Sept. 15, 1942. G. L. PARKHURST 2,295,752

CONVERSION OF HYDROCARBON GASES AND LIQUIDS TO MOTOR FUELS

Filed June 30, 1938 2 Sheets-Sheet 1

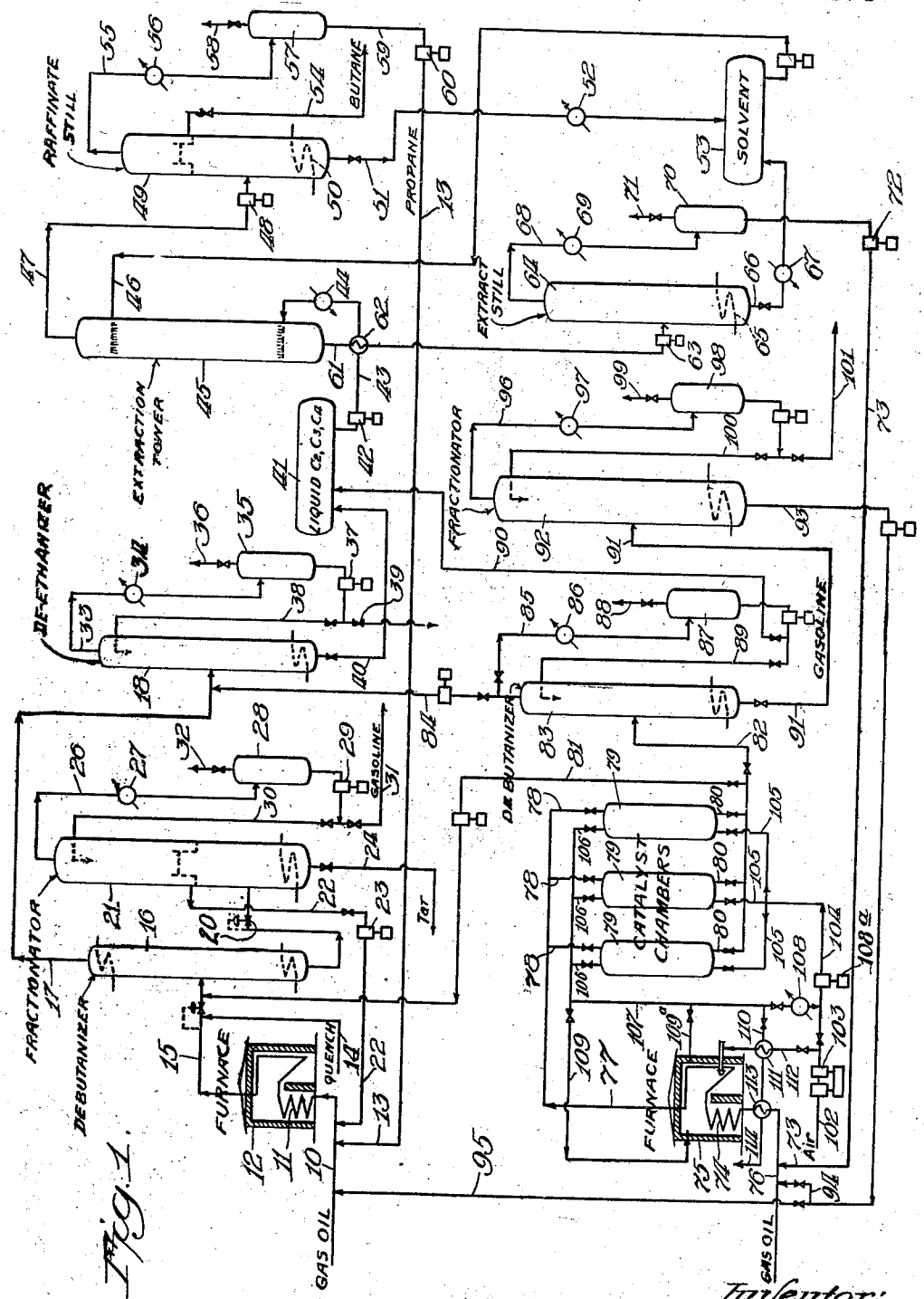

FIG. 1.

