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(1) Patent:

(54) METHODS OF PRODUCING GASES

(54) METHODES DE PRODUCTION DE GAZ

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ABSTRACT:

CLAIMS: [Show all claims](#)

*** Note: Data on abstracts and claims is shown in the official language in which it was submitted.

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Having described the invention and explained the purpose thereof, what is claimed is:

1. A continuous method for producing mixtures of CO and hydrogen suitable for use as a feed stock in the synthesis of hydrocarbons, the steps comprising subjecting a hydrocarbon oil to coking to form volatile hydrocarbon constituents and a coke, the coking operation being carried out in the presence of a fluidized, powdered solid inert material in a coking zone, withdrawing volatile hydrocarbon oils from said coking zone, simultaneously withdrawing the solid inert material containing coke deposited thereon, conducting the said solid material to a combustion zone, causing combustion of a portion of its coke whereby the temperature of the material is raised to water gas reaction temperatures, the solid material being in the form of a fluidized mass of solids in a gasiform material, withdrawing the highly heated solid material containing coke, conducting the same to a water gas synthesis reactor, treating the solids containing coke with steam at water gas reaction temperatures while the solids are in the form of a fluidized mass of solids in steam, and recovering from the last-named zone a mixture of hydrogen and CO.

2. The method of claim 1 in which the powdered material is pumice.

3. The method of claim 1 in which the powdered material is maintained in a fluidized state by limiting the velocity of the gasiform material passing up through the several zones within the limits of 1/2-10 feet per second.

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4. A continuous method for producing a mixture of CO and hydrogen which comprises first subjecting a highly viscous oil to coking in a coking zone containing a body of fluidized solid inert material wherein the said oil contacts the solids in a highly heated condition causing the release of vaporous hydrocarbons and the deposition of solid carbonaceous material on the inert material, withdrawing the latter from the coking zone suspending it in an oxygen containing gas and conducting it to a combustion zone where it is formed into a fluidized mass of coke containing inert material suspended in the said oxygen containing gas, permitting the coke containing inert material to remain resident in the combustion zone for a sufficient period of time to burn a portion of said coke, withdrawing the inert material containing unburned coke from the combustion zone and conducting it to a CO and hydrogen gas synthesis zone, discharging steam into said last-named zone to form therein a fluidized mass of inert material containing coke admixed with the said steam, permitting the inert material and the steam to remain in contact with each other for a sufficient period of time to form substantial quantities of CO and hydrogen, withdrawing the CO and hydrogen for product from the last-named zone and withdrawing the inert material from the last-named zone and conducting it to the coking zone for reuse therein as a repository for further quantities of coke.

5. The method set forth in claim 4 in which steam is injected into the coking zone for the purpose of aiding the release of volatile hydrocarbons.

6. The method of claim 4 in which a temperature of from 900° to 1100°F. is maintained in the coking zone.

7. An inexpensive method for manufacturing a mixture of CO and hydrogen of sufficient purity that it is adapted for use in the catalytic synthesis of normally liquid hydrocarbons, which comprises coking a highly viscous oil in the presence of a fluidized mass of finely divided solid material in a coking zone wherein volatile hydrocarbons and coke are formed, the latter being deposited on the said finely divided solid material, withdrawing solid material from said coking zone and conducting the same to a burning zone, causing combustion of a portion of the coke deposited on the said powdered material to raise the temperature of the powdered material to a value greater than 2000°F., conducting the powdered material containing unburned coke at a temperature in excess of 2000°F. to a synthesis gas generating zone, causing steam to contact the said powdered material containing coke in the last-named zone to form a fluidized mass of powdered material in steam, permitting the powdered material containing coke to remain resident in the last-named zone for a sufficient period of time to form substantial quantities of CO and hydrogen by chemical reaction between the said coke and the said steam, recovering from the last-named zone a mixture of CO and hydrogen and withdrawing from the last-named zone the powdered material and discharging the said material into the said coking zone for further use in the process.

8. The method of claim 7 in which at least a substantial portion of the heat required to support the coking reaction and the synthesis gas generation is supplied by burning a portion of the coke deposited on the inert material during the coking operation.

