PATENT SPECIFICATION

656,560

Date of Applications and filing Complete Specification: Jan. 21, 1948.
Nos. 1832/48 & 1833/48
Application made in United States of America on Feb. 5, 1947.
Application made in United States of America on July 21, 1947.
Complete Specification Published: Aug. 29, 1951.

2202

Index at acceptance:—Classes 1(i), F3a1a; and 2(iii), B1g, C3a(10a3 : 13a3).

COMPLETE SPECIFICATION

Improvements in or relating to Hydrogenation of Carbon Oxides

We, THE M. W. KELLOGG COMPANY, a corporation organized under the laws of the State of Delaware, United States of America, of Foot of Danforth Avenue, Jersey City, New Jersey, United States of America (Assignees of HENRY GEORGE MCGRATH, LUTHER RANDOLPH HILL, JOSEPH WARREN JEWELL, and WILLIAM BENEDICT JOHNSON), 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:—

This invention relates to an improved method and apparatus for hydrogenating carbon monoxide or dioxide to produce organic compounds. Primarily the improved process involves reacting hydrogen and carbon monoxide or dioxide under highly efficient conditions to produce hydrocarbons and/or oxygenated organic compounds. In the following description of the invention the hydrogenation of carbon monoxide will be specifically described but it will be understood, however, that the procedure described is substantially the same for carbon dioxide.

It has been known for some time that hydrogen and carbon monoxide may be made to react exothermically in the presence of certain catalysts and under specific reaction conditions to form hydrocarbons having more than one carbon atom per molecule and oxygenated organic compounds. In general, the synthesis of hydrocarbons by the hydrogenation of carbon monoxide is accomplished in the presence of a metal or an oxide of a metal, such as one chosen from Group VIII of the Periodic Table, as a catalyst at pressures below about 500 pounds per square inch gage and at temperatures below about 750° F.

Various methods have been practiced to effect the reaction of hydrogen and carbon monoxide to produce organic compounds. Among these methods are those known as fixed-bed catalyst operations and fluid-bed catalyst operations. The fixed-bed operation comprises passing a reaction mixture of hydrogen and carbon monoxide through a stationary bed of catalyst in a reaction zone, and the fluid-bed operation comprises passing a reaction mixture through a finely divided catalyst mass suspended in the reaction mixture in the reaction zone under conditions such that a so-called pseudo-liquid dense phase of solids is formed. Characteristically, certain reaction conditions are necessary for each of these processes and for the particular catalyst used.

The synthesis feed gas or reaction mixture comprises a mixture of about 1 to 5 mols of hydrogen per mol of carbon monoxide and may be prepared by various means including the catalytic conversion of natural gas, steam, and carbon dioxide.

The most recent development in the synthesis of organic compounds from hydrogen and carbon monoxide has been in the fluid-bed type operation. This type of operation has had several apparent advantages over the fixed-bed operation and has yielded organic compounds of high quality and in larger quantity per pound of catalyst. Operating at a temperature of about 600° F. and at superatmospheric pressures using a fluidized iron catalyst, contraction of reacting gases of about 41 per cent to about 70 per cent and a carbon monoxide disappearance of about 85 per cent to about 100 per cent have been observed. The selectivity of the reaction is dependent on the concentration of reactants but with relatively low H_2 : CO ratio about 25 to about 40 per cent of the CO is converted to CO_2, and oil and water yields of about 100 to 130 cc. per cubic meter of fresh feed and about 60 to 120 cc. per cubic meter of fresh feed, respectively, are obtainable.

Even in view of the relatively good results obtained by the fluid-bed type operation, certain inherent disadvantages have been found. In such fluid-bed opera-

tions in which the catalyst is suspended in the reaction mixture to form a pseudo-liquid dense phase of solids, classification of the solids often occurs causing partial deaeration of the catalyst bed and channeling of gas. There is also a tendency for the fluid-bed to settle after extended use of the catalyst as a result of the agglomeration of the catalyst particles caused by the presence of relatively high molecular weight organic compounds and carbonaceous deposits accumulating on the catalyst particles. This accumulation of such deposits on the catalyst also reduces the available active surface and consequently the conversion. It also reduces the density of the catalyst mass thereby requiring a greater volume for the same weight of catalyst.

Difficulty is also encountered in the removal of the exothermic heat of reaction from the fluid bed. The rate of reaction in the hydrogenation of carbon monoxide varies with temperature and there is considerable change in the production distribution in the higher range of operating temperatures as compared to the lower range of operating temperatures. The lower range of operating temperatures is more favourable to the production of higher-boiling products which have a tendency to condense on the catalyst particles. The condensed material on the catalyst particles may cause agglomeration and is potential coke, and, if the temperature increases above certain limits within the reaction zone, the formation of coke upon the catalyst particles is accelerated. Temperatures low enough to condense the relatively high-boiling products, and temperatures high enough to coke the condensed material can often occur in different parts of the fluid-bed. In a reactor with the fluid-bed of catalyst on the outside of the cooling tubes, the design space between the tubes must be made such that the catalyst particles will not to be cooled below the minimum allowable temperature or such that the catalyst particles will not be heated to an excessive temperature at any particular time. However, to insure cooling and at the same time to prevent overcooling of the catalyst, the tube spacing must be as close as mechanically practical and the coolant temperature must closely approach the catalyst bed temperature. Such a design obviously results in an expensive unit. On the other hand, if the fluid-bed of catalyst is inside the tubes, a velocity which will permit internal recycling or fluid-bed operation within the tubes will result in such a low-velocity in the zones under and above the tube sheet that the residence time of the reactants in excessive and overheating results. The overheating causes coke formation. It is desirable, therefore, to design or provide a system to overcome the tendency of overcooling or overheating fluid-bed systems.

Another inherent disadvantage of fluid-bed operation is the fact that the catalyst concentration in the fluid-bed cannot be controlled to any great extent since a considerable change in the gas feed volume is required to change the catalyst concentration in the fluid bed. Changes in the fluid-bed concentration may occur but usually do not occur at will but occur as a result of accumulations of deposits thereon or from local partial deaeration.

Still a further disadvantage of the fluid-bed technique is the fact that the catalyst is retained in the fluid-bed for an extended and prolonged length of time. If a portion of the catalyst is continuously or intermittently withdrawn for cooling and regeneration purposes, it follows that a portion remains in the fluid-bed in the reaction zone almost permanently. The prolonged residence time of the catalyst in the reaction zone results in considerable deactivation and changes in density of the catalyst as a result of such factors as the accumulation of carbonaceous deposits thereon, etc. Another disadvantage of uncontrolled residence time is that the high rate of accumulation of deposits on the catalyst limits the ratio of $H_2:CO$ to uneconomically high ratios. It is, therefore, much to be desired to provide a synthesis reactor and process in which the gas residence time, the catalyst residence time, and the temperature of reaction are under full and positive control.

It is an object of this invention to provide apparatus and a process for preventing or minimizing the above difficulties encountered with fluid-bed synthesis operations.

It is another object of this invention to produce hydrocarbons and/or oxygenated organic compounds by the interaction of carbon monoxide in the presence of a in the presence of a catalyst.

Another object of this invention is to provide an improvement in the synthesis of hydrocarbons from hydrogen and carbon monoxide in the presence of a finely-divided fluidized catalyst.

Still a further object is to provide a method for the synthesis of hydrocarbons using a relatively low feed ratio of hydrogen to carbon monoxide.

Still another object is to provide a fluidized process for the hydrogenation of carbon monoxide in which the catalyst life is extended and prolonged.

Another object is to provide an effective catalyst stripping zone to remove the

accumulation of high molecular weight organic compounds before the catalyst contacts fresh feed gas.

Yet another object is to provide a positive mixing zone where relatively cold feed gas can be contacted with relatively hot catalyst and insure preheating of the gas to the reaction temperature.

Various other objects and advantages will become apparent to those skilled in the art from the accompanying description and disclosure.

The process and apparatus of this invention provides a method for controlling the residence time of a finely-divided fluidized hydrogenation catalyst in a reaction zone for the hydrogenation of a carbon oxide. According to this invention a gaseous mixture comprising hydrogen and carbon monoxide or dioxide is flowed at a velocity of at least five feet per second in contact with a finely divided hydrogenating catalyst of such size that said catalyst is moved in the direction of flow of said gaseous mixture in a relatively dilute condition. The operation of the present process is such that all of the catalyst particles are continuously moved in the direction of flow of the gases through the reaction zone by entrainment in contrast to being held in suspension in a pseudo-liquid dense phase of solids according to conventional operations. In the conventional operation in which the suspended solids form a so-called pseudo-liquid dense phase, the finely divided solid particles are in a turbulent condition and are circulated or recycled within the dense phase itself. If any of the heavier particles in dense phase operation are circulated through the reaction zone, they are done so only by virtue of the bumping effect of the lighter particles which force the heavier particles through the reaction zone and the residence of such particles is indefinite.

In order to achieve continuous circulation of the catalyst particles through the reaction zone by entrainment in accordance with the teachings of this invention, a velocity of at least 5 preferably above 6 feet per second must be used. Still more preferably, the velocity is above about 8 or 10 feet per second and may be as high as 40 feet per second or higher. The actual velocity will depend upon the chemical and physical properties of the finely divided solid material and also upon the size of the solid particles. When a continuous catalyst phase of circulating catalyst particles is formed at the velocities described in accordance with this invention, the concentration of the finely divided catalytic material in the reaction zone is generally below about 35 pounds per cubic foot of gas at operating conditions of temperature and pressure. The residence time of the gaseous reactants and conversion products in the reaction zone should be sufficient to obtain the optimum yield of hydrocarbons and/or oxygenated organic compounds. The residence time of the catalyst may vary to a considerable extent and at very high velocities may be substantially the same as the residence time of the gases and reactants; however, the residence time of the catalyst is comparatively short with regard to fluid-bed operations, being a matter of seconds with the present operation, as compared to a matter of minutes or hours with fluid-bed operations and is under operating control over a wide range.

When a continuous catalyst phase of circulating catalyst particles is formed at the velocities described in accordance with this invention, the concentration of the finely divided catalytic material in the reaction zone is a function of actual velocity and characteristics of the vapor (such as density and viscosity) and is also a function of the average size, range of size, and physical characteristics of the catalyst and will vary between a figure proportional to the feed rate and a figure proportional to several (4—8) times the feed rate. By variation in cross section of the reaction zone in different sections thereof, concentration of catalyst may be varied in such sections. By varying the feed rate of the catalyst to any particular high velocity section of the circuit, the concentrations of catalyst in that section may be controlled. At any given fresh feed rate the concentration of catalyst may be varied by using more or less recycle vapor to change the velocity within the limits of the particular design.

