Feb. 9, 1926. 1,571,994

H. R. BERRY

PROCESS FOR THE CONSTRUCTIVE CONVERSION OF HYDROCARBONS

Filed Sept. 18, 1922 3 Sheets-Sheet 1

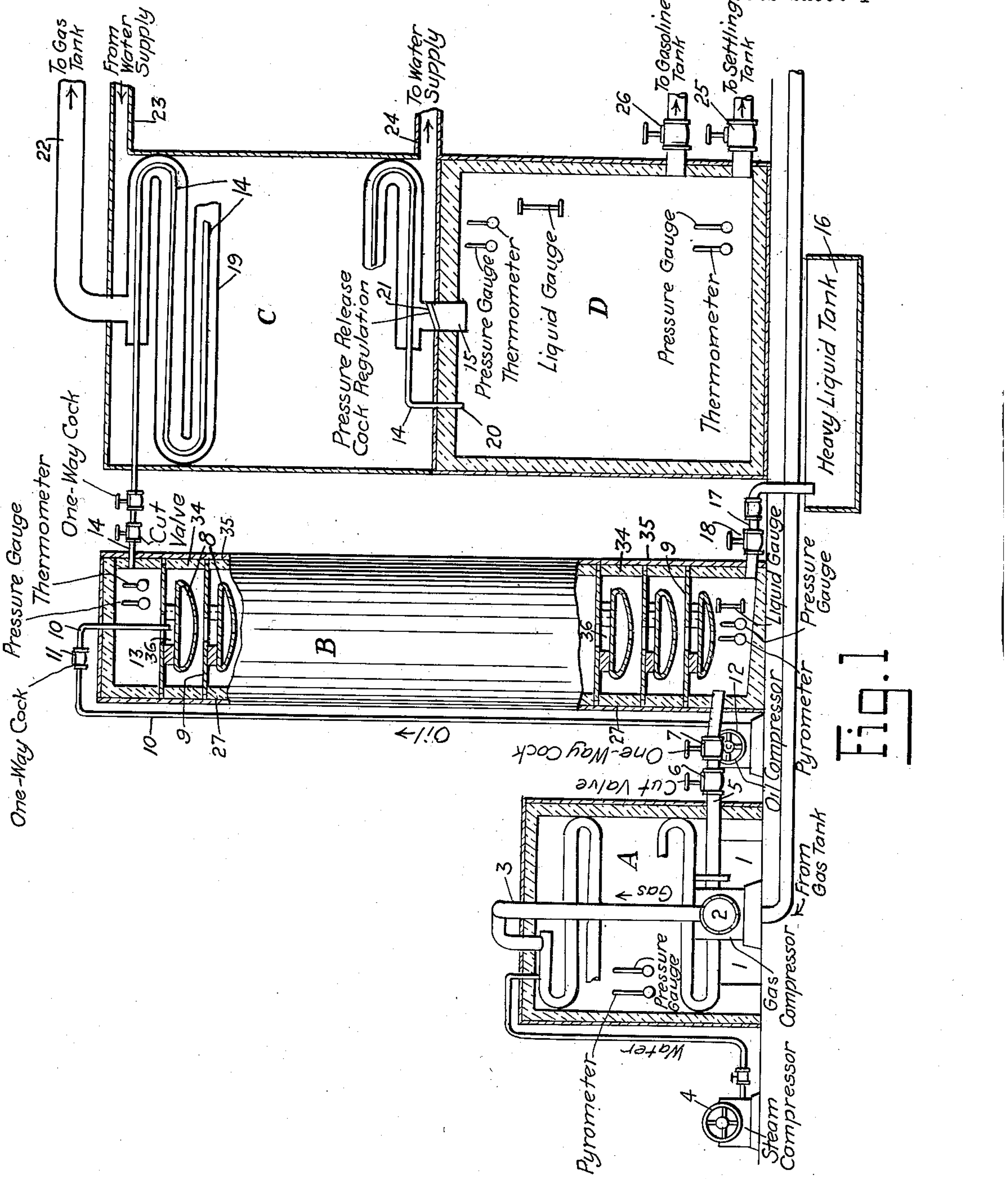

Fig. 1

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Filed Sept. 18, 1922 3 Sheets-Sheet 2

