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(54) ENGINE GENERATION OF SYNTHESIS GAS

(54) GEGERATION PAR MOTEUR DE GAZ DE SYNTHESE

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The present invention relates to the generation of synthesis gas comprising hydrogen and carbon monoxide by the partial combustion of a hydrocarbon with free oxygen in the combustion space of a cyclically operating, internal combustion engine. The process of this invention is particularly useful in the generation of carbon monoxide and hydrogen by partial combustion of a hydrocarbon gas with air, relatively pure oxygen, or oxygen-enriched air, the resulting products of which are suitable as a source of hydrogen or as feed gas for the synthesis of hydrocarbons, alcohols, or ammonia.

The present invention concerns the method of generating hydrogen and carbon monoxide in an internal combustion engine comprising introducing reactants to the engine combustion zone during the intake stroke or portion of the engine cycle in the proper proportions for partial combustion to hydrogen and carbon monoxide, subjecting the mixture to substantial compression, thereafter igniting the compressed mixture and causing it to burn with ensuing expansion of combustion products, withdrawing or exhausting product gas, preferably during contraction of the combustion zone, and continuously repeating the cycle to insure a continuing supply of product comprising hydrogen and carbon monoxide.

The reactants may be premixed or separately charged into the engine combustion zone, preferably during movement of the piston away from the cylinder head. When separately charged they may be introduced simultaneously or sequentially into admixture with one another within the combustion zone. With relatively pure oxygen and a hydrocarbon gas as reactants it is generally desirable to introduce the reactants separately into the combustion zone of the engine to avoid the hazards of charging an explosive mixture. However, this results in local concentrations of relatively pure oxygen in the combustion zone. Also, introduction of pure oxygen at the beginning of the intake portion of the cycle results in contact between the highly reactive pure oxygen and highly combustible residual product gas. The residual product gas in the combustion space of the engine is in contact with hot parts of the engine, particularly the exhaust valve, and with carbon deposits which are at a relatively high temperature. These conditions are conducive to preignition of the charge. We have found that preignition may be prevented by purging the combustion zone of combustion products and/or by cooling the combustion zone following the exhausting of product gas and prior to the introduction of oxygen.

The invention contemplates purging the combustion zone with a gaseous purging medium following the exhaust of combustion products therefrom and prior to the introduction of reactants thereto. Steam is especially suitable as a purging medium. When a purging medium is used we prefer overlapping the exhaust or product withdrawal portion of the cycle with the admission of the purging medium. The purging medium effects cooling of the hot spots in the combustion space of the engine as well as substantial purging of the product gases from the combustion space, and effectively prevents preignition of the charge gases. The use of steam is outstandingly advantageous in this connection, first, because water vapor constitutes a beneficial reactant in regulated, predetermined proportions, and second because any excess will simply carry over into the product gas, where it is readily removable by condensation. As a result, accurate metering of the steam is not mandatory. Preferably the steam is superheated prior to introduction into the combustion zone of the engine. Alternatively, but less desirably, air, hydrocarbon gas, or other purge media may be used.

We have also found that a liquid may be injected into the combustion chamber immediately following discharge of products of combustion and prior to introduction of oxygen to cool the combustion space and prevent preignition of the charge gas. Water and liquid hydrocarbons are especially useful in this connection.

Admission of the reactants into the engine combustion zone in consecutive order such that substantial admission of the hydrocarbon takes place prior to the admission of concentrated oxygen also serves to cool the residual gases and hot spots in the combustion zone and prevent preignition.

The amount of oxygen required for satisfactory operation of the engine is generally somewhat in excess of that amount theoretically required by stoichiometry for conversion of all of the hydrocarbon fuel to carbon monoxide and hydrogen. In general, from about 5 to about 50 per cent more oxygen is required than the theoretical amount. The oxygen requirements vary with engine design, being lower for high compression engines than for low compression engines. Oxygen requirements are best determined by trial for any given engine. Excessive oxygen causes misfiring or preignition while too little oxygen results in excessive carbon formation with resulting spark plug fouling. For highest yields of carbon monoxide and hydrogen it is desirable to operate with the oxygen feed as near that theoretically required as possible. A feature of our invention is the introduction of a minor proportion of the total oxygen charge into the combustion space of the engine in the immediate vicinity of the spark plug to prevent carbon deposition at this point and prevent fouling of the spark plug. This portion of the oxygen is injected following compression of the charge and at about the time of firing.

