerization and reforming reaction wherein provision is made for the control of temperature in the polymerization reaction;

Figure 4 shows a combined polymerization and reforming operation;

Figure 5 shows a design and flow sheet of a combined polymerization and reforming operation and a furnace structure for the control of temperature in the various coils of the furnace;

Figure 6 shows a simultaneous polymerization and reforming operation wherein the polymerization and reforming operations are carried on separately, and the products are combined and treated together.

Figure 1 represents a schematic flow sheet of a combined reforming and polymerization process in which the reforming is primarily conducted in one zone at relatively higher temperature and polymerization in another zone of relatively lower temperature. In Figure 1 gasoline, kerosene, or gas oil fractions having end points under 600–650° F. to be reformed are fed through line 1 by pump 2 through valve 3 and line 4 into the reforming coil 7 in furnace 8. The reforming catalyst may be added before passage to the heating coil through line 5 controlled by valve 6. The mechanism for the addition of the solid catalyst to the oil stream is shown schematically as indicated. Mechanisms for the addition of solid material to liquid being well known in the chemical engineering art. The reforming catalyst may be one of the previously mentioned catalysts or

may be a mixture of reforming and polymerization catalysts. The temperature of the reforming operation will be chosen to correspond with the catalyst used in accordance with the principles hereinabove discussed.

The reforming stream containing the catalysts may be treated in one of two ways. If the prior reforming operation was made in the presence of a catalyst or catalyst mixtures different from those which it is desired to have present in the polymerization zone, the stream is by-passed by closing valve 14 and opening valves 10 and 16. The stream of catalyst and oil vapor is then passed through line 9 and meets oil residuum such as fuel oil entering at 11 to act as a dousing medium to wash out entrained catalysts and separate the vapors from the dousing medium in the separator 12. The temperature maintained in the separator is about 500° F. to insure the vaporization of the gasoline fractions. The mixture of oil and catalyst is removed through valve controlled line 13, and the vapors of gasoline and lighter fractions including the hydrocarbons of four and less carbon atoms, pass through line 15 and valve 16 into line 9. However, if it is desired that the catalyst present in the reforming coil 7 and catalysts entrained in the vapors passing therethrough be also present in the polymerization zone, valves 10 and 16 remain closed and valve 14 is open. In the event the operation in chamber 12 is carried out, additional catalysts may be added through line 17 or provided as catalytic mass in the reactor chamber 29. It may be found desirable to add fresh catalysts to the reaction mixture. Also, in the event that the operation in chamber 12 is not carried out, the reaction mixture passes through line 9' in order to increase the concentration of active catalysts in the reaction mixture.

The reforming operation may be carried out with the omission of catalyst introduction through 5, and the entire reformed mixture may be passed either through 14 or by-passed to 12 and the separated gasoline sent to reactor chamber 29 in the same manner as previously described. The catalyst added through 17 is preferably chosen from among the polymerization catalysts herein previously disclosed. In order to increase the concentration of light hydrocarbons there may be added through line 18 liquid gases produced in the stabilizer 46 as will be hereinafter described. There may be also added at this point liquid gases from an extraneous source through line 21 and pump 22. These gases are preferably propenes, butenes, ethylene, or mixtures of these hydrocarbons with the saturated hydrocarbons of four or less carbon atoms. The mixture is formed in line 9'. In the event that the cooling operation in chamber 12 and the cooling effected by the addition of the liquid material through line 18 and vaporization of this material has reduced the temperature below the chosen reaction temperature, the mixture may be by-passed through line 23 and reheating coil 25 in furnace 8 by the proper manipulation of valves 9a, 24 and 27a. This control heater will then adjust the temperature in line 28 to the proper reaction temperature to be maintained in reactor 29. In the event that the reactor does not contain the mass catalysts in the form of a contact mass in the chamber, it becomes merely a reaction chamber to give reaction time to the mixture. In operating the reactor without the catalyst mass it would be advisable to direct the flow of vapors and entrained catalyst downwardly by adjusting the valves 28a in lines 28 and valved line 29' and valves 31a and 32a in line 31 so that the flow will be downward through the reactor and into fractionator 33. If the catalyst contact mass is used, it may be desirable to flow the vapors upwardly through the reactor and in which case by proper manipulation of the valves 29a, 28a, 31a and 32a, the flow may be properly directed. Gasoline thus formed will result from the reforming reactions operating on the charge to coils 7 and on polymerization of the reformed vapors and gases.