In conventional fluid-bed type operations the finely divided catalyst forms a so-called pseudo-liquid dense phase of catalyst in the reaction zone. The velocity of the gas stream passing through the pseudo-liquid dense phase of catalyst is sufficiently low to maintain the catalyst mass in the so-called dense fluidized condition and yet sufficiently high to maintain the finely divided catalyst in a turbulent condition in the dense phase. In this condition the catalyst mass may be said to be suspended in the gas stream but not entrained therein in the sense that there is continuous movement of the finely divided catalyst particles in the direction of flow of the gas stream. In the fluid-bed type operation a small proportion of the finely divided catalyst in the fluidized mass may become entrained in the gas stream emerging from the upper surface of the fluidized mass. Actually, therefore,

two phases are formed in the reaction zone; a dense pseudo-liquid catalyst phase in the lower portion of the reaction zone, and a dilute catalyst phase in the upper portion of the reaction zone. The concentration of the catalyst in the so-called dense phase is usually at least 25 pounds per cubic foot of gas and generally between about 50 and about 120 pounds per cubic foot of gas. The amount of catalyst in the so-called dilute phase is generally less than about 0.01 pounds per cubic foot of gas.

The catalyst employed in the present invention is a finely-divided powdered catalyst of a metal or metal oxide which is or becomes in the reaction zone a catalyst for the hydrogenating reaction. Finely-divided metallic iron or iron or a mixture of metallic iron and iron oxide are an example of the catalyst employed in this invention. Preferably, a metallic iron catalyst is used in the finely-divided form. Other metals and metal oxides may be employed which are effective in catalyzing the hydrogenation of carbon monoxide, such as cobalt, nickel, and other metals of Group VIII of the Periodic Table. While the catalyst powder usually consists of such catalytic metals or their oxides, it may also include a minor amount of promoting ingredients, such as alkalies, alumina, silica, titania, thoria, manganese oxide, and magnesia. Also, the catalyst may be supported on a suitable support, such as a bentonite type clay, the product known by the Registered Trade Mark, "Super-Filtrol," silica gel, alumina, and mixtures of these supports. In the following description, catalyst powders comprising a metal and/or a metal oxide and containing at most a minor proportion of promoters are referred to as finely-divided metal hydrogenation catalysts.

The exact chemical condition of the catalyst in its most active form is not certain. It may be that the active form is present when the metal is at an optimum degree of oxidation and/or carburization; consequently, a metallic iron catalyst which is in a reduced condition when first contacted with the reactants may reach its state of highest activity through being oxidized and/or carburized in the reaction zone. Therefore, in this specification and claims, the catalyst employed is described by reference to its chemical composition when first contacted with the reactants.

The catalyst is employed in a fine state of subdivision. Preferably, the powdered catalyst initially contains no more than a minor proportion by weight of material whose average particle diameter is greater than 250 microns. The greater proportion of the catalyst mass, preferably, comprises a material whose average particle diameter is smaller than 100 microns including at least 25 weight per cent of the material in a particle size smaller than 40 microns. An example of a desirable powdered catalyst is one which comprises at least 75 per cent by weight of material smaller than 150 microns and at least 25 per cent by weight of materials smaller than 40 microns.

The temperature of reaction for the hydrogenation of carbon monoxide is generally between about 300° F. and about 750° F. With a metallic iron catalyst, temperatures between 450° F. and 750° F. are usually employed. With a cobalt catalyst usually a temperature below 450° F. is sufficient for the hydrogenating reaction. However, within the broad range of temperatures it is a necessity to maintain the temperature within a close range, at some level, for optimum selectivity for any given reaction and a change in temperature may be desirable as the concentration of reactants changes, etc. Pressures employed are somewhat above atmospheric and range from about 10 pounds to as much as 500 pounds per square inch gage, preferably between about 80 pounds and about 300 pounds per square inch gage.

In effecting the reaction it may often become necessary to cool the reaction zone to maintain the relatively constant temperature necessary. Various methods of cooling the reaction zone itself, such as by external cooling means or by injection of a cooling medium, such as a vaporizable liquid or a gas, directly into the reaction mixture, may be practiced without departing from the scope of this invention. Furthermore, it may often become necessary to preheat the reaction mixture prior to entry into the reaction zone, and also the catalyst may be preheated before introduction in the reaction mixture. However, the cooling and preheating are factors which will be characteristic of the particular apparatus being used and the particular conditions under which the reaction is effected.

According to a preferred embodiment of this invention, a fresh feed gas having a hydrogen to carbon monoxide ratio higher than the ratio in which these compounds are converted to other compounds is employed and the ratio of hydrogen to carbon monoxide in the reaction zone itself may be increased above the ratio in the fresh feed gas and to a desired value by recycling a portion of the unconverted gas from the reaction zone, after removal of a part or all of the normally liquid pro-

duct by condensation. A ratio of hydrogen to carbon monoxide in the fresh feed gas is used in which only a portion of the hydrogen is converted to products of the process. A portion of the effluent after removal of the major proportion of the liquid product is recycled to the reaction zone in a volumetric ratio of recycle to fresh feed gas of about 0.5:1 to about 10:1, generally about 1:1 to about 5:1 or 6:1. However, depending on the character of the available feed gas or on the character of the desired product, it may or may not be desirable to recycle the non-condensed portion of the reaction effluent, and, therefore, once through or single pass operations are within the scope of this invention.

For efficient operation it is usually desirable to have a higher ratio of H_2:CO in the fresh feed than the ratio of consumption in the reactor. This insures sufficient surplus hydrogen to permit increasing the concentration by recycling which in turn insures the ability to attain economic conversion of the carbon monoxide.

The liability to accumulation of deposits on the catalyst which is characteristic of the fluid bed reactor is seriously aggravated by low H_2:CO ratios in the reactor feed, necessitating high recycle rates which sharply increase the cost of the equipment and the operation. The ratio of hydrogen to carbon monoxide in the reactor feed is usually about 0.7:1 to about 3:1 and according to this process may be maintained between about 0.7:1 and about 1.5:1 without detrimental effect on the synthesis reaction. The ratio of hydrogen to carbon monoxide in the fresh feed itself may be considerably lower than in the reaction zone or total feed and may range from about 0.7:1 to about 2:1 at relatively low conversions per pass.

The linear velocity of the gaseous reaction mixture passing upward through the reaction zone is conveniently expressed in terms of superficial velocity, which is the linear velocity the feed stream would assume if passed through the reactor in the absence of catalyst, and takes into account the shrinkage in volume caused by hydrogenation reaction.

The concentration of the catalyst in the gaseous reaction mixture in the reaction zone is less than about 18 pounds per cubic foot of gas at operating conditions for best operations, and at the preferred operating conditions with an iron catalyst is between about 3 pounds and about 12 pounds per cubic foot. Concentrations as low as one pound per cubic foot may be employed without departing from the scope of this invention. The actual concentration required in the above range will depend to a certain extent upon the amount of inert gas in the reaction zone and also upon the accumulation of carbon and wax on the catalyst particles as the operation proceeds. The accumulation of wax and carbon on the catalyst decreases the particle density and hence the weight of catalyst per cubic foot of gas at any given velocity. The above values represent the usual limits but the values may vary in accordance with the character of the catalyst and operating conditions.

Although the invention has been described with reference to an upward-flowing gaseous stream of reactants and catalyst, it should be understood that the catalyst and reactants may flow together downward, horizontally, or even angularly, through a reaction zone without departing from the scope of this invention. It has been found that by upward flowing of gas through a substantially vertical reaction zone the weight of catalyst per cubic foot of gas and the residence time of the catalyst can be controlled conveniently and accurately and for that reason is the preferable method of operation. It should be understood that the reaction continues in the down-flow operations although the catalyst concentration is less.

In operating a synthesis process under set conditions within the limits of this invention with an iron catalyst and at a temperature between about 550° F. and about 650° F. at relatively low superatmospheric pressures, a contraction of the catalyst gas of about 25 to about 85 per cent has been observed. The carbon monoxide disappearance is about 70 per cent to about 88 per cent and the selectivity of the reaction illustrated by the conversion of carbon monoxide to carbon dioxide is about 15 per cent to about 30 per cent. Condensed oil and water yields of about 80 to about 100 and about 80 to about 175 cc.'s per cubic meter of fresh feed gas, respectively, are obtained by operating according to the present process and may contain appreciable quantities of organic chemicals.

The invention will be described further by reference to the accompanying drawings which are views in elevation, partly in cross-section, of suitable apparatus for carrying out the process of the present invention. Fig. 1 of the drawings is an elevational view diagrammatically illustrating a reaction zone and suitable auxiliary equipment used for carrying out one embodiment of the present invention. Figures 2, 3, and 4 of the drawings are

other reaction chambers embodying the essential features of the present invention and may be substituted for the reaction chamber shown in Fig. 1 of the drawings.

In Fig. 1 of the drawings a synthesis gas comprising hydrogen and carbon monoxide present in a ratio between about 0.7:1 and about 1.4:1 is obtained from any suitable source. For example, a suitable source of hydrogen and carbon monoxide is the conversion of steam, carbon dioxide, and methane in the presence of a suitable catalyst, such as nickel. The resulting mixture of such a conversion usually contains sulphur and sulphur compounds, and the gas is preferably purified to remove such compounds therefrom. If a sulphur resistant catalyst is used the purification step is unnecessary. After purification in conventional manner known to those skilled in the art, the mixture of hydrogen and carbon monoxide is introduced into the lower end of a 26 foot length conduit or tubing 8 of Fig. 1. Conduit 8 is a curved conduit which has a major portion thereof positioned substantially vertically and is made of extra heavy 1 inch steel tubing having an inside diameter of 0.95 inches and an outside diameter of 1.31 inches. Conduit 8 is also lagged with about 6 inches of heavy lagging. The vertical section of conduit 8 is about 19 feet in length. The gaseous reaction mixture is passed upwardly through conduit 8 and catalyst from a standpipe 10 is introduced into the flowing gaseous stream in the lower portion of conduit 8, as shown. The velocity of the gas in conduit 8 is maintained above 5 feet per second in the vertical section in order to prevent the formation of a pseudo-liquid dense phase of catalyst in the vertical section of the conduit, but instead to form a continuous catalyst phase of relatively dilute concentration. The velocity of the gaseous stream in conduit 8 may be between about 12 and about 40 feet per second and at such velocities the catalyst is entrained in the gaseous stream and passes overhead into the upper portion of standpipe 10 with the gaseous stream itself. Since a continuous catalyst phase is present in conduit 8, the amount of catalyst taken overhead into the standpipe is approximately equivalent to the amount of catalyst introduced into the lower portion of conduit 8 from standpipe 10.