In commercial processes employing hydrogen, carbon monoxide or mixtures of hydrogen and carbon monoxide, it is generally desirable to have the gases available at elevated pressure. We have found that the internal combustion engine may be operated with exhaust pressures as high as 100 pounds per square inch gauge. We prefer to operate at pressures within the range of 50 to 100 pounds per square inch gauge. Corresponding elevated intake pressures are also employed.

In order to more specifically disclose the present invention in greater detail, reference is had to the attached drawing, wherin Figures 1 and 2 show, respectively, vertical and horizontal sectional views of a combustion engine cylinder embodying the principles of the present invention, and Figure 3 is a diagrammatic representation of a typical operating cycle.

In the engine disclosed in Figures 1 and 2, which may be of a multicylinder type, an individual cylinder designated by the reference numeral 10 receives a vertically reciprocating piston 11, attached through pin 12 and connecting rod 13 to a crank shaft, not disclosed, which delivers the available mechanical energy. A cylinder head 15 is provided, wherein four separate valves 16, 17, 18 and 19 lead respectively to individual manifolds 20, 21, 22, and 23.

The feed streams of oxygen is, as previously emphasized, advantageously enriched or rectified gas composed predominantly of molecular or free oxygen. Preferably, it contains over 80 per cent and desirably over 90 to 95 per cent oxygen. As a result, the product may comprise a high purity mixture of hydrogen and carbon monoxide substantially free from difficultly removable contaminating gases, such as nitrogen.

In the embodiment disclosed, manifold 20 receives a product gas through exhaust valve 16. Manifolds

21 and 23, respectively, supply a stream of pure oxygen and a stream of gaseous hydrocarbon. Manifold 22 supplies steam under pressure through valve 18.

Ignition is effected by means of a spark plug 25 connected with electrical igniting means, not shown, and timed as will hereinafter be disclosed in greater detail.

Valves 17, 18 and 19 are preferably shrouded as indicated at 26, 27, and 28 with annularly disposed projections arranged to insure high turbulence and therefore complete mixing of the admitted reactants by effecting admission or injection in about the same rotational direction with reference to the axis of the cylinder. It will be understood that the exact arrangement or construction of the mixing shrouds does not, per se, form an essential part of the present invention, and accordingly, this construction is not shown in detail. Actually, it has been found that shrouds extending annularly through 90-180° of the valve are effective when faced in generally the same rotational direction. However, this construction may obviously be varied widely to secure adequate mixing and alternatively, provision of directional intake ports and/or turbulence producing cylinder head arrangements may be substituted for this purpose.

In accordance with one embodiment of the present invention, provision, not shown, is made for timing the operation of the valves and ignition means in accordance with the diagram set forth in Figure 3.

Therein, progressing in a clockwise direction from the point "A" there is symbolized the complete cycle of operation in the case of a typical four-stroke cycle reciprocating engine. The vertical line 26 symbolizes the angular position of the combustion engine cylinder axis. Therefore, point 27 represents top dead center and point 28 bottom dead center. Accordingly, the angular movement on the right hand side of the line 26 covers the approximate intake and combustion or burning portions of the cycle, whereas the opposite side of the diagram relates, in general, to the compression and exhaust portions of the cycle.

Beginning with the exhaust portion of the cycle at the angular position "A" the exhaust valve opens, preferably though not necessarily, somewhat in advance of bottom dead center, and remains open throughout approximately the entire upstroke of the piston, as represented by the shaded area entitled "Exhaust", during which the product gas produced in a previous cycle of operation flows through outlet valve 16 into the exhaust manifold 20. In the cycle shown, the exhaust valve opens at 20° before bottom center, and closes at 10° before top center as indicated by the angular distance 30 and 31 respectively.

At a point of angular position "G" 30° before top center, that is, 20° before the exhaust valve is closed, steam injection valve 18 opens, sweeping the residual product gas through outlet valve 16.

At approximately top dead center, and preferably somewhat in advance thereof, at an angular position "B", both the hydrocarbon gas inlet valve 19 and the oxygen valve 17 open so the reactants under pressure enter from manifolds 21 and 23. Admission of the reactants, in the specific embodiment selected, takes place an angular distance 31 of 10° before top center and continues throughout the shaded portion of the cycle entitled "Admission of Reactants" to the angular position "F", preferably about or slightly after bottom dead center, and specifically 15° after bottom dead center as indicated by arc 35.