The reformed and polymer gasoline then passes through fractionator 33 containing the usual reflux cooler 42 which may be either internal or external. The heavy fraction, containing the suspended catalyst if this is combined in the vapors is removed from the tower through line 34 controlled by valve 35. The heavy gasoline fraction is removed through line 36, pump 37 for recycling to the reforming operation via line 19 or is removed from the system partially or totally. The reformed and polymer gasoline is removed through side stream take-off 38 into tank 39, passed by pump 40 through heater 41 and line 45 into the stabilizer 46. Uncondensed gas from the fractionator passes through line 43, compressor 43a and line 44 into the stabilizer 46. The gasolines and gas are separated into a stabilized gasoline removed through line 51, valve 52, and cooler 53 and the liquid gas fraction containing butanes, butylenes, propanes, propylenes, some ethane and ethylenes in liquid form pass into tank 56 and circulate by pump 57 through line 20 as previously described. Heat is supplied to the bottom of the tower by circulation from a lower tray through line 47, heater 49, and returned through line 50. The uncondensed and fixed gases are removed through line 54, controlled by valve 55.

The conditions to be maintained in heater 7 and in the reactor 29 are those previously described and must be adjusted for the stock and catalyst employed as will be well understood in the art.

In carrying out the process shown in Figure 1, any one of the catalysts here described may be employed, but the flow will be explained using one of the catalysts merely to illustrate the principle of carrying out the reaction.

It will be understood that the other catalysts may be used with the proper control of temperature and pressure according to the principles hereinabove fully described.

A kerosene fraction having an end point of about 550° F. is passed through line 3 and is intimately incorporated to form a slurry with molybdic acid, molybdenum sulfide, or calcium aluminate, and is heated to a temperature of about 930 to 1290° F. in coil 7. The mixture is then passed through line 9 into chamber 12 in which the catalyst and the oil are withdrawn and the vapors at a temperature of about 450° F. are withdrawn through line 15. Material is added through line 18 and the mixture at a temperature of about 350 to 400° F. is introduced into chamber 29 which is charged with a phosphoric acid catalyst in the form of orthophosphoric acid deposited upon a fuller's earth base. The pressure maintained in the coil 7 and the chamber 29 is about 500 to 1000 lbs.

Figure 2 shows an operation of reforming and polymerization wherein the reactions occur in the presence of an activating material which acts as a promoter to the reaction, or in the presence

of an extraneous material which aids in producing improved characteristics in the final product. As previously described the catalysts may be either added to the material entering the reforming operation or present in the reforming tubes or may be placed in the polymerization reactor. If the gas stream contains catalysts, it passes together with the catalysts through the polymerization reactor. It has been found that on using polymerization and reforming catalysts of the adsorbent clay type, such as fuller's earth or on using base catalysts like aluminum oxide, hydrochloric acid gas or alkyl chlorides which react at the temperature reaction in the presence of these catalysts activate these catalysts. It has been found additionally, that these alkyl chlorides are themselves quite readily polymerized into higher molecular weight hydrocarbons or chlorinated hydrocarbons. While this polymerization is shown as occurring in a catalyzed reaction, the alkyl chloride with or without mixture with the hydrocarbon feed as here shown, may be polymerized in tubes 7 in an uncatalyzed reaction. The action in reactor 29 if desired may be catalytic or the end product of the uncatalyzed polymerization in 7 may be digested to aid polymerization in chamber 29 free of catalyst.