Standpipe 10 comprises two substantially vertical, concentric, extra heavy steel pipes; an outside pipe 11 of approximately 4 inches in diameter and an inside tubing 10 having an inside diameter of 1.95 inches and an outside diameter of 2.5 inches. The outside 4 inch pipe 11 is welded at its ends to the inside tubing 10 to form an enclosing jacket which may be filled with a liquid as a cooling or heating medium. This jacket extends about 20 feet of the total length of 28 feet of tubing 10. The cooling or heating medium is introduced into the annular space formed by two concentric pipes through line 12 and may be withdrawn therefrom through line 15. In some instances the cooling or heating medium may be introduced through line 15 and removed through line 12, if desired. In another embodiment where the liquid introduced into the annular space is evaporated therein and the latent heat of evaporation is used to cool the catalyst, liquid is introduced through line 12 and vapors are removed, also through line 12.

Catalyst passes from conduit 8 into a conical section 14 which has a larger diameter than conduit 8 and thereby the velocity of the gases are diminished and the catalyst separates from the gaseous stream and flows downwardly into conduit 10. A slide valve 13 in the lower portion of standpipe regulates the flow of catalyst from conduit 10 into conduit 8. The upper end of conduit 10 is connected by means of a conical section 14 to an enlarged conduit 16 comprising a length of 8-inch extra heavy steel tubing having an inside diameter of about 7.63 inches. Conduit 16 facilitates the disengagement of the catalyst from the gas stream after the passage of the latter into conical section 14. Conduit 16 is connected by means of manifold 17 with conduits 18 and 19 which comprise other sections of extra heavy 8-inch steel tubing. Conduits 18 and 19 contain ceramic filters 20 and 21 which are constructed of porous material, such as alundum, permeable to the gases and vapors emerged from conduit 8 but impermeable to catalyst "fines" entrained in the gaseous effluent. Filters 20 and 21 are cylindrical and are closed at the bottom ends. A substantial annular space is provided between the wall of the filters and the wall of the enclosing conduit for the passage of gases and vapors and entrained catalyst upwardly through the annular space between the filters and conduits 18 and 19. The upper ends of filters 20 and 21 are mounted inside conduits 18 and 19 by means of enclosure means 22 and 23. The gases and vapors must pass through either or both filter 20 and filter 21 to reach outlet conduits 24 and 26. Each of the filters 20 and 21 is approximately 36 inches long and 4½ inches in outside diameter, the filter walls being approximately ¾ of an inch thick.

Union of the various conduits in the upper portion of the standpipe 10 is made

by welding.

When using a metallic iron catalyst in a finely-divided state, usually between about 40 and about 150 microns, the temperature of reaction in conduit 8 is between 550° F. and about 650° F. A pressure of about 30 pounds per square inch gage has been found to be quite satisfactory. However, various pressures above and below this may be used without departing from the scope of this invention. With a velocity greater than 10 feet per second in conduit 8 the reaction time is less than 3 seconds per pass. Operating at a gas velocity of about 15 feet per second in conduit 8 a loading of about 6 pounds of catalyst per cubic foot of gas entering conduit 8 will produce a concentration of about 12 pounds of catalyst per cubic foot of gas in the vertical section of conduit 8. Similarly, if the loading is cut to about 4 pounds per cubic foot of gas the concentration of catalyst in the vertical section of conduit 8 is about 8 pounds per cubic foot. In all cases the velocity of the gas passing through conduit 8 is maintained above 5 feet per second in order to prevent a formation of a dense pseudo-liquid phase of catalyst and to assure a continuous phase of catalyst in conduit 8. In operating at such high velocities the catalyst is entrained in the gaseous mixture and flows from the lower portion of conduit 8 to the upper portion thereof and settles or separates from the gaseous mixture in conical section 14 and enlarged conduit 16. The gaseous portion of the mixture from conduit 8 flows upwardly through the filters 20 and 21 and into the respective outlet conduits 24 and 26. Separated catalyst flows downwardly through conduit 10 and by the regulation of valve 13 is introduced in the conduit 8 at the desired rate. The density of the iron catalyst in conduit 10 is usually about 50 pounds to 110 pounds per cubic foot of volume.

In some instances, the heat of reaction may be removed by cooling the catalyst and using the sensible heat of the catalyst as a means for cooling the reaction mixture in the reaction zone. To accomplish this end, the catalyst in this particular apparatus may be cooled in conduit 10 by introducing a liquid, such as water or that known by the Registered Trade Mark "Dowtherm," through conduit 42 into the annular space between concentric conduits 10 and 11. The evaporation of the water or "Dowtherm" in the annular space removes a large portion of the heat in the catalyst. The cooled catalyst is then introduced into conduit 8 for recycling through the reaction zone or conduit 8. Conduit 8 may be cooled directly itself by indirect heat exchange (not shown) without departing from the scope of this invention. Various other methods known to those skilled in the art may be used to cool either the reaction mixture in conduit 8 or the catalyst in conduit 10 without departing from the scope of this invention.

Since the pressure differential between just below slide valve 13 and the upper portion of reaction zone 8 may vary to a considerable extent, it is necessary to control slide valve 13 to compensate for the pressure differential in order to obtain a constant flow of catalyst from standpipe 10 into conduit 8. This control of slide valve 13 is obtained by connecting a differential pressure recorder 28 by means of conduit 27 and 31 to the upper and lower portions of standpipe 10, as shown, and transmitting changes in pressure differential to slide valve 13 so that when the pressure differential is increased valve 13 is closed slightly and when the pressure differential is decreased valve 13 is opened slightly. The concentration of the catalyst per cubic foot of gas in the vertical section of conduit 8 may be determined by connecting a pressure differential recorder (not shown) on the vertical section of conduit 8 and calibrating the recorder readings in terms of concentration of catalyst. The gaseous effluent from either conduit 18 or 19 is passed through filters 20 and 21 into outlet conduit 24 and 26, respectively. Usually only one outlet conduit is used at a time. Thus, for example, the gaseous effluent passes through outlet conduit 24 to conduit 33, through condenser 34 where the effluent is cooled to about 40° F. at operating pressure and then passed to accumulator 36. In accumulator 36, gaseous components are separated from liquid components of the cooled effluent. Uncondensed components of the effluent, such as hydrogen, carbon monoxide, methane, propylene, butylene, light naphtha, and organic oxygenated compounds, are recycled by means of conduits 38 and 44 and a compressor or blower 45 to the lower portion of conduit 8 in a ratio of about 1:1 to about 5 or 6:1 of volumes of recycle to volumes of fresh synthesis gas. The amount of unreacted hydrogen and carbon monoxide in the recycle gas determines how much the ratio of carbon monoxide and hydrogen in the reaction zone itself will deviate from the ratio in the fresh feed. As shown, the recycle gas is introduced into the fresh feed before the catalyst is introduced into the gaseous mixture, however, the recycle may be introduced into the gaseous mixture after the catalyst is introduced into the feed stream or the feed gas may be

introduced into the gaseous mixture after the introduction of the catalyst without departing from the scope of this invention.

After passage of the gaseous effluent through filter 20 for a time, the filter becomes coated and clogged with catalyst fines which have not settled out from the gaseous effluent. In order to remove these fines from the catalyst filters so as to ensure continuous passage of the gaseous effluent through the filters and so as to recover the catalyst, the course of gaseous effluent is charged to flow through filter 21 and conduit 26 and a portion of the uncondensed effluent is passed from accumulator 36 by means of conduit 38, compressor 41, and conduit 24 to filter 20. The pressure of the gas blows the fines from the filter into conduit 18. The fines then settle in conduit 18 to standpipe 10. Other gases than the uncondensed effluent may be used to remove the fines from the filter and may be introduced through line 42, if desired.

Liquid condensate in accumulator 36 is passed through conduit 39 to separating means 48, which may represent various separating units, such as distillation columns, absorption units, extraction units, and the like. In separating means 48, water is separated from organic compounds and removed through line 49; oxygenated organic compounds are separated therein and removed through line 51; and hydrocarbons are separated and removed through line 52.

Uncondensed gas from accumulator 36 not used for recycle, etc., is removed from the system through conduit 40 and passed to oil and chemical recovery equipment not shown.

It has been found that operating a synthesis process according to this invention, in which the synthesis gas is passed through a reaction zone at a high velocity, good yields of products are realized. Ordinarily one would believe that insufficient catalyst for accomplishing the desired reaction would be carried by the gas at such high velocities, but it has been found that within the range indicated sufficient catalyst is carried by the gas to effect the reaction between hydrogen and carbon monoxide. If desired, the synthesis gas entering conduit 8 may be preheated; but it has been found that preheating the gas is unnecessary in most instances and that the contact of the hot catalyst from standpipe 10 with fresh feed gases entering conduit 8 does not cause baling or agglomeration of the catalyst mass. It has also been found, as previously mentioned, that the wax and carbon content of the catalyst with extended use is much less than that observed in the conventional fluid-bed operations.

Fig. 2 of the drawings is another arrangement of apparatus suitable for carrying out this invention. The apparatus shown in Fig. 2 may be substituted for conduit 8 and standpipe 10 of Fig. 1. The filter sections of Figures 1 and 2 are the same. Accordingly, a synthesis gas comprising hydrogen and carbon monoxide is passed into a reaction zone 70 through a line 68. Reaction zone 70 comprises a bundle of substantially vertical tubes 71 through which the gases pass upwardly into a cylindrical section 74 of a larger cross-sectional area than the total cross-sectional area of tubes 71. The outer surface of tubes 71 are sealed off to form an annular space 72 between the inner surface of the outer shell of reaction zone 70 and the outer surface of tubes 71. A cooling (or heating) fluid may be passed through annular space 72 to cool (or heat) the reaction mixture as it passes upwardly through tubes 71. Tubes 71 correspond to conduit 8 of Fig. 1. Upon reaching enlarged section 74 the velocity of the gaseous mixture is decreased to such an extent that the catalyst settles from the effluent and passes down through a standpipe 73 into the lower portion of reaction zone 70 where the catalyst falls or is drawn into a high velocity gaseous stream passing upwardly into tubes 71. The lower portion of reaction zone 70 and tubes 71 are of such a cross-sectional area that the catalyst is entrained in the gaseous stream.

