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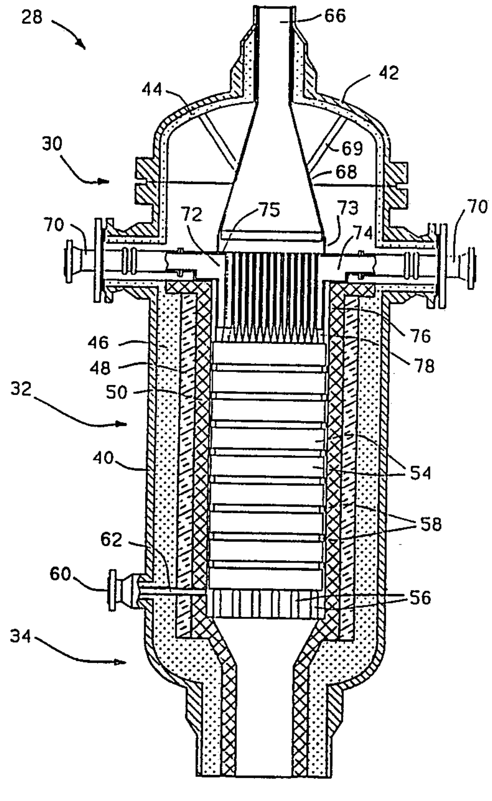
(54) Title: PRODUCTION OF METHANOL FROM HYDROCARBONACEOUS FEEDSTOCK

(57) Abstract

Methanol is produced from hydrocarbonaceous feedstock by a process which involves catalytically partially oxidizing the hydrocarbonaceous feedstock under temperature and steam conditions to produce a synthesis gas containing hydrogen, carbon monoxide and carbon dioxide without producing free carbon; reacting the hydrogen, carbon monoxide and carbon dioxide under methanol producing conditions; and recovering methanol.



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PRODUCTION OF METHANOL FROM HYDROCARBONACEOUS FEEDSTOCK

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to the production of methanol from hydrocarbonaceous feedstock by a process which includes the partial oxidation of hydrocarbonaceous feedstock to produce a synthesis gas containing hydrogen, carbon monoxide and carbon dioxide, which is further processed and fed to a methanol synthesis loop.

Description of the Prior Art

Methanol has long been produced by reacting hydrogen with carbon monoxide and/or carbon dioxide in the presence of a catalyst according to the equation:

$$CO + 2H_2 \longleftrightarrow CH_3OH \qquad (1)$$

Hydrocarbonaceous feedstock, such as natural gases recovered from sites near petroleum deposits, are convenient starting materials for the production of methanol. Typically, natural gases contain, as their principal constituent, methane, with minor amounts of ethane, propane and butane. Also included in the conversion in some instances, may be low-boiling liquid hydrocarbons.

In order to convert a hydrocarbonaceous feedstock into a feedstream suitable for introduction into a methanol synthesis reactor, the feedstock is first converted into a synthesis gas containing hydrogen, carbon monoxide and carbon dioxide. The synthesis gas can be treated to adjust the ratio of hydrogen to carbon monoxide and carbon dioxide in order to obtain the proper stoichiometric proportions for methanol synthesis. The treated gas stream is compressed and fed to the methanol synthesis loop, where the carbon monoxide, carbon dioxide and hydrogen are reacted in contact with a catalyst to produce methanol. The methanol is then purified by any of a number of conventional techniques.

Methods that have been employed to convert hydrocarbonaceous feedstock to synthesis gas in prior art methanol production processes include steam reforming, combined steam reforming/autothermal reforming, and partial oxidation. Steam reforming involves an endothermic reaction exemplified for methane by the equation:

$$CH_4 + H_2O \text{ ---> } CO + 3H_2 \qquad (2)$$

Partial oxidation involves an exothermic reaction exemplified for methane by the equation:

$$CH_4 + \tfrac{1}{2}O_2 \text{ ---> } CO + 2H_2 \qquad (3)$$

The product of both reactions (2) and (3) can be modified by the exothermic water gas shift reaction according to the equation:

$$CO + H_2O \text{ ---> } CO_2 + H_2 \qquad (4)$$

In steam reforming, desulfurized hydrocarbonaceous feedstock is mixed with between two and four moles of steam per mole of carbon and introduced into catalyst-filled tubes in a primary reforming furnace, where it is converted to synthesis gas containing mainly hydrogen, carbon monoxide, carbon dioxide and residual methane and steam. The composition of the synthesis gas at the exit of the reforming furnace is dependent on the steam-to-feedstock ratio at the inlet and the temperature and pressure at the outlet of the reforming furnace. Employing a high steam-to-gas ratio and a high temperature to increase production, however, also increases reformer fuel requirements, and low pressure operation increases the compression power requirement of the synthesis gas compressor which delivers the relatively low pressure synthesis gas into the higher pressure methanol synthesis loop. Typically, steam-to-carbon (in the feedstock) molar ratios in the range from 2.8:1 to 3.5:1 have been used with a reformer tube exit temperature in the range from 850°C to 888°C and an exit pressure in the range from 15 to 25 bar.

Under these operating conditions, the residual methane content in the synthesis gas is approximately 3-4 mole% (dry basis). Waste heat in the hot synthesis gas is recovered by raising steam and preheating boiler feedwater.

The endothermic heat of reaction is supplied by firing burners adjacent the catalyst-filled tubes in the refractory lined reforming furnace. Waste heat in the flue gas is recovered by raising and superheating steam and preheating combustion air. After heat recovery and final cooling, the synthesis gas is compressed in a centrifugal compressor to between 50 and 100 bar.

The fresh synthesis gas joins the gases circulating in the methanol synthesis loop at the suction of the circulation compressor. From the discharge of the circulation compressor, the bulk of the circulating gases are preheated to the reaction temperature of 210° to 270°C and fed to a catalytic methanol synthesis reactor. Formation of methanol at the operating conditions of the synthesis reactor is low, typically only 3.0-7.0%, depending upon the selected pressure of operation. This leads to the requirement for a circulating loop system where the reactants pass over the catalyst a number of times.

Gases leaving the reactor are used to preheat the circulating gas being fed to the reactor before crude methanol is condensed in a cooler and separated in a knock-out drum. The remaining gases return to the circulating compressor after removal of a purge gas stream by which the level of inert methane and excess hydrogen in the synthesis loop is controlled. The purge stream is utilized as fuel in the reforming furnace. Crude methanol is discharged via a let down valve to a low pressure separator where dissolved gases flash off and are passed to the reformer fuel system. The crude methanol is purified in a distillation system.

Conventional steam reforming processes produce a synthesis gas which is hydrogen rich for methanol synthesis. This excess hydrogen has to be compressed to methanol loop pressure and then purged from the loop to be used as fuel in the reforming furnace.

Steam reforming can be supplemented by autothermal reforming to produce a stoichiometric synthesis gas according to the following reactions:

$$CH_4 + H_2O \;{-}{-}{-}{>}\; CO + 3H_2 \qquad (2)$$

$$CO + H_2O \;{-}{-}{-}{>}\; CO_2 + H_2 \qquad (4)$$

$$CH_4 + \tfrac{1}{2}O_2 \;{-}{-}{-}{>}\; CO + 2H_2 \qquad (3)$$

$$CO + \tfrac{1}{2}O_2 \;{-}{-}{-}{>}\; CO_2 \qquad (5)$$

$$H_2 + \tfrac{1}{2}O_2 \;{-}{-}{-}{>}\; H_2O \qquad (6)$$

Desulfurized natural gas feedstock is split into two streams. The first stream is mixed with steam and introduced into the primary steam reformer. As excess methane is oxidized in the downstream secondary reformer, the primary reformer can be operated at higher pressure, lower temperature and lower steam to gas ratios than in the case of the single primary reforming furnace route. The synthesis gas from the primary steam reformer is mixed with the second stream of natural gas feedstock and introduced into the secondary reformer with preheated oxygen. Heat of reaction in the secondary reformer is supplied by combustion of methane, hydrogen and carbon monoxide. The exit temperature of the secondary reformer is typically 950-1000°C. Waste heat in the hot synthesis gas is recovered by raising steam, preheating boiler feedwater and providing distillation reboiler heat. Waste heat in the flue gas from the primary steam reformer is recovered by superheating steam, preheating feedstock and combustion air. The reduced flow rate of make-up synthesis gas is at a higher pressure than in the conventional route and therefore requires significantly less compression power. The methanol synthesis process is similar to that described above in conjunction with the steam reforming route.

Since reforming is carried out in the primary and secondary reformers, the size of the primary reforming furnace can be reduced by as much as 75%. The total natural gas usage (feedstock plus fuel) is reduced by approximately 6% due to reduced fuel requirement in the primary reforming furnace and reduced feedstock requirements as a result of more efficient utilization of the carbon contained in the feedstock. The capital cost is also reduced when compared to the conventional route as a result of the reduction in primary reforming furnace size, gas volumetric flow rates and compression power.

The autothermal reforming step requires a relative large volume of catalyst. Typically, space velocity requirements are between 8,000 and 12,000 hr.$^{-1}$ As used herein "space velocity" means the volumetric hourly throughput per volume of catalyst and the figures quoted herein refer to standard conditions of pressure and temperature.

Partial oxidation of hydrocarbonaceous feedstock represents one alternative to steam reforming in the production of synthesis gas. The partial oxidation processes that have been used in connection with methanol production have been non-catalytic processes. Non-catalytic partial oxidation reactions, however, are relatively inefficient. They operate at high temperatures, i.e., in the range of 2,200°F to 2,800°F (1205°C to 1340°C) and require large amounts of oxygen. Furthermore, free carbon is produced which is removed in a later step.

In methanol production processes of the prior art that employ partial oxidation, the feedstock is compressed to approximately 30-80 bar, heated and introduced to a partial oxidation generator. Preheated oxygen is injected into the generator burner. It has been reported that the feedstock is converted to carbon rich synthesis gas according to the following reactions:

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad (7)$$

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad (2)$$

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \quad (8)$$

The endothermic heat of reaction for the reforming reactions (2) and (8) is supplied by the combustion of some methane, reaction (7). This combustion reaction is highly exothermic. Heat contained in the synthesis gas leaving the generator at approximately 1400°C is recovered by raising steam before the gas is passed to a carbon scrubber where free carbon is removed.

In order to adjust the carbon/hydrogen ratio in the synthesis gas to that required for methanol synthesis, it is necessary to reduce carbon oxides such as by shifting carbon monoxide to carbon dioxide according to the reaction

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (4)$$

and then removing carbon dioxide by any of the conventional or proprietary acid gas removal processes, or by removing the carbon monoxide directly by pressure swing adsorption. Following additional heat recovery and adjustment of the carbon/hydrogen ratio, the synthesis gas is compressed to synthesis loop pressure. Since the gas is stoichiometric and at considerably higher pressure, the power required for synthesis gas compression is reduced. The saving in synthesis gas compression, however, does not necessarily result in overall cost savings. As a result of the higher generator operating pressure, oxygen compression costs are increased, and it is often necessary to include a natural gas compressor. This results in a net increase in power requirements, since substantial power, although reduced, is still required to run the methanol process gas compressor.

The additional power requirement and the less efficient utilization of carbon contained in the feedstock result in an increase in specific natural gas requirements (i.e. natural gas consumed per unit of methanol produced) when compared to the conventional steam reforming process.

Conversion efficiency of oxidation processes can generally be improved by the use of catalysts; but where the oxidation process in only partial, i.e. with insufficient oxygen to completely oxidize the hydrocarbon, then the catalyst is subject to carbon deposit and blockage. Carbon deposits can be avoided by using expensive catalyst materials in generally uneconomical processes. For example, U.S. Patent 4,087,259, issued to Fujitani et al., describes employment of a rhodium catalyst in a process wherein liquid hydrocarbonaceous feedstock is vaporized and then partially oxidized in contact with the rhodium catalyst at a temperature in the range of 690° to 900°C with optional steam added as a coolant at rate not more than 0.5 by volume relative to the volume of the liquid hydrocarbon in terms of the equivalent amount of water. The rhodium catalyst enables partial oxidation without causing deposition of carbon, but at temperatures greater than 900°C, thermal decomposition ensues producing ethylene or acetylene impurities. When steam is added, the quantity of hydrogen produced is increased while the yield of carbon monoxide remains constant due to catalytic decomposition of the steam to hydrogen gas and oxygen. A "LHSV" (Liquid Hourly Space Velocity) from 0.5 to 25 1/hour is disclosed; particularly, a high yield from partial oxidation of gasoline vapor, without steam, is produced at a temperature of 725°C and at a LHSV of 20, and with steam, is produced at temperatures of 700°C and 800°C and at a LHSV of 2.

The use of catalysts in partial oxidation processes requires that the reaction be carried out within a specific range of space velocity. In order to obtain acceptable levels of conversion using catalytic partial oxidation processes of the prior art it has been necessary to use space velocities below about 12,000 hr.$^{-1}$ For example, U.S. Patent No. 4,522,894, issued to Hwang et al., describes the production of a hydrogen-rich gas to be used as fuel for a fuel cell. The process reacts a hydrocarbon feed with steam and an oxidant in an autothermal reformer using two catalyst zones. The total hourly space velocity is between 1,960 hr.$^{-1}$ and 18,000 hr.$^{-1}$. Because the prior art processes must be carried out at low space velocity, catalytic partial oxidation reactors of the prior art have had to have large catalyst beds in order to achieve the throughput desired in commercial operation. This increases the size and cost of the partial oxidation reactor.

It is an object of the present invention to provide a process for the production of methanol from hydrocarbonaceous feedstock which is energy efficient, is capable of using low cost catalysts and employs relatively small, inexpensive equipment volume to achieve commercially acceptable throughput.

It is a further object of the invention to provide a process for the production of methanol from hydrocarbonaceous feedstock with a relatively low oxygen demand, thereby increasing throughput of hydrocarbonaceous feed.

These and other objects of the invention are achieved by a process which is described below.

Summary of the Invention

The invention provides a process for producing methanol from hydrocarbonaceous feedstock in a manner which uses relatively smaller and less costly equipment and operates at a relatively higher level of efficiency, in terms of feedstock conversion, than prior art processes for methanol production.

This invention provides a process for the production of methanol in which synthesis gas is generated by the catalytic partial oxidation of a hydrocarbonaceous feedstock, such as natural gas, with an oxidant stream under temperature and steam conditions producing essential no free carbon at a space velocity in the range from 20,000 hour^{-1} to 500,000 hour^{-1}; hydrogen, carbon monoxide and carbon dioxide in the synthesis gas are reacted under methanol-producing conditions; and methanol is recovered. If necessary, the ratio of hydrogen to carbon monoxide and carbon dioxide in the synthesis gas is adjusted by removal of carbon monoxide and/or carbon dioxide to provide the proper stoichiometric amounts of reactants for the methanol production reaction.

In one embodiment, the invention provides a process for producing methanol from hydrocarbonaceous feedstock which comprises:

(a) introducing to a catalytic partial oxidation zone a gaseous mixture of a hydrocarbonaceous feedstock, oxygen or an oxygen-containing gas and, optionally, steam in which the steam-to-carbon molar ratio is from 0:1 to 3.0:1 and the oxygen-to-carbon molar ratio is from 0.4:1 to 0.8:1, said mixture being introduced to the catalytic partial oxidation zone at a temperature not lower than 200°F (93°C) below its autoignition temperature and preferably at or above its autoignition temperature;

(b) partially oxidizing the hydrocarbonaceous feedstock in the catalytic partial oxidation zone to produce a gas consisting essentially of methane, carbon oxides, hydrogen and steam by passing the mixture through a catalyst capable of catalyzing the oxidation of the hydrocarbons, said catalyst having a ratio of surface area to volume ratio of at least 5 cm^2/cm^3 and a volume sufficient to produce a space velocity in the range from 20,000 $hour^{-1}$ to 500,000 $hour^{-1}$;

(c) reacting the hydrogen, carbon dioxide and carbon monoxide under methanol-producing conditions, thereby producing a product stream containing methanol; and

(d) recovering the methanol.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is an elevated cross-section view of a catalytic partial oxidation reactor having at its input a mixer and distributor suitable for introducing the reactants to the catalyst bed.

FIG. 2 is an enlarged elevational cross-section view of broken-away portion of the mixer and distributor of FIG. 1.

FIG. 3 is a top view of a broken-away quarter section of the mixer and distributor of FIG. 1.

FIG. 4 is a bottom view of a broken-away quarter section of the mixer and distributor of FIG. 1.

FIG. 5 is a diagrammatic elevational cross-sectional illustration of a broken-away portion of the mixer and feeder of FIGS. 1 and 2 showing critical dimensions.

FIG. 6 is a graph plotting oxygen-to-carbon molar ratio vs. steam-to-carbon molar ratio in the catalytic partial oxidation reaction for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

FIG. 7 is a graph plotting the hydrogen-to-carbon monoxide molar ratio in the catalytic partial oxidation reaction product vs. the steam-to-carbon molar ratio for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

FIG. 8 is the graph plotting the volume % methane in the catalytic partial oxidation product vs. the steam-to-carbon molar ratio for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

FIG. 9 is a graph plotting the volume % carbon dioxide in the catalytic partial oxidation product vs. steam-to-carbon molar ratio for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

FIG. 10 is a graph plotting the molar ratio of total hydrogen and carbon monoxide in the catalytic partial oxidation product to total hydrogen and carbon vs. steam-to-carbon molar ratio in the feedstock for three different operating temperatures at an operating pressure of 400 psig (2760 KPa).

FIG. 11 is a flow diagram of a process for producing methanol from a hydrocarbonaceous feedstock in accordance with the invention

FIG. 12 is a sectional view of a tube cooled converter for use in producing methanol in accordance with the invention.

