

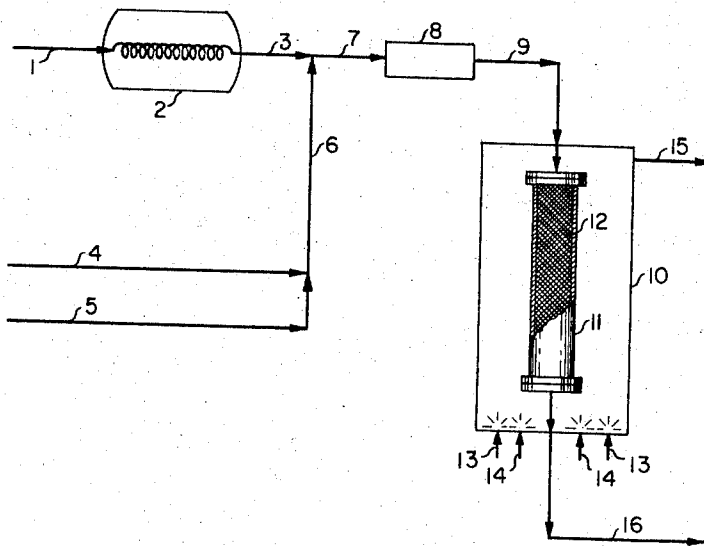
Nov. 7, 1967

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3,351,563

PRODUCTION OF HYDROGEN-RICH SYNTHESIS GAS

Filed June 5, 1963



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3,351,563
**PRODUCTION OF HYDROGEN-RICH
 SYNTHESIS GAS**

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Filed June 5, 1963, Ser. No. 285,672
 6 Claims. (Cl. 252-373)

This invention relates to the catalytic steam-reforming of naphtha, to produce a hydrogen-rich synthesis gas. A process has been developed which features the cracking and partial thermal reforming of naphtha vapor, by reaction with superheated steam under controlled conditions of temperature and reaction time. The formation and accumulation of free carbon is avoided by limiting the reaction time prior to catalysis to prevent attainment of reaction equilibrium, while the formation of lower hydrocarbons by thermal cracking is also controlled and becomes a transient phenomenon. After catalytic steam reform, the final process gas stream contains only a negligible proportion of unreacted lower hydrocarbons.

Naphtha is a relatively volatile petroleum refining product or intermediate, which is generally defined in terms of boiling range. Thus, according to a crude oil survey in *Industrial and Engineering Chemistry*, 44, #11 (November 1952) p. 2578, naphtha is defined as follows: "Naphtha content (of crude oil) is the total distillate recovered in the U.S. Bureau of Mines routine analysis at a vapor temperature of 392° F." A more detailed definition of naphtha appears in "Petroleum Refining With Chemical" by Kalichevsky & Kobe (1956). A discussion of naphtha on pp. 21-23 of this text indicates that different naphthas may have boiling ranges from a low point of 122° F. to a maximum of 400° F. Thus "naphtha" is defined as a general term which is applied to fractions boiling in the gasoline or low kerosene range. In general then, naphtha is a low-boiling and readily volatilized liquid hydrocarbon cut, derived from crude oil distillation in petroleum refining. This material consists mostly of straight chain paraffinics in the C-5 to C-9 range, however, up to about 30% naphthenics together with up to 10% aromatics and unsaturates may also be present. In addition, naphtha also generally contains a significant proportion of sulfur in the form of COS and mercaptans.

Naphtha may be utilized in a variety of ways. Thus, crude naphtha may be further refined and upgraded to yield a variety of finished petroleum solvents. In many refineries, naphtha is "reformed" in the petroleum sense of the term. In this case, the crude naphtha is cracked, and hydrocarbon molecules are re-assembled in the presence of platinum or other suitable catalyst, so as to yield a substantial proportion of branched chain or aromatics molecules. This material is then blended with other refinery cuts for gasoline usage. In the terminology of the present invention, the word "reforming" has an entirely different meaning, as will appear infra.

