

July 12, 1938.

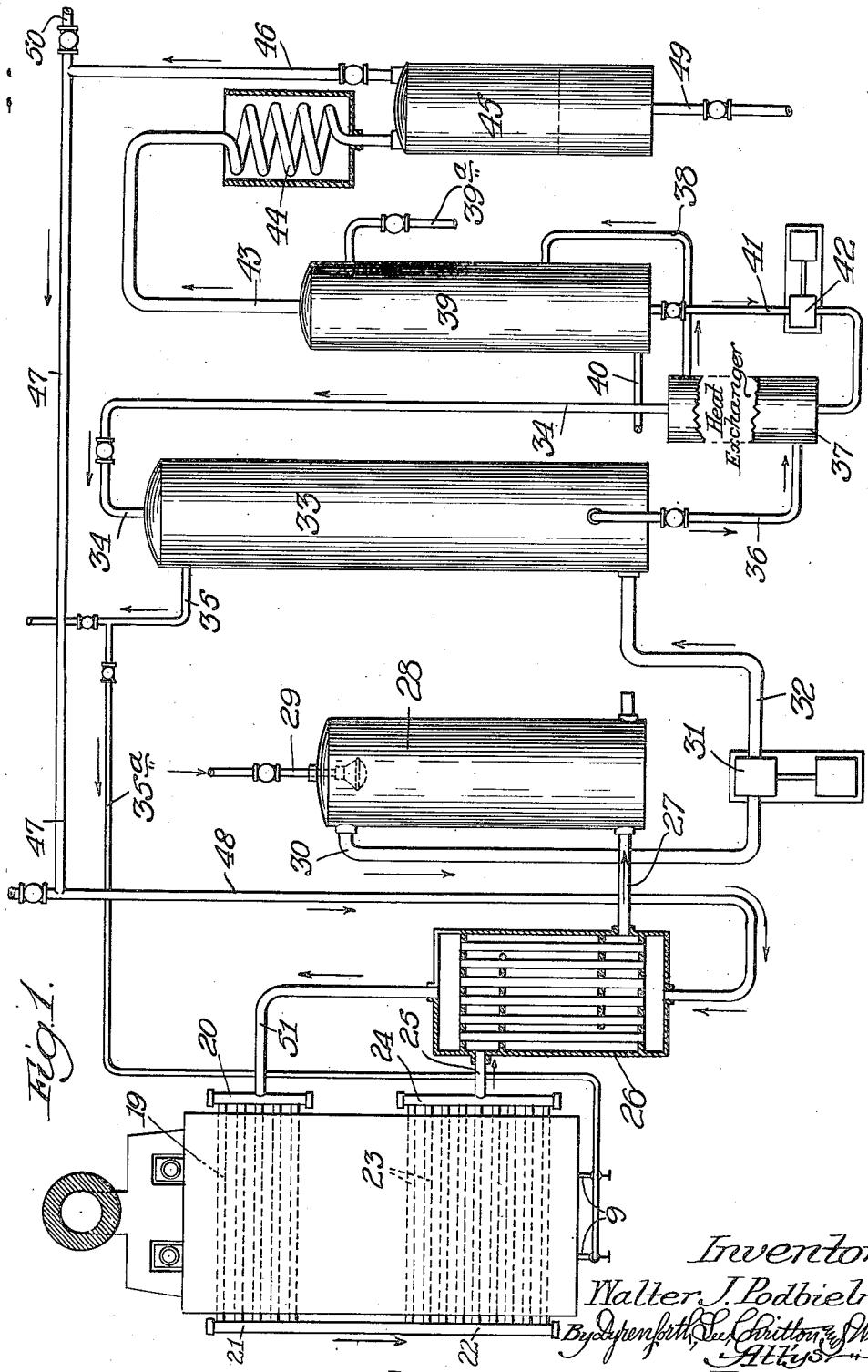
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## HEAT TREATMENT OF HYDROCARBON GASES