Following this point, with the valves closed, the engine goes through almost a complete revolution in which the mixed gases are compressed, subjected to ignition at point 40, and thereafter burned as indicated in the line designated as "Compression and Burning" which continues to angular position "A", at which the four-stroke cycle of operation is repeated.

As above indicated, the period of opening of the steam injection valve is not extremely critical since any small amounts of steam or water vapor carried off with the product gas through the outlet manifold 20 are readily removable by condensation.

It is to be understood that there is a wide permissible variation of valve and ignition timing from those disclosed in the above specific example. For example, opening of the exhaust valve usually takes place anywhere from 40° before to 40° after bottom center, but preferably, at least 10° in advance of bottom center, While the exhaust valve normally closes at about top dead center, it may be adjusted in accordance with engine characteristics to close from 20° in advance to 20° beyond top center.

In order to effect efficient charging of reactants, the hydrocarbon gas valve and oxygen valve advantageously open about or before top center, as for example, as much as 20° in advance. The oxygen and hydrocarbon gas inlet valves may close before, or preferably, somewhat after bottom center, as for example, 10° or even as much as 20° thereafter. The ignition point 40 depends on known principles of engine design and operation which, per se, form no part of the present invention. Therefore, spark timing is preferably adjusted for development of maximum mechanical energy with due regard to engine speed and other engine characteristics.

Example

Natural gas is used as fuel in an engine gas generator. The composition of the natural gas follows:

Methane	84.6	mol	per	cent
Ethane	7.3	"	"	"
Propane	5.1	"	"	"
Carbon dioxide	1.6	"	"	"
Air	1.4	"	"	"

The gas is admitted to the cylinder of the engine from and intake manifold maintained at 53 pounds per square inch gauge. Oxygen of 99.5 mol per cent purity is introduced from and intake manifold maintained at 77 pounds per square inch gauge. The natural gas and oxygen are fed in the relative ratio of 1.50 O/C or 0.75 mols of oxygen per mol of carbon in the feed gas.

A

Steam at 60 pounds per square inch gauge is used as purge.

The product gas is discharged from the engine at 40 pounds per square inch gauge. The product gas has the following composition:

Carbon monoxide	32.0 mol per cent
Carbon dioxide	8.2 " " "
Hydrogen	59.2 " " "
Nitrogen	0.4 " " "
Methane	0.2 " " "

The steam purge results in smooth, predictable operation without carbon formation. There is no tendency of the engine to misfire or knock. No trouble is experienced with spontaneous ignition.

As above indicated, the invention especially contemplates feeding the engine with a normally gaseous hydrocarbon such as methane, and the C_2-C_4 hydrocarbons, such, for example, as are found in natural gas. Broadly, however, the feed may include gasiform or vaporform hydrocarbons, for instance, normally liquid hydrocarbons which are fed in a gasiform condition under a substantial preheat.

Preheating of either or all the reactants and steam to temperatures of 300-600°F. and higher is specifically contemplated as a means of improving thermal efficiency. It is to be understood that in spite of the preheating, the temperature of the steam is substantially lower than that of the residual combustion mixture so that an initial cooling or quenching occurs to a range at which uncontrolled ignition is

A

inhibited. Therefore, it is manifest that the present process enables a substantial and desirable preheating of the reactants without the misfiring or preignition tendency which otherwise would accompany the simultaneous introduction of relatively high temperature methane and oxygen streams into the combustion zone.

In spite of the fact that the detailed examples have been given in terms of a four-stroke cycle engine, it should be apparent that the disclosure in its broadest aspect is not so limited since injection of the reactants may be effected prior to, during, or after compression and before ignition, in accordance with known engine practice. For example, provision may be made for injecting steam, methane and oxygen at the bottom of the exhaust stroke in a two-cycle engine such that the oxygen and methane are admitted after steam injection.

The injection of the steam results in metered inclusion of a predetermined amount of water vapor in the reactant mixture which is subjected to ignition. In general, the proportion of water vapor which may be included may range up to about 100 per cent of the molar volume of free molecular oxygen supplied to the engine.

In the foregoing detailed description of a preferred embodiment of this invention steam has been taken as an illustration of the cooling and purging medium. It is to be understood that other gaseous purging media, for example carbon dioxide, methane, air or other gases which are not detrimental to the product may be introduced through manifold 22 as the cooling and/or purging medium. Similarly, as indicated hereinabove, the valve 19 may be opened prior to opening of valve 17 to permit introduction of the gasiform hydrocarbon fuel into the combustion zone of the engine prior to introduction of relatively pure oxygen from manifold 21.

