# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION.

## Improvements in or relating to the Production of Synthesis Gas Mixtures containing Carbon Monoxide and Hydrogen.

We, Standard Oil Development Company, a corporation duly organised and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention, and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:

The present invention relates to methods of preparing a mixture of carbon monoxide and hydrogen suitable for use in hydrocarbon synthesis.

At the present time there is a great deal of interest in the problem of manufacturing synthetic fuels. The Government and the large oil companies have taken cognizance of the fact that the known petroleum oil reserves may be exhausted in the not too distant future. At the present rate of increase in use, the known petroleum oil reserves will be insufficient to supply the demand in the foreseeable future. In seeking other possible sources of fuel, the oil industry has considered several possibilities including the hydrogenation of coal, the distillation of shale and/or tar sands, and the synthesis of hydrocarbons from carbon monoxide and hydrogen, the carbon monoxide and hydrogen being prepared either from natural gas by reforming or partial oxidation, or by coking a heavy oil and subjecting the coke thus formed to a water-gas reaction, or by treating a solid carbonaceous material at elevated temperatures with steam.

As previously stated, the present improvements relate to the preparation of a mixture of carbon monoxide and hydrogen which may be reacted to form hydrocarbons and also oxygenated hydrocarbons. The materials which are used are liquefiable bituminous carbonaceous materials such as heavy tars and pitches and natural asphalts, which, in quantity, equal the estimated reserves of oil and natural gas. For example, there are natural deposits of pitches readily available in localities such as in Trinidad and also there are considerable quantities of pitches for which heretofore there has been found no use, such as pitches which result from the distillation of Venezuelan crude. Any of these asphalt pitches and tars may be used as well as other liquefiable bituminous carbonaceous materials.

It is a main object of the invention, therefore, to produce carbon monoxide and hydrogen of a purity sufficient for the hydrocarbon synthesis more cheaply than has heretofore been possible.

More specifically, the invention involves the use of tars, pitches and other liquefiable bituminous carbonaceous material as the starting material for the production of carbon monoxide and hydrogen.

Other and further objects of the invention will appear from the following more detailed description and claims.

In the accompanying drawings, a reactor is shown in which carbon monoxide and hydrogen is produced according to the invention.

In brief, the invention comprises broadly a process for producing carbon monoxide and hydrogen in which the reaction is performed by changing a liquefied bituminous carbonaceous raw material in a single reaction vessel containing a fluidized bed of powdered refractory material and by partially burning the raw material in the presence of substantially pure oxygen and regulated quantities of added steam adapted to supply hydrogen, to make for any hydrogen deficiency in the carbonaceous material so as to produce finally a product containing from one to two mols of hydrogen per mol of carbon monoxide and limited quantities of carbon dioxide.

Referring in detail to the drawing, 1 represents a reaction vessel or retort, cylindrical in shape having a convex crownpiece and a conical base and being provided in its lower section with a foraminous member G. Within the reactor 1 is maintained a dense, turbulent suspension of powdered refractory material, such as silica, alumina and magnesia, the refractory material having an average particle size of from 20 to 80 mesh per linear inch and being maintained in the dense, turbulent suspension or "fluidized" state by causing gasiform material to flow upwardly therethrough at a relatively low superficial velocity. A mixture of oxygen and steam from an outside source is introduced through a line 3 and the gaseous mixture is discharged into the bottom of reactor 1 where it passes upwardly through the grid G and flows through the reactor thereafter at a superficial velocity (i.e., the gas velocity were the reactor empty) of from ½ to 1½ feet per second. The manner of fluidizing solids to form the dense suspension referred to is now well known to those skilled in several arts, including the petroleum and related arts, and this technique has by now been in commercial use for several years in the oil cracking art. Sufficient powdered material is added or maintained within the reactor 1 to form a dense suspension having an upper level at L. A heavy oil such as the non-vaporizable material resulting from the vacuum distillation of the bottoms of a Venezuelan crude is introduced through line 5. Considerable quantities of this material are available in a locality called Aruba (in the Caribbean Sea, near Venezuela) for which no practical use has been found up to this time. The non-vaporizable material or pitch is converted into a flowable state by heating to a temperature condition of from 200 to 450°F. In order to further increase the flowability of the heavy pitch, it is admixed with steam from line 6, which steam is injected into line 5 and this mixture is atomized in a spray head 7 disposed within the reactor as shown. In the drawing there is shown the spray nozzle or atomizer disposed within the dense phase but this may be located above L so as to spray the atomized pitch on to the top of the dense phase suspension. Instead of having a single spray there may be several disposed peripherally around the inner wall of the reactor 1. The oxygen fed into the reactor, as stated, causes a partial combustion of the atomized pitch to form carbon monoxide, hydrogen and a minor quantity of carbon dioxide. Since pitch is usually low in hydrogen content, steam is included with the oxygen, the amount of steam added being 0.5 to 5 mols per mol of oxygen added. The proportions of oxygen and steam used will vary in accordance with the desired ratio of hydrogen to carbon monoxide in the product, the preferred proportions of oxygen to steam being 0.3 pounds of oxygen and 1.5 pounds of steam per pound of pitch to produce a $H_2/CO$ ratio of about 1.8. By increasing the oxygen to 0.9 pounds per pound of pitch and reducing the water pro rata, the $H_2/CO$ ratio in the product may change to about 1.0. During the partial combustion of the pitch in the dense phase suspension in the reactor, a temperature of from about 1,500 to 2,000°F. prevails and the pressure of from about 0 to 300 pounds per square inch gauge with pressures of 115 to 300 pounds preferred. Digressing for a moment, it should be pointed out that in the actual synthesis of the hydrocarbons and the oxygenated hydrocarbons from carbon monoxide and hydrogen, in the interest of suppressing carbon formation on the catalyst in that synthesis reaction, it has been found advisable to operate at superatmospheric pressure and in this present reaction it is preferred to operate at superatmospheric pressure so as to produce a gas which will be under superatmospheric pressure and can be delivered in that state to the synthesis reactor.

