

May 29, 1956

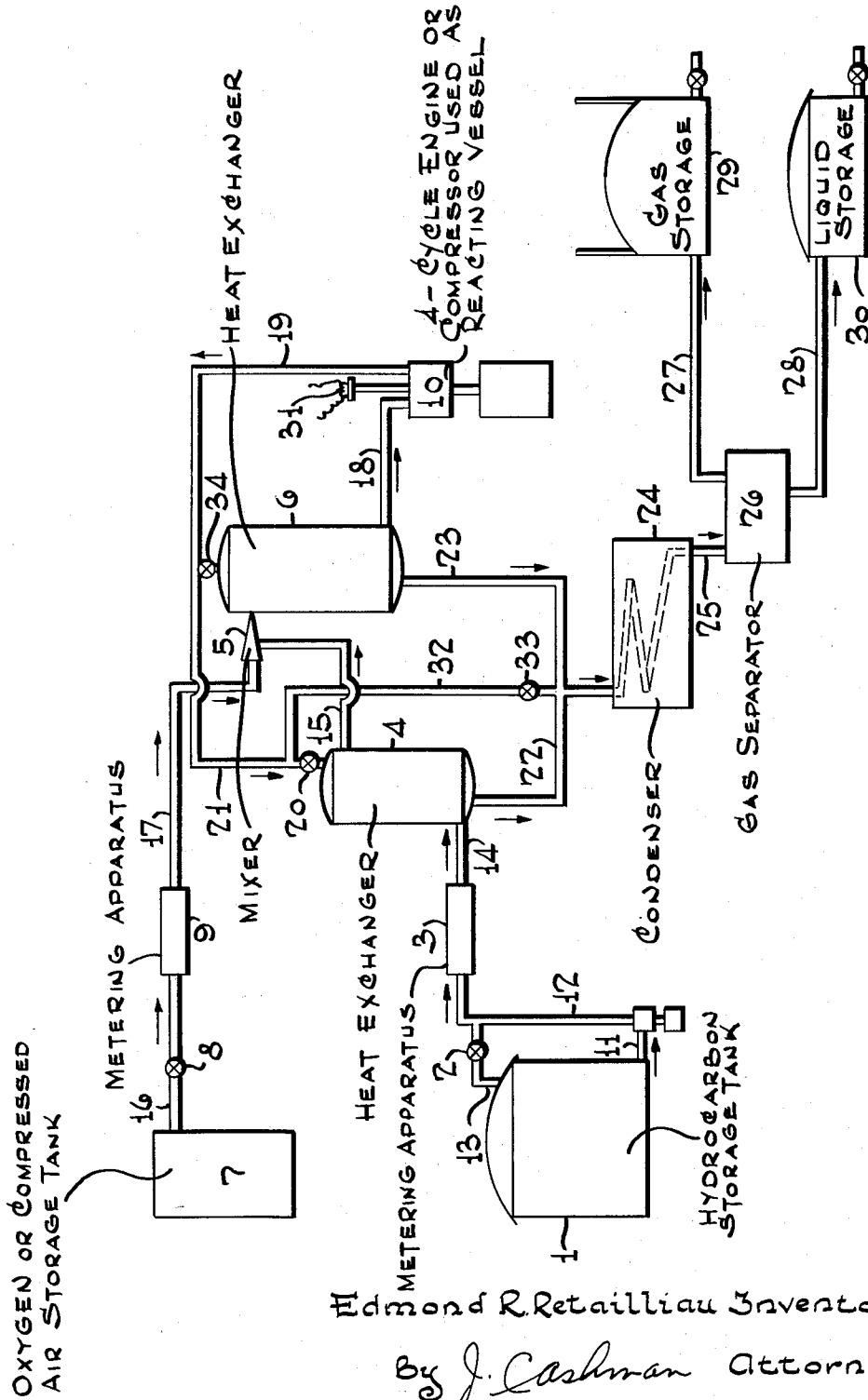
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GAS MANUFACTURE