9. The method set forth in claim 7 in which the powdered material is pumice.

10. The method set forth in claim 7 in which the said highly viscous oil is a hydrocarbon oil having a gravity of 10° API or less.

11. The method set forth in claim 7 in which the ratio of solids to steam is from about 5-150 pounds of solid powdered material per pound of steam.

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12. A continuous method for producing a mixture of CO and hydrogen which comprises subjecting a highly viscous oil to coking in a coking zone containing a body of fluidized solid material wherein the said oil contacts the solids in a highly heated condition causing the release of vaporous hydrocarbons and the deposits of solid material on the inert material, withdrawing the latter from the coking zone, suspending it in an oxygen-containing gas and conducting it to a combustion zone where it is formed into a fluidized mass of coke containing inert material suspended in the said oxygen-containing gas, permitting the coke containing inert material to remain resident in the combustion zone for a sufficient period of time to burn a portion of said coke, withdrawing the inert material containing unburned coke from the combustion zone and conducting it in part to a CO and hydrogen gas synthesis zone, discharging steam into said last-named zone to form therein a fluidized mass of inert material containing coke admixed with the steam, permitting the inert material and the steam to remain in contact with each other for a sufficient period of time to form substantial quantities of CO and hydrogen, recovering the CO and hydrogen for product from the last-named zone, discharging that portion of the inert material withdrawn from the combustion zone which is not discharged into the CO and hydrogen synthesis zone into the coking zone, withdrawing solids from the CO and hydrogen gas synthesis zone and conducting the solids thus withdrawn to the combustion zone.

13. The method set forth in claim 12 in which steam is injected into the coking zone with the purpose of aiding the release of multiple hydrocarbons.

14. The method set forth in claim 12 in which the solid powdered material issuing from the coking zone is at a water gas reaction temperature.

15. The method set forth in claim 12 in which the solid inert material is pumice.

16. A continuous method of producing CO and hydrogen by the water gas reaction, which comprises providing three vessels, each containing a fluidized mass of solid inert material, all intercommunicating and being, respectively, a coking zone, a combustion zone, and a water gas forming zone, disposing the combustion zone at a vertical position above the other two said zones so that solids may proceed by natural flow from the combustion to the other two zones, discharging a highly viscous oil into said coking zone maintained at a temperature sufficiently high to cause coke formation and deposition on said inert solids, withdrawing said solids from said coking zone, conducting them pneumatically to the said combustion zone in a gas stream containing free oxygen, permitting contact between the fluidized solid inert material containing coke and the oxygen-containing gas for a sufficient period of time to raise the temperature of the solid inert material to water gas reaction temperature, withdrawing the thus highly heated inert material from the combustion zone, discharging it into the water gas zone, discharging steam in the last-named zone to form the fluidized mass, permitting contact between steam and the coke-containing solids therein for a sufficient period of time to effect the water gas reaction, withdrawing solids from the said water gas reaction zone and returning them to said combustion zone, and recovering for product from the water gas forming zone a mixture of CO and hydrogen gas.

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17. A continuous method for producing a mixture of carbon monoxide and hydrogen which comprises subjecting a hydrocarbon oil to coking in a coking zone containing a body of fluidized solid material wherein the said oil contacts the solids in a highly heated condition causing the release of vaporous hydrocarbons and deposits of coke on the inert material withdrawing the latter from the coking zone, conducting it to a water gas forming zone where it contacts steam while in the form of a fluidized mass of said inert material in said steam, permitting the inert material containing coke and the steam to remain in contact with each other for a sufficient period of time to form substantial quantities of carbon monoxide and hydrogen, recovering the carbon monoxide and hydrogen for product from the said water gas forming zone, withdrawing inert material from the said water gas forming zone, conducting a portion of the thus withdrawn inert material to the coking zone, conducting another portion of the inert solids withdrawn from the water gas forming zone to a combustion zone, forming in said last-named zone a fluidized mass of inert material containing coke admixed with an oxygen-containing gas, permitting contact between the coke containing inert material and said oxygen-containing gas for a sufficient period of time to effect substantial combustion of said coke on said inert material and withdrawing inert material from said combustion zone and conducting it to said water gas forming zone.