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Fig. 2

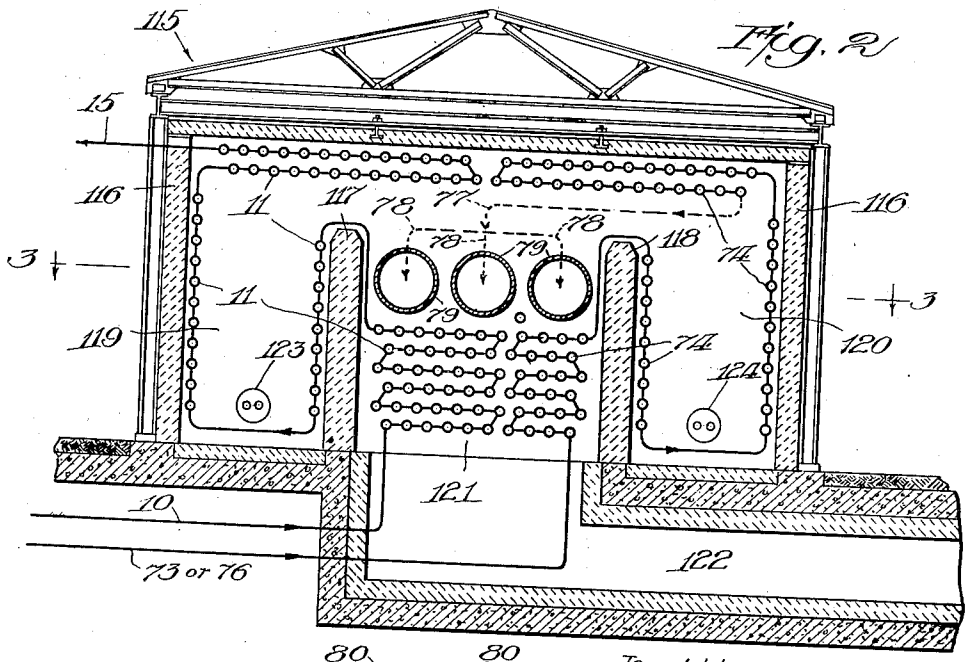
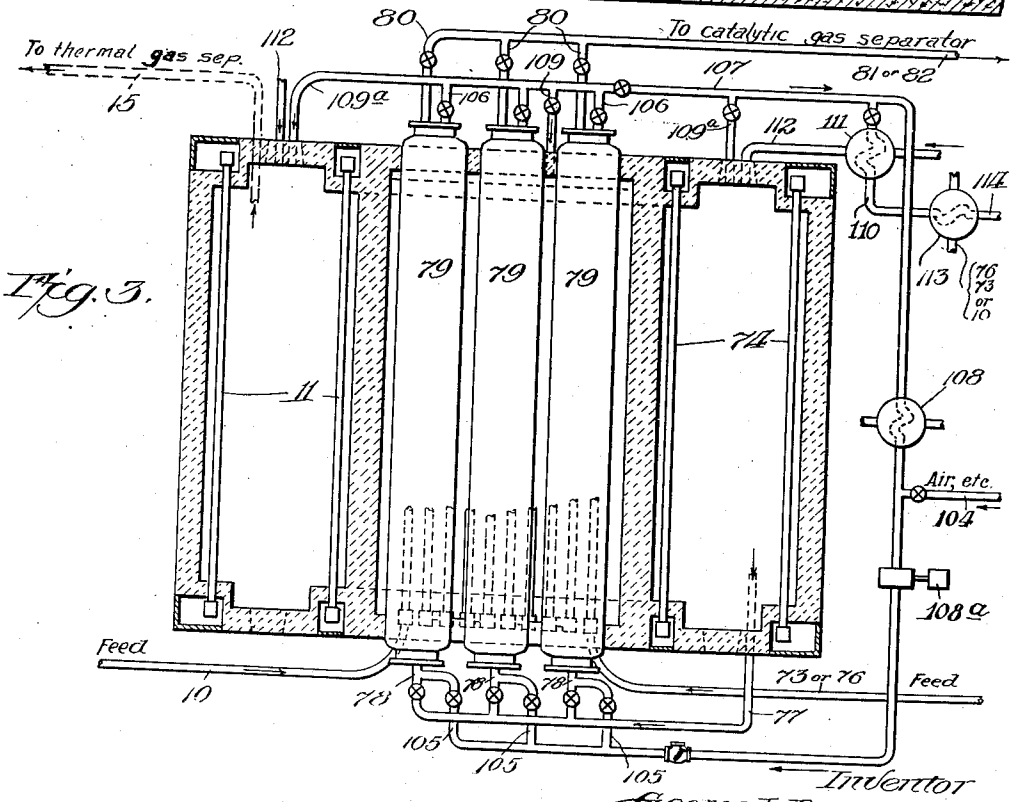