FIG. 13 is a process flow diagram of a first portion of a large methanol plant in accordance with the invention.

FIG. 14 is a process flow diagram of a second portion of the large methanol plant of FIG. 13.

FIG. 15 is a process flow diagram of a third portion of the large methanol plant of FIG. 13.

FIG. 16 is a process flow diagram of a first portion of a small methanol plant in accordance with the invention.

FIG. 17 is a process flow diagram of a second portion of the small methanol plant of FIG. 16.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Essentially, the process of the invention involves three steps: conversion of the hydrocarbonaceous feedstock into synthesis gas containing hydrogen, carbon dioxide and carbon monoxide by catalytic partial oxidation under temperature and steam conditions avoiding production of free carbon; reaction of the hydrogen, carbon dioxide and carbon monoxide under methanol producing conditions; and recovery of methanol. Additionally, it may be necessary to adjust the molar ratio of hydrogen to carbon dioxide and carbon monoxide in the gas undergoing conversion to methanol, in order to provide stoichiometric amounts of these reactants in the methanol synthesis step. This may be done at any of three points in the process.

Catalytic Partial Oxidation

The catalytic partial oxidation of hydrocarbonaceous feedstock is carried out according to a process described in copending, commonly assigned U.S. application Serial No. 085,160 filed August 14, 1987 in the names of M. Dunster and J.D. Korchnak.

One particular aspect of the invention is the substantial capital cost savings and/or advantageous operating economy resulting from the employment of catalytic partial oxidation to produce the raw synthesis gas employed in the methanol producing process. This is made possible by the discovery that catalytic partial oxidation performed at a temperature, as measured at the exit of the catalytic reaction zone, equal to or greater than a minimum non-carbon-forming temperature equal to or greater than a minimum temperature selected as a linear function which includes a range from 1600°F (870°C) to 1900°F (1040°C) corresponding to a range of the steam-to-carbon molar ratio from 0.4:1 to 0:1 and at a space velocity in the range from

20,000 hour^{-1} to 500,000 hour^{-1} produces essentially no free carbon deposits on the catalyst. Further, it is found that products of the partial catalytic oxidation in the process of the invention consist essentially of hydrogen, carbon monoxide and carbon dioxide at oxidation temperatures equal to or greater than the minimum temperature, rhodium catalysts are not required to prevent carbon formation. For example in FIG. 6, dotted line 25 represents a generally linear function which, at a steam/carbon ratio of 0, corresponds to a minimum partial oxidation temperature of about 1900°F (1040°C), and at a steam/carbon ratio of 0.4 corresponds to a minimum partial oxidation temperature of about 1600°F (870°C); favorable catalytic partial oxidation without producing free carbon occurs at temperatures and steam/carbon ratios equal to or greater than points on the line. Further, lower minimum temperatures at corresponding steam/carbon ratios greater than 0.4 can be extrapolated from the linear function represented by line 25.

Generally the catalytic partial oxidation is performed at a temperature, as measured at the exit of the catalyst, in the range from 1400°F (760°C) to 2300°F (1260°C). Preferably, the catalytic partial oxidation temperature, as measured at the exit, is in the range from 1600°F (870°C) to 2000°F (1090°C). At temperatures below about 1400°F (760°C), uneconomic quantities of methane are left unconverted, and at temperatures above 2300°F (1260°C), excessive amounts of oxygen are used.

The pressure at which the partial oxidation takes place is generally above 150 psig (1030 KPa) and preferably above 300 psig (2060 KPa). The pressure can be up to or above the methanol synthesis loop pressure. Preferably, the pressure does not exceed the methanol synthesis loop pressure by more than that necessary to provide synthesis gas flow through the processing equipment into the methanol synthesis loop.

Essentially little or no reforming reactions are employed in the process of the invention; that is, the process of the invention relies essentially solely on partial oxidation and the water gas shift reaction (equation 4) to convert hydrocarbonaceous feedstock to synthesis gas. Catalytic partial oxidation of uniformly premixed feedstock and oxygen does not require any reforming reactions to take place. The catalyst is selected to promote the partial oxidation reaction, and not necessarily any reforming reaction. The steam reforming reaction (equation 3) generally requires a low space velocity, i.e. generally below about 12,000 hour^{-1}, and the employment of space velocities above 20,000 hour^{-1} in the present process precludes efficient steam reforming of the feedstock. It is believed that increased hydrogen production, above that attributable solely to partial oxidation, is due more to the water gas shift reaction (equation 4) than to the steam reforming reaction (equation 2).

The process of the invention can be employed to convert hydrocarbonaceous feedstock to synthesis gas with very low levels of hydrocarbon slippage (unreacted feedstock), i.e. as low as 2% or lower, if desired. Because the rate of reaction in the partial oxidation reactor is mass transfer controlled, the process of the invention can be carried out efficiently using relatively small volumes and relatively inexpensive catalyst materials, provided that the surface area-to-volume requirements of the invention are met. In accordance with the process of the invention the reactant gases are introduced to the reaction zone, i.e. the catalyst bed, at an inlet temperature not lower than 200°F (93°C) less than the autoignition temperature of the feed mixture. The autoignition temperature of the feed depends on the composition and conditions of the feed mixture and on the catalyst employed. Preferably the reactant gases are introduced at a temperature at or above the autoignition temperature of the mixture. A further essential feature of the catalytic partial oxidation reaction is that the reactants shall be completely mixed prior to the reaction taking place. Introducing the thoroughly mixed reactant gases at the proper temperature ensures that the partial oxidation reactions will be mass transfer controlled. Consequently, the reaction rate is relatively independent of catalyst activity, but dependent on the surface-area-to-volume ratio of the catalyst. It is possible to use any of a wide variety of materials as a catalyst, provided that the catalyst has the desired surface-area-to-volume ratio. It is not necessary that the catalyst have specific catalytic activity for the steam reforming reaction. Even materials normally considered to be non-catalytic can promote the production of synthesis gas under the reaction conditions specified herein when used as a catalyst in the proper configuration. The term "catalyst", as used herein, is intended to encompass such materials.

The catalytic partial oxidation step can be understood with reference to the figures. The catalytic partial oxidation zone is typically the catalyst bed of a reactor such as that illustrated in FIG. 1. As shown in FIG. 1, a reactor for partially oxidizing a gaseous feedstock includes an input mixing and distributor section indicated generally at 30. The mixer and distributor 30 mixes the feedstock with an oxidant and distributes the mixture to the entrance of a catalytic reactor section indicated generally at 32 wherein the feedstock is partially oxidized to produce a product which is then passed through the exit section indicated generally at 34.

The reactor includes an outer shell 40 of structural metal such as carbon steel with a top 42 secured thereon by bolts (not shown) or the like. A layer 43 of insulation, such as 2300°F (1260°C) BPCF ceramic fiber insulation, is secured to the inside of the upper portion of the shell 40 including the top 42. In the lower portion of the mixing section 30 in the reactor section 32 and outlet section 34, there are secured layers 46, 48 and 50 on the inside of the shell. The layer 46 is a castable or equivalent insulation such as 2000°F (1090°C) ceramic insulation. The layer 48 is also a castable or equivalent layer of insulation but containing 60% alumina for withstanding 3000°F (1650°C). The internal layer 50 is a refractory or equivalent layer such as 97% alumina with ceramic anchors or 97% alumina brick for withstanding the interior environment of the reactor section.

The catalytic reactor section 32 contains one or more catalyst discs 54. As shown, the reactor contains a sequence of discs 54 separated by high alumina rings 58 between each adjacent pair of discs. The stack is supported by a grill with high alumina bars 56. A sample port 60 is formed in the lower end of the reaction section and has a tube, such as type 309 stainless steel tube 62 extending below the bottom refractory disc 54 for withdrawing samples of the product.

The outlet section 34 is suitably formed for being connected to a downstream heat recovery boiler (not shown) and/or other processing equipment.

The catalyst comprises a high surface area material capable of catalyzing the partial oxidation of the hydrocarbonaceous feedstock. The catalyst is in a configuration that provides a surface area to volume ratio of at least 5 cm^2/cm^3. Preferably, the catalyst has a geometric surface area to volume ratio of at least 20 cm²/cm³. While there is no strict upper limit of surface area to volume ratio, it normally does not exceed about 40 cm²/cm³. A wide variety of materials can be used in the construction of the catalyst including materials not normally considered to have catalytic activity, provided that the catalyst configuration has the desired surface area to volume ratio.

The catalyst disc 54 can be, for example, a monolithic structure having a honeycomb type cross-sectional configuration. Suitable monolithic structures of this type are produced commercially, in sizes smaller than those used in the process of the invention, as structural substrates for use in the catalytic conversion of automobile exhausts and as catalytic combustion chambers of gas turbines or for catalytic oxidation of waste streams. Typically, the monolithic structure is an extruded material containing a plurality of closely packed channels running through the length of the structure to form a honeycomb structure. The channels are typically square and may be packed in a density as high as 1,200 per square inch of cross section. The monolithic structure can be constructed of any of a variety of materials, including cordierite ($MgO/Al_2O_3/SiO_2$), Mn/MgO cordierite ($Mn-MgO/Al_2O_3/SiO_2$), mullite (Al_2O_3/SiO_2), mullite aluminum titanate ($Al_2O_3/SiO_2-(Al,Fe)_2O_3/TiO_2$), zirconia spinel ($ZrO_2/MgO/Al_2O_3$), spinel ($MgO/Al_2O_3$), alumina ($Al_2O_3$) and high nickel alloys. The monolithic catalyst may consist solely of any of these structural materials, even though these materials are not normally considered to have catalytic activity by themselves. Using honeycombed substrates, surface area to volume ratios up to 40 cm²/cm³ or higher can be obtained. Alternatively, the monolithic substrate can be coated with any of the metals or metal oxides known to have activity as oxidation catalysts. These include, for example, palladium, platinum, rhodium, iridium, osmium, ruthenium, nickel, chromium, cobalt, cerium, lanthanum and mixtures thereof. Other metals which can be used to coat the catalyst disc 54 include noble metals and metals of groups IA, IIA, III, IV, VB, VIB, or VIIB of the periodic table of elements.

The catalyst discs 54 may also consist of structural packing materials, such as that used in packing absorption columns. These packing materials generally comprise thin sheets of corrugated metal tightly packed together to form elongate channels running therethrough. The structural packing materials may consist of corrugated sheets of metals such as high temperature alloys, stainless steels, chromium, manganese, molybdenum and refractory materials. These materials can, if desired, be coated with metals or metal oxides known to have catalytic activity for the oxidation reaction, such as palladium, platinum, rhodium, iridium, osmium, ruthenium, nickel, chromium, cobalt, cerium, lanthanum and mixtures thereof.

The catalyst discs 54 can also consist of dense wire mesh, such as high temperature alloys or platinum mesh. If desired, the wire mesh can also be coated with a metal or metal oxide having catalytic activity for the oxidation reaction, including palladium, platinum, rhodium, iridium, osmium, ruthenium, nickel, chromium cobalt, cesium, lanthanum and mixtures thereof.

The surface area to volume ratio of any of the aforementioned catalyst configurations can be increased by coating the surfaces thereof with an aqueous slurry containing about 1% or less by weight of particulate metal or metal oxide such as alumina, or metals of groups IA, IIA, III, IV VB, VIB and VIIB and firing the coated surface at high temperature to adhere the particulate metal to the surface, but not so high as to cause sintering of the surface. The particles employed should have a BET

(Brunnauer-Emmett-Teller) surface area greater than about 10 m²/gram, preferably greater than about 200 m²/gram.

A gaseous mixture of hydrocarbonaceous feedstock, oxygen or an oxygen-containing gas such as air, and, optionally, steam is introduced into the catalytic partial oxidation zone at a temperature not lower than 200°F (93°C) below its autoignition temperature. Preferably, the gaseous mixture enters the catalytic partial oxidation zone at a temperature equal to or greater than its autoignition temperature. It is possible to operate the reactor in a mass transfer controlled mode with the reactants entering the reaction zone at a temperature somewhat below the autoignition temperature since the heat of reaction will provide the necessary energy to raise the reactant temperature within the reaction zone. In such a case, however, it will generally be necessary to provide heat input at the entrance to the reaction zone, for example by a sparking device, or by preheating the contents of the reactor, including the catalyst, to a temperature in excess of the autoignition temperature prior to the introducing of the reactants in order to initiate the reaction. If the reactant temperature at the input to the reaction zone is lower than the autoignition temperature by more than about 200°F (93°C), the reaction becomes unstable.

When the reactant mixture enters the catalytic partial oxidation zone at a temperature exceeding its autoignition temperature, it is necessary to introduce the mixture to the catalyst bed immediately after mixing; that is, the mixture of hydrocarbonaceous feedstock and oxidant should preferably be introduced to the catalyst bed before the autoignition delay time elapses. It is also essential that the gaseous reactants be thoroughly mixed. Failure to mix the reactants thoroughly reduces the quality of the product and can lead to overheating. A suitable apparatus for mixing and distributing the hydrocarbonaceous feedstock and oxygen or oxygen-containing gas so as to provide thorough mixing and to introduce the heated reactants into the reaction zone in a sufficiently short time is illustrated in Figs. 1-5 and described in more detail in copending commonly assigned U.S. patent application Serial No. 085,159 filed August 14, 1987 in the names of J.D. Korchnak, M. Dunster and J.H. Marten.

Referring to Fig. 1, one of the feed gases, i.e. hydrocarbonaceous gas or oxygen-containing gas, is introduced into the input section 30 through a first inlet port 66 through the top 42 which communicates to an upper feed cone 68 which forms a first chamber. The cone 68 is fastened by supports 69 in the top 42. The other feed gas is introduced into the input section 30 through second inlets 70 extending through side ports of the shell 40 and communicating to a second chamber 72 which is interposed between the upper chamber 68 and the inlet of the catalyst reaction section 32. A ring 73 mounted on the central portion of an upper wall 75 of the chamber 72 sealingly engages the lower edge of the cone 68 so that the wall 82 forms a common wall between the upper chamber 68 and lower chamber 72. The chamber 72 has an upper outer annular portion 74, see also Figs. 2 and 3, which is supported on the top surface of the refractory layer 50. A lower portion of the chamber 72 has a tubular wall 76 which extends downward in the refractory sleeve 50. The bottom of the chamber 76 is formed by a cast member 78.

Optionally, steam can be introduced into either or both of the hydrocarbonaceous feedstock and oxygen or oxygen-containing gas. The gases are fed to the reactor in relative proportions such that the steam-to-carbon molar ratio is in the range from 0:1 to 3.0:1, preferably from 0.8:1 to 2.0:1. The oxygen-to-carbon ratio is from 0.4:1 to

0.8:1, preferably from 0.45 to 0.65. Although air may be used as the oxidant in the process of the invention, it is preferred to use oxygen or an oxygen-rich gas, in order to minimize the inert ingredients such as nitrogen that must be carried through the system. By "oxygen-rich" is meant a gas containing at least 70 mole.% oxygen, preferably at least 90 mole.% oxygen.

The reactant mixture preferably enters the catalytic reactor section 32 at a temperature at or above its autoignition temperature. Depending on the particular proportions of reactant gases, the reactor operating pressure and the catalyst used, this will generally be between about 550°F (290°C) and 1,100°F (590°C). Preferably, hydrocarbonaceous feedstock and steam are admixed and heated to a temperature from 650°F (340°C) to 1,200°F (650°C) prior to passage through inlet port(s) 70 or 66. Oxygen or oxygen-containing gas, such as air, is heated to a temperature from 150°F (65°C) to 1200°F (650°C) and passes through the other inlet port(s) 66 or 70.

Referring again to FIG. 1, the mixing and distributing means comprises a plurality of elongated tubes 80 having upper ends mounted in the upper wall 75 of the chamber 72. The lumens of the tubes at the upper end communicate with the upper chamber 68. The bottom ends of the tubes 80 are secured to the member 78 with the lumens of the tubes communicating with the upper ends of passageways 84 formed vertically through the member 78. Orifices 86 are formed in the walls of the tubes 80 for directing streams of gas from the chamber 72 into the lumens of the tubes 80. The inlets 66 and 70, the cone 68, the supports 69 are formed from a conventional corrosion and heat resistant metal while the chamber 72, tubes 80 and member 78 are formed from a conventional high temperature alloy or refractory type material.

The number of tubes 80, the internal diameter 90 (see FIG. 5) of the tubes 80, the size and number of the orifices 86 in each tube are selected relative to the gas input velocities and pressures through inlets 66 and 70 so as to produce turbulent flow within the tubes 80 at a velocity exceeding the flashback velocity of the mixture. The minimum distance 92 of the orifices 86 from the bottom end of the tube 80 at the opening into the diverging passageways 84 is selected to be equal to or greater than that required for providing substantially complete mixing of the gas streams from chambers 68 and 72 under the conditions of turbulence therein. The size of the internal diameter 90 of the tubes 80 as well as the length 94 of the tubes is designed to produce a sufficient pressure drop in the gas passing from the chamber 68 to the reaction chamber so as to provide for substantially uniform gas flow through the tubes 80 from the chamber 68. Likewise the size of the orifices 86 is selected to provide sufficient pressure drop between the chamber 72 and the interior of the tubes 80 relative to the velocity and pressures of the gas entering through inlets 70 so as to provide substantially uniform volumes of gas flows through the orifices 86 into the tubes 80.

The diverging passageways in the member 78 are formed in a manner to provide for reduction of the velocity of the gas to produce uniform gas distribution over the inlet of the catalyst. The rate of increase of the cross-section of the passageway 84 as it`proceeds downward, i.e., the angle 98 that the wall of the passageway 84 makes with the straight wall of the tubes 80, must generally be equal to or less than about 15° and preferably equal to or less than 7° in order to minimize or avoid creating vortices within the passageways 84. This assures that the essentially completely mixed gases, at a temperature near to or exceeding the autoignition temperature, will pass into the catalyst bed in a time preferably less than autoignition delay time. The configuration of the bottom end of the passageways, as shown in FIG. 4, is circular.

