April 13, 1965 F. J. DENT ETAL 3,178,272

GASIFICATION OF HYDROCARBON-CONTAINING OILS

Filed Sept. 25, 1959 2 Sheets-Sheet 1

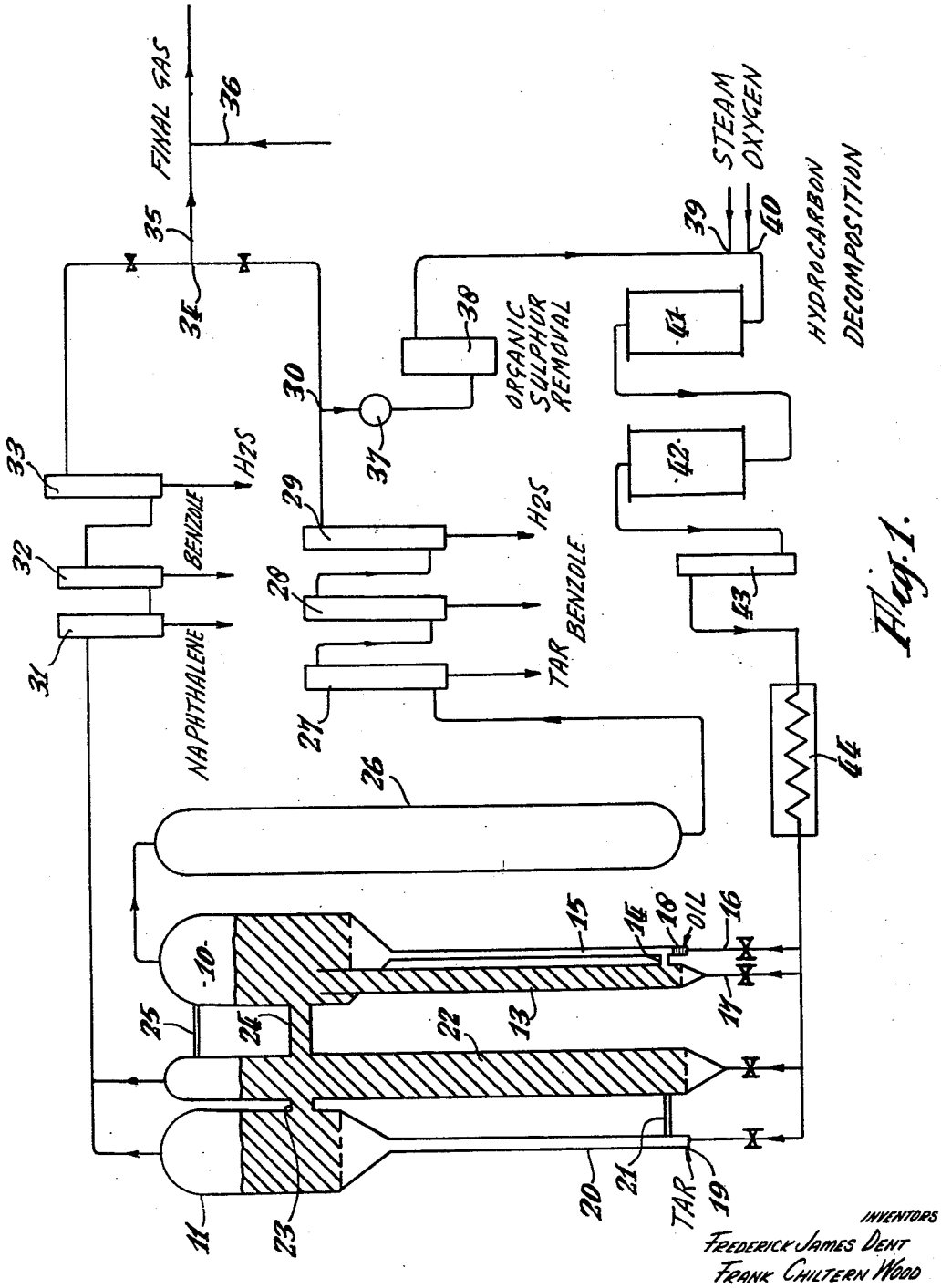


Fig. 1.

