PATENT SPECIFICATION

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3557

COMPLETE SPECIFICATION

Synthesis of Hydrocarbons

We, STANDARD OIL DEVELOPMENT COMPANY, a Corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

The present invention relates to the manufacture of valuable synthetic products by the catalytic conversion of gas mixtures containing hydrogen and carbon monoxide produced from solid carbonaceous materials. The invention is more particularly concerned with improvements in synthesis gas production and hydrocarbon synthesis which cooperate to afford substantial savings and increased thermal efficiencies in the catalytic synthesis of hydrocarbons on the basis of coal or other carbonaceous solids such as lignites, brown coals, peat, oil shale, tar sands, cellulosic materials including lignin, all types of cokes, including oil coke, etc.

The catalytic synthesis of hydrocarbon oils and valuable chemicals from carbon monoxide and hydrogen has been assuming increasing importance in recent years as a source of fuels and raw materials supplementing and potentially replacing the steadily decreasing crude oil resources. The hydrocarbon synthesis may be operated on the basis of either natural gas and other hydrocarbon gases or carbonaceous solids such as coal, etc. for the production of synthesis gas containing carbon monoxide and hydrogen. Coal is the most plentiful, least expensive and, as such, the most desirable raw material. However the hydrocarbon synthesis based on coal has not as yet advanced to a state of development at which the products of the synthesis could be manufactured at a cost fully competitive with that of similar products recoverable from crude oil.

This is particularly true for the synthesis of high octane motor fuels in the form of substantially unsaturated hydrocarbons which may be produced from carbon monoxide and hydrogen in the presence of iron catalysts at elevated pressures. Extensive research and development work within the last ten years has demonstrated that the most desirable procedure with respect to thermal efficiency as well as product yields and quality involves application of the so-called fluid solids technique wherein the catalyst is maintained in the form of a dense highly turbulent mass of finely divided solids fluidized by upwardly flowing gases to resemble a boiling liquid having a well defined upper level. This technique, particularly when applied to iron-type catalysts, involves the use of relatively high pressures above about 250 lbs. and preferably of about 400—600 lbs. per sq. in. to prevent catalyst carbonization and fluidization difficulties. One of the most serious obstacles in the path of using coal as the basis for an iron-catalyzed fluid type high pressure hydrocarbon synthesis has been the high cost anticipated for the production from coal of a synthesis gas of a composition and at a pressure suitable for this type of hydrocarbon synthesis. Another difficulty is presented by the problem of adapting the synthesis operation to the characteristics of the synthesis gas produced from coal so as to accomplish results comparable to those attainable on the basis of natural gas as the raw material. The present invention overcomes these difficulties.

The specification of British Patent No. 330,918 discloses and claims a method of obtaining a gaseous mixture of carbon monoxide, carbon dioxide and hydrogen by passing a mixture of oxygen and water vapour over carbon substantially free from volatile impurities at a reaction temperature not exceeding about 750° C. It is stated that for practical purposes the pressure in the gas generator should be limited to below 15 to 20 atmospheres.

The specification of Patent No. 504,529 also discloses a method of producing a synthesis gas by the action of an oxygen-steam mixture on a fuel under a pressure of several atmospheres, for example 5 to 50 atmospheres.

The specification of Patent No. 516,555 discloses and claims a process of synthesising hydrocarbons, in which coal, coke or other suitable carbonaceous material is gasified under pressure with steam and the products of gasification are reacted with evolution of heat in a water-cooled reaction chamber or chambers including the step or steps of using low pressure steam produced by heating of the cooling water and/or contained in the products of reaction for the production of high pressure steam and using the latter in the gasification step. The steam used in the gasification step is stated to have a pressure of 9 to 12 atmospheres.

The specification of our earlier Patent No. 631,319, which was not published at the date of application of the present case claims a process for controlling the liquid/gas product distribution in the production of liquid and gaseous fuels by the conversion of carbonaceous materials into a gaseous mixture containing carbon monoxide and hydrogen, and the subsequent catalytic treatment of said mixture to produce normally liquid hydrocarbons and a a fuel tail gas wherein the said fuel tail gas is recovered and a portion thereof in excess of the desired requirement of fuel gas is recycled to the reaction for converting the carbonaceous material into the carbon monoxide-hydrogen mixture.

The Specification of another of the prior patents of the present applicants' Patent No. 640,907, which also was not published at the date of the present case claims a process for the production of fuel gases of high heating value which comprises passing a gas mixture containing carbon monoxide and hydrogen at conversion conditions of temperature, pressure and through-put conducive to the predominant formation of normally gaseous hydrocarbons, particularly methane, to a conversion zone containing a highly turbulent, dense, fluidized mass of finely divided solid hydrogenation catalyst capable of promoting the conversion of carbon monoxide and hydrogen predominantly to said normally gaseous hydrocarbons at the conversion conditions, preheating the said gas mixture to substantially said conversion temperature to its entry to the conversion zone, withdrawing heat from the conversion zone to maintain the conversion temperature at the desired level, and recovering normally gaseous hydrocarbons from the conversion zone.

It has now been discovered that particularly desirable hydrocarbons and oxygenated organic compounds are obtainable when the gas generation step and the subsequent hydrocarbon synthesis step are conducted at approximately the same pressure. This feature is not disclosed in any of Patent Specifications Nos. 330,918, 504,529 or 516,555, or claimed in either of Patent Specifications Nos. 631,319 or 640,907.

The present invention therefore provides a process for the production of hydrocarbons and oxygenated organic compounds comprising contacting carbonaceous solids with an oxidising gas containing steam so as to generate gas mixture containing carbon monoxide and hydrogen and passing the gas mixture so formed to a hydrocarbon synthesis zone wherein it is catalytically converted to a mixture of hydrocarbons and oxygenated organic compounds, the gas generation step being conducted at approximately the same pressure as the subsequent hydrocarbon synthesis step, both pressures being between 150 and 700 pounds per square inch, preferably between 300 and 600 pounds per square inch.

Preferably the gas mixture from the generation step is passed in a single pass operation through a number of hydrocarbon synthesis stages each of which are operated at a pressure substantially the same as that of the gas generation step.

The gasification conditions should be such as will produce a synthesis gas having a relatively low $H_2:CO$ ratio of about 0.7—1.5 which may be supplied to the synthesis reactor without further compression and without extensive CO_2 scrubbing. The synthesis process is operated without tail gas recycle in once-through fashion. The synthesis tail gas which is obtained under the synthesis pressure is advantageously utilized for pressurizing in the gas generator stage of the process.

The advantages of this procedure are considerable in number and importance. When carbonaceous solids are gasified with steam and oxygen to produce gas mixtures containing H_2 and CO in the relatively low ratios indicated above, it is not necessary to remove completely the CO_2 from the synthesis gas prior to its entry into the synthesis reactor. Production of the synthesis gas substantially at synthesis pressure makes superfluous further compression of the gas between gas generator and synthesis reactor. In this manner mechanical compression is required only on the oxygen used in the gas generator for heat generation, which means a reduction of about 75—80% in the volume of gas to be compressed assuming the use of oxygen of about 95% purity. Furthermore, recent experimental work indicates that the rate of reaction between carbon and steam increases as the pressure and the weight of carbonaceous solids held up in the gas generator increase. Thus the increase in gasification pressure results in an increased reaction rate or in a decrease of the carbon hold-up requirements or, for a given carbon hold-up, in a possible decrease in reaction temperature. Further considerable saving in compressor investment is realized by the use of the high pressure synthesis tail gas for pressurizing the feed solids for the gas generator.