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18. The method set forth in claim 17 in which sufficient excess air is present in the burning zone or in the combustion zone so that the oxides and carbon in the effluent flue gas resulting from the combustion predominate in carbon dioxide.

19. A continuous method for producing a mixture of carbon monoxide and hydrogen from a heavy hydrocarbon oil which comprises providing fluidized and separated masses of powdered inert material in three separated zones comprising respectively a coking zone, a burning zone, and a water gas forming zone, feeding a heavy hydrocarbon oil to said coking zone where it contacts said powdered inert material at elevated temperatures, permitting said oil to remain resident in said coking zone for a sufficient period of time to effect the desired conversion, causing flow of said powdered solid inert material through the several zones, forcing a gasiform material upwardly through each of the several zones at a flow rate such that the powdered inert material is maintained in the said fluidized state, the gasiform material being a free oxygen-containing gas in the burning zone and steam in the other two zones, regulating the flow of powdered material through the several zones so that said powdered material containing coke is fed to the burning zone and the water gas forming zone, permitting sufficient residence time of the powdered inert material containing coke in the combustion zone in contact with the said oxygen-containing gas to generate heat by burning coke on said powdered material to the extent that when it is withdrawn from the combustion zone and forced into the water gas forming zone and the coking zone, it contains sufficient sensible heat to supply at least a portion of the heat necessary to support the endothermic reactions taking place in the last named zones, and permitting the powdered inert material containing coke to remain resident in the water gas forming zone in contact with the said steam to form substantial quantities of carbon monoxide and hydrogen, and withdrawing a mixture of carbon monoxide and hydrogen from the water gas forming zone.

The present invention relates to the novel featured hereinafter fully disclosed in the specification and claims considered in connection with the accompanying drawing.

The main object of this invention is to produce a gas consisting essentially of carbon monoxide and hydrogen adapted for conversion into hydrocarbons by known catalytic processes.

In general, the object of this invention is accomplished by (1) subjecting a hydrocarbon oil to coking, withdrawing the petroleum coke from the coking zone, (2) causing it to be heated to temperatures wherein it will react with steam, and (3) conveying it to a gas generator where it is treated with the said steam under conditions such that a water gas reaction takes place resulting in the formation of appreciable quantities of CO and hydrogen, the entire operation being carried out using the fluid-solids method of operation. The solid in the form of a powder is caused to be formed into a dense suspension with a gas in a treating zone by controlling the upward linear velocity of the gas so as to permit slippage or delayed settling of the solids, all of which will be more fully explained hereinafter.

In the accompanying drawing we have shown in

Figures I to III three vessel systems adapted for use in the production of a mixture of carbon monoxide and hydrogen from a heavy hydrocarbon oily material; the vessels shown being 1) a coking vessel in which the coking is performed in the presence of a powdered solid material which acts as a coke receiver, 2)-a combustion vessel in which a portion of the coke formed in the coking vessel is burned to supply heat for the process and 3) a generator wherein the productive reaction occurs; namely, the water gas reaction to form carbon monoxide and hydrogen. For simplicity purposes, Figures II and III are fragmentary showings in that the preheating equipment and the showing of the apparatus adapted for treating the carbon monoxide and hydrogen product have been omitted from the latter two figures. The three figures together show a plurality of methods for carrying these inventions into effect; the main difference between the several modifications residing in the sequence in which the powdered solid material flows continuously through the three vessels, all of which will more fully and at length appear hereinafter.

Similar reference characters refer to similar parts in the several views.