Filed Feb. 15, 1935

2 Sheets-Sheet 1



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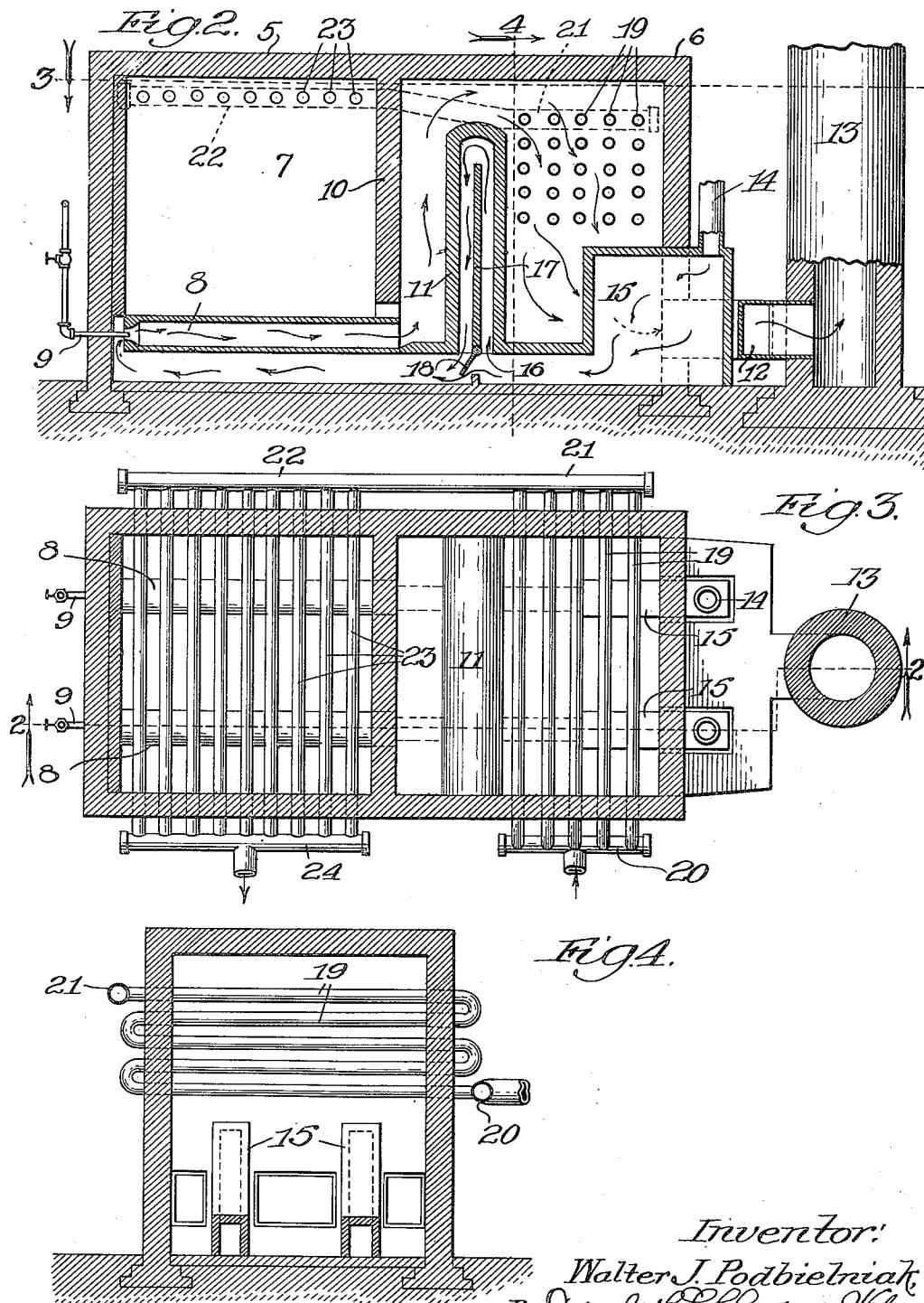
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HEAT TREATMENT OF HYDROCARBON GASES

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2 Sheets-Sheet 2



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## UNITED STATES PATENT OFFICE

2,123,799

HEAT TREATMENT OF HYDROCARBON  
GASES

Walter J. Podblejniak, Chicago, Ill.

Application February 15, 1935, Serial No. 6,748  
In Canada October 16, 1931

13 Claims. (Cl. 196—10)

The present invention relates to improvements in the heat treatment of hydrocarbon gases for the conversion of hydrocarbon constituents thereof and, more particularly, for the production of liquid hydrocarbon products. It will be fully understood from the following description illustrated by the accompanying drawings, in which—

Figure 1 is a diagrammatic illustration of apparatus suitable for carrying the invention into effect;

Fig. 2 is a vertical sectional view through the furnace shown in Fig. 1 on line 2 in Fig. 3;

Fig. 3 is a horizontal sectional view through the furnace on the line 3 of Fig. 2; and

Fig. 4 is a vertical sectional view through the furnace on line 4 of Fig. 2.

In accordance with the present invention, a suitable hydrocarbon gas containing gaseous hydrocarbons, generally including methane and some or preferably a large proportion of which have two to four or even five carbon atoms, are subjected to heat treatment under conditions hereinafter set forth, to form unsaturated and cyclic compounds, and preferably liquid products such as benzol, toluol, and the like. In such operations, as hitherto conducted commercially, the conditions of operation have required the use of heating devices of heavy, refractory material of low heat conductivity, although it has been proposed, in the production of gaseous olefins, to employ heavy metallic tubings of various alloys, particularly high chromium alloys, which have been made of substantial wall thickness. In such operations, the apparatus required has been expensive, frequent replacements are necessary, and the conditions of heating hitherto employed have been such as to lead, at temperatures at which conversion becomes extensive, to the production of substantial proportions of hydrogen, together with large quantities of methane and correspondingly reduced yields of liquid products or of unsaturated gaseous olefins. It has likewise been proposed to employ refractory checker-work or packings, alternately heated to a high temperature and then employed as a heating means for the gas to be treated; but in such operations uniform conditions of heating and proper control thereof cannot be secured, excessive quantities of hydrogen, tars and carbon are produced and inadequate yields of the desired end products are secured.