Reaction conditions suitable for the production of a synthesis gas having an $H_2:CO$ ratio of about 0.7—1.5:1 include temperatures of about 1600°—2000° F., preferably about 1700°—1900°F., steam feed rates of about 10—45 lbs. of steam per 1000 standard cu. ft. of $CO+H_2$ produced at steam conversion rates of about 90 to 40%, and oxygen feed rates of about 200—250 standard cu. ft. of O_2 per 1000 standard cu. ft. of $CO+H_2$ produced based on oxygen of about 95% purity. The most favorable conditions within the ranges indicated depend on the exact $H_2:CO$ ratio desired, the character and reactivity of the feed solids, the preheat of the gaseous and solid reactants and the thermal efficiency of the system, and may be readily determined for any specific practical case. The $H_2:CO$ ratio of the product gas may be further adjusted toward increased CO production by the controlled addition to the gas generator of CO_2 which may be readily obtained by suitable scrubbing of the generator gas or from synthesis tail gas. In many cases recycle of synthesis tail gas as such to the gas generator may serve the same purpose.

A substantially complete catalytic conversion of this synthesis gas predominantly into normally liquid synthetic products in once-through fashion is preferably carried out in multi-stage series flow operation with liquid product recovery, CO_2 scrubbing, and, if desired, an adjustment of the $H_2:CO$ ratio to the desired value of about 0.7 to 1.5:1 between stages. The individual synthesis stages are preferably operated by the fluid solids technique at pressures within the limits of this invention, i.e., from 150—700 lbs. per sq. in., preferably 300—600 lbs. per sq. in., using conventional finely divided synthesis catalysts, preferably those of the iron type which are most suitable for high pressure operation and the production of high octane motor fuels. Operating conditions of this type of hydrocarbon synthesis are well known in the art and need not be specified for a proper understanding of the present invention by those skilled in the art. Any conventional method of converting hydrocarbon gases of the type present in synthesis tail gas such as methane, ethane, gaseous olefins, etc. into H_2 and CO such as catalytic reformation with steam and/or CO_2, oxidation with free oxygen and/or a metal oxide, and combinations of these methods may be used together with CO_2 control to adjust the $H_2:CO$ ratio between synthesis stages to the desired value of about 1:1. However, for the process of the present invention partial oxidation is usually preferable to reformation since the equipment is more readily adapted to high pressure operation.

An important element of the present invention is a proper control of the CO_2 content of the gases fed to the individual synthesis reactors and to the primary and secondary synthesis gas generators in order to maintain the desired $H_2:CO$ ratio in the synthesis gases and to assure satisfactory efficiency of the once-through synthesis operation. Assuming an $H_2:CO$ ratio of about 1:1 in the synthesis gases supplied to each individual synthesis reactor, the CO_2 content of these gases should be kept below about 15% by volume but need not be reduced below about 5% by volume for efficient once-through operation. Carbon dioxide concentrations of about 7—12% by volume are generally most desirable for this purpose. When carbon formation in the primary or any subsequent synthesis reactor rises high enough to cause fluidization difficulties or to affect conversion to desired products, small amounts of steam, say about 5—15 volume per cent steam, may be added to the synthesis gas or the CO_2 concentration may be reduced by more intensive scrubbing.

The presence of excess quantities of CO_2 in the synthesis gas will tend to reduce the H_2 content of the gases by reacting to form CO and H_2O so as to establish water gas equilibrium. This then would cause a decreased H_2 partial pressure in the reactor and thus be conducive to carbon formation. Therefore, control of the CO_2 content of the gases provides a method for indirectly controlling the $H_2:CO$ ratio in synthesis gas. While CO_2 concentrations within the ranges mentioned above may be readily maintained in the primary synthesis gas by proper operation of the primary water gas generator followed by only insignificant CO_2 scrubbing the relatively high CO_2 concentration of synthesis tail gas and of the gas produced by oxidation of synthesis tail gas makes more extensive CO_2 scrubbings necessary between synthesis stages in order to maintain the CO_2 content of the synthesis gases fed to the individual synthesis stages within the ranges indicated and also to prevent the formation of excessive proportions of CO in the intermediate tail gas reformation or oxidation stages. For example, the CO_2 concentration of the tail gas subjected to oxidation with free oxygen between synthesis stages may be about 30% by volume.

Final stage high pressure synthesis tail gas is used at least in part for pressurizing the solids fed to the primary gas generator. Pressurized lock hoppers operating on short cycles of about 10—20 minutes have been found to be suitable for this purpose and afford substantial savings in investment requirements for the lock hoppers. Thereafter, the tail gas is available as a fuel gas or to drive waste gas turbines or for any other desired use. Any suitable part of the tail gas may either prior or after its use as a pressurizing gas and, if necessary after CO_2 adjustment, be supplied to the primary gas generator to control the $H_2:CO$ ratio of the primary synthesis gas.

Having set forth its general nature and objects, the invention will be best understood from the more detailed description hereinafter in which reference will be made to the accompanying drawings in which

Figures 1, 1A, and 1B show the flow plan of a system suitable for carrying out the present invention; and

Figures 2 and 3 show modifications of the coal gasification stage.

Referring now in detail to Figures 1, 1A, and 1B the system illustrated therein essentially comprises a lock hopper system 12, 14, 22; a primary synthesis gas generator 30; a gas scrubbing system 88, 94; a primary synthesis reaction 120; a tail gas oxidizer 156; a secondary synthesis reactor 180; and CO_2 absorbers 142 and 168 in the synthesis system. The functions and cooperation of these elements will be forthwith explained using as an example the production of about 13,600 bbl. per stream day of gasoline range hydrocarbons from a bituminous coal employing the fluid solids technique in both the coal gasification and synthesis stage. It should be understood, however, that the system may be operated in a generally analogous manner using other carbonaceous solids such as coke, petroleum coke, lignites, shales, etc., as the starting material.

For purposes of illustration it is assumed that the bituminous coal used as the starting material has a composition about as follows:

	By Weight
Moisture	5.0%
Carbon	62.4%
Hydrogen	4.2%
Oxygen	5.5%
Nitrogen	1.3%
Sulfur	1.6%
Ash	20.0%

About 7,130 tons of the coal per stream day is supplied through line 1 to crusher 2 wherein it may be crushed to pass through a 30 mesh screen. Any other fluidizable particle size falling within the wide range of ½ in. to 200 mesh may be used depending on the specific design and operation of gas generator 30. From crusher 2 the ground coal is hoisted or conveyed in any suitable manner to coal storage bin 6, via line 4 which may have the form of a vertical bucket conveyor. Bin 6 may have a capacity of about 34,000 cu. ft. corresponding to a coal hold up of about 2 hours and may be held at atmospheric pressure.

Coal from hopper 6 flows by gravity alternately through valved lines 8 and 10 to lock hoppers 12 and 14 which are alternately charged at about atmospheric pressure and discharged at about 500 lbs. per sq. in. in cycles of about 15 minutes each. For this purpose lock hoppers 12 and 14 may have a capacity of about 2600 cu. ft. each, corresponding to a coal hold up time of about 7.5 minutes. Lock hoppers 12 and 14 are pressurized by means of high pressure synthesis tail gas supplied through lines 13, 15 and 17 as will appear more clearly hereinafter. The tail gas released during the depressuring cycles may be vented to any existing fuel system.

The feed coal now under process pressure flows from hoppers 12 and 14 through valved lines 16 and 18 and line 20 to a large buffer lock hopper 22 which may have a capacity of about 10,500 cu. ft. corresponding to a coal hold up time of about 30 minutes. A pressure drop of about 10 lbs. per sq. in. may exist between lock hoppers 12 and 14, on the one hand, and hopper 22, on the other hand. Lock hopper 22 permits the continuous flow of coal through valved line 24 to generator 30 at a rate of about 300 tons per hour and at a pressure of about 480 lbs. per sq. in. Line 24 may have the form of an aerated standpipe receiving and aerating gas such as steam, synthesis tail gas, etc. through tap 26 in order to facilitate the solids flow through line 24.

