

1

2

3,252,774
PRODUCTION OF HYDROGEN-CONTAINING GASES

Joseph F. McMahon, Iselin, and Ernest Solomon, Upper Montclair, N.J., assignors to Pullman Incorporated, New York, N.Y., a corporation of Delaware
No Drawing. Filed June 11, 1962, Ser. No. 201,248
20 Claims. (Cl. 48-214)

This invention relates to a novel and improved process for producing hydrogen-containing gases from liquid hydrocarbons.

Hydrogen-rich gases including those containing carbon monoxide are useful for the synthesis of hydrocarbons boiling in the gasoline boiling range or oxygenated organic compounds such as alcohols and ketones. Hydrogen-rich gases also are useful in hydrogenation, hydro-treating and hydrocracking processes, ammonia synthesis, as well as for the reduction of metallic oxides and as fuel for domestic and industrial uses. As the demand for industrial and hydrogen-containing gases increases, it becomes increasingly important to find new sources of raw materials. Considerable efforts are also being expended to develop commercial methods for producing synthetic gases of high heating value. It is of importance, therefore, to find methods capable of utilizing raw materials other than natural gas for the production of hydrogen-rich gas which is either useful in the synthesis of gas of high-heating value or which is itself useful as a domestic fuel. Among the raw materials which the petroleum industry has long sought to use advantageously are heavy low-valued hydrocarbons. Most modern methods described in the prior art for the production of hydrogen and carbon monoxide from heavy oils involve partial oxidation of the oil with oxygen in the presence or absence of a catalyst. One major drawback to such oxidative methods is that an oxygen plant is necessitated. A method whereby liquid hydrocarbons are gasified without the necessity for using oxygen is, therefore, highly desirable. Although satisfactory catalytic methods have been devised for the conversion of methane and other normally gaseous paraffins to hydrogen and carbon monoxide, such methods which usually involve the use of steam, are recognized in the art as being unsatisfactory for the conversion of heavier hydrocarbons which usually contain catalyst poisons such as sulfur and coke-forming metal contaminants such as iron, nickel, vanadium, copper, etc., which deposit on the catalyst causing deactivation, loss of selectivity and operational difficulties.

It is an object of this invention, therefore, to provide an improved method for the production of hydrogen-containing gas from normally liquid hydrocarbons.

Another object is to provide a method for gasification of normally liquid hydrocarbons using steam which method does not require the use of oxygen.

Another object is to provide a process for the gasification of normally liquid hydrocarbons which is readily adapted to continuous operation and by which substantially complete conversion of hydrocarbon to product gas comprising hydrogen and low molecular weight hydrocarbons including methane and unsaturated compounds such as ethylene is realized.

A further object is to provide a medium for the gasification of heavy petroleum oils such as reduced crude, the nature of the medium being such that residual ash constituents, metal impurities, sulfur, etc., can be discharged without interruption of the gasification process.

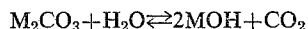
A further object is to provide a process for the gasification of normally liquid hydrocarbons which can be controlled so as to yield hydrogen gas consisting essentially of hydrogen and carbon oxides.

Various other objects and advantages of this invention will become apparent to those skilled in the art from the accompanying description and disclosure.

Accordingly, the above objects are generally accomplished by the process which comprises contacting a normally liquid hydrocarbon feed in the presence of steam with a melt comprising an alkali metal compound under conditions including a temperature between about 800° F. and about 1800° F. such that hydrogen-containing product is produced.