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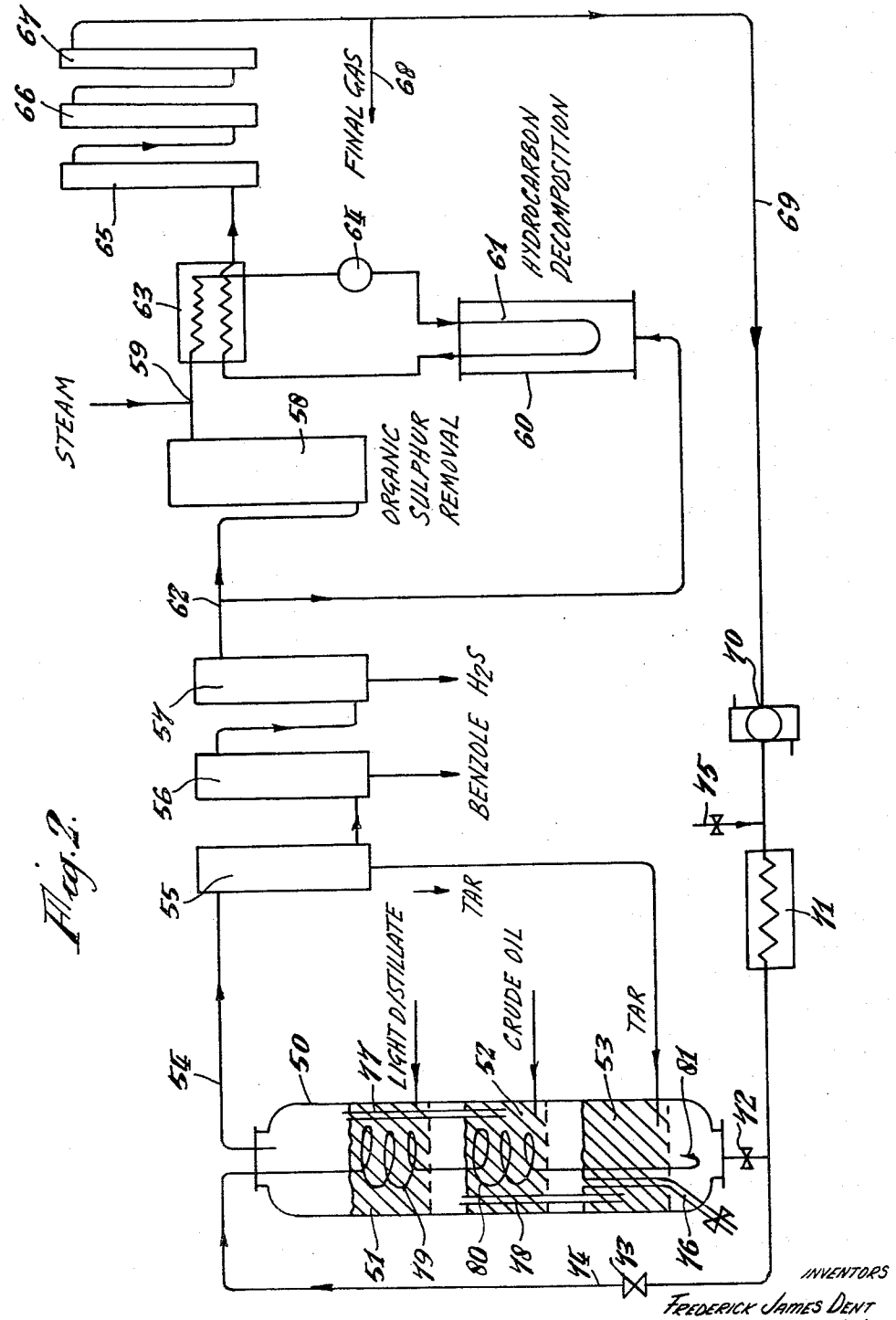


Fig. 2.

