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COMPLETE SPECIFICATION

Improvements in or relating to Gasoline Hydrocarbons and Process for the Manufacture thereof

I, ARTHUR HAROLD STEVENS, a British Subject, of the Firm of Stevens, Langner, Parry & Rollinson, Chartered Patent Agents, of 5/9, Quality Court, Chancery Lane, London, W.C.2, do hereby declare the nature of this invention (Communication from Hydrocarbon Research, Inc., a Corporation organised under the laws of the State of New Jersey, United States of America, of 115, Broadway, New York, 6, State of New York, United States of America) and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to the production of normally liquid hydrocarbons from a gaseous mixture consisting essentially of carbon monoxide and hydrogen. More particularly, the invention relates to the production of liquid motor fuel of high antiknock value.

The invention contemplates the utilization of normally gaseous hydrocarbons of low molecular weight, such as methane, ethane, etc., and also heavy hydrocarbons as well as other carbonaceous materials in the generation of synthesis gas, i.e. a mixture of carbon monoxide and hydrogen the synthesis of hydrocarbons from such gas and the working up of the synthesis products to obtain a maximum yield or normally liquid hydrocarbons of which the major portion is a motor fuel of high antiknock value. The invention makes considerable point of maintaining a high efficiency of utilization of the gaseous hydrocarbon or other carbonaceous feed in terms of desired liquid hydrocarbons produced.

The prime object of the invention is to provide a novel and simple process for reacting carbon monoxide and hydrogen to form liquid hydrocarbons in the motor fuel range.

Another principal object is to provide a synthesis process in which the several steps are so integrated that the major product is a motor fuel or gasoline of high antiknock value and at the same time a high utilization efficiency of the gaseous hydrocarbon feed is realized.

Another object is to conduct the conversion of gaseous hydrocarbons to liquid hydrocarbons of high antiknock rating in equipment which is simple and cheap.

In accordance with the invention, a continuous process is provided for the manufacture of gasoline hydrocarbons which comprises generating a synthesis gas consisting essentially of carbon monoxide and hydrogen, passing said synthesis gas in contact with a fluidized synthesis catalyst comprising iron in a synthesis reaction zone, effecting said contact at elevated temperature and under super-atmospheric pressure such that carbon monoxide and hydrogen undergo substantial conversion into normally liquid hydrocarbons with formation of oxygen-containing compounds, withdrawing an effluent stream of reaction products from said synthesis reaction zone, separating from said effluent a normally liquid fraction rich in gasoline hydrocarbons and containing a substantial amount of oxygen-containing compounds, subjecting said fraction to contact with a solid contact agent of the mineral type to effect dehydration in a treating zone in the presence of a substantial amount of carbon dioxide at a temperature generally in the range of 700 to 950° F. thereby effecting conversion of such hydrocarbons into gasoline hydrocarbons of improved antiknock value, removing from the contact treating zone a product mixture containing improved gasoline hydrocarbons, gaseous hydrocarbons and gas including carbon dioxide, and recovering gasoline hydrocarbons therefrom. In carrying out the invention a normally gaseous hydrocarbon, e.g. natural gas and refinery waste gases, is converted to synthesis gas, a mixture of carbon monoxide and hydrogen, by any of the known procedures which permit the recycling of carbon dioxide in order to form additional carbon monoxide. It is preferred to conduct the conversion by the reaction of the gaseous hydrocarbon with controlled quantities of oxygen at a temperature in the vicinity of 2000° F. to 2400° F. and under a pressure of about 250 pounds or in the range of about 100—500 pounds per square inch gauge. Advantageously the oxygen and hydrocarbon gas are separately preheated to at least 600° F. and preferably as high as possible. The synthesis gas is then passed through a reactor containing an iron catalyst. While the desired conditions of synthesis are generally well understood, great difficulty is experienced in attaining them in commercial-scale equipment. It has been found preferable, therefore, to conduct the synthesis step in accordance with the fluidization technique whereby the synthesis gas is passed up through a mass of powdered catalyst at such velocity that the powder is maintained in a suspended state without appreciable quantities of the powder being carried out of the reactor by the effluent gases.