The process of this invention is applicable to the conversion of a wide range of normally liquid hydrocarbons. The term "normally liquid hydrocarbons" as used herein is intended to include hydrocarbons whose atmospheric pressure boiling points are greater than about 100° F. and includes naturally occurring petroleum oils, fractions thereof produced during refining operations, and individual hydrocarbons. Thus the feedstock may be a single normally liquid hydrocarbon including acyclic and alicyclic aliphatic hydrocarbons and aromatics such as pentanes, pentenes, hexanes, heptanes, etc., cyclohexanes, benzene, toluenes, xylenes, naphthalenes, and mixtures thereof. The process is especially valuable for the conversion of various normally liquid or liquid-containing petroleum fractions from light to heavy oils and tars. Typical examples of such fractions are gas oils including straight run gas oil (boiling range of between about 400° F. and about 800° F.), thermally cracked gas oil and heavy gas oil, cycle oils such as fluid catalytically cracked cycle oil, light naphtha (boiling range from about 100° F. to about 250° F.), heavy naphtha (boiling range of 200° F. to about 400° F.), straight run gasoline, kerosene, diesel oil, whole crude and residual fractions such as reduced crude. The term "reduced crude" as used herein is intended to mean a crude oil from which the light materials and gasoline boiling range constituents have been removed and which has then been distilled to remove the gas oils present therein. The initial boiling point of such an oil is usually between about 500° F. and about 800° F. although this may vary somewhat. The process of this invention is also applicable to the conversion of shale oil, tar sand oil, asphalt tar and other liquid-containing heavy or viscous materials, including petroleum wax fractions.

The molten medium with which the hydrocarbon feed is brought into contact comprises an alkali metal compound which is molten within the aforesaid temperature range between about 800° F. and about 1800° F. and which is of sufficiently low volatility such that loss of the alkali metal compound with product gas is minimized. Suitable alkali metal compounds are, for example, the alkali metal carbonates, hydroxides, nitrates, sulfides and oxides, of which the carbonates and hydroxides are preferred. Under the reaction conditions employed herein and due to the presence of substantial amounts of steam in the reaction zone and carbon dioxide in the product gas, the melt is converted in situ to an equilibrium mixture of alkali metal carbonates and hydroxides according to the following equation:



wherein M is an alkali metal. Thus the reaction zone is charged either with a preformed carbonate-hydroxide mixture or with a mixture of an alkali metal compound convertible to the reactive carbonate-hydroxide mixture in situ. Typical examples of suitable combinations of alkali metal compounds which are charged to the reaction zone are admixtures of: sodium carbonate-sodium hydroxide; potassium carbonate-sodium hydroxide; sodium carbonate-potassium carbonate; sodium carbonate-lithium carbonate; sodium carbonate-potassium hydroxide; sodium carbonate-sodium nitrate; as well as admix-

http://www.PatentGopher.com

tures of more than two compounds such as mixtures of the carbonates of sodium, potassium and lithium, and mixtures of sodium carbonate, sodium hydroxide and lithium carbonate.

In preparing the preferred molten medium, the higher melting alkali metal compounds such as sodium and potassium carbonates are admixed with between about 10 and about 90 weight percent of the lower melting compounds such as the hydroxides of sodium, potassium and lithium, or lithium carbonate.

Also included within the scope of this invention is the use of a molten salt medium comprising the alkali metal compound in admixture with other types of compounds such as the carbonates, oxides or hydroxides of the alkaline earth metals.

The gasification reaction of this invention is effected within a temperature range from about 800° F. to about 1800° F., using a large excess of molten salt in relation to the hydrocarbon feed to be converted. The hydrocarbon feed is introduced into the reaction zone at a space velocity within the range from about 0.001 to about 1 pound of normally liquid hydrocarbon feed per hour per pound of molten salt and more usually at a rate from about 0.01 to about 0.5. Within these space velocities, the steam-carbon ratio, defined as the number of mols of steam charged to the reaction zone per atom of carbon of the hydrocarbon feed, is between about 1 and about 20 or higher and is usually between about 1 and about 15.

The process is effected within the aforesaid temperature range at a pressure between about 14 and about 1000 pounds per square inch absolute (p.s.i.a.). The particular pressure employed depends largely upon economic considerations and the end use of the gas product. For example, for many significant uses of the hydrogen gas product, elevated pressures are required and it is advantageous, therefore, to conduct the reaction at substantially super-atmospheric pressure such as from about 50 to about 850 p.s.i.a. so as to reduce subsequent compression.

In accordance with one embodiment of the process of this invention, the hydrocarbon feed and steam are bubbled up through a molten pool of salt. However, also included within the scope of this invention is the method whereby the salt is sprayed into the reactor or trickled down the reactor walls.

