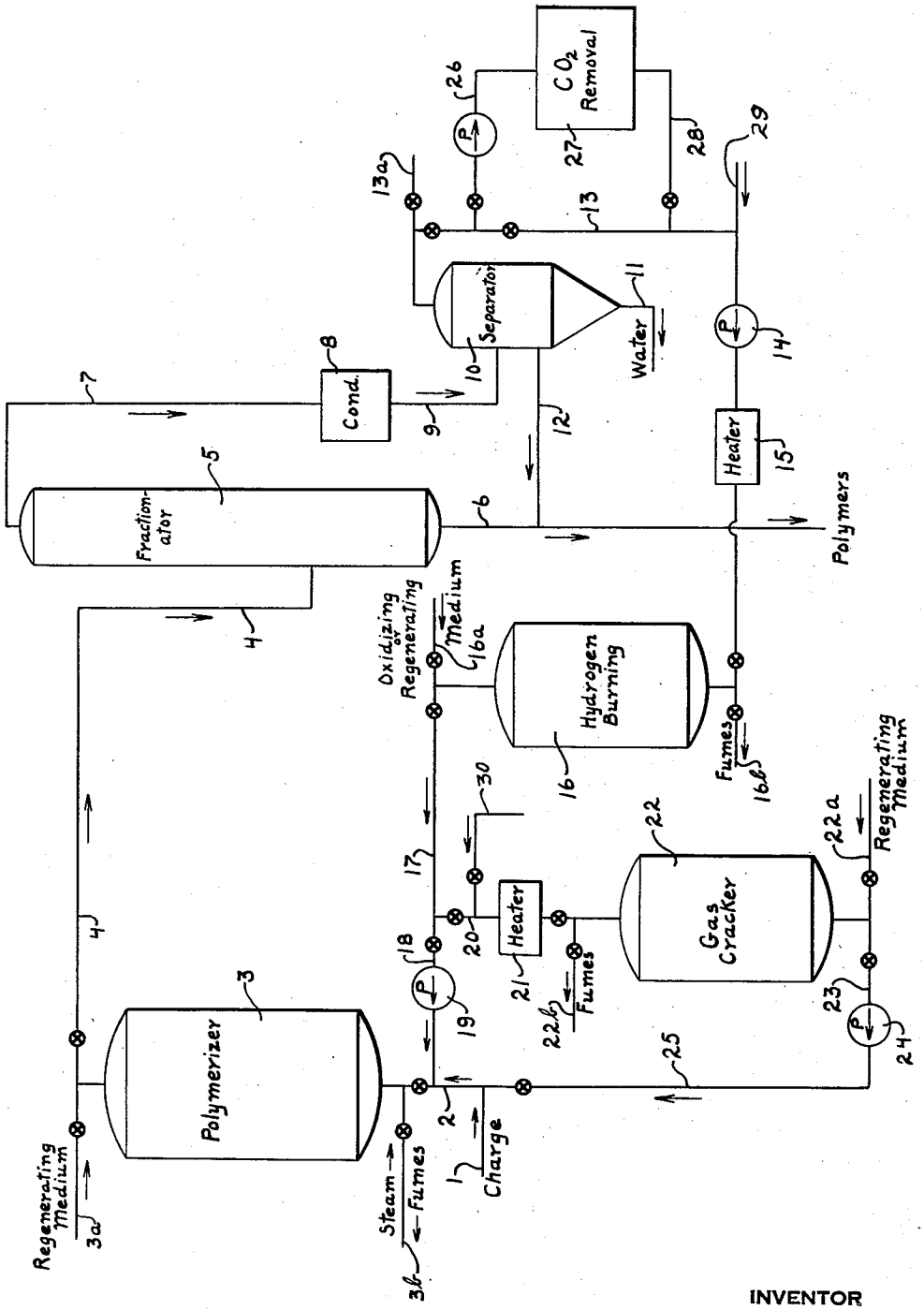
Sept. 3, 1940. E. J. HOUDRY 2,213,247

PRODUCTION OF POLYMER GASOLINE

Filed April 20, 1937



INVENTOR

Eugene J. Houdry

BY

Ira L. Nickerson

ATTORNEY

Patented Sept. 3, 1940 2,213,247

UNITED STATES PATENT OFFICE

2,213,247

PRODUCTION OF POLYMER GASOLINE

Eugene J. Houdry, Haverford, Pa., assignor to Houdry Process Corporation, Wilmington, Del., a corporation of Delaware