A desirable fluid reactor comprises a vertical reaction vessel containing cooling surfaces one side of which surface is in contact with fluidized catalyst and reactants while the other side is in contact with a suitable heat carrier fluid such as water or a mixture of diphenyl and diphenyl ether flowing thereover for the purpose of absorbing heat liberated by the reaction and removing it from the reaction zone. The fluidized catalyst powder and reactants advantageously occupy space in the channels between vertical cooling tubes. It is desirable that such reaction channels have an effective size of pipe having an internal radius of not less than about 0.5 inch and not more than about 4 inches. By effective pipe size it is means that in any tubular reaction channel, the furthest catalyst particle shall be not less than about 0.5 inch and not more than about 4 inches away from the closest wall of cooling surface. Preferably the effective pipe size of the reaction channel is not less than about 1 inch and not more than about 2 inches in internal radius.

The synthesis catalyst comprises iron containing suitable promoters such as the oxides of magnesium, thorium, alumina, etc. The reaction may be carried out at temperatures in the range of about 500 to 700° F. and under pressures ranging from 100 to 500 pounds per square inch gauge.

An important phase of the invention is the treatment of the reaction products to stabilize them and to improve their antiknock value. For this purpose a catalytic treating unit is employed, through which the reaction products are passed. As is known, the oil or hydrocarbon layer obtained from a catalytic synthesis process frequently contains as much as about 5% by weight of oxygen and rarely less than about 3%. The oxygen is present in the form of alcohols and other oxygenated compounds which remain dissolved in the oil layer when separated from the water of reaction which holds in solution an even larger proportion of oxygenated compounds. An oxygen content of about 3% by weight generally means that the oil contains about 10% by volume of alcohols and other oxygenated compounds. The presence of oxygenated compounds in a motor fuel is detrimental to both stability and antiknock rating. Accordingly, from a commercial viewpoint, it is found imperative to treat such synthetic gasoline so that the oxygen in the product is eliminated. Passage of the synthetic oil in vapour phase through a mass of solid dehydration catalyst, such as activated alumina or bauxite, or a synthetic silica-alumina type of catalyst, at temperatures above about 700° F. leads to the splitting off of water from the oxygenated compounds and, consequently, to improvement of the gasoline stability and antiknock value. At temperatures of about 700 to 750° F., the catalytic treatment is essentially a dehydration operation, water being split out from the oxygenated compounds. As the temperature of this treatment is raised the dehydration is accompanied by an increasing amount of reforming or cracking of the product. Thus, at a temperature of about 950° F. the hydrocarbon fraction is not only deoxygenated but also materially reformed. The temperature selected for this catalytic treatment, generally in the range of 700 to 950° F. and preferably in the range of about 800 to 900° F., depends upon the nature of the oil produced by the synthesis step and the quality of the motor fuel which is desired as the end product. Such catalytic treatment to improve the motor fuel leads to the deposition of carbonaceous matter on the catalyst which must be removed in order to maintain catalyst activity. The regeneration of spent catalyst is conventionally conducted by burning the carbonaceous deposit with a stream of air. In the process of the invention, however, substantially pure oxygen (i.e., not less than about 95% by volume of oxygen) has been adopted as the regeneration gas so that the resultant flue gas from the regeneration step is essentially carbon monoxide and carbon dioxide, usually in the ratio of one volume of monoxide to two volumes of dioxide. This gas which contains all of the carbon laid down on the catalyst and which normally would represent a loss in the utilization of the gaseous hydrocarbon feed to the process, is in a form admirably suited for recycling either to the synthesis gas generator or to the synthesis reactor or to both. In this manner a higher utilization efficiency is effected for the feed to the process than has been possible by any prior process directed to the production of motor fuel of high antiknock value. As is known, the synthesis reaction produces both gaseous hydrocarbons, e.g., hydrocarbons having three or four carbon atoms, as well as heavier hydrocarbons beyond the ordinary range of motor fuels. The catalytic treating step, when carried at reforming or cracking conditions, has the added advantage of appreciably reducing the quantity of heavier hydrocarbons which, in fact, may be reduced to any desired limit. A fraction suitable for diesel oil manufacture may be separated from the synthesis reaction products prior to the foregoing catalytic treatment.