The normally liquid hydrocarbon feed and steam are charged to the reaction zone in admixture or individually at one or more points. It is preferred to admix the hydrocarbon and steam prior to introduction into the molten reaction medium. The hydrocarbon feed may be vaporized, partially vaporized, or, as is more usual in the case of heavy oils such as reduced crude, the oil is in the form of droplets of liquid dispersed or suspended in a stream of steam. The oil may be preheated by passing it through a furnace or other suitable heating means prior to being admixed with pre-heated steam, or it may be injected at ambient temperature into a stream of super-heated steam such that condensation of the steam is substantially prevented. Thus the liquid hydrocarbon may be heated to a temperature between about 200° F. and about 800° F. The particular temperature selected depends largely upon the volatility of the hydrocarbon feed and its stability to heat.

In accordance with the preferred mode of operation, hydrocarbon feed is admixed with steam just prior to being charged to the molten reaction medium, the admixture flowing at a velocity sufficiently high such that it is injected into the molten medium as a jet-like stream or streams or as a spray. A preferred device for charging the feed to the reaction zone is a two-fluid nozzle comprising two relatively long tubular conduits in concentric relationship with an annular space therebetween, the outer tube having a tapered outlet which extends beyond the outlet of the inner tube. The outlet may be at the surface of the reactor or may extend into the molten medium in which case it usually has an outer protective casing which is relatively inert to the molten medium. Preferably the

hydrocarbon feed is passed through the internal tube while steam is passed through the outer tube, contact being made at a point between the respective outlets of the outer and internal tubes.

The linear velocity at which the hydrocarbon or steam or admixtures thereof is introduced into the molten reaction medium ranges between about 30 and about 600 feet per second, and more usually is between about 200 and about 400 feet per second.

Heat necessary to melt and maintain the reaction medium in the molten state and to provide the requirements for the heat of reaction is supplied to the reactor either from an external source, such as a gas furnace, or the molten salt may be circulated between the reaction zone to which the hydrocarbon and steam are charged and from which hydrogen product is withdrawn, and a second zone in which heat is generated by burning of coal, fuel oil, etc. In this manner the temperature of the endothermic reaction zone is maintained at the desired level by liberation of the sensible heat of the circulating molten salt.

The reaction zone is preferably provided with means positioned in the upper portion such as a cyclone to prevent entrainment of the molten salt in the product vapor.

The use of molten salt as reaction medium, for conversion of normally liquid hydrocarbons and steam to hydrogen-rich gas is a highly efficient system and offers many advantages over prior art methods. One advantage, of course, is that an oxygen plant is not a necessary adjunct of the process. Another advantage is that the reaction proceeds without troublesome carbon deposition as often occurs when the feed is contacted with solid catalytic materials, the prior art methods usually requiring intermittent removal of the carbon deposits from the solid catalyst by oxidation and reactivation treatments. A related advantage, particularly with respect to the conversion of heavy oils such as whole or reduced crudes, is that inorganic constituents which build up after prolonged operation are readily removed from the reaction zone. Such constituents include heavy metals such as vanadium, iron, nickel, copper, and ash, the principal constituents of which are silica, alumina, calcium oxide, magnesia, titania, iron oxide, and other such materials. In using prior art solid catalysts to effect conversion of heavy oils, heavy metal constituents and ash accumulate on the catalyst, causing a gradual poisoning and deactivation of the catalyst. To avoid this poisoning effect, the oil is usually subjected to costly demetallization procedures prior to use. Due to the nature of the molten medium employed in the process of this invention such inorganic materials are readily removed. A certain portion of the ash residue such as iron oxide, for example, has been found to be only partially soluble or insoluble in the molten medium and is readily removed by withdrawing an ash-rich stream from the molten salt, this stream also containing the metal contaminants. The purged stream can be subjected to further separation to recover alkali metal compounds. Soluble ash constituents such as silica are readily removed as required by discharging molten salt and passing it to a recovery zone in which the melt is cooled and treated with water to dissolve the alkali metal salts leaving ash-insoluble residue including heavy metal contaminants. In this manner the content of inorganic constituents in the molten salt system can be controlled and discharged without interruption of the process.