Filed Oct. 25, 1951

3 Sheets-Sheet 1



May 29, 1956

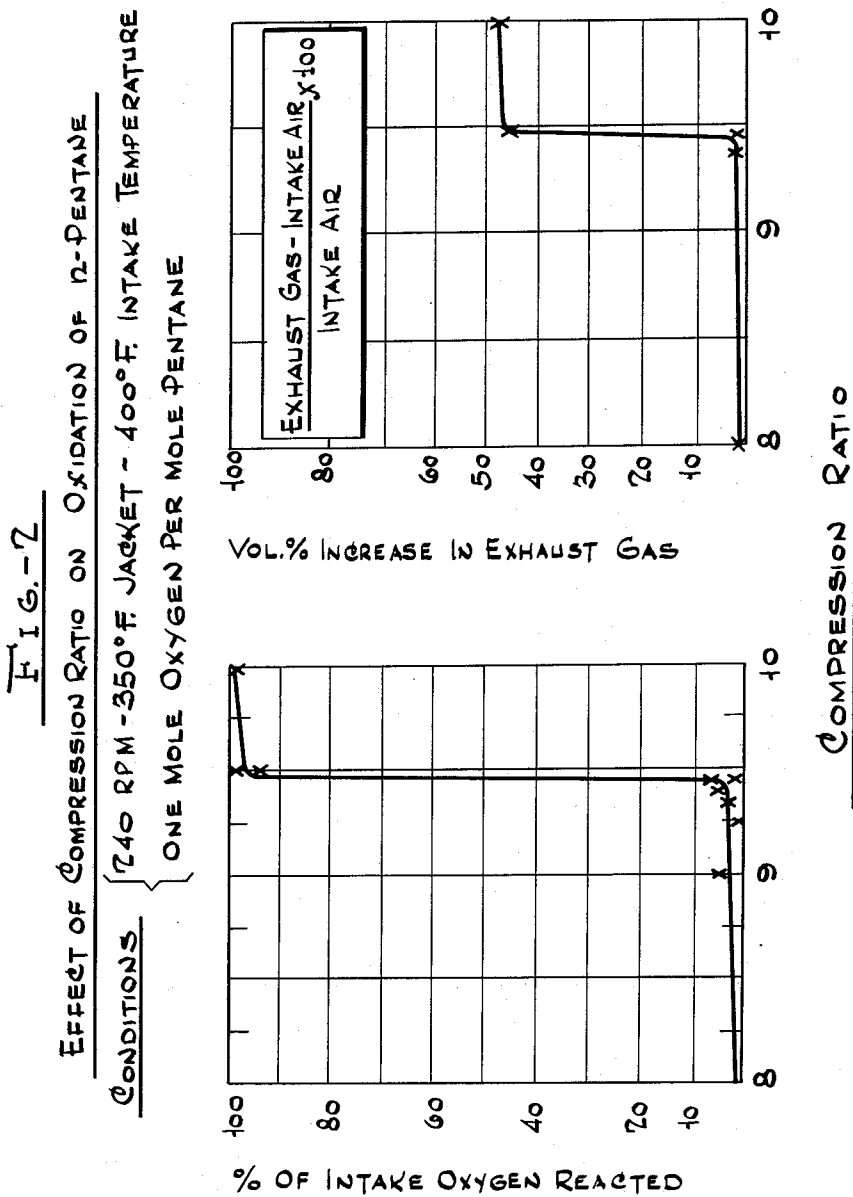
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GAS MANUFACTURE

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3 Sheets-Sheet 2



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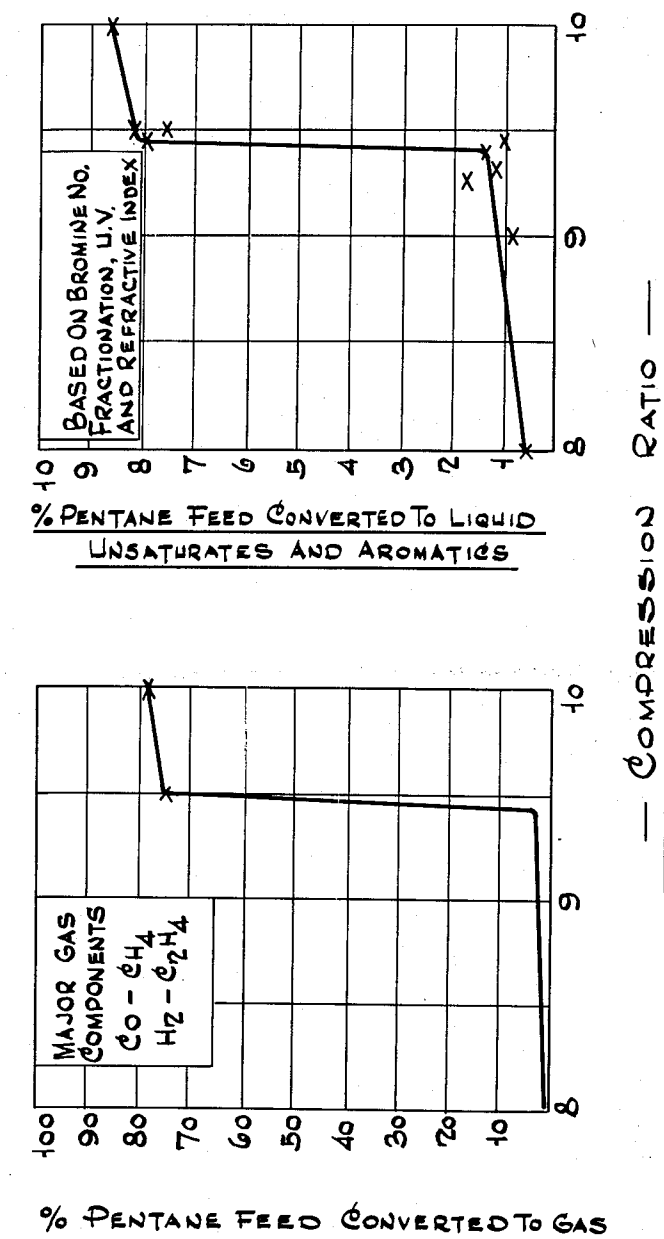
GAS MANUFACTURE