The coal feed enters generator 30 at a point above distribution means 32 arranged in the lower portion of generator 30. Simultaneously, generator 30 receives from line 34, through distributor 32, a mixture of steam and oxygen preheated at generator pressure to a temperature of about 1000°—1500° F. as will appear more clearly hereinafter. The gas mixture enters the main section of generator 30 at a superficial linear velocity of about 0.3—1 ft. per second adapted to maintain the solids above distributor 32 in the form of a dense turbulent fluidized mass having a well defined upper level L_{30}.

The absolute and relative proportions of steam and oxygen are so chosen that about 70—95% of the carbon fed to generator 30 is gasified at a steam conversion of about 40—90% and about 5—30%, preferably 10—20%, of the carbon gasified is burned to CO_2 to supply the heat required by the water gas reaction and to maintain a gasification temperature of about 1600°—2000° F., preferably about 1800° F. Amounts of about 0.3—1.5 lbs. of steam and about 0.416 to 0.544 pounds of oxygen per pound of coal supplied to generator 30 are generally adequate for this purpose and for the production of a gas mixture having an H_2:CO ratio of about 0.7—1.5:1. For example the gas mixture supplied through line 34 may be composed of about 83.4 million standard cu. ft. per stream day (MMSCF/SD) of oxygen (95% purity) and about 8.1 million pounds per day of steam, for a generator bed height of about 30 feet. Depending on the reactivity of the carbonaceous charge, reaction temperature and pressure, the bed height may vary between about 5 and about 40 feet.

An amount of about 2100 tons per day of solid gasification residue containing about 20—50% by weight of carbon is withdrawn through bottom drawoff well 36 and passed through standpipe 38 aerated through tap 40 substantially at generator temperature to one or more ash drums 42 maintained at about generator pressure. From ash drums 42 the solid residue may be fed through line 44 by any suitable means to boiler house 46 wherein the remainder of the carbon may be burned to produce steam for any desired use.

Water is introduced through line 48 (Fig. 1A) at a temperature of 300°—310° F. and a pressure of about 500 psig., into preheater 50. The water at saturation temperature flows from heat exchanger 50, through line 52 into the boiler 54, where 500 psig. steam is produced. The steam generated in 54 flows through line 56, heat exchanger 58 and line 60 to line 34 which it enters at a temperature of about 1800° F. Simultaneously, oxygen of about 95% purity is produced in oxygen plant 62 and pumped by compressor 64 at a pressure of about 500 lbs. per sq. in. through line 66, heat exchanger 68 and line 70 to line 34 which it enters at a temperature of about 800° F. to make up therein the oxygen-steam mixture described above. Higher oxygen preheat temperatures may be employed where the heat exchanger material so permits.

Returning now to generator 30, an amount of about 515 MMSCF/SD of product gas is withdrawn overhead from level L_{30}. The gas containing some entrained solids leaves through line 72 at about generator temperature. It may have a composition about as follows:

CO_2	9.4%
CO	34.0%
H_2	34.0%
H_2O	17.8%
H_2S	0.5%
N_2	1.3%
CH_4	3.0%

The product gas then flows through heat exchangers 58 and 68 wherein it gives off heat to steam and oxygen respectively to enter a third heat exchanger 74 at a temperature of about 1370°—1400° F. from which it is passed to a cyclone separator 76. Heat exchanger 74 serves to reheat the synthesis gas after scrubbing as will appear hereinafter. In cyclone separator 76 entrained solids are separated and may be withdrawn through line 78 and returned through a lock hopper 80 and line 82 to lock hoppers 12 and 14 or withdrawn from the system.

Product gas now at about 1000° F. leaves cyclone 76 through line 84 and passes through heat exchangers 54 and 50 to produce steam and preheat boiler feed water and through line 86 at a temperature of about 410°—420° F. to a conventional water scrubber 88 for scrubbing of solids and further cooling to about 100° F. A slurry of scrubbed solids in water leaves the system through line 90.

Product gas is withdrawn through line 92 and passed to the bottom of a conventional CO_2 and/or H_2S absorber 94 wherein it flows countercurrently to a suitable absorbent such as triethanolamine supplied through line 96 from a conventional reactivator 98 to the top of absorber 94. Rich absorbent is withdrawn through line 100, passed to the top of reactivator 98 and reactivated therein by the application of heat, all in a manner known *per se*.

Carbon dioxide and H_2S leave reactivator 98 through line 102 and a liquid trap 104 from which absorbent may be returned through line 106 to reactivator 98. Carbon dioxide and H_2S leave the system through line 108, to be discarded or recovered in any conventional manner. For the purpose of the present example absorber system 94, 98 is preferably so operated that about 5 MMSCFSD of CO_2 and about 3 MMSCFSD of H_2S are withdrawn through line 108 to reduce the H_2S content to practically nil. A triethanolamine circulation of about 1500 gals. per minute is suitably for this purpose. Any portion of the CO_2 recovered from line 108 may be returned to generator 30 to adjust the $H_2:CO$ ratio of the gas produced if desired.

The purified gas leaves absorber 94 through line 110 at about 100° F. and passes through heat exchanger 74 wherein it may be reheated to about 600° F. in heat exchange with raw hot product gas. The reheated gas may then be passed through line 112; mixed with about 3000 SCFM of air supplied by compressor 114 at a pressure of about 450 lbs. per sq. in., and then passed through one or more drums 116 filled with an iron oxide type desulfurization catalyst for the removal of organic sulfur in a conventional manner. The purified gas which may amount to about 417 MMSOFSD and is now ready for use in the synthesis stage of the process leaves drums 116 through line 118 at a pressure of about 430 lbs. per sq.in. and a temperature of about 600° F. It may have a composition about as follows:

CO_2	10.4%
CO	42.0%
H_2	42.0%
CH_4	3.7%
N_2	1.6%
H_2O	0.3%

This gas may be supplied through line 118 to the lower portion of a conventional fluid type synthesis reactor 120 (Figure 1B) which it enters through a distributing grid 122 at a superficial velocity above the grid of about 0.5—1 ft. per sec. Reactor 120 preferably contains a finely divided iron-type catalyst such as alkali-promoted sintered and reduced pyrites ash or red iron oxide, or the like having a particle size of about 20—200 microns, predominantly 50—100 microns. At the flow velocities indicated the catalyst is converted into a dense, turbulent, fluidized mass forming a well defined upper level L_{120} and may have an apparent density of 20—150 lbs. per cu. ft., preferably 40—100 lbs. per cu. ft. The pressure is kept at about 400—430 lbs. per sq. in. so that no further compression of the synthesis gas supplied through line 118 is required. The temperature of the exothermic reaction may be controlled by heat exchange means 124 or any other conventional means of heat withdrawal, at a level of about 600°—800° F. preferably at about 650° F. Reactor 120 may be designed to permit the throughput of the entire output of gas generator 30 in a single vessel or in several vessels arranged in parallel to obtain a CO-conversion of about 80—98% in a single pass. Gasiform synthesis products and unconverted reactants are withdrawn overhead from Level L_{120} and passed through a cyclone separator 126 from which separated catalyst fines may be returned through line 128 or discarded through line 129. Gases substantially free of solids pass through line 130 through a conventional product recovery system which may comprise a condenser 132, a gas liquid separator 134 and a water-oil settler 136. To prevent plugging of condenser 132, liquid product may be recycled through connection 131 to wash down the solids. Several condensers may be used in series with heavier products removed after the first condenser; or a fractionating tower with bottom scrubber section may be used alternatively. Tail gas is withdrawn through line 133. Liquid product passes from separator 134 through line 135 to settler 136 from which hydrocarbons are withdrawn through line 137 and an aqueous layer containing oxygenated compounds through line 139, for further work-up in a conventional manner.