The gas exiting the catalytic partial oxidation reactor contains hydrogen, carbon dioxide, carbon monoxide and some methane. The synthesis gas leaving the catalyst zone is first cooled by heat exchange, either by heating the hydrocarbon and steam feed stock, by heating the oxidant stream, by super heating steam, by raising steam in a boiler, by preheating boiler feed water or any combination thereof.

Adjustment of Hydrogen to Carbon Oxide Ratio

The gas stream that is converted to methanol in the methanol synthesis loop contains hydrogen and carbon oxides, i.e. carbon dioxide and carbon monoxide. The molar ratio of hydrogen to carbon oxides in the gas to be converted can be expressed as the methanol stoichiometric synthesis gas ratio (MSSGR). The MSSGR is defined as the following molar ratio:

$$\text{MSSGR} = \frac{H_2}{2\,CO + 3CO_2}$$

The MSSGR should have a value of at least 0.8 and preferably from about 0.95 to 1.1 for methanol synthesis. Normally, the synthesis gas from the catalytic partial oxidation reactor will be slightly carbon-rich, that is, the MSSGR is somewhat lower than that ideally desired. In order to correct the stoichiometry, carbon is removed, either from the synthesis gas passing to the methanol synthesis loop, the methanol loop or the purge gas from the methanol synthesis loop.

Carbon dioxide can be removed from the synthesis gas stream by any know method. For example, the gas stream can be passed through a countercurrent liquid stream of a carbon dioxide absorbing medium. Commercial processing units for carbon dioxide removal are available, for example, under the trademarks Selexol, Amine Guard, and Benfield

Since the amount of carbon dioxide in the synthesis gas is relatively small it may be necessary to remove a portion of the carbon monoxide in order to achieve the desired MSSGR. Any known method for carbon monoxide removal can be employed. One suitable method involves converting at least a portion of the carbon monoxide to carbon dioxide by water gas shift reaction and then removing the carbon dioxide from the gas stream. The water gas shift reaction is known, and suitable equipment for carrying out the reaction is commercially available.

An alternative method for removing carbon oxides is pressure swing absorption. This procedure can be employed not only to remove the desired amount of carbon monoxide and/or carbon dioxide, but also to remove components of the gas stream that are not required for methanol production such as methane and nitrogen. Pressure swing adsorption involves the adsorption of components to be removed at high pressure followed by their desorption at low pressure. The process operates on a repeated cycle having two basic steps, adsorption and regeneration. Not all the hydrogen is recovered as some is lost in the waste gas during the regeneration stage, but by careful selection of the frequency and sequence of steps within the cycle the recovery of hydrogen is maximized.

Regeneration of the adsorbent is carried out in three basic steps.

(a) The adsorber is depressurized to the low pressure. Some of the waste components are desorbed during this step.

(b) The adsorbent is purged at low pressure, with the product hydrogen removing the remaining waste components.

(c) The adsorber is repressurized to adsorption pressure ready for service.

Pressure swing adsorption is most effectively employed to remove carbon oxides and inert materials, for example, methane and nitrogen, from the methanol synthesis loop.

Methanol Synthesis

The hydrogen, carbon dioxide and carbon monoxide are reacted under methanol-producing conditions. Any known procedure for reacting hydrogen, carbon dioxide and carbon monoxide to produce methanol can be used. Preferably, they are reacted in a medium pressure process in a circulating catalytic reactor at a pressure from about 50 atm (5070 KPa) to 120 atm (12160 KPa), more preferably from about 70 atm (7090 KPa) to 100 atm (10130 KPa). This type of synthesis and equipment for carrying it out are known in the art.

The synthesis gas is compressed to between 50 atm (5070 KPa) and 120 atm (12160 (KPa), preferably between 70 atm (7090 KPa) and 100 atm (10130 KPa). The gas enters a methanol synthesis vessel in which it is admixed with recycle gas. The gas then passes into a catalytic methanol converter. The methanol converter typically comprises a pressure vessel containing a catalyst bed and facilities for moderating the exothermic reaction of hydrogen with the carbon oxides to produce methanol, for example by injecting cold gas at intervals within the catalyst bed.

Any commercially available catalyst which is capable of catalyzing the reaction of hydrogen, carbon monoxide and carbon dioxide to produce methanol can be employed. Such catalysts are manufactured, for example, by Imperial Chemical Industries, Katalco, and Haldor Topsoe, Inc. Preferred catalysts for methanol synthesis are composed of zinc oxide and copper oxide. The methanol synthesis reaction generally takes place at a temperature in the range from about 410°F (210°C) to 570°F (300°C), depending on the activity of the particular catalyst employed.

The exit gas from the methanol converter is passed through a condenser in which it is cooled with water and then through a separator. The bottoms product of the separator contains methanol condensate. An amount of gas is purged from the methanol synthesis loop in order to maintain the concentration of inert gases circulating within the loop at acceptable levels. The remaining gas is admixed with incoming synthesis gas to be recycled to the methanol converter.

As previously indicated, carbon monoxide and/or carbon dioxide can be removed either from the circulating gas in the methanol synthesis loop or from the purge gas in order to maintain the desired MSSGR, preferably between 0.96 and 1.10, entering the converter. When carbon oxides are removed from the purge gas, the remaining hydrogen-rich gas is recycled to the methanol synthesis loop.

The crude methanol containing water is then purified by conventional means to obtain essentially pure methanol. Preferably, the methanol condensate is purified in one or more distillation columns.

The process of the invention can be understood further by reference to the flow diagram of FIG. 11.

When compared to present day commercial processes, the catalytic partial oxidation process offers the following advantages.

(1) The high cost steam reforming furnace is eliminated.

(2) Low catalyst volume when compared to either steam reforming or autothermal reforming.

(3) Low oxygen consumption when compared to conventional non-catalytic partial oxidation processes.

(4) Low water consumption when compared to steam reforming or steam reforming plus autothermal reforming. The process is therefore particularly suitable either when water is not available (e.g. in desert locations) or is expensive (e.g. must be produced by desalination).

(5) Reduced area requirement when compared to the steam reforming route to methanol (particularly suitable for offshore application).

(6) High efficiency in terms of feedstock conversion when compared to present processes (either reforming or partial oxidation).

(7) Lower in capital cost then all present commercial processes.

A process flow diagram of a methanol plant designed for maximum efficiency is shown in FIGS. 13-15. Hydrocarbonaceous feedstock, such as natural gas stream 200, FIG. 14, is optionally desulfurized using conventional methods. Desulfurization may, for example, be conveniently carried out by preheating the hydrocarbonaceous feedstock to a temperature between about 250°F (120°C) and 750°F (400°C) and absorbing the sulfur compounds into zinc oxide contained in one or several desulfurization vessels 202. The desulfurization vessel 202 is located upstream of a feedstock saturator 204 in the embodiment shown in FIG. 14; alternatively, the desulfurization vessel 202 can be located downstream of the synthesis gas compressor, as shown in the embodiment in FIG. 16.

The desulfurized hydrocarbonaceous feedstock is saturated with water vapor in the forced film saturator 204. The forced film saturator 204 is a distinctive feature of the process and results in reduced capital cost and power requirements when compared with the more conventional packed tower type of saturator presently employed in commercial installations. The forced film saturator 204 consists of a vertical shell and tube exchanger and a water circulation system 206. The desulfurized hydrocarbonaceous feedstock and water enter the top head 208 of the exchanger and flow vertically downward through the tubes 210. The feedstock is heated as it flows though the tubes, for example to a temperature of about 400°F (206°C), and as it is heated, its water vapor content increases due to vaporization of the circulating water. The heating medium, in this case methanol reactor effluent gas stream 330, passes to the shell side of the tubes 210 in the forced film saturator at the bottom and flows countercurrent to the feedstock flow to emerge at a lower temperature at the top outlet of the shell. The desulfurized hydrocarbonaceous feedstock and unvaporized water emerge from the exchanger tubes 210 at the bottom and are separated in the bottom head 212. Recovered water is recirculated by the pump 206 to the top 208 of the forced film saturator and the saturated hydrocarbonaceous feedstock passes to saturated feedstock line 220. Makeup water 216 is added to the recycle water stream, and blowdown line 218 for the saturator water recycle stream is provided.

The major advantages of the forced film saturator 204 over the conventional packed bed saturator are: (1) The forced film saturator has a considerably lower water circulation rate and hence lower power consumption. (2) The forced film saturator has a simpler design and consequently improved operability and reliability. (3) The capital cost of the forced film saturator is less than that of the packed bed type.

As shown in FIG. 13, the saturated feedstock passes through line 220 to coil 222 of a fired heater 224 where the saturated feedstock is preheated to a temperature in the range from 650°F (340°C) to 1200°F (650°C), for example to 1100°F (595°C), by combustion of fuel in the fired heater with air. The fuel 225 can be one or more waste gas streams from the methanol plant, such as fusel oil stream 226 from distillation, flash gas stream 228 from the ammonia synthesis loop, PSA purge gas stream 230, and light ends stream 232 from distillation which are combusted with air 227.

The heated saturated feedstock on line 234 from the heater 224 is fed to the catalytic partial oxidation (CPO) reactor 28 where it is mixed with an oxygen or oxygen-containing stream 236 as has been described hereinbefore. The oxygen stream 236 is obtained from an air separation plant 238 and preheated to a temperature in the range from 150°F (65°C) to 1200°F (650°C), for example, 300°F before being mixed with the natural gas and steam feedstock passing to the CPO catalyst. High pressure steam is used to preheat the oxygen in a heat exchanger 240. The main overall reactions taking place within the CPO reactor 28 are the partial oxidation reactions:

$$C_nH_{2n+2} + {}^{n}/_{2}O_2 \text{ ---> } nCO + (n + 1)H_2 \qquad (9)$$

and the water gas shift reaction:

$$CO + H_2O \text{ ---> } CO_2 + H_2 \qquad (4)$$

FIG. 6 shows oxygen consumption for the above process, as a function of the steam-to-carbon molar ratio of natural gas feedstock, for reaction temperatures of 1,600°F (870°C), 1,750°F (950°C) and 1,900°F (1040°C) and an operating pressure of 400 psig (2760 KPa). It can be seen from the graph that oxygen consumption, expressed as oxygen-to-carbon molar ratio, is relatively low for the process of the invention as compared with present commercial partial oxidation processes. The dashed line 25 in FIG. 6 represents the minimum temperature and steam conditions, i.e. the minimum temperature is a linear function of the steam-to-carbon ratio, which have been discovered to prevent formation of carbon deposits on the catalyst. Generally, a lower temperature of reaction is preferred, such as an exit temperature of 1700°F (925°C) at a pressure of about 415 psig (2860 KPa). Conveniently, the saturator 204 provides the total quantity of steam necessary to achieve a steam-to-carbon molar ratio of approximately 1.3 to 1.0 and additional make-up steam is not required to enable the catalytic partial oxidation reaction at the desired temperature in accordance with the invention.

FIG. 7 shows the molar ratio of hydrogen, as H_2, to carbon monoxide in the product as a function of steam-to-carbon ratio for reaction temperatures of 1,600°F (870°C), 1,750°F (950°C) and 1,900°F (1040°C).

FIGS. 8 and 9, respectively, show the amounts of methane and carbon dioxide, as volume %, in the product as a function of steam-to-carbon ratio for reaction temperatures of 1,600°F (870°C), 1,750°F (950°C) and 1,900°F (1040°C).

FIG. 10 shows the effective H_2 production of the process, expressed as total moles of H_2 and carbon monoxide in the product divided by total moles of H_2 and carbon in the feedstock as a function of steam-to-carbon ratio for reaction temperatures of 1,600°F (870°C), 1,750°F (950°C) and 1,900°F (1040°C).

The reactor effluent 244 is first cooled by generating steam in a boiler 246 which receives water from a high pressure steam drum 248 and returns steam to the drum. The drum 248 operates at a high pressure of, for example, about 1550 psig (10700 KPa). Water supply 250 for the steam drum is first heated in coils 252 of the heater 224 and then fed to the drum through line 254. Steam output 256 from the drum 248 is further heated in coils 258 to produce superheated steam 260 which can be used to operate steam turbines or provide heating for process steps. Line 262 to a blow down drum (not shown) provides for blow down of the drum 248.

The reactor effluent is passed by line 264 to distillation column reboiler 266, by line 268 to distillation column reboiler 270, by line 272 to demineralized water heater 274, and by line 276 to synthesis gas cooler 278 for further cooling, for example, to 100°F (38°C), by recovering and utilizing the heat in the synthesis gas. Water in the process stream is condensed and the stream passes to knockout drum 280 where the water 281 is separated from the synthesis gas. Alternative cooling and heat recovery schemes can be used.

After water removal, the synthesis gas in line 282 is mixed with hydrogen 284 from PSA unit 286, FIG. 14, and passes to make-up compressor unit 288 where the synthesis gas is compressed to the methanol loop pressure, for example, to 1220 psig (8410 KPa). The make-up compressor unit of FIG. 13 includes compressor 290, heat exchanger 292, knockout drum 294, and compressor 296 to produce the make-up gas stream 298 which is passed to the methanol synthesis loop in FIG. 14. The compressors 290 and 296 can conveniently share a common steam turbine drive 300 with methanol loop circulator 302, FIG. 14.

The make-up synthesis gas 298 from the compressor unit 288 joins the gas circulating in the methanol synthesis loop at the discharge 304 of the circulator 302. The loop stream 306 is preheated in loop heat interchanger 308 before passing in line 310 to tube cooled methanol converter 312. Start-up heater 314 is provided so that, upon start up of the methanol converter, the incoming process stream can be heated to the reaction temperature until the methanol converter becomes hot enough due to the heat generated by the reaction to heat the incoming gases, whereupon operation of the start-up heater 314 can be discontinued.

The tube cooled converter, shown in detail in FIG. 12, is a distinctive feature of the process and includes a simple gas-to-gas heat exchanger with no high differential pressure tubesheets. The vessel shell 314 is designed to retain the process pressure. Inlet 316 connects through distributor 318 to intermediate branch tubes 320 which, in turn, are connected through distributors 322 to a plurality of tubes 324 extending vertically upward through the catalyst bed 326. The catalyst bed is supported on a bed of ceramic balls 328 which are separated from the outlet 330 by screen support 332. The reactant gas is fed though inlet 316 into the bottom of the converter where it is distributed by distributors 318, intermediate branch tubes 320, and distributors 322 to the vertical tubes 324. The gas is heated as it flows upward by heat exchange through the tube and distributor walls. From the exits 334 of tubes 324 at the top of the vessel, the reactant gas pass downward, through the catalyst, which is packed in the space between the tubes 324. The gas flow through the tubes 324 is countercurrent to the gas flow through the catalyst bed. The temperature profile against methanol concentration is quasi-isothermal and is very favorable in terms of reaction rates and conversion.

The main features of the tube cooled converter are: (1) The design is mechanically simple with no high differential pressure across the tube material and no tubesheet construction problems. (2) Catalyst loading is simple. (3) A single reactor can be constructed capable of producing methanol at high capacity of over 2000 tons

(1,815,000 kg) per day. (4) Methanol synthesis loop circulating gas rates are reduced when compared to a conventional quench type of reactor. (5) Heat recovery is simplified; boiler feedwater preheating, steam raising or feedstock saturation may be employed. (6) Control is simplified. (7) Catalyst volume is reduced.

From the tube cooled converter 312, the effluent gas 330 passes to the shell side of the forced film saturator 204, where the gas is cooled, for example to a temperature of about 340°F (170°C), by heat transfer to the circulating water and incoming natural gas stream flowing through the tubes 210. The converter effluent gas emerges from the saturator in line 336 and passes to the heat exchanger 308 where the effluent gas is further cooled by heat exchange with the loop feed for the converter. Then the gas from the converter is fed over line 338 to loop condenser 340 which is cooled by water to condense the methanol in the methanol loop stream. Condensed methanol is separated from the methanol loop in separator 342, and passed over line 344 to pressure letdown vessel 346 before being passed in crude methanol stream 348 to the distillation section 350 in FIG. 15.

The gas stream 354 from the separator is split into a recycle stream 356 passing to the suction inlet of the circulator 302 and a purge stream 358 taken through valve 360 to maintain the concentration of inert material in the methanol loop at acceptable levels. Hydrogen is recovered from the purge gas stream 358 by the pressure swing adsorption unit 286 to generate the hydrogen recycle stream 284 used to improve stoichiometry of the methanol loop stream. The flash gas 228 is taken through valve 262 and the purge gas 230 is taken from the pressure swing adsorption unit 286 to form a portion of the fuel to the fired heater 224.

In the distillation section 350, FIG. 15, the crude methanol 348 is passed to a distillation column 364 where light end materials such as absorbed gases are removed. The overhead 366 from the column 364 is passed through water cooled condensers 368 and 370 with the condensate passing to drum 372 from which it is drawn by pump 374 to form a reflux stream for the column. The noncondensed light ends 232 are passed as fuel to the fired heater. Bottom streams from the column 364 are recycled through reboilers 266 and 374 heated by the synthesis gas stream and steam, respectively. The methanol stream 378 is passed by pump 380 to distillation column 382 where the stream is separated into the fusel oil stream 226, a water stream 384, and the product methanol stream 386. The distillation column has reboilers 270 and 388 heated by the synthesis gas stream and steam, respectively. The overhead 389 is withdrawn under vacuum produced by vacuum pump system 390. The overhead vapors are condensed by water cooled condenser 392 and separated in reflux drum 394 before being passed by pump 396 back to the distillation column as a reflux stream. The vacuum pump system 390 includes pump 398 circulating water from collector 400 through water cooled heat exchanger 402. Excess water is passed by line 404 from the collector 400 back to the bottom of the distillation column 382. The water stream 384, withdrawn by pump 406 from the bottoms of column 382, is further cooled by heat exchanger before discharge in line 410.