In carrying out the process shown in Figure 2 the feed is described as being made up of gasoline fractions to which may be added the alkyl chlorides. It is of course possible that the feed may be composed of alkyl chlorides alone. However, it is preferred to operate the process in Figure 2 whereby the alkyl chlorides are added to the gasoline and in the event the alkyl chlorides are used as a promoter in the catalytic polymerization reaction they will be added to the reaction mixture entering the polymerization zone. Heavy gasoline or kerosene passes through line 1, pump 2, to be passed with stock added through valve 3 and pass then into line 4 and valve 3 into reforming coils 7 in furnace 8. Alkyl halides may be fed through line 60 and valve 60*a* into reaction coil 7, or in the event that the feed is composed entirely of these halides, material is not introduced in line 1. If it is desired instead of feeding halides through line 60, valve 60*a* may be closed and the halides may be introduced into line 9. Polymerization catalyst is introduced into the stream passed into line 4 as previously described by any well known solid feeding mechanism. The point of introduction should be prior to the introduction of the stream into coil 7 unless the catalyst is contained inside the coils. Reformed material passes through line 9. Before entering line 9 it meets liquid gas introduced through line 18. These liquid gases may be introduced from stabilizer 46 as later described or may come from an extraneous source or may be both. The reactor 29 may be used either as an additional contact catalytic zone in which case the catalyst is maintained in the reactor as a contact mass or the reactor may be empty and merely provide reaction time. The material passes through line 9 controlled by valve 9*a* and through the reactor 29, passes through line 32 and valve 32*a* to fractionator 33. In the event that reaction is completed in coils 7, reactor may be by-passed by closing valves 9*a* and 32*a* and the vapors passed through line 31, controlled by valve 31*a* directly into fractionator 33. In fractionator 33 material is separated into a heavy residual fraction and is withdrawn through line 34. The bottoms are reheated by circulation through lines 23, pump 23*a*, heater 25 and line 27. Incompletely converted gasoline is withdrawn through line 36 and pump 37 to act as recycle stock as previously described. The reformed and polymer gasoline is withdrawn through line 38 into tank 39 and passed through pump 40 and heater 41 to stabilizer 46. The gases uncondensed by cooler 42 pass through line 43, compressor 43*a* into stabilizer 46. In stabilizer 46 the gasoline and gases are separated into a stabilized, reformed and polymerized gasoline which is withdrawn through line 51 and cooler 53. Bottoms are circulated through line 47, heater 49 and line 50 to provide heat in the base of the column. Liquid fractions composed of butane, butylene, propane, propylene, ethane and ethylene are withdrawn in liquid form into tank 56 and passed to line 20 into line 61 as will be hereinafter described. The uncondensed and fixed gases are withdrawn through line 54 controlled by valve 55, cooled and condensed to provide a reflux to column 46. The liquefied gases are withdrawn through line 20 to which may be added from an extraneous source, preferably unsaturated normally gaseous hydrocarbons or mixtures of said hydrocarbons and saturated normally gaseous hydrocarbons. The gases may be separated in the following fashion: A portion may be introduced through line 18 and valve 18*a* as previously described. Another portion may be passed through line 61 controlled by valve 61*a* to the reaction chamber 62 for conversion into the halide.

It has been found that unsaturated hydrocarbons in the nature of propylene, butylene, amylene will react with hydrochloric acid in the presence of activated fuller's earth or aluminum oxide at temperatures from 32–390° F. to form alkyl halide. Propylene will add in the presence of hydrochloric acid at temperatures from 32–390° F. to hydrochloric acid very smoothly. The alkyl chloride thus formed may be introduced into the reaction stream by passing through line 63, valve 64 and line 65. In passing through 65 it passes as a vapor and may be introduced into line 9 to activate the polymerization in reactor 29. It has been found that as much as from one-tenth to five-tenths percent of isopropyl chloride when added to the gases entering the polymerizer reactor chamber 29 accelerates polymerization reaction markedly. The chloride may be passed via line 60 and valve 60*a* into coils 7. Instead of passing the isopropyl chloride as a gas the isopropyl may be condensed by passing through line 63*a*, valve 64 remaining closed to cooler 66, collector 67 and uncondensed gases may be removed through valved line 68; the condensate is fed by pump 69 through valved line 70 as previously described. The hydrochloric acid may be added into the stream entering the reactor 62 through line 71. In operating in the presence of isopropyl chloride, it would be advisable to insure that the gases and liquid are moisture free. Provision will have to be made for separating free hydrochloric acid from the vapors in 54 and from the various condensates withdrawn from the system by treatment with sodium hydroxide.