Application April 20, 1937, Serial No. 137,900

11 Claims. (Cl. 196—10)

This invention relates to the formation and recovery of liquid polymers from hydrocarbon gases with removal of hydrogen from the circuit and with or without cracking of gases to produce unsaturates capable of polymerization.

One object of the invention is to effect the desired operations wholly or largely in vapor phase and at low or moderate pressures. Another object is to arrange the operations in such order as to effect heat economies. Other objects and advantages will appear from the detailed description which follows.

In order to illustrate the invention and the manner of its use one concrete embodiment thereof is shown in a diagrammatic manner in the single figure of the accompanying drawing.

Fresh charge in the form of hydrocarbon gases containing unsaturates capable of polymerization from any source, as for example, natural gas, ordinary refinery gases and preferably a propane-butane cut from fractionating or stabilizing equipment, may be sent into the circuit by line 1 to be mingled with other material of similar characteristics in line 2, so as to enter the reaction zone of polymerizer 3 under suitable reaction conditions. Polymerizer 3, which may be of any suitable or desired type, discharges its products through line 4 which leads to suitable separating equipment, such as fractionator 5, wherein the liquid polymers in the gasoline boiling range and heavier are removed from the lower end of the fractionator by line 6, while the gases are withdrawn overhead by outlet line 7 which leads to condenser 8. The discharge line 9 from condenser 8 leads to separator 10, from which water may be drawn through bottom outlet line 11 and liquid polymers in a side stream are conducted by line 12 which joins polymer line 6 from fractionator 5. A portion or all of the hydrogen and hydrocarbon gases leaving the top of the separator by line 13 are forced by pump 14 through a heater 15 and thence into the reaction zone of a hydrogen burning case 16. When only a portion of the gases in line 13 are admitted to hydrogen burning case 16, the remainder may be rejected from the system by line 13a. In case 16 the hydrogen is removed from the gaseous stream without the necessity of adding any oxidizing medium to the stream, the burning being effected through the action of catalytic material which promotes the combustion of the hydrogen and supplies the required oxygen. The gases stripped of hydrogen leave case 16 by line 17. A part may be sent by line 18 through pump 19 to be added to the fresh charge in line 2 passing to polymerizer 3. The remainder or all of the gases in line 17 may pass through line 20, through heater 21 and thence under reaction conditions into gas cracking case 22 which operates thermally or catalytically and in which the saturated hydrocarbons are dehydrogenated or cracked to produce unsaturates capable of polymerization. The products of the gas cracking zone are discharged through line 23 and forced by pump 24 into line 25 and then into line 2, to be mingled with the fresh charge or gases entering by line 1 to make up the mixture of gaseous material going to polymerizer 3 and to impart some or all of the heat necessary to bring such material to reaction conditions.

For continuous operation of the system, two or more catalytic units will be provided wherever necessary so that one or more units for each operation may be on-stream, while the other or others are in regeneration. However, to simplify the disclosure, only one unit for each operation is indicated in the drawing. Regeneration in polymerizing zone 3 may be effected by a regenerating medium admitted to one end of the case as by line 3a while the products or fumes of regeneration are withdrawn from the opposite end as by line 3b. The latter line may be utilized during on-stream periods, if desired, for the admission of extraneous material, such as steam, as a diluent, for temperature control, or to minimize coke deposition. Similarly, for the hydrogen burning case 16 an oxidizing or regeneration medium may be sent into the case when not on stream through valved line 16a, while the fumes are withdrawn through valved line 16b. Also, for gas cracker 22 the regenerating medium may be admitted by line 22a and the fumes withdrawn by line 22b. The hydrogen burning step often produces, in addition to steam, which is condensed and removed from the system by line 11, a small amount of carbon dioxide. This gas may be continuously removed from the system by diverting all or a portion of the stream in line 13 through line 26 to CO_2 removal zone 27 of any desired type and then returning the gases freed of CO_2 to line 13 by line 28. If desired, CO_2 removal zone 27 may be operated periodically, as for example, when the accumulated CO_2 content of the gases in line 13 reaches 5 to 10%.