The cooling medium is introduced into the annular space 72 through line 76 and is withdrawn therefrom through line 77.

The reaction effluent from reactor 70 passes upwardly through conduits 17, 18, and 19 of which the latter two contain filters as previously discussed with reference to Fig. 1. Conduits 17, 18, and 19 are the same as conduits 17, 18, and 19 of Fig. 1. The gaseous effluent passes from conduits 18 and 19 through outlet conduits 24 and 26 to conduit 33. The effluent in conduit 33 of Fig. 2 is condensed and separated according to the description of Fig. 1 and a portion of the uncondensed gases may be recycled (not shown) to conduit 68, if desired.

The cross-sectional area of conduits 71 with respect to the quantity of gases flowing therethrough is such that the velocity of the gases is greater than about 8 feet per second, while the cross-sectional area of enlarged section 74 is such that the velocity of the gases is below about 5 feet per second so that the catalyst may settle from the gaseous effluent. In section 74, the catalyst may form a dense pseudo-

liquid catalyst phase having a concentration of catalyst greater than about 20 pounds or 25 pounds per cubic foot of gas. In such a case, reactor 70 has two reaction sections, tubes 71 in which the gas flows at a relatively high velocity and with a relatively low concentration of catalyst and enlarged section 74 in which the gas flows at a relatively low velocity and with a relatively high concentration of catalyst. The same effect may be achieved in the apparatus of Fig. 1 of the drawings by extending the length of section 16 and adjusting the cross section thereof such that the velocity of the gases therein is appropriate for the formation of a dense pseudo-liquid catalyst phase. In this manner, a high velocity continuous catalyst phase will exist in conduit 8 and a dense pseudo-liquid catalyst phase will exist in section 16.

A movable valve 69 is provided at the lower end of standpipe 73 to control the flow and dispersion of the catalyst into the gaseous stream. Valve 69 may cause an aspiration effect by the deflection of the gases passing by and as a result of which the catalyst is drawn into the gaseous stream.

Fig. 3 gives a diagrammatic illustration in elevation of another arrangement of apparatus for the synthesis of hydrocarbons according to the present invention. The apparatus in Fig. 3 is very similar in operation to the apparatus of Fig. 1 and Fig. 2 and thus only a brief discussion of its operation will be included. A synthesis gas passes through a conduit 104 to a reaction chamber 106. Reaction chamber 106 comprises a bundle of reaction tubes 107 surrounded by a shell 108 to form an annular space 109 between the outside diameter of tubes 107 and shell 108. Annular space 109 is for the circulation of cooling fluid around reaction tubes 107 in order to maintain the temperature of reaction substantially constant. The cooling fluid, such as "Dowtherm," enters annular space 109 through conduit 113. The pressure in annular space 109 is such that the "Dowtherm" boils below the desired temperature of reaction in tubes 107. The vaporized "Dowtherm" passes from annular space 109 through conduit 112 to an accumulator 114. From accumulator 114 vapors pass through line 115 to a condenser 116 in which substantially all of the "Dowtherm" vapor is condensed. Condensate from condenser 116 passes to accumulator 114 through conduit 118. From accumulator 114 liquid "Dowtherm" is recycled to annular space 109 through conduit 113. Any uncondensable vapors are removed from the system through conduit 117.

A reaction effluent comprising reaction products and finely-divided catalyst entrained in the reaction effluent is passed to a settling and accumulation chamber 120 through conduit 111. Chamber 120 comprises an upper settling chamber 121 and a lower accumulator chamber 128. The cross-sectional area of settling chamber 121 is such that substantially all of the catalyst separates from the gaseous effluent and flows downwardly through a funnel-shaped septum 127 into the lower portion of accumulation chamber 128. Gases containing a small amount of fine catalyst pass upwardly in settling chamber 121 into a cyclone separator 122. Gases from cyclone separator 122 are removed therefrom by conduit 123 and may be treated in the manner heretofore described. Separated fine catalyst is removed from cyclone separator 122 by means of a conduit 124 and passed to funnel-shaped septum 127, as shown. Finely divided catalyst accumulates in accumulation chamber 128 to a level above the end of the funnel 127 in order to prevent the passage of the gaseous effluent downwardly through funnel 127. An aeration gas, such as hydrogen or recycle gas, is introduced into the lower portion of accumulation chamber 128 through conduit 132 and is injected into the accumulated catalyst therein by means of dispersion means 133 which may comprise a perforated conduit or the like. Accumulator 128 may be maintained at a substantially higher pressure than settling chamber 121 by introducing a gas therein through conduit 131, if desired. By maintaining the pressure higher in chamber 128 than in chamber 131 passage of gaseous effluent into the accumulated catalyst is prevented. Pressuring gas and aeration gas may be passed, if desired, from chamber 128 to chamber 121 through conduit 134. Alternatively, aeration gas may be passed from chamber 128 to conduit 131 if that conduit is not being used for the introduction of a pressuring gas.

Accumulated catalyst in accumulator 128 passes through a standpipe 129 to conduit 104 to be mixed with fresh feed.

Cyclone separator 122 may be omitted and in its place another type of separating means may be used, such as the filter means of Figures 1 and 2. Various other modifications of Fig. 3 may become obvious to those skilled in the art without departing from the scope of this invention.

Assuming a reactor inlet gas volume of 25,000 standard cubic feet per hour, a reactor consisting of four tubes having an inside diameter of 2 inches would operate at a maximum linear velocity of 9 feet

per second. Using a tube length of 36 feet, a velocity of 9 feet per second would correspond to about 4 seconds of contact time per pass, allowing for contraction. A reactor capable of a 40 feet per second linear velocity and 5 seconds contact time per pass would involve a flow path of about 200 feet in length. A single tube having a 2 inch inside diameter might be substituted for the four tubes having a 1 inch inside diameter with substantially the same velocity and throughput.

The invention will be described further by reference to Figure 4 of the accompanying drawings which is a view in elevation partly in cross section diagrammatically illustrating apparatus for effecting the hydrogenation of a carbon oxide according to the present invention for a minimum capacity of 19,000 standard cubic feet of gas per hour and for a minimum velocity of 7 feet per second at reaction conditions in the vertical upflow section of the equipment.

In Figure 4 a synthesis feed gas comprising hydrogen and carbon monoxide present in a ratio of about 2:1 is introduced into conduit 211. In conduit 211 the gas stream picks up finely divided hydrogenation catalyst, such as reduced iron, from standpipe 249. Conduit 211 is a standard 2 inch steel pipe and is about 2½ feet in length from the point of introduction of the catalyst. The catalyst loading into conduit 211 is regulated by a conventional slide valve 251. At the minimum velocity of about 28 feet per second in conduit 211, intimate mixing of finely divided catalyst and reactants is achieved and reaction is effected immediately. In order to prevent overheatng of the reaction mixture in conduit 211 as the result of the liberation of the exothermic heat of reaction therein, the residence time of the reactants between the catalyst introduction and the first cooler should be less than about 2 seconds, preferably at the minimum velocity about 1.5 seconds, for relatively high CO concentrations, such as above 30 per cent. While the hydrogenation of the carbon oxide is progressing in conduit 211, the gaseous mixture of reactants and products of reaction are passed to a first cooler 216 through a standard 4 to 2 inch reducer 212 and a standard 4 inch diameter pipe 213. Standard 4 inch diameter pipe 213 provides a minimum velocity of about 7 feet per second at reaction conditions for the design capacity of 19,000 standard cubic feet of passing through per hour. Cooler 216 comprises a cylindrical shell surrounding a bundle of seven standard one inch diameter pipes 217. Pipes 217 are held in place by tube sheets (not shown) at each end of cooler 216. Cooler 216 is connected to conduit 213 by means of a standard reducing fitting 214 and to a conduit 222 by a reducing fitting 221. Reducer 212, conduit 213, and fitting 214 together are about 10 feet 8 inches in length. Cooler 216 is approximately 12 feet in length. A cooling liquid, such as "Dowtherm" or other suitable coolant, is introduced into the annular space between tubes 217 and the shell of cooler 216 by means of inlet conduit 218, or the equipment may be arranged as a boiler in which the flow of coolant is preferentially upward. The cooling medium flows downward in indirect contact with the upward flowing gaseous reaction mixture in tubes 217 and is removed from the lower portion of cooler 216 by means of outlet conduit 219. Prior to entry into cooler 216 the gaseous reaction mixture is at the maximum temperature desired, about 600° F. While the reaction proceeds in cooler 216 the rate of heat removal is in excess of the rate of heat release due to reaction; the reaction mixture leaves the cooler at a desired lower temperature, about 590° F. The linear gas velocity in cooler 216 is greater than the linear gas velocity in conduit 213 and is usually above about 24 feet per second. A cooled reaction mixture at a temperature of about 590° F. and containing entrained catalyst is passed from cooler 216 through reducer 221 into a standard 4 inch diameter pipe 222 in which pipe the reaction proceeds. The length of conduit 222 is such with regard to the velocity of the gaseous stream therein that the temperature of reaction will not rise above the maximum temperature desired before entering a second cooler 224. Conduit 222 may contain a restricted section of about 2 inches in diameter to aid in mixing the catalyst and gases. In the present design the length of conduit 222 including reducing fittings 221 and 223 is about 7 feet 8 inches. At the outlet of conduit 222 the temperature of the gaseous reaction mixture is about 600° F. The gaseous mixture is introduced into the second cooler 224 through reducing fitting 223. Cooler 224 is similar to cooler 216 and comprises a cylindrical shell surrounding a bundle of tubes 226 through which the gaseous reaction mixture and entrained catalyst flow. A cooling medium is introduced into the annular space between tubes 226 and the cylindrical shell of cooler 224 by means of inlet conduit 227. Cooling medium passes counter-currently and in indirect heat exchange with the flowing gaseous mixture in tubes 226. The cooling medium is removed from cooler 224 through outlet conduit 228. Cooler 224 is approximately

12 feet in length. The reaction mixture in cooler 224 is cooled from about 600° F. to an outlet temperature of about 590° F. The cooled reaction mixture containing entrained catalyst is removed from cooler 224 and passed through a standard reducing fitting 229, a standard 4 inch pipe 231, into catalyst separator 232. The gaseous mixture in conduit 231 achieves a temperature of about 620° F. before discharging into separator 232. This relatively high temperature aids in stripping some of the unvaporized product components from the catalyst. The total length of conduit 231 is about 25 feet. The horizontal section of conduit 231 may be of a smaller diameter than the vertical section, for example about 2 inches in diameter, in order to minimize or prevent the tendency of the catalyst to settle in the horizontal section.