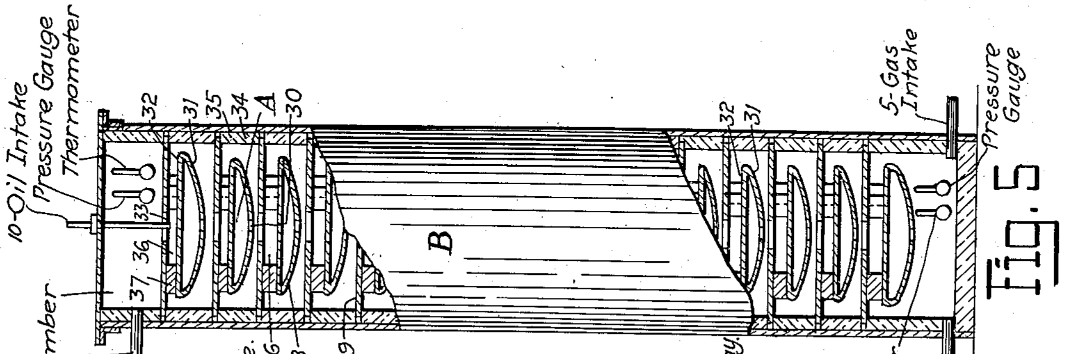

Fig. 5

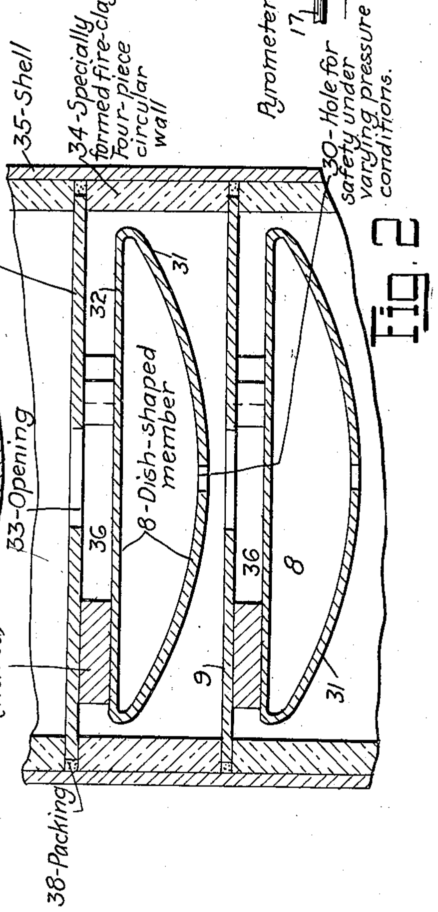

Fig. 2

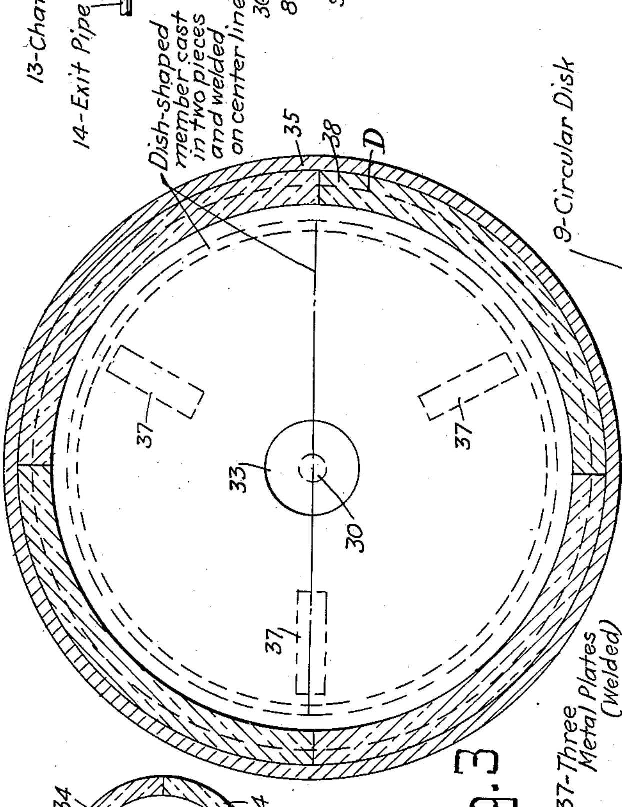

Fig. 3

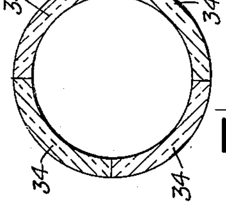

Fig. 4

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PROCESS FOR THE CONSTRUCTIVE CONVERSION OF HYDROCARBONS

Filed Sept. 18, 1922 3 Sheets-Sheet 3

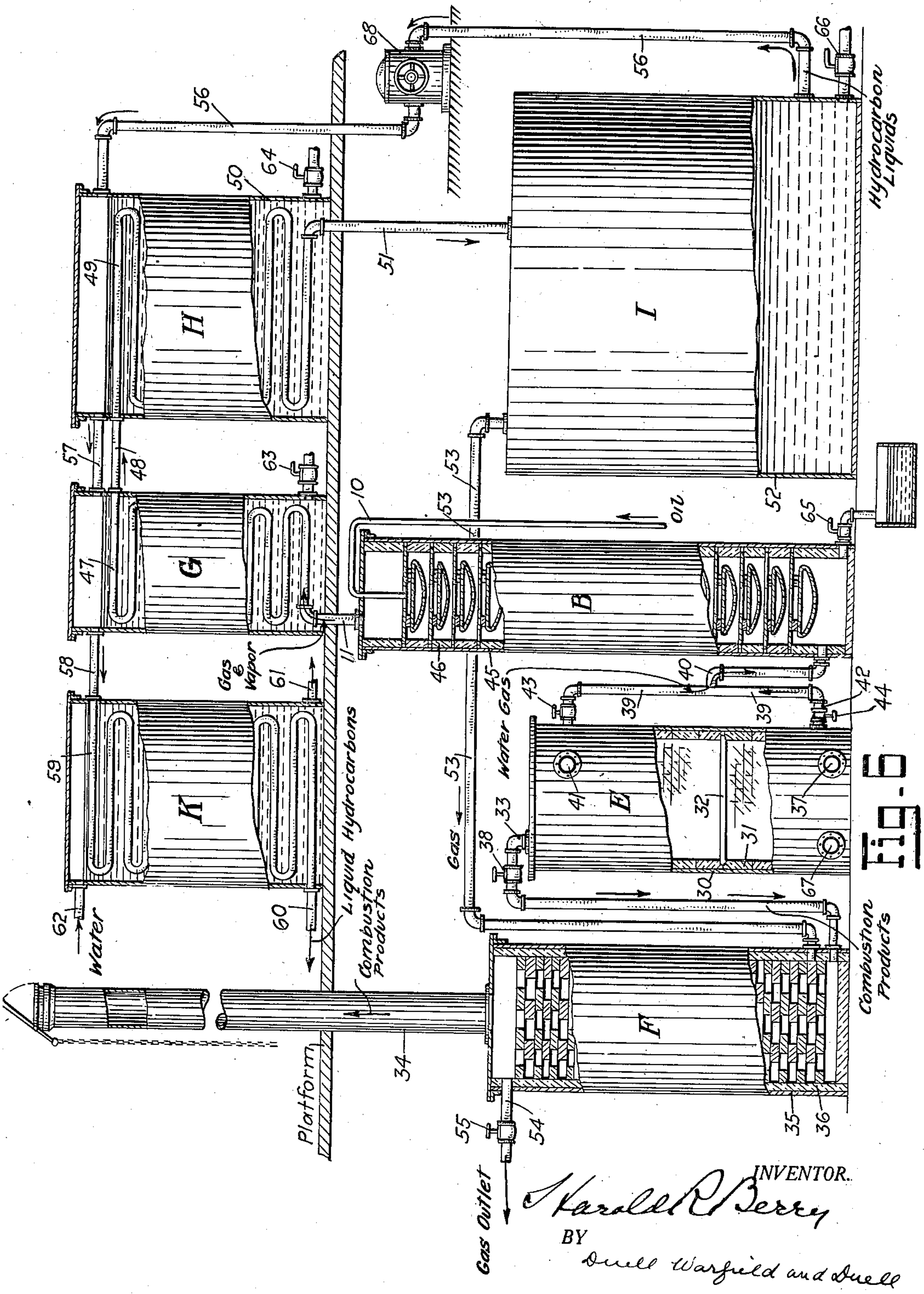

Fig. 6

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Patented Feb. 9, 1926. **1,571,994**

UNITED STATES PATENT OFFICE.

HAROLD R. BERRY, OF BROOKLYN, NEW YORK.

PROCESS FOR THE CONSTRUCTIVE CONVERSION OF HYDROCARBONS.

Application filed September 18, 1922. Serial No. 588,848.

To all whom it may concern:

Be it known that I, HAROLD R. BERRY, a citizen of the United States, residing at Brooklyn, in the county of Kings and State of New York, have invented certain new and useful Improvements in a Process for the Constructive Conversion of Hydrocarbons, of which the following is a full, clear, and exact description, such as will enable others skilled in the art to which it appertains to make and use the same.

This invention pertains to a process for the constructive conversion of hydrocarbons. The purpose is the conversion of the oil and other materials treated into a hydrocarbon product of the type and gravity selected and predetermined.

Essential differentiation is claimed from fractional distillation, and the practiced methods of oil cracking.

The materials used are crude petroleum or its heavy-gravity fractions, in conjunction with natural gas, overly rarefied resultants of fractional distillation, artificial gases, preferably water gas or hydrogen, derived as a product from superheated steam in contact with suitable metallic oxidizing reagents, or otherwise. Any of these may be used in combination, and with or without the addition of water or steam.

The process contemplates operation with or without pressure, but a method is submitted for determining the proper coefficients of pressure and temperature requirements, dependent upon analysis of the oil to be treated.

The required heat for the operation is supplied preferably by superheating the gaseous material employed.

In carrying out the invention, the liquid and gaseous materials are preferably counterflowed against each other in any suitable apparatus, in such manner that the oil introduced for treatment is subjected to ever-increasing temperature, and the gaseous material is subjected to ever-decreasing temperature, as heat is gradually, though constantly, transferred to the oil through contact.

The process contemplates the unstabilizing of various substantially different hydrocarbon compounds in heterogeneous relationship and their readjustment into a predetermined and selected hydrocarbon product, which for all commercial purposes is substantially uniform or commercially homogeneous.

The preferred method for accomplishing these results includes any kind of means for causing the various hydrocarbon compounds to be hydrogenized at or above their points of molecular instability, and for withdrawing such part of the treated mass as has attained desired hydrogenization. The process continues treatment of the residue until total desired hydrogenization of the entire mass is effected.

It is preferred to accomplish this result by utilizing a pressure, temperature and gravity zone of such character that it will not receive and pass hydrocarbon products until they have been reconstituted into a state which is commercially uniform or substantially homogeneous.

The process contemplates the vaporization of each differentiated compound of the oil mass, as its respective boiling-point temperature is attained, the amount of pressure utilized being sufficient to raise the boiling point to equal or exceed the temperature of molecular instability, whereby hydrogenization and molecular readjustment occur.

As each succeeding compound attains vaporization, it ceases to follow the direction of the oil, but counter-flows, as vapor, with the hydrogenous, gaseous material used in the operation, and encounters constantly cooler temperature zones.

The ultimate and coolest temperature is regulated and maintained at the boiling point of the selected and predetermined product. Such compounds of the oil mass as are not sufficiently hydrogenized during vaporization, liquefy and flow with the oil mass, and undergo revaporization. The process continues until attainment of exit conditions is met, when escapement follows.

The operation of the process will be described in connection with the production of a specific product, gasoline, for instance, from heavy petroleum fractions in conjunction with, for instance, natural gas.

The principles and reasons governing the process and its application will be set forth. The apparatus described is one, among others, capable of being so manipulated as to carry out the process and method presented.

The principles underlying this invention are:

1. The specific gravity and the boiling point of the hydrocarbon found in petroleum, are decreased, by increasing the ratio of the hydrogen content.

The variation of these properties of the hydrocarbon compound is illustrated in the following:

Compound.		Hydrogen per cent.	Boiling point.	Specific gravity.
Nonodecane	$C_{19}H_{40}$	14.93	635° F.	.8122
Octodecane	$C_{18}H_{38}$	14.96	607°	.8017
Heptadecane	$C_{17}H_{36}$	15.00	578°	.794
Hexadecane	$C_{16}H_{34}$	15.04	549°	.7911
Tridecane	$C_{13}H_{28}$	15.22	453°	.775
Undecane	$C_{11}H_{24}$	15.38	351°	.7411
Heptane	$C_{7}H_{16}$	16.00	209°	.7304

As the ratio of hydrogen content increases, specific gravities and boiling points decrease; thus specific gravities and boiling points are raised or lowered inversely with the increase or decrease of the hydrogen content of the molecule.

2. Reason presents but two ways in which the hydrogen ratio can be increased. In an oil composed of so much hydrogen and so much carbon, the ratio of the hydrogen to the mass can be increased either (*a*) by taking some of the carbon out, in which case the hydrogen sustains an increased ratio to the remaining mass, or (*b*) by adding hydrogen to the compound; (*a*) is accomplished by so-called cracking; (*b*) by the method presented herein. The product of (*a*) is largely olefine, smoky and rarely sweet; the product of (*b*) is sweet, clear, and paraffine.

3. Each hydrocarbon compound occurent in petroleum has distinctive characteristics, distinguishing it from other such compounds. The characteristics include, not only differentiations in specific gravities, molecular weights, hydrogen contents, and boiling points, but also characteristic differences in the temperature required to produce instability of the molecular organization.

In the processes of cracking, by the application of heat and usually, pressure, molecular instability is carried to the point of molecular dismemberment, by which the atomic constituents are thrust asunder. There is a correspondent state of inter-atomic agitation within the molecule for any heat condition established. With additional heat, the molecule becomes more and more agitated and less stable, resulting, with sufficient heat, in disassociation, but during this period of agitation and nonstability, other elements, properly conditioned, easily enter the oil, with accompanying molecular readjustment. The temperature of instability for each compound, is, then, that temperature, below the cracking point, at which molecular readjustment and incorporation of new elements is most easily effected.

4. The application of pressure, in the heat treatment of a liquid, elevates its boiling point. It is therefore possible to regulate pressure so that the boiling point of a hydrocarbon compound may be elevated to equal or exceed its temperature of molecular instability. In this case, the resultant vapor emanates in a state of instability, and is susceptible of hydrogen assimilation.

5. Concerning saturation: it has become quite the practice to use the term "saturated compound" to indicate a hydrocarbon compound, thoroughly impregnated with the maximum hydrogen coefficient for the carbon present. In the paraffine series, C_n+H_{2n+2} it is found that, given any specific carbon content, the hydrogen accompanying the specific carbon quantity is greater in amount in this series than in any other.

	Per cent hydrogen.
Paraffine—butane	C_4H_{10}—17.2
Olefine—butylene	C_4H_8 —14.2
Acetylene—crotonylene	C_4H_6 —11.1
Aromatics—benzine	C_6H_6 — 7.3

"Paraffine series" is thus customarily used interchangeably with "saturated series".

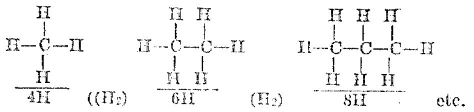
As every constituting member of the olefine series contains 14.28% hydrogen, conversion, through hydrogenization into another olefine may not be effected, but the incorporation of hydrogen into its molecule makes it a paraffine.

$$C_4H_8+2H=C_4H_{10}, \text{ a paraffine.}$$

Following the sequence of the chief petroleum hydrocarbons in their relationship to the hydrogen molecule H_2 we find:

$$C_nH_{2n-6}\text{ (diacetylenes)}+2H=C_nH_{2n-4}\text{ (olefinacetylenes)}$$
$$C_nH_{2n-4}\text{ (olefinacetylenes)}+2H=C_nH_{2n-2}\left\{\begin{matrix}\text{diolefines}\\ \text{acetylenes}\end{matrix}\right\}$$
$$C_nH_{2n-2}\left\{\begin{matrix}\text{diolefines}\\ \text{acetylenes}\end{matrix}\right\}+2H=C_nH_{2n}\text{ (olefines)}$$
$$C_nH_{2n}\text{ (olefines)}+2H=C_nH_{2n+2}\text{ (paraffines)}$$

In the paraffine compounds the sequence continues.



The principle involved is, though the paraffine possesses for its carbon content, in comparison with other family groupings, the greatest ratio of hydrogen incorporation; nevertheless, each compound of the paraffine series possesses a different and characteristic percentage of hydrogen.

In the direction of methane the hydrogen content constantly increases and is accompanied by reduced boiling point and specific gravity.