While in the process of the invention the catalytic treating step is relied on to deliver a motor fuel of high antiknock value and to curtail the production of heavy hydrocarbons, it is advantageous also to provide a polymerization step to produce an additional gasoline fraction from the normally gaseous hydrocarbons from the synthesis step. Any residual, unreacted hydrocarbon gases from this step are returned to the synthesis gas generator wherein they are utilized for the production of synthesis gas and in the subsequent synthesis step additional liquid hydrocarbons are formed. It is evident that the foregoing integration and inter-relation of the several steps results in a process in which the gaseous hydrocarbon feed is converted to a major quantity of gasoline of high antiknock value and good stability and a minor quantity of valuable oil, e.g., diesel grade, while attaining a high utilization efficiency for the gaseous hydrocarbon feed in terms of the liquid hydrocarbons produced.

In the accompanying drawing there is schematically shown a plant in which the process of the invention may be carried out continuously for the production of motor fuel from natural gas.

A natural gas containing about 90% methane is drawn from a source not shown through a pipe 1 and conducted to a generator 2. Simultaneously, oxygen of about 98% purity is drawn from an oxygen plant 4 and conducted through pipe 5 to the generator.

Advantageously, the generator 2 comprises a refractory-lined, unpacked vessel wherein the natural gas and oxygen are reacted at a temperature of about 2000° F. and under a pressure of approximately 250—275 pounds per square inch gauge. As will be mentioned later, recycle gas obtained from subsequent stages in the process may be passed to the generator.

The resulting synthesis gas containing about 85—95% carbon monoxide and hydrogen in the ratio of about 2 mols of hydrogen to 1 mol of carbon monoxide is delivered through a pipe 6, cooler 7 and pipe 8 to a synthesis reactor 9. The synthesis gas is cooled to about 600° F. prior to introduction to the reactor 9. Provision may be made for injecting fresh feed gas at a plurality of succeeding points by passage through pipe 11 and branch pipes 12, 13 and 14.

The reactor 9, operating at a pressure of about 250 pounds per square inch gauge and a temperature of about 650° F., is of the type in which powdered iron catalyst is suspended in an upward flowing stream of synthesis gas and forms a relatively dense fluidized mass. It is advisable to pass the gases through the fluidized catalyst mass at an average velocity of about 1 foot per second and to effect a contact time of 30—50 seconds. Powdered iron containing 2—3% of potassium oxide (K_2O) and alumina (Al_2O_3) as promoters is a desirable catalyst. Preferably all of the powder should pass through a 200 mesh screen and about 85% should pass through a 325 mesh screen. Temperature control is attained through a suitable heat exchange device such as a coil 10 disposed within the fluidized catalyst mass.

The reaction gases containing some entrained catalyst powder leave reactor 9 through a pipe 15 and pass to a separator 16. This separator may comprise any suitable means for separating dust from gases, such as filtration, centrifugal or electrical precipitation, or a combination of such means. The separated catalyst powder is removed through a pipe 17 and injected into the recycle gas stream flowing through pipe 23 by which means it is returned to the lower portion of the reactor 9.

The effluent gases, from which entrained catalyst has been removed, pass through pipe 18 and cooler 19 into a flash drum 20 to effect a crude separation of products at a temperature in the range of about 70—150° F. and while still under substantially the pressure prevailing in reactor 9. About half of this product mixture is water of reaction while a quarter of it may be carbon dioxide.

A water layer containing an appreciable quantity of alcohols and other oxygenated reaction products is drained from the bottom of drum 20. An upper oil layer also containing oxygenated products is withdrawn through pipe 21. This oil layer holds about 10—15% of absorbed carbon dioxide and about 80—85% thereof comprises a naphtha fraction boiling below about 400° F. which naphtha fraction contains about 40—50% olefins. Uncondensed gases flow from the top of the drum 20 through a pipe 22. This gas stream may comprise as much as about 20—30% carbon dioxide, 20—40% hydrogen, and up to about 2% carbon monoxide by volume, the remainder being mainly light hydrocarbons having from 1 to about 5 carbon atoms per molecule.