Coolers 216 and 224 may be independently operated such that the reaction effluent may be cooled to different outlet temperatures. The outlet temperature of the reaction effluent from cooler 216 may be lower than the outlet temperature from cooler 224; and, *vice versa*, the outlet temperature from cooler 216 may be higher than the outlet temperature from cooler 224 without departing from the scope of this invention. Conveniently, the cooling medium from conduits 219 and 228 and coolers 216 and 224, respectively, may be passed to a common cooling unit (not shown) comprising a conventional indirect heat exchange unit. After cooling of the cooling medium, the cooling medium may be passed to an accumulator (not shown), and from there recycled back to coolers 216 and 224 through conduits 218 and 227, respectively. Alternatively, coolers 216 and 224 may be independently operated with separate cooling means for cooling the cooling medium and with separate accumulators. Although countercurrent heat exchange with the reaction mixture has been shown and described, concurrent heat exchange may be employed without departing from the scope of this invention.

Separator 232 comprises an upper enlarged cylindrical section 233, an intermediate conical section 234, and a lower, preferably cylindrical, section 236. Enlarged section 233 comprises a standard 24 inch pipe in which section a larger proportion of the catalyst is separated from the reaction effluent. Lower section 236 comprises a standard 10 inch pipe and constitutes an accumulation zone for separated catalyst. A catalyst bed is maintained in accumulator or lower section 236 at a level indicated by numeral 243. Conduit 231 preferably terminates above or adjacent to level 243 such that the effluent gases issuing therefrom cause a highly turbulent action in the catalyst bed in accumulator 236. This turbulent action caused by the effluent gases from conduit 231 prevents bridging or caking of the catalyst in the accumulation zone 236, which caking or bridging would hinder the flow of the catalyst downward into stripping section 246. A conventional cyclone separator is positioned inside enlarged section 233. Gases containing finely divided entrained catalyst pass into cyclone separator 238 wherein the finely divided entrained catalyst is separated from the gases. Catalyst passes from cyclone separator 238 downward through a standpipe 239 into the lower portion of accumulator 236. Standpipe 239 comprises a ¾ inch standard pipe and terminates below the bed level 243. Gases substantially free from entrained solids are removed from cyclone separator 238 through conduit 241 and gate valve 242. Conduit 241 is a standard 1½ inch steel pipe.

Catalyst which has separated from the gaseous effluent is passed to a stripping section 246 by means of a standard reducer 244. Stripping section 246 comprises a standard 2½ inch steel pipe approximately 2 feet in length. A stripping gas, such as hydrogen, carbon dioxide, steam or recycle gas, is introduced into stripping section 246 through conduit 247. The stripped finely divided catalyst is passed from stripping section 246 by means of a standard reducer 248 into a standpipe 249 comprising a 2 inch standard pipe. A standard 2 inch slide valve 251 is provided in the lower portion of standpipe 249 to regulate the flow of catalyst into conduit 211.

Cold synthesis gas and/or recycle gas may be injected into conduit 222 and/or into conduit 231 without departing from the scope of this invention. The injection of such gases into the reaction section of the apparatus aids in controlling the temperature of reaction and also aids in controlling the composition of the reaction effluent with regard to hydrogen, carbon monoxide, and diluent gases.

The gaseous effluent comprising the products of the hydrogenation reaction and unreacted hydrogen and/or carbon monoxide is passed through conduit 249 to conventional separation units (not shown) for the separation of the products of the process from the effluent. Unreacted reactants recovered in the separation unit may be recycled to conduit 211, if desired.

With regard to temperature, using a high velocity system, as shown in the

drawings the cooling surface is swept clean of catalyst particles with the result that none of the catalyst has sufficient time of contact to overcool, and with the result that the cooling surface is more efficient. The relatively clean cooling surface permits using a lower temperature coolant without danger of overcooling the catalyst as with conventional fluid-bed operations. Furthermore, with temperatures under full control the design minimum and maximum operating temperatures can safely cover a relatively wide range without local excessive deviation from the permissible range of temperatures.

The system of the present invention is also much more flexible than conventional fluid-bed systems because the catalyst feed rate and the coolant flow rate can be changed independently. No preheating of the synthesis gas is required in most instances since the mixing of the reactants and catalyst at the catalyst pick-up is so efficient that all of the gases come to the theoretical mixing temperature almost instantaneously.

The multi-stage cooling of the apparatus of Figure 4 has several distinct advantages. By multi-stage cooling in a high velocity system, the temperature range through the reaction zone can be kept relatively closer to an average or can be varied at will. The divided capacity of the catalyst coolers also makes it possible for fixed tube sheet bundles to be employed, which results in a decrease in cost of apparatus. The conical sections into and out of the coolers are highly efficient mixers at the velocities of the present process and are, therefore, ideal reaction zones for the most efficient utilization of the catalyst.

The catalyst concentration in the reaction zone, such as in conduits 211, 222, and 231 of Figure 4 may be accurately controlled according to this process by varying the catalyst loading rates through slide valve 251. The concentration is a function of both the velocity and the loading rate, except at the higher velocities within range disclosed when the concentration is a function primarily of the loading rate.

Still another advantage of the present system is the fact that the accumulation of unvolatilized organic compounds of relatively high molecular weight, such as heavy polymers, on the catalyst, which compounds are potential coke, can be minimized by stripping the circulating catalyst in accumulator 120 of Figure 3 and in stripper 246 of Figure 4. Since the catalyst has a relatively short residence time in the reaction zone in which it contacts the hydrogen and carbon monoxide, the wax deposits thereon may be stripped before the accumulations become excessive and before coke is formed. The catalyst is in the reaction zone in the present system only a matter of seconds before it is withdrawn, separated from the reactants and reaction products, and then stripped of wax deposits. After stripping, the catalyst is again returned to the reaction zone. The intermediate stripping operation maintains the catalyst at its maximum activity and results in substantially prolonged life of the catalyst. The combination of short residence time and stripping enables the operation of the process without frequent intermittent or continuous regeneration of the catalyst by oxidation and-or reduction. The process may be operated for prolonged periods with substantially the sole source of catalyst to the reaction zone being the stripped recycle catalyst. A small amount of fresh catalyst may be added to the system to compensate for the loss of catalyst with the reaction effluent, such as through line 241 of Figure 4.

Various minor modifications and alterations of the apparatus shown in the drawing may be practiced by those skilled in the art without departing from the scope of this invention. Various coolers, condensers, distillation units, and other means for treating the reaction effluent have not been shown for a matter of convenience and simplicity but their presence and use will be obvious to those skilled in the art.

The following example is offered as a means of better understanding the application of the present invention to the hydrogenation of carbon monoxide and the specific recitation of certain limitations therein is not considered unnecessarily limiting to the present invention.

EXAMPLE.

In accordance with this invention an iron catalyst was prepared in the following manner. About 13,600 grams of powdered Alan Wood Ore was mixed with 69 grams of TiO_2 and 175 grams of KOH by forming a solution of the potassium hydroxide dissolved in 1600 ml. of distilled water and adding the solution to the Alan Wood Ore. The titanium dioxide was added to the mixture of potassium hydroxide solution and the entire mixture thoroughly agitated for about 15 or 20 minutes. The wet mix was dried overnight in porcelain dishes at about 210° F. to about 220° F. The resulting hard dry cake was ground to about 20 mesh in a disc mill. The finely-ground material was fused at a temperature of about 2600° F. to about 2800° F. After fusing, the

material was broken up into large chunks and ground again in a disc mill and pulverized in a ball mill.

The pulverized material was then pelleted to about $\frac{3}{16}$ inch to $\frac{1}{2}$ inch pellets and was reduced with hydrogen at about 1400° F. to 1500° F. for about ten hours.

After reduction of the pellets with hydrogen, the pellets were repowdered in a ball mill. The reduction of the fused mixture was carried out in a fixed-bed operation in which the catalyst formed a stationary bed of pellets in the reaction zone.

Alan Wood Ore comprises about 1 per cent to 2 per cent alumina, about 1 per cent silica, and less than 1 per cent titanium oxide, and the remainder iron oxides. The resulting catalyst contains in addition to metallic iron, alumina, titanium dioxide, and silica, about 1.2 per cent to about 1.4 per cent potassium calculated as the oxide. The size of the prepared catalyst is shown in Table I below:

TABLE I.

POWDERED IRON CATALYST PARTICLE SIZE.

Screen Analysis Mesh	Weight Per Cent
+40	—
40/100	2.5
100/200	5.1
200/Pan	13.2
	79.2
	100.0
Roller Analysis Microns	
0—10	16.2
10—20	17.0
20—40	19.2
40—60	24.0
60+	23.6
Recovery—%	98.8
Density (basis water)	6.8

Having prepared a catalyst of the desired properties and the required size, the catalyst was introduced into a conduit, similar to conduit 8 of Fig. 1 of the drawings, in which a mixture of hydrogen and carbon monoxide was flowing upwardly at a relatively high velocity. The conditions of reaction and the analysis of the product is shown in Table II below. In substantially all respects the apparatus used for obtaining the data shown in Table II was the same as the apparatus of Fig. 1 of the drawings. In obtaining data various gas velocities as well as concentrations of catalyst in the reaction zone (conduit 8) were used to determine their effect on the reaction and product. Also it will be noted that the pressures used varied from 80 to 150 pounds per square inch gage. In some runs, especially the later runs, the temperature of the inlet feed gas was decreased to a relatively low value to determine the effect of contact between relatively hot catalyst and relatively cold gas and whether temperature conditions could be maintained in the reaction zone. The reaction effluent was withdrawn from the reaction zone after a relatively short contact time with the catalyst. The catalyst separated by gravity from the effluent in an enlarged section of the apparatus and passed by means of a standpipe, such as conduit 10 of Fig. 1, to the point of introduction of the catalyst into the synthesis gas stream. The effluent passed through filters to separate fine catalyst therefrom. The filters were cleaned intermittently or continuously by flowing recycle gas back through them as previously explained with reference to Fig. 1 of the drawings. The effluent then passed through a condenser at 40° F. and at operating pressure and uncondensed gases were recycled to a point just before the first contact of catalyst and synthesis gas.