Finally, naphtha may also be utilized as a hydrocarbon raw material for the manufacture of hydrogen or synthesis gas which is employed in the catalytic synthesis of ammonia or methanol. There are two general approaches to the conversion of the various types of hydrocarbons to synthesis gas, namely, steam reforming and partial oxidation. In steam reforming, a normally gaseous hydrocarbon such as methane is mixed with steam, and the mixture is then passed through an externally heated bed of nickel-containing reform catalyst. An endothermic reaction takes place between the hydrocarbon and steam, resulting in the formation of a "synthesis gas" product stream containing principally hydrogen, carbon monoxide and carbon dioxide.

In the case of partial oxidation, a hydrocarbon raw material is reacted with oxygen or oxygen-enriched air at a highly elevated temperature. The product stream is then quenched, to yield a crude synthesis gas stream. A catalyst is not employed in conventional partial oxidation practice, since essentially complete reaction of the hydrocarbon is readily accomplished at the high temperature levels generated in this process. In addition, a variety of hydrocarbons may be employed in partial oxidation, including liquid or even powdered solid hydrocarbons as well as gases.

As is well known in the art, catalytic steam reforming is generally limited to the usage of gaseous hydrocarbons, due to such problems as partial conversion and carbon deposition, when vaporized liquid hydrocarbons are employed. One approach to the steam reforming of higher hydrocarbons such as naphtha is described in U.S. Patent No. 2,940,840. In this process, the formation of free carbon in the catalyst bed is purposely brought about by overloading the catalyst. Although this process is cyclic and requires a regeneration period during which the deposited carbon is oxidized for removal, it is claimed that the overall process efficiency is better than in prior practice. Another recent approach to the problem is described in U.S. Patent 2,943,062. A partial oxidation effect is obtained in a catalytic process by adding oxygen to a stream of hydrocarbon vapor or partially reformed gas, immediately before the stream is passed through a catalyst bed. The bed is not externally heated, instead the process is carried out in a refractory-lined chamber as in conventional partial oxidation. It will be evident that this procedure is subject to the principal economic drawback of all partial oxidation processes, namely, that an air separation plant is required.

In the present invention, naphtha is catalytically steam reformed to produce a hydrogen-rich synthesis gas. In one embodiment, carbon dioxide is employed together with process steam, to yield a synthesis gas having the proper ratio of hydrogen to carbon oxides for usage of the product gas stream in methanol synthesis. The process of the present invention depends on a unique balance of reaction conditions to achieve the catalytic steam reforming of naphtha, since this is accomplished without accumulated deposition of free carbon. In addition, no significant amount of unreacted hydrocarbon is present in the final synthesis gas. The process is carried out in two stages, a gasification-conditioning stage and a catalytic steam reform stage. These stages of the process are distinctly co-acting and dependent, in that it has been found that the conditioning stage must be of short duration in order to prevent reactants from reaching equilibrium with resultant deposition of free carbon in the catalyst bed. It has also been found that the reactants must be preheated in order to provide a minimum temperature level in the conditioning stage. Thus, in the present invention, process streams of naphtha and steam are preheated and mixed. A partial reaction ensues, and the mixed process stream, now containing a variety of intermediate components but not in final reaction equilibrium, is passed through an externally heated bed of reform catalyst. A final process stream is produced by steam reforming of residual naphtha and intermediate lower hydrocarbons. This final process stream consists of a synthesis gas containing principally hydrogen, carbon monoxide, carbon dioxide and steam. The stream is essentially free of unreacted hydrocarbons or solid particulate carbon.

The process of the present invention possesses several significant advantages. A primary advantage is that naphtha is catalytically steam reformed to a hydrogen-rich synthesis gas, without the concomitant accumulation of free carbon or tars, and without the production of lower

hydrocarbons as a significant component of the final process stream. Thus, no recycle or side stream disposal is required. The process is continuous rather than cyclic or intermittent. In addition, one major economic cost in partial oxidation processes, namely an air separation plant or other source of free oxygen, is not required in the process of the present invention. Finally, conventional steam reformer apparatus rather than a special or costly apparatus design may be employed in the catalytic reforming stage of the present invention.

It is an object of the present invention to produce a synthesis gas for usage in hydrogen production by steam reform of naphtha.