Fig. 3.



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CONVERSION OF HYDROCARBON GASES AND LIQUIDS TO MOTOR FUELS

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Application June 30, 1938, Serial No. 216,707

7 Claims. (Cl. 196—116)

This invention relates to an improved process and apparatus for converting hydrocarbon gases and liquids into high quality motor fuels.

One object of my invention is to increase the quality and yield of gasoline obtainable from hydrocarbon gases, petroleum oils, shale oils, oils obtained from carbonaceous materials by hydrogenation or carbon monoxide synthesis, etc.

A further object is to provide an improved method and means for utilizing both liquid and gaseous hydrocarbons in the most effective and efficient manner in the production of large yields of high octane number gasoline. A still further object is to provide a flexible integrated unit adapted to process all types of hydrocarbon materials, in which unit each of the materials is processed under conditions most suitable for that material.

Another object is to provide an improved combination of systems for converting hydrocarbon gases and liquids into motor fuels and for separating hydrocarbon gases into paraffinc and olefinic fractions so that each fraction may be converted in the system most suited to that fraction. It is also an object to provide an integrated gas conversion unit including both thermal and catalytic systems, wherein one of said systems may be used for polymerization while the other system is used for gas reversion, the products from each system being fractionated on the basis of relative saturation (i. e. into olefins and paraffins) as well as on the basis of boiling point. A further object is to provide an improved and integrated unit for separately processing mixtures containing normally gaseous components and for blending both the liquid and the gaseous reaction product for the most effective utilization thereof.

It is also an object of the invention to provide an improved method and means for utilizing the heat of catalyst regeneration to supply a part of the heat required for catalytic or thermal conversion. Other objects will become apparent as the detailed description of my invention proceeds.

Thermal gas reversion or polymerization is capable of utilizing paraffinic gases in the manufacture of gasoline, while catalytic gas reversion or polymerization can best utilize the olefinic gases. In practising my invention I combine a catalytic gas reversion system with a thermal gas reversion system, segregate the C_2 to C_4 hydrocarbons (hydrocarbons having from two to four carbon atoms per molecule) from the reaction products produced by each system and then fractionate these C_2 to C_4 hydrocarbons on the basis of their saturation, the paraffinic fraction being returned to the thermal conversion process and the olefinic fraction being returned to the catalytic conversion process. Since butanes are valuable components of gasoline I prefer to segregate the butanes from the propane and ethane and only return the latter hydrocarbons to the thermal conversion process, keeping the butanes for blending with the final fuel. The butylenes, propylene and ethylene are returned to the catalytic conversion process where they are most effectively utilized for the production of high quality motor fuel.

My combination of systems comprises a thermal gas reversion system wherein normally liquid hydrocarbons are reacted with propane at a temperature of about 1000 to 1150° F., and wherein the C_2 to C_4 fraction of the reaction products is segregated from the other components of the reaction mixture. The combination also includes a catalytic system wherein olefinic hydrocarbon gases are reacted with normally liquid products in the presence of a catalyst to effect their conversion into motor fuel. The C_2 to C_4 fraction from the gas reversion processes usually contains large amounts of paraffinc hydrocarbons and in such cases I combine the C_2 to C_4 fraction from the thermal system with the C_2 to C_4 fraction from the catalytic system, and separate the paraffinc from the olefinic gases in the combined fractions by means of a selective solvent such as phenol, cresylic acid, nitrobenzene, furfural, dichlorethyl ether, sulfur dioxide, etc. From the raffinate which consists essentially of paraffinic hydrocarbons I segregate the butane and return the propane and ethane for further thermal treatment. The unsaturated hydrocarbons which are freed from the solvent are recycled to the catalytic conversion process.