Catalyst in the standpipe was maintained at about 800° F. by means of electrical heating elements wound around the 4 inch jacket surrounding the 2 inch standpipe. Various predetermined loadings of the catalyst into the synthesis gas stream were used and the tendency for variation in loadings for any particular run caused by variation in differential pressure in the reaction zone was minimized by controlling a slide valve on the bottom of the standpipe by a conventional differential pressure recorder responsive to the differential pressure between the top and bottom of the standpipe. The differential pressure recorder was set at various readings of inches of water depending upon the catalyst loading desired. The concentration of catalyst in the reaction zone or elongated conduit was determined by the differential pressure in a 15 foot vertical section of the conduit. The overall length of the reaction zone was about 26 feet and 8½ inches, i.e., from the point the catalyst was first contacted with the synthesis gas and the point where the catalyst was separated from the reaction effluent.

The velocity of the gas stream was so great that the catalyst was entrained in the synthesis gas stream throughout the reaction zone in a continuous phase without the formation of the conventional dense pseudo-liquid phase of catalyst.

Gas bleeds into the instrument lines were used to prevent catalyst from clogging instrument lines and instruments. In some cases recycle gas was used as the bleed gas, in other instances hydrogen or

fresh feed gas were used.

The catalyst in the standpipe was aerated with recycle gas or combined inlet gas in most instances, however other gases, such as carbon dioxide, hydrogen, nitrogen, and steam could have been used if desired.

TABLE II—Part 1

Run No.	1	2	3	4	5	6
Hours on Run	6	6	6	16	18	18
Operating Conditions						
Pressure, P.S.I.	80	80	80	80	80	80
Ratio of Recycle to Fresh Feed	6.0	6.4	7.7	1.7	1.8	6.2
Fresh Feed, CF/H	83	137	143	150	155	191
Gas Ratio, H_2:CO						
Fresh Feed	3	3	3	3	3	3+
Inlet to Reaction Zone	—	—	—	—	4.5	14
Standpipe						
Temp. °F.	583	597	598	598	596	605
Density, P.C.F.	97	97	100	103	99	102
Lin. Velocity, F.P.S.O.	0.4	0.4	0.4	0.10	0.17	0.18
Reaction Zone						
Aver. Temp. °F. in zone	585	593	595	594	596	603
Gas Inlet Temp. °F.	572	591	616	604	603	605
Lin. Velocity, F.P.S. (Superficial)	15	15	19	7	8	15
Catalyst Loading (inches of water)	35	55	56	53	35	49
Concentration of Catalyst, P.C.F.	3.5	5.5	5.9	3.5	3.0	4.2
Results						
Contraction—%	—	—	54	26	23	32
CO Disappearance	85	75	79	87	54	81
Observed Oil, cc/m^3 of fresh feed	20	80	19	28	31	44
Water, cc/m^3 of fresh feed	167	176	105	81	80	—
Selectivity CO—CO_2	12.5	13.8	14.7	22.4	15.4	—

TABLE II—Part 2

Run No.	7	8	9	10	11	12
Hours on Run	150	5	12	24	18	24
Operating Conditions						
Pressure, P.S.I.	150	150	150	150	150	150
Ratio of Recycle to fresh feed	4.92	4.9	4.7	5.0	7.1	8.5
Fresh Feed, CF/H	251	234	224	188	139	106
Gas Ratio, H_2:CO						
Fresh Feed	3	3	2	2	1.4	1.4
Inlet to Reaction Zone	4.9	4.8	3.9	3.3	2.5	2.0
Standpipe						
Temp. °F.	597	595	597	602	597	596
Density, P.C.F.	106	75	87	88	87	87
Lin. Velocity, F.P.S.	0.14	0.20	0.13	0.13	0.11	0.11
Reaction Zone						
Aver. Temp. °F. in zone	601	602	600	603	602	600
Gas Inlet Temp. °F.	576	614	603	596	602	600
Lin. Velocity, F.P.S. (Superficial)	14.3	14.2	13.4	13.1	11.8	10.5
Catalyst Loading (inches of water)	70	70	70	70	70	70
Concentration of Catalyst, P.C.F.	8.4	7.7	8.0	8.4	8.0	8.7
Results						
Contraction—%	35	41	37	38	25	35
CO Disappearance	88	—	67	59	39	71
Observed Oil, cc/m³ of fresh feed	38	20	41	46	55	101
Water, cc/m³ of fresh feed	135	61	110	114	126	165
Selectivity:						
CO—CO_2%	13.2	—	20.5	25.8	39.5	23.2
CO—CH_4	—	—	—	—	—	18

TABLE II—Part 3

Run No.	13	14	15	16	17	18
Hours on Run	22	6	18	24	24	18
Operating Conditions						
Pressure P.S.I.	150	150	150	150	150	150
Ratio of Recycle to fresh feed	6.5	8.1	6.6	6.4	6.0	6.5
Fresh Feed, CF/H	123	105	127	130	136	135
Gas Ratio, H_2:CO						
Fresh Feed	1.4	1.4	1.4	1.4	1.4	1.4
Inlet to Reaction Zone	2.2	2.0	2.2	2.0	—	2.6
Standpipe						
Temp. °F.	597	601	600	600	601	604
Density, P.C.F.	82	80	78	90	52	69
Lin. Velocity F.P.S.	0.11	0.08	0.10	0.10	0.09	0.10
Reaction Zone						
Aver. Temp. °F. in zone	604	604	602	604	602	602
Gas Inlet Temp. °F.	600	600	600	600	575	550
Lin. Velocity F.P.S. (Superficial)	10.4	10.2	10.3	10.2	10.0	10.8
Catalyst Loading (inches of water)	70	75	80	74	60	59
Concentration of Catalyst, P.C.F.	9.4	10.1	11.2	9.8	8.7	8.2
Results						
Contraction—%	46	37	43	44	47	48
CO Disappearance	74	—	83	—	79	—
Observed Oil, cc/m^3 of fresh feed	60	93	80	73	79	63
Water, cc/m^3 of fresh feed	142	168	129	140	148	141
Selectivity:						
CO—CO_2%	23.2	—	11	26.6	29.5	17.4
CO—CH_4	14.5	—	17.8	11.8	—	12.9

TABLE II—Part 4

Run No.	19	20	21	22	23	24
Hours on Run	24	24	24	24	21	48
Operating Conditions						
Pressure, P.S.I.	150	150	150	150	150	150
Ratio of Recycle to Fresh Feed	6.4	5.6	5.4	5.5	6.5	6.6
Fresh Feed CF/H	128	145	148	144	131	126
Gas Ratio H_2:CO						
Fresh Feed	1.4	1.4	1.4	1.4	1.4	1.4
Inlet to Reaction Zone	2.6	1.7	2.0	2.0	2.0	2.1
Standpipe						
Temp. °F.	598	600	595	590	590	559
Density P.C.F.	67	67	66	66	60	55
Lin. Velocity, F.P.S.	0.09	0.09	0.11	0.11	0.11	0.10
Reaction Zone						
Aver. Temp. °F. in zone	595	590	585	575	570	540
Gas Inlet Temp. °F.	500	450	400	350	300	150
Lin. Velocity, F.P.S. (Superficial)	9.8	8.9	9.5	8.6	8.2	8.5
Catalyst Loading (inches of water)	58	59	58	57	58	57
Concentration of Catalyst, P.C.F.	8.4	8.7	8.0	8.0	8.0	8.0
Results						
Contraction—%	49	49	44	53	53	43
CO Disappearance		79				
Observed Oil, cc/m³ of fresh feed	70	69	—	56	65	50
Water—cc/m³ of fresh feed	160	121	—	100	139	95
Selectivity:						
CO—CO_2%	17.4	20.0	—	—	—	17.9
CO—CH_4	12.9	7.4	—	—	—	—

TABLE II—Part 5

Run No.	25	26	27
Hours on Run	24	24	18
Operating Conditions			
Pressure, P.S.I.	150	150	150
Ratio of Recycle to fresh feed	5.8	3.6	4.8
Fresh Feed, CF/H	171	271	206
Gas Ratio, H_2:CO Fresh Feed	1.4	1.4	1.4
Standpipe			
Temp. °F.	591	593	607
Density, P.C.F.	49	43	49
Lin. Velocity, F.P.S.	0.12	0.13	0.11
Reaction Zone			
Average Temp. °F. in zone	602	593	604
Gas Inlet Temp. °F.	615	610	604
Lin. Velocity, F.P.S. (Superficial)	10.1	10.5	10.6
Concentration of Catalyst, P.C.F.	5.8	3.6	4.8
Results			
Contraction—%	62	68	83
Observed Oil, cc/m³ of fresh feed	98	70	17
Water—cc/m³ of fresh feed	154	106	84

From the above data it is apparent that the product and results in general compare favourably with fluid-bed operations using a conventional dense phase of catalyst. It should be noted that a considerably lower ratio of hydrogen to carbon monoxide in the fresh feed gas is used than is usually practiced in fluid-bed operations.

It is assumed that a catalyst slip of about 50 per cent is present in the vertical section of the reaction zone. Actually, therefore, the catalyst loading of pounds of catalyst per cubic foot of gas may be about half the concentration of catalyst in the reaction zone. Thus, for a concentration of 8 pounds per cubic foot of gas, the catalyst flow was calculated to be about 1000 pounds per hour.

When operating at 1.4 ratio of hydrogen to carbon monoxide, as in runs 13 to 23, with a recycle ratio of about 5:1 to 6:1 the gas inlet composition (including fresh feed and recycle gas) was about 18 per cent carbon monoxide and a ratio of H_2:CO of about 2:1 to 2.5:1 existed in the reaction zone.

In certain runs, it was found that with a catalyst loading represented by a differential pressure of 80 inches of water the flow of catalyst in the reaction zone was too great to permit uniform settling in the standpipe. However, with a larger diameter or longer standpipe or bigger

slide valve, loadings higher than that represented by 80 inches of water could be used satisfactorily. In run 24 a combined inlet gas temperature of 150° F. was used. When operating at a combined recycle and fresh feed gas temperature as low as 150° F. it was necessary to maintain the catalyst temperature at least 560° F. to ensure a sufficiently high reaction temperature. The catalyst was maintained at about 560° F. in the standpipe by heating the catalyst electrically, as previously discussed. With the equipment used for these runs, the catalyst could not be maintained to a high enough temperature to permit a lower inlet gas temperature. An inlet gas temperature as low as 100° F. or lower could be used if the catalyst could be maintained at 600° F. in the standpipe.