The catalyst employed may be fuller's earth or aluminum oxide, and preferably, the aluminum oxide formed by the co-precipitation of alumina and silica by the interaction of sodium silicate and aluminum sulfate, as previously described. Reaction chamber 62 is charged with activated fuller's earth or aluminum oxide as previously described. The temperature main-

tained in reactor 62 is as described, under 390° F. Dry hydrochloric acid gas is fed through 71 and alkyl chloride is introduced into line 18. The material entering line 4 is a slurry of the fuller's earth or aluminum oxide and oil. The temperature maintained in reactor 7 is in the neighborhood of 930–1020° F. and the temperature in reactor 29 is from 640–730° F. This temperature is maintained by the introduction of material through 20 or through cooling the gases entering through 9 by an interchanger, as will be understood although not shown in the drawings, or by the control in the reactor 29 as shown in Figure 3. Cooling in line 9 may be provided as shown in Figures 3, 4 and 6. Pressure maintained in reactors 7 and 29 is in the neighborhood of 500–1500 lbs.

Figure 3 shows schematically a combined process of reforming and polymerization process in which separate reforming and polymerization zones are provided. A reforming zone is provided in coil 7 in which coil polymerization may also be effected if desired. Provision is made for the control of the temperature in the polymerization zone 29. The polymerization, being exothermic, the temperature in the reaction chamber 29 tends to rise, and it is desirable to control the temperature to prevent excessive increases in temperature.

Feed is introduced under pressure through line 1 and may pass either through line 1a and valve 2a or through line 1b and valve 1c, or through both to the reforming coils 7. It is preferred, in the event that the feed is a mixed feed containing a wide range of boiling fractions such as gasoline, kerosene and gas-oil, to rectify the feed by introducing it through line 1b and valve 1c into the fractionating chamber 33. In this chamber it meets the hot vapors from the reaction zones and aids in the fractionation of these vapors to form a heavy residual fraction 28 composed of the heavy ends of the charging stock and the heavy ends of the polymerized and reformed gasoline. A side cut of intermediate boiling fractions is removed through line 19b and circulated through line 19 to meet any portion of material by-passed through line 1a if any such is by-passed. If desired, a portion of the liquid gases which are to be polymerized are introduced through line 80 and the mixture is then passed through line 1a, heat exchange coil 3a, line 4 into the reforming coils 7 positioned in furnace 8. At the outlet of coil 7 the reformed gasoline is doused by contact with relatively cold heavy oil such as fuel oil entering through line 11 and the partially cooled gases are then passed through heat exchanger 3b from which point they may be passed directly to the polymerizing chamber 29 via line 9', or first passed through the separator 12. In separator 12 the heavy ends are removed through line 13 and the vapors withdrawn from line 15. The stripping of the bottoms to insure the removal of the gasoline fractions is aided by the introduction of fixed gases such as hydrogen, methane, carbon dioxide or liquid gases used in the polymerization reaction in chamber 12. With some catalysts where steam is either an aid or is not a detriment to the polymerization reaction, steam may be used at this point. A spray of wash oil 12a is passed over the mist extraction and fractionating elements 12b to insure separation of entrained materials and heavy ends of the vapors. Instead of passing the vapors through this chamber, the chamber may be by-passed by proper control of valve 10 in line 9 and valve 9a in line 9' to pass the vapors around the separator. The vapors are then passed to the polymerizing zone 29. Instead of passing the gases through the reforming zone, or in addition to passing the gases through the reforming zone, they may be added to the vapor in line 9' through by-pass line 16 by proper control of valve 16a and valve 80a. The mixed gases and vapors are then passed through line 9' into the reaction zone 29.

In order to control the temperature in the reaction zone 29, the liquid gases may be expanded through spray 81 by proper control of valves 82 and also by circulation of cooling fluid through the cooler 83 via lines 83a and 83b. In operating the separator 12 in such manner that only the light fractions of gasoline are separated, the temperature of the outlet vapors may sometimes be below the desired temperature in the polymerization chamber 29. Thus for instance, the vapors issuing through line 15 may be in the neighborhood of 400–450° F. while the reaction zone may be of a temperature of 600° F. and above. Under those circumstances it may be desirable to heat the reaction chamber 29 instead of cooling it. To do this the cooler 83 may be converted to a heater by circulating a heating fluid through the coils of the cooler 83. This cooler may be of the closed tube sheet type, the cooling fluid circulating out of contact of material in the reaction chamber 29. The gases entering through valves 82 and spray 81 may be heated by passing through valves 84 and 86 and heater 85 by the proper manipulation of valve 87'. Any desired proportion of the gases to be added for polymerization may be added in this way. Such gases thus added are not subject to the reactions occurring in the reforming coils 7. If it is desired to polymerize these gases without subjecting them to the reforming operation all the gases may be introduced in this manner.