In the illustrated description above, the preferred valve shrouding is aligned to produce a unidirectional swirl. As there intimated, however, the highly desirable intimate admixing of the reactants may be realized by arranging the valve shrouds in rotationally opposed directions so as to induce opposing swirling of the introduced reactants. Actually, it appears at the present time that opposed swirling provides somewhat more thorough mixing. Accordingly, the invention contemplates any combination of swirling actions effective to realize the desired mixing and combustion.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. In a process for the generation of hydrogen and carbon monoxide by the reaction of a gasiform hydrocarbon with oxygen in an internal combustion engine wherein said reactants are charged into the combustion space of a cyclically operating internal combustion engine in relative proportions for the formation of a partial combustion product composed essentially of hydrogen and carbon monoxide, mixed and compressed therein, subjected to reaction with the generation of mechanical energy, and the product hydrogen and carbon monoxide thereafter exhausted as a relatively pure stream, the improvement which comprises introducing a cooling medium into the combustion space following the exhausting of at least the major portion of the product therefrom and prior to the introduction of oxygen into the combustion space.

2. A process according to Claim 1 in which said gasiform hydrocarbon is admitted to the combustion space as said cooling medium following discharge of said product therefrom and prior to the introduction of oxygen thereto.

3. A process according to Claim 1 or 2 wherein a major portion of the required oxygen is charged to the combustion space prior to compression of the hydrocarbon and oxygen mixture therein, said compressed mixture is subjected to spark ignition to initiate said reaction, and a minor amount of additional oxygen is introduced into the combustion space in the immediate vicinity of the point of spark ignition following compression and at about the time of ignition.

4. A process according to Claim 1 in which water is admitted to the combustion space as said cooling medium following discharge of reaction products therefrom and prior to the introduction of fresh reactants.

5. A process according to Claim 1 in which a liquid hydrocarbon is admitted to the combustion space as said cooling medium following discharge of said product therefrom and prior to the introduction of said reactants.

6. In a process for the generation of hydrogen and carbon monoxide in an internal combustion engine by the reaction of a gasiform hydrocarbon with oxygen wherein said reactants are charged to the combustion space of a cyclically operating internal combustion engine in relative proportions for the formation of a partial combustion product composed essentially of hydrogen and carbon monoxide, compressed therein, subjected to reaction with the generation of mechanical energy, and the product hydrogen and carbon monoxide thereafter exhausted as a relatively pure stream, the improvement which comprises cooling and purging the combustion space by charging a gaseous cooling medium thereto during the latter portion of the period in which the products of reaction are being exhausted therefrom.

E.L 7. A process according to Claims 1 or 6 in which steam is charged to the combustion space as said cooling medium following exhausting of said product and prior to the introduction of said reactants.

8. A process according to Claims 1 or 6 wherein the reactants are charged to the combustion space of the engine in consecutive order such that the gasiform hydrocarbon is first admitted and the admission of the free oxygen later initiated after substantial prior admission of the hydrocarbon.

B

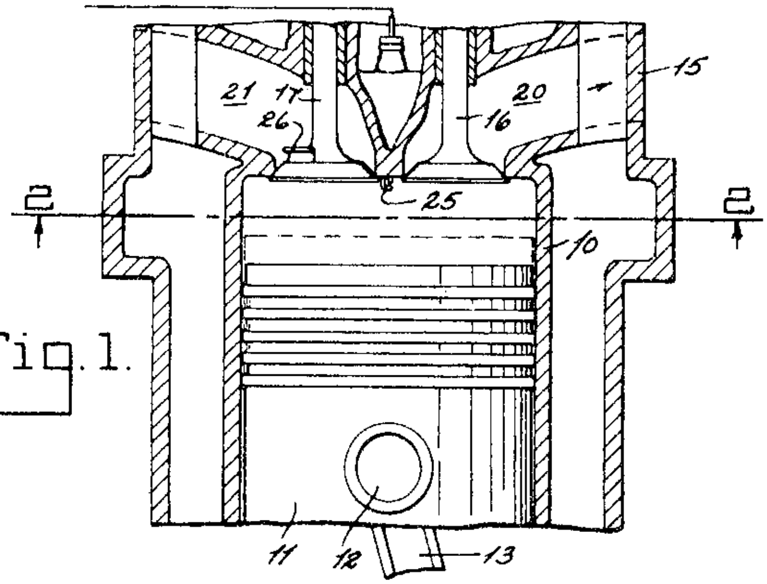

Fig.1.