A portion of this gas stream is diverted through a pipe 23 and forced by compressor 23a into the reactor 9. The volume of gas so recycled may range from about 1 to 3 volumes or more per volume of fresh feed gas flowing through the pipe 8.

The remainder of this gas stream flowing through pipe 22 is conducted through pipe 24 to an absorber 25. The residual gases from a polymerization plant referred to hereinafter may be mixed in whole or in part with the gases flowing through the pipe 24 into the absorber 25.

The gases rise through the absorber 25 counter-currently to lean oil, the enriched oil being withdrawn through a pipe 26 and into a lean oil still 28. Steam injected at the bottom of still 28 displaces the gaseous hydrocarbons which are scrubbed from the gases processed in absorber 25. The hydrocarbon vapors flow from still 28 through a pipe 29 and cooler 30 into a separator 31 wherein condensed and uncondensed fractions are separated. Oil is returned by way of pipe 32 to the top of still 28 while a water layer is drawn off at the bottom of drum 31.

The stripped oil flows from the bottom of still 28 through pipe 34 and after passage through a cooler not shown is returned to the top of absorber 25 thus completing the cyclic flow of the absorption medium.

The residual gas leaving the top of the absorber 25 contains a large amount of carbon dioxide, for example as much as 40%. A portion of this gas may be vented while the remainder is diverted into a pipe 35 through which it may be forced by a compressor 36 either into a branch pipe 37 for recycling to the reactor 9, or into a branch pipe 38 for recycling to the generator 2. Recycling to the reactor is advantageous as regards obtaining maximum conversion of synthesis gas into desired products. If desired, this gas may be recycled to both the reactor 9 and the generator 2.

The vented gas has some fuel value and may be utilized to provide heat in the plant or elsewhere.

The recovered gaseous hydrocarbons flowing from the top of the separator 31 through a pipe 39 comprise mainly hydrocarbons ranging from about 3 to 5 or 6 carbon atoms per molecule. This gas stream, which contains a substantial amount of carbon dioxide, is conducted through pipe 39a and mixed with the oil stream flowing through pipe 21. The resulting mixture is passed through a heater 40 wherein the temperature is raised to about 900° F. The heated stream is conducted through a pipe 41a to the bottom of a treater 42. This treater advantageously involves a unitary reactor in which a fluidized mass of a powdered treating catalyst, e.g., Cyclocel, a bauxite catalyst, is divided by an upright baffle into a conversion zone 43 and a contiguous combustion zone 44. The gas stream rises through the conversion zone 43 at a velocity of about 1 foot per second and the contact time is about 20—30 seconds. A stream of oxygen is supplied from plant 4 by way of pipe 45 to the combustion zone 44 of treater 42 in order to burn off carbonaceous deposits formed on the catalyst during treatment of the gaseous hydrocarbons in zone 43.

By maintaining different fluid-static aids, e.g., by producing different densities of the fluidized catalyst mass in zones 43 and 44, cyclic flow of the fluidized catalyst through these zones is established.

With the aid of the heat of combustion liberated in zone 44 and the heat carried by the pipe 40, a temperature of about 850° F. is maintained in zone 43. As a result of the catalytic treatment, oxygenated products are chemically dehydrated, i.e., molecules of water are split out of the oxygenated compounds, and compounds such as aldehydes, ketones and acids decompose producing additional carbon dioxide and carbon monoxide. In addition, the octane value of the hydrocarbons is materially increased while reforming of heavier hydrocarbons is also effected.

The carbon dioxide present in the oil undergoing clay treatment at elevated temperature acts as a diluent and reduces the partial pressure of the hydrocarbons thereby giving rise to conditions favorable to realizing maximum octane improvement while voiding side reactions which would give rise to excessive carbon formation. To obtain these results, it is advantageous to provide from about 2 to 10 mols of carbon dioxide per mol of normally liquid hydrocarbons passing to the treater 42.