Another object is to reform naphtha in a continuous process, without accumulated deposition of tars or free carbon.

A further object is to reform naphtha by catalytic reaction with steam.

An additional object is to react naphtha with steam by a two-stage mixing and catalytic reform process, whereby naphtha is completely reformed and a gas stream principally containing hydrogen, carbon monoxide, carbon dioxide and steam is produced.

Still another object is to gasify and reform naphtha to a hydrogen-rich synthesis gas suitable for methanol synthesis using steam and carbon dioxide as process reactants.

These and other objects and advantages of the present invention will become evident from the description which follows. Referring to the figure, stream 1 is a liquid naphtha, derived from petroleum refining or other types of crude oil processing. Thus, as described supra, stream 1 consists principally of paraffinic hydrocarbons in the C-5 to C-9 range, together with naphthenics as well as minor amounts of aromatics and sulfur compounds. The liquid stream 1 is vaporized and preheated in heater 2, to form naphtha vapor stream 3. Vapor stream 3 may be produced at any suitable temperature, ranging from the boiling point of naphtha up to about 1000° F. Above this temperature level the naphtha vapor may become unstable, and certain portions or components will readily crack to smaller molecules with concomitant carbon deposition. Stream 3 thus is preferably produced at a temperature ranging from 400° F. to 800° F.

Stream 4 consists of highly superheated steam, preheated to a temperature above 1000° F., and preferably to the range of 1500° F. to 1800° F. Although lower ratios are feasible, it has been found that a range of molar steam/carbon ratios between 5 to 1 and 6 to 1 is desirable in proportioning the relative flow rates of streams 4 and 3, in order to prevent accumulated deposition of carbon under normal operating conditions.

Optional stream 5 consists of carbon dioxide, preheated usually to a temperature above 1000° F. The proportion of carbon dioxide employed in the process is quite small, thus carbon dioxide is used only to provide a suitable molar ratio of hydrogen to carbon oxides in the final synthesis gas stream when methanol synthesis gas is the desired product. In such instances, the molar ratio of carbon dioxide to naphtha carbon will generally be in the range of 0.1 to 1.0. The streams 4 and 5 are preferably combined, to form a mixed steam-carbon dioxide stream 6 at a temperature of at least 1500° F. Stream 6 is now combined with naphtha vapor stream 3, and the mixed stream 7 is immediately passed into residence or gas conditioning chamber 8. It will be appreciated that streams 3, 4 and 5 may be separately passed into chamber 8, however pre-mixing of the carbon dioxide and steam to form stream 6 is a preferable procedure since this results in better and more rapid mixing of the several streams. Thus, stream 3 is more rapidly dispersed and diluted due to the mixing with stream 6, prior to entry of the naphtha vapor into residence chamber 8. Consequently, the possibility of transient carbon formation or deposition due

to cracking of the naphtha is reduced by the pre-mixing step.

In chamber 8, simultaneous reactions take place between and among the several reactants and intermediate components. A portion of the naphtha is non-catalytically steam reformed due to the high temperature and high steam concentration in chamber 8. This endothermic reaction serves to produce free hydrogen, and also causes a temperature decline. A further portion of the naphtha is thermally cracked to lower hydrocarbons, due also to the high temperature level. However, simultaneous deposition and accumulation of free carbon does not instantaneously occur. Instead, the unstable lower hydrocarbons are selectively hydrogenated to a certain extent due to the in situ formation of hydrogen, which may possibly be formed in the nascent state. Thus, the resultant gaseous stream 9 contains significant proportions of steam, hydrogen, carbon dioxide, carbon monoxide, unsaturated hydrocarbons (mostly ethylene), methane and ethane. It should be understood, however, that these components are present on a transient or instantaneous basis. If stream 9 is allowed to reach stable equilibrium under these process conditions, significant formation and accumulated deposition of free carbon will take place.