Referring in detail to Figures I to III, (1) represents a coking vessel or drum. The oil to undergo coking enters the system through line (10), and thereafter

may be pumped through a fired coil (12) disposed in a suitable furnace setting (13) where the oil is heated to a temperature, say, up to 300°F. (to avoid coking, the oil should not be heated above 300°F.) and then is withdrawn through line (14) and sprayed or otherwise injected into the coking drum (1). It may be advisable to charge the oil into coking drum (1) without passing through the heating coil (12) for (1), as will subsequently appear, contains a body of highly heated powdered material which may contain sufficient sensible heat to support the coking operation. The oil may be any hydrocarbon oil. We find, however, that this invention is especially well adapted for the processing of high-boiling residual oils. For instance, the oil charged is preferably a high-boiling hydrocarbon oil such as crude bottoms, Bunker C fuel oil, or any other heavy oily material. A good way to inject the oil is to spray the same, admixed with the superheated steam from line (15), through a spray nozzle (16) in atomized condition onto the powdered solid.

In the case of normally liquid free flowing oil, it may be caused to flow from line (10), through lines (19) and (15) into the coker (1). It is preferable, however, to mix the oil with the hot solids entering the coker through line (32) after the control valve (33). Thus, the oil may pass from line (19) via line (19a) into line (32) as shown.

There is maintained, as indicated, within the coking zone a body of powdered material, such as pumice, crushed rock, sand, ash, or any other inert material chosen from a group of materials which will not fuse at temperatures existing in a burning vessel (53) hereinafter described, upon the particles of which the coke formed in the process deposits. As previously indicated, this powdered, inert material is maintained in fluidized state, that is to say, it is maintained in a dense, turbulent suspension by causing a gasiform material, such as steam, from line (15) to flow through line (17) into the bottom of the drum (1) through a perforated member (6) and then upwardly through the said drum, the linear velocity being controlled within the limits of $1/2$ -10 feet per second, but preferably from 1-3 feet per second, whereupon the powder is maintained in the dense suspension or fluidized mass mentioned. By controlling the amount of powdered material charged to (1) and the gas or vapor velocity, an upper level (L) of the dense suspension may be obtained, above which the concentration of the powdered material is much more dilute so that the volatile constituents issuing through line (20) may contain only a very minor amount of entrained solids.

We shall now set forth the manner of introducing the powdered material continuously into the coking zone and withdrawing the same. Hot inert powdered material of the character indicated, at a temperature of as high as 2200°F., is withdrawn through a standpipe (32) controlled by a valve (33) and discharged into the side of the

reactor (1) at any convenient point. The standpipe (32) carries a number of branch pipes (34) into which a gas, such as steam, may be slowly bled, for the purpose of inducing free flow in the standpipe, thus preventing bridging and plugging of the material therein.

Simultaneously, powdered material contaminated with coke is continuously withdrawn from the vessel (1) through line (50), and then discharged into a line (52) containing a flowing stream of an oxygen-containing gas. The inert material coated with coke formed in the coking operation in (1) forms a suspension in the air or other oxygen-containing gas and this is conveyed into a burning zone (53) wherein again the particles of solid material are formed into a dense suspension by controlling the linear velocity of the gas, in the same manner as was done in coking vessel (1). In this vessel (53) a portion of the coke is burned whereby the temperature of the particles is raised from 1800°F. to 2400°F. and then the highly heated particles containing coals are withdrawn through standpipe (60) and conducted into a reaction vessel (62) where it forms with steam introduced through line (70), a third fluidized mass of solids in the gasiform material. A substantial portion of the coke or carbon remaining on the powdered material reacts with the steam to form CO and hydrogen and this material is recovered overhead through line (71) and delivered to hydrocarbon synthesis (72). If desired, the steam entering the reactor (62) through line

(70) may be admixed with a minor amount of air or other oxygen-containing gas, although it is preferable to exclude nitrogen from the reaction zone.

Also, air or oxygen, or oxygen diluted with inert gas may be introduced into the bottom of coker (1) via line (18) to supply heat in situ by coke combustion. Obviously the amount of air thus introduced must be carefully controlled to prevent excessive burning and/or explosions. Enough air or oxygen is recommended merely to burn a few percent of the coke formed in coker (1).

It will be noted that coking vessel (1), combustion vessel (53), and synthesis gas generator (62) are provided with elements E, G₁, and G₂, respectively. These elements are grids, screens or other perforated members, and the gasiform material entering the vessels passes through these perforated members. The function of the said members is substantially to secure uniform distribution of the gas in the several treating zones.