In the catalytic gas reversion process it is necessary from time to time to regenerate the catalyst by burning the carbon therefrom under controlled temperature conditions. From the standpoint of heat economy it is essential that the heat so generated be utilized and in practising my invention I utilize this heat directly in either the thermal or catalytic furnace. I prefer to mount the catalyst chambers in the convection section of the furnace above the convection tubes and at a point at which the temperature conditions are approximately those required for catalytic gas reversion. The hot regeneration gases may be employed for heating air or fuel charged to the furnace, it may be introduced directly into the combustion chamber

of a furnace, or it may be introduced into the convection section for maintaining the temperature of the catalyst chambers and to supply heat in the convection furnace coils.

The invention will be more clearly understood from the following detailed description read in connection with the accompanying drawings which form a part of the specification and in which similar parts are designated by like reference characters. In these drawings:

Figure 1 is a flow diagram of my improved gas gas reversion unit;

Figure 2 is a vertical section through a combination thermal-catalytic furnace showing the position of the catalyst chambers in the convection section; and

Figure 3 is a horizontal section of the furnace shown in Figure 2.

My invention will be described in connection with the manufacture of high octane gasoline from Mid-Continent gas oil and ordinary refinery gases, particularly cracking still gases. It should be understood, however, that other liquid charging stocks may be employed, ranging from heavy naphthas to stocks which are even more viscous than gas oils. The gaseous hydrocarbons may be obtained from natural gas or from any other source of paraffinic or olefinic C_2 to C_4 hydrocarbons.

Gas oil is charged to the system through line 10 to the coils 11 of thermal conversion furnace 12 under a pressure of about 500 to 3000, preferably 1000, pounds per square inch. A liquefied gas mixture consisting chiefly of propane, but also containing some ethane and butane is introduced through line 13 into line 10 or into another bank of tubes in the thermal conversion furnace, in which case the separately heated gases are preferably combined with the heated gas oil charge at incipient gas reversion temperature. The mixture is then raised to gas reversion temperature—about 1000 to 1150° F., preferably 1050° F. The reaction time is relatively short, and in order to prevent undesired side reactions I prefer to introduce a quench oil through line 14 to transfer line 15 at the point wherein the pressure is reduced to about 250 to 350, preferably about 300, pounds per square inch prior to the introduction of the reaction mixture into debutanizer tower 16.

The relative proportions of gas oil and liquefied gas may be varied throughout a relatively wide range—I prefer to employ equal parts by volume, but the amount of liquefied gas may range from 10% to 200% of the volume of the liquid charging stock. The amount of quench oil is usually rather small, about 5% to 10% of the combined charging stocks. The quench oil is preferably a gas oil, a portion of the charging stock or a cycle oil produced as hereinafter described.

Debutanizer tower 16 is preferably operated with a bottom temperature of about 850 to 900° F. and at a pressure of about 250 to 350, preferably about 300, pounds per square inch. By providing a sufficient amount of cooling in the upper part of this tower, either with cooling coils or by the introduction of a reflux liquid, as sharp a fractionation as possible is made between hydrocarbons from C_1 to C_4 and hydrocarbons heavier than C_4. The C_1 to C_4 fraction is withdrawn through line 17 to deethanizer tower 18 which is also operated at this high pressure. The heavier fraction is withdrawn through pressure-reducing valve 20 to fractionator 21, which is preferably operated at about atmospheric to 50 pounds per square inch pressure, with a bottom temperature of about 750 to 900° F. Cycle stock is withdrawn as a side stream through line 22 and is returned by pump 23 back to line 10 for admixture with the gas oil feed, or preferably to the particular coils in the furnace in which the oil is at about the temperature of the recycle oil. Tar is withdrawn from the base of the fractionator through line 24. It should be understood, however, that instead of using a single tower for separating tar and gas oil I may employ a separate tar flash tower, and withdraw the gas oil and gasoline fractions from the top of the tar flash tower to a bubble tower fractionator.