A process flow diagram of a methanol plant designed for low capital cost is shown in FIGS. 16 and 17. Hydrocarbonaceous feedstock, such as natural gas stream 420, FIG. 17, is passed to a feedstock saturator 422 which is similar to the saturator 204 in the embodiment shown in FIG. 14. Water is recirculated by pump 424 to the top of the forced film saturator where it flows with the feedstock stream through the tubes of the saturator. The saturated feedstock is separated from the water in the bottom of the saturator to form saturated feedstock stream 425 and the water recycle stream. Makeup water for the recycle water stream comes from synthesis gas condensate 426 and distillation bottoms 428. Methanol converter effluent stream is fed to the shell side of the saturator to heat the water and feedstock stream. Line 430 provides for blowdown of the saturator water.

As shown in FIG. 16, the saturated feedstock 425 passes through coil 434 of a fired heater 436 where the saturated feedstock is preheated by combustion of waste fuel 438 with air 439. The heated saturated feedstock on line 440 from the heater 436 is fed to the catalytic partial oxidation (CPO) reactor 28 where it is mixed with an oxygen or oxygen-containing stream 442 and subjected to catalytic partial oxidation to produce synthesis gas as has been described hereinbefore.

The reactor effluent 444 is first cooled by generating steam in a boiler 446 which receives water from a steam drum 448 and returns steam to the drum. A second steam drum 450 has water flow boiled in coils 452 of the fired heater 436. Steam outputs 454 and 456 of the steam drums 448 and 450 are combined to produce the steam 458 used in the process. Lines 460 and 462 provide for boiler blowdown from the drums 448 and 450. Boiler feedwater 464 branches into streams 466 and 468 feeding the respective drums 448 and 450. The branch 466 is preheated in heat exchanger 472 by the reactor effluent in line 470 from the boiler 446 before passing in line 474 to the drum 448. The synthesis gas in line 476 from the heat exchanger 472 is further cooled by water in condenser 478 and then passed through line 480 to synthesis gas separator 482 where water condensate 484 is removed by pump 486 to provide the condensate stream 426.

After water removal, the synthesis gas in line 490 is compressed to the methanol loop pressure by compressor 492 to produce feed 494 to the desulfurization vessel 202. The output 496 of the desulfurization vessel 202 forms the make-up gas for the methanol loop of FIG. 17.

The make-up synthesis gas 496, in FIG. 17, joins the gas circulating in the methanol synthesis loop at the discharge 498 of the methanol loop circulator 500. The loop stream 502 is preheated in heat exchanger 504 by steam before passing in line 506 to tube cooled methanol converter 508 which substantially similar to tube cooled methanol converter 312 of FIG. 14. Line 510 from the loop heater 504 provides heated loop gas to the top of the converter 508 during initial start-up of the methanol converter.

From the tube cooled converter 508, the effluent gas 512 passes to the shell side of the forced film saturator 422, where the gas is cooled by heat transfer to the circulating water and incoming natural gas stream flowing through the saturator. The converter effluent gas emerges from the saturator in line 514 and passes to water cooled condenser 516 to condense the methanol in the methanol loop stream line 518. Condensed methanol is separated from the methanol loop in separator 520 and passed over line 522 and valve 524 to pressure letdown vessel 526

The gas stream 528 from the separator 520 is split into a recycle stream 530 passing to the suction inlet of the circulator 500 and a purge stream 532 taken through valve 534 to maintain the concentration of inert material in the methanol loop at acceptable levels. Flash gas 536 through valve 538 from the let-down vessel 526 is combined with the purge stream 532 to form the waste fuel stream 488 to the fired heater 436.

From the let-down vessel 526, crude methanol 540 is passed to a distillation column 542 where the stream is separated into a light ends stream 544, a water stream 546, and the product methanol stream 548. The distillation column has a reboiler 550 heated by steam. The overhead 552 is cooled by water cooled condenser 554 producing a condensed methanol stream 556, a portion of which is used as a reflux stream through pump 558. The remaining portion of the condensed methanol stream 556 is combined with the fusel oil fraction 560 to form the product stream 548. The water stream 546 from the bottoms of column 542, is cooled in cooler 562 and passed by pump 564 to the stream 428 feeding the saturator 422.

The following examples are intended to illustrate further the invention described herein and are not intended to limit the scope of the invention in any way.

EXAMPLE I

A methanol plant in accordance with FIGS. 13, 14 and 15 is operated to produce 2000 tons (1,800,000 kg) of methanol per day. The following TABLES I, II, and III set forth moles/hour, mole percent, and parameters of pressure, temperature, water/steam, and heat transfer for the plant. The moles/hour are lb moles/hour (0.4536 kg moles/hour).

TABLE I

Moles / Hour

DESCRIPTION	CO	CO2	H2	CH4	C2H6	N2	Ar	O2	H2O	CH3OH	C4H9OH	CH3OCH3	TOTALS
Natural Gas (line 200)		3.7		6236.0	9.4	6.3							6255.4
S. Nat. Gas (line 220)		3.7		6236.0	9.4	6.3			8303.7				14559.1
Oxygen (line 236)							16.0	3186.1					3202.1
CPO out (line 244)	4017.5	1652.9	12264.2	591.2		6.3	16.0		7360.2				25908.3
Loop Make-Up (line 298)	4019.6	1653.8	12869.0	591.2		6.3	16.0		30.8				19186.7
Converter In (line 310)	9803.5	10861.9	62624.4	35614.5		407.6	946.0		55.0	492.2	1.0	30.7	120836.8
Converter Out (line 330)	5876.1	9451.9	50539.5	35614.5		407.6	946.0		1493.5	5787.0	8.1	37.8	110162.0
Sep. Liquid (line 344)	4.4	103.5	34.5	63.2		0.3	2.0		1468.9	5287.3	7.1	6.6	6977.8
Sep. Gas Out (line 354)	5871.7	9348.4	50505.0	35551.3		407.3	944.0		24.6	499.7	1.0	31.2	103184.2
Loop Recycle (line 356)	5783.9	9208.1	49755.4	35023.3		401.3	930.0		24.2	492.2	1.0	30.7	101650.1
Purge Gas (line 358)	87.8	140.3	749.5	528.0		6.0	14.0		0.4	7.5		0.5	1534.1
PSA Hydrogen (line 284)	2.1	0.9	604.8										607.8
PSA Purge (line 230)	85.7	139.4	144.8	528.0		6.0	14.0		0.4	7.5		0.5	925.3
Flash Gas (line 228)	3.8	61.5	34.1	58.5		0.3	1.9		0.3	6.5		0.4	167.3
Crude Methanol (line 348)	0.6	42.0	0.4	4.7			0.1		1468.6	5230.3	7.1	6.2 (NO2)	6810.5

TABLE I (CONTINUED)

Moles / Hour

DESCRIPTION	CO	CO_2	H_2	CH_4	C_2H_6	N_2	Ar	O_2	H_2O	CH_3OH	C_4H_9OH	CH_3OCH_3	TOTALS
Total Fuel (line 225)	80.1	242.9	178.3	591.2		6.3	16.0		50.4	93.3	7.1	7.1	1283.7
Comb. Air (line 227)						6821.4	82.7	1829.6	257.1				8990.8
Heater Flue (233)		1060.1				6827.7	98.7	308.6	1912.6				10207.7
Light Ends (line 232)	0.8	42.0	0.4	4.7			0.1			25.6		6.2	79.6
Fusel Oil (line 226)									49.7	53.7	7.1		110.5
Distillation In (line 378)									1468.6	5255.2	7.1		6730.9
Column Bottoms (line 410)									1418.9				1418.9
Product Methanol (line 386)										5201.5			5201.5

TABLE II
Mole Percent

DESCRIPTION	CO	CO2	H2	CH4	C2H6	N2	Ar	O2	H2O	CH3OH	C4H9OH	CH3OCH3
Natural Gas (line 200)		0.06		99.69	0.15	0.10						
S. Nat. Gas (line 220)		0.03		42.83	0.06	0.04			57.04			
Oxygen (line 236)							0.50	99.50				
CPO out (line 244)	14.51	6.38	47.34	2.28		0.02	0.06		28.41			
Loop Make-Up (line 298)	20.95	8.62	67.08	3.08		0.03	0.08		0.16			
Converter In (line 310)	8.11	8.99	51.82	29.47		0.34	0.78		0.05	0.41		0.03
Converter Out (line 330)	5.33	8.58	45.88	32.33		0.37	0.86		1.36	5.25	0.01	0.03
Sep. Liquid (line 344)	0.06	1.49	0.49	0.91			0.03		21.05	75.78	0.10	0.09
Sep. Gas Out (line 354)	5.69	9.06	48.95	34.46		0.39	0.92		0.02	0.48		0.03
Loop Recycle (line 356)	5.69	9.06	48.95	34.46		0.39	0.92		0.02	0.48		0.03
Purge Gas (line 358)	5.69	9.06	48.95	34.46		0.39	0.92		0.02	0.48		0.03
PSA Hydrogen (line 234)	0.35	0.15	99.5									
PSA Purge (line 230)	9.25	15.05	15.64	57.00		0.65	1.51		0.04	0.81		0.05
Flash Gas (line 228)	2.27	36.75	20.38	34.96		0.18	1.14		0.18	3.39		0.24
Crude Methanol (line 348)	0.01	0.52	0.01	0.07					21.56	77.54	0.10	0.09

TABLE II (CONTINUED)

Mole Percent

DESCRIPTION	CO	CO_2	H_2	CH_4	C_2H_6	N_2	Ar	O_2	H_2O	CH_3OH	C_4H_9OH	CH_3OCH_3
Total Fuel (line 225)	7.02	18.92	13.97	46.05		0.49	1.25		3.93	7.27	0.55	0.55
Comb. Air (line 227)						75.87	0.92	20.35	2.86			
Heater Flue (233)		10.39				66.88	0.97	3.02	18.74			
Light Ends (line 232)	0.75	52.77	0.50	5.90			0.13			32.15		7.78
Fusel Oil (line 226)									44.98	48.59	6.43	
Distillation In (line 378)									21.82	78.07	0.11	
Column Bottoms (line 410)									100.00			
Product Methanol (line 386)										100.00		

TABLE III
Parameters

DESCRIPTION	Pressure		Temperature		Water/Steam		Net Heat Transfer	
	PSIG	KPa	DEG F	DEG C	LBS/HR	KG/HR	MMBTU/HR	KCAL 10^6/HR
Natural Gas 200	450	3103	60	16				
Saturator 204							176.4	44.5
Make-up water 216			228	109	157040	71230		
Blowdown 218					7450	3380		
Saturated Gas 220	444	3061	401	205				
Coil 222							114.3	28.8
Fusel oil 226			128	53				
Flash gas 228			105	41				
PSA purge 230			100	38				
Light ends 232			100	38				
Heated Feedstock 234			1100	593				
Oxygen 236	535	3689	300	149				
Heater 240							5.5	1.4
CPO out 244	413	2848	1700	927				
Heat exchanger 246							46.8	11.8
Steam Drum 248	1550	10687	601	316				
Heater coils 252							65.5	16.5
Water 254			432	222	305530	138590		
Heater coils 258							68.7	17.3
Steam 260	1500	10342	850	454				
Blowdown 262					3030	1370		
Process stream 264			650	343				
Reboiler 266							46.8	11.8
Process stream 268			422	217				
Reboiler 270							161.1	40.6
Process stream 272			200	93				
Heat exchanger 274							23.2	5.8
Process stream 276			137	58				
Condenser 278							11.9	3.0
Condensate 281			100	38	132040	59890		
Process stream 282	403	2779	100	38				

TABLE III (CONTINUED)
Parameters

DESCRIPTION	Pressure		Temperature		Water/Steam		Net Heat Transfer	
	PSIG	KPa	DEG F	DEG C	LBS/HR	KG/HR	MMBTU/HR	KCAL 10^6/HR
Hydrogen recycle 284	485	3344	100	38				
Make-up gas 298	1219	8405	219	104				
Circulator out 304			114	46				
Process stream 306			128	53				
Heat exchanger 308							186.0	46.9
Converter feed 310			311	155				
Converter out 330	1161	8005	509	265				
Process stream 336			339	171				
Process stream 338			201	94				
Condenser 340							153.9	38.6
Crude methanol 348	75	517	100	38				
Overhead 366	8	55	170	77				
Condenser 368							37.5	9.5
Condenser 370							7.0	1.8
Reboiler 376							normally nil	
Condensate stream 384			176	80				
Product methanol 386			105	41				
Reboiler 388							31.9	8.0
Overhead 389	5	34	104	40				
Condenser 392							205.3	51.7
Heat exchanger 408							1.9	0.5
Column bottoms 410			100	38				

EXAMPLE II

A methanol plant in accordance with FIGS. 16 and 17 is operated to produce 102,000 lbs. (46,400 kg) of methanol per day. The following TABLES IV, V, and VI set forth moles/hour, mole percent, and parameters of pressure, temperature, water/steam, and heat transfer for the plant. The moles/hour are lb moles/hour (0.4536 kg moles/hour).

TABLE IV
Moles / Hour

DESCRIPTION	CO	CO2	H2	N2	O2	Ar	CH4	C2H6+	CH3OH	C2H5OH+	CH3OCH3	H2O	TOTALS
Natural Gas (line 420)		0.20		2.13			160.56	1.28					164.17
S. Nat. Gas (line 425)		0.20		2.13			160.56	1.28				176.21	340.38
Oxygen (line 442)				9.63	86.66								96.29
CPO out (line 444)	116.42	37.21	322.01	11.76			10.40					159.04	656.86
Loop Make-Up (line 496)	116.42	37.21	322.01	11.76			10.40					1.44	499.24
Converter In (line 506)	469.28	459.39	1658.63	529.65			454.00		16.99		1.05	2.62	3591.61
Converter Out (line 512)	360.94	434.42	1367.05	529.65			454.00		149.24	0.18	1.22	28.30	3325.00
Sep. Gas Out (line 528)	360.73	431.61	1366.46	529.45			453.50		17.37		1.08	1.21	3161.41
Loop Recycle (line 530)	352.86	422.18	1336.63	517.89			443.60		16.99		1.06	1.13	3092.39
Purge Gas (line 532)	7.87	9.43	29.83	11.56			9.90		0.38		0.02	0.03	69.02
Flash Gas (line 536)	0.19	1.10	0.56	0.19			0.39		0.12		0.01	0.01	2.57
Waste Gas (line 488)	8.06	10.53	30.39	11.75			10.29		0.50		0.03	0.04	71.59
Crude Methanol (line 540)	0.02	1.72	0.03	0.02			0.11		131.75	0.18	0.15	27.08	161.05

TABLE IV (CONTINUED)

Moles / Hour

DESCRIPTION	CO	CO_2	H_2	N_2	O_2	Ar	CH_4	C_2H_6+	CH_3OH	C_2H_5OH+	CH_3OCH_3	H_2O	TOTALS
Comb. Air (line 439)				166.70	44.72	2.03						6.27	219.72
Ingress Air (line 441)				15.15	4.06	0.18						0.57	19.96
Heater Flue (443)		29.44		193.60	8.13	2.21						58.94	292.32
Light Ends (line 544)	0.02	1.72	0.03	0.02			0.11		0.15		0.13		2.18
Fusel Oil (line 560)									2.25	0.06		0.95	3.26
Column Bottoms (line 428)									0.08	0.05		24.92	25.05
Product Methanol (line 557)									129.27	0.07	0.02	1.21	130.57
Blended Product (line 548)									131.52	0.13	0.02	2.16	133.83

TABLE V
Mole Percent

DESCRIPTION	CO	CO_2	H_2	N_2	O_2	Ar	CH_4	C_2H_6+	CH_3OH	C_2H_5OH+	CH_3OCH_3	H_2O
Natural Gas (line 420)		0.12		1.30			97.80	0.78				
S. Nat. Gas (line 425)		0.06		0.63			47.17	0.37				51.77
Oxygen (line 442)				10.00	90.00							
CPO out (line 444)	17.72	5.67	49.02	1.79			1.58					24.22
Loop Make-Up (line 496)	23.32	7.45	64.50	2.36			2.08					0.29
Converter In (line 506)	13.07	12.79	46.18	14.75			12.64		0.47		0.03	0.07
Converter Out (line 512)	10.85	13.07	41.11	15.93			13.65		4.49	0.01	0.04	0.85
Sep. Gas Out (line 528)	11.41	13.65	43.22	16.75			14.35		0.55		0.03	0.04
Loop Recycle (line 530)	11.41	13.65	43.22	16.75			14.35		0.55		0.03	0.04
Purge Gas (line 532)	11.41	13.65	43.22	16.75			14.35		0.55		0.03	0.04
Flash Gas (line 536)	7.39	43.80	21.79	7.39			15.18		4.57		0.39	0.39
Waste Gas (line 488)	11.26	14.71	42.45	16.41			14.38		0.70		0.04	0.05
Crude Methanol (line 540)	0.01	1.07	0.02	0.01			0.07		81.81	0.11	0.09	16.81

TABLE V (CONTINUED)

Mole Percent

DESCRIPTION	CO	CO2	H2	N2	O2	Ar	CH4	C2H6+	CH3OH	C2H5OH+	CH3OCH3	H2O
Comb. Air (line 439)				75.87	20.36	0.92						0.57
Ingress Air (line 441)				75.87	20.36	0.92						0.57
Heater Flue (443)		10.07		66.23	0.76	2.78						20.16
Light Ends (line 544)	0.92	78.90	1.38	0.92			5.05		6.88		5.96	
Fusel Oil (line 560)									69.02	1.84		29.14
Column Bottoms (line 428)									0.32	0.20		99.48
Product Methanol (line 557)									99.00	0.05	0.02	0.93
Blended Product (line 548)									98.27	0.10	0.01	1.61