The solids contained in gas synthesis vessel (62) are continuously withdrawn through a standpipe (32) and returned to coking drum (1) as previously indicated, thus completing a cycle of operations.

It is pointed out, of course, that like standpipe (50), (60) should be provided with taps into which a gasiform material may be forced to fluidize the material therein flowing, that is, to prevent it from bridging or plugging. Thus standpipe (50) is provided with a plurality

of such taps (51), and standpipe (60) is provided with a plurality of taps (61).

Referring back to line (20) in communication with the coking vessel (1), of course, valuable hydrocarbon oil may be recovered through this line and subjected to refinement of various kinds, including condensing, distilling, and the like, to recover gasoline, gas oil and normally gaseous hydrocarbons, according to known refinery practice. To simplify the explanation of the present invention, a full description of the best and most economical manner of treating the volatile hydrocarbons in line (20) has not been included, for these are well known and understood by the competent petroleum engineer.

In Figure II, a modification of the invention has been shown, in which hot solids from the combustion vessel (53) flow both to the water gas vessel (62) and to the coking vessel (1). In other words, in this modification solids from line (60) may be passed in part via line (60a) into the coking vessel (1), the remainder passing to the water gas set (62). The solids drawn from the bottom of coking vessel (1) pass, as in Figure I, into line (52), but the solids from the bottom of the water gas set (62) also discharge into line (52) and flow with the solids from vessel (1) to the combustion vessel (53). The advantages of this modification of this invention are that hot solids pass directly from the combustion vessel to the coking vessel, thus insuring an ample heat supply in the coking

vessel and permitting operation in said coking vessel (1) without the necessity of preheating the oil before it enters the said vessel.

In Figure III a still further modification of this invention has been shown in which the hot solids containing coke are withdrawn from coking vessel (1) via line (50), mixed with steam, introduced through line (52a) and thence conducted to the water gas vessel (62) where the steam reacts with the coke on the inert solids to cause the water gas reaction to take place. Solids which are withdrawn from the water gas vessel (62) through line (32) in this modification, may be mixed with air introduced through line (52b) and delivered to line (52b), discharging into the bottom of combustion vessel (53). In combustion vessel (53) most, if not all, of the coke on the solids is burned to carbon dioxide so that the flue gas, exiting from the vessel (53), contains little, if any, carbon monoxide. The advantage of this modification is that a greater quantity of heat is made available for the process per pound of carbon burned. The burnt solid powdered material containing very little, if any, coke, but heated to a high temperature, is withdrawn through line (50) and delivered to the water gas set (62) so that the latter contains a mixture of solids delivered to it directly from the coking vessel (1) and hot solids delivered to it from the combustion vessel (53). Instead of delivering all of the solids issuing from the water gas set (62) to the

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combustion vessel (53), a portion of said solids may be delivered to the coking vessel (1) via line (32a), controlled by valve (32v).

As to operating conditions, the following conditions are maintained in coking vessel (1):

	<u>Broad Range</u>	<u>Preferred Range</u>
Temperature	900-1100°F.	925-975°F.
Pressure	Atmospheric--100 PSIG*	5-30 PSIG
Feed Rate (Oil)**	0.4-32	0.4-2.0
Solids to Oil Ratio to Coking Drum	1-10	1-5

The oil may be a reduced crude or high-boiling cracked tar or pitch.

The conditions maintained in the burning zone (53) are as follows:

	<u>Broad Range</u>	<u>Preferred Range</u>
Temperature	At least 50°F. above water gas producer temperature and dependent on solids-oil weight ratio, up to 2500°F.	Same
Pressure	Atmospheric--100 PSIG	5-30 PSIG
Residence Time	Varies with products desired.	0.1-10 W/Hr/W (feed rate)

* PSIG is pounds per square inch gauge.