The temperature in the top of fractionator 21 is regulated by cooling coils or the introduction of reflux to take over substantially all of the gasoline fraction and to return substantially all of the gas oil as hereinabove described. The gasoline vapors are withdrawn through line 26 to condenser 27 and receiver 28 from which a portion of the condensate may be recycled by pump 29 and line 30 as reflux, and a portion withdrawn through line 31 for storage or blending. Uncondensed gases from receiver 28 may be withdrawn through line 32 to a suitable holder and/or compressed and introduced into the liquefied gas storage tank which will be hereinafter described.

As hereinabove described, the C_1 to C_4 fraction is introduced into deethanizer tower 18 at a pressure of about 300 pounds per square inch. The bottom temperature of this tower may range from about 150 to 250° F. but the top is preferably maintained at about 100° F., by the use of cold reflux. Methane and ethane are withdrawn from the top of the deethanizer through line 33, partially condensed in cooler 34 and then introduced into receiver 35, the methane with some of the ethane being vented to suitable gas lines through valved line 36, and the liquefied ethane being returned by pump 37 either to reflux line 38 or liquefied gas draw-off 39. The C_3 and C_4 hydrocarbons, with perhaps small amounts of C_5 and C_2 hydrocarbons are withdrawn from deethanizer 18 through line 40 to liquefied gas storage tank 41. The gases in this storage tank consist essentially of a mixture of ethane, ethylene, propane, propylene, butane, iso-butane, butene-1, butene-2, iso-butylene and perhaps a very small amount of C_5 hydrocarbons. The exact composition will vary throughout a relatively wide range, but it will usually be about 20% to 50% olefins.

In order to separate the paraffinic from the olefinic liquefied gases I introduce the liquefied gases by pump 42, line 43 and heat exchanger 44 to solvent extraction tower 45 in which the liquefied gases are passed counter-current to a selective solvent which is introduced in the upper part of the tower through line 46. The temperature and pressure conditions in the tower will depend upon the particular solvent employed. I prefer to use phenolic solvents such as phenol, cresylic acid, cresols, etc., or chlorinated phenolic solvents such as monochlorphenol, although it should be understood that any selective solvent may be used if the proper conditions are provided to effect the desired phase separation. The phenolic solvents may be used at about room temperatures and they offer the advantage of being easily separable from the extract and raffinate respectively, in the solvent recovery systems. Sulfur dioxide is an excellent solvent but its boiling range is so close to that of the gases

that separation is difficult. Chlorex (dichlorethyl ether), nitrobenzene, furfural, chloraniline, etc. are further examples of solvents which may be used.

Raffinate from the extraction tower is withdrawn through line 47 and introduced by pump 48 into raffinate still 49 which is provided with a suitable heating means 50. The solvent is withdrawn from the base of the still through line 51 and cooler 52 to solvent storage tank 53. Since butane and pentanes are valuable components of motor fuels, such products are preferably removed as a side stream through line 54. The remaining paraffinic gases which consist chiefly of propane, smaller amounts of ethane and butanes are withdrawn from the top of the tower through line 55 and condenser 56 to receiver 57, uncondensed gases being vented through line 58, and the condensed paraffinic gases being returned through line 59 by means of pump 60 to line 13 and furnace coils 11.

The extract from tower 45 is withdrawn through line 61 and heat exchanger 62 and is forced by pump 63 into extract still 64 which is likewise provided with suitable heating means 65. Solvent from the extract still is returned through line 66 and cooler 67 to solvent storage tank 53. The olefinic gases from the top of extract still 64 are withdrawn through line 68 and conductor 69 to receiver 70, the uncondensed gases being vented through line 71.