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3,178,272

GASIFICATION OF HYDROCARBON-CONTAINING OILS

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Claims priority, application Great Britain, Dec. 7, 1954, 35,466/54
1 Claim. (Cl. 48—213)

This application is a continuation-in-part of application Serial No. 551,144, filed on December 5, 1955, and now abandoned.

This invention relates to the gasification of hydrocarbon materials which are liquid at temperatures ranging from ordinary temperatures to 500° C. and consist wholly or mainly of hydrocarbons including aliphatic hydrocarbons, for example, liquid or fusible bitumens, such as an oil or tar obtained by the distillation of coal, petroleum oil or a liquid or fusible fraction obtained therefrom.

An object of this invention is to gasify such hydrocarbon-containing oils by a hydrogenation treatment, which involves the splitting and hydrogenation of hydrocarbons, to produce gases which contain gaseous hydrocarbons consisting of methane with or without other gaseous hydrocarbons, such as ethane. A further object is to produce from the hydrocarbon-containing gases, hydrogen-containing gases consisting mainly of hydrogen or of hydrogen and carbon monoxide.

In the process for gasifying a hydrocarbon-containing oil, in accordance with this invention, the oil is subjected to interaction with hydrogen to produce a gas containing gaseous hydrocarbons by passing the oil and a gas comprising hydrogen under a pressure within the range of 20 to 50 atmospheres through a bed of non-catalytic particulate solid maintained in the fluidised state by the gas and having a temperature within the range of about 700° C. to 800° C.

Under these conditions of temperature and pressure the relatively reactive, that is to say the aliphatic constituents of which the oil may be wholly or partly composed, are converted into gaseous hydrocarbons, principally methane. It has been found that the less reactive constituents that may be present in hydrocarbon oils, and are not converted into gaseous hydrocarbons under the aforesaid conditions can be so converted in a bed of a fluidised non-catalytic particulate solid at temperatures above 800° C. and not exceeding about 900° C. under pressures within the range of 20 to 50 atmospheres or at temperatures above about 900° C. and not exceeding 1100° C. under pressures higher than 50 atmospheres, for example, up to or exceeding 200 atmospheres.

There may be used as the hydrogenating gas, for example, a mixture of carbon monoxide and hydrogen, such as water gas, produced by the gasification of solid carbonaceous fuel with steam. It may be of advantage to increase the hydrogen content of such a mixture by reacting a part or the whole of the carbon monoxide contained therein with steam in accordance with the known water gas switch reaction, and subequently removing the carbon dioxide formed.

There may also be used a gas containing gaseous hydrocarbons, in addition to hydrogen, and the hydrogen content of such a gas may be increased by known methods to convert a part or the whole of the hydrocarbons into hydrogen and carbon monoxide, for example, by reacting the hydrocarbons with steam or oxygen or with both steam and oxygen. The oxygen may be used in the form of air, but it is preferable to use it undiluted or mixed with air. If desired, a part or the whole of the carbon monoxide so formed may be reacted with steam as described above, in order still further to increase the hydrogen content of the gas.

Instead of deriving the hydrogenating gas from a separate source, it may be obtained by treating a part of the hydrocarbon-containing gas produced to convert a part or the whole of the hydrocarbons therein into hydrogen. Such conversion of hydrocarbons includes conversion as described above into hydrogen and carbon monoxide with or without subsequent reaction of a part or the whole of the carbon monoxide so formed with steam to produce further hydrogen.

The non-catalytic particulate solid of which the fluidised bed is composed may be, for example, a siliceous material or carbon, for example, coke dust, and it may include particles of carbon deposited during the reaction between the oil and the hydrogen.