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3 Sheets-Sheet 3

FIG. - 3

EFFECT OF COMPRESSION RATIO ON OXIDATION OF 12-PENTANE
 CONDITIONS { 740 RPM - 350° F. JACKET - 400° F. INTAKE TEMPERATURE
 ONE MOLE OXYGEN PER MOLE PENTANE



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GAS MANUFACTURE

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9 Claims. (Cl. 260—673)

The present invention relates to the oxidation of relatively low molecular weight hydrocarbons. More particularly, the present invention relates to the conversion of relatively low molecular weight hydrocarbons which are normally resistant to reforming reactions, into products valuable as fuel and as intermediates for conversion into products of high octane value. More specifically, the present invention relates to the generation of city gas and hydrocarbon synthesis gas comprising hydrogen and carbon monoxide, as well as the preparation of valuable olefins and aromatics, by oxidative cracking of said low molecular weight hydrocarbons in the presence of gaseous oxygen in the combustion space of a cyclically operating unfired internal combustion engine.

Whereas it is well known in the art that hydrocarbon material may be reacted with oxygen to yield various oxygenated compounds as well as hydrocarbons of lower molecular weight, great difficulties have been encountered in attempting to carry out such reactions on a commercial scale. This is largely due to the fact that the reactions of oxygen with hydrocarbons are highly exothermic and that the heat thus evolved is locally so high as to cause many undesirable side reactions with the result that the yields of the desirable products are extremely low, usually less than 1.0% on the hydrocarbon feed. In the few cases where such oxidation has been carried out in commercial plants, it has been found necessary to dilute the reactants with enormous amounts of unreactive diluent material in order to obtain some control of the reaction towards forming the desired compound. The size of the equipment required is very large with regard to the volume of the chemical compound produced and its cost consequently extremely high; because of this, the oxidative treatment of hydrocarbon material has found application only in cases where the relatively high value of the oxygenated compound obtained could provide some return on the investment. It has now been found that conversion of cheap hydrocarbon material by a comparatively inexpensive oxidation procedure may be performed so as to give relatively high yields of valuable products such as aromatic and olefinic hydrocarbons together with some oxygenated compounds such as carbonyls and alcohols. As the source of hydrocarbon material, there may be employed either gaseous hydrocarbons such as methane, ethane and propane or liquid hydrocarbons such as n-butane, n-pentane, n-hexane and the like, which do not lend themselves easily to reforming processes and these are converted in good yields to the above mentioned classes of valuable compounds. The light unsaturated hydrocarbons are particularly valuable for alkylating purposes and thus will contribute to increase the supply of aviation blending agents as will the aromatics produced in the process. On the other hand, the process may be so operated as to produce a mixture of hydrocarbons highly suitable for illuminating purposes and the present application is particularly concerned with these objects.