A further advantage of the process of this invention is that the molten medium does not require regeneration and can be used for prolonged periods. Generally the addition of fresh salt is required only to make up for any losses which may be caused by purging of ash-rich streams. Thus the process of this invention is to be distinguished from methods in which alkali metal compounds such as sodium carbonate serve as the primary source of oxygen found in the carbon oxides of the product gas and in which regeneration of the carbonate is required. In the process of this invention, on the other hand, the primary source of oxygen found in the carbon oxides is steam which is

used in substantial amounts, i.e., in amounts equivalent to steam-carbon ratios of at least 1.

The following examples are offered as a better understanding of this invention and are not to be construed as unnecessarily limiting thereto. In the following experiments, alkali metal salt was charged to an Inconel reactor having an inner diameter of 1½ inches and being 47.5 inches in length, positioned within a resistance furnace. The salts were then melted, the quiescent depth of molten salt within the reactor being about 15 inches. The hydrocarbon feed was mixed with nitrogen and pumped upwardly through the internal pipe of an Inconel two-fluid nozzle about 20¼ inches in length. Steam was passed through the annular space around the internal pipe. The hydrocarbon-nitrogen and steam streams were brought into contact at a series of orifices drilled in the internal pipe over 1½ inches of length ending ½ inch from the nozzle tips and the combined stream was sprayed into the molten bath contained in the reactor. That portion of the nozzle tip exposed to the molten salt was coated with an insulating sleeve composed of castable chrome brick. A perforated cone deflector positioned in the upper section of the reactor served as a trap to minimize entrainment of salt in the product vapors. Dry gas product was separated from the reaction zone effluent, collected and analyzed by mass spectrometer. The residence times reported in the following examples are nominal and are based on the volume of quiescent molten salt.

Example 1

The above-described reactor was charged with 1100 grams of a mixture consisting of 15 weight percent lithium carbonate and 85 weight percent sodium carbonate. The mixture was melted and the melt maintained at a temperature of about 1650° F. Mid-Continent gas oil was used as the hydrocarbon feed and is characterized by an API gravity of 34.3, the boiling range being as follows as determined by ASTM distillation:

Boiling range:	Temperature, ° F.
IBP -----	392
5% off -----	503
10% off -----	519
20% off -----	540
30% off -----	556
40% off -----	574
50% off -----	588
60% off -----	604
70% off -----	626
80% off -----	651
90% off -----	690
95% off -----	726
EP percent off -----	730

The Mid-Continent gas oil was admixed with steam as described above, such that the steam-carbon ratio was 5.8. The oil-steam mixture was charged to the molten salt bath at a space velocity of about 33 grams of oil plus water per hour per 1000 grams of molten salt, such that the residence time of the feed in the molten salt was 9 seconds. Under these conditions the conversion was 20 weight percent based on the amount of gas oil reacted. Analysis of the product gas showed that it consisted essentially of hydrogen (75.5 mol percent) and carbon oxides, the contents of carbon dioxide and carbon monoxide being 19.2 and 4.9 mol percent, respectively, and only 0.2 mol percent methane.

Example 2

The above-described reactor was charged with 1200 grams of a mixture consisting of 19 weight percent lithium carbonate and 81 weight percent sodium carbonate. The mixture was melted and the melt maintained at a temperature of about 1375° F. Mid-Continent reduced crude was used as the hydrocarbon feed and is characterized by an API gravity of 17.9, an ash content of 0.082 weight percent and a Ramsbottom carbon residue of 8.3 weight per-

cent, the boiling range being as follows as determined by the Vacuum Engler method:

Boiling range:	Temperature, ° F.
IBP -----	498
5% off -----	694
10% off -----	770
20% off -----	846
30% off -----	900
40% off -----	952
50% off -----	(975 at 42%)
60% off -----	---
70% off -----	---
80% off -----	---
90% off -----	---
95% off -----	---
EP percent off -----	---