Condensed olefinic gases from receiver 70 are introduced by pump 72 and line 73 into coils 74 of furnace 75. This furnace may be either a gas reversion, alkylation or polymerization furnace. If it is employed for gas reversion, gas oil is introduced through line 76 and the mixture of gas oil with olefinic gases may be passed through the entire furnace concurrently or they may be heated in separate coils and combined after they have reached a temperature of incipient gas reversion, which for catalytic gas reversion is about 800 to 900° F.

In transfer line 77 the temperature is maintained at about 800 to 1000° F., preferably at about 900° F. At this temperature the mixture is introduced through one or more of the lines 78 into one or more of the catalyst chambers 79. The catalyst chamber is preferably a cylindrical vessel packed with any conventional catalyst such as activated hydrosilicate of alumina or acid-treated clay which has been formed into pellets and dried at a temperature of about 1000 to 1050° F. Examples of suitable clays include bentonite, Olmstead clay, Attapulgus clay, Death Valley clay, Floridin earth, montmorillonite, Filtrol, fuller's earth, etc. Synthetic clays may be prepared by precipitating sodium silicate with hydrochloric acid, washing free from chlorides, and impregnating with a solution of a salt of copper, cadmium, or nickel, boric acid or other solutions of metal salts or acids, the catalyst then being dried. Butyl bromide or other alkyl halides or halogen acids may be used as promoters or as homogeneous catalysts, either alone or in conjunction with the heterogeneous catalysts hereinabove described. I do not limit myself to any particular catalyst and any known gas reversion catalyst may be employed.

As hereinabove indicated, my process is not limited to gas reversion in the catalyst chambers—I may employ these catalyst chambers for polymerization, alkylation or other known conversion processes which utilize olefinic hydrocarbons and hydrocarbon gases for the production of motor fuels.

If polymerization is to be effected an excellent catalyst is phosphoric acid on kieselguhr or clay, and with such a process and catalyst the temperature in transfer line 77 will be maintained at about 250 to 600° F., preferably about 450° F. and pressures of 100 to 1000 pounds per square inch. The gas oil charge is, of course, omitted.

For alkylation I may employ sodium aluminum chloride, phosphoric acid etc. as catalysts at a temperature of about 300 to 500° F., preferably 400° F. and pressures of 750 to 2000 pounds per square inch. A suitable liquid charging stock can be introduced through line 76 if desired.

In accordance with conventional practice one catalyst chamber is on stream while others are being purged, revivified or recharged. The reaction products leave the chambers through lines 80 and thence through line 81 to debutanizer 16 or through line 82 to debutanizer 83. If a separate debutanizer 83 is employed it may be operated at about atmospheric to 50 pounds per square inch pressure with a bottom temperature of about 400 to 450° F., sufficient cooling or reflux being provided at the top to knock back any appreciable amounts of C_5 or heavier hydrocarbons. The C_4 and light hydrocarbons may be withdrawn from the top of this debutanizer through line 84 and introduced into deethanizer 18. It will be understood that if gases are transferred through lines 81 and 84 to debutanizer 16 or deethanizer 18, respectively, suitable compressors must be employed to boost the gas pressure to the required pressure.

Alternatively, the overhead from debutanizer 83 may be withdrawn through line 85, partially condensed in cooler 86 and introduced into receiver 87, the methane and other uncondensed gases being vented through line 88, a part of the condensate being returned through line 89 for use as reflux, and the remainder of the condensate being introduced through line 90 to the liquefied gas storage tank 41.

The heavy fractions from the base of debutanizer 83 are withdrawn through line 91 to fractionator column 92 which may operate under about the same conditions as tower 21. Since the catalytic process produces substantially no tarry materials, the bottoms from this fractionator may be recycled through line 93 and 94 to the coils 74 in furnace 75 or preferably through line 95 to the coils 11 of furnace 12.

The overhead from fractionator 92 is withdrawn through line 96, condenser 97 to receiver 98, uncondensed gases being vented through line 99 to storage and/or compressed and introduced into liquefied gas storage 41. A part of the condensate from receiver 98 may be recycled through line 100 as reflux and the rest of it withdrawn through line 101 to storage or for blending.