In accordance with the present invention, these defects in prior methods of operation are largely or completely avoided. The operation may be

conducted in apparatus which is more durable and much more economical, both in first cost and in replacement; uniform and completely controlled heating conditions are secured; hydrogen formation is substantially completely eliminated, carbon formation is materially reduced, and the yields of the desired products, and particularly of liquid aromatic hydrocarbons, are substantially increased.

The gas to be treated may be, for example, natural gas, the residue gas from a natural gasoline plant, the vent gas from a natural gasoline stabilizing plant, refinery gas or the like. The raw material may of course be produced and this process carried out in a continuous one stage process if desired. In carrying out the invention the gas is heated, but only to a temperature below that at which conversion of the gaseous constituents takes place rapidly, for example, to a temperature of 1200 to 1300° or 1350° F. (or as high as 1400° to 1450° with methane gas) by any suitable means, such as by heat exchange with products of reaction, in pipe heaters or the like. The gases are then caused to pass through the conversion passages or tubes in which, in a single passage, they are subjected to the desired heating conditions to effect conversion of constituents of the gas into liquid aromatic hydrocarbons, unsaturated liquid or gaseous hydrocarbon or other desired products. In passage through the heating tube, it is necessary to rapidly heat the gas to an outlet temperature to secure the desired conversion, say, from 1500° F. upwardly, and preferably to from 1650° F. to 1850° F. in continuous, unobstructed flow in less than 0.5 second and preferably in as little as 0.1 to 0.3 second (referred to velocities of heated cracked gases).

In order to secure the necessary high heat input, I employ as the reaction or conversion conduits, unobstructed tubes having thin, metallic walls, the metal employed being of a highly refractory and heat-resistant type. Although it has hitherto been generally accepted that nickel, in contact with hydrocarbon gases at such high conversion temperatures, has a catalytic effect in the direction of the production of hydrogen and carbon, I have found, on the contrary, that most satisfactory results can be secured and the formation of hydrogen largely substantially reduced or avoided by employing for the metallic walls of the conversion tubes a heat-resistant metal consisting largely of nickel, or of cobalt, alloyed with chromium or with mixtures of chromium and other metals such as iron. Minor proportions of other metals or iron-metallic elements may

also be present. For example, alloys of 80% nickel and 20% chromium, 85% nickel and 15% chromium, and of 68% nickel, 17% chromium and 15% iron, or similar alloys with cobalt substituted for the nickel are typical of metallic alloys which I have found satisfactory for use in accordance with the present process. The tubes employed are preferably of small diameter, in general, not over 2 to 2.5 inches internal diameter and with thin walls, for example, of one-sixteenth to one-eighth inch thickness. By the use of such thin walled, metallic heating conduits, I am enabled to secure an extremely high rate of heat transfer to the gas under treatment while in rapid, unobstructed flow.

It has also been discovered that alloys consisting largely of nickel or cobalt and alloyed with chromium or with mixtures of chromium and other metals such as iron, have a very considerable catalytic effect in the production of liquid products from the cracking of gaseous hydrocarbons. This effect is produced whether the reaction be carried out in tubes comprised of the alloys herein described, or whether the tubes be inert and the alloy distributed throughout in small particles. Particularly valuable catalytic results for the formation of liquid products have been produced with tubes containing 80% nickel, 19 plus per cent. chromium, and with tubes containing 80% nickel, 14% chromium and 6% iron. Reactions carried out in tubes of this character produced very considerable quantities of liquid products, whereas similar reactions carried out in the presence of lead, magnesium, or chromium, produce little or much less liquid products.

The conversion tubes, suitably of the character hereinbefore described, are heated by any suitable means so as to secure a substantially uniform wall temperature and substantially uniform heat conditions throughout their entire lengths within the heating zone. In order to secure the maximum transfer of heat, I prefer to heat the conversion tubes by exposing them to radiant heat; for example, from a highly heated body of refractory material in which surface combustion is taking place or which is made the target of a burning fuel mixture, from direct flame, or from a highly heated, carborundum combustion chamber. If desired, in addition to radiant heat, more or less additional heat may be supplied to the conversion tubes by direct induction from combustion gases. By operating under the conditions hereinbefore set forth, a rapid and highly effective heating of the gases under treatment may be secured, as indicated by the fact that with gas outlet temperatures as high as 1760° to 1800° F., the tube wall temperature may be kept to a temperature as low as from 100° to 150° F. higher. The use of thin walled metallic passages is particularly important in increasing effectiveness of heat transfer and securing the desired conversion with minimum formation of hydrogen and carbon and with lowest possible tube wall temperatures. With lower outlet temperatures for the gases under treatment, a higher temperature differential between the gas outlet temperature and the wall tube temperature is permissible with increased capacity and shorter time of passage through the tube.