TABLE VI
Parameters

DESCRIPTION	Pressure PSIG	Pressure KPa	Temperature DEG F	Temperature DEG C	Water/Steam LBS/HR	Water/Steam KG/HR	Net Heat Transfer MMBTU/HR	Net Heat Transfer KCAL 10^6/HR
Natural Gas 420	500	3450	60	16				
Saturator 422							4.12	1.04
Condensate 426					2840	1290		
Bottoms water 428					455	206		
Blowdown 430					121	55		
Saturated Gas 425	430	2960	390	200				
Coil 434							2.78	0.70
Waste Fuel 438	41	283	104	40				
Heated Feedstock 440	420	2900	1100	593				
Oxygen 442	420	2900	285	141				
CPO out 444	1700	11720	375	191				
Boiler 446							6.36	1.60
Coils 452							3.81	0.96
Steam 454	610	4210	491	255	7826	3550		
Steam 456	610	4210	491	255	3963	1798		
Boiler Blowdown 460					78	35		
Boiler Blowdown 462					40	18		
Boiler Feed Water 464			275	135	11907	5400		
Boiler Feed 466					7904	3585		
Boiler Feed 468					4003	1815		
Process Stream 470			550	288				
Heat Exchanger 472							1.17	0.29
Boiler Feed 474			415	213				
Process Stream 476			315	157				
Condenser 478							3.93	0.99
Process Stream 480			104	40				
Synthesis Gas 490	357	2590	104	40				
Compressed Syngas 494	904	6230	310	154				
Make-Up Gas 496	894	6160	310	154				

TABLE VI (CONTINUED)

Parameters

DESCRIPTION	Pressure PSIG	Pressure KPa	Temperature DEG F	Temperature DEG C	Water/Steam LBS/HR	Water/Steam KG/HR	Net Heat Transfer MMBTU/HR	Net Heat Transfer KCAL 10^6/HR
Circulator Output 498	894	6160	115	46				
Loop Heater 504							4.85	1.22
Converter Feed 506			309	154				
Converter Out 512	867	5980	509	265				
Process Stream 514			363	184				
Condenser 516							9.60	2.42
Condenser Output 518	849	5850	104	40				
Flash Gas 536	75	520	104	40				
Crude Methanol 540	75	520	104	40				
Dist. Column 542	15	100	250	121				
Light Ends 544			104	40				
Blended Product 548			104	40				
Reboiler 550							4.40	1.10
Overhead 552	5	35	164	73				
Condenser 554							4.20	1.06
Fusel Oil 560			194	90				
Bottoms Cooler 562							0.08	0.02

Since many modifications, variations, and changes in detail may be made to the above described embodiments without departing from the scope and spirit of the invention, it is intended that all matter described above and shown in the accompanying drawings be interpreted as illustrative and not in a limiting sense.

CLAIMS

1. A process for producing methanol which comprises: forming a homogeneous gaseous mixture of a hydrocarbonaceous feedstock, an oxidant, and optional steam wherein the oxygen-to-carbon molar ratio is in the range from 0.4:1 to 0.8:1 and the steam-to-carbon molar ratio is in the range from 0:1 to 3.0:1; catalytically partially oxidizing the mixture at a temperature equal to or greater than a minimum temperature selected as a linear function which includes a range from 870°C to 1040°C corresponding to a range of the steam-to-carbon molar ratio from 0.4:1 to 0:1 thereby producing a synthesis gas containing hydrogen, carbon monoxide and carbon dioxide; reacting the hydrogen, carbon monoxide and carbon dioxide under methanol-producing conditions; and recovering methanol.

2. A process as claimed in Claim 1, wherein the gaseous reaction mixture passes through the total volume of catalyst employed for the production of synthesis gas from hydrocarbonaceous feedstock with a space velocity in the range from 20,000 hour^{-1} to 500,000 hour^{-1}.

3. A process as claimed in Claim 1, wherein the catalytic partial oxidation is carried out at a steam-to-carbon molar ratio in the range from 0.8:1 to 2.0:1 and an oxygen-to-carbon molar ratio in the range from 0.45:1 to 0.65:1.

4. A process as claimed in Claim 1, where in the oxidant in the catalytic partial oxidation step is an oxygen-rich gas containing at least 70 mole % oxygen.

5. A process as claimed in Claim 1, wherein the oxidant in the catalytic partial oxidation step is an oxygen-rich gas containing at least 90 mole % oxygen.

6. A process as claimed in Claim 1, wherein the oxidant in the catalytic partial oxidation step is air.

7. A process as claimed in Claim 1, wherein the catalytic partial oxidation takes place at a temperature between about 760°C to 1260°C.

8. A process as claimed in Claim 7, wherein the catalytic partial oxidation takes place at a temperature between about 870°C to 1090°C.

9. A process as claimed in Claim 1, wherein the gas which undergoes methanol synthesis is treated to adjust the molar ratio of hydrogen to total carbon monoxide and carbon dioxide such that the ratio

$$\frac{H_2}{2CO + 3CO_2}$$

has a value of at least 0.8.

10. A process as claimed in Claim 9, wherein the ratio

$$\frac{H_2}{2CO + 3CO_2}$$

has a value of between 0.90 and 1.1.

11. A process as claimed in Claim 9, wherein the ratio

$$\frac{H_2}{2CO + 3CO_2}$$

is adjusted by adding hydrogen recovered from methanol loop purge gas.

12. A process as claimed in Claim 9, wherein the ratio

$$\frac{H_2}{2CO + 3CO_2}$$

is adjusted by adding hydrogen recovered from a combination of methanol loop purge gas and synthesis gas produced by catalytic partial oxidation.

13. A process as claimed in claim 1 which uses a

forced film saturator to recover heat of reaction from methanol synthesis.

14. A process as claimed in claim 1 which uses a tube cooled converter in which reactions producing methanol are performed.

15. A process as claimed in claim 1 which uses a single packed column for distillation of crude methanol to produce refined methanol.

16. A process for producing methanol from a hydrocarbonaceous feedstock which comprises:

(a) introducing to a catalytic partial oxidation zone an essentially completely mixed gaseous mixture of a hydrocarbonaceous feedstock, oxygen or an oxygen-containing gas and, optionally, steam in which the steam-to-carbon molar ratio is in the range 0:1 to 3.0:1 and the oxygen-to-carbon molar ratio is in the range from 0.4:1 to 0.8:1, said mixture being introduced to the catalytic partial oxidation zone at a temperature not lower than 93°C below its catalytic autoignition temperature;

(b) partially oxidizing the hydrocarbonaceous feedstock in the catalytic partial oxidation zone to produce a gas consisting essentially of methane, carbon oxides, hydrogen and steam by passing the mixture through catalyst capable of catalyzing the partial oxidation of the hydrocarbons, said catalyst having a ratio of geometric surface area to volume of at least 5 cm^2/cm^3 and a total volume corresponding to a space velocity of between 20,000 $hour^{-1}$, thereby producing a synthesis gas containing hydrogen, carbon monoxide and carbon dioxide;

(c) reacting the hydrogen, carbon monoxide and carbon dioxide under methanol producing conditions; and

(d) recovering the methanol.

17. A process as claimed in Claim 16, wherein the steam-to-carbon molar ratio is in the range from 0.8:1 to

2.0:1 and the oxygen-to-carbon molar ratio is in the range from 0.45:1 to 0.65:1.

18. A process as claimed in Claim 16, wherein the methanol-producing reaction is carried out at a temperature from about 210°C to 302°C with the reactants in contact with a catalyst containing zinc oxide and copper oxide.

19. A process as claimed in Claim 16, wherein the gas which undergoes methanol synthesis is treated to adjust the molar ratio of hydrogen to total carbon monoxide and carbon dioxide such that the ratio

$$\frac{H_2}{2CO + 3CO_2}$$

has a value of at least 0.8.

20. A process as claimed in Claim 19, wherein the ratio

$$\frac{H_2}{2CO + 3CO_2}$$

has a value between about 0.95 and 1.1.

21. A process for producing methanol from a hydrocarbonaceous gas containing principally methane, the process comprising:

(a) mixing the hydrocarbonaceous gas with steam and an oxygen-containing gas at a steam-to-carbon molar ratio in the range from 0:1 to 3.0:1, and at an oxygen-to-carbon molar ratio in the range from 0.4:1 to 0.8:1 under conditions providing thorough even mixing without combustion;

(b) partially oxidizing the hydrocarbonaceous gas, steam and oxygen gas mixture in a catalytic partial oxidation zone having a catalyst capable of catalyzing the partial oxidation of the methane, said catalyst having a ratio of geometric surface area to volume of at least 5 cm^2/cm^3 and a total volume corresponding to a space velocity in the range from 20,000 to 500,000 $hour^{-1}$, thereby producing a synthesis gas containing hydrogen, carbon monoxide and carbon dioxide;

(c) reacting the hydrogen, carbon monoxide and carbon dioxide under methanol producing conditions; and

(d) recovering the methanol.

22. A process as claimed in Claim 21, wherein the catalytic partial oxidation is carried out at a steam-to-carbon molar ratio in the range from 0.8:1 to 2.0:1 and an oxygen-to-carbon molar ratio in the range from 0.45:1 to 0.65:1; the oxidant in the catalytic partial oxidation step is an oxygen-rich gas containing at least 70 mole % oxygen; and the catalytic partial oxidation takes place at a temperature in the range from 870°C to 1090°C.

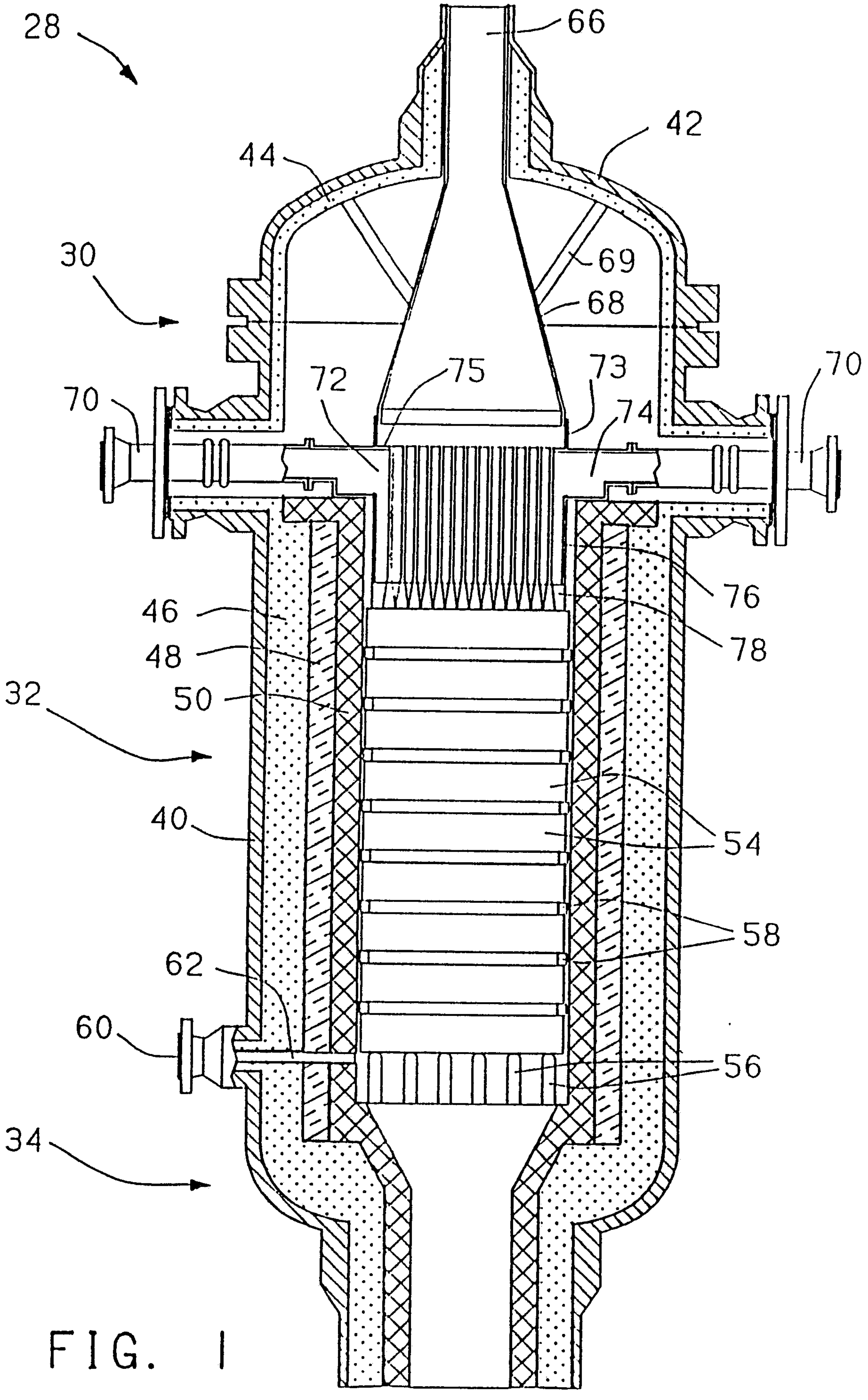
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FIG. 1

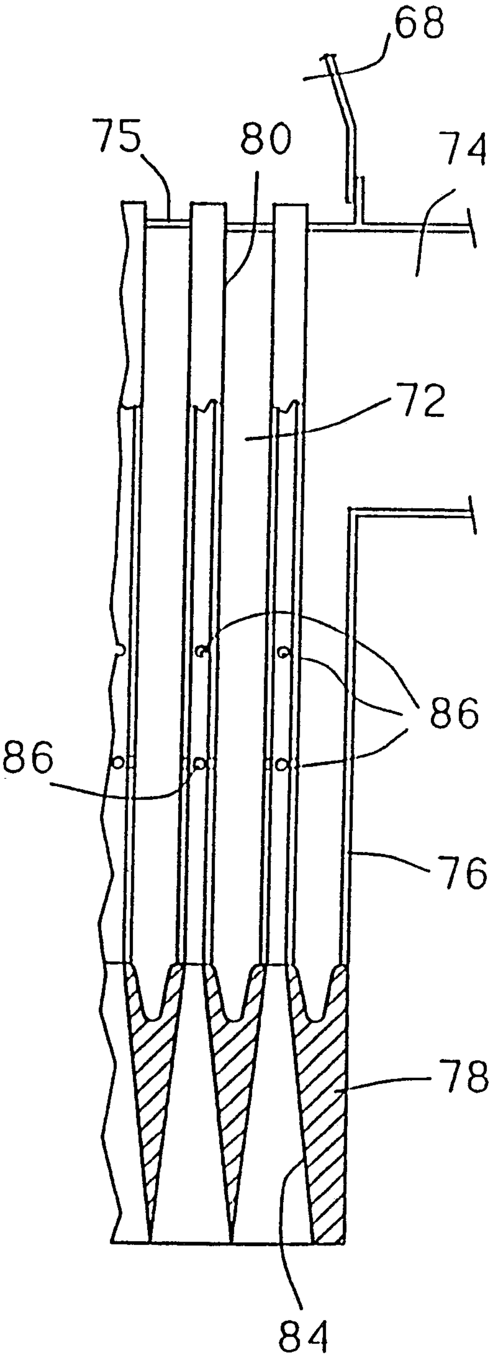


FIG. 2

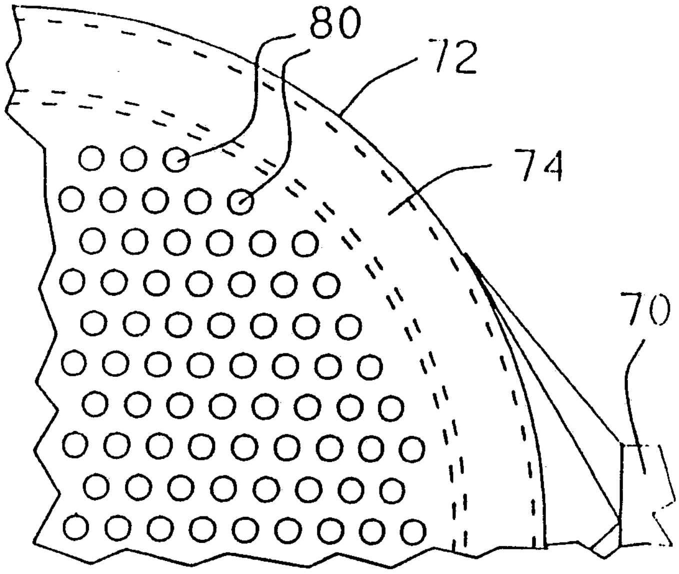


FIG. 3

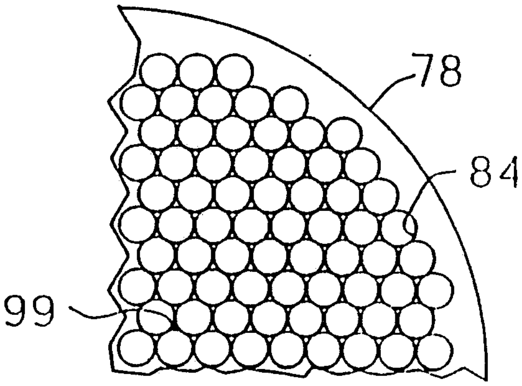
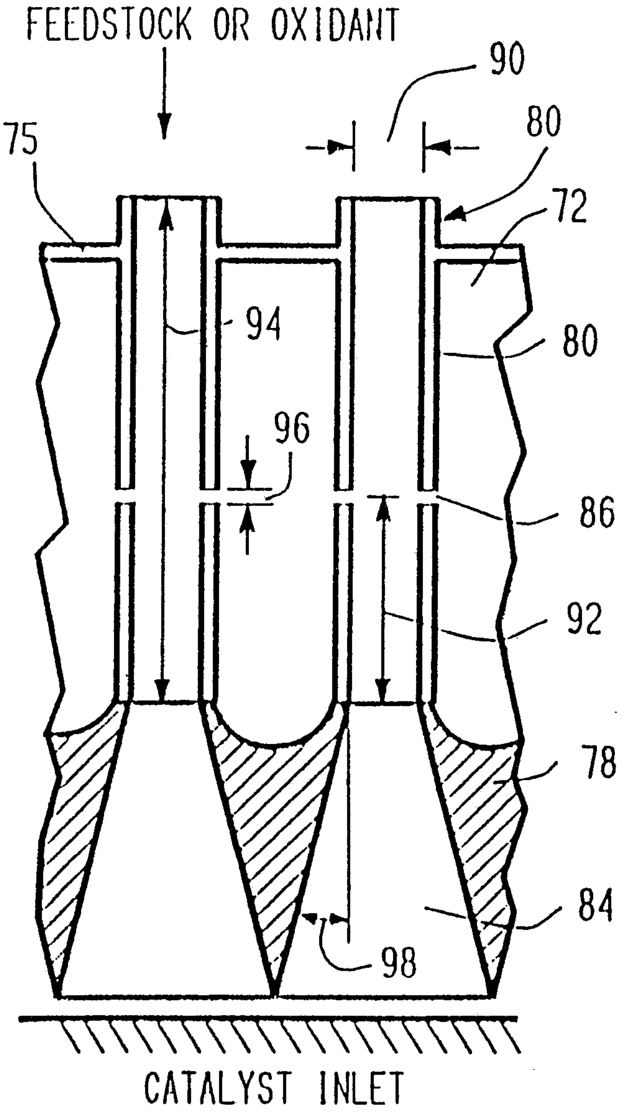