Compound.	Hydrogen.	B. P.—C.	Sp. gr.
Nonodecane $C_{19}H_{40}$	14.93%	330°	.777
Octodecane $C_{18}H_{38}$	14.96	317	.7765
Heptadecane $C_{17}H_{36}$	15.00	303	.776
Hexadecane $C_{16}H_{34}$	15.04	287.5	.7758
Pentadecane $C_{15}H_{32}$	15.09	270	.7756
Tetradecane $C_{14}H_{30}$	15.15	252	.7754
Tridecane $C_{13}H_{28}$	15.22	234	.775
Dodecane $C_{12}H_{26}$	15.29	214	.7745
Undecane $C_{11}H_{24}$	15.38	194	.774

One pound of carbon occurrent in tridecane is incorporated with .1795 pounds of hydrogen.

One pound of carbon occurrent in hexane is incorporated with .1943 pounds of hydrogen.

Both are paraffine.

Both are termed saturated.

Discussion which departs from customary usage of the word, "saturation", I find may not be had at this time and under these circumstances, but I quote from Richter's Organic Chemistry, 1922 edition, published by P. Blakiston's Son & Co., vol. 1, page 68,

"They (carbon compounds) are further classified into saturated and unsaturated compounds. In the first of these, called also limit compounds or paraffins, the directly united quadrivalent carbon atoms are linked to each other by a single bond, so that the number of affinities still remaining to be satisfied in a chain of *n* carbon atoms is 2_n+2. Their general formula is, therefore, expressed in the form C_nX_{2n+2}, where X represents the affinities of the elements or groups directly combined with carbon."

In increasing the hydrogen content of the paraffine and thereby reducing its gravity and boiling point, the problem is not that the carbon content has assimilated all the hydrogen chemically incorporatable with the amountof carbon present. The requirement is to unstabilize the single bond union of the paraffine through inter-atomic activity produced by the proper coefficient of heat and pressure.

6. The relationship between hydrogen content, boiling point, and specific gravity of the paraffines has been noted. The infinitesimal increase of hydrogen content in each succeeding compound of the series, in the direction of methane, has been shown.

It may now be stated that any condition of pressure and temperature, maintained in a suitable apparatus, has its coefficient in one of the series as the perfect balance for the condition developed. It will be found that the higher the temperature, the more rarefied the coefficiental compound. With properly adjusted conditions, and an available supply of needed elements afforded, equilibrium prevails, and the products are paraffine; disarrangement of these conditions produces the conglomerate of over-rarefication, carbon fixation, and heavy olefine percentages.

It is not contended, necessarily, that the paraffine compound is directly hydrogenized into lighter members of the series. It is altogether probable that the ascent is brought about by a number of reactions. Molecular instability, brought about by the heat and pressure conditions, may be followed by the occurrence of olefine, chain, and other non-paraffine structures. Such series, however, being comparatively unstable at best, rapidly saturate into the lighter paraffines.

Description of the apparatus and its functions.

In the accompanying drawings:

Figure 1 is a diagrammatic view, mostly in cross-section, of an apparatus operative by the process and method presented herein.

Figure 2 is a vertical section, showing part of the generator and filmenting plates.

Figure 3 is a plan view, partly in horizontal section, looking down on the construction shown in Figure 2.

Figure 4 is a section on a smaller scale, showing the manner of assembling the fire-clay wall sections.

Figure 5 is a view, partly in section and partly in elevation, showing the entire generator.

Figure 6 is a view, partly in cross-section and partly in elevation, showing the general assemblage of an apparatus for using water gas and crude petroleum, or its heavier fractions, for the manufacture conjointly of an enriched water gas product and a liquid hydrocarbon combustion fuel.

Like reference numerals indicate corresponding parts in the different figures of the drawing.

From left to right, in Figure 1, the elements of the apparatus are;

1st—a heater—A.
2nd—a generator—B.
3rd—a refrigeration system—C.
4th—a collecting tank—D.

The heater, A, may be of any suitable construction. In this instance, the walls of the heater are constructed of fire-clay and brick within, and steel casing without, and it contains a nest of high-pressure piping, with the heat delivered at the fire box, 1, and distributed throughout the interior of the heater. The heater, A, is supplied with any hydrogen-containing gas, for instance natural gas, by means of the centrally located compressor, 2, at desired pressure. The gas is delivered at the top of the heater through the pipe, 3, and passes down through the coil system as shown. The small compressor, 4, to the left, is utilized for delivering water at a point adjacent to the delivery point of the gas within the top part of the heater, A, as shown. If the operation is conducted without the use of steam, the supply is closed in any suitable manner by pet-cock, for instance, as shown. There is generated a temperature, corrected to the pressure used, exceeding the degree of heat required for vaporizing the heavy hydrocarbons contained in the oil to be introduced into the apparatus for treatment. The exit pipe, 5, passes from the bottom-most part of the heater, A, and gives exit to the superheated gas under the pressure maintained. The exit pipe, 5, is controlled with a cut-off valve, 6, and a combined, one-way valve and regulative pressure valve cock, 7, of any suitable character.

There is thus discharged in the bottom of the second apparatus, B, the heated gas, which ascends through the filmenting construction of the generator. Figures 2, 3, 4, 5, are generator B in greater detail than shown in Figure 1.

In Figure 2 the filmenting member, 8, is constructed of any suitable substantial material. It may be made of fire-clays, terra cotta, carborundum, metals, or other suitable materials. It may be of solid or hollow construction. In the design shown, it is hollow and of cast iron construction. It is equipped with a small hole, 30, centrally located in the dish-shaped side, 31, to allow for equalization of pressure conditions.

In this construction the member is cast in two pieces, such as are formed by a plane passing through the circumference and the center of both the top and the lower dish-shaped side. The two halves after being cast, are welded together at their like edges, constituting thereby the hollow, enclosed, dish-shaped figure, represented in the drawing by 8.

As constituting another part of the unit, there is a circular disk member, 9, constructed of any suitable substantial material. In the design submitted, it is of cast iron.

The disk is equipped with a central opening, 33, of such size as operating conditions require. This circular disk is of larger diameter than that of the dish-shaped or filmenting part, sufficient to allow the circular-disk part to extend over and rest upon the insulating material, 34, within the shell, 35.

Circular disk, 9, and the dish-shaped filmenting member, 8, are attached one to the other, having the intervening space, 36, of any suitable amount for working condition. The connection is made by any suitable means utilizing any material or materials.

In the construction illustrated, three metal blocks, 37, for instance 8%×2″×2″, are placed on the top of the dish-shaped member, 8, so that a line bi-secting the length of the blocks will coincide with a radius of the upper or flat circular side of the dish-shaped part, 8, the three blocks being equidistant one from the other. Thus placed, the blocks are welded to the top surface of the dish-shaped member, and to the bottom surface of the circular disk, 9.

In installing the unit, the insulating wall, 34, may be made in a number of pieces, four, for instance, as shown in Figure 4. When placed in position within the generator, and properly cemented together, the circular disk, 9, may rest upon the top surface so formed. The circular disk does not touch the shell of the generator.

The space, 38, between the circumference of disk, 9, and the shell, 35, provides room for expansion and contraction under the heat conditions maintained; the space thus remaining is filled with suitable packing, 38.

In a series, these units are placed one upon top of the other, each unit supported by the insulating wall, Figure 5.

The top surface, 32, of the dish-shaped member is level and parallel with the circular disk, 9.

In operation, oil delivered upon the upper level surface of the dish-shaped member will spread with maximum slowness, because of no declevity, to the circle forming the boundary of the circular area.

When the oil, thus filmed, attains the circumference or rim of the top surface and flows onward, it does not fall downward, but, by adhesion, clings to the lower surface, 31, of the dish-shaped member. Thus the member supports a fine film of oil covering the surfaces on top and on bottom.

Hot gas, entering from the central hole in the lower plate, 9, Figure 2, sustains intimate contact with the oil film encasing the dish-shaped section, 8. Maximum intercourse follows, as the only course open for the gas to follow is around the edges and over the top surface of the dish-shaped member.

The upward push of the gas is as upon a roof. Such film disturbance as is caused by the onward rushing of gas, which results in dripping, causes precipitation upon the upward surface of plate, 9, Figure 2.

The only impediments encountered are the three 8″×2″×2″ bars, 37, joining the parts of the member. The function of this member is to produce maximum intimacy of contact between the oil and gas.

There is supplied at the top of the generator, B, through pipe, 10, Figure 1, the oil delivered for treatment. The pipe is equipped with one-way cock, 11, and the oil supply is delivered by compressor, 12. Oil, thus delivered, passes in a state of fine filmentation from filmenting member to filmenting member in its downward journey.

Heated hydrogen-containing gas is introduced into generator B, at the lower intake, 5, and proceeds constantly upward passing alternately through the central openings, 33, in the disks, 9, and then encompassing the film of oil around and about the filmenting member, 8, over its top surface and through the next higher central opening, 33.

Operation presents certain considerations. Crude petroleum is a conglomerate mass. It is not homogeneous, but is a mixture of many hydrocarbon compounds. Each constituent possesses distinctive characteristics, varying one from the other in boiling point, specific gravity, density, and temperature of non-stability. The mass is rendered further complex by carrying through absorption the most rarefied of gases, and by suspension some of the heaviest of the hydrocarbon group. Any laboratory analysis presents the large range of these differences.

Introducing heated gas at the lower intake, 5, and introducing oil to be treated at the upper intake, 10, the oil proceeds downward, encountering the filming construction, and the heated gas rises in a close-contact counter-flow.

It is evident that with oil thus journeying downward with an initial, comparatively cool temperature, and with hot gas thus journeying upward, the farther downward the oil travels, the greater is the quantity of gas with which it has had contact. Contrariwise, the greater elevation attained by the gas, the greater is the quantity of oil with which the gas has had contact. The farther the oil journeys, therefore, the greater becomes its temperature.

With the gas, the higher it rises, the more heat it has imparted, and the cooler it becomes. It thus results that in operation, the coolest part of the generator is at the top, the hottest at the bottom, the two temperatures graduating into each other throughout the vertical length of the apparatus.

The condition developed is, that the oil introduced to treatment on its downward journey is subjected to ever-increasing gradation of temperature, and the gas in its ascendency is subjected to ever-decreasing temperature. The oil thus experiences a gradual, yet ever-increasing temperature. When any one of the differentiated hydrocarbons of the oil encounters its boiling point temperature, it is vaporized, and as a vapor is relieved from further heat condition as it joins the upward stream of gas into cooler zones.

Thus, as it were, each compound in the oil mass is afforded the opportunity to choose its needed temperature for vaporization, and in this sense the operation might be termed selective distillation.