The hydrogenation may be carried out in a single fluidised bed or in a plurality of fluidised beds at different temperatures. A plurality of fluidised beds may be used for the treatment of a composite oil containing two or more fractions of different reactivities, by introducing the composite oil into a bed operated under conditions suitable for hydrogenating substantially only the most easily reactive fraction, that is to say, at a temperature within the range of about 700° C. to 800° C. under a pressure of 20 to 50 atmospheres. The remaining fraction or fractions are then separated from the resulting gas and treated in a bed or beds operated under the appropriate conditions, that is to say at a temperature above 800° C. and not exceeding about 900° C. under 20 to 50 atmospheres, or at a temperature above about 900° C. and not exceeding 1100° C. When more than one fraction remains after the first treatment, they may be supplied in admixture to a succession of separate beds operated under conditions of successively increasing severity to hydrogenate the several fractions in turn in the order of decreasing reactivity. Alternatively, when several fractions remain after the first treatment, they may be separated from one another and treated separately in beds operated under conditions suitable for the respective fractions.

If it is attempted to hydrogenate the whole of a composite oil in a single bed at the higher temperature required for the less reactive constituents, the difficulty often arises that only the more reactive constituents undergo hydrogenation, while the less reactive constituents undergo decomposition without hydrogenation, thereby being wasted and leading to the deposition of carbonaceous solids.

The several fluidised beds may be separately supplied with hydrogenating gas, or the hydrogenating gas may be passed in succession through a series of fluidised beds. Thus, for example, a series of two or three beds may be operated at progressively decreasing temperatures in the direction of flow of the gas from one bed to the next, the hydrogenating gas being introduced into the first bed. A composite oil containing two fractions, one more reactive than the other, may be introduced into the second bed in which substantially only the more reactive fraction is hydrogenated. The less reactive fraction, which is carried away with the gases leaving the second bed, is separated by condensation from the gases and introduced into the first bed, which is operated at a higher temperature and concentration of hydrogen appropriate for hydrogenating the less reactive fraction. If a third bed is used, a light hydrocarbon oil, which is more readily hydrogenated than the fraction hydrogenated in the second bed, may be hydrogenated in the third bed by means of the residual hydrogen in the gases from the second bed. Alternatively, a third bed may be used for slightly cool-

ing the gases from the second bed, for example, to 500° C.

The oil should be as far as possible in the form of vapour in the fluidised bed in which it is treated. For this purpose the oil may be introduced directly into the fluidised bed, but is preferably injected into the fresh hot hydrogenating gas passing to a fluidised bed or into a hot hydrogen-containing gas passing from one fluidised bed to another. In the case of oils which can be completely vaporised, they are preferably introduced as vapour into the hydrogenating gas. In the case of oils which contain constituents that undergo thermal decomposition to form carbon or solid carbonaceous products at the temperature to which the oil must be heated, it may be undesirable to introduce such oils directly into a fluidised bed, as such solid products may cause agglomeration of the fluidised particles. Moreover, when such oils are introduced into a hydrogen-containing gas being supplied to a fluidised bed, such decomposition products may be deposited in and block the gas conduit.

In order to overcome this difficulty it is of advantage to inject the oil into a stream of solid particles suspended in and being carried along with the hot gas being supplied to a fluidised bed. In this manner any solid decomposition products formed when the oil is injected into the hot gas are carried along with the suspended particles and the gas, and are distributed in the fluidised bed in an innocuous manner. The suspended particles for this purpose are advantageously derived from the fluidised bed by causing a part of the particles to flow under gravity in fluidised condition from the bed into an upwardly flowing stream of the hydrogenating gas passing into the bed, so that the said particles become suspended in and carried along with the gaseous stream. The particles so entering the gaseous stream being at a high temperature assist in vaporising the oil injected into the gaseous stream, in addition to carrying away decomposition products as described above.

Since the hydrogenation reaction is exothermic the temperature required can usually be maintained by suitably adjusting the temperature to which the hydrogenating gas is preheated. If desired, additional heat may be supplied by heat exchange between the hot hydrocarbon-containing gas produced and the oil and/or hydrogenating gas. Additional heat can also be supplied, if necessary, by introducing oxygen separately or together with the hydrogenating gas.

In order to produce a gas containing hydrogen, for example, at least 50 percent of hydrogen, a gas containing gaseous hydrocarbons is produced by the process described above, and the resulting gas is treated as described above to convert hydrocarbons into hydrogen, that is to say, first into hydrogen and carbon monoxide, followed, if desired, by the conversion of carbon monoxide by reaction with steam into hydrogen and carbon dioxide and the removal of carbon dioxide part of the hydrogen-containing gas so obtained is withdrawn as the product gas and the remainder, if desired, after converting carbon monoxide, when present, into hydrogen and carbon dioxide and removing the latter, is used for hydrogenating the oil.