** Pounds of oil per hour per pounds of solids in reactor

With respect to the conditions maintained in the synthesis gas generator (62), they are as follows:

	<u>Broad Range</u>	<u>Preferred Range</u>
Temperature	1800°-2500°F.	1800°-2200°F.
Pressure	Atmospheric--100 PSIG	5-30 PSIG
Ratio* of solids to steam	5-150	75-100

To recapitulate briefly, a method of producing synthesis gas suitable for use as feed stock in an operation designed to synthesize hydrocarbons from CO and hydrogen has hereinbefore been set forth. The outstanding features of this invention are the following:

- 1) Continuity of operation.
- 2) Flexibility inherent in the fluid-solids type of reaction.
- 3) Use of an inexpensive source of carbon.
- 4) Extension of utility of crude oil natural resources supply.
- 5) The procurement of coke in a highly reactive state.

These modifications of the invention have been shown in the drawing and these modifications have heretofore been described. We wish to point out that there are other modifications falling within the scope of this invention and among these are the following; to wit:

- 1) A modification of the design shown in Figure 1 in which a portion of the material withdrawn from the burning zone and discharged into the water gas pot is returned to

* Pounds of solids per pounds of steam.

the burning zone.

2) A modification in which solids are withdrawn from the coker and passed to the water gas set, thence passed from the water gas set to the burning zone and thence a portion of the solids are withdrawn from the burning zone and returned to the coking zone, while the remainder of the solids are withdrawn from the burning zone and passed to the water gas set.

3) A modification in which a portion of the solids are withdrawn from the coking zone, discharged into the burning zone, thence withdrawn from the burning zone and returned to the coking zone; while another portion of the circulating solids passes from the coking zone directly to the water gas set and thence back to the coking zone.

4) A modification in which solids pass from the coking zone to the water gas set, then pass in part to the burning zone and returned to the coking zone, the portion of the solids passing from the water gas set but not to the burning zone being returned to the coking zone.

5) A modification in which a part of the solids withdrawn from the coking zone are passed to the burning zone, thence passed to the water gas set, thence passed to the coking zone, the portion of the solids withdrawn from the coking zone and not passed to the burning zone passing to the water gas set.

6) A modification in which all solids withdrawn from the coking zone pass to the burning zone directly while a portion of the solids withdrawn from the burning zone passes immediately to the coking zone while the remainder of the

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solids withdrawn from the burning zone passes mediately to the coking zone via the water gas set.

7) A modification in which a portion of the solids withdrawn from the coking zone passes immediately to the burning zone but the remainder of the solids withdrawn from the coking zone passes mediately to the burning zone via the water gas set; while all of the solids withdrawn from the burning zone pass immediately to the coking zone.

8) A modification in which the total solids withdrawn from the coking zone pass mediately to the burning zone via the water gas set and are returned from the burning zone immediately to the coking zone.

It will be understood that in the eight modifications which are summarized in words immediately above that, of course, the solids remain resident in the respective zones for a sufficient period of time to accomplish the purpose for which they are delivered to the several zones; for example, they remain resident in the burning zone for a sufficient period of time to effect the desired degree of burning and they remain resident in the water gas zone for a sufficient period of time to effect the required degree of conversion taking place in that zone. Of the eight modifications described in words immediately heretofore, those modifications numbered 1, 2, 5, and 6 are preferred over the others because of the fact that the water gas set can be maintained at a higher temperature than can the coker.

Numerous other modifications of this invention may be made by those skilled in this art without departing from the spirit thereof.