FIG. 4

3/15


FEEDSTOCK OR OXIDANT
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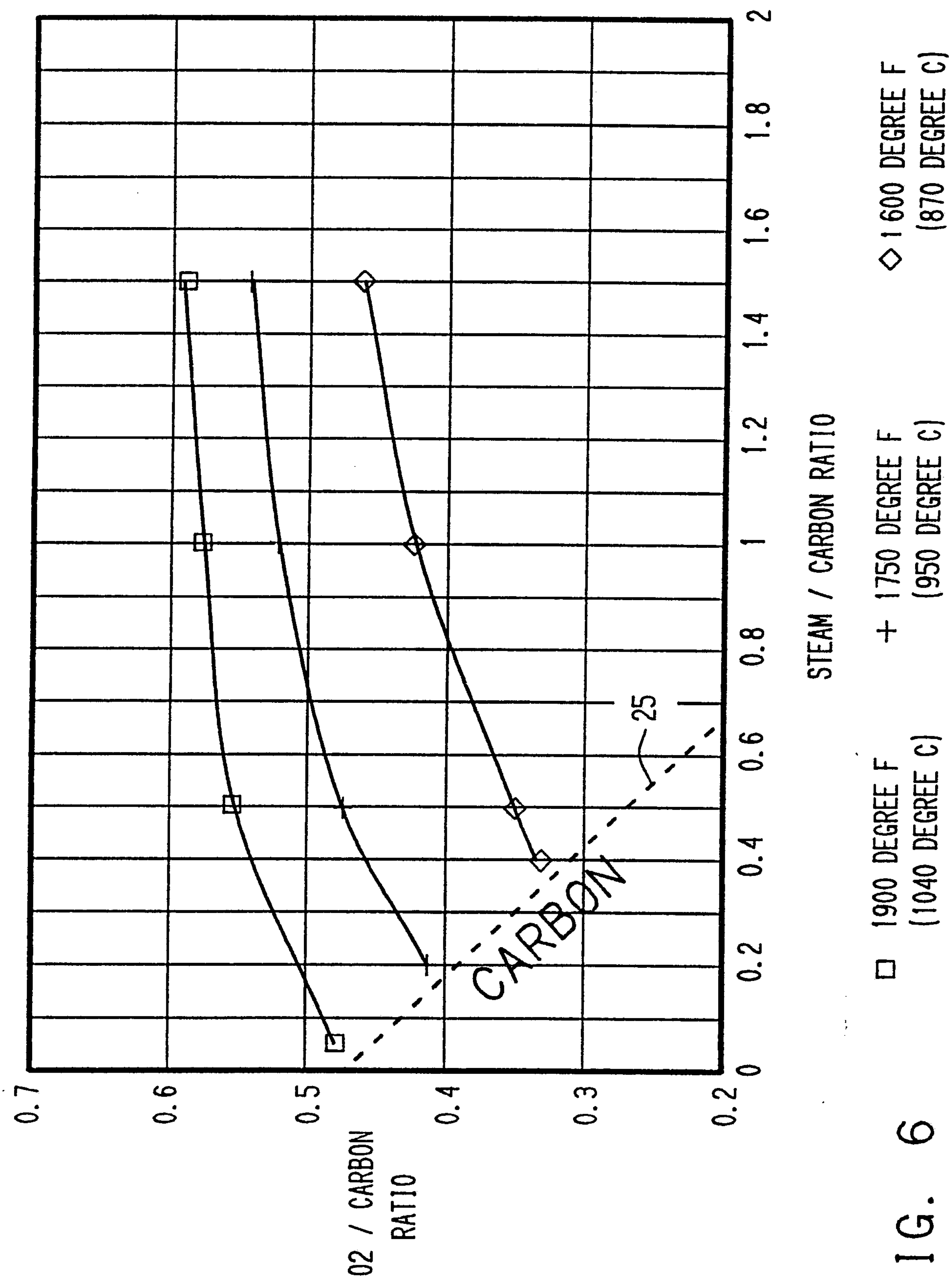
80
72
94
80
96
86
92
78
84
98
CATALYST INLET

FIG. 5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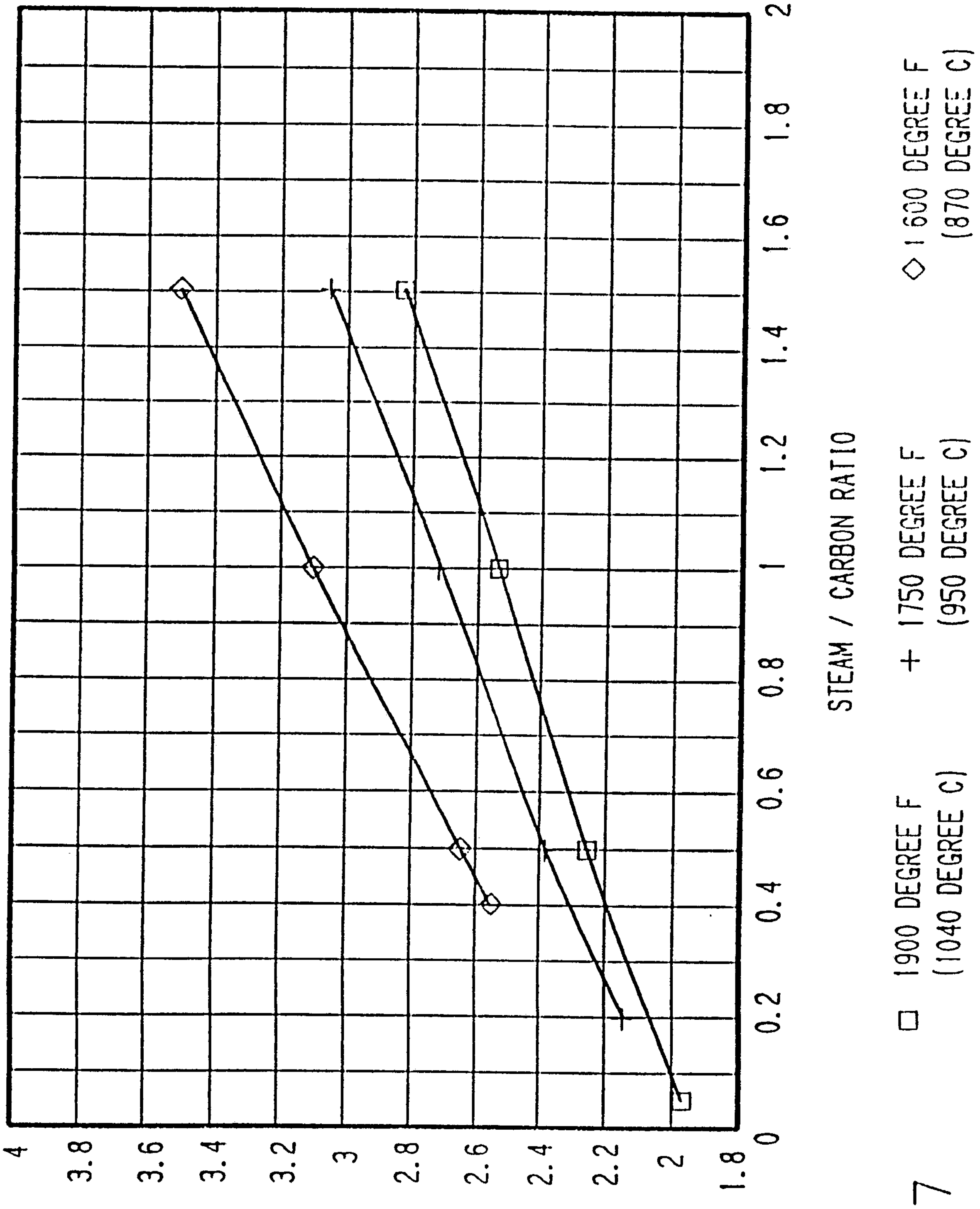
0.6
0.5
0.4
0.3
0.2
O2 / CARBON RATIO
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
STEAM / CARBON RATIO
CARBON
25
□ 1900 DEGREE F (1040 DEGREE C)
+ 1750 DEGREE F (950 DEGREE C)
◇ 1600 DEGREE F (870 DEGREE C)

FIG. 6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3.6
3.4
3.2
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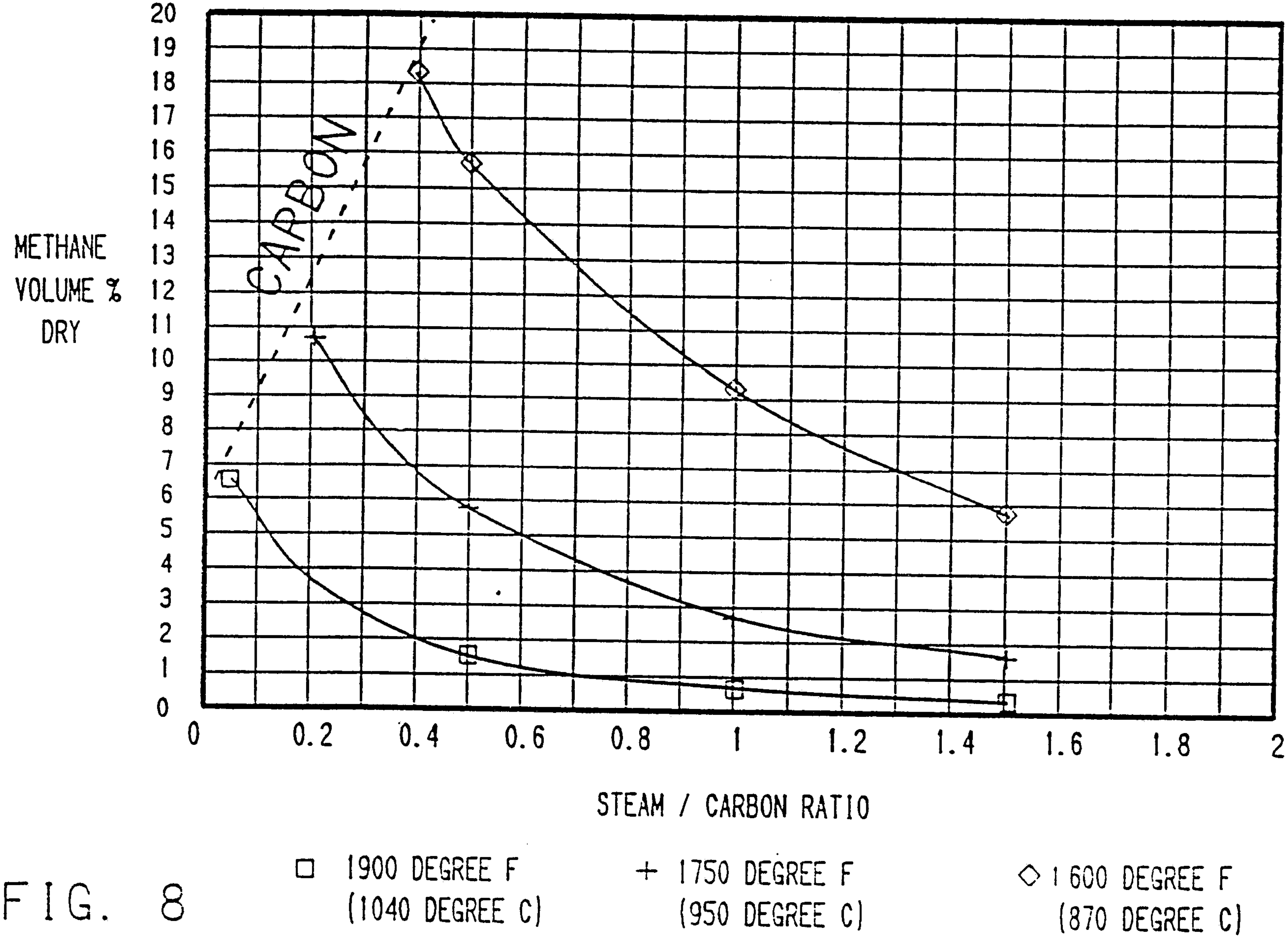
2.8
2.6
2.4
2.2
2
1.8
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
STEAM / CARBON RATIO
□ 1900 DEGREE F (1040 DEGREE C)
+ 1750 DEGREE F (950 DEGREE C)
◇ 1600 DEGREE F (870 DEGREE C)

FIG. 7


METHANE
VOLUME %
DRY
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19
18
17
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
CARBON
STEAM / CARBON RATIO
□ 1900 DEGREE F
(1040 DEGREE C)
+ 1750 DEGREE F
(950 DEGREE C)
◇ 1600 DEGREE F
(870 DEGREE C)

FIG. 8

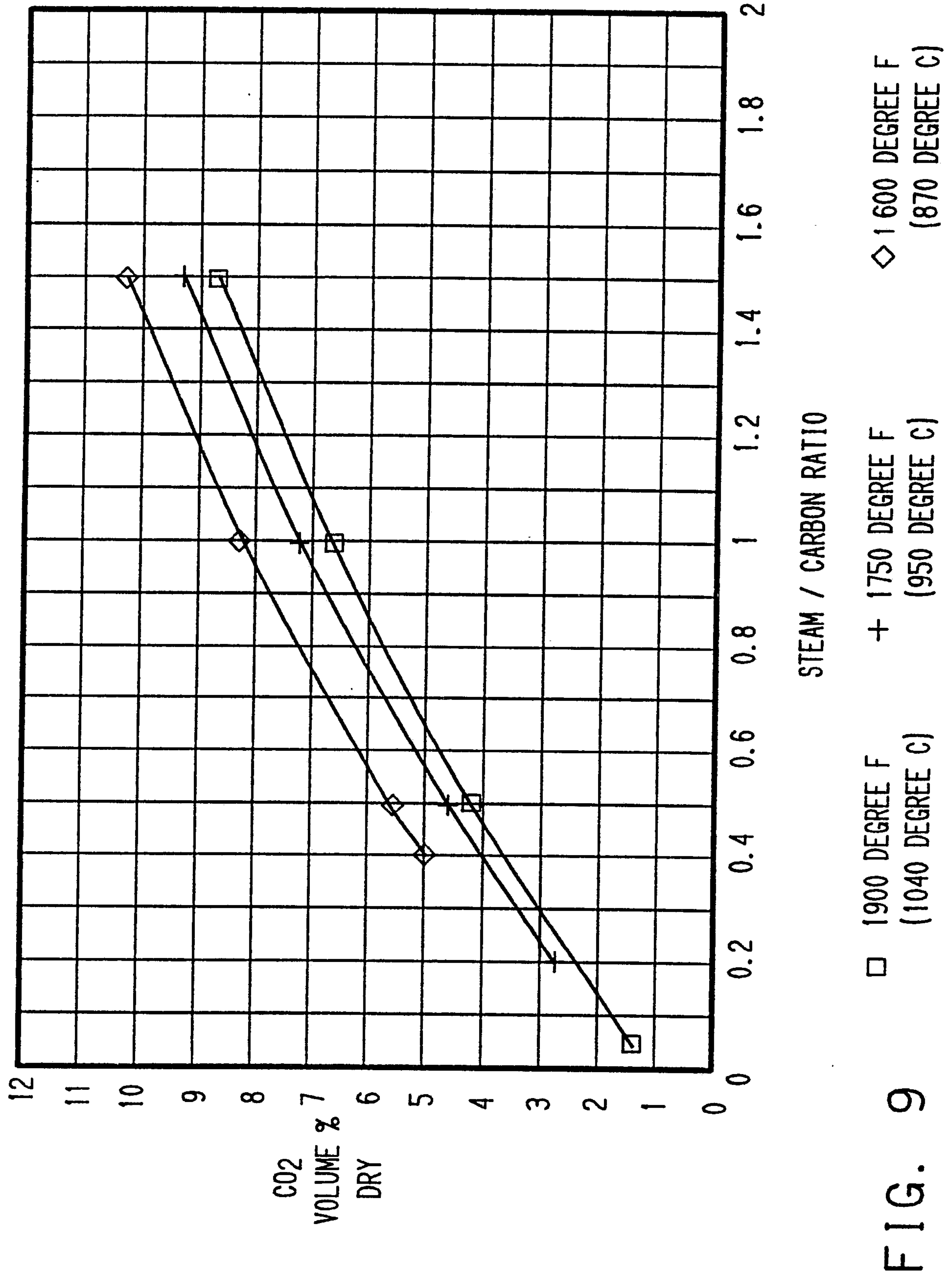

CO2
VOLUME %
DRY
0
1
2
3
4
5
6
7
8
9
10
11
12
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
STEAM / CARBON RATIO
□ 1900 DEGREE F (1040 DEGREE C)
+ 1750 DEGREE F (950 DEGREE C)
◇ 1600 DEGREE F (870 DEGREE C)