In accordance with the present invention, a low molecular weight hydrocarbon, such as n-pentane for example,

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is vaporized and blended with a predetermined amount of oxygen-bearing gas such as ordinary air, although pure oxygen may be used for certain purposes if desired. This mixture is then conditioned by a suitable heat treatment prior to being conducted into the cylinder of a compressor or of an unfired reciprocating engine where, as a result of the heat generated by compression of said mixture, the hydrocarbon is brought to a satisfactory level of activation for causing it to react with the oxygen present and produce a gas eminently suitable for use as city gas. The B. t. u. value of the gas so produced is controlled by the quantity of oxygen-containing gas added and by the choice of oxygen or air. With the use of air, the diluent nitrogen serves to reduce the B. t. u. value to the values used in city gas distribution which is usually around 500 B. t. u. On the other hand, if desired, a high B. t. u. gas suitable for the replacement of natural gas can be obtained by partial or complete removal of the nitrogen diluent by the additional use of suitable absorption processes or by using steam instead of nitrogen as diluent.

The lack of availability of fuel gas or city gas at isolated points has long been felt. It has not been feasible to build pipe lines or mains from centers wherein gas producer units are located, to distant areas. The use of compressed city or natural gas is cumbersome and not feasible on a large scale. By operating in accordance with the present invention, by setting up a compressor, or series of compressors or engines, at isolated points, manufactured gas of any desired B. t. u. value may be produced in volume suitable for the load conditions required.

Particularly useful as the hydrocarbon in this operation are the normally low molecular weight liquid hydrocarbons, such as n-pentane, n-hexane, and the like. These hydrocarbons are difficult to convert into useful products; for instance, it is either extremely difficult or impossible to convert n-pentane into a cyclic hydrocarbon by hydroforming or reforming and it is very difficult to perform this operation on n-hexane. In the past, these materials have been employed for solvents or they have been subject to isomerization reaction and thus converted into a gasoline blending agent. In accordance with the present invention, this type of hydrocarbon is oxidatively cracked in the compressors located at isolated spots, whereby a large supply of manufactured gas is thus available without the heavy cost entailed in building coal gas manufacturing plants or the cost of constructing gas mains and lines and piping gas large distances.

The size of compressors required to produce such gas by the process to be described in detail below is moderate. Thus, a single compressor having about a 13½ inch piston diameter and a 20 inch stroke and operating at 200 R. P. M. will produce over a million cubic feet per day of gas; if two or three compressors are employed, their size would be correspondingly smaller. Smaller compressors would also be employed if higher compression speeds are used. The cost of a single compressor for producing a million cubic feet per day is in the range of about \$15,000 to \$20,000 and thus, it is readily seen that the process of the invention provides a convenient and inexpensive method of supplying small communities with manufactured gas. Also, if it is contemplated to employ the manufactured gas as hydrocarbon synthesis gas, i. e. gas mixture comprising essentially of carbon monoxide and hydrogen which is catalytically converted into high octane motor fuel by passage over a group VIII catalyst, this affords another means of converting a low octane hydrocarbon into a high octane material.

Although the exact mechanism by which n-pentane is converted by oxygen into a multiplicity of other compounds (chiefly among which carbon monoxide, hydro-

gen, methane and aromatics were found) is not thoroughly understood, it is believed that the initial reaction of the pentane with oxygen results in the formation of peroxides at a certain stage of the compression stroke when the activation of the molecules has reached a sufficient level. These peroxides, in turn, decompose upon further heating (as the compression stroke proceeds farther) to yield a number of free radicals and the reaction then proceeds at an accelerated rate by a chain mechanism process. Because of the deficiency of the mixture in oxygen, a large proportion of the free radicals formed from the decomposition of the peroxides combine with one another to form stable hydrocarbon or other molecules such as methane, ethylene, benzene, or hydrogen, etc., rather than reacting with additional oxygen. The identification of benzene and toluene in the reaction products is indicative of the formation of highly dehydrogenated radicals such as =CH- or -CH=CH- , etc., which have combined to form the stable aromatic nucleus. However, the present invention is not intended to be dependent upon this or any other possible explanation of the reaction mechanism.

An important feature of the invention is that an unfired rather than a fired engine is employed. The reason for this is that use of an electric spark for promoting the reaction of oxygen with the hydrocarbon always results in the formation of increased amounts of carbon dioxide without appreciably increasing the hydrocarbon conversion. The net effect of sparking the hydrocarbon-air mixture being to convert part of the desirable carbon monoxide initially formed into useless carbon dioxide, it is obviously advantageous to prevent such product degradation and hence, operation of the engine without spark is a valuable feature of the present invention. If, however, it is desired to increase the production of carbon dioxide as, for example, for the supplemental manufacture of Dry Ice, a spark could then be used without departing from the principles of this invention.