Under some conditions, the temperature in unit 8 may be in the range of 1450° F. to 1500° F. However, with such low reaction temperatures, the formation of free carbon may readily occur, unless the residence time is kept in the range of 0.05 to 0.33 second. With such short residence times, unreacted naphtha may passing to the following catalytic stage of the process, however, as will appear infra, the formation of free carbon is readily prevented in the catalytic stage by maintenance of a temperature level above 1600° F. In general, the residence time in chamber 8 must be kept below 1.0 second, and preferably in the range of 0.05 to 0.33 second, in order to achieve the desired reactions without carbon formation. In addition, the instantaneous mix temperature of stream 7 must be kept above 1000° F., since it has been found in practice that the various competing reactions will tend to form free carbon if the initial mix temperature is below 1000° F. This initial or instantaneous mixture temperature should preferably be in the range of 1400° F. to 1700° F., in order to preclude carbon formation due to process upsets. It will be evident that chamber 8 may actually, in terms of apparatus design, consist merely of an insulated pipe section extending between the point of mixing of the reactant streams and the entry of the conditioned gas stream into the catalyst bed section.

Stream 9 now passes into the catalytic reformer unit 10. Reformer 10 may be a unit of conventional design, such as shown in U.S. Patent 2,660,519. Thus, unit 10 is provided with a plurality of reformer tubes such as 11 having a bed or charge of reform catalyst 12, usually consisting of nickel or cobalt deposited on a suitable carrier. Tube 11 is externally heated by such means as combustion of fluid hydrocarbon streams 13 with air streams 14, with flue gas removal via 15.

As mentioned supra, it has been found that the temperature of the catalyst in bed 12 must generally be kept above 1600° F., in order to prevent carbon accumulation. As the process stream 9 passes into bed 12, endothermic steam reforming of hydrocarbons immediately takes place. In order to prevent a concomitant sudden drop in the in situ process temperature at the inlet end of bed 12, the equivalent linear velocity of the process stream in the bed 12 is maintained above 5 ft./second. "Equivalent" linear velocity refers to the gas velocity which would exist at normal operating conditions, if the tube was not filled with catalyst. It has been determined that this linear velocity should preferably be in the range of 10 ft./sec. to 30 ft./sec., in order to effectively spread out the reforming reaction through the bed 12 and thereby effectively prevent carbon deposition. Various other expedients may be adopted in this respect. Thus, the apparatus concept em-

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bodied in U.S. 2,801,159 may alternatively be employed in the present invention in order to more effectively disperse stream 9 into bed 12. Other modifications, such as diluting the upper portion of catalyst bed 12 with inert material such as porcelain, so as to reduce the amount of hydrocarbon reformed per unit volume of catalyst, may also be adopted in order to extend the reforming reactions through bed 12 and thereby prevent localized temperature decrease and concomitant carbon deposition.

The resultant reformed gas stream is removed from tube 11 via 16. Stream 16 contains essentially only hydrogen, carbon monoxide, carbon dioxide and steam. A typical analysis of stream 16 is as follows: 72.4% hydrogen, 14.7% carbon dioxide, 11.5% carbon monoxide, 1.0% methane and 0.0% unsaturates. This analysis was on a dry basis, the total product stream generally contained about 50% steam on a total volume basis. In order to produce a finished synthesis gas, stream 16 is now processed by conventional technology, not shown. This will include the usual process steps of CO-oxidation, carbon dioxide removal, etc., if hydrogen gas is the desired final product. It will be understood that the process of the present invention may be carried out without carbon dioxide as process reactant, when hydrogen gas is the desired product.

It has been found that operating pressure does not appear to be a significant variable in the process of the present invention, and the process may be operated at atmospheric pressure. Although pressure is not critical, an operating pressure in the range of 1 to 22 atmospheres is preferable since reform plant equipment size is reduced, and also because subsequent compression costs are reduced. In addition, reforming at elevated pressure yields a high pressure process gas which thus may be directly treated for carbon dioxide removal by hot potassium carbonate scrubbing.