After leaving the conversion tube, the gases are rapidly cooled, preferably by heat exchange with the gas to be subjected to treatment, soot and tarry matter are settled out, and the liquefiable hydrocarbons separated from the residue gas by compression, absorption or other suitable means.

In operating in accordance with the present invention, the residue gas is substantially free from hydrogen, and consequently has a high B. t. u. value.

The accompanying drawings illustrate apparatus suitable for carrying the invention into effect. In the drawings the numeral 5 indicates the furnace, suitably formed of two sections, a preheater section 6 and a conversion section 7. In the conversion section, a plurality of tunnels 8, of carborundum or other suitable, highly conductive refractory material are provided, in which the fuel mixture to be burned is directed by the burners 9. The carborundum tunnels 8 are brought to an extremely high temperature and 15 radiate heat to the conversion tubes which are located in the furnace chamber 7 as hereinafter described. The carborundum tunnels 8 open beyond the bridge wall 10 which separates the two sections of the furnace, and the hot combustion 20 gases pass over a hollow bridge wall 11 and downwardly to the flues 12 leading to the stack 13. Air for combustion is forced through the conduit 14 into the preheater 15 in the path of the gases passing to the stack, and from the preheater the 25 air passes through flue 16 to the burner. A partition 17 is provided in the hollow bridge wall 11, forming passages communicating with the flue 16 and a damper 18 in the flue may be used to direct all or part of the air passing to the burner 30 through the passages thus formed in the hollow bridge wall 11 for further preheating.

A number of preheating pipes are disposed in the preheater or convection section 6 of the furnace, these being arranged in vertical rows, the 35 pipes of each vertical row being connected in series by suitable return bends. The gas to be treated enters a manifold 20, from which it flows in parallel through the pipes 19 of each vertical row. From the latter it passes into the 40 manifold 21 by which the gas is conducted to the manifold 22 and from the latter it passes in parallel flow to the conversion tubes 23 in the conversion or radiant heat section 7 of the furnace. The manifolds 20 and 21 are preferably 45 lagged with any suitable insulating material to prevent loss of heat.

As hereinafter more fully pointed out, temperatures of the order of 800° to 1350° F. and generally, of 1250° to 1350° F. are attained by 50 the gas in passing through the tubes 19 in the preheating section of the furnace. These tubes may be formed of the ordinary metals used in high temperature oil treatment, such as calorized iron, heat resistant steel alloys and the like. 55 The conversion tubes 23 are, as pointed out hereinbefore, unobstructed tubes of thin-walled, highly conductive material, preferably a highly resistant alloy. Thus I have found that tubes formed of an alloy of 80% nickel or cobalt, and 20% chromium, or of an alloy of 68% nickel, 17% chromium and 15% iron, of 1.5 inches internal diameter with walls one-sixteenth inch thick to be suitable for a capacity of fifteen to twenty-five thousand cubic feet of raw gas treated (measured cold) per twenty-four hours with inlet temperatures ranging from 800° F. to 1350° F. and outlet temperatures exceeding 1500° F., say from 1550° F. to 1850° F. Tubes having walls of one-eighth or three-sixteenth inch thickness may be employed, but I prefer to employ the thinner-walled tubes, say from one-sixteenth to one-eighth inch thick, as I am enabled thereby to secure higher rates of conversion into the desired products with substantial prevention of hy- 70 75

drogen formation. I have found the use of such thin-walled tubes to be particularly effective with a radiant heat source in securing effective conversion and rapid attainment of the desired conversion temperature, as with heavier-walled conduits or non-metallic conduits excessive hydrogen and carbon formation occur and the effective application of the heating means is greatly reduced. The internal diameter of the tubes may vary, in accordance with the desired capacity, from one-half inch upwardly, and in general I prefer to employ tubes not over 2-2.5 inches internal diameter.

In flow through the conversion tubes 23, the gases are brought to the desired conversion temperature, and enter the header 24, from which they pass through pipe 25 to the heat exchanger 26, in which they are cooled by heat exchange with the incoming raw gas to be treated, the latter being at the same time heated somewhat prior to their introduction into the preheating section 6 of the furnace. The cooled, treated gases pass from the heat exchanger 26 through line 27 into the spray tower 28, into the upper portion of which a water spray is directed by means of the pipe 29. Any remaining carbonaceous matter and tar is removed from the gases by the water spray, and the gases are further cooled in the spray tower 28. From the latter, the gasses pass out through the line 30 to pump 31, by which they are forced under pressure through line 32 into the lower portion of the absorber tower 33. A suitable absorber oil, such as heavy naphtha or mineral seal oil is forced into the absorption tower 33 through the line 34, and descends the tower countercurrent to the ascending gases, removing condensable liquid hydrocarbons, such as benzol, toluol and heavier aromatics from the gases. It is preferred that sufficient pressure be maintained on the absorber tower to cause normally gaseous hydrocarbons having two or more carbon atoms to be absorbed with the normally liquid products, these being separated at a later stage of the process and returned to the heating and conversion tubes for retreatment. The stripped gases pass out of the upper portion of the tower through the line 35. The enriched absorption oil passes out of the tower through the line 36, to heat exchanger 37 in which it is partly preheated by heat exchange with the hot, lean absorber oil as hereinafter more fully shown, and the enriched oil then passes through the line 38 into the distillation tower 39. In the latter, the absorbed hydrocarbons are distilled off from the absorber oil, steam being supplied as a heating medium for this purpose through the line 40. The lean absorber oil is drawn from the distillation tower 39 through the line 41 by pump 42 and forced to the heat exchanger 37, in which it is cooled by the rich absorber oil from tower 33. The cooled oil then passes through the line 34 into the absorption tower for reuse therein.