The reaction within the engine is critically sensitive to temperature, contact time, compression ratio, and above all, to the ratio of oxygen to hydrocarbon. A relatively long contact time or low R. P. M. of the driving motor produces carbon dioxide and water rather than a fuel gas. A high preheat temperature, for instance, above about 400°F. , causes a pre-reaction which may have an unfavorable effect. A low proportion of oxygen such as below an 0.5 mol ratio, shows little reaction at 350°F. , whereas almost complete utilization of the oxygen is obtained at 1.0 ratio and above. However, large carbon formation resulted from operation at 2.0 mol ratio. Furthermore, as detailed more fully below, in a systematic series of experiments made at 1.0 oxygen to hydrocarbon mol ratio (that is, with one-eighth the theoretical amount of oxygen required for complete combustion of this particular hydrocarbon) at 400°F. intake temperature, during which the compression ratio was increased in small increments, it was shown that there was practically no reaction until a certain critical temperature is reached at which the reaction proceeds with an explosive velocity. Under the experimental conditions employed, this critical compression temperature was calculated from the actual peak compression of the air-fuel mixture to be 898°F. and was reached at a compression ratio of 9.49 to 1. Thus, during most of the compression or at low compression ratios, there is no reaction and only when compression is brought to that stage high enough for the heat generated to activate the reaction are desired reaction products obtained. Thus, by operating in accordance with the present invention, the prerequisite of an extremely short reaction time followed by extremely rapid cooling is obtained. These are not available with ordinary equipment.

The process of the invention may best be illustrated in accordance with the Figure 1 which shows one embodiment of the present invention. For the purpose of the example, normal pentane is employed though it will be understood that other hydrocarbons such as the normally gaseous paraffinic hydrocarbons or normally liquid paraffinic hydrocarbons as n-butane, n-hexane and the like, or liquid naphthenic hydrocarbons may also be used.

The n-pentane is pumped from storage tank 1 through lines 11 and 12 to a metering device 3, and thence through line 14 to heat exchanger 4 where it is vaporized; the flow of pentane is regulated by means of valve 2 and by-pass line 13 through which the excess pentane is returned to the storage vessel 1. From heat exchanger 4, the vaporized pentane is led through line 15 into a mixing chamber 5 where it is blended with the required amount of air (or oxygen, if desired) bled from storage tank 7 through line 16 and valve 8 into the metering device 9 and thence through line 17 into mixer 5. This mixing vessel may be of any conventional design for intimately blending gaseous components and, for example, may be of the ejector or carburetor type. The gaseous mixture of pentane vapors and oxygen-containing gas is then preheated to a predetermined temperature in heat exchanger 6 and thence conducted through line 18 into the intake manifold of the compressor or of the unfired single or multicylinder engine 10 (or a battery of such compressors or engines) employed for causing the hydrocarbon to react with the oxygen by compression of the heated mixture. The pistons of these compressors or engines are externally actuated to provide for alternate compression and expansion of the reacted gases. This may be achieved by any suitable means such as an electric motor or diesel engine, etc. Inasmuch as the present invention does not reside in the type of engine used, the latter will not be described in detail, but is of conventional design save for the fact that spark plugs or other means of ignition are not essential; for example, single cylinder or multi-cylinder engines of the diesel or spark ignition types or 4-cycle compressors are suitable for the purpose of the invention.

Following the reaction occurring during the compression stroke, the gaseous mixture produced is partially cooled during the expansion stroke and then expelled during the exhaust stroke, the jacket cooling medium temperature being adjusted to leave sufficient heat in the exhaust gases for adequate preheating of the incoming feed. The hot exhaust gases are thus conducted counter-currently to the incoming feed in heat exchangers 4 and 6 through lines 19 and 21 and are finally cooled in condenser 24 which may be of any desired conventional design employing any suitable coolant. The cooled gases are then separated from the condensed hydrocarbons in gas separator 26 from which both products are sent to their respective storage tanks, the condensed liquid to tank 30 through line 28 and the gas to gas holder 29 through line 27. Suitably located valves such as valves 20, 33 and 34 are used for regulating the amount of exhaust gas diverted to the heat exchangers as required to preheat the incoming mixture to the desired temperature.

A single cylinder CFR engine, equipped with either the regular CFR head for determination of octane numbers of motor gasolines or with a diesel head, was used for demonstrating the process using substantially the layout shown in Figure 1, except that the heating of vessels 4 and 6 was obtained by electrical means rather than by heat exchange with the exhaust products as would be the case in commercial operation. When the regular CFR head was employed the spark ignition system was disconnected. In addition, heating of the jacket of these engines was accomplished by circulating a suitable liquid heated to the desired temperature. Air was usually the

oxygen-bearing gaseous medium utilized in this work. In order more readily to establish the various reactions occurring during the oxidation of hydrocarbons, n-pentane of high purity (better than 99.0% pure) was employed in most of this work although light virgin fractions which are extremely refractory to reforming processes were also successfully used. A considerable number of experiments were performed for the systematic investigation of the influence of the many variables involved in this novel method of hydrocarbon conversion.