It will be evident to those skilled in the art that the significant process variables in steam reforming of naphtha according to the present invention are closely inter-related. Thus, the required minimum preheat temperatures of the reactant streams prior to chamber 8 will depend principally on the residence time in 8 prior to entry of the mixed stream via 9 into bed 12. With lower residence times in the range of 0.05 to 0.10 seconds, it has been found that the process may be successfully carried out with a residence chamber temperature in the range of 1450° F. to 1500° F. However, if a longer residence interval up to 1.0 seconds is required, then the initial streams 3, 4 and 5 must be preheated to higher levels so as to provide a temperature range of 1650° F. to 1690° F. in chamber 8, in order to prevent accumulated deposition of free carbon in actual operation of the process.

Similarly, it will be recognized that a minimum steam/carbon ratio of 2:1 is generally required, in order to satisfy material balance considerations by providing sufficient steam for complete reaction with the naphtha. However, a steam/carbon ratio in the range of 5:1 to 7:1 has been found to be optimum in providing complete reaction, satisfactory reaction rate, and minimum tendency for carbon formation due to process upsets.

The reactions of naphtha cracking and steam reform are carried out in the first stage of the process of the present invention. It has been determined that, by maintenance of reaction conditions within certain critical ranges, these reactions may be carried out without carbon accumulation. In addition, the resulting unstable process stream, when passed to catalytic steam reforming before further reaction ensues, is successfully steam reformed to yield further hydrogen and carbon monoxide in a second stage without carbon accumulation. In summary, the present invention essentially accomplishes the steam reforming of naphtha by a process which partially gasifies the naphtha vapor using preheated steam. It has been determined that the resulting mixed gas stream may be successfully converted to a synthesis gas by conventional

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endothermic catalytic steam reforming without accumulated deposition of carbon, if the mixed gas stream is passed into contact with a catalyst bed before final process equilibrium is reached. Thus, as discussed supra, the critical features of the present invention essentially involve the maintenance of the several inter-related process variables within operating limits in which the new result of the present invention is achieved, namely the continuous steam reforming of naphtha.

Following are examples of industrial application of the process of the present invention.

A naphtha feedstock was steam reformed to produce a synthesis gas of high hydrogen content in accordance with the present invention. The data was taken at above normal throughputs for units used in conventional practice. Catalyst bed volume was 1.5 cubic feet. The naphtha was successfully reformed in a continuous manner without carbon formation. Following are the results obtained.

20 TABLE I.—NAPHTHA REFORMING TO PRODUCE HYDROGEN

Run No.	1	2
Naphtha Feed Rate, gals./hr.	18	20
Pressure, p.s.i.g.	290	305
Catalyst Bed Temp., ° F.	1,630-1,680	1,560-1,650
Steam Preheat Temp., ° F.	1,240	1,220
Naphtha Preheat Temp., ° F.	550	600
Inlet Steam to Carbon Ratio	5.4	5.28
Product Gas Content, Volume Percent:		
Carbon Dioxide	15.3	14.7
Hydrogen	71.6	72.4
Carbon Monoxide	11.9	11.5
Methane	0.7	1.0

It is evident that if a very high purity hydrogen product is required, the methane leakage can be lowered by decreasing the throughput. A slight increase in the steam to carbon feed ratio can also lower the methane leakage.

The process of the present invention was also applied to the production of methanol synthesis gas. In this case, the final gas stream must have a lower hydrogen to carbon monoxide ratio than shown in Table I supra. This is accomplished by lowering the process steam ratio and injecting carbon dioxide into the feed stream. Following are the results obtained.

45 TABLE II.—NAPHTHA REFORMING TO PRODUCE METHANOL SYNTHESIS GAS

Inlet steam to carbon ratio	1.7
Inlet carbon dioxide to carbon ratio	0.2
Pressure, p.s.i.g.	105
Catalyst bed temperature, ° F.	1600
Product gas volume:	Percent
Carbon dioxide	6.1
Carbon monoxide	30.3
Hydrogen	63.3
Methane	0.3

Following is an analysis of the commercial naphtha employed in the runs. It is evident that naphthas of varying compositions and analyses may be successfully reformed by suitable selection of process variables within the scope of the present invention.