Now that the circuit has been described, attention will be given to details of various elements used therein and the operating conditions necessary to produce the desired results.

The polymerization effected in case 3 is preferentially a gas phase operation in the tempera-

ture range of 600 to 825° F. at low or moderate pressures, as up to about 200 pounds per square inch gauge. The reaction zone is charged with catalytic material, preferably in the form of bits, fragments or molded pieces having selectively adsorptive properties and capable of effecting the desired combining of unsaturated gases to produce liquid polymers, especially those in the gasoline boiling range. Material which will effect up to 50% or more polymerization of unsaturates in a charge presented under the above temperature and pressure conditions comprises blends of silica and alumina from natural or artificial sources, as by chemical or other treatment of clays, or by synthetic production of silica-alumina gels. The rate of feed to the catalytic zone may be in the range of 2 to 25 cu. ft. of gas per hour per liter of catalyst, the preferential range being from 10 to 18 cu. ft. per hour in the preferential temperature range of about 700 to 750° F. and under a pressure of about 100 pounds per square inch. In many instances and with some charging stocks, the addition of steam up to 30% by weight of the charge has little effect in holding down coke deposit and frequently decreases the rate of polymerization. Under proper operating conditions, the coke deposit is low and it is usually possible to remain on stream for periods up to an hour in length. Toward the end of the period, there is frequently a serious falling off in the polymerization rate, in which case it is usually desirable to shorten the on-stream period.

In the polymerizing operation described in the preceding paragraph, there is no adverse effect from the presence of hydrogen in the charge. However, some hydrogen may be released during the polymerizing operation and considerable amounts of hydrogen will be produced during the gas cracking operation in case **22**, so that there will be a tendency for hydrogen to build up in the circuit. Accordingly, the hydrogen burning cases **16** are provided continuously to remove this excess. The burning of hydrogen in cases **16** is effected at low or atmospheric pressure and in the temperature range of 500 to 700° F., preferentially 500 to 600° F. Contact material is utilized which will readily give up oxygen and promote burning with little or no destruction of hydrocarbon material. By using such catalytic material it is unnecessary to add any oxidizing medium, such as air, to the circuit which would increase the quantity of gas in the circuit and would produce oxidation of certain of the hydrocarbons. The oxides of certain metals, such as copper, nickel and manganese, have the desired properties mentioned above, especially when in finely divided form and on or in a suitable porous support. A preferential catalytic mass for the hydrogen burning operation is made up of copper oxide mixed with china clay or kaolin in the weight ratio of about 1:4 and formed in small molded pieces. The rate of feed to the hydrogen burning zone should be within the range of 5 to 30 cu. ft. per hour of gas per liter of catalyst with a preferential rate in the range of 10 to 25 cu. ft. The metallic oxide gives up its oxygen to combine with the hydrogen in the gases to effect burning and produce water, thus reducing the oxide to metallic form. The metal is restored to its oxide form during the regenerating operation by passing air through the catalytic bed.

A good operation for the gas cracking zone in case **22** is one effected catalytically at low pressure and in gas or vapor phase. The catalyst is preferably a blend of chromium oxide and aluminum oxide which may or may not be on a suitable support, such as aluminum silicate. A preferred catalyst is formed from aluminum chromite, aluminum chromate or chromium aluminate incorporated in comminuted form in a support comprising china clay or kaolin and molded in pieces of uniform size and shape to facilitate regeneration. The operating temperature is in the range of 900 to 1000° F. and preferentially in the range of 925 to 975° F. The pressure is kept as low as possible, usually below 30 pounds per square inch. The charge is sent in vapor phase at a rate of 12 to 32 cu. ft. of gas per hour per liter of catalyst. The lower rate is utilized for the lower temperatures in the operating range; for a temperature of 970° F., the feed rate is usually about 25 cu. ft. of gas per hour per liter of catalyst. The percentage of conversion to unsaturates is usually from 17 to 21% per volume of outlet gases or from 22 to 26% by weight of saturates in the charge to the gas cracking zone.