The reaction products along with the products of combustion which are largely carbon monoxide and carbon dioxide in the proportions of 1 and 2 volumes respectively, leave the top of the treater 42 through a pipe 46. This stream is introduced to a fractionator 47 for the purpose of separating from the treated products a distillate fraction comprising gases and hydrocarbons boiling in the range of motor fuel, and a residual fraction comprising gas oil or hydrocarbons boiling above 400° F. The latter is drawn off through a pipe 48. Any catalyst entrained in the effluent gases from the treater 42 is recovered as a slurry in the gas oil stream drawn off from the bottom of the fractionator.

The distillate fraction is conducted through pipe 49 and cooler 50 to a separator 51 wherein uncondensed gases are separated from liquid. The liquid forms a lower liquid layer which is withdrawn at the bottom of the separator, and an oil layer which is partly returned by way of pump 52 and pipe 53 into the top of the fractionator 47. The rest of the oil layer is forced by pump 54 through pipe 55 and heat exchanger 56 into the lower portion of a stabilizer 57. The uncondensed gases from the top of the separator 51 are conducted through a pipe 58 and injected into the upper portion of stabilizer 57.

The stabilized gasoline is withdrawn from the bottom of the stabilizer 57 by way of heat exchanger 56 and pipe 60. A gaseous stream is removed from the top of the stabilizer through a pipe 61 and cooler 62 from which it is discharged into a separator 63 which removes uncondensed gases from a liquid fraction which is returned by way of pipe 64 and pump 65 to the top of the stabilizer.

The uncondensed gases containing a large amount of carbon dioxide, some carbon monoxide and hydrogen and light hydrocarbons ranging mainly from 1 to about 4 carbon atoms per molecule are drawn off from the separator 63 through a pipe 66. This stream contains valuable olefins predominantly in the range 3 to 4 carbon atoms per molecule.

From the pipe 66 the gas stream flows into an absorber 67. Lean oil flows countercurrently to the gases in the absorber 67 for the purpose of separating the C_3 and higher hydrocarbons from carbon dioxide and other gases. The enriched oil stream is withdrawn through pipe 68 and passed into a still 69 wherein the absorbed hydrocarbons are stripped from the lean oil by the injection of steam at the bottom of the still.

The stripped oil is withdrawn through a pipe 70 and after suitable heat exchange, not shown, returned to the top of the absorber 67. The unabsorbed gases, containing carbon dioxide, leaving the top of the absorber 67 flow through a pipe 71 which communicates with the previously mentioned pipe 35 for recycling either to the reactor 9 or the generator 2 as may be desired.

The effluent gases from the still 69 pass through a pipe 72 and cooler 73 into a separator 74 wherein uncondensed gases are separated from a liquid fraction. The liquid fraction forms a lower water layer which is withdrawn at the bottom of the separator, and an oil layer which is returned by way of pipe 75 to the top of the still 69 as reflux liquid.

The gases discharged from the top of the separator 74 pass through pipe 80 to a heater 81 and from there through pipe 82 to a polymerizer 83. The hydrocarbons are subjected to contact therein with a suitable polymerizing catalyst such as a phosphoric acid type catalyst at a temperature in the range of 375—500° F. and under a pressure in the range of 500—2000 pounds so as to effect polymerization of olefins.

The gas flowing through pipe 80 may contain substantial amounts of carbon dioxide, and therefore provision, not shown, may be made for extracting carbon dioxide therefrom prior to polymerization. Carbon dioxide so removed may be recycled to the pipe 35.

The reaction products pass through a pipe 84 and cooler 85 into a stabilizer 86 wherein polymer gasoline is separated from light hydrocarbon gases and is withdrawn through a pipe 87 as an end product.

A gas fraction is removed from the top of the stabilizer 86 through a pipe 90 and cooler 91 and discharged into a separator 93 wherein condensate is separated from the gases and returned by pipe 94 and pump 95 to the top of the stabilizer.

The gases leaving the top of the separator 93 and consisting essentially of C_4 and lighter hydrocarbons flow through a pipe 100 and may be diverted all or in part through pipe 101 to the absorber 25 hereinabove described. On the other hand, a portion of this gas stream may be passed through a pipe 102 and compressor 103 to the generator 2. If desired, a portion of the gas flowing through pipe 100 may be discharged from the system. Provision may also be made for passing some of this gas back through pipe 104 as a diluent to the polymer feed flowing through pipe 82.