From the above description it will appear that I have produced three different stocks for blending purposes: gasoline from the thermal conversion process (line 31), gasoline from the catalytic conversion process (line 101) and butanes from the raffinate still (line 54). These three products have very different characteristics and may be blended in any desired amounts to produce motor fuel for particular purposes.

It should also be noted that any pentanes which are not knocked back in the debutanizers are eventually recovered with the butanes from the raffinate still (line 54) before the gases are re-

cycled. The withdrawal of butanes and pentanes at this point effects a material savings in operating costs and provides valuable components in the final motor fuel blend.

Referring back to the catalytic conversion step—since most catalysts tend to lose their effectiveness after a certain period of use because of the deposition of carbon thereon, I revivify the catalyst periodically by burning out this carbon with air at a temperature which depends on the nature of the particular catalyst and which in the case of the hydrosilicate of alumina is preferably about 1000, but not above 1050° F. Air from line 102 is forced by blower 103 through line 104 and the proper line 105 to the catalyst chamber undergoing revivification, the combustion gases being withdrawn from the chamber through line 106 and recycled through line 107 and heat exchanger 108 by means of supplementary compressor 108a. The recycled gases are cooled in heat exchanger 108 and mixed with incoming air in such proportions as to maintain the desired temperature during the revivification step.

Since large amounts of the hot gases are not required for recycling, I may utilize the heating value of such gases by introducing them through line 109 to the convection section or line 109a to the radiant section of furnace 12, as will hereinafter be described. When the gas contains large amounts of carbon monoxide or other combustible material, it may well be introduced into the radiant section through line 109a, but ordinarily full advantage and benefit may be taken of the sensible heat of these gases by introducing them into the convection section through line 109. Also, or alternatively, I may pass such hot gases through line 110 and heat exchanger 111 to preheat incoming air which passes through line 112 to the furnace burners. The hot gases may also, or alternatively, be passed through heat exchanger 113 to preheat incoming charging stock to the furnace, the final cooled gases being vented through line 114. It should be understood that heat exchangers 111 and 113 may be used in place of heat exchanger 108, i. e., the recycle gases may be used to preheat air for supporting combustion or to preheat charging stock.

The gases which are not used for recycling are preferably introduced into the convection section of the furnace where the heat may be absorbed by the convection tubes and/or by the catalytic reactors which may be mounted in such section as shown in Figures 2 and 3.

Instead of building furnace 12 and furnace 76 as independent and separate units, they may be built as a single furnace 115 (Figures 2 and 3). Between outer walls 116 are transverse baffles 117 and 118. Space 119, between baffle 117 and the outside wall, forms the radiant section for the thermal heating step. Space 120, between baffle 118 and the outside wall, forms the radiant section for the catalytic heating step. Space 121, between baffles 117 and 118, may serve as a convection section for both the catalytic and thermal heating steps, and since the temperature at the top of this zone is about that which is employed for catalytic gas reversion, the catalytic reaction chambers may be mounted in this convection section of the combination furnace. The flue gases leave the bottom of the convection section through flue 122. Heat is supplied for the thermal radiant section by burner 123 and to the catalytic radiant section by burner 124.

By mounting the catalytic reaction chambers in the convection section of the furnace I avoid the expense of insulation which would otherwise be required and at the same time I obtain effective temperature regulation because this section of the furnace is held at substantially constant temperature. The hot gases which have been used to burn carbon from the catalyst chambers may be passed directly into the convection section through line 109 or into one or both radiant sections through line 109a, as shown in Figure 3, or they may be used to preheat incoming air for supporting combustion, or to preheat charging stock.

By employing a common convection section for both the thermal and catalytic heating systems I may connect any number of tubes in the section with the system, and as shown in Figure 2, the thermal conversion heating step usually requires more tubes than the catalytic step.