In carrying out this process an oil containing more reactive and less reactive constituents, for example a crude petroleum oil, may be treated at a high pressure of, say, 30 atmospheres in a series of two or three beds in a single vessel as described above. The crude oil is injected into the second bed, and the unreacted tar is separated from the hydrocarbon-containing gas produced and injected for hydrogenation into the first bed in which the temperature and the concentration of hydrogen are higher than in the second bed. The third bed, if used, may serve for hydrogenating a light distillate or for cooling as described above.

In order to convert gaseous hydrocarbons present in the gas into hydrogen and carbon monoxide, the gas is mixed with steam, and the mixture subjected under about 5 atmospheres pressure to the action of a suitable catalyst at 800–900° C., the catalyst vessel being externally heated. The resulting gas may then be subjected to the water gas switch reaction in a separate vessel at about 300° C. A part of the hydrogen-rich gas so obtained is withdrawn as product gas, and another part is compressed to 30 atmospheres and used as the hydrogenating gas, after removing the carbon dioxide at any desired stage.

Instead of expanding the hydrocarbon-containing gas, it may be reacted with oxygen or oxygen and steam at 30 atmospheres pressure. The resulting gas is then treated as described above, but at the same pressure and without the need of external heating, to convert carbon monoxide by reaction with steam into hydrogen and carbon dioxide.

In order to produce a heating gas, for example, town gas, rich in gaseous hydrocarbons, mainly methane, a hydrocarbon oil, for example, petroleum oil, containing more reactive constituents and less reactive, for example, aromatic, constituents, is treated as described above in a fluidised bed to hydrogenate only the more reactive constituents and yield a gas rich in gaseous hydrocarbon, having, for example, a hydrocarbon content of at least 40 percent, the unreacted constituents are separated from the resulting gas and hydrogenated in a separate fluidised bed to yield a gas poorer in gaseous hydrocarbon, a part of the hydrocarbon-rich gas is treated as described above to convert hydrocarbon into hydrogen, the resulting hydrogen-containing gas is used as the hydrogenating gas, and the gas poorer in hydrocarbons is mixed with the remaining hydrocarbon-rich gas to form the calorific gas.

In this process the treatment of the oil containing the more reactive and less reactive constituents, and the hydrogenation of the less reactive constituents, are carried out in separate fluidised beds to which hydrogenating gas is separately supplied and from which the gases produced are separately withdrawn. Thus, the hydrogenation conditions are readily controllable to suit the requirements of the different constituents. For example, the less reactive constituents may be hydrogenated under a higher pressure than that used for hydrogenating the more reactive constituents. The use of the gas richer in hydrocarbons for producing the hydrogenating gas enables less steam to be used than would be necessary if the gas poorer in hydrocarbons were used.

The following examples illustrate the invention, the processes described in these examples being carried out with the apparatus shown diagrammatically in FIGS. 1 and 2 of the accompanying drawings.

Example 1

This is an example of the process for the production of a hydrocarbon-containing gas suitable as a heating gas, such as town gas, in accordance with the invention, and is carried out in the apparatus shown in FIG. 1.

In this process a heavy fuel oil having a viscosity of 3000 seconds Redwood (No. 1) is treated in a fluidised bed within a vessel **10** to hydrogenate the more readily reactive constituents at 750° C., and the tar is recovered from the gases produced and hydrogenated at 900° C. in a fluidised bed within a vessel **11**. The fluidised beds are composed of coke particles having a grain size of 32–72 mesh B.S.S. The hydrogenation in both beds is carried out at 50 atmospheres' pressure.