The reduced crude was admixed with steam as described above such that the steam-carbon ratio was 14.5. The oil-steam admixture was charged to the molten salt bath at a space velocity of 60 grams of oil plus water per hour per 1000 grams of molten salt such that the nominal residence time of the oil in the molten salt was about 5 seconds. Under these conditions the conversion was 100 percent, based on the amount of reduced crude reacted. Upon analysis, it was found that the product gas had the following composition expressed on a mol basis: 41.3 percent hydrogen, 20.3 percent methane, ethane (0.2 percent), 24.9 percent carbon dioxide, 2.8 percent carbon monoxide, the remainder consisting essentially of unsaturates, namely ethylene (9.2 percent), propylene (0.5 percent), butadiene (0.2 percent), benzene (0.4 percent) and acetylene (0.1 percent).

Inspection of the results obtained in accordance with the above examples shows that normally liquid hydrocarbon feeds can be converted by the process of this invention to synthesis gas consisting essentially of hydrogen and carbon oxides. For example, the results obtained in Example 1 show that at the higher temperature of 1650° F. and maintaining a partial conversion of the normally liquid hydrocarbon feed, the gas product contained a high percentage of hydrogen; the selectivity of the process, defined as the percent carbon reacted appearing as carbon monoxide or carbon dioxide, was also high (99 percent). The results of Example 2 show that at the milder temperatures such as 1375° F. and at high conversions of normally liquid hydrocarbon feed per pass the gas product contained, in addition to hydrogen and carbon oxides, substantial amounts of methane, making the gas useful for general fuel use, and of unsaturated hydrocarbons. These results show, therefore, that in the conversion of normally liquid hydrocarbons by the process of this invention, product gas containing hydrogen as the major or predominant component is obtained by operating at a temperature from about 1300° F. to about 1800° F., the hydrogen content increasing with increasing temperature, and that hydrogen-containing gas also containing substantial amounts of unsaturates, i.e., about 10 mol percent and higher, is obtained by operating at a temperature between about 800° F. and about 1400° F., the yield of unsaturates such as ethylene increasing with decrease in temperature.

In contrast to the above, it has been found that when the normally gaseous hydrocarbon, methane, is used as the feed, low impracticable conversions are obtained as illustrated by the following Examples 3-5. In these examples commercial methane having the following composition, on a mol basis, was employed: 93.3 percent methane, 3.7 percent ethane, 0.7 percent propane, 0.7 percent butane, 1.0 percent carbon dioxide, 0.2 percent carbon monoxide and 0.4 percent hydrogen.

Example 3

In this example the commercial methane was admixed with steam in a steam-carbon ratio of 2.1 and was charged to the above-described reactor to which 1480 grams of an

admixture consisting of 29 weight percent lithium carbonate and 71 weight percent of sodium carbonate was charged, the mixture being in the molten state prior to introduction of the feed. The methane-steam feed was contacted with the molten salt maintained at a temperature of 1375° F., the nominal residence time of the feed in the molten salt being 7 seconds. Under these conditions, the conversion of methane was 2 percent. Analysis of the product gas showed it to consist essentially of unreacted methane (83.1 mol percent), the remainder being hydrogen (8.2 percent), carbon dioxide (4.1 percent), carbon monoxide (0.3 percent), ethylene (3.5 percent), ethane (0.5 percent), and propylene (0.3 percent).

Example 4

In this example commercial methane admixed with steam in a steam-carbon ratio of 0.9 was introduced into the same molten medium consisting essentially of lithium carbonate and sodium carbonate employed in Example 3. The melt was maintained at a temperature of 1500° F., the nominal residence time of the feed in the molten salt being 5 seconds. Under these conditions the conversion of methane was 3 percent. The analysis of the product gas showed it to contain 11.0 percent hydrogen, 79.0 percent unreacted methane, 1.3 percent carbon monoxide, 5.1 percent carbon dioxide, 3.1 percent ethylene, 0.2 percent ethane and 0.3 percent propylene.