The heavy polymers formed in the reaction zone and which are not volatile at the temperature in chamber 29 are withdrawn through 34a and the vapors are withdrawn through line 34 to be passed to fractionator 33. There they pass countercurrent to the feed 1b and the reflux formed by cooling coils 42. In addition to the heavy cut 19b, a reformed and polymer gasoline is withdrawn through the side cut into tank 39 and passed by pump 40 through heater 41 into the stabilizer 46. The uncondensed vapors pass through line 43, compressor 43a into the stabilizer 46. In the stabilizer, the gasoline is separated into a stabilized gasoline, withdrawn through 51 and cooler 53. The bottoms are reboiled by circulation through line 47, heater 49 and return line 50. A liquid light hydrocarbon fraction withdrawn through line 56a into chamber 56 and composed of the fractions containing four or lower carbon atoms, both of the saturated and unsaturated types. Fixed gases are withdrawn through line 54, condenser 54b and recycled as a reflux through line 54a. The liquid gas is circulated through line 20 by pump 57 and meets additional gases through valve 87 coming from storage 89. These liquid gases are similar to those in 20 and are derived from other refinery sources. These gases may be sent through line 88' or 80 as previously described.

In operating the process according to this flow sheet the temperature in coil 7 may be from 600–1000° F. Thus, for instance, it may be operated at about 980° F., cooled by the dousing me-

dium to about 650° F. and further cooled to about 500° F. and separated in 12. Vapor withdrawn through line 15 may be in the neighborhood of 425° F. and the chamber 29 maintained at about 600° F. In employing a catalyst requiring a polymerization temperature of 350–450° F. the reaction chamber is cooled. Catalyst may be omitted in the reforming operation and the temperature then employed may be from 950–1200° F.

The reaction shown in Figure 2 may also be carried out in Figure 3 in which case the reforming catalysts may be fed as a slurry in line 4, separated in chamber 12, and the polymerization catalyst be disposed as a contact catalyst mass in chamber 29. The temperatures and pressures discussed with relation to Figure 2 may be applied to the process of Figure 3.

The catalysts to be used in the reforming operation may be either introduced into line 1a by a feeder as previously described or may be positioned in the coils of reforming coils 7. The reaction chamber 29 may be charged with contact mass catalysts or the catalysts may be introduced into line 9' to pass with the vapors through line 9'. It is preferred, however, in the structure shown in Figure 3, to charge reaction chamber 29 with catalysts.

In the operation according to the flow sheet shown in Figure 4, the polymerization and the reforming operation are carried out in one zone. The feed which consists of kerosene and gasoline fractions containing added thereto propane, butane, propene, butene, ethane, and ethylene produced as previously described, is passed under pressure together with the catalyst, if an entrained catalyst be used, through lines 1 and 20 and through heater exchange 3a, line 4, coil 7 positioned in chamber 8. Instead of using an entrained catalyst I may use coils charged with catalytic mass. Polymerized and reformed gasoline is then doused by contact with heavy fuel oil entering through 11 passed into the heat exchange 3b and through separator 12. The heavy fractions are withdrawn through line 13 and the vapors are passed through mist extractor and fractionator elements 12b and washed with oil introduced through 12a to separate the heavy ends of the vapors. The vapors then pass through line 15 to the fractionator 33 in which the heavy oil is withdrawn through line 28 and vapors refluxed by reflux produced by cooler 42. The polymer and reformed gasoline are withdrawn into side stream receiver 39, and passed by pump 40 through the heater 41 and introduced into the stabilizer 46. The uncondensed vapors through line 43 are also introduced into stabilizer 46 by compressor 43a. In the stabilizer the vapors are separated into a stabilized gasoline, withdrawn through 51 and cooler 53. The bottoms are heated by circulating through line 47, heater 49 and line 50. Reflux is obtained by the condensation of the vapors, withdrawn through by-pass 54, valve 55, condenser 54b and condensate collected in 54' returned through 54a as a reflux. Liquid fraction withdrawn through 56a contains the hydrocarbons ranging from butanes and butylenes, propane and propylenes to ethane and ethylene. These are recirculated through line 20 to be sent to reformer coils 7.

The temperature chosen in Figure 4 in operating with fuller's earth may be in the neighborhood of 840–1020° F.; the pressure in the neighborhood of 500–5000 lbs. The other conditions will follow those described with regard to Figure 3.