Were it possible, in all instances, for the temperature which produces sufficient molecular activity to vaporize an oil, to be sufficient also to intensify inter-atomic agitation to the point of instability of the molecule, the act of vaporizing, in the presence of hydrogen-containing gases, would result in hydrogen incorporation and reduction of specific gravity. However, certain compounds, later mentioned, at vaporization temperatures exhibit so slight an increase of inter-atomic movement as to be insufficient for rapid hydrogenization.

The primary necessity is to unstabilize the paraffine, so additional hydrogen may be assimilated, and this must be accomplished with an apparatus sufficiently sensitive to adapt itself to the varying requirements of the different compounds making up the oil undergoing treatment.

Customarily, it is said that a process operates with so much temperature and so much pressure, and to the question as to why the particular temperature and the particular pressure are chosen, the answer is that best results are found to obtain under such conditions.

The fact is, however, that because of the heterogeneous character of the constituting compounds of a petroleum mass, there can be no uniform condition to satisfy such widely differentiated requirements. At best, any single condition can be but an average, and in this, it is too great for certain requirements and insufficient for others. The customary procedure is to give it the maximum requirement and let it go at that.

The table following is presented as the solution of our problem. In it will be found molecular weights, vaporization temperatures (boiling points), and temperatures of molecular instability.

The last of these is the degree of heat at which the strings of attraction between the atomic constituents, making the hydrocarbon molecule, are strained to a point of non-equilibrium. It is the critical temperature for hydrogen absorption and molecular readjustment, the most favored condition for gravity reduction.

Carried to excess, however, with violent and ill-adjusted excess of heat, the atomic constituents break asunder, even as the molecules separate in the process of vaporization. This excess results in over-rarefication and carbonization.

1			2	3	4	5	6
NAME		SYMBOL	MOL. WTS.	BOILING POINTS (x)	TEMPERATURES OF NON-STABILITY (y)	PRESSURE (lb. per sq. in) TO RAISE BOILING PT TO EQUAL TEMP. OF NON-STABILITY. (z)	SPECIFIC GRAVITY
PENTANE	GASOLINE	C_5H_{12}	72	96.8	750	5815	.6365
HEXANE		C_6H_{14}	86	156.2	731.8	3175	.6494
HEPTANE		C_7H_{16}	100	209	713.6	1760	.6619
OCTANE		C_8H_{18}	114	258	695.2	1065	.6740
NONANE		C_9H_{20}	128	302	678	590	.6838
DECANE		$C_{10}H_{22}$	142	342	661	320	.6943
UNDECANE	KEROSINE	$C_{11}H_{24}$	156	381	642.1	216	.6939
DODECANE		$C_{12}H_{26}$	170	418	628	119	.7025
TRIDECANE		$C_{13}H_{28}$	184	453	590.7	51.6	.7114
TETRADECANE		$C_{14}H_{30}$	198	486	565	20.8	.7187
PENTADECANE	GAS AND FUEL OIL	$C_{15}H_{32}$	212	518	545	14.6	.7252
HEXADECANE		$C_{16}H_{34}$	226	549	515	—	.7319
HEPTADECANE		$C_{17}H_{36}$	240	578	496	—	.7369
OCTADECANE		$C_{18}H_{38}$	254	607	475	—	.7425
NONADECANE		$C_{19}H_{40}$	268	635	455.2	—	.7466
EICOSANE		$C_{20}H_{42}$	282	662	437	—	.7507
HENEICOSANE		$C_{21}H_{44}$	296	688	419	—	.7534
DOCOSANE		$C_{22}H_{46}$	310	714	404	—	.7553
TRICOSANE		$C_{23}H_{48}$	324	739	391	—	.7571
TETRACOSANE		$C_{24}H_{50}$	338	763	382	—	.7583
PETACOSANE		$C_{25}H_{52}$	352	788	376	—	.7597

(x) - The Non-Benzenoid Hydrocarbons-B. T. Brooks-U. S. Bureau of Mines-Redwood last edition, 1st volume 304-12

(y) - Deductively from, Engler-Höfer-Das Erdöl

(z) - Pressure-Temperature Equations - F. S. Mortimer, J. A. C. S. July 1922, p. 1429

$$\log P_c = 1.1633 + \frac{4S(t_c - t_b)}{9[(273 + \frac{4}{9}t_c)(273 + \frac{4}{9}t_b)]}$$

S = Constant for each gas calculated from boiling temperature

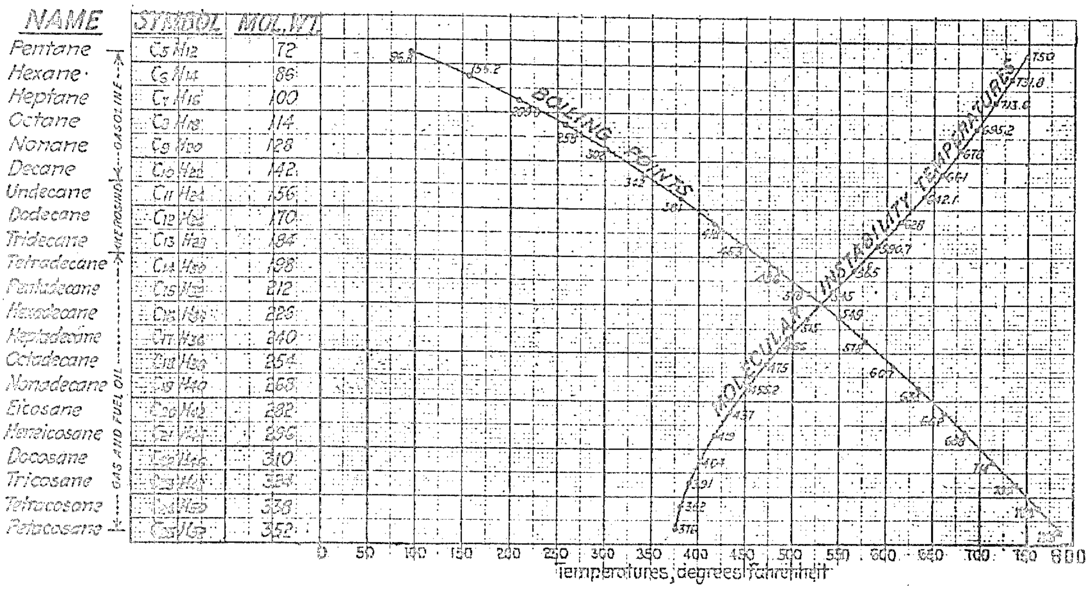
P_c = Cracking Pressure $S = 1267 + 2.849t_b + 0.00015t_b^2$

t_c = Cracking Temperature

t_b = Boiling Temperature

It is observable that in hexane C_7H_{16}, a gasoline compound, 209° F. (boiling point), 713.6° F. (instability temperature), tetradecane $C_{14}H_{30}$, a gas oil compound 486° (boiling point), 570° (instability temperature), the low boiling point is accompanied with high instability temperature; likewise in undecane $C_{11}H_{24}$, a kerosene compound, 381° (boiling point), 642° (instability temperature), nonodecane $C_{19}H_{40}$, a fuel oil compound, 626° (boiling point), 455° (instability temperature).

A sequence is observable in this: the lower the boiling point, the higher the temperature of instability; the higher the boiling point, the lower the temperature of instability. The reason for this seems to lie in the fact that the intermolecular contact is more intimate in the heavy compounds than in the light, and the transfer of energy produced by heat, is more effectually made through the instrumentality of heavy mass than with the lighter construction of slight comparative density. The curve of this relationship is superposed as follows:



The curves cross between pentadecane, b. p. 518° F., and hexadecane, b. p. 550°. All lighter compounds possess lower boiling points than temperatures of instability; all heavier compounds are unstable before attaining boiling point.

The last shown table includes a list of pressure coefficients by which the boiling temperatures of the compounds are elevated to the temperature of instability.

The enormous pressures indicated for the first few compounds of the series are all within the gasoline group. They are set forth simply to show the intensity of the parabolic curve. No operation, of course, is contemplated for the hydrogenization of these compounds. The lightest of the family for which treatment by the submitted process is considered, would be decane, which is the lightest of the kerosene series.

The method for arriving at temperature and pounds pressure requirements for operation of the system and apparatus submitted, is:

Determine first the character of oil to be treated, by simple laboratory boil-over and condensation test; carry the percentages to an approximate dry. Compute tables of ready reference as above. Estimate the pressure needed to elevate the boiling point of the lightest component of the oil to a temperature equalling the temperature of instability for the particular compound. All compounds heavier than the lightest occurrent in the oil, will have lower temperatures of instability. The result is, that with the establishment of a pressure which causes the lightest component to become unstable before vaporizing, this will effect instability in all components prior to their vaporization.

In case of extremely heavy petroleums, or refinery residual oils, if their boiling point is above 525 degrees F., no pressure whatever is needed, because it has been shown that compounds possessing such a boiling point and over, attain the state of instability prior to boiling.

The purpose of this regulation, as is apparent consists in establishing conditions so that when the oil vaporizes, it vaporizes in a state of non-stability, in which condition it is susceptible to molecular readjustment and the incorporation of the heat-imparting and surrounding hydrogen-carrying gases.

In addition to the tabulated information for calculating pressure and temperature requirements, is needed a table of saturated steam coefficients, contained in Kent or any other pocket manual. The reason is this: Pressure is regulated to raise the boiling point of the lightest compound to its temperature of instability, so that the vapor is unstable. This heat will exceed the instability temperature of all other fractions of the oil, rendering them unstable.

But the pressure which raises the boiling point of the lightest compound possessing the lowest boiling point, has also raised the boiling point of the other hydrocarbons. The other hydrocarbons without additional heat, therefore, cannot boil. The maximum and minimum within the generator must be conditioned to serve all compounds in the oil, the selective feature of the operation giving each the desired equation, but all conditions must be furnished.

With instability established, boiling is not an absolute essential, but the operation is hastened by the intimacy of contact afforded.

The pressure condition is established by the pounds per inch needed to cause the lightest compound to unstabilize before vaporizing. The temperature condition is established by ascertaining a new boiling point for the compound requiring the greatest heat to vaporize, under pressure conditions thus established.

The formula is:

h. c.=heaviest compound.
b. p.=heaviest compound boiling point (°F.)
P=pounds per square inch pressure.
S=steam boiling point, same pressure.
T=maximum required heat.

$$T=\frac{S-212}{\text{Sp. gr. h. c.}}+\text{b. p.}$$

This formula is not submitted as completely accurate, but furnishes sufficiently reliable an index for heat requirements to answer the necessities of practical operation.

Illustration:

=1=laboratory boil-over

Below 350°= 0%
350–400°=19%
400–500°=23%
500–600°=40%
600–700°=15%
Over 700°= 3%

Pressure.