A specific example of the use of the invention is as follows: A refinery propane-butane cut derived from the stabilization of gasoline and containing approximately 23% unsaturates was admitted under a pressure of approximately 100 lbs. per square inch gauge to polymerization zone **3** containing a catalytic mass maintained at about 700° F. and comprising a hydrosilicate of alumina which had been activated by acid treatment. The products from the polymerization zone were separated from unpolymerized or residual gases by fractionation in tower **5** and separator **9**. A portion of the residual gases was heated to approximately 520° F. in heater **15** and sent, under substantially atmospheric pressure and without the addition of oxygen-bearing fluid, to hydrogen burning zone **16** containing a contact mass comprising kaolin and copper oxide in the weight ratio of substantially 4:1. The products from the hydrogen burning zone, which issued therefrom at a temperature of about 600° F., were further heated to approximately 935° F. in heater **21**, and, at that temperature and substantially atmospheric pressure, were subjected in case **22** to the dehydrogenating action of a catalyst comprising essentially a precipitated blend of chromium and aluminum oxides, prepared as chromium aluminate. The reaction products from the dehydrogenating zone were compressed to about 100 lbs./sq. in. and used as cycle stock, sufficient fresh feed being added to bring the mixture to the proper temperature (about 700° F.) for admission to the polymerization zone. During the period of balanced operation, a recycle ratio of dehydrogenated gas to fresh charge of approximately 3:1 was maintained, and the rate of feed of charge to the reaction zones was about 12, 20 and 17 cubic feet per liter of catalyst per hour to the polymerization, hydrogen burning and dehydrogenation zones, respectively.

In this operation, the material issuing from the dehydrogenation zone provided all the sensible heat necessary to raise the temperature of the aforesaid fresh charge from approximately 120° F. to the desired polymerization temperature of 700° F. After establishment of balanced operating conditions, the charge to the polymerizing step contained approximately 19% unsaturates, substantially 90% of which were converted into higher boiling materials, about 55% being higher boiling materials having boiling range and other characteristics of gasoline. The residual gases remaining after fractionation of polymerization

products contained approximately 14% hydrogen which was reduced in the hydrogen burning zone to approximately 2%. The hydrogen burning step produced steam and a small amount of carbon dioxide which were removed from the system after fractionation of products of the polymerizing step. The dehydrogenating or gas cracking operation provided approximately 18% unsaturates and about 17% hydrogen in the material issuing from that zone. The catalyst used in each of the reaction zones was periodically revivified in situ using air as the regenerating medium; the periods between revivifications in the hydrogen burning and dehydrogenating zones were about thirty minutes, while the on-stream or run periods for the polymerization zone were approximately one hour.

From the above it will be apparent that the system of the present invention effects heat economies at several points. When it is in balanced operation, the fresh charge to the polymerizing zone is brought to reaction temperature by the recycled material. After polymerization and fractionation to remove the polymers, the unconverted gases are merely heated up sufficiently to start the hydrogen burning. Instead of using a separate heater as shown in the drawing, the heating can be effected in whole or in part by bringing the charge to this zone into heat exchange relation with the hydrogen burning catalyst in suitable manner, as by heat exchange members embedded in the catalytic mass as indicated, for example, in Patent No. 1,987,636, issued to T. B. Prickett and myself on January 15, 1935, or as indicated in my copending application Ser. No. 78,542, filed May 8, 1936. Thereafter no heat is added except a small amount for the gases which are sent to the gas cracking zone, the products of which are recycled through the system after suitable temperature regulation by the addition of a proper amount of fresh charge. The elimination of hydrogen by selective burning of the same at low temperature with very little or no destruction of hydrocarbons and with a very small production of CO_2 is an important feature of the invention.