Briefly summarized, it was discovered using a 4-stroke cycle engine, that long reaction times resulting from very low engine speeds, as from 20 R. P. M. to about 200 R. P. M., were unfavorable since a large proportion of the oxygen used was converted to carbon dioxide, an undesirable product from the point of view of the present invention. On the other hand, speeds from 200 to 900 R. P. M. were highly satisfactory and preferably engine speeds of from 200 to 300 R. P. M. are used. Since in a 4-stroke cycle engine one compression stroke occurs for every two revolutions of the engine crankshaft, these engine speeds correspond to 100-450 and to 100-150 compressions per minute, respectively. In a 2-stroke cycle engine, the revolutions of the engine per minute are the same numerically as the number of compression strokes per minute. Although the engine jacket temperature may be varied from about 200 to 500° F., temperatures of from 250 to 350° F. are more advantageous and similarly preheating of the hydrocarbon-air mixture to from about 200° to 400° F. is preferred, although higher temperatures may be useful in certain cases. The importance of properly choosing the compression ratio at which to carry out the oxidation reaction is best emphasized by the data plotted in Figs. 2 and 3, from which it is seen that, with the engine employed in this particular series of tests, activation of the reactants requires a minimum compression ratio of at least about 9.5:1 and that further increases in compression ratio brought only relatively insignificant additional changes in the various products.

As indicated previously, the ratio of oxygen to hydrocarbon is highly critical with regard to the end products obtained. For the preparation of a city gas, for example, there is used an amount of air which will give an oxygen to hydrocarbon ratio of from about 0.5 to about 1.5, and preferably about 1.0 whereas, if it is desired to prepare a synthesis gas for use in the manufacture of synthetic gasoline by the Fischer-Tropsch process, the proportion of oxygen is increased and there is used air in amounts corresponding to about from 1.5 to 2.8 mols of oxygen per mol of hydrocarbon; preferably about 2.0 mols of oxygen per mol of hydrocarbon in the case of n-pentane, which was used in the present case, since these proportions give hydrocarbon-air mixtures safely above the upper explosive limit of n-pentane. It will be noted that an oxygen to pentane mol ratio of 1.0 corresponds to 12.5% of the amount required for complete combustion of pentane to carbon dioxide and water, while a ratio of 2.8 corresponds to 35% of this theoretical amount. In the commercial application of the process, safety devices well known in the art would naturally be used for automatic control of the respective flows of reactants and prevention of the formation of explosive mixtures.

Having thus fully described the various effects of the main variables involved in the operation of the process, there will now be described the properties of the products obtained. As examples, there are shown the production of a city gas and of a synthesis gas which were obtained under the same engine operating conditions except for the fact that the oxygen to pentane mol ratio was different. Typical products are presented in Table I, following:

TABLE I

Oxidation of ni-pentane in a single cylinder CFR engine operated without spark ignition at 240 R. P. M.

	Manuf- acture of City Gas	Manuf- acture of Synthesis Gas
Experimental Conditions:		
Intake Temperature, °F.....	400	400
Jacket Temperature, °F.....	350	350
Compression Ratio.....	10:1	10:1
Oxygen: Pentane Mol Ratio.....	1:1	2:1
Percent of Oxygen Feed Reacted.....	98.5	100
Products Recovered:		
(a) Liquid Phase, Volume Percent of Feed.....	18.7	17.4
(b) Gaseous Phase, Volume Percent of Feed.....	81.3	82.6
Properties of Liquid:		
Bromine Number, cc./g.....	34.0	12.0
Saponification Number.....	3.0	0.0
Neutralization Number.....	Below 1.0	0.0
Specific Gravity, 60/60.....	0.7250	0.6413

COMPOSITION OF DRY EXHAUST GAS (BY MASS SPECTROGRAPH)

	Mol Percent	B. t. u./ Cubic Foot	Mol Percent
Hydrogen.....	5.2	326.2	22.0
Methane.....	11.3	1009.0	4.9
Ethane.....	1.7	1764.4	0.2
Propane.....	0.1	2572.0	0.1
Pentane.....	1.2	4035.6	0.1
Ethylene.....	9.9	1631.0	0.6
Propylene.....	2.1	2347.2	0.1
Carbon Monoxide (By Infrared).....	13.6	323.5	15.5
Carbon Dioxide.....	0.6		1.1
Nitrogen.....	53.7		55.3
Oxygen.....	0.2		0.0

From the above composition and B. t. u. value of the individual components, it is readily calculated that the city gas produced has an approximate value of 467 B. t. u. per cubic foot; it can readily be enriched to the desired value of 550 B. t. u./cubic foot by addition of 2.7% of pentane.