The vessels **10** and **11** are associated with means hereinbefore described for dealing with an oil containing constituents that decompose to produce solid carbonaceous material at the temperatures used. Thus, a standpipe **13** opens at its upper end into the fluidised bed in the vessel **10**, and communicates through a passage **14** at its lower end with the lower end of an ascending pipe or upriser **15**, through which hydrogenating gas is passed from a line **16** into the vessel **10** so as to maintain the solid particles in the fluidised state. The fluidised material from the vessel **10** descends into the standpipe **13**, in

which the material is kept fluidised by hydrogenating gas introduced from a line **17**. Owing to the hydrostatic pressure due to the height of the fluidised material above the level of the passage **14**, a small amount of this material passes into the upriser **15** where it is carried along in suspension in the ascending gas stream, the temperature of the material being substantially the same as that of the material in the vessel **10**. The oil is injected at **18** into the upriser **15** so that the bulk of the atomised oil is vaporised and solid carbonaceous decomposition products are carried along in suspension with the suspended particles from the standpipe **13** into the vessel **10**. The oil is thus rapidly mixed with the hydrogenating gas and vaporised by the sensible heat of the suspended coke particles and of the gas, and this favours hydrogenation of a high proportion of the oil. The tar, which is to be hydrogenated in the vessel **11**, is similarly injected at **19** into the lower end of an upriser **20** together with solid particles derived from a passage **21** communicating with the lower end of a wide standpipe **22**, which communicates at its upper end through a passage **23** with the fluidised bed in vessel **11**. Hydrogenating gas is passed through the standpipe **22** to maintain the material therein fluidised, and also to hydrogenate solid carbonaceous decomposition products admixed with the coke particles derived from the vessel **11** and also from the vessel **10** through a passage **24** communicating with the wide standpipe **22**. The diameter of the standpipe **22** must be large enough to give the particles a residence time therein adequate for hydrogenation of the said decomposition products, and normally this diameter should not be less than half the diameter of the fluidised bed in vessel **11**. A small passage **25** connects the spaces above the fluidised beds in the vessel **10** and standpipe **22** for the purpose of pressure equalisation.

The greater part of the hydrogenation of the more reactive constituents of the oil occurs in the vessel **10**, and completion of the reactions is brought about by passing the gases from the top of the vessel **10** into an empty vessel **26**. The methane-containing gas from vessel **26** is then passed through a cooler **27**, in which tar is condensed, and a second cooler **28** in which benzole is condensed. Then hydrogen sulphide is removed in known manner in a washer **29**, for example, by washing with ethanolamine. The tar from the cooler **27** is introduced at **19** for hydrogenation in the vessel **11**.

A part of the hydrocarbon-containing gas from the washer **29** is tapped off at **30** for treatment to form the hydrogenating gas as described below. Since the gas produced in the vessels **10** and **26** is richer in hydrocarbons than the gas derived from the hydrogenations in the vessels **11** and **22**, the former gas is utilised for producing the hydrogenating gas. The gas from the vessels **11** and **22** are passed first through a cooler **31** to remove a tar, which in this case consists mainly of crude naphthalene which can be purified to yield a marketable product. Benzole is recovered in a second cooler **32** and hydrogen sulphide is removed in a washer **33**. The gas from the washer **33** is mixed at **34** with the portion of the gas from the washer **29**, which is not used for producing the hydrogenating gas. The mixed gas in the line **35** is diluted with nitrogen (obtained during the production of the oxygen referred to below) introduced from the line **36** in a proportion suitable to produce a town gas of appropriate calorific value and density.

The hydrocarbon-rich gas tapped off at **30** for producing the hydrogenating gas is passed by a blower **37** through a vessel **38**, in which organic sulphur compounds are removed in known manner, for example, by means of alkaline iron oxide at 220° C. Steam and oxygen are then admixed with the purified gas at **39** and **40**, respectively, and the gaseous mixture is passed into vessel **41** in which the gaseous hydrocarbons are decomposed in known manner by means of a nickel catalyst at 900° C. into hydrogen and carbon monoxide. The carbon monoxide is then converted in known manner by reaction with the excess of steam in the gas in a vessel **42**, and the carbon dioxide is removed from the gas in known manner in a vessel **43**. The resulting hydrogenating gas is then preheated to 350–400° C. in a preheater **44** before being supplied to the hydrogenation vessels **10** and **11** and the standpipes **13** and **22**.