In normal operation, fresh charge containing considerable amounts of unsaturates will be added to the system by line 1. If small amounts of gases are available and it is desirable to utilize these in the production of polymer gasoline, any such gases containing saturates and considerable amounts of hydrogen may be sent into the circuit by line 29 in advance of pump 14 and hydrogen burning zone 16. Saturated gases can also be added to the circuit by line 30 in advance of heater 21 and gas cracker 22.

I claim as my invention:

1. Process of producing liquid polymers from lower boiling unsaturated hydrocarbons comprising sending a hydrocarbon charge containing unsaturates under polymerizing conditions into a polymerizing zone, separating the resulting liquid polymers from unpolymerized material, subjecting at least a portion of the latter to promoted combustion in the presence and with the aid of a contact mass capable of supplying oxygen to the combustion simultaneously to effect burning of hydrogen in said unpolymerized material and to increase the temperature thereof toward dehydrogenation temperature, subjecting hot products of said controlled combustion to dehydrogenation effected at higher temperature than said combustion, and adding products of said dehydrogenation to said hydrocarbon charge to raise the temperature of the latter toward that desired for polymerization and to provide a charge to the polymerization zone comprising fresh feed and dehydrogenated material while effecting heat economies.

2. Process of producing liquid polymers from lower boiling unsaturated hydrocarbons comprising sending a hydrocarbon charge containing unsaturates under polymerization reaction conditions into a polymerizing zone, separating resulting liquid polymers from unpolymerized material, effecting controlled combustion of the latter simultaneously to burn hydrogen contained therein and to increase the temperature thereof, subjecting a portion of the products of said combustion at still higher temperature to cracking to produce polymerizable unsaturates, adding hot products of said cracking and another portion of products of said combustion to said charge thereby to utilize heat content of both the cracked and burned materials to raise the temperature of said charge toward that desired for polymerization.

3. In the polymerization of unsaturated hydrocarbons involving dehydrogenation of unpolymerized material to produce unsaturates and recirculation of unsaturates so made through the polymerization zone, the steps comprising separating liquid polymers from unpolymerized hydrocarbons, subjecting the latter successively to hydrogen burning and cracking steps effected at progressively higher temperatures, adding fresh charge containing unsaturates to hot cracked material entering the polymerization zone whereby the heat content of said dehydrogenated material is utilized to adjust to reaction temperature the charge to the polymerization zone, and removing CO_2 from unpolymerized material before it enters the hydrogen burning zone.

4. Process of producing liquid polymers within the gasoline boiling range from a charge of lower boiling hydrocarbons containing unsaturates and saturates which comprises passing said charge into a confined polymerizing zone maintained under reaction conditions, thereby to produce a substantial proportion of higher boiling hydrocarbons by the polymerization of unsaturates or olefins, withdrawing products of reaction from said polymerizing zone and separating higher boiling hydrocarbons comprising components within the gasoline boiling range from the remaining lower boiling gaseous material, effecting removal of hydrogen from the hydrocarbons of said gaseous material under conditions so as to bring about a rise in temperature of said hydrocarbons to a level approaching that desired in a subsequent gas cracking step, then passing the resulting hydrocarbon gaseous material into a confined cracking zone maintained under conditions so as to produce a substantial proportion of unsaturates and so as further to increase the temperature of the hydrocarbon gaseous material, mixing products from said cracking zone with the aforementioned charge, thereby to bring up the temperature of the latter, and passing the resulting mixture into said confined polymerizing zone, thereby to produce a high amount of liquid polymers from the aforementioned charge while effecting heat economies.