350–400°—undecane, b. p. 381.2°; temperature of instability 642.1°; pressure requirement to elevate boiling point to temperature of instability, 221 pounds. (Pressure 221=250 lbs.)

Temperature.

Over 700°—docosane, b. p. 714°; specific gravity .7553; pressure 250 pounds.

$$T=\frac{S-212}{\text{Sp. gr.}}+\text{b. p.}=\frac{207.8-212}{.7553}+714°=960° \text{ Fahr., temperature required.}$$

Illustration:

=2=laboratory boil-over

Below 450°= 0%
450–500°=18%
500–600°=32%
600–700°=30%
700–750°=16%
Over 750°= 4%

Pressure:

450–500°—tridecane; b. p. 453.2°; temperature of instability 590°; pressure required to elevate boiling point to temperature of instability 66.6 pounds. (Pressure 66.6=75 lbs.)

Temperature:

Over 750°—tetracosane; b. p. 788°; specific gravity .7597; pressure 75 pounds.

$$T=\frac{S-212}{\text{Sp. gr.}}+\text{b. p.}=\frac{320-212}{.7597}+788^\circ=930^\circ \text{ Fahr., temperature required.}$$

The operations within the generator, then, are as follows:

The oil mass starts downward from its inlet, 10, maintaining a state of fine filmentation in the presence of the superheated gases introduced at the gas intake, 5, at the bottom of the generator.

As the oil mass proceeds downward, encountering ever-increasing temperature, such hydrocarbon components as require the least temperature for vaporization, under the pressure conditions provided, are vaporized. Prior to the occurrence of this vaporization, a temperature has been encountered equalling the state of instability, the state in which molecular equilibrium is disrupted. Thus, the vapor formed emanates in a state of molecular instability. In the presence of the heat-imparting, hydrogen-containing gas, equilibrium is sought between the two, resulting in mutual interchange, producing hydrogenization of the unstabilized, vaporized liquid.

Each successively heavier compound attains greater penetration of the generator. Attainment of each respective boiling point temperature vaporizes the particular compound, and insures its release from temperature in excess of that required. As a vapor, the oil rises to cooler zones. The results, successively, are instability, vaporization, and hydrogenization.

Through regulation of the quantities of comparatively cool oil introduced into the generator, the quantities of hot gas introduced, and the temperature of the gases when introduced, the temperature of the top chamber, 13, of the generator, into which is attached the exit pipe, 14, is regulatable.

Thus, presuming the desired product to be a type of gasoline with an average 200° boiling point: the heat condition of the top exit chamber, 13, is regulated to this temperature, corrected, however, in adjustment with the pressure condition maintaining. The result is that only such hydrocarbons as exist in a volatile state at the selective temperature, can escape through the exit pipe.

Such vapors can only be gasoline vapors of the pre-selected, average grade, or lighter elements, with lower boiling points.

In the downward course of the oil, so conditioned, the lighter hydrocarbons with the lower boiling points are the first to vaporize. The further the journey of the oil into the generator, the more and more is it constituted of the heavier fractions.

Unless each compound, when vaporized, assimilates sufficient hydrogen to lower its boiling point to the selective temperature of the top chamber, it liquefies before reaching the selective temperature. The result is that the oil resumes the downward course, as a liquid. Revaporization occurs at its new and lower boiling point temperature, when it again ascends, eventually complying with the regulative conditions of the exit chamber, and is released.

The gentleness of the operation avoids over-rarefication and carbon deposit. The administration of heat through hydrogen-containing gas is much different from the delivery of like temperature through metallic contact. A sponge thrown on a cook stove with a 500° surface heat, will become a cinder, but suspended in a steam jet, at the same temperature, it saturates. A heavy hydrocarbon, squeezed with pressure and excessive metal-delivered heat, drops carbon and gives off gas, but stimulated by intimate contact with hot hydro-containing gas, saturation follows.

It is, of course, apparent that the operation outlined is not intermittent, but continuous.

In the drawing, Figure 1, the receiving tank, D, below the condenser, C, receives the products of the operation. The regulative discharge from the generator denies exit to all else than a vapor or gas at the selected temperature. Such of this as liquefies, through the condenser, C, is precipitated on the floor of the receiving tank, D. Such part as remains gaseous, finds exit through the roof of the tank, at 15. Pressure release cocks are installed at both places.

Gas from the tank is conducted to a single-lift holder, not shown. From the gas holder, the gas is compressed into the heater, A, at working pressure conditions, determined as before outlined. A working surplus of several thousand feet is maintained in the holder.

Additional gas is taken into the holder, without pressure, to the extent of the actual gas consumed, and incorporated, during operation. The flow of gas through the generator is in excess of the requirements of quantitative reaction with the oil.

To the extent that any of the oil introduced may be composed of such heavy constituents and impurities as not to vaporize, there is provided a tank, 16, below, for containing such liquid. The same is drained through the pipe, 17, and cut-off valve, 18.

In the event of it being desired to produce a number of different predetermined and selected products, this result may be accomplished by using a number of generators, B, as above described, each governed by such regulations that the temperature at the bottom and the top of the generator will produce the product desired. These generators may be operated individually or in tandem, or otherwise, as desired.

The method for condensing, in this particular apparatus, utilizes the expansion of gas released from pressure, supplemented by water, as the agencies.

The pipe, 14, carrying the discharged products of the generator, B, passes through an encompassing pipe, 19, of larger diameter. The vaporous products delivered into pipe, 14, are refrigerated to atmosphere or below, so that the vapors are converted into a liquid to the extent of their capacity to assume such form. They are delivered at the terminus, 20, in the collecting tank, D.

That part of the gas which does not liquefy then obtains outlet through the larger pipe, 15, which is equipped with a release pressure cock, 21, so regulatable that it permits discharge at a fraction less pressure than the pressure appearing in the top of the generator, B, minus friction. At this point of discharge, above the cock, 21, the pressure is released and expansion and refrigeration take place.

The gas, having discharged its refrigeration functions, is then conducted from exit 22, to the gas holder, of ordinary construction, not necessary to be shown. For supplementary refrigeration, water may be supplied to the tank, C, through pipe 23, finding exit through pipe 24.

The container, D, Figure 1, the fourth element, scarcely needs description, as it consists simply of a tank constructed for the purpose, amply strong to withstand the required pressures. It is equipped with double discharge valves, 25—26, as in case steam has been used in the operation, quantities of water will settle to the bottom. The entire apparatus is equipped with pyrometers, thermometers, liquid and pressure gauges, at the several appropriate and necessary points.

The compressor, 2, receives its gas supply from the gas-holder (not illustrated). The gas-holder receives the exhaust gas from pipe 22, augmented by gas supplied from outside sources as required.

Such details as the use of heated gas for warming the crude oil before introduction into the generator, B, are not indicated, but it is to be understood that any suitable appliance for this purpose may be employed.

It is to be understood that the foregoing description is merely one way in which the results indicated can be obtained from the principles involved in the operation of this particular apparatus. It is not the purpose to give in exact detail the needs of a commercial apparatus operated on the principles indicated.

It is to be further understood that many changes in the arrangement, order, and steps of the process and method, and in the apparatus as herein set forth, can be made within the scope of the claims, and as indicated by the variations in the different claims, without departing from the spirit of the invention.

There is submitted an apparatus consisting mainly of a fire-clay-lined shell, equipped within with certain oil filmenting members.

By the introducing of relatively cool oil at the top and heated, hydrogen-containing gas at the bottom, the counter-flow of the two is designed to make the top of this generator the coolest, and the bottom the hottest. Thus conditioned, the farther the oil penetrates toward the bottom of the generator, the greater is the heat experienced, and the higher the gas rises, the cooler are the zones it encounters.

This is based upon the premise of the complex character of petroleum or its heavier fractions, in that their composition is one of a mixture of differentiated hydrocarbons. The purpose is that, by continuous operation, as the boiling point of any particular compound is reached in temperature, because of the fineness of its filmentation, vaporization follows, and the vapor ascends to cooler zones, each compound being permitted, in this way, the opportunity to select its needed temperature for vaporization.

There is presented, as the needed pressure equation, the degree of pressure needed to raise the boiling point to the temperature of instability of the molecule constituting the most rarefied of the petroleum mass undergoing treatment. This fraction is determined by simple laboratory boil-over analysis. The heat equation is determined by the temperature needed to boil the heaviest fraction under the pressure condition thus established.

The principle of this regulation is that when vaporization occurs, each respective compound will vaporize in a condition of non-stability, enabled thereby to undergo molecular readjustment in the presence of the hydrogen-containing gas, which adds to its hydrogen content, producing lower boiling point and specific gravity. The top regulative chamber is maintained at such temperature, taking into consideration the pressure regulation, as to permit, only in the form of vapor, exit of hydrocarbon compounds susceptible of maintaining the state of vaporization under the conditions maintained.

The result claimed is that the operation of the generator makes possible pre-determination of the product to be delivered, and the graduation of temperature administered, gives to each constituting carbon of the oil mass the selective temperature needed for unstabilized vaporization, and hydrogenous incorporation.

There may be employed, in this operation, any hydrogen-containing gas; for instance, natural gas, overly rarefied products of fractional distillation, or other refinery processes; artificial gas, particularly water gas, containing upwards of fifty per cent, by volume, in hydrogen; free hydrogen as a derivative, for instance, of superheated steam in contact with metallic, oxidizing reagents, or otherwise.

The remaining parts of the apparatus, consisting of gas super-heater, condensation coils, reception tank for product delivered, and gas-holder, are merely adjuncts necessary to the operation of the generator, and may be of any suitable type.

It might also be added that any hydrocarbon compound of the oil mass, unable at initial vaporization to become sufficiently hydrogenized to maintain vapor state at the regulative temperature of the topmost regulative chamber, liquefies in the cooler zones before attaining this chamber, and is thus subjected to revaporization, the process being repeated until adequate hydrogenization is had to enable the compound in its new form to pass the requirements of the regulative chamber.

The time element needed for all reactions is increased, when need be, by elongation vertically of the generator, and an increase in the number of filmenting members.

Distinguished from cracking.

Customarily, cracking is a term applied to a process involving an active state of a heated oil mass, in which pronounced dismemberment is in progress. The scope of the word, in some instances, has been enlarged to include the products of the process: rare gas, carbon depositing, and lower specific gravity of the residue. The process submitted is not cracking.

In cracking, the temperature is so intensive that inter-atomic agitation is carried beyond the point of molecular instability, to molecular dismemberment.

The process submitted contemplates no severance of the constituting hydrogen and carbon, but the principle involved finds entire application during the period of molecular instability.