In carrying out the process by way of example the temperature of the fluidised bed in the vessel **10** is maintained at 750° C. by adjusting the temperature of the hydrogenating gas admixed with the oil at **18** to, say, 390–400° C. The temperature of the bed in the vessel **11** is maintained at 900° C. by adjusting the temperature of the hydrogenating gas to 340–350° C.

In unit time 37,625 cubic feet of hydrogenating gas are supplied to the vessel **10** per 100 gallons of oil. The compositions of the hydrogenating gas and of the resulting methane-rich gas, having a calorific value of 676 B.t.u. per cubic foot, are as follows:

	Hydrogenating gas, percent by volume	Methane-rich gas, percent by volume
CO_2	1.9	0.2
CO	4.8	6.8
H_2	89.4	51.7
CH_4	3.9	31.0
C_2H_6		10.3
	100.0	100.0

183 pounds of tar are recovered from the vessel **27** and 90 pounds of benzole from the vessel **28**. Calculation showed that about 41 pounds of solid carbonaceous products were deposited on the coke particles, most of which products would flow into the standpipe **22** to become hydrogenated.

The 183 pounds of tar so recovered are passed for hydrogenation into the vessel **11**. 14,570 cubic feet of the hydrogenating gas are supplied to the vessel **11**, and 3660 cubic feet to the standpipe **22** for the hydrogenation of solid carbonaceous products. The mixed gases derived from the vessel **11** and standpipe **22** have the composition

	Percent by volume
CO_2	0.1
CO	8.4
H_2	57.3
CH_4	34.2
	100.0

On cooling the gas, 45 pounds of tar (mainly consisting of naphthalene suitable for refining and so not recirculated) and 31 pounds of benzole are obtained from the vessels **31** and **32**, respectively.

The two methane-containing gases mixed together at **34** yield 22,100 cubic feet of mixed gas having a calorific value of 594 B.t.u. per cubic foot. Dilution with nitrogen from **36** gives a town gas of calorific value 500 B.t.u. per cubic foot and having a density of 0.45 (air=1). It has the composition:

	Percent by volume
CO_2	0.2
CO	6.8
H_2	46.9
CH_4	28.6
C_2H_6	2.6
H_2	14.9

924 pounds of steam and 5883 cubic feet of oxygen are introduced at **39** and **40**, respectively, for the decomposition of the gaseous hydrocarbons.

Example 2

This example illustrates a process for the production of a hydrogen-rich gas in accordance with the invention, and the process is described with reference to FIG. 2.

Within a vessel **50** three fluidised beds **51**, **52** and **53** of coke particles of 32–75 mesh B.S.S. are maintained by an upward current of hydrogenating gas. Into the middle bed **52** is introduced Kuwait crude petroleum oil the more reactive constituents of which are hydrogenated in the bed at about 800° C. A light petroleum distillate is hydrogenated in the uppermost bed **51** at about 700° C. Tar from the beds **51** and **52** is hydrogenated at about 900° C. in the lowermost bed **53**. The hydrogenations are carried out at 30 atmospheres' pressure.

The hydrocarbon-containing gas from the top of the vessel **50** is passed through a line **54** into a cooler **55**, in which the tar is condensed, and then supplied to the bed **53**. Benzole and hydrogen sulphide are removed from the gas in a cooler **56** and a washer **57** as described in Example 1. The gas is then passed through a vessel **58** for the removal of organic sulphur compounds. Steam under high pressure is mixed with the purified gas at **59**, and the gaseous mixture is treated in a vessel **60** to decompose the gaseous hydrocarbons with the steam to form hydrogen and carbon monoxide at 900° C. over a nickel catalyst. The tubes, represented diagrammatically at **61**, which contain the catalyst are heated by a small supply of the methane-containing gas tapped off at **62**. Before entering the catalyst tubes **61**, the gaseous mixture is preheated to 700° C. in a preheater **63** by heat exchange with the hot gases leaving the catalyst tubes, and is then expanded in a turbine **64** to 5 atmospheres.