5. Process of producing liquid polymers within the gasoline boiling range from a charge of lower boiling hydrocarbons containing unsaturates and saturates which comprises passing said charge

into a confined polymerizing zone containing a solid adsorptive polymerizing catlyst and maintained under conditions of reaction so as to produce a substantial proportion of hydrocarbons within the gasoline boiling range, the temperature of such polymerizing zone being below approximately 825° F., withdrawing products of reaction from said polymerizing zone and separating higher boiling hydrocarbons comprising components within the gasoline boiling range from the remaining lower boiling gaseous material, passing the major proportion of said remaining gaseous material at a sufficient temperature through a confined hydrogen burning zone containing a solid oxide compound which will yield up oxygen in the presence of hydrogen so as selectively to oxidize the latter without substantially affecting hydrocarbons which are admixed therewith, thereby to effect an exothermic removal of hydrogen from the remaining hydrocarbons, withdrawing hydrocarbons from the last-mentioned zone, further heating them and passing them into a confined cracking zone maintained under conditions so as to produce a substantial proportion of unsaturates therefrom and so as further to increase the temperature of the hydrocarbon gaseous material, mixing products from said cracking zone with the afore-mentioned charge, thereby to bring up the temperature of the latter, and passing the resulting mixture into said confined polymerizing zone, thereby to produce a high amount of liquid polymers from the aforementioned charge while effecting heat economies.

6. Process of producing liquid polymers within the gasoline boiling range from a charge of lower boiling hydrocarbons containing unsaturates and saturates which comprises passing said charge into a confined polymerizing zone containing a polymerizing catalyst comprising an adsorptive blend of silica and alumina and maintained under conditions of reaction so as to produce a substantial proportion of hydrocarbons within the gasoline boiling range, the temperature of said polymerizing step being substantially within the range of 600° to 825° F., withdrawing products of reaction from said polymerizing zone and separating higher boiling hydrocarbons comprising components within the gasoline boiling range from the remaining lower boiling gaseous material, passing at least the major proportion of said remaining gaseous material at a sufficient temperature through a confined hydrogen burning zone maintained substantially within the temperature range of 500° to 700° F. and containing as a contact material a solid oxide compound which will yield up oxygen in the presence of free hydrogen so as selectively to oxidize the latter without substantially effecting hydrocarbons which are admixed therewith, thereby to effect an exothermic removal of hydrogen from the remaining hydrocarbons, withdrawing hydrocarbons from the last-mentioned zone, further heating at least the major proportion thereof and passing the resulting further heated hydrocarbons into a confined cracking zone at a temperature substantially above that of said hydrogen burning zone and of at least approximately 900° F., under conditions so as to produce a substantial proportion of unsaturates from the hydrocarbon material charged thereto, mixing products from said cracking zone with the aforementioned charge, thereby to bring up the temperature of the latter, and passing the resulting mixture into said confined polymerizing zone, thereby to produce a high proportion of liquid polymers within the gasoline boiling range from the aforementioned charge while effecting heat economies.

7. Continuous process of producing liquid polymers from gaseous hydrocarbons which comprises subjecting gaseous material containing unsaturates to a catalytic polymerizing operation between 600 and 825° F., removing the liquid polymers so formed from the circuit, subjecting the unpolymerized gases to a hydrogen burning operation induced by a solid contact material which, in the presence of free hydrogen, will yield up oxygen selectively to combine with such hydrogen while leaving the hydrocarbons in said gaseous material substantially unaltered, said hydrogen burning operation being conducted at temperatures below those of the polymerizing reaction and without the addition of an oxidizing medium, subjecting at least a part of the gases from the hydrogen burning operation to a gas cracking reaction at temperatures above those of said polymerizing operation, and mingling hot products of the gas cracking reaction with fresh gases prior to recirculation through the system thereby continuously to present charging material at approximately reaction conditions to said polymerizing operation.

8. Continuous process of producing liquid polymers from gaseous hydrocarbons which comprises subjecting gaseous material containing unsaturates to a catalytic polymerizing operation between 600 and 825° F., removing the liquid polymers so formed from the circuit, subjecting the unpolymerized gases to a selective hydrogen burning operation in the temperature range of 500 to 700° F. and without the addition of any gaseous oxidizing medium, said hydrogen burning being induced by a solid contact material which, in the presence of free hydrogen, will yield up oxygen selectively to combine with such hydrogen while leaving the hydrocarbons in said gaseous material substantially unaltered, subjecting at least a part of the gases from the hydrogen burning operation to a catalytic gas cracking operation in the temperature range of 900 to 1000° F., continuously preparing material for the circuit by mingling fresh gases with the products of said hydrogen burning and gas cracking operations thereby to present to said polymerizing operation a mixture at reaction conditions, and repeating the above operations.