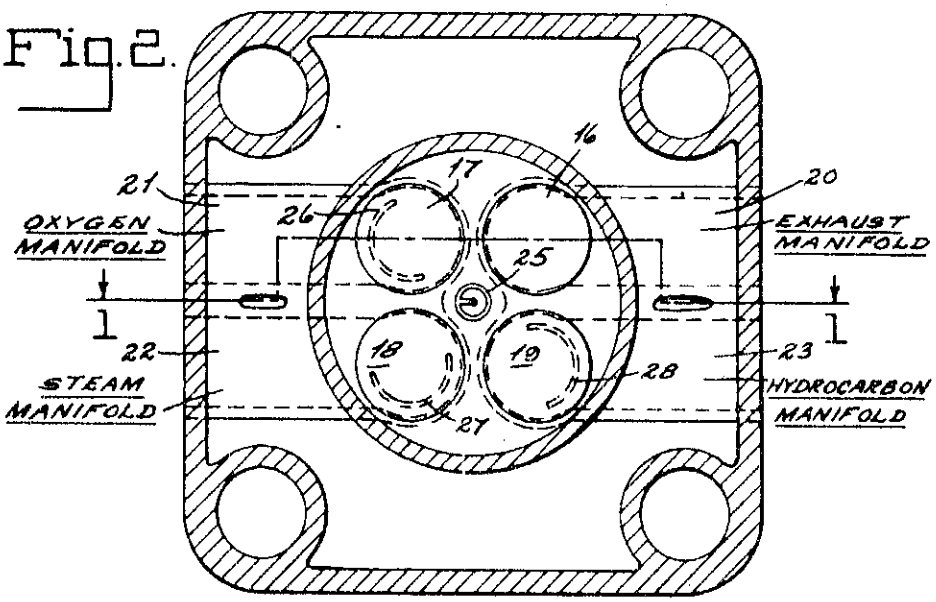

Fig.2.

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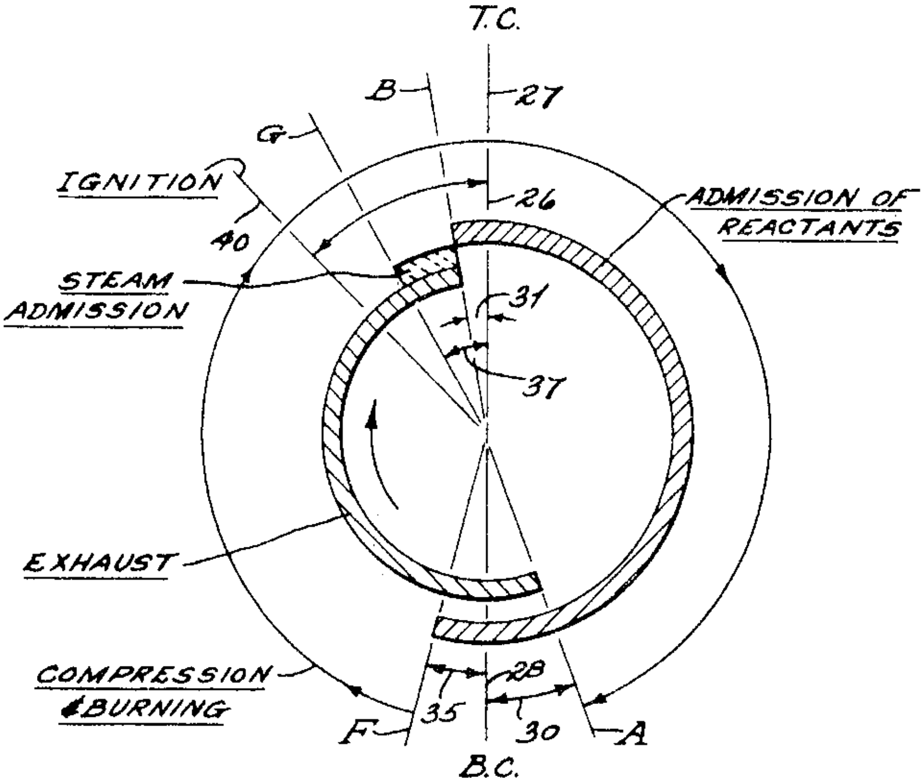

Fig.3.

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