Example 5

In this example commercial methane admixed with steam in a steam-carbon ratio of 2.2 was introduced through the same molten medium consisting of lithium carbonate and sodium carbonate employed in Example 3. The temperature of the molten medium was maintained at 1500° F., the nominal residence time of the methane-steam feed in the molten salt being 6 seconds. Under these conditions the conversion of methane was 4 percent. Analysis of the product gas showed it to contain 17.0 percent hydrogen, the remainder consisting essentially of unreacted methane (70.3 percent) and containing 9.6 and 1.3 percent carbon dioxide and carbon monoxide, respectively, 1.6 percent ethylene, 0.1 percent ethane and 0.1 percent propylene.

The results of Examples 3-5 show that in each case the conversion of feed per pass was very low. Comparison of the results obtained in Examples 4 and 5 shows that increasing the steam-carbon ratio from a value of less than 1 to a higher value of about 2.2 led to substantially higher yields of carbon oxides but the conversion of methane feed was still at an infeasible level. Thus it is seen that the use of methane as feed necessarily requires further processing of the product gas to obtain useful hydrogen-containing gas such as by fixed bed catalytic steam-methane reforming. On the other hand, the process of this invention offers particular advantage for the conversion of normally liquid hydrocarbon feeds to hydrogen-rich gas which is useful as such, the liquid feeds in the first instance being only difficultly converted by conventional fixed bed catalytic steam reforming, or to hydrogen-containing gas containing substantial yields of valuable olefins such as ethylene.

It is to be understood that although the above description of the invention is drawn primarily to the use of molten media comprising the alkali metal carbonates or hydroxides, any alkali metal compound convertible to an equilibrium mixture of the carbonate and hydroxide under the reaction conditions may be charged to the reaction zone initially. From the standpoint of operability, therefore, other salts such as the alkali metal sulfates, chlorides, etc., are usable. However, due to the fact that these latter compounds are highly corrosive they are usually not employed unless the equipment with which the molten medium is brought into contact is made of, or lined with, a high temperature inert material such as ceramics, brick, etc.

Various alterations and modifications of the process of

this invention may become apparent to those skilled in the art from the accompanying description and disclosure without departing from the scope of this invention.

Having described our invention, we claim:

1. A process for the production of hydrogen-containing gas which comprises contacting a molten reaction medium comprising at least 10 weight percent of an alkali metal carbonate, with steam and a normally liquid hydrocarbon in a form ranging from its liquid to vaporized form, said hydrocarbon and steam reacting in the molten reaction medium to produce hydrogen-containing gas as a product of the process.
2. The process of claim 1 in which said normally liquid hydrocarbon is a gas oil.
3. The process of claim 1 in which said normally liquid hydrocarbon is a naphtha fraction.
4. The process of claim 1 in which said normally liquid hydrocarbon is reduced crude oil.
5. The process of claim 1 in which said normally liquid hydrocarbon is cycle oil.
6. The process of claim 1 in which said normally liquid hydrocarbon is a tar.
7. The process of claim 1 in which said alkali metal carbonate is sodium carbonate.
8. The process of claim 1 in which said alkali metal carbonate is potassium carbonate.
9. The process of claim 1 in which said alkali metal carbonate is lithium carbonate.
10. A process for the production of hydrogen-containing gas which comprises introducing a dispersion of a normally liquid hydrocarbon in a form ranging from its liquid to vaporized form in steam into a molten reaction medium comprising an alkali metal carbonate in an amount of at least 10 weight percent, maintaining said molten reaction medium at a temperature between about 800° F. and about 1800° F., the steam to carbon ratio being at least 1, to produce hydrogen-containing gas, and recovering said hydrogen-containing gas as a product of the process.
11. A process for the production of hydrogen-containing gas which comprises introducing a feed consisting essentially of a normally liquid hydrocarbon in a form ranging from its liquid to vaporized form and steam into a molten reaction medium comprising between about 90 and about 10 weight percent of sodium carbonate and between about 10 and about 90 percent by weight of a lower melting alkali metal compound, maintaining said medium at a temperature between about 800° F. and about 1650° F., the steam to carbon ratio being at least 1, to produce hydrogen-containing product.
12. A process for the production of hydrogen-containing product which comprises contacting a normally liquid hydrocarbon in a form ranging from its liquid to vaporized form and steam with a molten reaction medium comprising at least 10 weight percent of an alkali metal carbonate, and maintaining said molten reaction medium at a temperature between about 800° F. and about 1400° F. such that product is produced containing hydrogen and substantial amounts of unsaturated hydrocarbons.
13. A process for the production of hydrogen-containing gas which comprises charging steam and a normally liquid hydrocarbon in a form ranging from its liquid to vaporized form and containing inorganic impurities to a reaction zone maintained at an elevated temperature and containing a molten reaction medium comprising at least 10 weight percent of an alkali metal carbonate, the steam to carbon ratio being at least 1, to produce hydrogen-containing gas, withdrawing a stream of molten medium rich in said inorganic impurities from said reaction zone, and recovering said hydrogen-containing gas as a product of the process.
14. A process for the production of hydrogen-containing gas which comprises introducing a normally liquid hydrocarbon in a form ranging from its liquid to vaporized form and steam to a reaction zone containing a molten