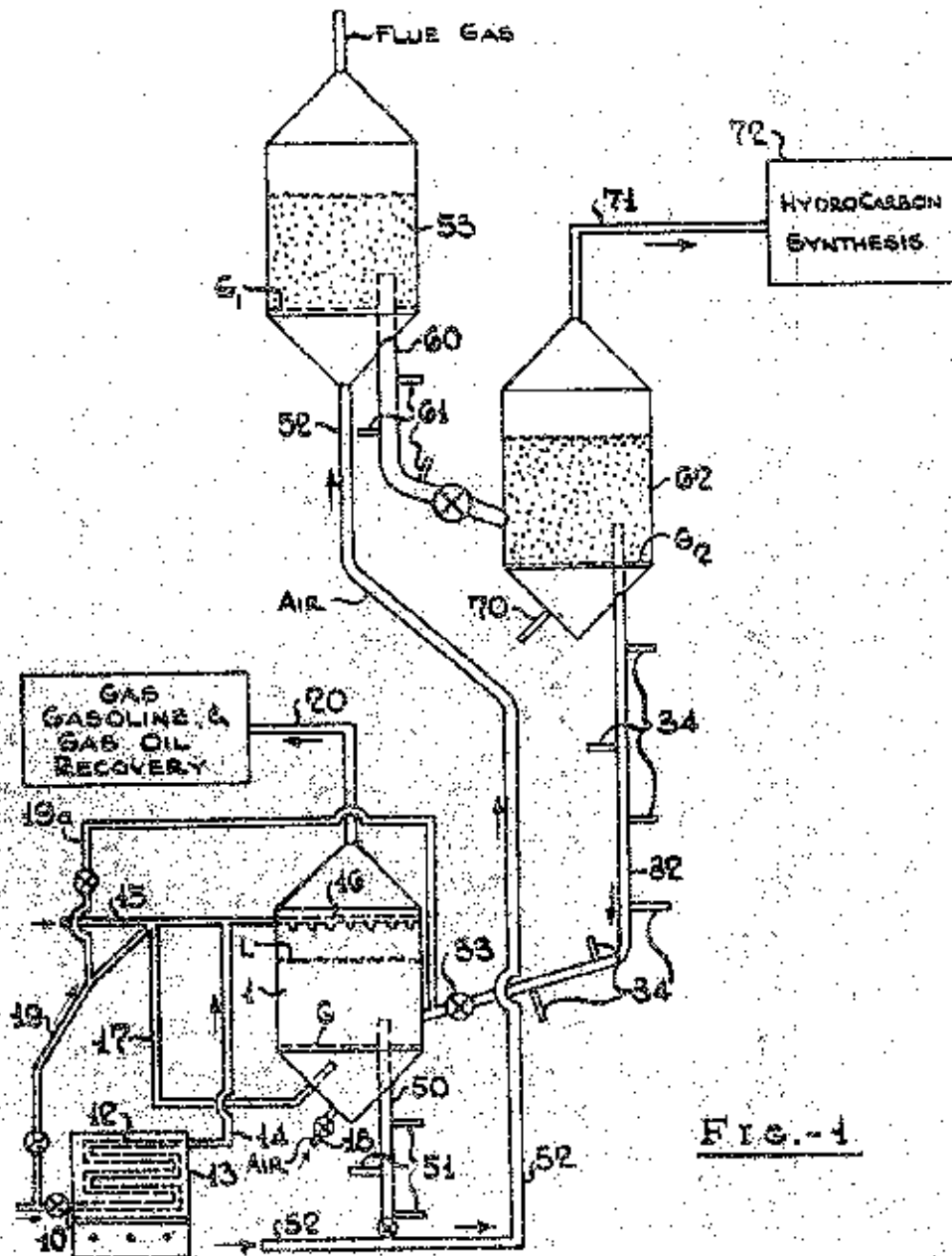


FIG.-1

*Standard Oil Development
Company*

Certified to be the drawings referred to
in the specification hereunto annexed.