It is of great interest to note that the amount of carbon dioxide produced was very small in both cases and that, therefore, the oxygen was employed almost quantitatively for useful purposes; the fact that the city gas produced in this manner is, for all practical purposes, oxygen-free, is quite important since it makes it quite safe for use in cold climates in contrast to some other methods previously disclosed where air is blended with gaseous and condensable hydrocarbons.

It should be further pointed out that, while air was used as the source of oxygen in the example given above, the invention is by no means restricted to such source of oxygen. Indeed, other diluents, carbon dioxide, flue gas, and the like, may be used for the purpose of the present invention without departing from its spirit and, for example, should a gas of greater heating value be desired, steam would be used as the preferred diluent for the oxygen-bearing gas. It will be obvious that when steam is the diluent, the gaseous hydrocarbon mixture will be most readily separated from the condensed steam and a gas of heating value far in excess of that of natural gas will be produced by this process.

Finally but not least important is the fact that the liquid hydrocarbon layer recovered is a most valuable by-product since it contains a large proportion of aromatics. Indeed, analysis of this hydrocarbon layer indicates that it contains 40% of aromatics, more than 90% of which is benzene and the rest is toluene; in addition it contains 13.4% of conjugated diolefins which are valuable synthetic rubber intermediates, 4.1% of oxygenated compounds (including those recovered from the small amount of water condensed together with the hydrocarbon layer) and 1.8% of mono-olefins which are valuable addition agents for motor gasoline. Since all these constituents of the hydrocarbon layer may be readily separated by simple fractionation from the unreacted pentane

which constitutes the remaining part of the hydrocarbon layer, it is seen that a relatively important source of revenue is available which will make the manufacture of city gas by this procedure relatively inexpensive and well adapted to the purpose intended. The unreacted pentane so separated can either be used for increasing the heating value of the city gas manufactured when using air as the source of oxygen-bearing gas or may be recycled to the process for the further production of additional city gas.

The formation of aromatics is favored when about 1 mol oxygen per mol pentane is employed in the engine or compressor and when the dilution of the oxygen with an inert gas is relatively small, being from about 4 to 8 times its own volume. On the other hand, if the molar ratio of oxygen to pentane is doubled but the dilution of the oxygen with an inert gas is simultaneously considerably increased to about 14 to 18 times its own volume, the pentane or other paraffinic hydrocarbon may be converted to a substantial extent, to the corresponding olefin, as well as other valuable products without degradation to methane, carbon dioxide and light paraffins. Although oxidative dehydrogenation of paraffins has been known for years, it has not been used on a commercial scale because of the very low yields of the desired olefins obtainable and because of the large extent of degradation of the original paraffin to useless gaseous products such as CO₂, CH₄ and the like. By contrast, a substantial amount of the paraffin is converted to the corresponding olefin by means of the present process without significant degradation to undesirable products but with the production of lower olefins which are particularly advantageous for the manufacture of high octane gasoline components by the conventional alkylation or polymerization processes. Thus, using pentane as the feed to a CFR engine equipped with a diesel head and operating this engine as a compressor, in the presence of two mols of oxygen (air) per mol of pentane and 200% dilution of the air with nitrogen (or steam) and preheating the whole gaseous mixture to 200° F., before entering the engine cylinder, and operating at a compression ratio of 11.5, there was converted 31% of the n-pentane in a single pass, the amount of pentenes formed amounting to about 21% of the pentane converted. At the same time, about 41% of other valuable olefins, such as ethylene, propylene and butylenes and 25% of valuable oxygenated hydrocarbons were formed. This is summarized in Table II.