In view of the fact that the polymerization reaction using certain catalysts as previously described, operates best at temperatures lower than the reforming operation, the form of heater shown in Figure 5 provides for reaction zones of alternately high and low temperatures in which the reaction mass is first passed through high temperature and then low temperature zones. The reforming catalysts may be positioned in the high temperature zone and polymerizing catalysts in the low temperature zone or the mixed catalysts may be used in both zones. The furnace 8 is divided by vertical partition walls 100 to form chambers 8a and 8b. The coils 7 are positioned in both zones, the flow being first passed through the coils in zone 8a and then zone 8b, and then zone 8a, etc. as shown until the vapors exit. The furnace is heated by burner 101 in combustion tunnel 101a and the gases escape through conduit 102. The combustion gases may be split by proper manipulation of dampers 103 and 104. A portion may be passed through conduit 105 passing into the flue 109 leading to the stack. Combustion air which is also used for cooling the chamber 8b is circulated through conduits 110 and 111 by fan 112 passed through low temperature zone 8b and conduit 113. A portion of the thus preheated air is split by proper manipulation of dampers 114 and 115, and passes through conduit 116 to provide combustion air for burner 101. In this fashion cold air, and if desired, flue gases recycled by the circulation of the portion of combustion stream from conduit 102, is circulated over the coils in chamber 8. Chamber 8b is therefore maintained at considerably lower temperature from chamber 8a. Wall 100 is preferably made of heat insulating material which is suitable for high temperature operation such as fire brick or diatomaceous earth bricks. By proper circulation of air any desired difference in temperature may be maintained. It is understood that instead of passing the reaction material first through the coils in chambers 8a, then through chamber 8b and then through chamber 8a, etc., the vapors may be passed in any number of passes through the coils in chamber 8a, and then to chamber 8b to pass in the chosen number of passes. Thus, the vapors may be passed to chamber 8a to carry on the reforming reaction, and then passed through chamber 8b for polymerization. The gases after exiting from chamber 8b are then treated as shown in Figure 4. It will be understood that the furnace construction and flow shown in Figure 5 may also be used in place of the furnaces shown in Figures 1, 2 and 3.

In operating the reaction in Figure 5, the coils in chamber 8a shall be maintained from 930–1020° F. while the coils in chamber 8b shall be at about 640–720° F. In this case the catalyst may be fuller's earth or activated fuller's earth, or aluminum oxide, or the precipitated oxide previously described.

While the descriptions of the preferred operation in Figs. 4 and 5 are given with relation to catalyzed reactions, the process there described may also be carried out as an uncatalyzed reaction by omitting the catalyst. In the case of Fig. 5 uncatalyzed operation, the temperature plane in zone 8a should be relatively higher in the range of 1000–1300° F. and the temperature in zone 8b should be lower in the range of 750–950° F.

Figure 6 shows a modification wherein the reforming and polymerization reaction is separated, and the polymerized and reformed materials are combined for treatment to produce a blended,

stabilized, polymerized and reformed gasoline. Feed composed of petroleum fractions, for instance kerosene and gasoline, is introduced through line 1, into fractionator 33. A side cut having an intermediate boiling range is withdrawn through line 1a by pump 2 and sent through heat exchange 3a into reforming chamber 7 positioned in furnace 8. Reformed gasoline is then contacted with the dousing oil composed of fuel oil introduced through 11, where it is partially cooled and then passed through heat exchange coil 3b. It meets in line 9 polymerized material introduced through line 90. The mixture of polymerized and reformed gasoline passes into separator 12 and through mist extractor 12b. The heavy ends are withdrawn through 13 and the uncondensed vapors of a temperature from 425–450° F. are removed through line 15, then passed into the stripper and fractionator 33 where, by the aid of the feed 1 and the reboiler 33a and reflux coil 42 in fractionating chamber 33b, it is fractionated into heavy ends 28, recycle stock 1a and the side cut of reformed polymerized gasoline withdrawn through line 39a. Reflux is provided by coil 42. The uncondensed vapors are withdrawn through line 43. The side cut 39a is passed by pump 40 into heater 41 and into the stabilizer 46. The uncondensed vapors are passed by pump 43a, line 43, into the stabilizer 46. In this stabilizer the gasoline is stabilized by the aid of reboiler 46a and reflux provided by the condensation of gases withdrawn through valve 55, line 54 and 54a and condenser 54b. Stabilized gasoline is withdrawn through 51, and liquefied gases containing the butanes, propanes, butylenes, propylenes, ethane and ethylenes pass through line 56a into collecting chamber 56 for recycling by pump 57 through line 20 into line 80. In this line it meets additional like materials through line 87. The commingled gases are then passed into heat exchanger 91a into polymerization coil 91 positioned in furnace 92. The hot gases are doused by mixing with a dousing medium such as gas oil, fuel oil, or kerosene, or gasoline introduced through 93 and passed through heat exchanger 91b and through 90 as previously described.