The hot gases from the decomposition pass from the preheater **63** into a vessel **65**, in which carbon monoxide is converted by reaction with excess of steam in the gas by means of an iron-chromium catalyst at 300° C. into hydrogen. The carbon dioxide so formed is removed in known manner in a vessel **66**, and the gas is cooled to atmospheric temperature in a cooler **67**. A part of the hydrogen-rich gas so produced is withdrawn as product gas at **68**. Another part of the hydrogen-rich gas is passed through a line **69** to a compressor **70**, which compresses the gas to 30 atmospheres. The compressed gas is preheated at 400° C. in a preheater **71**, and then used as the hydrogenating gas.

In order to start the process the plant is first filled with hydrogenating gas at 30 atmospheres' pressure. The vessel **50** is then warmed by passing through it hydrogenating gas preheated in **71** to 400–500° C., the gas being introduced at the bottom of the vessel through a valve **72**, a valve **73** in a line **74** being closed. The coke particles, which are to form the fluidised beds, are introduced into the hydrogenating gas at **75**. When the vessel **50** is almost full of coke particles, the latter are caused to form the three fluidised beds by withdrawing surplus particles through an overflow pipe **76**, which determines the upper level of the bed **53**, the upper levels of the beds **51** and **52** being determined by overflow pipes **77** and **78**. A small amount of air for combustion is then admitted to the lowermost bed **53**, and the air is ignited by the preheated coke particles. The supply of hydrogenating gas is then changed by closing valve **72** and opening valve **73**, so that it passes through the line **74** and passes downwardly through coils **79** and **80** in the beds **51** and **52**, and is finally discharged at **81** into the space beneath the lowermost bed **53**. The supply of air is continued until the temperature in the bed **53** approaches 800° C. The oil is then supplied to the bed **52** and the final working temperature is reached with the assistance of the exothermic heat of hydrogenation. The air supply is then shut off.

During normal operation the hydrogenating gas is preheated to 400° C. in the preheater **71**, and is further preheated to 750° C. in passing downwards through the coils **79** and **80** in the beds **51** and **52**, which have reached their working temperatures. The preheated gas then passes upwardly through the three beds in series so as to hydrogenate the tar and oils being supplied.

To illustrate the results obtainable, for every 1000 cubic feet of hydrogenating gas, 22.6 pounds of petroleum oil are supplied to the middle bed **52**, 4.25 pounds of light petroleum distillate to the upper bed **51**, and 4.05 pounds of recovered tar to the lower bed **53**. 905 cubic feet of methane-containing gas are obtained from the washer **57**, having the composition:

	Percent by volume
CO	6.9
H_2	29.9
CH_4	53.2
C_2H_6	10.0
	100.0

3.07 pounds of benzole are recovered from the cooler **56**. The hydrogen-rich gas produced amounts to 2160 cubic feet having the composition

	Percent by volume
CO_2	2.0
CO	4.3
H_2	91.0
CH_4	2.7

Of this gas 1160 cubic feet are withdrawn at **68** as the product gas, and the remaining 1000 cubic feet are passesd through the line **69** and used as the hydrogenating gas.

During operation, coke particles are continually withdrawn from the lowermost bed **53** through the pipe **76** and returned to the upper bed **51**, so that there is a continual downward movement of the particles through the series of beds. In this way solid carbonaceous products deposited on the coke particles from the oil in the middle and uppermost beds are hydrogenated in the lowermost bed due to the higher temperature and concentration of hydrogen in that bed.

We claim:

A process for the gasification of a hydrocarbon material which is liquid at a temperature within the range from ordinary temperatures to 500° C. and contains aliphatic hydrocarbons, which comprises subjecting the hydrocarbon material to interaction with a proportion of hydrogen sufficient to convert substantially the whole of the aliphatic hydrocarbon into gaseous saturated hydrocarbons by passing the material and a gas comprising the said proportion of hydrogen under a pressure within the range of 20 to 50 atmospheres through a bed of non-catalytic particulate solid maintained in the fluidised state by the gas and having a temperature within the range of about 700° C. to 800° C.

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