60 TABLE III.—SPECIFICATION OF TESTED NAPHTHA

Initial boiling point (° F.)	130
End point (° F.)	380
Specific gravity @ 60° F.	0.725
Sulfur content (p.p.m.)	4

We claim:

1. A process for reforming naphtha to produce a hydrogen-rich gas, suitable for methanol synthesis and containing essentially only hydrogen, carbon monoxide, carbon dioxide and steam, and substantially free of hydrocarbons, which consists of vaporizing and preheating naphtha to a temperature below 1000° F., superheating steam to a temperature above 1000° F., and preheating carbon dioxide to a temperature above 1000° F.; combining said streams

of naphtha vapor, steam and carbon dioxide to form a mixed gaseous stream at a temperature in the range of 1400° F. to 1700° F., said mixed stream consisting of a mixture of naphtha vapor, steam and carbon dioxide and having a molar steam to carbon ratio in the range of 1.7 to 6.0 and a molar carbon dioxide to carbon ratio in the range of 0.1 to 1.0, reacting said mixture non-catalytically for an interval in the range of 0.05 to 1.0 seconds whereby said naphtha is simultaneously cracked to lower hydrocarbons, reacted with carbon dioxide, and partially steam reformed without accumulated deposition of free carbon, and catalytically reforming the resulting gas mixture in contact with a hydrocarbon reforming catalyst selected from the group consisting of nickel and cobalt deposited on a carrier, at a linear gas velocity of at least 5 ft./sec., said catalyst being externally heated to maintain a reaction temperature of at least 1600° F., whereby a final reformed gas mixture is produced substantially free of hydrocarbons and without accumulated deposition of free carbon, said final gas mixture having the proper ratio of hydrogen to carbon oxides for methanol synthesis and containing essentially only hydrogen, carbon monoxide, carbon dioxide and steam.

2. A process for producing a hydrogen-rich synthesis gas suitable for methanol synthesis and containing essentially only hydrogen, carbon monoxide, carbon dioxide and steam, and substantially free of hydrocarbons, from naphtha which consists of vaporizing and preheating naphtha to a temperature in the range of 400° F. to 800° F., superheating steam to a temperature in the range of 1500° F. to 1800° F., and preheating carbon dioxide to a temperature above 1000° F., combining said streams of naphtha vapor, carbon dioxide and steam to form a mixed gaseous stream at a temperature in the range of 1400° F. to 1700° F. and total pressure in the range of 1 to 22 atmospheres, said mixed stream consisting of a mixture of naphtha vapor, carbon dioxide and steam and having a molar steam to carbon ratio in the range of 5.0 to 6.0 and a molar carbon dioxide to carbon ratio in the range of 0.1 to 1.0, reacting said mixture non-catalytically for an interval in the range of 0.05 to 0.33 second, whereby said naphtha is simultaneously cracked to lower hydrocarbons and partially steam reformed without accumulated deposition of free carbon, and catalytically reforming the resulting gas mixture in contact with a hydrocar-

bon reforming catalyst selected from the group consisting of nickel and cobalt deposited on a carrier, at a linear gas velocity in the range of 10 to 30 ft./sec., said catalyst being externally heated to maintain a reaction temperature of at least 1600° F., whereby a final reformed gas mixture is produced substantially free of hydrocarbons and containing essentially only hydrogen, carbon monoxide, carbon dioxide and steam, said reformed gas mixture being produced without accumulated deposition of free carbon and having the proper ratio of hydrogen to carbon oxides for methanol synthesis gas.

3. The process of claim 2, in which the mixed gas stream produced after said reaction interval is divided into a plurality of partial streams and said partial streams are passed into contact with said catalyst in a catalyst bed at a plurality of spaced intervals, whereby the resulting catalytic reforming reaction takes place at a substantially uniform rate throughout said catalyst bed and localized temperature depression is prevented.

4. The process of claim 2, in which said catalyst is disposed in a bed having progressively increasing catalytic activity per unit volume of bed in the downstream direction of gas flow.

5. The process of claim 2, in which said streams of naphtha, steam and carbon dioxide are combined by first mixing together the steam and carbon dioxide to form a first mixed stream at a temperature of at least 1500° F., and thereafter combining said first mixed stream with the vaporized naphtha.

6. The process of claim 4, in which said bed is vertically oriented and said mixed gas stream is passed downwards through the bed.

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