In Runs No.'s 20 through 23 the selectivity appeared to be good with 21 per cent $CO \rightarrow CO_2$ and a similar amount of $CO \rightarrow CH_4$. Analysis of the product of run 20 indicated that about 40 per cent of the condensed oil comprised oxygenated compounds of which 15 per cent were acids. The water contained about 14 per cent chemicals, approximately half of which were acids. A yield of about 40 cc./m.³ of total oxygenated compounds was obtained.

Operations at 250 pounds per square inch pressure have proved to be successful with results somewhat similar to those at lower pressures.

As will be noted, no external cooling of the reaction system was used during the runs for the hydrogenation of carbon monoxide with the apparatus of Figure 1. In fact, heat was added to the system through the catalyst standpipe by electrical heating coils around the jacket of the standpipe which contained "Dowtherm" under pressure. The reaction zone was heavily lagged and electrically wound to produce substantially adiabatic conditions in that zone. If the entire assembly of apparatus had been completely adiabatic, and if the runs had been carried out on a larger scale, cooling of the standpipe or the reaction zone would have been necessary. Such cooling could have been carried out by contact with a cooling medium surrounding the reaction zone, such as cooling with water or "Dowtherm," or by introducing relatively cold feed gas or cold recycle gas or both.

Prior to run 12 an iron catalyst similar to that previously described, but which had been used in conventional dense-phase, fluid-bed operation for about 400 hours, was substituted for the original catalyst in carrying out the process. The composition of this catalyst prior to use in the process is shown in column 1 of Table III. After the catalyst had been used for a period of two days, five days, and nine days, analysis of the catalyst was made to determine the effect of this type of reaction on the carbon and oil content of the catalyst, and also upon the catalyst size. This data is shown in Table III.

TABLE III.

CATALYST ANALYSIS.

Chemical Analysis	Charged	2 days	5 days	9 days
Oil + Wax	4.0	4.5	5.5	5.2
Carbon	23.1	23.5	26.4	24.0
Total Iron	65.3	65.2	63.4	62.0

Holler Analysis Microns	Weight per cent		
0—10	0.9	1.0	1.2
10—20	0.9	2.8	2.7
20—40	7.5	10.2	12.9
40—80	32.4	33.3	38.4
80+	58.3	52.7	44.8
Density	3.4	3.1	3.2

The data of Table III indicates only a slight change in chemical composition and size of the catalyst from the original material introduced at the beginning of run 12. The wax content increased about 1.5 per cent and the fixed carbon content increased about 3.3 per cent. A decrease of less than 2 per cent in the total iron

was noted. The particle size analysis indicates that the catalyst became slightly finer on use. From these results the catalyst composition in the circulating system of the present invention was probably more stable than with the conventional dense-phase operation using a fluid-bed.

This invention has been described with particular reference to specific apparatus and to specific conditions of operation. however, various modifications of the apparatus and various operating conditions may be used within the limits disclosed without departing from the scope of this invention. Essentially, the apparatus design itself must permit high velocity of gases in at least a portion of the reaction section.

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 hydrogenating carbon monoxide or dioxide which comprises flowing a gaseous mixture comprising hydrogen and carbon monoxide or dioxide at a velocity of at least 5 feet per second in contact with a finely divided hydrogenating catalyst of appropriate particle size such that said catalyst is moved in the direction of flow of said gaseous mixture in a condition more dilute than the condition of the catalyst in a conventional pseudo-liquid dense phase type of operation under comparable conditions.

2. A process according to claim 1 in which the gaseous mixture is continuously passed through a plurality of alternate uncooled and cooled reaction zones and the finely divided hydrogenation is continuously introduced into said gaseous mixture.

3. A process according to claim 2, in which the residence time of said catalyst and said gaseous mixture between the point of introduction of catalyst and the inlet to the first cooled reaction zone is less than about 2 seconds.

4. A process according to claims 2 or 3 in which the gaseous mixture is passed upwardly through an elongated reaction zone, and the finely divided hydrogenating catalyst is entrained in said gaseous mixture in an amount less than about 25 pounds per cubic foot of gas, suitable conditions of temperature and pressure for the production of organic compounds being maintained in said reaction zone.

5. A process according to claim 4 which includes continuously withdrawing from the upper portion of the reaction zone an effluent comprising organic compounds produced therein and entrained catalyst.

6. A process according to claim 5 which includes separating entrained catalyst from the effluent, recycling the separated catalyst, and recovering organic compounds from said effluent as products of the process.

7. A process according to any of the preceding claims, in which said finely-divided hydrogenating catalyst comprises iron.

8. A process according to any one of claims 1 to 6 in which said finely-divided hydrogenating catalyst comprises cobalt.

9. A process according to any one of claims 1 to 6 in which said finely-divided hydrogenating catalyst comprises nickel.

10. A process according to any of claims 4 to 9 in which the gaseous mixture comprises hydrogen and carbon monoxide or dioxide in a mol. ratio of at least about 1:1 and a temperature and pressure of reaction between about 300° F. and about 750° F. and between about atmospheric and about 500 pounds per square inch gauge is maintained in the reaction zone.

11. A process according to any of claims 4 to 9 in which the hydrogen and carbon monoxide or dioxide in a ratio between 0.7:1 and about 2.5:1 are introduced into an elongated substantially vertical zone, the gaseous mixture being passed upwardly through said reaction zone at a velocity between about 8 and about 40 feet per second.

12. A process according to claim 11 in which the finely-divided hydrogenating catalyst comprises iron having the greater proportion thereof of less than about 100 microns so that the catalyst is entrained in the gaseous mixture in an amount between about 1 pound and about 12 pounds per cubic foot of gas and forms a continuous phase in the reaction zone.

13. A process according to claim 12 in which a temperature of reaction between about 450 and about 750° F. and a pressure between about 10 pounds and about 500 pounds per sqare inch gauge is maintained in said reaction zone.

14. A process according to any one of claims 1 to 7 which comprises introducing the hydrogen and carbon monoxide or dioxide into a first reaction zone, passing the gaseous mixture comprising hydrogen and carbon monoxide or dioxide upwardly through said first reaction zone, continuously introducing into the lower portion of said first reaction zone the finely divided hydrogenating catalyst, continuously withdrawing from said first reaction zone a gaseous effluent containing catalyst therein, introducing said gaseous effluent containing catalyst into a second reaction zone having a larger cross-sectional area than said first reaction zone

such that the velocity of the gases in said second reaction zone is less than the velocity of the gases in said first reaction zone, passing gases upwardly through said second reaction zone at a velocity such that non-continuous dense pseudo-liquid catalyst phase is formed, withdrawing an effluent substantially free from catalyst from the upper portion of said second reaction zone, withdrawing catalyst from the lower portion of said second reaction zone and recycling same to said first reaction zone, and recovering organic compounds from said effluent from said second reaction zone as products of the process.

15. A process according to any one of claims 1 to 5, which includes cooling and condensing the effluent and separating resulting condensate from uncondensed vapors comprising unreacted reactants, and recycling at least a portion of said uncondensed vapors to the reaction zone in a ratio of recycle gas to hydrogen and carbon oxide introduced into said reaction zone between about 1:1 and about 5:1.

16. The process of hydrogenating carbon oxides substantially as hereinbefore described.

Dated this 24th day of January, 1948.

For:
THE M. W. KELLOGG COMPANY,
Stevens, Langner, Parry & Rollinson,
Chartered Patent Agents,
5—9, Quality Court, Chancery Lane,
London, W.C.2, and at
120, East 41st Street,
New York, 17, N.Y., U.S.A.

Leamington Spa: Printed for His Majesty's Stationery Office, by the Courier Press.—1951.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies, price 2s. per copy; by post 2s. 1d. may be obtained.

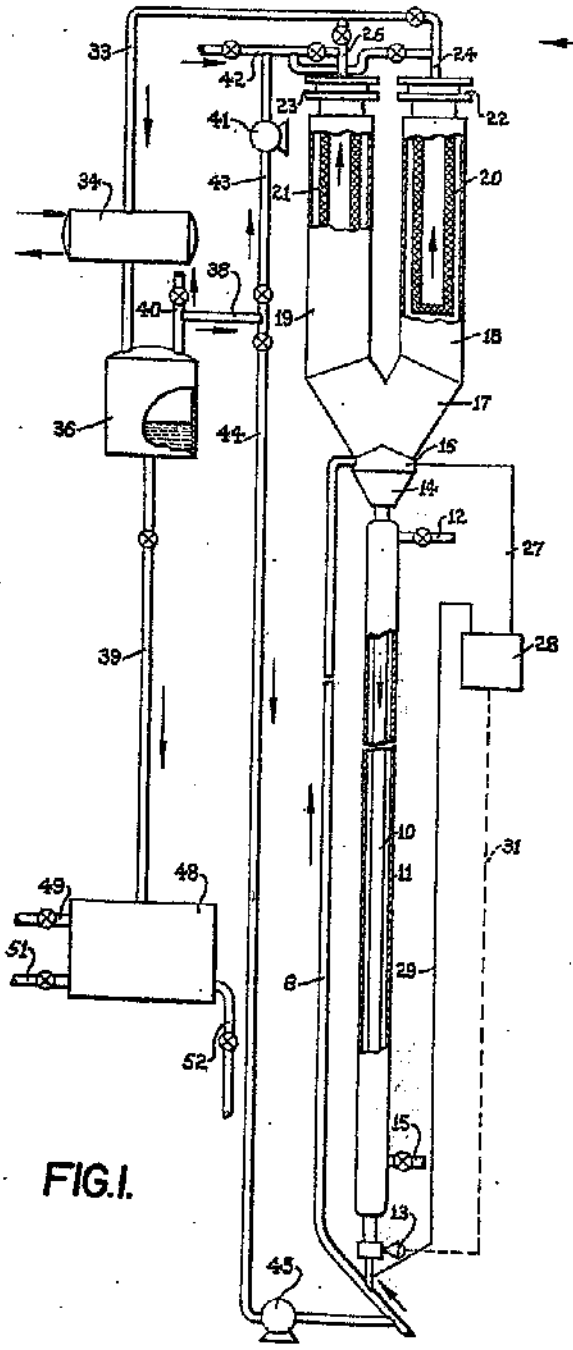


FIG.1.