Assuming a CO conversion of about 98%, the yields from the first synthesis stage at the conditions specified above may be about as follows:

Gasoline, bbl./stream day	9,898
Gas Oil ,, ,, ,,	1,392
Alcohols (Raw)	1,543
Tail Gas, MMSCF/SD	170

The tail gas may have about the following composition:

	By Vol.
H_2	14.7%
CO	2.1%
CH_4	12.9%
C_2+	2.5%
N_2	6.5%
CO_2	61.1%
H_2O	0.2%

Gas of this composition is not suitable for an efficient conversion into further amounts of valuable liquid products and is, therefore, converted without substantial pressure loss into a synthesis gas of a more desirable composition, preferably by partial oxidation with free oxygen. Large amounts of CO_2 such as those just specified tend to decrease the H_2:CO ratio of the gas obtainable from the oxidation process. As a general proposition the CO_2 content of the first stage tail gas prior to oxidation with free oxygen should be adjusted to about 25—35% by volume when operating with a synthesis gas having an H_2:CO ratio of about 1:1 in both synthesis stages.

In the case of the present example the tail gas in line 133 is, therefore, passed through line 140 to a CO_2 absorber 142 which cooperates with an absorbent reactivator 144 in a manner similar to that described in connection with the CO_2 absorption system 94, 98. In absorber 142 the CO_2 content of the tail gas may be reduced to about 30% by volume and the removed CO_2 amounting to about 75 MMSCF/SD may be recovered through line 146 to be used in the primary gas generator, if desired. A by-pass line 148 around absorber 142 may be used when the CO_2 content of the first stage tail gas is within the desirable ranges specified above.

After adjustment of its CO_2 content the tail gas passes through line 150, heat exchanger 152 and line 154 to a conventional high pressure oxidizer 156 which it enters at a temperature of about 860° F., being preheated in heat exchanger 152 by exchange with hot product gas from oxidizer 156. An amount of about 20—25 MMSCFSD of oxygen of about 95% purity is supplied to oxidizer 156 from compressor 64 (Fig. 1) via lines 66, 67 and 158, preferably after preheating to about 800° F. in heat exchange with any of the hot process streams. Oxidation of the tail gas takes place at about 1800°—2500° F. and pressures similar to or somewhat lower than in synthesis stage 120. About 165—180 MMSCFSD of a synthesis gas is produced.

This gas is withdrawn through line 160, passed through heat exchanger 152, line 162, gas reheater 164 and line 166 to a CO_2 absorption system schematically indicated at 168 wherein the CO_2 content may be reduced if desired. Carbon dioxide may be recovered through line 170 for any desired use. If no CO_2 adjustment is required, by-pass line 172 may be used. A scrubber or filter may be desirable for removing traces of soot from the gas leaving the oxidizer and prior to its entry into the scrubber 168. The gas, after CO_2 removal to a CO_2 content of about 5—15%, passes through line 174 to reheater 164 wherein it may be reheated to about 600° F. The reheated gas entering secondary synthesis reactor 180 through line 176 has about the following composition:

H_2	40.3%
CO	40.3%
CO_2	8.7%
CH_4	0.7%
N_2	9.8%
H_2O	0.2%

Reactor 180 is designed and operated substantially as outlined in connection with reactor 120, a distributing grid 182, a cooling device 184, a cyclone separator 186 and fines return and withdrawal pipes 188 and 189 being provided as before. The reaction conditions may be substantially those specified for reactor 120 to accomplish a CO conversion of about 80—98% so that total conversion based on original CO produced in generator 30 closely approaches 100%.

Products and unconverted reactants are withdrawn through line 190 and treated in condenser 192, separator 194 and settler 196 as described in connection with the recovery system 132, 134, 136. Liquid hydrocarbons are withdrawn through line 197 to be combined with those in line 137 and the aqueous layer containing oxygenated compounds flows through line 199 to join the product in line 139.

The secondary stage tail gas leaves separator 194 through line 195 and may be returned substantially at the pressure of reactor 180 through line 198 to line 13 and lock hoppers 12 and 14, if desired via CO_2 absorption system 200 or via by-pass line 202. Any desired portion of the tail gas may be withdrawn from the system to be used as a fuel gas or for any other suitable purpose. The total secondary tail gas may amount to about 50—60 MMSCFSD and may have a composition about as follows:

	Vol. %
H_2	13.2
CO	1.9
CO_2	54.9
CH_4	5.0
C_2+	2.2
N_2	22.6
H_2O	0.2

It has a heating value of about 120—140 BTU per cu. ft. which may be increased to about 250—310 BTU per cu. ft. by CO_2 removal.

The system illustrated by the drawing permits of various modifications, some of which will be briefly explained below.

Whenever it appears desirable for design considerations, the primary gas generator stage may comprise a plurality of generators of the type of generator 30, arranged for parallel flow of gas and solids feed. Instead of generating the heat required in generator 30 by conducting a combustion reaction using oxygen of 95% purity within generator 30, the necessary heat may be generated by circulating generator residue to a separate fluid type combustion zone which may be supplied with air rather than oxygen, and supplying heat to generator 30 in the form of sensible heat of solid combustion residue recirculated to generator 30. When it appears advisable to carbonize the coal prior to the gasification stage, a fluid type carbonization zone operated in a manner similar to that described for generator 30, but at a lower temperature and pressure suitable for efficient carbonization, may be interposed preferably between bin 6 and lock hoppers 12 and 14.

In certain cases it may be more desirable to place heat exchanger 54 which normally may act as a waste heat boiler ahead of product gas reheater 74 in the direction of product gas flow, in order to make more heat available for high pressure steam generation. In place of water scrubber and cooler 88 an indirect heat exchanger may be used, the water condensing from the cooled product gas serving to scrub out entrained solids fines. Water scrubbing, steam stripping and energy recovering means such as a Pelton wheel may be used in addition to or in place of the gas purification system 94, 98, as will be readily understood by those skilled in the art. In using an energy recovery device such as a Pelton wheel the absorbents flowing from the absorbers would be expanded to stripping pressure through the energy recovery device, thereby providing some of the energy necessary for pumping the stripped absorbent up to process pressure.

While heat exchangers 50, 54 and 58 have been shown as means for producing and preheating steam to nearly the gas generator temperature, substantial advantages may be realized by using direct heat exchange with hot solid generator residue withdrawn through line 38.

In this case, countercurrent flow of solid residue and steam should be attained for best efficiency. In this way the residue can be cooled to a low temperature, while the steam is preheated essentially to generator temperature. Countercurrent flow may be obtained by means of a high ratio of length to diameter (L/D) in the contactor, for example L/D greater than 5, or baffles, contacting plates, packing, or other known means may be used.

The heat exchange may be effected in one or more preferably fluid-type vessels in parallel or series taking the place of drum 42 which may receive steam and/or water through line 205 and connect directly into the bottom of the generator or may be connected thereto by means of conduits such as line 207. In some cases better control will be obtained when using several vessels with series flow. Various arrangements may be used for this purpose. A plurality of vertical fluid type contactors may be used connecting into the bottom of the generator. Liquid water and/or steam may be introduced near the lower end of the contactor and pass out the top directly into the generator section. The hot ash flows down the contactor and is cooled and removed at the bottom. A series of contacting plates, or an arrangement of vertical baffles may be used to reduce back mixing of the solids to a tolerable level. Gas velocity in the contacting section will usually be maintained between 0.1 and 2.0 ft. per second at operating conditions. The contacting vessels may operate at gasifier pressure, or a depressuring step may be included to allow use of a lower pressure.

The inlet steam may also be contacted with spent char in the generator zone beneath distributor 32 in which case well 36 would feed into this lower space and pipe 38 would withdraw solids from this lower space. The oxygen would then be introduced separately into the generator. Well 36 may also have the form of an external pipe fitted with suitable valves. Other arrangements may appear to those skilled in the art.

Procedures of this type offer the important advantage of providing steam generation and superheating without requiring exchanger surface. Thus, expensive surface for cooling spent char may be eliminated as well as the surface required for generating and preheating the steam. Because of the excellent heat transfer, the steam can be heated practically to generator temperature if desired. This type of contactor has particular advantages when the gasification is operated at relatively low pressures because excellent heat transfer is obtained even at low pressures, for example atmospheric pressure. Another important feature is that the water used for steam generation may contain oxygenated products formed in the synthesis step. Since no heat transfer surface is required, corrosion is no problem. By returning the product water containing unrecovered oxygenated compounds from the work-up of the liquid in line 139 to the system, the overall efficiency of the process is improved. Also the problem of recovery or waste disposal is avoided.