reaction medium comprising at least 10 weight percent of an alkali metal carbonate such that said mixture is brought into contact with said molten medium to produce product containing hydrogen and supplying the endo-

15. A process for the production of hydrogen-containing gas which comprises charging a reaction zone with (1) an alkali metal carbonate of the group consisting of sodium carbonate and potassium carbonate, and (2) another alkali metal compound having a melting point below that of said alkali metal carbonate, heating said alkali metal carbonate and lower melting compound to obtain a molten admixture thereof, said molten admixture containing from about 10 to about 90 weight percent of said alkali metal carbonate (1), introducing a normally liquid hydrocarbon in a form ranging from its liquid to vaporized form and steam into said molten reaction medium at a steam to carbon ratio of at least 1, supplying heat to said reaction zone to maintain the reaction medium in the molten state and at a temperature between about 800° F. and about 1800° F. and withdrawing normally gaseous effluent from said reaction zone comprising hydrogen and an oxide of carbon.

16. The process of claim 15 in which said lower melting alkali metal compound is lithium carbonate.

17. The process of claim 15 in which said lower melting alkali metal compound is an alkali metal hydroxide.

18. A process for the conversion of a normally liquid hydrocarbon to hydrogen and normally gaseous hydrocarbons which comprises contacting a normally liquid hydrocarbon in a form ranging from its liquid to vaporized form and steam with a molten reaction medium comprising an admixture of an alkali metal carbonate and an alkali metal hydroxide, the alkali metal carbonate being present in an amount of at least 10 weight percent, maintaining said reaction medium in the molten state and at a temperature from about 800° F. to about 1400° F., the normally liquid hydrocarbon and steam reacting to pro-

duce gaseous product comprising hydrogen, an oxide of carbon and at least 10 mol percent of normally gaseous hydrocarbons.

19. A process for the production of hydrogen-containing gas which comprises charging alkali metal carbonate to a reaction zone as the sole added alkali metal compound, in said reaction zone maintaining said alkali metal carbonate in the molten state, contacting the molten alkali metal carbonate with steam and a normally liquid hydrocarbon in a form ranging from its liquid to vaporized form, the hydrocarbon and steam being fed to the molten reaction medium at a steam-to-carbon ratio of at least one, supplying heat to said reaction zone to maintain the alkali metal carbonate in the molten state and at a temperature between about 800° F. and about 1800° F., and withdrawing from said reaction zone normally gaseous effluent comprising hydrogen and an oxide of carbon.

20. The process of claim 19 in which the alkali metal carbonate is sodium carbonate.

References Cited by the Examiner

UNITED STATES PATENTS

701,186	5/1902	Faulkner	48—92
2,015,085	9/1935	Oberle	202—18
2,031,987	2/1936	Sullivan.	
2,628,890	2/1953	Shapleigh	23—212
2,794,709	6/1957	Kirkbride	23—212 X

FOREIGN PATENTS

7,718	1910	Great Britain.
8,426	6/1892	Great Britain.
322,959	12/1929	Great Britain.
465,548	5/1937	Great Britain.

MORRIS O. WOLK, Primary Examiner.

MAURICE A. BRINDISI, Examiner.

A. J. STEWART, D. GANTZ, J. SCOVRONEK, Assistant Examiners.