It will thus be seen that the thermal and catalytic systems are integrated and interdependent in the heating step, as well as in the gas recovery and fractionation steps and the solvent extraction step. An outstanding feature of this combination is the treatment of gases from both the catalytic and thermal process in a common extraction system, so that the paraffinic gases may be returned to the thermal process and the olefinic fraction to the catalytic process, respectively. By employing the solvent extraction step in conjunction with the inter-related conversion processes I can return those fractions to each system which are best adapted for conversion in that system. This is a feature of the invention which is impossible of accomplishment by any of the recycling system heretofore known.

While I have described in detail a preferred embodiment of my invention, it should be understood that I do not limit myself thereto except as defined by the following claims which should be construed as broadly as the prior art will permit.

I claim:

1. In apparatus of the class described, a furnace containing a radiant section and a convection section, heating coils in said radiant section, a plurality of catalyst chambers mounted in said convection section, means for passing hydrocarbons first through said coils and thence through said catalyst chambers, means for burning carbonaceous materials from spent catalyst in said chambers thereby producing hot gases, and means for utilizing the heat of said hot gases in the radiant section of said furnace.

2. The apparatus of claim 1 which includes means for fractionating products leaving the catalyst chambers and for separately recovering a motor fuel fraction and a C_2 to C_4 fraction, means for solvent extracting said C_2 to C_4 fraction and for separately recovering paraffinic and olefinic C_2 to C_4 fractions, respectively, and means for returning said olefinic C_2 to C_4 fractions to the coils in said radiant section.

3. A hydrocarbon conversion system which comprises a furnace provided with a radiant section and a convection section, a bank of tubes in said radiant section, a bank of tubes in said convection section, a plurality of catalyst chambers in said convection section, means for connecting said tubes and said catalyst chambers whereby hydrocarbons may be passed through the tubes in the convection section and the tubes in the radiant section respectively and then introduced into one of said catalyst chambers, means for transferring the introduction of hydrocarbons from said tubes into another of said catalyst

chambers when the catalyst in one of said chambers has become spent, means for introducing an oxygen-containing gas into the catalyst chamber which has become spent whereby hot regeneration gases are formed in said spent catalyst chamber and means for introducing said hot regeneration gases into the radiant section of said furnace.

4. In a hydrocarbon conversion system a pipe still furnace having a radiant section, a plurality of tubes in the radiant section of said furnace, a plurality of catalyst chambers, means for connecting said tubes with one of said catalyst chambers whereby hydrocarbons pass first through said tubes and thence into one of said catalyst chambers, means for transferring the introduction of hydrocarbons from said tubes to another of said catalyst chambers when the catalyst in one of said chambers has become spent, means for regenerating the spent catalyst in said chamber whereby hot regeneration gases are produced and means for transferring heat from said hot regeneration gases to said tubes in the radiant section of said furnace.

5. The apparatus of claim 4 wherein the furnace contains both a radiant section and a convection section and wherein the catalyst chambers are mounted in said convection section.

6. In a hydrocarbon conversion system a furnace provided with a radiant section and a convection section, banks of tubes in said radiant section and said convection section respectively, a plurality of catalyst chambers, means for connecting said tubes and said chambers whereby a hydrocarbon may be passed through said tubes and thence into one of said catalyst chambers, means for transferring the introduction of said hydrocarbon from said tubes into another of said catalyst chambers when the catalyst in one of said chambers has become spent, means for regenerating spent catalyst in said chambers whereby hot regeneration gases are produced and means for transferring heat from said hot regeneration gases to the tubes in the radiant section of said furnace.

7. In a hydrocarbon conversion system a pipe still furnace, a plurality of tubes in said furnace, a plurality of catalyst chambers, means for connecting said tubes with one of said catalyst chambers whereby hydrocarbons pass first through said tubes and thence into one of said catalyst chambers, means for transferring the introduction of hydrocarbons from said tubes to another of said catalyst chambers when the catalyst in one of said chambers has become spent, means for regenerating the spent catalyst in said chamber whereby hot regeneration gases are produced, a heat exchanger, means for passing said hot regeneration gases through said heat exchanger, means for passing air through said heat exchanger to be preheated by said hot regeneration gases and means for introducing said preheated air into said furnace for supporting combustion therein.

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