Whether or not the steam generated in this manner represents more or less than the process steam requirement depends upon the particular conditions under consideration. It may be greater than, exactly equal to, or less than the process steam requirement.

Further modifications of the coal gasification system which permit substantial improvements with respect to thermal efficiency, particularly when the carbonaceous solids feed is to be carbonized prior to gasification, are illustrated in Figures 2 and 3.

The high pressure coal gasification system illustrated in Figures 1 to 1B requires considerable high temperature alloy exchanger surface and in addition a substantial investment for oxygen production. Some 35% of the heat generated by oxygen is used for preheating coal and steam going to the gas generator. Thus, advantage is not taken of the fact that the sensible heat content of the product gas and spent ash streams may be sufficient to allow preheating the reactants to reaction temperature, and at the same time supply the heat required for coking. The subsequent disclosure shows an efficient and practical method for effecting an improved heat transfer by cooling the product streams while preheating the feed streams. An important feature of this embodiment of the invention is that all of the heat transfer may be effected without using exchanger surface. The required heat transfer is carried out by countercurrent contacting of process solids with gas streams. It will be apparent from a study of the following disclosures that they afford substantial improvements in the coal gasification process, including a considerable reduction in plant investment and operating costs, and at the same time a material increase in the thermal efficiency of the entire process. These improvements amount to an appreciable saving in the gasification section and in addition the investment for oxygen production may be about 25% lower.

In this embodiment of the invention, direct contacting of solids and gases is used to transfer heat from the streams leaving the gas generator to the reactants. The same mechanism is used to carry heat into a coking vessel where valuable liquid and gaseous products are recovered from the coal before gasification. It is noted that the coking operation may be carried out without requiring any vessels other than those already in the system described above. Thus, a coking process may be added to the system without requiring an additional investment, other than for recovery of coking products.

Figures 2 and 3 illustrate two applications of the principles involved, similar reference characters being used to identify apparatus elements similar to those shown in Figures 1 and 1A. In Figure 2 the coal feed flows to a low pressure storage hopper 6 where it may be preheated in any suitable manner. For example, product streams from synthesis, coking, etc. can be employed using indirect heat transfer in coil 7. Aeration steam or gas is added to this hopper through taps *t*. Preheating the coal by exchange with product streams has the advantage of saving on cooling water. In some cases it will be preferable to preheat the coal by using circulating gas or solids streams, or the preheating can be omitted. Coal flows from low pressure hopper 6 through lock hoppers 12 and 14 to build up the desired pressure and it then mixes in line 20 with a hot char stream from line 21 which supplies the heat to maintain the coking zone 22 at the desired temperature. Products from coking are under pressure and flow through line 23 to heat exchange, tar recovery equipment, etc., not shown. Char from coker 22 flows through line 25 to a heat exchange tower 27 where it is contacted countercurrently with the product gas leaving generator 30 through line 72. Part of the char is withdrawn at an intermediate point of this tower and recycled through line 21 to the coking vessel for temperature control. The feed flow of char continues down the tower and is preheated to a temperature approaching that of the gasifier. The preheated char then flows through line 29 to the generator 30. Packing and/or baffles can be used in heat exchange tower 27 to improve the countercurrent action in a manner known *per se*.

Oxygen and steam are added to generator 30 through line 34 as described above. Spent ash from generator 30 is removed through a lower heat exchange section 30a where it is cooled by contacting with part or all of the steam used for gasification. The cooled spent ash leaving the bottom of the heat exchange section 30a through line 38 can then be depressured and used in the boiler house. In some cases the heat capacity of the spent ash normally withdrawn will not be sufficient to preheat all the steam that is used. In such a case, part of the cooled spent ash can be recycled to the coking vessel 22 or to the first mentioned heat exchange tower 27 thereby making more hot solids available for preheating steam. Suitable solids and gas distribution means may be employed in heat exchange section 30a together with packing and/or baffles to reduce back mixing.

Figure 2 also shows a convenient arrangement for making steam by direct contact with hot solids. The top section of the heat exchange tower may be used to preheat solids by exchange with the product gases. The hot solids then flow through a standpipe 31 to generate the desired pressure and are then mixed with water supplied through line 33. The suspension flows up through line 35 to a disengaging drum or settler 37 from which the solids are returned to the top of the tower through line 39. If desired, spent ash or other solids of suitable particle size may be added through line 36 in order to establish a desired particle size distribution in the solids returned through line 39 to tower 27. Steam containing a small amount of dust may be withdrawn from the settling drum 37 and this steam may flow through line 41 directly back to the heat exchange section in the bottom of generator 30. If desired, filters and/or cyclones may be used to remove solids from the steam and such steam may be used for other purposes. Alternatively, the steam may be cleaned by scrubbing with water which may then be used for generating the steam. The process as disclosed provides for gasification of coal with a minimum of equipment and with high heat economy. At the same time, coking is carried out with very little additional equipment and without increasing the oxygen requirement of the process.

Figure 3 is similar to Figure 2 except that preheating is accomplished in a separate high pressure storage hopper 22a. With this arrangement the steam generated by drying the coal feed may be used in the gas generator 30. It will be noted that the coal feed is preheated in high pressure hopper 22a in a manner similar to that described in connection with hopper 6 of Figure 2. The coal is simultaneously dried in 22a and the steam so generated is supplied through line 41 to the bottom section of generator 30 as described above. Preheated coal flows through line 20a wherein it is admixed with hot char from line 21, and thence to coker 22. The remainder of the operation is substantially as outlined in connection with Figure 3. If desired, the amount of steam generated in hopper 22a may be increased by adding liquid water to an upper portion of hopper 22a through line 43.

For purposes of illustration, operating temperatures have been indicated for the various elements of Figure 3. It will be understood, however, that other temperatures may be used to obtain essentially similar results. For example, coking can be carried out at temperatures within the range of 800°—1500° F.

Other modifications in the process can be made. For example, heat for gasification may be supplied by introducing the oxygen to a separate heater vessel as previously indicated. This allows operation of the heater vessel to give any desired ratio of CO_2 to CO. Also the fact that the CO_2 is excluded from the gas generator permits operation at higher steam conversion in the gasifier and with a corresponding reduction in steam requirement. When air is used in a separate heater vessel, the flue gases may be used to preheat air, coal, etc. before flowing to a flue gas turbine. In this case, it may not be necessary to use oxygen for the reformation or oxidation of the tail gas from the first synthesis stage. Instead this first stage tail gas, after CO_2 adjustment, if necessary, may be contacted with hot solid residue from the heater vessel to form CO and hydrogen by a reduction and cracking reaction. Temperature may be maintained by solids circulation through the heater and steam may be added to the tail gas prior to contact with the heater residue to further adjust the H_2 : CO ratio. The secondary gas so produced may be desulfurized in any conventional manner prior to its use in the secondary synthesis stage.

It has been indicated above that water containing oxygenated products may be recycled from the product recovery plant of the synthesis stage to the system. In further substantiation of this modification, it may be pointed out that in the conventional product recovery system in hydrocarbon synthesis plants, complete recovery of oxygenated materials is generally uneconomic, consequently substantial amounts of these compounds are wasted. When the unrecovered oxygen compounds are returned to the system and used better overall utilization may be achieved, even though the recovery in the product section is incomplete.

The lean water stream from the product recovery system still containing some oxygen compounds may be used to generate steam which is used in the process. For example, this steam may be fed directly or indirectly to reactor 30 of the coal gasification section as indicated above. If desired, the steam may be reacted with hydrocarbons and CO_2 for production of synthesis gas. Also the lean water stream after partial separation of oxygen compounds may be employed for extracting more oxygen compounds from the oil layer.