TABLE II

Selectivity of n-pentane to various compounds under conditions of controlled oxidation

Experimental conditions:	
Diesel head—900 R. P. M.—11.5 compression ratio	
200° F. intake and 350° F. jacket temperature	
2.0 oxygen/pentane mol ratio	
200% nitrogen dilution of air intake	
Products recovered:	
1911 cubic feet of exhaust gas	
1425 ml. of aqueous solution	
495 ml. of hydrocarbon layer	
Pentane conversion:	
30.98% on pentane feed or 36.45% on pentane accounted for by recovered products.	
Selectivity:	
A. To carbon oxides:	Percent of pentane reacted
CO ₂	3.82
CO.....	7.64
B. To olefins:	
Ethylene.....	15.29
Propylene.....	17.32
Butylenes.....	7.64
Pentenes.....	21.36
Hexenes.....	0.22
C. To Paraffins: Hexanes.....	1.89
D. To oxy compounds as a group.....	24.79
or individually:	
To Acids as acetic acid.....	6.45
Aldehydes as formaldehyde.....	4.53
Ketones as MEK.....	8.29
Alcohols as butyl alcohol.....	5.52
E. Summary: Selectivity to olefins + oxy compounds = 86.62%	

This process, therefore, provides a valuable means for converting normal paraffins which have little value as motor fuel components into derivatives of far greater value. Its versatility is well demonstrated by the fact that olefins and oxygenated compounds are produced under the conditions just described without degradation to useless compounds, whereas, under different conditions, aromatics are obtainable besides providing the synthesis gas or city gas described in Table I.

10 What is claimed is:

1. An improved process for converting low molecular weight, normally liquid hydrocarbons into valuable, predominantly hydrocarbon fuels, which comprises the steps of preheating to a temperature in the range of 200°–400° F. a gaseous feed mixture comprising said hydrocarbons and a limited amount of a free oxygen-containing gas, the ratio of free oxygen to hydrocarbon being in the range of about 0.5 to 2.8 mols of oxygen per mol of hydrocarbon, and being insufficient to support complete combustion; passing at least a portion of said mixture to an externally unheated reaction zone; compressing said mixture in said zone rapidly to about $\frac{1}{10}$ to $\frac{1}{20}$ of the original volume of said reaction zone about 100 to 450 times a minute for a reaction period of less than about 0.005 minute so that its temperature is increased substantially exclusively by said compression to a level conducive to a limited reaction during said compression between the hydrocarbon and the free oxygen to produce carbon compounds having less hydrogen per molecule than the hydrocarbon; rapidly thereafter expanding the reaction products to reduce their temperature; and withdrawing reaction products from said zone having a greater number of molecules than the gaseous feed mixture, and comprising valuable, predominantly hydrocarbon fuel products.

2. The process of claim 1 wherein said mixture of oxygen and hydrocarbon is diluted with an inert gas.

3. The process of claim 1 wherein said inert gas is steam.

40 4. The process of claim 1 wherein said inert gas is nitrogen.

5. The process of claim 1 wherein said hydrocarbon is a low octane, low molecular weight paraffinic compound having up to 6 carbon atoms in the molecule.

45 6. The process of claim 1 wherein said mixture is compressed to $\frac{1}{11.5}$ of its original volume.

7. The process of claim 1 wherein said oxygen-containing gas is air, diluted with added nitrogen to the extent of about 200%.

50 8. The process of claim 1 wherein steam is added to said feed mixture.

9. The thermal process of converting a low molecular weight normally liquid hydrocarbon feed stock containing 55 paraffinic hydrocarbons to produce a hydrocarbon mixture of improved motor fuel value without substantial degradation to methane, which comprises preheating to about 200° to 400° F. a feed mixture of said hydrocarbon and an oxygen-containing gas, the ratio of oxygen to hydrocarbon in said mixture being between about 1.5 and 2.8/1, rapidly compressing said mixture to a maximum of $\frac{1}{10}$ of its original volume and maintaining the compressed mixture at an elevated temperature due to said compression for a period of less than about 0.005 minute, thereafter rapidly cooling the resultant mixture including reaction products containing an increased number of molecules as compared to the feed mixture by expanding, and recovering therefrom a product including 70 a normally liquid hydrocarbon fraction produced during the compression step of improved octane value having a substantially increased total content of olefinic and aromatic hydrocarbons.

(References on following page)

References Cited in the file of this patent

UNITED STATES PATENTS

1,808,168	Hopkins	June 2, 1931
1,872,931	Goldsborough	Aug. 23, 1932
1,984,519	Chappell	Dec. 18, 1934
2,143,380	Klein et al.	Jan. 10, 1939

2,274,204

2,362,196

5

217,747

Kipper Feb. 24, 1942

Frey Nov. 7, 1944

FOREIGN PATENTS

Great Britain June 26, 1924