The vapors of the hydrocarbons distilled off in the distillation tower 39 pass out through the line 43 to condenser 44, and the condensate, together with any uncondensed gases are discharged into the receiver and separator 45. The uncondensed gases and vapors pass out of the receiver 45 through the line 46, by which they are conducted to the manifold 47 which leads to the line 48, by which the raw gas to be treated is supplied to the heat exchanger 26, to enter the system. The liquid condensate is drawn off from the receiver 45 through the line 49 and conveyed

to a suitable stabilizing or fractionating device (not shown). Uncondensed vapors from such stabilizing or fractionating device may be led through line 50 to the manifold 47, by which they are returned to the system.

The raw gas to be treated, together with any recycled gas from previous treatment in the system, is supplied through line 48 to the heat exchanger 26, through which it passes in indirect heat exchange with the gases coming from the conversion tubes 23, being thereby preheated. The gases, thus preliminarily heated, pass from the heat exchanger 26 through line 51 to the manifold 20 leading to the preheating pipes 19

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In flow through the conversion tubes 23, the gases are brought to the desired conversion temperature, and enter the header 24, from which they pass through pipe 25 to the heat exchanger 26, in which they are cooled by heat exchange with the incoming raw gas to be treated, the latter being at the same time heated somewhat prior to their introduction into the preheating section 6 of the furnace. The cooled, treated gases pass from the heat exchanger 26 through line 27 into the spray tower 28, into the upper portion of which a water spray is directed by means of the pipe 29. Any remaining carbonaceous matter and tar is removed from the gases by the water spray, and the gases are further cooled in the spray tower 28. From the latter, the gasses pass out through the line 30 to pump 31, by which they are forced under pressure through line 32 into the lower portion of the absorber tower 33. A suitable absorber oil, such as heavy naphtha or mineral seal oil is forced into the absorption tower 33 through the line 34, and descends the tower countercurrent to the ascending gases, removing condensable liquid hydrocarbons, such as benzol, toluol and heavier aromatics from the gases. It is preferred that sufficient pressure be maintained on the absorber tower to cause normally gaseous hydrocarbons having two or more carbon atoms to be absorbed with the normally liquid products, these being separated at a later stage of the process and returned to the heating and conversion tubes for retreatment. The stripped gases pass out of the upper portion of the tower through the line 35. The enriched absorption oil passes out of the tower through the line 36, to heat exchanger 37 in which it is partly preheated by heat exchange with the hot, lean absorber oil as hereinafter more fully shown, and the enriched oil then passes through the line 38 into the distillation tower 39. In the latter, the absorbed hydrocarbons are distilled off from the absorber oil, steam being supplied as a heating medium for this purpose through the line 40. The lean absorber oil is drawn from the distillation tower 39 through the line 41 by pump 42 and forced to the heat exchanger 37, in which it is cooled by the rich absorber oil from tower 33. The cooled oil then passes through the line 34 into the absorption tower for reuse therein.

The gas treated in accordance with the present invention may be any suitable hydrocarbon gas containing gaseous hydrocarbons. Thus, I may employ natural gas, stripped natural gas after removal of natural gasoline therefrom, refinery gases, vent gases from the stabilizing of natural gas gasoline, refinery pressure distillates and the like or other available hydrocarbon gases. I have found the operation particularly advantageous in its application to vent gases from the stabilizing of natural gas gasoline.

The gas to be treated is brought by preliminary heat treatment, for example, in the heat exchanger 26 and the preheating tubes 19, to a temperature somewhat below the desired rapid conversion temperature, say to 1250 to 1350° F., and the preheated gases are then forced through the conversion tubes under the conditions hereinbefore set forth. In the tubes by reason of the extremely rapid heat input secured therein, the gases are brought to the desired outlet temperature in an extremely short interval of time in passage through an unobstructed conduit. If it is desired to secure predominantly a conversion into gaseous olefin hydrocarbons, outlet temperatures up to 1500 to 1550° F. are suitable. At higher temperatures, larger proportions of condensable hydrocarbons are secured, and by operating with outlet temperatures of above 1600° to 1650° F. and preferably from 1700° to 1850° F., substantial proportions of liquid aromatic and unsaturated hydrocarbons in the gasoline boiling point range are secured. By operating in accordance with the present invention, I am enabled to secure outlet temperatures as high as 1750° to 1850° F. with highly efficient heat transmission, as indicated by tube wall temperatures which are only from 100° to 150° higher than the outlet temperature and with substantial elimination of hydrogen formation and reduction or elimination of carbon formation in a time of passage through the conversion tubes based on the volume of the heated gases less than 0.5 second, and in general below 0.3 second. It has not hitherto been possible to secure such conversion temperatures, except by the use of heating surfaces of refractory ceramic materials and with the production of large proportions of hydrogen. Lower outlet temperatures may be secured in even shorter time intervals.