By reusing the oxygen compounds in

the process it becomes possible to go to a substantially lower or even zero per cent recovery of oxygenated products from the synthesis reactor, whereby the recovery equipment is simplified. In effect the oxygen compounds are recycled and if they are passed through the gasification reactor they will be decomposed, so that the net result is to convert the oxygen compounds into additional synthesis gas from which hydrocarbons are produced. In some cases it will be desirable to include a step for concentrating the lean water stream before recycling to the system. This would be the case, for example, when the process water requirement is less than that represented by the lean water stream, so that it becomes necessary to reject water from the system.

With respect to the operation of reactors 120 and 180 it is noted that in fluid hydrocarbon synthesis operations over an iron catalyst, it is desirable from the standpoint of carbon formation to operate with as high a reactor hydrogen partial pressure as possible and at the lowest reactor temperature that is consistent with satisfactory feed gas conversion. However, at reactor pressures approaching or exceeding 600 psig. and temperatures of 650° F. and lower, poor fluidization exists and the process may become inoperable because the heavy oil products are not driven off from the reaction zone. Poor fluidization has been frequently encountered at the bottom of the fluid bed causing a partial plug across the reactor under these conditions. The catalyst from this portion of the reactor then contains considerably more material soluble in benzene than the main bulk of the catalyst. Higher reactor temperatures tend to overcome this difficulty, but carbon formation may be greater, thus off-setting the advantage of the high hydrogen partial pressure. These difficulties may be overcome by operating the fluid reactor at 600—1000 psig. and 600°—650° F. and by continuously removing a stream of catalyst along with the heavy oil adhering to it from the bottom of the reactor into a stripper vessel that operates at reactor temperature or higher, and may be at a lower pressure such as 100—400 psig. The stripping medium may consist of hydrogen or tail gas. The catalyst, stripped of its heavy oil may then be returned to the high pressure synthesis reactor vessel through a system of lock hoppers as will be readily understood by those skilled in the art.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of hydrocarbons and oxygenated organic compounds comprising contacting carbonaceous solids with an oxidising gas containing steam so as to generate gas mixtures containing carbon monoxide and hydrogen and passing the gas mixture so formed to a hydrocarbon synthesis zone wherein it is catalytically converted to a mixture of hydrocarbons and oxygenated organic compounds, the gas generation step being conducted at approximately the same pressure as the subsequent hydrocarbon synthesis step, both pressures being between 150 and 700 pounds per square inch, preferably between 300 and 600 pounds per square inch.

2. A process as claimed in Claim 1 wherein the gas mixture from the generation step is passed in a single pass operation through a number of hydrocarbon synthesis stages each of which are operated at a pressure substantially the same as that of the gas generation step.

3. A process as claimed in Claim 1 or Claim 2 in which the gas mixture from the gas generation step is contacted with a synthesis catalyst in a first synthesis zone to produce normally liquid synthetic products and a tail gas containing H_2, CO, CO_2 and normally gaseous hydrocarbons in proportions unsuitable for hydrocarbon synthesis, said tail gas is subjected to a succession of oxidation and synthesis treatments in which the tail gas from each synthesis treatment is contacted with an oxidizing agent in a conversion zone to produce a further gas mixture containing H_2 and CO in a ratio suitable for hydrocarbon synthesis and said further gas mixture is contacted in a further synthesis zone with a synthesis catalyst to produce additional amounts of normally liquid synthetic products and a further tail gas.

4. A process as claimed in Claim 3 in which the further tail gas is recovered from the final synthesis zone at substantially said pressure and supplied at substantially said pressure to a confined space containing said carbonaceous solids so as to place said carbonaceous solids substantially under said pressure.

5. A process as claimed in any of the preceding claims wherein the oxidising gas used in the gas generator zone includes carbon dioxide and/or oxygen.

6. A process as claimed in Claim 5 wherein the oxidising gas includes carbon dioxide recovered from the gaseous product from the gas generation zone or from the tail gas from one or more of the synthesis zones.

7. The process as claimed in any of Claims 1 to 6 wherein the quantity of

oxidizing gas added to the gasification zone is controlled such that from 70 to 95% of the carbonaceous materials is converted into synthesis gas.

8. The process as claimed in any of Claims 1 to 7 wherein part of the oxygen supplied to the gasification zone is employed to burn from 5—30% of the carbonaceous material to generate the heat required for the gasification of the remainder.

9. The process as claimed in any of Claims 1 to 8 wherein the initial gasification reaction is carried out under conditions of temperature, pressure and oxidizing gas feed rate to produce a gas mixture containing hydrogen and carbon monoxide in the proportion of 0.7 to 1.5 volumes of hydrogen to 1 volume of carbon monoxide.

10. The process as claimed in any of Claims 1 to 9 wherein the initial gasification reaction is carried out at a temperature between 1600 and 2000° F. and preferably between 1700 and 1900° F.

11. A process as claimed in any of Claims 3 to 10 wherein the tail gas from each synthesis zone is adjusted to a carbon dioxide content before subjection to the succeeding oxidation reaction to produce a second synthesis gas mixture containing from 5 to 15% carbon dioxide.

12. A process as claimed in Claim 11 wherein the tail gas from each synthesis zone is adjusted to have a carbon dioxide content between 25 and 35% by volume before subjection to the succeeding oxidation conversion reaction.

13. A process as claimed in Claim 11 or 12 wherein the tail gas from each synthesis zone is scrubbed to remove some of the carbon dioxide.

14. A process as claimed in any of Claims 3—13 wherein each oxidation conversion process is carried out to produce a synthesis gas containing hydrogen and carbon monoxide in the proportion of 0.7 to 1.5 volumes of hydrogen per 1 volume of carbon monoxide.

15. The process as claimed in any of Claims 3—14 wherein at least part of the tail gas from the final synthesis zone is recycled to the initial gasification zone.

16. The process as claimed in any of Claims 2—15 wherein from 5 to 15% by volume of steam is added to the synthesis gas mixture fed to each of one or more of said synthesis zones.

17. The process as claimed in any of Claims 3—16 wherein the oxidizing agent used in the oxidation conversion zones is free oxygen.

18. The process as claimed in any of the preceding claims in which at least a portion of the steam employed is generated by contacting water directly with hot solids withdrawn from said gasification zone.

19. The process as claimed in Claim 18 in which said water contains oxygenated products produced in said synthesis zones.

20. The process as claimed in any of the preceding claims in which at least a portion of the steam supplied to the gasification zone is contacted with solids withdrawn from said gasification zone prior to its entry into said gasification zone.

21. The process as claimed in any of the preceding claims in which the carbonaceous solids in the initial gasification zone are solids withdrawn from a carbonization zone.

22. The process as claimed in Claim 21 wherein the carbonaceous solids comprise the carbonaceous residue from contacting finely divided fluidized carbonizable materials with hot solids withdrawn from the said gasification zone in a carbonization zone under carbonization conditions of temperature and pressure.

23. The process of Claim 21 in which at least a portion of the oxidizing gas is directly contacted with hot solids withdrawn from said carbonization zone, prior to its supply to said gasification zone.

24. The process as claimed in any of the preceding claims wherein the catalyst used in the synthesis zones is a synthesis catalyst of the iron type.

Dated this 9th day of November, 1949.