An apparatus constructed and operated in accordance with the process presented, constantly affords opportunity for hydrogen increase in the oil mass, simultaneously with attainment by any constituting compound of sufficient instability for its reception. As the oil constituents penetrate farther and farther into the apparatus and into greater heat, each differentiated member encounters its required temperature for the purpose. Increase of hydrogen content lowers the boiling point, and immediate relief, as vapor, is had from the excess temperature which rends asunder the molecule. The essence of this process is not to crack.

The comparison requires, possibly, reference to the readjustment occurrent in cracking. How can the dismemberment, or cracking of a molecule, composed of hydrogen and carbon, resulting in the release of its carbon as a solid, and of its hydrogen as a gas, decrease the specific gravity of the oil mass undergoing treatment?

The happening is this: By application of heat and pressure conditions, certain compounds are burst asunder; carbon is precipitated as a solid, and the hydrogen which had been unified with it to make a hydrocarbon, is released. This released hydrogen, taking advantage of the stirred-up condition of the other hydrocarbons, joins them, forcing its way into other molecules because of their receptivity produced by temperature and pressure. This entrance of hydrogen increases the hydrogen content, reducing thereby specific gravity. The molecule in a state of agitation is increasing its hydrogen content.

It must be remembered that the higher the boiling point, the lower the cracking point. Thus, in cracking processes, the molecules constituting the heaviest hydro-carbons, first reach the point of such intensified oscillation as to burst asunder. Their carbon is deposited, their hydrogen incorporated by members of lower boiling point and higher cracking point.

The new hydrogen incorporation still further lowers the boiling point, and increases the dismemberment temperature for the molecule, so that the heavier constituents are hydrogenizing the lighter.

The cracking process is the dismemberment of the heavy for the hydrogenization of the lighter, the active agency lying in the dismemberment in cracking. In the process presented, hydrogenization is otherwise provided to the unstable molecule, and the essence is not to crack.

In the process submitted, the state of receptivity is established in which hydrogen is assimilative, and the hydrogen is supplied. One is destructive distillation, the other constructive conversion.

The apparatus submitted is virtually self-regulative. Arrange the requirements of the two extremes of the oil-constituting compounds, and each constituent chooses its own requirements.

Cracking apparatuses, in their various forms, impose conditions based upon dismembering, or cracking, certain parts of the oil mass, while no such conditions are present in apparatuses operated by this process.

It is important to note that, as cracking effects the elimination of certain fractions, the residuary bulk is of decreased amount. The method proposed adds to the bulk, making greater quantity as the specific gravity is reduced.

Oil sample, weight per gallon 7.21 pounds.

Boil-over:
400- 500°—26%; 500-600°—42%; 600-700°—30%; over 700°—2%.

	C	*H*	
400- 500°—$C_{13}H_{28}$—7.21×.26=1.87=	1.59 lb.	.28 lb.	Oil, one gallon 7.21 lb.
500- 600°—$C_{16}H_{34}$—7.21×.42=3.03=	2.58 lb.	.45 lb.	
600- 700°—$C_{20}H_{42}$—7.21×.30=2.16=	1.83 lb.	.33 lb.	
Over 700°—$C_{23}H_{48}$—7.21×.02= .15=	.13 lb.	.02 lb.	
	6.13 lb.	1.08 lb.	

Gas sample, by volume 250 cubic feet.

(Methane 85%; ethane 10%; propane 3.5%; nitrogen and impurities 1.5%)

			C	*H*	
Methane CH_4	$\frac{250\times.85}{23.6}$	=9 lb.	=6.75 lb.	2.25 lb.	Gas 250 cu. ft.
Ethane C_2H_6	$\frac{250\times.10}{12.5}$	=2 lb.	=1.60 lb.	.40 lb.	
Propane C_3H_8	$\frac{250\times.035}{8.5}$	=1.3 lb.	=1.06 lb.	.24 lb.	
			9.41 lb.	2.89 lb.	12.30 lb.
			15.54 lb.	3.97 lb.	19.51 lb.

Reaction.

Gasoline series:			*C*	*H*	
Pentane	C_5H_{12}	b. p. 96.8°— 2.4 lb.=	2. lb.	.4 lb.	
Hexane	C_6H_{14}	b. p. 156.2°—12.0 lb.=	10. lb.	2. lb.	
Heptane	C_7H_{16}	b. p. 209. °— 2.8 lb.=	2.34 lb	.46 lb,	
Octane	C_8H_{18}	b. p. 258. °— 1.5 lb.=	1.2 lb.	.3 lb.	
			15.54 lb.	3.16 lb.	18.70 lb.
				Free hydrogen	.81 lb.
					19.51 lb.

Pentane, hexane, heptane, and octane, in above proportions, form a gasoline. Gasoline b. p. 96.8°–258°, avg. 200°; sp. gr. .65; wt. per gallon 5.40 lbs. Allowance factor 25%, to include cost of heat generation and apparatus loss. Quantities:

$$\frac{18.70\times.75}{5.40}=2.5 \text{ gallons gasoline}-.81 \text{ lb. hydrogen.}$$

It should be mentioned that great saving is found in the use of the methods and type of apparatus presented, as a substitute for the usual checker-brick form of carburetor as incorporated as part of the standard equipment for generating artificial gas.

Generator B is incorporated between the gas generator and superheater of the ordinary sets, U. G. I.—Wilkinson and others. The heated gas from the gas generator is delivered at the bottom of generator B, and the oil to be used for enrichment purposes at the top, through pipe 10. No pressure is required. The vaporized oil and gas introduced enter the superheater of the set through pipe 14, where fixation occurs.

The term "hydrogen-containing gas" as used herein means a gas or vapor in which hydrogen is occurrent either in a free state or in chemical combination.

The process presented will be referred to in the claim as "constructive conversion" because by its use hydrocarbon compounds are converted into others by a constructive method of addition in contrast to the destructive method of substraction or cracking.

The phrase "carbon deposit" as used means carbon as deposited by molecular dismemberment or cracking of the hydrocarbon compounds.

In the phrase "a process for the constructive conversion of hydrocarbons of higher boiling points and hydrogen containing gases into liquid hydrocarbons of lower boiling points the words "hydrocarbons of higher boiling points" and "hydrocarbons of lower boiling points," both refer to hydrocarbons which are liquid at atmospheric pressure and temperature.

The expression "substantially homogeneous product" as used does not mean that the compounds of the hydrocarbon product shall have the same boiling points. I refer to such a product as commercial gasoline as a substantially homogeneous product, although some of its constituent compounds have boiling points as low as approximately 100° and others as high as approximately 280°.

The term pressure as used in the claims is intended to mean pressure above atmosphere.

The thickness of the oil films in the apparatus will be determined by the viscosity of the oil, as will readily be understood.

It will be understood that in using unrefined petroleum and flowing the same into the increasing temperatures, there is first vaporized in substantially an unchanged state the gasoline content of the petroleum.

Referring to increase of the hydrogen content of the hydrocarbon molecules: it is apparent that when the boiling point of the lightest hydrocarbon compound of an oil is raised to its corresponding instability temperature all of the members of the series possessing higher boiling point must have been raised to or beyond their instability temperature because as the boiling points increase instability temperatures decrease.

The operation of the process submitted includes hydrogenization of the heavier compounds of the oil undergoing treatment at temperatures less than that of their respectively advanced boiling points. By this operation it becomes apparent that through increase of the hydrogen content of such compounds their boiling points become reduced and vaporization effected.

It is observable that in the operation of the process presented, the resultant products, liquid and gaseous, are jointly delivered to a product-receiving container, for instance receiving tank D, as shown in Figure 1.

From such product container, exits are provided in the upper part for the gaseous, and in the lower part for the liquid materials.

The process described herein and the apparatus as shown in Figures 1, 2, 3, 4, and 5, may be operated for the purpose of manufacturing, in a single operation, both a heating and illuminating gas for commercial use, and a liquid hydrocarbon of predetermined character.

Artificial gas, as manufactured by methods in use for domestic consumption, is so low in thermal value that the practice is to cause its enrichment by the addition of gasified petroleum fractions. The enrichment is customarily effected in an apparatus unit called a carburetor, consisting of an insulated steel shell containing checker-brick, broken tile, or other filming device.

Filmed oil and heated gas are afforded contact in the carburetor, and the resultant vapors and gases are conveyed to a superheater for fixation.

In these specifications it is set forth that any hydrogen-containing gas may be used in applying and operating the process described herein.

In Figure 6 there is presented, mostly in cross-section, an apparatus for using water-gas and crude petroleum or its heavier fractions, for the manufacture conjointly of an enriched water-gas product, and a liquid hydrocarbon combustion fuel.

In Figure 6, element E is a water-gas generator, of any type, consisting of a steel shell, 30, insulated with any suitable material, 31, having a fire-grate, 32. The charge of coal, or coal and coke, is deposited on grate 32, and ignited, and air in comparatively large volume is forced through opening, 67, causing a rapid and hot burning of the coal-charge. Pipe 33 conveys the exhaust heat from the water-gas generator, E, into and through superheater F, and thence through stack 34.

Superheater F is a shell made of steel, or other suitable material, 35, with suitable insulation, 36. The interior of F is filled with checker-brick or broken tile, or with other suitable material for heat absorption.

Upon attainment of the proper state of partial combustion and intense heat, through ignition of the coal-charge placed on grate 32, Figure E, the air supply through inlet 67 is cut off and steam is introduced through opening, 37.

Coincidental therewith, valve 38 is closed. The steam passing through the ignited coal, or coal and coke, gives up its oxygen to the carbon present, producing a gaseous result, approximately, by volume, hydrogen 50%, CO_2 10%, and CO 40%. This gas then passes through pipes 39 and 40, into the bottom-most part of element B.

Inlet 41 is provided for reversing the steaming charge. In this, steam-inlet 37 is closed, and steam-inlet 41 is open, causing the steam to proceed downward through the fire-bed and through exit pipes 42, and 40, into the bottom-most part of element B.

Stop-cocks 43 and 44 are respectively opened and closed for directing the water-gas produced through pipe 40, dependent upon whether the steam-charge is delivered above or below the grate, 32.

Element B consists of an outer shell, 45, insulated with any suitable material, 46, and filled within with any suitable means for oil filming: checker-brick, broken tile, or otherwise, but preferably with a vertical series of dish-shaped members, as described in Figures 2, 3, 4, and 5.

Oil supplied through inlet-pipe, 10, is thus counter-flowed within element B against the heated water-gas delivered through pipe 40.