Immediately upon leaving the conversion tubes and entering the manifold 24, rapid cooling of the treated gases begins. They are further cooled by heat exchange with the entering raw gas to be treated in the heat exchanger 26, being reduced therein to, say, 200° F. Soot or carbon from the cracking operation, together with suspended tar, deposit in the heat exchanger and any remaining in the gas is removed by the water spray to which

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it is subjected in the spray tower 28, in which the gases are further cooled to, say, 70 to 90° F.

In passing through the heating and conversion system, it is not desired to subject the gases to substantial pressures. The outlet pressure at the conversion-tubes does not exceed 50 lbs., and is preferably approximately atmospheric, or a partial vacuum may be drawn, for example, by the action of the pump 31.

10 The cooled gases, after leaving the spray tower 28, are put under pressure by the pump 31, say about 45 lbs., and forced to the absorption column 33, in which the condensable constituents, such as benzol, toluene and the like, together with 15 normally gaseous hydrocarbons having two or more carbon atoms, are removed by the absorption liquid or wash oil supplied to the pipe 34. The enriched absorber liquid is then subjected to distillation in the still or column 39, the absorbed 20 hydrocarbons resulting from the heat treatment of the gas being vaporized, cooled and the condensate collected in the receiver 45, from which they may be withdrawn for further stabilization, rectification or the like. The uncondensed gases 25 which separate from the condensable liquids in the separator 45 and in any further stabilizing and fractionating operations to which it is subjected, are returned through the line 47 to the stream of raw gas entering the conversion system for treatment.

I have found the process particularly advantageous in the treatment of rich gases such as stabilizer vent gases which are of very high specific gravity and B. t. u. value, since by the operation 30 of the present process, I am enabled to produce from such gases substantial quantities of valuable liquid hydrocarbons such as benzol, toluol and the like in quantities in excess of 2.5-3 gallons per thousand cubic feet of gas treated, and I am enabled to secure a residue gas, of adequate B. t. u. 35 value, substantially free from hydrogen or very low therein, in volumes ranging from two to three times the volume of raw gas treated.

For example, in a typical operation, I have 40 treated a stabilizer vent gas of specific gravity 1.5 (air equals one) and with a B. t. u. value of 2500 per cubic foot. The gas was brought in passage through the heat exchanger and preheating section of the furnace to a temperature of approximately 1300° F. The conversion tubes employed 45 had an effective length of twelve feet within the furnace, 1.5 inches internal diameter and a wall thickness of one-sixteenth inch, and were heated uniformly, largely by radiant heat. With 50 a flow of approximately 22000 cubic feet per twenty-four hours through each such tube, an outlet temperature of 1760° F. was secured with a tube wall temperature of 1860° F., such temperature being uniform over the entire wall surface, as indicated by an optical pyrometer. The 55 time of passage through the conversion tube was, on the basis of the volume of the heated and cracked gases, in the order of 0.1 second. After cooling and separation of tar from the treated 60 gases, a yield of 3.10 gallons per thousand (based on raw gas treated) of condensable aromatic hydrocarbons was secured, the liquid containing about 60% benzol and the remainder toluol and higher homologues, substantially entirely boiling 65 below 425° F. in addition to carbonaceous matter, tars, and the like, which were separately removed. The residue gas, after removal of the condensable liquids, contained less than 1% hydrogen, had a gravity of 0.72 and a heating value exceeding 1000 B. t. u. per cubic foot. The vol-

ume of residue gas secured amounted to 2110 cubic feet for each 1000 cubic feet of raw gas treated.

As hereinbefore indicated, the relative proportions of liquid hydrocarbons and olefine gases 5 may be widely varied by varying the temperature of conversion, time of reaction, and other factors in operation. Thus, in a similar operation, with an outlet temperature from the thin-walled conversion tube of about 1650° F., the tube wall 10 temperature being about 1820° F., the yield of light aromatic hydrocarbons was 2.13 gallons per thousand cubic feet of gas treated, and the effluent gas was substantially hydrogen-free and amounted to 1980 cubic feet per thousand treat- 15 ed, its gravity being about 0.77 and being correspondingly richer in olefines. Less than 70% thereof consisted of methane. With an outlet temperature from the conversion tube of 1520° F., with a wall temperature of about 1775° F. 20 and a throughput of 21,700 cubic feet per twenty-four hours per tube, the liquid yield was reduced to about 0.55 gallon per thousand and about 1520 cubic feet of treated gas of a density of approxi- 25 mately 1 were secured per thousand of gas treat- ed. This residue gas consisted largely of olefine hydrocarbons, containing less than 2% hydrogen and about 34.5% methane.