On the basis of charging the aforesaid natural gas to the generator at the rate of about 580 mols per hour, the plant has a daily production capacity of about 355 barrels of synthesized gasoline, 178 barrels of polymerized gasoline (containing butane) and 48 barrels of gas oil. The synthesized gasoline has an octane number of 76 or 77 by the ASTM test method (CFR motor). The composite resulting from blending the polymerized and synthesized gasolines has an octane rating of 80 or over.

In connection with the synthesis reactor operation it is contemplate that provision may be made for recycling a portion of the product gases without cooling and separation of products. Thus, a portion of the effluent stream flowing through the pipe 18 may be diverted through a pipe 18a and thus recycled directly to the reactor. If desired the effluent stream flowing through pipe 16, with or without recycling a portion thereof to the reactor through pipes 18 and 18a, may be passed directly to the heating coil 40. In this case carbon dioxide which was present in the effluent, will pass through the treater 42 for recovery and recycling as previously described.

While the foregoing operation has been described with reference to the use of natural gas as a feed to the process, nevertheless it is contemplated that the synthesis gas may be prepared from any suitable carbonaceous material other than natural gas. For example, it may be obtained from coal, coke, lignite, peat, shale and heavy fuel oils.

It is also contemplated that provision may be made for recovering oxygenated compounds from the synthesis reaction products. These may be recovered from the water phase leaving the separator 20 and may also be extracted from the hydrocarbon phase flowing through the pipe 21 prior to treatment of the hydrocarbons with the clay type catalyst at elevated temperature.

It is also contemplated that a diesel oil fraction may be separated from the synthesis hydrocarbons either prior to or following such high temperature clay treatment.

The treater 42 may comprise two separate cylindrical vessels in one of which the contact catalyst is used to effect the treatment of the hydrocarbon stream and in the other of which the used catalyst is regenerated, provision thus being made for continuously drawing off used catalyst from the vessel in which the hydrocarbons undergo treatment and passing it to the companion vessel in which the used catalyst is regenerated, following which the regenerated catalyst is returned to the treating vessel.

If desired, the treater 42 may be of the stationary catalyst bed type wherein the hydrocarbon stream flows through one catalyst vessel for a period of time and is then switched to another vessel while the catalyst mass in the off-stream vessel is regenerated.

As previously indicated, the generator 2 is of the open or unpacked type. However, when nature gas is the feed, it may contain a mass of granular refractory material such as alundum, and this refractory may comprise a catalytic agent for the reaction between methane and carbon dioxide or steam and which may be desirable in the event that carbon dioxide is being recycled in substantial amount to the generator, or steam is being added thereto.

The synthetic product treatment step of the process may employ any of several contact agents, such as acid-treated clays and bauxite, synthetic cracking catalysts and activated alumina. The procedure of regenerating spent catalyst by burning off the carbonaceous deposit with oxygen makes it feasible to utilize this carbon which has been formed at the expense of gaseous hydrocarbons entering the process and which ordinarily when burning with air would be lost in the flue gases vented into the atmosphere. Accordingly, the process of the invention averts such loss and contributes to the attainment of a high utilization efficiency for the gaseous hydrocarbon feed. Furthermore, the absence of a large volume of atmospheric nitrogen permits the mixing of the gases leaving the conversion and regeneration zones of the catalytic treater. In a system embodying the fluidizing principle, such mixing obviates expensive catalyst separators, e.g., cyclone separators and electrical precipitators. The use of oxygen for catalyst regeneration also decreases the size of the equipment. Marked economies in installation and maintenance costs are therefore realized.