The hottest part of element B is at the bottom, the coolest part at the top, hence as the oil delivered through pipe 10 progresses downward, constantly acquiring additional temperature, its respective constituting hydrocarbon compounds are vaporized as the required boiling-point temperatures are encountered. Thus, there is delivered at the bottom of a dephlegmating device, element G, the emanating hydrocarbon gases and vapors.

Element G consists of a coil, 47, of suitable material, containing within, the gaseous material emanating through pipe 11, element B, the coil being surrounded with cooling liquid material, the temperature being so regulated that escapement from element G is denied all hydrocarbons unable to exist in vapor form at a predetermined and regulated temperature.

Such vapors as are unable to remain in vapor state at the regulative exit temperature, return downward through coil, 47, element G, and thence into element B, where revaporization occurs. All such compounds as maintain a state as gas or vapor at the selected exit-temperature established in element G, pass through pipe 48, into coil 49, element H.

Element H is a condenser, consisting of an outer shell, 50, and containing coil 49, made of any suitable material, the coil being surrounded by relatively cool liquid.

There is then discharged from element H, through pipe 51, the liquid and gaseous material which has passed through condenser H, which material, liquid and gaseous, is discharged through the top of element I.

Element I is a receiving tank for the liquid and gaseous resultants of the dephlegmator, G, and condenser, H. It consists of a shell, 52, of any suitable material.

The liquid discharged from pipe 51, into the top of element I, goes to the bottom of element I, and exit is provided for the gaseous material through pipe 53, where it is conveyed to the bottom of superheater, F. Superheater F possesses high temperature, normally, in the average water-gas operation approximating 1400 degrees.

The gaseous material thus ascends through the heated checker-brick construction, where gas fixation occurs, and the gas is discharged as a permanent gas through pipe 54, which conducts the gaseous product, through suitable scrubbing and purifying tanks, and refrigeration apparatus, to a gas-holder of any suitable construction, not shown in the drawing.

Valve 55, element F. is closed when ignition is in progress of the coal-charge on grate 32, Figure E, or blowing period, and is automatically opened during the steaming or gas-making period.

The liquid material deposited in the bottom of receiving tank, I. is delivered through pipe 56, by use of a small pump, 68, into the top of the condensing member, H. The liquid fills the space in condenser H intervening between the encompassed coil and the walls of the member. The liquid then flows over through pipe 57, into the dephlegmating member, G.

The liquid thus contained within members G and H is redistilled, and as a vapor passes through pipe 58 into condenser K, through coil 59, and finds exit at the coil terminal, 60, from which it is conducted to storage tanks.

The cooling medium employed in condenser K is water, which is supplied at opening, 62, and afforded egress through opening, 61.

There is thus delivered through exit 60 a double-distilled liquid hydrocarbon, possessed of such gravity as the adjustment of heat and pressure conditions during the operation produces, for instance, gasoline of a predetermined and selected grade.

Pet-cocks 63, 64, 65, 66 are opened from time to time to discharge sediment, impurities, and other refractories.

A supplementary water-cooled dephlegmator may be added above and as a continuation of element G, Figure 6.

A supplementary water-cooler-condenser may be added below and as a continuation of Element H, Figure 6.

A second water-gas generator, element E, Figure 6, may be installed, and the two so operated that while one blows, the other steams, effecting thereby non-intermittent delivery of water-gas.

The delivery of superheated gas from element E, to element B, may be supplemented by passing gas from the gas-container (not shown) through a superheater, and introducing the gas into element B.

Any suitable method for preheating the oil introduced, or increasing available temperatures by any suitable means, and for scrubbing, purifying or redistilling of any of the products, may be employed.

I know of no water-gas set which is operated with pressure conditions imposed. The only pressure occurrent is that produced by gas expansion within the generator, which serves merely to drive the gas through the apparatus to the gas-holder, and is measured in ounces.

In operating the apparatus, Figure 6, with petroleum fractions as heavy as or heavier than pentadecane, no pressure condition is imposed, because the lines of molecular instability and boiling points cross at about 535° F., see diagrammatic drawing, page 18.

In operating the apparatus with oils containing lighter fractions than pentadecane, or with crude oil, pressure conditons may also be eliminated. The result is that fractions with lower boiling points than 535° F. will vaporize before attaining temperatures of molecular instability, and appear liquefied in the bottom of element I, Figure 6.

To convert this aggregate of liquid compounds into gasoline, or other substantially homogeneous product, the liquid is subjected in another apparatus to treatment by the method illustrated in the apparatus, Figure 1.

The oil so derived is fed into a supplementary apparatus, designed as shown in Figure 1, through pipe 10, Figure 1. Hydrogen-containing gas is available from the gas-holder, not shown, and is fed into the apparatus through pipe 5, Figure 1.

In operating the apparatus, Figure 6, with oil containing fractions with a lower boiling point than approximately 535° F., or with crude petroleum, pressure conditions may be introduced, governed by the same principles and adjustments as heretofore fully described herein, as applying to the operation of the apparatus, Figure 1.

Concerning operation of apparatus, Figure 6, it is to be understood that the foregoing description is merely one way in which the results indicated can be obtained from the principles involved in the operation of this particular apparatus. It is not the purpose to give in exact detail the needs of a commercial apparatus operated on the principles indicated.

It is to be further understood that many changes in the arrangement, order, and steps of the process and method, and in the apparatus as herein set forth, can be made within the scope of the claims, and as indicated by the variations in the different claims, without departing from the spirit of the invention.

Illustration:

Oil sample, weight per gallon 7.21 pounds.

Boil-over: 400°-500°, 26%; 500°-600°, 42%; 600°-700°, 30%; over 700°, 2%

			C	*H*
400°-500°	$C_{13}H_{28}$	7.21 x 5 x .26= 9.35 lb.=	7.95 lb.	1.40 lb.
500°-600°	$C_{17}H_{34}$	7.21 x 5 x .42= 15.15 " =	12.90 "	2.25 "
600°-700°	$C_{20}H_{42}$	7.21 x 5 x .30= 10.80 " =	9.15 "	1.65 "
Over 700°	$C_{23}H_{43}$	7.21 x 5 x .02= .75 " =	.65 "	.10 "
Quantities:			30.65 "	5.40 "

Oil five gallons 7.21 x 5= 36.05 lb.

Water-gas, by volume 1,000 cubic feet.

Hydrogen 50%; CO 40%; CO_2 10%.

			H	*CO*	*CO_2*
Hydrogen	$\frac{500}{188}$	= 2.66 lb.=	2.66 lb.		
Carbon monoxide	$\frac{400}{13.5}$	=29.63 " =		29.63 lb.	
Carbon dioxide	$\frac{100}{8.8}$	=11.36 " =			11.36 lb.
		30.65 "	8.06 "	29.63 "	11.36 "

Water gas 1,000 cubic feet 43.65 lb. 79.70 "

Reaction—Gasoline.

				C	*H*
Pentane	C_5H_{12}	b.p. 96.8°	= 2.4 lb.=	2. "	.4 "
Hexane	C_6H_{14}	" 156.2°	=12.0 " =	10. "	2. "
Heptane	C_7H_{16}	" 209.0°	= 2.8 " =	2.34 "	.46 "
Octane	C_8H_{18}	" 258.0°	= 1.5 " =	1.2 "	.3 "
				15.54 "	3.16

Gasoline.
b.p. 96.8-258°, avg. 200°
sp. gr. .65
wt. per gal. 5.40 lb.
loss factor 25%

Gasoline sp. gr. .65 2.5 gallons 18.70 lb.

$$\text{Quantities: } \frac{15.54+3.16\times(1.00-.25)}{5.40}=2.5 \text{ gallons.}$$

Enriched water-gas.

			C	*H*	*CO*	*CO_2*
Methane	CH_4	=14.45 lb.=	10.84 lb	3.61 lb.		
Ethane	C_2H_6	= 3.21 " =	2.57 "	.64 "		
Propane	C_3H_8	= 2.08 " =	1.70 "	.38 "		
Hydrogen	H_2	= .27 " =		.27 "		
Carbon monoxide	CO	=29.63 " =			29.63 lb.	
Carbon dioxide	CO_2	=11.36 " =				11.36 lb.
Quantities:		61.00 "	15.11 "	4.90 "	29.63 "	11.36 "

Volume and B.t.u.			*cu. ft.*		*B.t.u.*
Methane	14.45 lb. x	23.6=	341	x 1009=	344,069
Ethane	3.21 " x	12.5=	40	x 1764=	70,560
Propane	2.08 " x	8.6=	18	x 2521=	45,378
Carbon monoxide	29.63 " x	13.5=	400	x 323=	129,200
Carbon dioxide	11.36 " x	8.6=	100	x ----=	-------
Free hydrogen	.27 " x	188. =	51	x 325 =	16,575
			950 cu. ft.		605.782 B. t. u.

950 cu. ft. 635 B. t. u. gas 61 lb.

Recapitulation.

	C	*H*	*CO*	*CO_2*	
Oil	30.65 lb.	5.40 lb.			
Water-gas		2.66 "	29.63 lb.	11.36 lb.	
Quantities·	30.65 "	8.06 "	29.63 "	11.36 "	79.70 lb.

Reaction.

Gasoline	15.54 "	3.16 "			
Enriched water-gas	15.11 "	4.90 "	29.63 "	11.36 "	
	30.65 "	8.06 "	29.63 "	11.36 "	79.70 "

5 gals. heavy oil+1000 cu. ft. 300 B. t. u. water-gas←→2½ gals. .65 sp. gr. gasoline+950 cu. ft. 635 B. t. u. gas.

What is claimed as new is:

1. A process for the constructive conversion of liquid hydrocarbons of higher boiling points, into liquid hydrocarbons of lower boiling points, simultaneously with the adding of carbon in chemical union with hydrogen to hydrogen-containing gas, which consists in introducing into a confined space hot hydrogen-containing gas, and liquid hydrocarbons, and causing the same to counterflow in intimate contact, so that the liquid hydrocarbons constantly enter increasing temperature, and the hydrogen-containing gas constantly enters reduced temperature,

with conditions of heat and pressure so regulated that part of the hydrogen-containing gas combines with the liquid hydrocarbon, and part of the liquid hydrocarbon combines with the hydrogen-containing gas, thus decreasing the gravity of the liquid hydrocarbon, and increasing the gravity of the hydrogen-containing gas, and so conditioning the operation that substantially the entire liquid and gaseous materials are withdrawn as a heavier gas and a lighter liquid.