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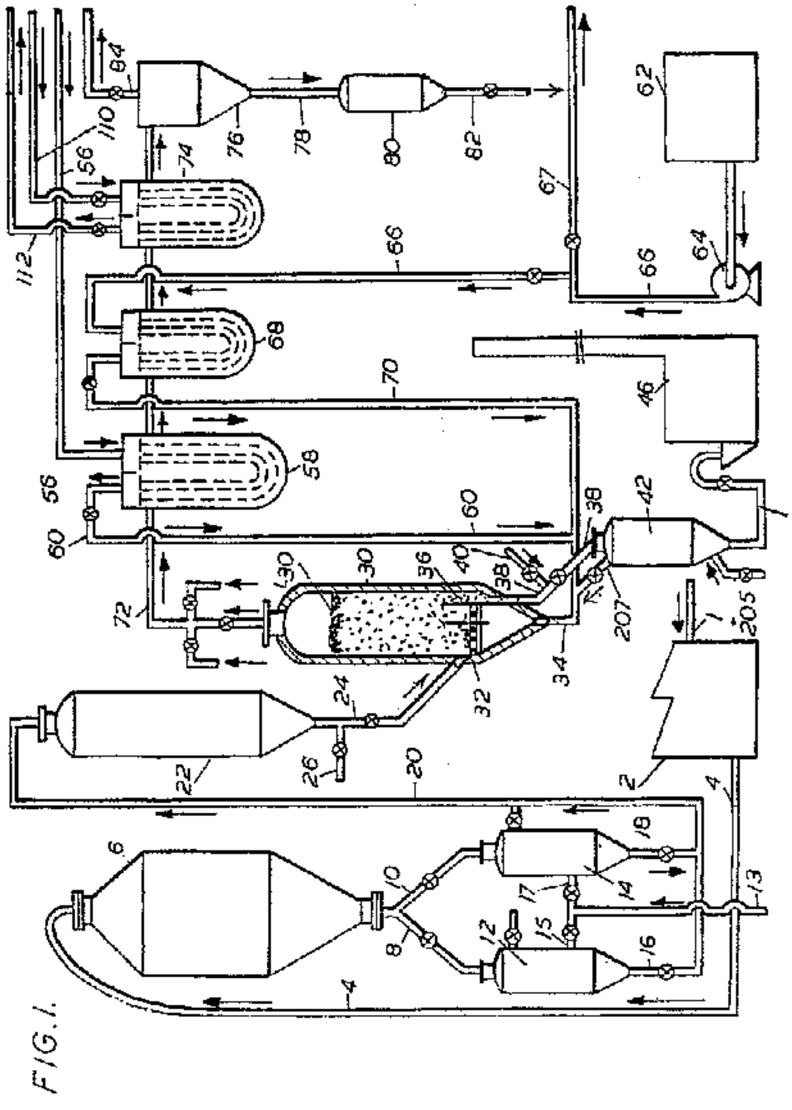
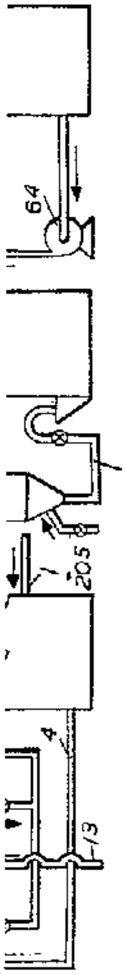


FIG. 1.

5 SHEETS

SHEET 1



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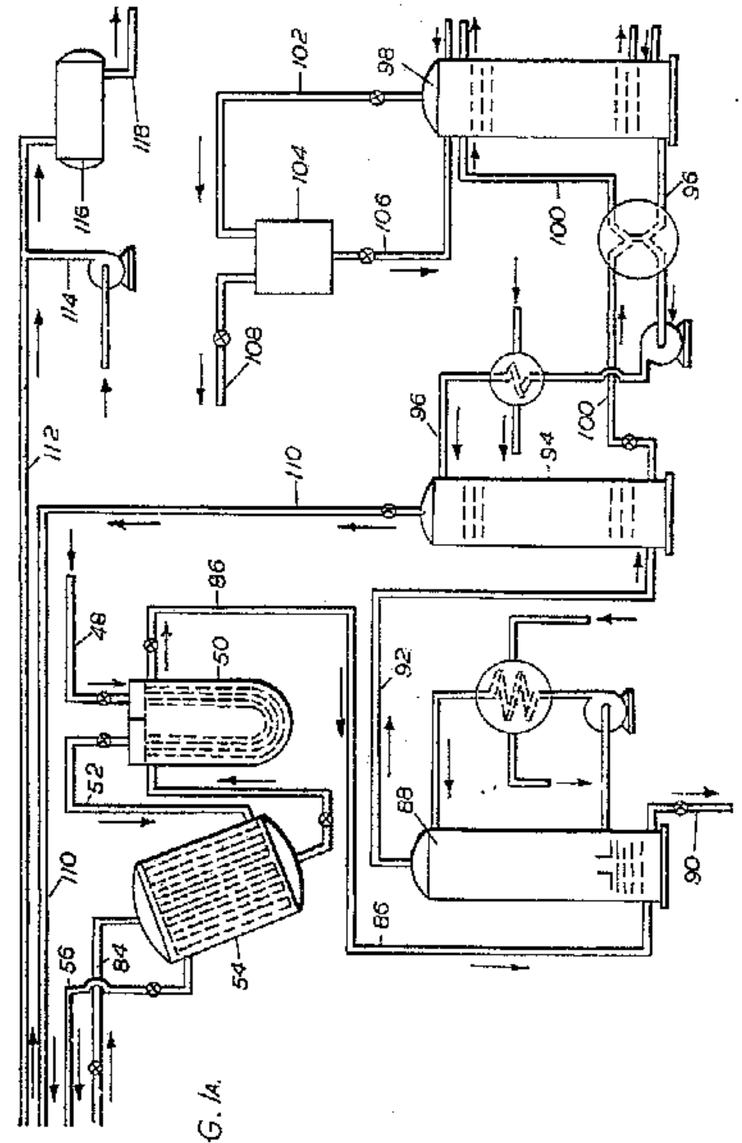

F/G. 1A.

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FIG. 1.

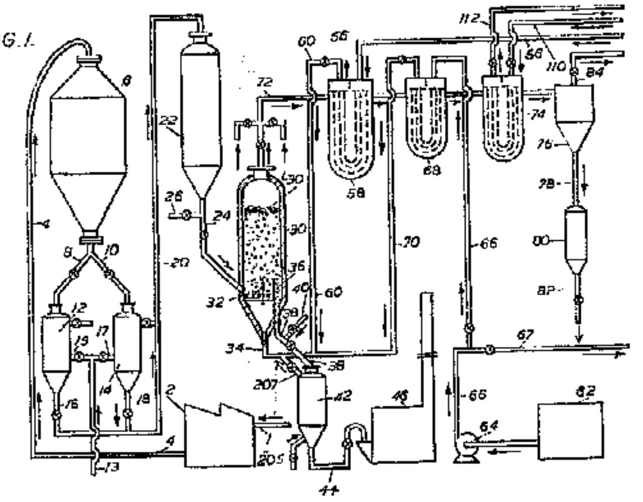

FIG. 1A.