Those skilled in the regeneration of spent catalysts of the type contemplated for the dehydration step appreciate that the combustion of the carbonaceous deposit on the spent particles must be carried out below the deactivation temperature of the catalyst selected. The deactivation temperature, i.e., the point at which thermal injury or deactivation of the catalyst begins, varies with the catalyst used. Generally, the deactivation temperature is in the vicinity of about 1100° F., but some catalysts, e.g., the synthetic silica-alumina type, have deactivation temperatures as high as about 1300° F. In any case, however, the regeneration temperature should not be permitted to fall below about 800° F. In regenerating spent catalyst with substantially pure oxygen, cooling coils or tubes may be used to control the temperature within the desired limits but preferably, when using a fluidized system, thermal regulation may be effected through the control of the rates of oxygen introduction and of circulation of catalyst between the regenerating zone and a heat-abstracting zone, e.g., the endothermic conversion zone 43 of the drawings or a conventional cooler for fluidized catalysts.

While a preferred form of the invention and modifications thereof are described, it is understood that these are by way of illustration only and various changes may be made without departing from the scope of the claims.

Having now particularly described and ascertained the nature of my said invention, as communicated to me by my foreign correspondents, and in what manner the same is to be performed, I declare that what I claim is:—

1. A continuous process for the manufacture of gasoline hydrocarbons which comprises generating a synthesis gas consisting essentially of carbon monoxide and hydrogen, passing said synthesis gas in contact with a fluidized synthesis catalyst comprising iron in a synthesis reaction zone, effecting said contact at elevated temperature and under superatmospheric pressure such that carbon monoxide and hydrogen undergo substantial conversion into normally liquid hydrocarbons with formation of oxygen-containing compounds, withdrawing an effluent stream of reaction products from said synthesis reaction zone, separating from said effluent a normally liquid fraction rich in gasoline hydrocarbons and containing a substantial amount of oxygen-containing compounds, subjecting said fraction to contact with a solid contact agent of the mineral type to effect dehydration in a treating zone in the presence of a substantial amount of carbon dioxide at a temperature generally in the range of 700 to 950° F. thereby effecting conversion of said hydrocarbons into gasoline hydrocarbons of improved antiknock value, removing from the contact treating zone a product mixture containing improved gasoline hydrocarbons, gaseous hydrocarbons and gas including carbon dioxide, and recovering gasoline hydrocarbons therefrom.

2. A process according to claim 1, in which said fraction rich in gasoline hydrocarbons and containing oxygen-containing compounds is separated from said withdrawn effluent while still under pressure.

3. A process according to claims 1 or 2, in which at least a portion of said effluent containing oxygen-containing compounds is recycled to the synthesis reaction zone.

4. A process according to claims 1, 2 or 3, in which said gas including carbon dioxide is recovered from the product mixture and recycled to the synthesis reaction zone.

5. A process according to any of claims 1 to 4, which includes a separately recovering olefins from said product mixture, subjecting the recovered olefins to polymerization so as to form a polymer product containing polymer gasoline and gaseous hydrocarbons, removing polymer gasoline from said product and recycling gaseous hydrocarbons from said polymer product to said gas generating zone.

6. A process according to claim 5, in which the polymerization is effected by subjecting a gaseous fraction of said product mixture containing olefins to contact with a polymerization catalyst at elevated temperature.

7. A process according to claim 5 or 6, in which residual light hydrocarbons from said polymerization reaction are recycled to the gas generating zone.

8. A process according to claims 5, 6 or 7, which includes first subjecting said removed product mixture to fractionation to separate therefrom a stabilized gasoline fraction and a secondary gas fraction containing unsaturated light hydrocarbons and carbon dioxide, and separating light hydrocarbons from said secondary fraction, said separated light hydrocarbons then being subjected to said polymerization step.

9. A process according to any of claims 1 to 8, in which the solid contact agent is bauxite.

10. A process according to any of claims 1 to 9, in which said contact agent is fouled by the deposition of carbonaceous matter during treatment of said fraction rich in gasoline hydrocarbons, but is reactivated by combustion of said carbonaceous matter with substantially pure oxygen to yield combustion gases consisting essentially of carbon oxides, said combustion gases being mixed with the effluent stream from said treatment step.

11. A continuous process for the manufacture of gasoline hydrocarbons substantially as hereinbefore described.

12. Gasoline hydrocarbons whenever

manufactured by the process claimed in any of claims 1 to 11.

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