FIG. 9

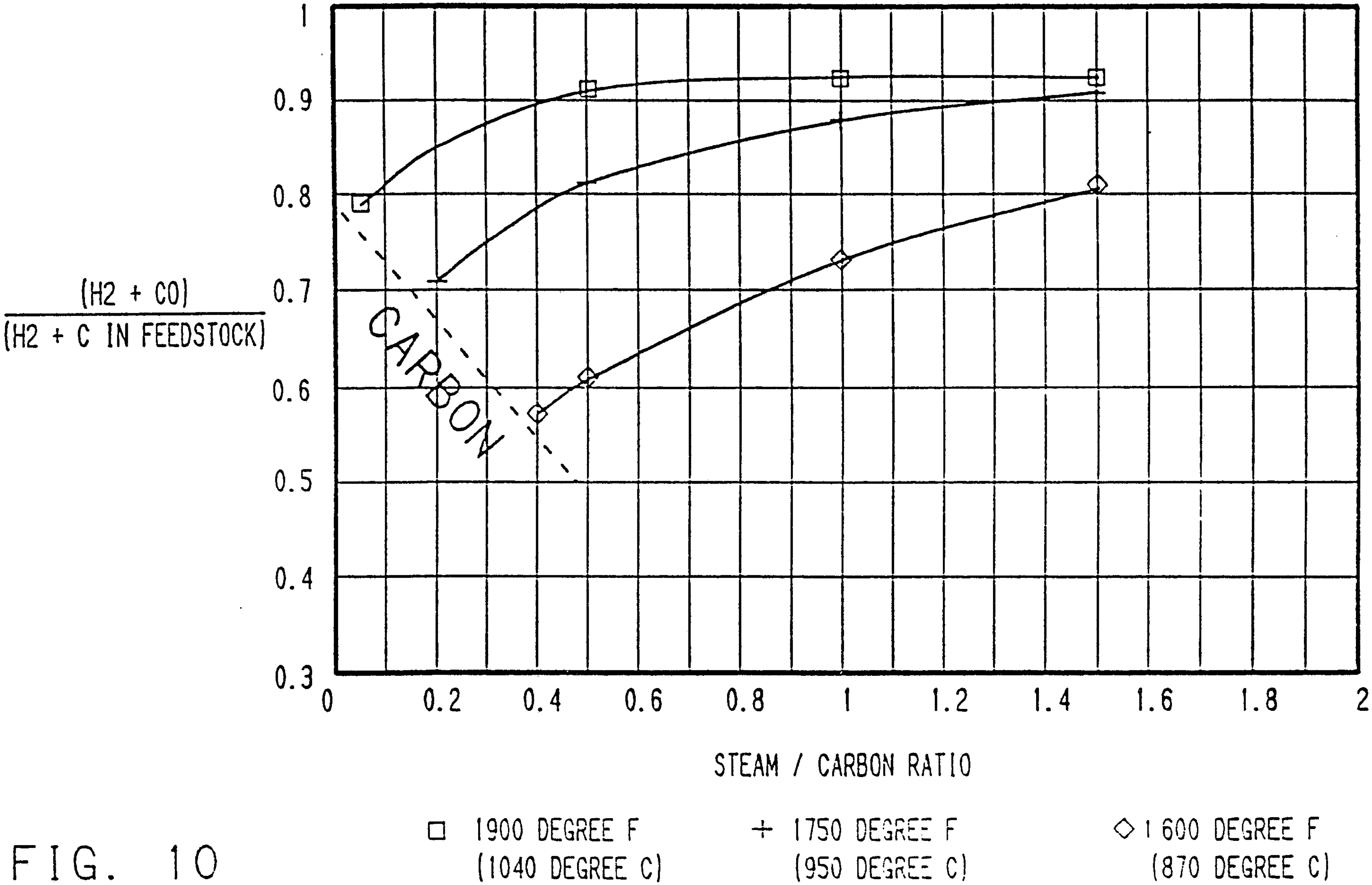

(H2 + CO)
(H2 + C IN FEEDSTOCK)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
CARBON
STEAM / CARBON RATIO
□ 1900 DEGREE F (1040 DEGREE C)
+ 1750 DEGREE F (950 DEGREE C)
◇ 1600 DEGREE F (870 DEGREE C)

FIG. 10

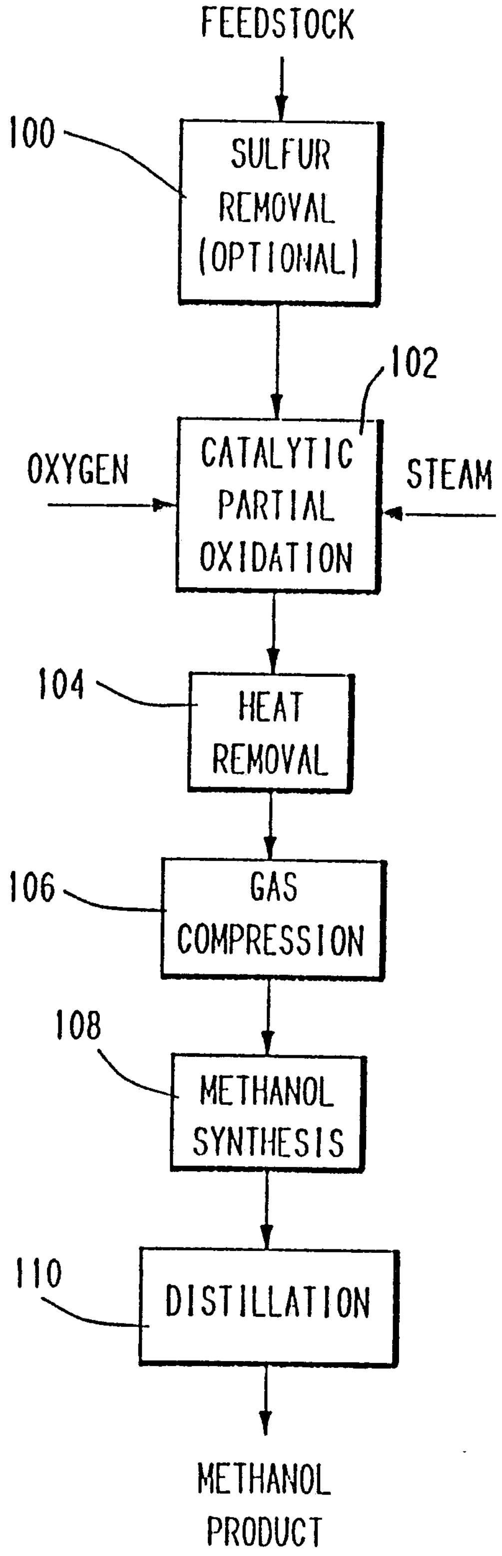

FEEDSTOCK
100
SULFUR REMOVAL (OPTIONAL)
102
OXYGEN
CATALYTIC PARTIAL OXIDATION
STEAM
104
HEAT REMOVAL
106
GAS COMPRESSION
108
METHANOL SYNTHESIS
110
DISTILLATION
METHANOL PRODUCT

FIG. 11

10/15

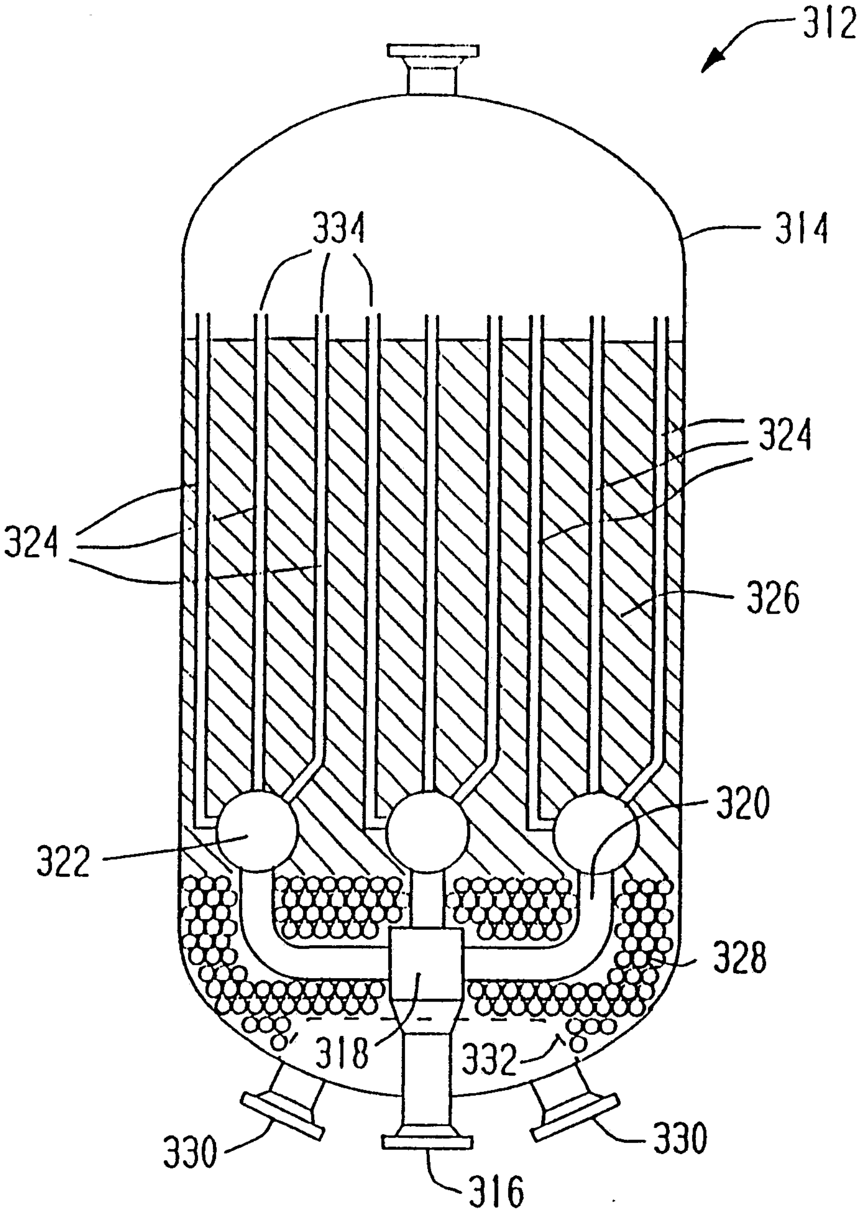
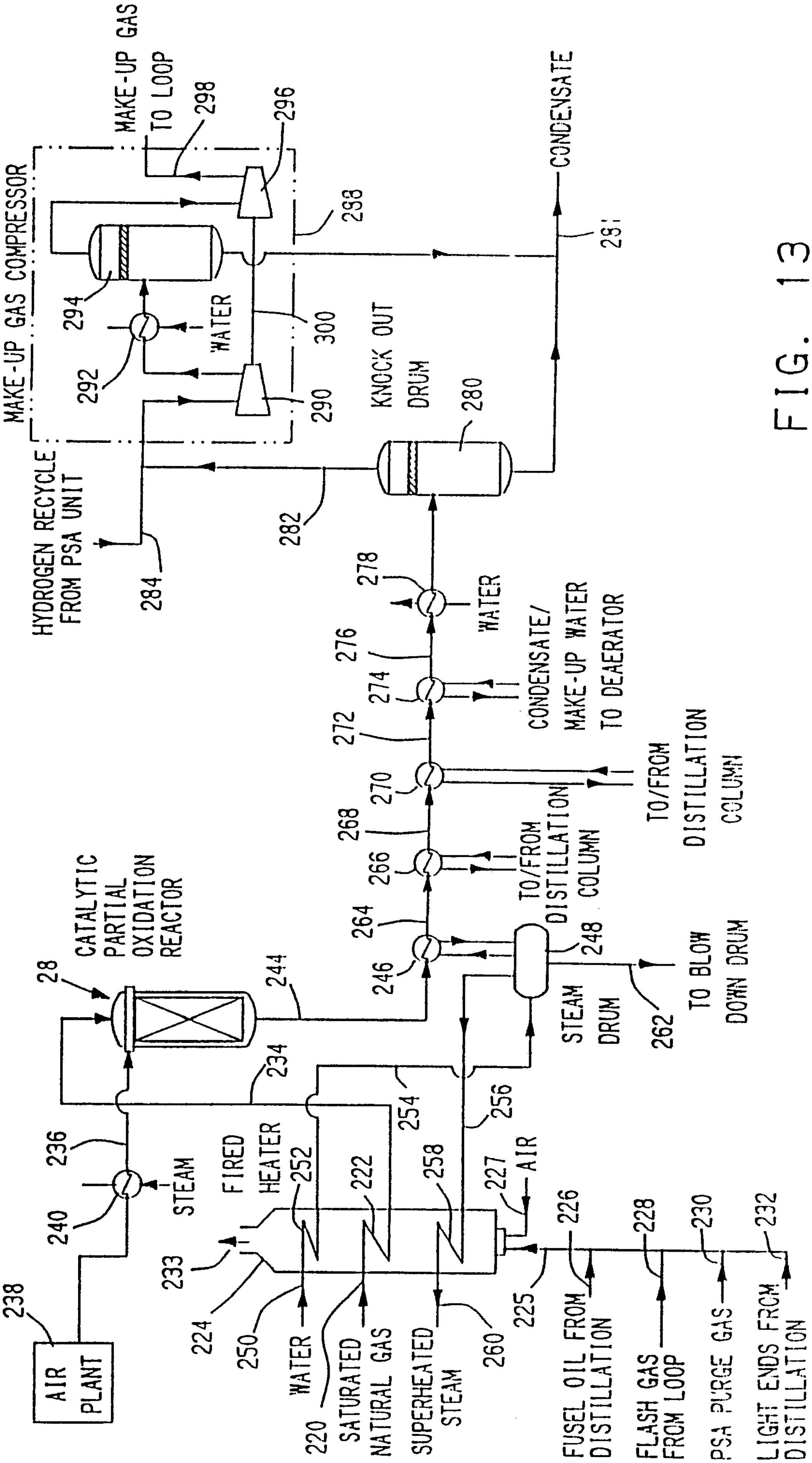


FIG. 12



MAKE-UP GAS TO LOOP
298
296
MAKE-UP GAS COMPRESSOR
288
294
292
WATER
300
290
CONDENSATE
281
KNOCK OUT DRUM
280
HYDROGEN RECYCLE FROM PSA UNIT
284
282
278
WATER
276
274
CONDENSATE/ MAKE-UP WATER TO DEAERATOR
272
270
TO/FROM DISTILLATION COLUMN
268
266
TO/FROM DISTILLATION COLUMN
264
246
248
244
CATALYTIC PARTIAL OXIDATION REACTOR
28
STEAM DRUM
TO BLOW DOWN DRUM
262
234
254
256
236
240
STEAM
FIRED HEATER
252
222
258
227
AIR
226
228
230
232
238
AIR PLANT
233
224
250
220
260
225
WATER
SATURATED NATURAL GAS
SUPERHEATED STEAM
FUSEL OIL FROM DISTILLATION
FLASH GAS FROM LOOP
PSA PURGE GAS
LIGHT ENDS FROM DISTILLATION