The condensable liquid hydrocarbons thus secured may be substantially entirely used in the 30 production of motor fuel, for example, by blending with natural gas gasoline, or by incorporating therewith butane or other light fractions from raw natural gas gasoline. However, in general 35 it is preferred to fractionate the product to separate the benzol, toluol and other hydrocarbons therein and employ them in accordance with market conditions. The relative proportions of benzol and toluol may be varied somewhat by control of the temperature of operation; for ex- 40 ample, at higher temperatures, larger proportions of toluols may be secured. Similar results may be secured by reducing somewhat the velocity of flow of the gas to the conversion tubes. Such changes in operation, however, result in 45 some reduction in volume of liquid products secured and increase in hydrogen formation in the process.

In the treatment of gases consisting largely or entirely of methane, higher temperatures of operation 50 may be employed for conversion into liquid products than when gases richer in heavier hydrocarbons such as ethane, propane, butane and the like, are present in substantial proportions. In such operations, it is preferred to employ cobalt alloys in the construction of the 55 tubes.

The conversion tubes employed in accordance with the present invention are of high endurance, notwithstanding the high temperatures and 60 severe heating conditions to which they are subjected. Thus such tubes have been found to withstand operation for periods exceeding 400 hours; and may, when found defective, be repaired or straightened and put back into service quickly 65 and at a low cost.

In the operations as described, much smaller carbon deposits were secured in the conversion tubes than when attempts were made to secure similar outlet temperatures with tubes of steel 70 alloys, chrome-iron alloys, calorized iron, and the like, and such tubes rapidly choked with carbon deposits, and burned out quickly.

Although the carbon deposits in the apparatus are small in operations in accordance with this 75

invention, it is found desirable at suitable intervals to pass steam or air through the heating system to effect removal of carbon. It is preferred to use a small percentage of steam, say 5 1% by volume, in the gases during the cracking operation instead of intermittently passing steam through the system.

It is a particular advantage of operations in accordance with the present invention that the 10 production of hydrogen, and likewise the production of carbon, which is correlated thereto, are greatly reduced or substantially eliminated. Thus, in the conversion operation, even at high 15 temperatures for the production of liquid aromatic hydrocarbons, I have been able to reduce the production of hydrogen to less than 5% in effective operation, and in many instances to less than 1% or to substantially eliminate it. At the same time, in operating in accordance with this 20 process, I am enabled to secure substantially increased yields of liquid products. Thus, whereas hitherto the yields of light condensable aromatic hydrocarbons from the heat treatment of gases such as stabilizer vent gases have been of the 25 order of 1.75 to 2 gallons per thousand cubic feet, as pointed out hereinbefore, I am able to secure yields in excess of 3 gallons per thousand cubic feet. Furthermore, by operating in accordance 30 with the present invention, I am able to avoid the use of refractory ceramic tubing for the conversion operation, and of cracking or filling for the retort or conduit in which the conversion is effected.

It should be understood, of course, that while 35 it is possible to secure very high yields of olefines by operating in accordance with the present process and while securing little or no hydrogen, in the upper portion of the time range the olefines already formed apparently react or polymerize to form liquid products and at the same time produce additional hydrogen. However, by operating within the time range herein disclosed, the amount of hydrogen secured for a given yield of liquid products is very substantially less than 40 in prior processes. In fact yields up to 30% or more of liquid products by weight have been secured under the present process with yields of hydrogen only 15-20% by volume. In obtaining such high yields of liquid products the gaseous olefines such as ethylene are substantially 45 eliminated. For example 35% ethylene by volume has been secured in a cracked gas with a corresponding liquid yield of about 20% by weight referred to the raw material. On the 50 other hand, when this percentage of liquid product was increased to 33%, the percentage of ethylene in the gas declined to about 5%.

This application is a continuation in part of my copending application Serial Number 489,617, 55 filed October 18, 1930.

What I regard as new and desire to secure by Letters Patent is:

1. The method of heat treatment of hydrocarbon gases to effect conversion of constituents thereof which comprises passing such gases at a temperature below rapid conversion temperature into and through a passageway having thin metallic walls, the separation of said walls being 60 a substantial distance not substantially over 2.5 inches, and heating said walls externally largely by radiant heat while flowing the gas therethrough at a velocity exceeding 15,000 cubic feet (cold gas treated) for a 12 foot pipe in twenty- 65 four hours for each 1.77 square inches cross sec-

tion of the passage to bring the gas to the desired conversion temperature.