The reaction coil 7 may be uncatalyzed or catalyzed. If catalyzed, the catalyst may be any one of the reforming catalysts hereinabove indicated. The temperature may be regulated independently of coil 91. The pressure in coil 91 may be independently controlled by regulating valve 90a. The temperature in coil 7 may, depending upon the catalyst, be from 850–1050° F. and the pressures from about 150–500 lbs. If uncatalyzed, the temperature may be between 900–1250° F., while in coil 91, the pressures may be around 500–5000 lbs., and the temperatures from 230–750° F., depending upon the catalyst employed. Any of the polymerizing catalysts previously described may be employed. Mixed catalyst slurry is removed through chamber 12. This will depend on the catalyst and stock chosen as will be understood from what has been said previously. If the reactions in coil 91 are uncatalyzed, the temperature may range from 850°–950° F.

The foregoing description of the several modifications of my invention described above are not to be considered as limiting since many variations may be made within the scope of the following claims by those skilled in the art without departing from the spirit thereof.

The present application is a division of my copending application, Serial No. 35,702, filed August 12, 1935.

I claim:

1. A process for the production of reformed and polymer gasoline which comprises heating at a gasoline reforming temperature in a series of coils in a restricted stream and without separation of vapors a slurry of comminuted catalyst and petroleum hydrocarbons having an end point not to exceed 650° F. and containing gasoline fractions and substantially completely reforming said gasoline fractions, separating the reformed gasoline from the heavier fractions to produce a vapor mixture of gasoline and lighter hydrocarbon fractions including the normally gaseous hydrocarbons, subjecting said mixture to a polymerizing reaction apart from substantial quantities of materials having end points above 650° F. by maintaining said mixture at an elevated temperature for a period of time to cause polymerization of said normally gaseous hydrocarbons, and separating the mixture of polymer and reformed gasoline from said mixture.

2. A process for producing cracked and polymer gasoline which comprises passing a stream of vaporized petroleum stock through a cracking zone, carrying a finely divided catalyst in said stream of hydrocarbons from a point of introduction into said cracking zone to a point remote from said point of introduction, subjecting said vapor in said cracking zone to temperature and pressures adapted to crack said petroleum stock, separating and removing said catalyst in a zone in which no substantial cracking occurs from vapors and gases, commingling said vapors and gases with a second catalyst adapted to polymerize hydrocarbons of four and less carbon atoms contained in said vapors and gases and subjecting said mixture to pressures and temperatures adapted to polymerize said hydrocarbons of four and less carbon atoms and polymerizing said hydrocarbons in the presence of gasoline hydrocarbons formed by said first mentioned cracking and separating cracked and polymer gasoline from said mixture of hydrocarbons.

3. A process for producing cracked and polymerized gasoline which comprises passing a stream of vaporized petroleum stock through a cracking zone into a polymerizing chamber and in said polymerizing chamber, polymerizing gaseous hydrocarbons produced by said passage through said cracking zone and passing an oxygen-containing gas with said vapors passing through said cracking zone and polymerizing chamber to remove by reaction therewith diolefines and other gum-forming constituents from said vapors and gases.

4. A process for producing cracked and polymerized gasoline which comprises subjecting a vaporized petroleum stock to cracking reaction in a cracking zone in the presence of a catalyst which is not poisoned by the presence of oxygen or water vapors, subjecting the products of said cracking reaction to polymerization reaction in a polymerization zone to polymerize gaseous hydrocarbons formed by said cracking reaction, passing an oxygen-containing gas with said vapors and gases through said cracking and polymerization zones to remove by reaction therewith undesirable gum-forming constituents such as diolefines and separating a cracked and polymer gasoline from said reaction products.

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