FIG. 13

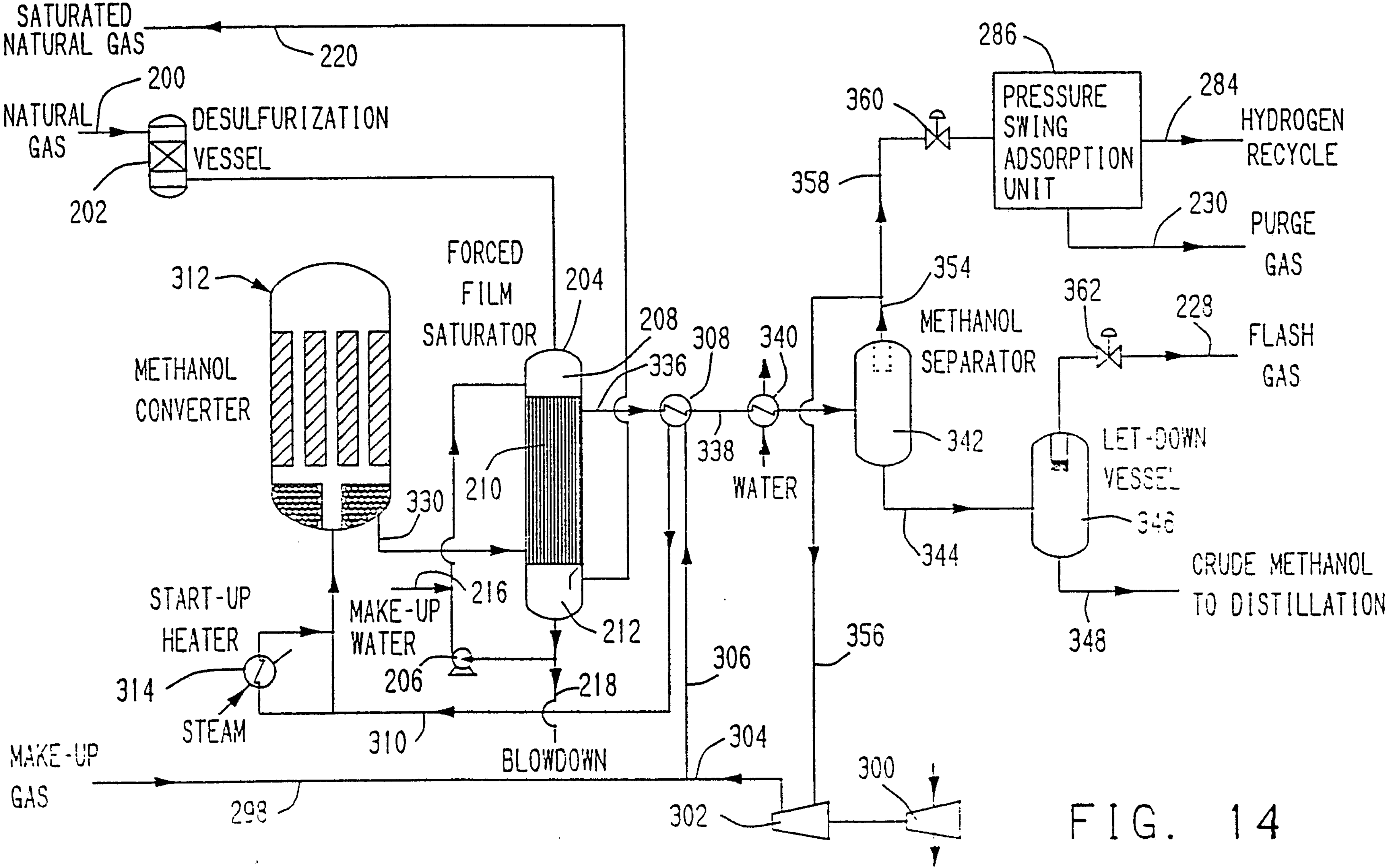

SATURATED NATURAL GAS
220
200
NATURAL GAS
DESULFURIZATION VESSEL
202
286
PRESSURE SWING ADSORPTION UNIT
284
HYDROGEN RECYCLE
360
358
230
PURGE GAS
312
METHANOL CONVERTER
FORCED FILM SATURATOR
204
208
336
308
340
354
METHANOL SEPARATOR
362
228
FLASH GAS
210
330
338
WATER
342
LET-DOWN VESSEL
346
344
CRUDE METHANOL TO DISTILLATION
348
216
START-UP HEATER
MAKE-UP WATER
212
206
218
314
STEAM
306
356
310
BLOWDOWN
304
300
MAKE-UP GAS
298
302

FIG. 14

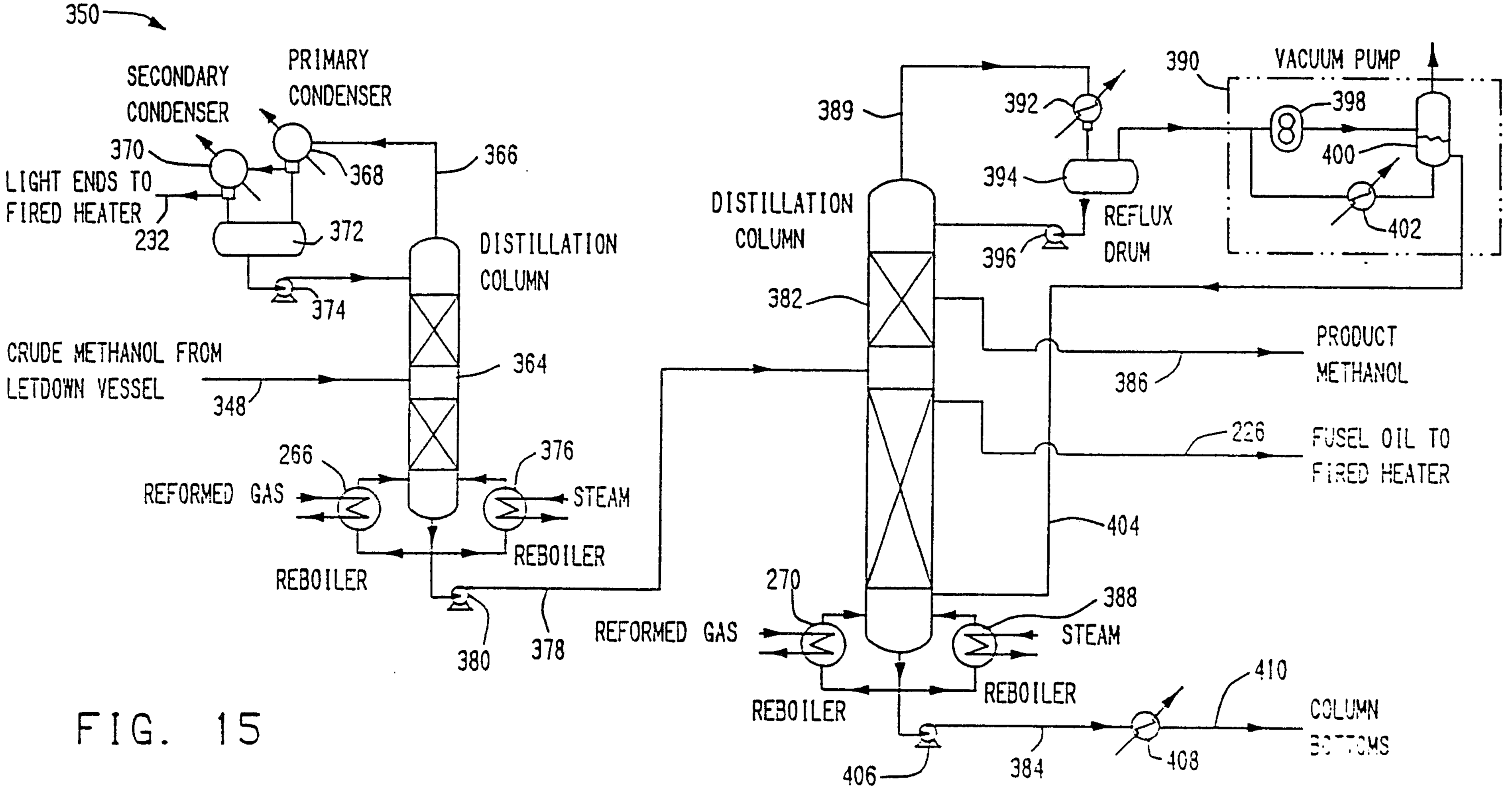

350
SECONDARY CONDENSER
PRIMARY CONDENSER
370
368
366
LIGHT ENDS TO FIRED HEATER
232
372
374
DISTILLATION COLUMN
CRUDE METHANOL FROM LETDOWN VESSEL
348
364
266
376
REFORMED GAS
STEAM
REBOILER
REBOILER
380
378
389
392
390
VACUUM PUMP
398
400
402
394
396
REFLUX DRUM
DISTILLATION COLUMN
382
PRODUCT METHANOL
386
226
FUSEL OIL TO FIRED HEATER
404
270
388
REFORMED GAS
STEAM
REBOILER
REBOILER
406
384
408
410
COLUMN BOTTOMS

FIG. 15

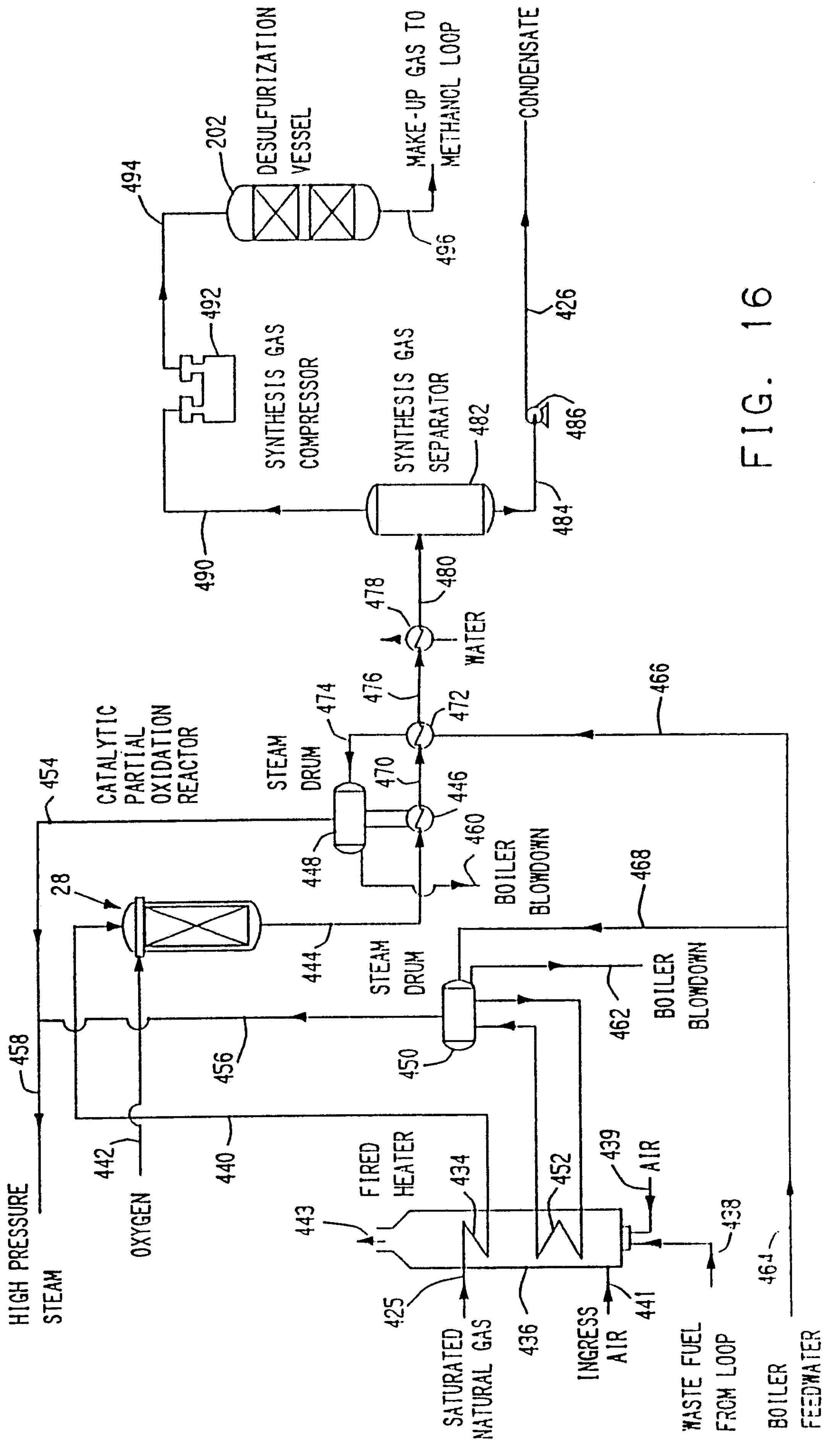

HIGH PRESSURE STEAM
OXYGEN
SATURATED NATURAL GAS
INGRESS AIR
WASTE FUEL FROM LOOP
BOILER FEEDWATER
FIRED HEATER
AIR
CATALYTIC PARTIAL OXIDATION REACTOR
STEAM DRUM
STEAM DRUM
BOILER BLOWDOWN
BOILER BLOWDOWN
WATER
SYNTHESIS GAS SEPARATOR
SYNTHESIS GAS COMPRESSOR
DESULFURIZATION VESSEL
MAKE-UP GAS TO METHANOL LOOP
CONDENSATE
28
202
425
426
434
436
438
439
440
441
442
443
444
446
448
450
452
454
456
458
460
462
464
466
468
470
472
474
476
478
480
482
484
486
490
492
494
496

FIG. 16

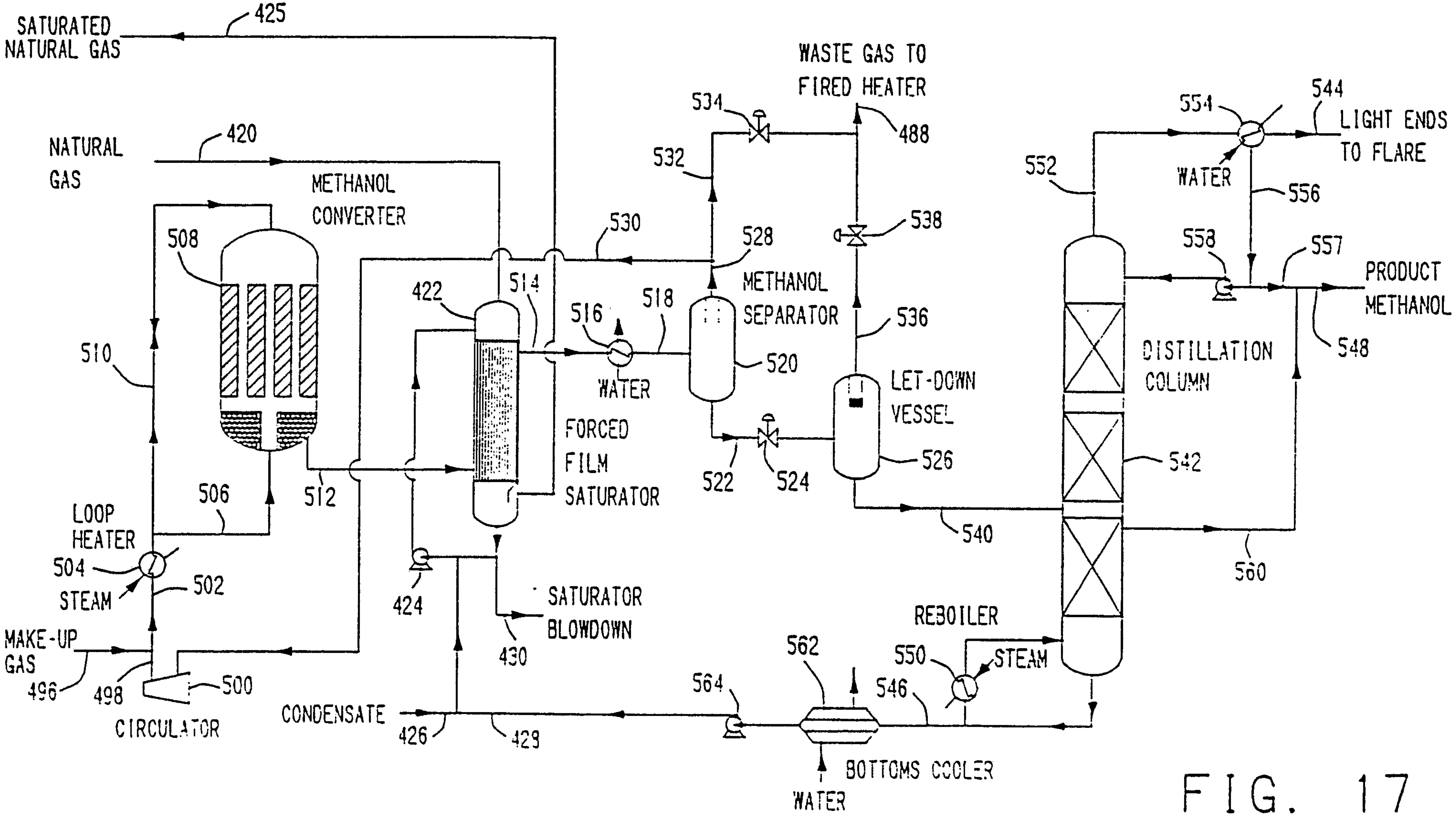

SATURATED NATURAL GAS
425
NATURAL GAS
420
METHANOL CONVERTER
508
510
506
512
LOOP HEATER
504
STEAM
502
MAKE-UP GAS
496
498
500
CIRCULATOR
CONDENSATE
426
429
422
514
424
430
SATURATOR BLOWDOWN
FORCED FILM SATURATOR
516
WATER
518
530
532
534
528
METHANOL SEPARATOR
520
522
524
WASTE GAS TO FIRED HEATER
488
538
536
LET-DOWN VESSEL
526
540
552
554
WATER
544
LIGHT ENDS TO FLARE
556
558
557
PRODUCT METHANOL
548
DISTILLATION COLUMN
542
560
REBOILER
550
STEAM
546
562
BOTTOMS COOLER
WATER
564

FIG. 17

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 89/05370

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: C 07 C 31/04, C 07 C 29/15

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	C 07 C 29/00, C 07 C 31/00

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	EP, A, 0067491 (STAMICARBON) 22 December 1982 see page 1, lines 17-34; page 2, line 19 page 3, line 30; page 5, lines 3-23; page 7, example; pages 8-9, claims; figures 1/1	1,3-5, 7-13,16-22
	--	
X	EP, A, 0111376 (STAMICARBON) 20 June 1984 see page 1, line 20 - page 2, line 10; page 2, line 36 - page 3, line 10; page 3, line 33 - page 4, line 14; figures 1/1; pages 6-7, claims	1,3-5, 7-13,16-22
	--------------	

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search 21st March 1990	Date of Mailing of this International Search Report 12 APR 1990
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer Mme N. KUIPER

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 8905370
SA 32913

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 06/04/90
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A- 0067491	22-12-82	NL-A- 8102840	03-01-83
		CA-A- 1241666	06-09-88
		JP-A- 58000923	06-01-83
		US-A- 4464483	07-08-84
EP-A- 0111376	20-06-84	NL-A- 8204820	02-07-84
		CA-A- 1242749	04-10-88
		JP-A- 59167527	21-09-84

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82