9. Continuous process of producing liquid polymers from gaseous hydrocarbons which comprises subjecting gaseous material containing unsaturates to a catalytic polymerizing operation of the order of 700 to 750° F., removing the liquid polymers so formed from the circuit, subjecting the unpolymerized gases to a selective hydrogen burning operation at a temperature of from approximately 500 to 600° F., said hydrogen burning operation being induced by solid contact material which, in the presence of free hydrogen, will yield up oxygen selectively to combine with such hydrogen while leaving the hydrocarbons in said gaseous material substantially unaltered, subjecting at least a part of the gases from the hydrogen burning operation to a gas cracking operation at 900° F. or somewhat higher, and continuously presenting gaseous material at about 700° F. and under reaction conditions to said polymerizing operation by mingling fresh gases in suitable amount with the products of said hydrogen burning and gas cracking operations.

10. Continuous process of producing liquid

polymers from gaseous hydrocarbons which comprises subjecting gaseous material containing unsaturates to a catalytic polymerizing operation between 600 and 825° F., removing the liquid polymers so formed from the circuit, subjecting the unpolymerized gases to a selective hydrogen burning operation in the temperature range of 500 to 700° F. and without the addition of any gaseous oxidizing medium, said hydrogen burning operation being an exothermic one carried out in the presence of solid contact material which, in an atmosphere of free hydrogen, will yield up oxygen to the extent required for the burning of hydrogen and will selectively catalyze the burning of such hydrogen while leaving the hydrocarbons which are admixed therewith substantially unaltered, subjecting at least a part of the gases from the hydrogen burning operation to a catalytic gas cracking operation in the temperature range of approximately 900 to 1000° F., continuously preparing material for the circuit by mingling fresh gases with the products of said hydrogen burning and gas cracking operations thereby to present to said polymerizing operation a mixture at approximately reaction conditions, the polymerizing operation being effected at a moderate pressure not in excess of 200 lbs./sq. in. gauge while the hydrogen burning and gas cracking operations are effected at low pressures approximating that of the atmosphere, the rate of feed of reactants to all said operations being adjusted to temperature and pressure conditions but at all times being within the range of 2 to 30 cu. ft. of gas per hour per liter of catalyst or contact material.

11. Continuous process of producing liquid polymers from gaseous hydrocarbons which comprises subjecting gaseous material containing unsaturates to a catalytic polymerizing operation of the order of 700 to 750° F., removing the liquid polymers so formed from the circuit, subjecting the unpolymerized gases to a selective hydrogen burning operation at 500 to 600° F., said hydrogen burning operation being an exothermic one carried out in the presence of solid contact material which, in the atmosphere of free hydrogen, will yield up oxygen to the extent required for the burning of the hydrogen and will selectively caalyze the burning of such hydrogen while leaving the hydrocarbons which are admixed therewith substantially unaltered, subjecting at least a part of the gases from the hydrogen burning operation to a catalytic gas cracking operation at 900° F. or somewhat higher, and continuously presenting gaseous material at about 700° F. and under reaction conditions to said polymerizing operation by mingling fresh gases in suitable amount with the products of said hydrogen burning and gas cracking operations, the polymerizing operation being effected at a pressure of about 100 lbs. per square inch gauge while the hydrogen burning and gas cracking operations are effected at lower or atmospheric pressures, the feed rates to the operations being in the range of 10 to 18 cu. ft. of gas per hour per liter of catalyst for polymerization, 10 to 25 cu. ft. per hour per liter for hydrogen burning, and 12 to 32 cu. ft. per hour for gas cracking.

EUGENE J. HOUDRY.