2. The method of heat treating hydrocarbon gases to effect conversion of constituents thereof which comprises passing the gas through a thin-walled metallic tube while heating the walls of said tube, largely by radiant heat, to a substantially uniform external temperature and bringing said gas from a temperature of about 1200° to 1350° F. to the desired conversion temperature in a time of passage not exceeding one second for a temperature of about 1750° to 1850° F. with a differential between the outlet gas temperature and the wall temperature of not over 100° to 150° F., the said temperature differential increasing at lower attained conversion temperatures, and cooling said gas, the total time during which said gas is at the desired conversion temperature not exceeding one second. 10 15

3. The method of heat treating hydrocarbon gases to effect conversion of constituents thereof which comprises passing the gas through a thin-walled metallic tube while heating the walls of said tube, largely by radiant heat, to a substantially uniform external temperature and bringing said gas from a temperature of about 1200 to 1350° F. to the desired conversion temperature in a time of passage not exceeding one second for a temperature of about 1750° to 1850° F., and a wall temperature of not substantially over 2000° F., and cooling said gas to a temperature below a conversion temperature, said gas being over a conversion temperature not over one second. 20 25 30

4. The method of treating hydrocarbon gases 35 to effect conversion of constituents thereof into hydrocarbons of higher carbon content, which comprises forcing the gas in a continuous stream and in contact with an alloy predominantly of a metal of the class consisting of nickel and cobalt and containing chromium through a confined passageway and heating said passageway to bring the gas from a temperature below 1200-1450° F. to a conversion temperature substantially in the range from 1500-1850° F., and immediately cooling said gas below 1200-1450° F., said heating and cooling being carried out at such a rate that said gas does not remain at a rapid conversion temperature in excess of .1 to .5 second, said lower time corresponding to the 40 45 50 higher temperature and vice versa.

5. The method of treating hydrocarbon gases to effect conversion of constituents thereof into hydrocarbons of higher carbon content, which comprises forcing the gas in a continuous stream 55 through a confined passageway the gases in their passage through the passageway being contacted with a catalyst of an alloy predominantly composed of a metal from the group consisting of nickel and cobalt and containing chromium and heating said passageway to bring the gas from a temperature below 1200-1450° F. to a conversion temperature substantially in the range from 1500-1850° F., and immediately cooling said gas below 1200-1450° F., said heating and cooling being carried out at such a rate that said gas does not remain at a rapid conversion temperature in excess of .5 second. 60 65

6. The method of treating hydrocarbon gases to effect conversion of constituents thereof into hydrocarbons of a higher carbon content which comprises forcing the gases in a continuous stream and in contact with an alloy predominantly of a metal of the class consisting of nickel and cobalt and containing chromium and iron, 70 75

through a confined passageway and heating said passageway to bring the gas from a temperature below 1200-1450° F. to a conversion temperature substantially in the range from 1500-1850° F. and 5 immediately cooling said gas below 1200-1450° F., said heating and cooling being carried out at such a rate that said gas does not remain at a rapid conversion temperature in excess of .1 to .5 second, said lower time corresponding to the higher 10 temperature and vice versa.

7. The method as set forth in claim 6 in which the heated gas is contacted with an alloy comprising 68-80% nickel, 17 to 20% chromium, and 15 to 0% iron.

15 8. The method of treating hydrocarbon gases to effect conversion of constituents thereof into hydrocarbons of higher carbon content which comprises forcing the gas in a continuous stream through a thin walled metallic tube having walls 20 of a substantial thickness not substantially exceeding  $\frac{1}{8}$  inch and a substantial diameter not substantially exceeding 2 $\frac{1}{2}$  inches and heating the passageway so formed to bring the gas from a temperature below 1200 to 1450° F. to a conversion 25 temperature substantially in the range from 1500 to 1850° F., and immediately cooling said gas below 1200 to 1450° F., said heating and 30 cooling being carried out at such a rate that said gas does not remain at a rapid conversion temperature in excess of .1 to .5 second, said lower time corresponding to the higher temperature and vice versa.

9. The method as set forth in claim 8 in which the metallic tubes are predominantly of a metal of the group comprising nickel and cobalt, and containing chromium.

10. The method as set forth in claim 8 in which the metallic tubes comprise 68 to 80% nickel or cobalt, 17 to 20% chromium, and 15 to 0% iron.

11. Apparatus for converting hydrocarbon gases, comprising a metallic tube having walls of a substantial thickness not substantially greater than  $\frac{1}{8}$  inch and a substantial diameter not substantially greater than 2 $\frac{1}{2}$  inches; means for passing said gases through said tube; means for heating said gases within said passageway from a temperature below rapid conversion temperature to a conversion temperature substantially in the range of from 1500 to 1800° F. for a time not in excess of .5 second, said means including a source of heat yielding primarily radiant heat, and means for immediately cooling said gases to a temperature below rapid conversion temperature. 15

12. Apparatus as set forth in claim 11 in which the tube is composed of an alloy predominantly composed of a metal from the group comprising nickel and cobalt, and containing chromium. 20

13. Apparatus as set forth in claim 11 in which the tube is composed of an alloy comprising 68 to 80% nickel or cobalt, 17 to 20% chromium and 15 to 0% iron. 25

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