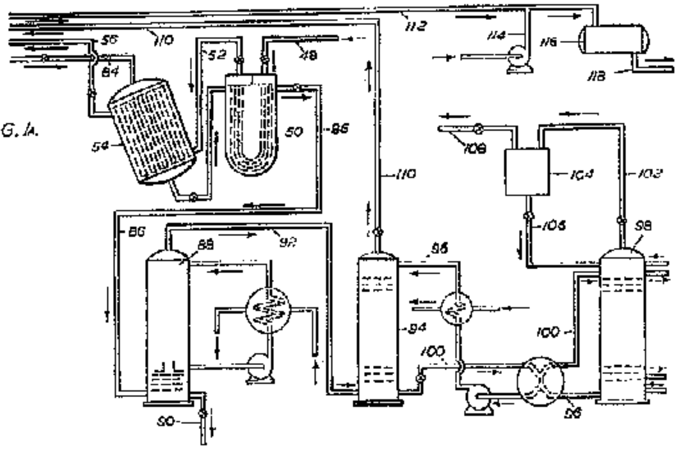

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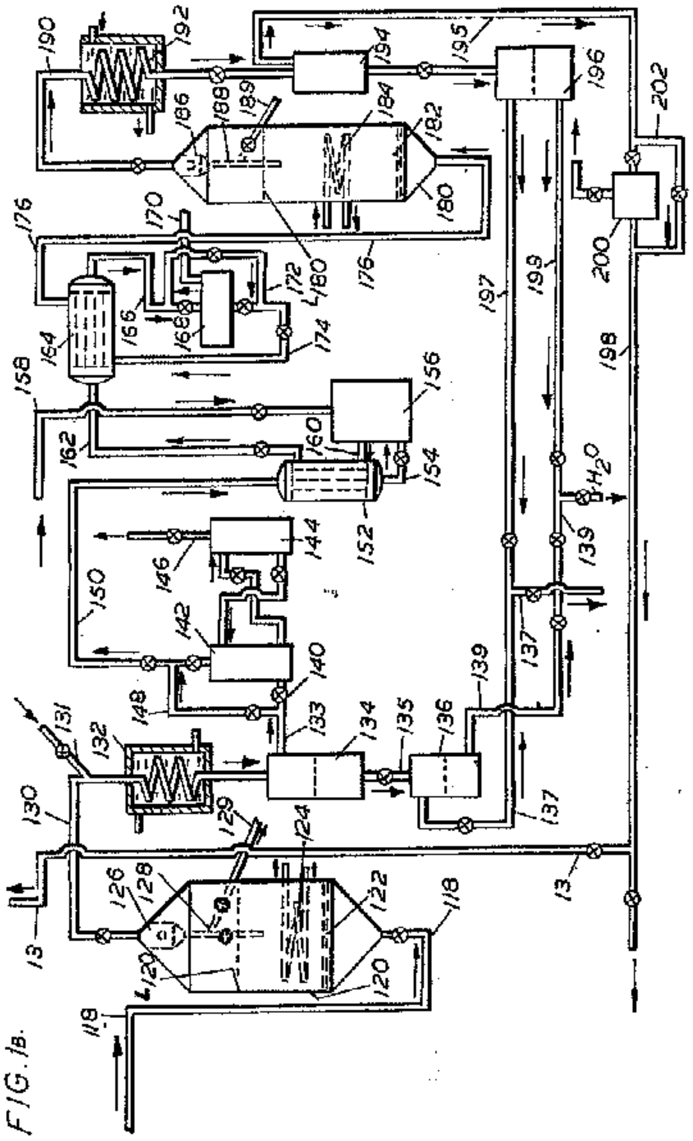
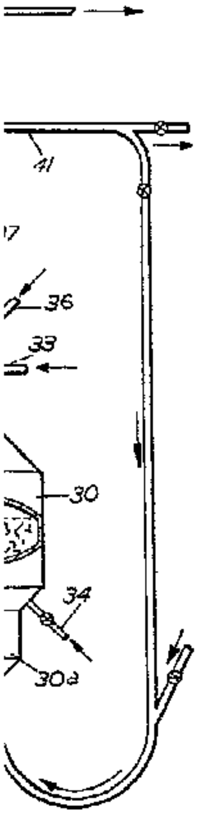
FIG. 1B.

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F/G. 3.

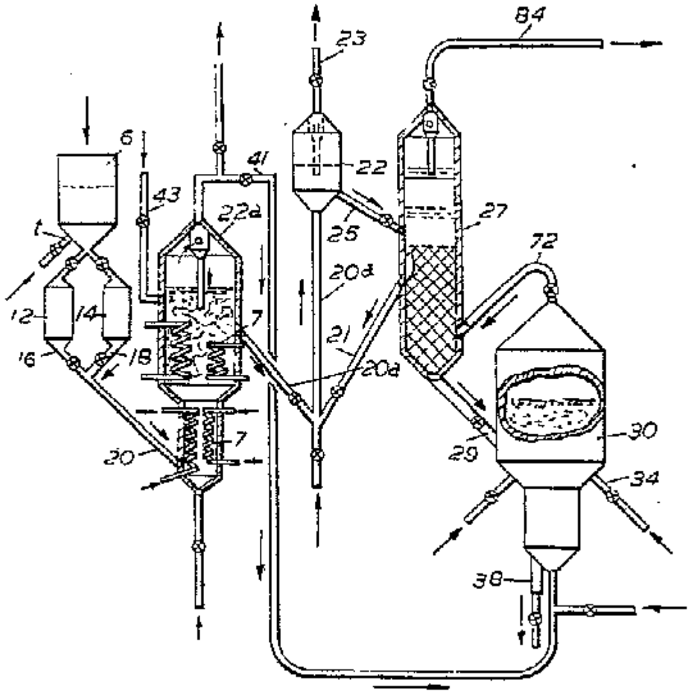
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FIG. 2.

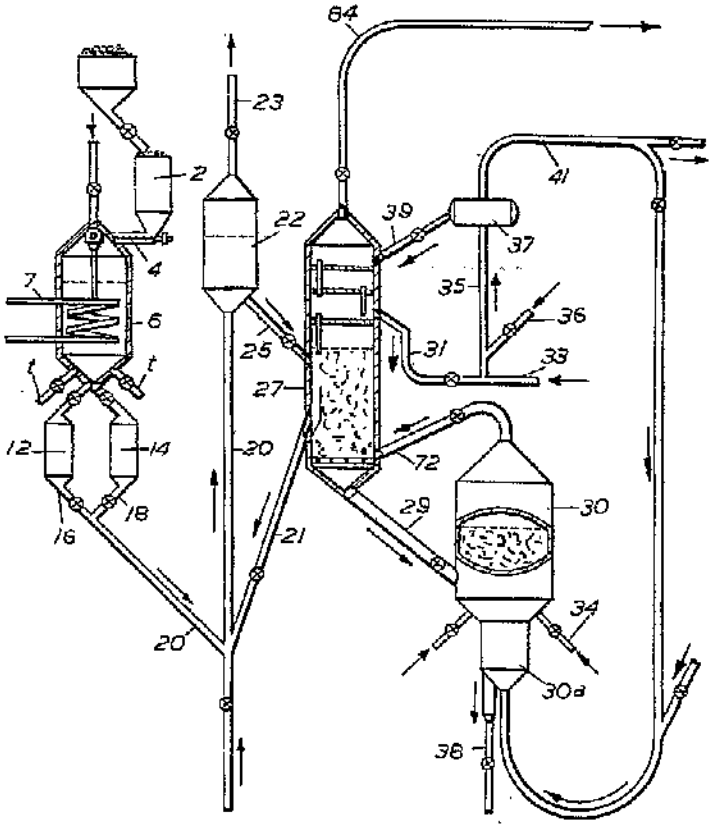


FIG. 2.

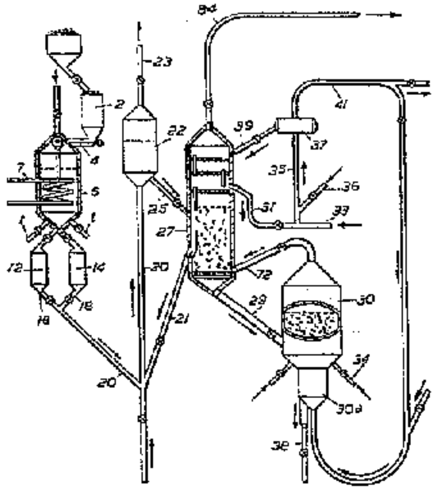
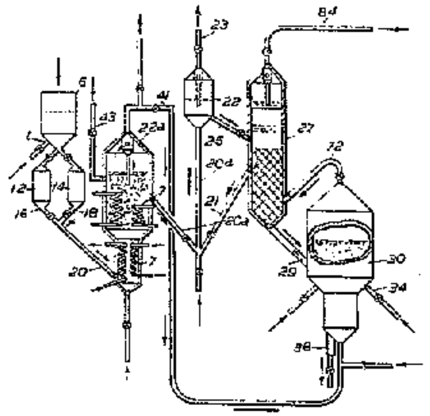


FIG 3



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