Referring again to the reaction in the dense phase, it should be pointed out that along with the carbon monoxide, hydrogen, and carbon dioxide formed, substantial quantities of soot and vaporizable hydrocarbons are formed due to cracking. The products of the reaction ascend from the dense phase into the upper portion of the reactor, and in the said upper portion of the reactor, that is, above the dense phase level L a quantity of secondary oxygen is added through a line 10 for the purpose of partially oxidizing the lighter hydrocarbons and the soot or solid carbonaceous material. A temperature in the upper portion of the secondary burning zone which extends from L to the top of the reactor of from 2,000 to 3,000°F. is attained. The amount of secondary oxygen added per pound of pitch fed is from 0.1 to 0.5 pounds. The products of the reaction are withdrawn from the retort through line 15, thence discharged into a waste heat boiler 17 where a substantial quantity of sensible heat is recovered and the products are withdrawn from the waste heat boiler at a temperature of about 400°F. through a line 20 and discharged into one or more gas-solids contacting devices such as "cyclones" 22, for the purpose of separating out entrained fines which may unavoidably pass up through the reactor and exit with the products. The separated fines are returned via standpipe 25 to the reactor at a point preferably below L. The products are finally recovered for use in the synthesis reaction through a line 30. The products in line 30 may be cooled to as low as 100°F. or at least below the condensation temperature of steam before introduction into the hydrocarbon synthesis reaction zone (not shown herein) for the purpose of condensing out and separating water.

Referring again to the reactor 1, attention is directed to the fact, as shown in the drawing, that the upper portion 1a of the retort is of greater internal diameter than the lower section. This expanded upper section is necessary because of the additional oxygen added thereto as well as the additional expansion of the gases due to the higher temperature resulting from the addition of the secondary oxygen. The diameter of the upper section should be such that the gas velocity therein is less, say, in the order of ½ of the velocity in the lower section. In other words, as stated, where the superficial gas velocity in the lower section is from ½ to 1½ feet per second, the gas velocity in the upper expanded section should be of the order of ¼ to ¾ of a foot per second.

Then, it may, and often does happen that the pitch which is introduced through line 5 contains substantial quantities of salts along with other metallic compounds, such as vanadium, calcium, and iron, which may exist as chlorides, oxides, or metallo-organic compounds. It is desirable, therefore, to continuously supply fresh powdered refractory material to the retort and to remove refractory material contaminated with the aforementioned compounds. To this end, therefore, a hopper 40 is provided in communication with a standpipe 42 through which standpipe refractory material may be fed from the hopper 40 to the reactor or retort. At the same time contaminated solids are withdrawn from the reactor through the draw-off pipe 45.

It will be noted in the design which has been described that in the lower portion of the retort a temperature not exceeding about 2,000°F. exists, and at this relatively lower temperature any salts or other compounds which may be present in the hydrocarbon feed do not ordinarily melt or flux and, therefore, it is an important advantage of the invention to maintain the lower section of the retort at a temperature below that at which the fluxing ash of the salts and other compounds which might be present in the oil would impair the fluidized solids. Of course, in the case where the oil is not contaminated with the salts, it will not be necessary ordinarily to continuously add fresh powdered solids and withdraw the same.

Another important phase of the invention is that in some instances to produce the gas of a certain composition, it may be desirable to introduce carbon dioxide into the bottom section of the reactor with the oxygen and steam.

Having now particularly described and ascertained the nature of our said invention, and in what manner the same is to be performed, we declare that what we claim is:—

1. A method of producing a mixture of gases containing a preponderance of carbon monoxide and hydrogen which comprises providing a fluidized bed of a powdered refractory material in a confined reaction zone, charging to said reaction zone a liquified bituminous carbonaceous material, separately charging a mixture of oxygen and steam to said reaction zone, maintaining a temperature in the fluidized bed of powdered refractory material sufficiently high to cause a reaction between the bituminous material, the oxygen and the steam to form a gaseous mixture containing carbon monoxide, hydrogen, carbonaceous residue and unconverted carbonaceous material, withdrawing a gaseous product containing the carbon monoxide, the oxygen and the hydrogen from the said fluidized bed, discharging the mixture into a space disposed in the upper portion of said reaction zone above said dense suspension of powdered refractory material, supplying oxygen to said space and converting the carbonaceous residue and unconverted carbonaceous material therein to produce additional quantities of carbon monoxide and hydrogen, and recovering from said space a gaseous material containing a preponderance of carbon monoxide and hydrogen.

2. A method according to Claim 1, wherein the temperature in the lower portion of the reaction zone is maintained below the fusion point of the ash contained in or formed from the said bituminous material.

3. A method according to Claim 1 or 2, wherein the bituminous material is normally solid.

4. A method according to any one of Claims 1—3, wherein the bituminous material is petroleum pitch.

5. A method according to any one of Claims 1—4, wherein said reaction zone is maintained under superatmospheric pressure.

6. A method according to any one of the preceding claims, wherein a tempera-

ture from 1,500 to 2,000°F. prevails in the lower portion of the reaction zone and a temperature up to 3,000°F. prevails in the upper portion thereof.

Dated this 19th day of May, 1947.

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