Ottawa, April 12 1946

Brack & Sibley

ATTORNEYS

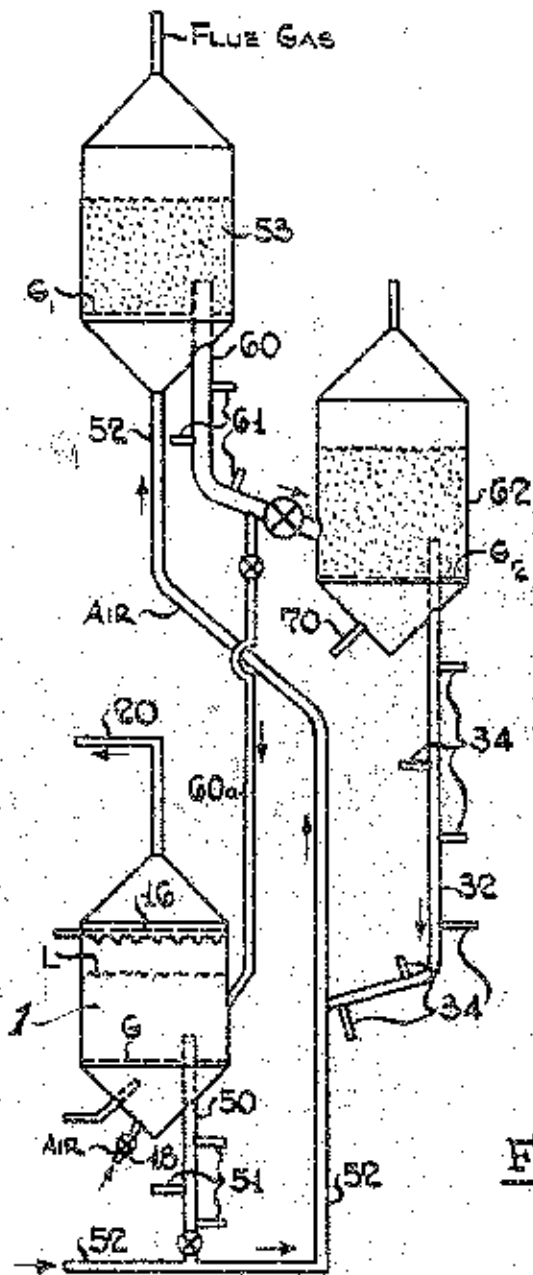


FIG.-2

Standard Oil Development Company

Certified to be the drawings referred to in the specification herewith annexed.

Ottawa, April 12 1946

Mark A. Oliver

ATTORNEY

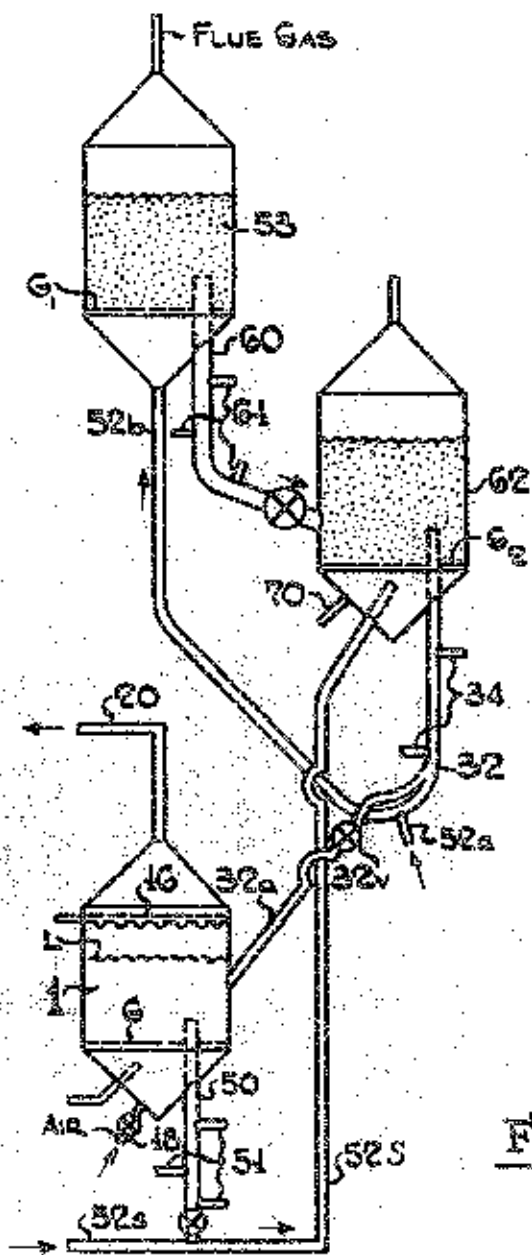


FIG.-3

*Standard Oil Development
Company*

Certified to be the drawings referred to
in the specification herewith annexed.

Ottawa, April 12, 1946

Maxwell

ATTORNEYS