2. A process for conjointly enriching water-gas, and reducing the specific gravity of liquid hydrocarbons, which consists in counterflowing relatively cool liquid hydrocarbons, against heated water-gas, in intimate contact, within a confined space, and so regulating conditions of temperature and pressure that part of the water-gas is caused to combine with the liquid hydrocarbons, and parts of the liquid hydrocarbons are caused to combine with the hydrogen of the water-gas, thus increasing the ratio of hydrogen in the liquid hydrocarbons, and causing the introduction of carbon in chemical union with hydrogen into the artificial gas, and so conditioning the operation that the enriched gas and the vaporized, hydrogenized liquid hydrocarbons may be withdrawn, passed through a condenser, whereby the liquid hydrocarbon vapors are separated as a liquid from the enriched water-gas, and both products made available.

3. A process for conjointly enriching water-gas, and manufacturing gasoline, consisting of introducing crude petroleum or its heavier fractions, and hot water-gas, into a confined space, exit from which may be had only by gases and vapors possessing boiling points less than a selected exit temperature, and counterflowing the oil against the hot gas in close contact within the confined space, so that part of the hydrogen of the water-gas enters into chemical combination with the oil, and part of the oil enters into chemical combination with the hydrogen of the water-gas, thereby lowering the gravity of the oil and enriching with hydrocarbon addition the hydrogen content of the water-gas, and so regulating the exit conditions that the gas may escape, but none of the oil, save as vapors as light as or lighter than the heaviest compound entering into the grade of gasoline selected to be produced, and causing all such gases and vapors as escape, to pass through a condenser and into a product-receiving receptacle, from which the enriched gas and gasoline may be respectively withdrawn.

4. A process for conjointly enriching water-gas, and converting petroleum fractions heavier than the gasoline series, into hydrocarbons of reduced gravity, which consists in introducing crude petroleum or its heavier fractions, and hot water-gas, into a confined space, in which the oil experiences constantly increasing temperature, and the gas and vapors experience constantly decreasing temperatures, and establishing a state of sufficient molecular instability to permit hydrogen to enter into the liquid hydrocarbon, and hydrocarbons to combine with the hydrogen of the water-gas, and so conditioning exit requirements that only gases and vapors possessing boiling points less than a selected exit temperature, may escape.

5. A process for conjointly enriching water-gas, and manufacturing gasoline, which consists in commingling in a confined space, hydrocarbons in liquid and vapor states, and water-gas, filming the liquid hydrocarbons and administering heat thereto through the medium of hot water-gas, under regulations of temperature and pressure so that sufficient molecular instability is established for part of the hydrogen contained in the water-gas to combine with the introduced liquid hydrocarbons, and part of the introduced liquid hydrocarbons to combine with the hydrogen of the water-gas, and preventing cracking or dismemberment of the liquid hydrocarbons through their intimate contact with the hydrogen of the gas, and so regulating exit conditions that only a predetermined grade of gasoline vapor, and the enriched water-gas, may escape.

6. A process for conjointly adding hydrocarbons to a hydrogen-containing gas, and adding hydrogen to liquid hydrocarbons of higher boiling points, which consists in commingling hydrogen-containing gas in a confined space, with petroleum or its heavier fractions, causing sufficient molecular instability by regulation of temperature and pressure, to produce molecular readjustment and increase of the hydrogen content of the liquid hydrocarbons, and hydrocarbons addition to the hydrogen-containing gas, without dismembering or cracking the liquid hydrocarbon compounds, and subjecting the resultant hydrocarbon vapors to decreasing temperatures, and maintaining such regulation of exit conditions that only a substantially homogeneous liquid hydrocarbon vapor, and enriched hydrogen-containing gas, may escape.

7. A process for adding hydrocarbons to a hydrogen-containing gas, and adding hydrogen to liquid hydrocarbons of higher boiling points, which consists in establishing within a confined space a counterflow of heated hydrogen-containing gas, against relatively cool oil filmed to fineness, so that the oil flows into increasing temperatures and the gas and vapors into decreasing temperatures, and through regulation of heat and pressure conditions causing sufficient molecular instability to cause molecular readjustment, whereby hydrogen is added to

the liquid hydrocarbon, and hydrocarbons are added to the hydrogen-containing gas, thus effecting the lowering of the boiling points of the liquid compounds, and the enrichment and increase of thermal value of the hydrogen-containing gas, the liquid hydrocarbons not being permitted to attain sufficient temperature for molecular disruption and carbon deposit.

8. A process for adding hydrocarbons to a hydrogen-containing gas, and adding hydrogen to liquid hydrocarbons of higher boiling points, which consists in bringing together in a confined space, an oil, a hydrogen-containing gas, and hydrocarbon vapors, so that intimate contact is established between the oil and the gaseous material, and counterflowing the gas and oil, with heat and pressure conditions so adjusted that the oil in liquid form experiences constantly increasing temperature, and the gas and vapors experience constantly decreasing temperature, the degree of heat and the amount of pressure being so adjusted and supplied that the boiling points of the liquid compounds are retarded to equal or exceed a temperature at which inter-atomic activity is sufficiently accelerated to cause molecular readjustment and the addition of hydrogen to the liquid hydrocarbons, and the addition of hydrocarbons to the hydrogen-containing gases, without permitting dismemberment or cracking of the oil compounds, and then withdrawing the enriched gas and substantially homogeneous hydrocarbon vapors.

9. A process for adding hydrocarbons to a hydrogen-containing gas, and adding hydrogen to liquid hydrocarbons of higher boiling points, which consists in establishing in a confined space, the presence of hydrogen-containing gaseous material, and non-gaseous hydrocarbons, and successively and continuously heating each compound of the non-gaseous hydrocarbons to a temperature of molecular instability by regulation of heat and pressure conditions, and maintaining intimate contact between the gaseous and non-gaseous materials, so that sufficient temperature is attained, without molecular dismemberment or cracking of the oil, to effect the incorporation of hydrogen into the non-gaseous material, and the incorporation of hydrocarbons into the gas, by establishing sufficient molecular instability to permit molecular readjustment, thus lowering the boiling points of the non-gaseous compounds and increasing the thermal value of the gas, and causing through resultant vaporization of the oil, contact by the oil vapors with decreasing temperature, and so conditioning the operation that substantially the entire volatile, non-gaseous hydrocarbons are converted into a substantially homogeneous product of reduced boiling point, and the gas enriched and its specific gravity increased and boiling point elevated.

10. A process for converting liquid hydrocarbons and hydrogen, into liquid hydrocarbons of reduced boiling points and gaseous hydrocarbons, which consists in establishing intimate contact, within a confined space, between liquid hydrocarbons and hydrogen, under such heat and pressure conditions as to cause a state of sufficient molecular instability as to cause part of the hydrogen to combine with the liquid hydrocarbon compounds, and part of the liquid hydrocarbons to combine with the hydrogen, through resultant molecular readjustment, in such manner that the molecules constituting the liquid hydrocarbons are not permitted to become dismembered or cracked, and exit conditions so regulated that escape is denied excepting to gases and vapors not exceeding in boiling points a predetermined temperature.

11. A process, without pressure, for enriching water-gas and constructively converting petroleum fractions whose temperatures of molecular instability are less than their boiling points, into lighter hydrocarbons whose temperatures of molecular instability are not less than their boiling points, consisting of commingling crude petroleum or its heavier fractions, and hot water-gas, in intimate contact, within a confined space, and causing the liquid oil to encounter constantly increasing temperature, and the gas and vapor to encounter constantly decreasing temperature, and employing such temperature regulation as to vaporize with substantially no molecular change, substantially all of the liquid hydrocarbons possessed of boiling points lower than their temperatures of molecular instability, and unstabilizing such volatilizable liquid hydrocarbons as possess a lower temperature of molecular instability than their boiling points, without molecular dismemberment or cracking, and causing part of the hydrogen contained in the water-gas to combine with part of such heavier oil fractions, and part of such heavier oil fractions to combine with the hydrogen contained in the water-gas, and establishing temperature exit conditions at substantially the temperature at which boiling points and temperatures of molecular instability coincide, so that there may escape from the confined space, in gaseous and vapor states, elements and compounds whose boiling points are equal to or less than the temperature at which boiling points and the temperatures of molecular instability coincide, and returning for retreatment compounds unable to maintain a vapor state at the regulative exit temperature, and retreating same until they comply with such exit temperature regulation, so that there results an enriched

water-gas and a liquid hydrocarbon, the constituting compounds of which possess boiling points not greater than their temperatures of molecular instability.

12. A process for enriching water-gas, and manuufacturing gasoline, without pressure, consisting of commingling crude petroleum or its heavier fractions, and hot water-gas, in intimate contact, within a confined space, in such manner that the liquid oil encounters constantly increasing temperature, and the gas and vapors encounter constantly decreasing temperature, and employing such temperature regulation as to vaporize with substantially no molecular change, substantially all of the liquid hydrocarbons possessed of boiling points lower than their temperatures of molecular instability, and unstabilizing such volatile liquid hydrocarbons as possess a lower temperature of molecular instability than their boiling points, without molecular dismemberment or cracking, and causing part of the hydrogen contained in the water-gas to combine with part of such heavier oil fractions, and part of such heavier oil fractions to combine with the hydrogen contained in the water-gas, and establishing temperature exit conditions at substantially the temperature at which boiling points and temperatures of molecular instability coincide, so that there may escape from the confined space, in gaseous and vapor states, elements and compounds whose boiling points are equal to or less than the temperature at which boiling points and the temperatures of molecular instability coincide, so that there results by refrigeration to atmospheric temperature of the gases and vapors so emanating, an enriched water-gas, and a liquid hyrdocarbon composed of compounds whose boiling points are equal to or less than the coincident temperatures of boiling points and temperatures of molecular instability, and so treating the said liquid, by constructive conversion, that the said liquid is converted into a gasoline of predetermined grade.

13. A process for enriching hydrogen-containing gas, and converting petroleum or its heavier fractions into any selected, substantially homogenous hydrocarbon product, consisting of commingling crude petroleum or its heavier fractions, and hot hydrogen-containing gas, in intimate contact, within a confined space, so that the liquid oil encounters constantly increasing temperature, and the gas and vapors encounter constantly decreasing temperature, and maintaining such regulation of pressure and temperature as to produce sufficient molecular instability without molecular dismemberment or cracking, to produce molecular readjustment, whereby hydrogen is added to the oil, and hydrocarbons are added to the gas, and establishing such temperature exit conditions that there may escape from the confined space only the enriched hydrogen-containing gas, and liquid hydrocarbon compounds able to maintain a vapor state at the predetermined and established conditions of temperature and pressure required for exit, and returning for retreatment such compounds as are unable to maintain a vapor state at such regulative exit conditions, and retreating the same until they comply with the given conditions and gain exit, so that there results an enriched hydrogen-containing gas, and liquid hydrocarbon vapors of predetermined and selected character.

In testimony whereof I affix my signature.

HAROLD R. BERRY.