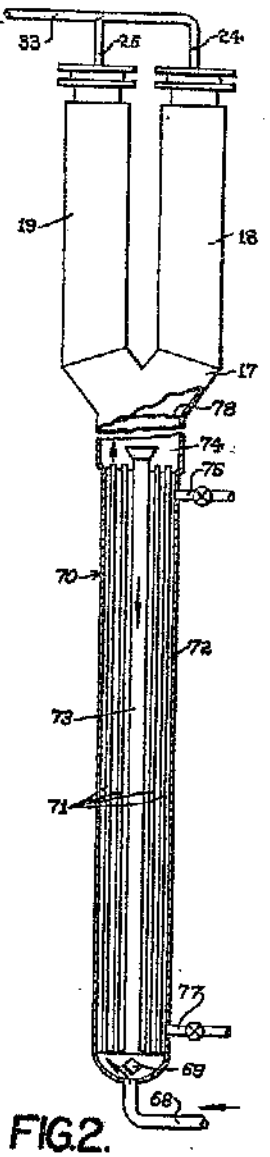
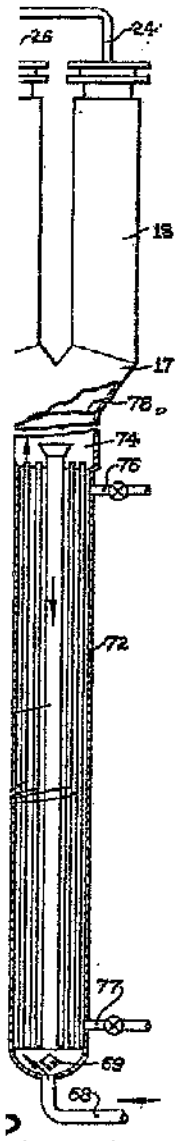


FIG.2.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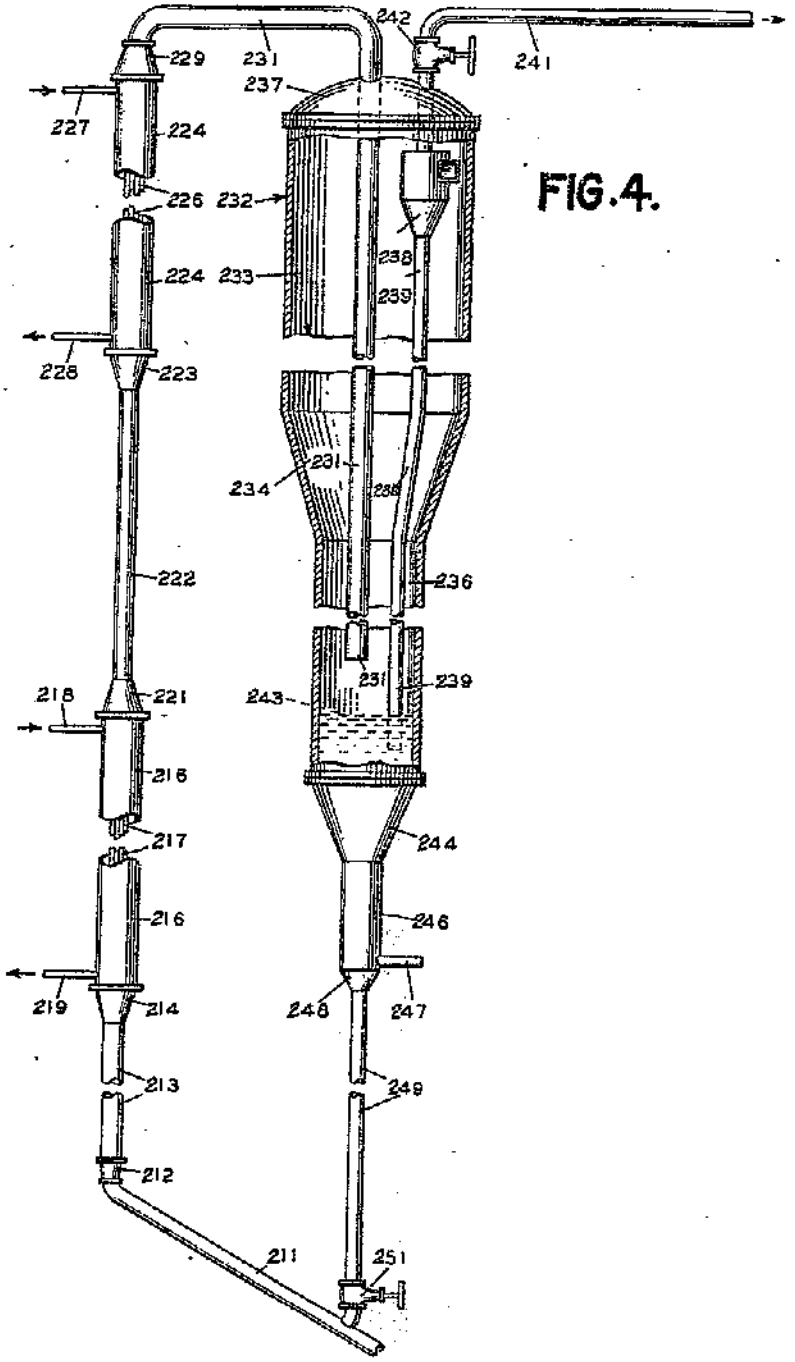
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FIG.4.

656,560 COMPLETE SPECIFICATION

SHEET 1

3 SHEETS
SHEET 3

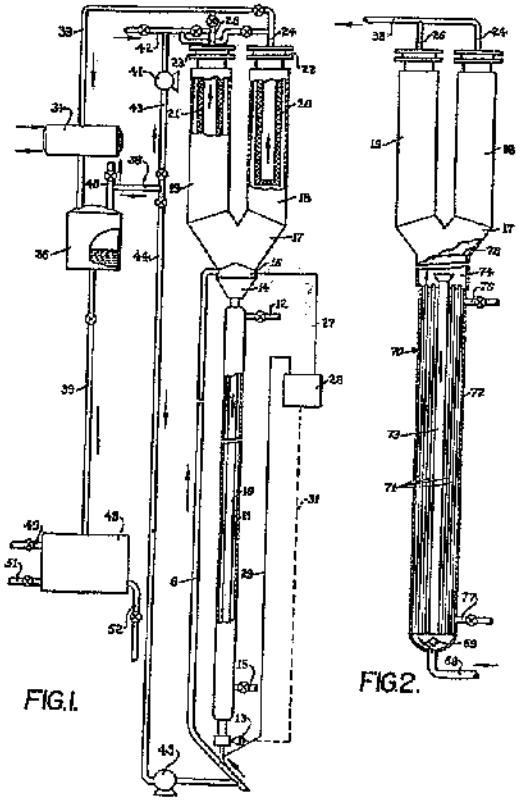

FIG.1.

FIG.2.

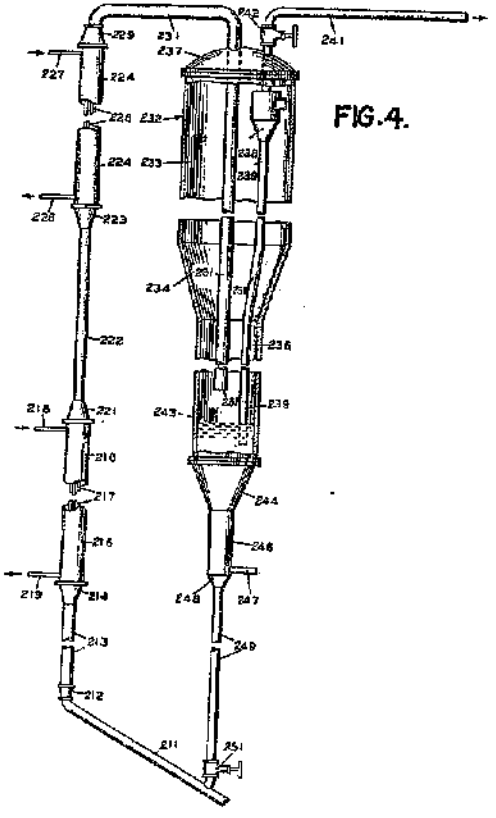

FIG.4.

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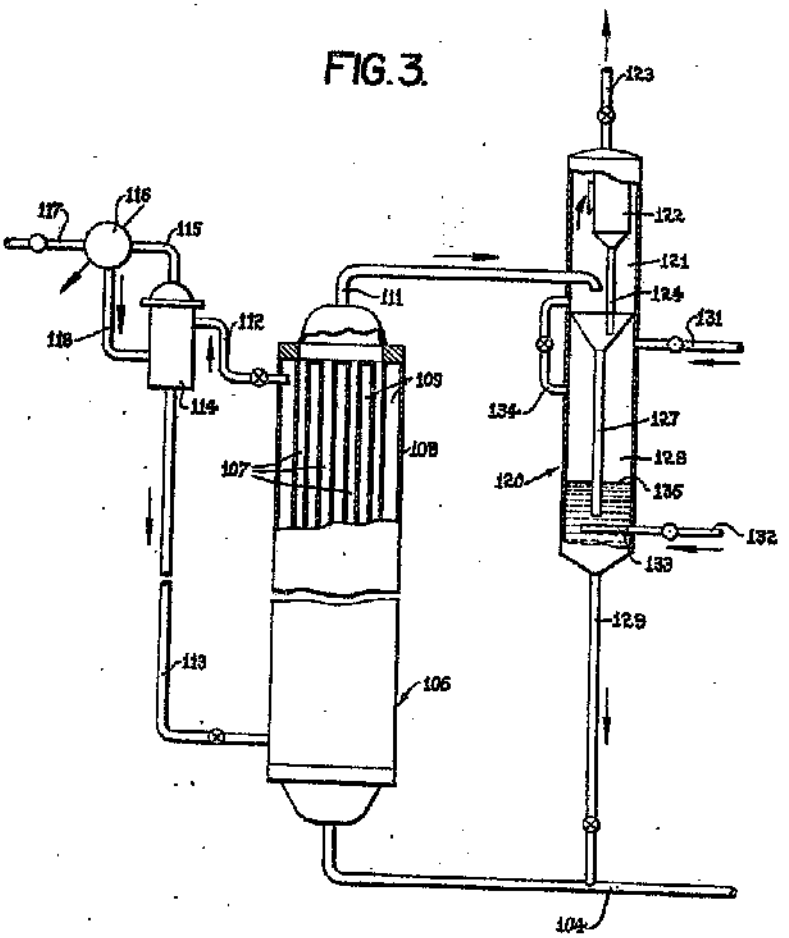
FIG. 3.



H.M.S.O. (M.F.P.)