AMENDED SPECIFICATION

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PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Improvements in or relating to Process for Hydrogenating Carbon Oxides

We, THE M. W. KELLOGG COMPANY, a corporation organised 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, 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 improvements in the hydrogenation of carbon oxides. The improved process is particularly applicable to the large-scale production of hydrocarbons and oxygenated compounds by the hydrogenation of carbon monoxide.

The catalysts which are effective to promote the hydrogenation of carbon oxides include principally the metals of group VIII of the periodic system, particularly iron, cobalt, nickel and ruthenium. These hydrogenating metals may be employed as such but ordinarily the catalysts other than iron in this group are employed in combination with suitable supports. Iron, also, may be employed in combination with a support. The supporting materials employed comprise inert adsorbents such as kieselguhr and clay. These catalysts also may have combined therewith small proportions of suitable promoters in the form of metal oxides, such as alkalies, alumina, silica, titanium, thoria, magnesia and manganese oxide. For example, a catalyst extensively employed comprises metallic cobalt in combination with approximately twice its weight of kieselguhr and approximately one-tenth its weight of magnesia or thoria. In forming such composite catalytic material, the hydrogenating metal is precipitated as its oxide on the supporting material. Any promoting oxide which is employed may be precipitated on the inert support at the same time. The resulting mixture is then further treated to convert it to the form necessary for promoting the catalytic reaction.

The hydrogenating metals, and particularly those having an atomic number higher than 26, ordinarily exhibit their maximum activity in promoting the reaction when put into use in a substantially completely reduced condition.

In accordance with the present invention a process is provided for hydrogenating a carbon oxide by contacting a gaseous reaction mixture comprising hydrogen and a carbon oxide with a finely divided contact material comprising a catalytic hydrogenating metal, which comprises passing a stream of a reducing gas upwardly through a mass of said finely divided contact material containing said catalytic hydrogenating metal in an oxidized condition, in the case of an iron contact material, said oxidized condition having been obtained other than by passing the contact material after its contact with the hydrogen and carbon oxide mixture to a separate oxidizing zone where it is oxidized, flowing said stream of reducing gas through said mass at a velocity effective to suspend said mass in said stream in a dense fluidized pseudo-liquid condition, permitting a sufficient time of contact at a temperature level effective to cause substantial reduction of the oxidized hydrogenating metal, and thereafter contacting the finely divided contact material thus subjected to reducing treatment with an upwardly flowing stream of said reaction mixture comprising hydrogen and a carbon oxide under conditions effective to suspend a mass of said finely divided contact material in said stream of reactants in a dense fluidized pseudo-liquid condition at a temperature level effective to produce the desired catalytic reaction.

In carrying out the process of the invention the catalytic contact material, which has been prepared in a substantially unreduced form outside the reactor and treated to convert it to a finely divided powdered form, may be charged to the reactor in the finely divided form without a prior reduction treatment. In the reactor, the unreduced finely divided contact material is subjected to reducing conditions, while being maintained in a relatively dense fluidized, pseudo-liquid condition, to effect substantial, or complete, reduction of the oxide of the hydrogenating metal. Thereafter, and without permitting substantial oxidation of the reduced contact material, the reaction mixture, in a gaseous or vaporous form, may be contacted with the reduced contact material while the latter is maintained in the dense fluidized, pseudo-liquid condition.

The dense pseudo-liquid condition is brought about by passing upwardly through the reaction zone and through the mass of finely divided contact material a stream of gases or vapours which flows at a linear velocity effective to suspend the mass of contact material in the gas stream in the dense fluidized condition. If the linear velocity of the gas stream is properly regulated the mass of finely divided contact material assumes a condition which may be described as "pseudo-liquid," since the mass exhibits many of the properties of a true liquid, particularly as to flowability and density.

The linear velocity of the gas stream which is necessary to produce this condition depends somewhat upon the character and condition of the contact material. It is preferred ordinarily to pass the gas stream through the mass of contact material at a velocity which is sufficiently low to produce the condition described above but sufficiently high to produce turbulence in the fluidized mass whereby the particles circulate at a high rate throughout the mass of finely divided contact material.

Under the conditions described above, the fluidized mass of contact material is quite dense, resembling in this respect a settled mass of the same material. The density of the fluidized mass may be as much as one-half that of the settled mass. The fluidized catalyst mass is suspended in the gas stream but there is no movement of the catalyst mass as a whole along the path of flow of the gas stream. The fluidized catalyst mass is suspended in the gas stream it is not entrained therein. However, a small proportion of the particles of the fluidized mass may become entrained, and carried away, in the gas stream emerging from the dense pseudo-liquid catalyst mass.

To produce the fluidized catalyst mass, the gas stream is passed into the bottom of the reactor, through a relatively small inlet, at an inlet velocity such that solids in the reactor are prevented from passing downwardly out of the reactor through the gas inlet. The horizontal dimension of the reactor and the rate of flow of the gas stream into the reactor are controlled to produce in the reactor a gas velocity effective to maintain the catalyst mass in the fluidized condition. This velocity is defined ordinarily in terms of the velocity of the gas stream through an empty reactor, which is referred to as the superficial velocity. Ordinarily superficial velocities of 0.1 to 10 feet per second are employed.

It is preferred that the reactor volume be considerably greater than the desired volume of the fluidized catalyst mass. In such a large reactor the contact material forms the relatively dense fluidized mass, described above, which occupies the lower part of the reactor, and which is referred to hereafter as the dense phase. In the upper part of the reactor the concentration of solids in the gas is substantially less and of a different order of magnitude than the concentration of solids in the dense phase. In this upper, or diffuse, phase there is substantial disengagement by settling of solids which are lifted above the dense phase by the gas stream. Such settling may effect substantially complete disengagement of solids from the gas stream. Ordinarily, however, some of the particles comprising the catalyst mass have free settling rates lower than the superficial velocity of the gas stream, whereby a small proportion of the catalyst is carried from the reactor in the exit gas stream, in the absence of special means to effect separation of the suspended solids from the gas stream.

Between the dense catalyst phase and the upper diffuse phase there is a visual interface which is a relatively narrow zone in which the concentration of solids in the gas stream changes from the high concentration of the dense plate to the low concentration of the diffuse phase.

In order to produce the desired turbulent pseudo-liquid condition in the dense phase it is desirable that at least a substantial proportion of the contact material consist of particles whose free settling rates are lower than the superficial velocity of the gas stream. The mass of contact material may consist advantageously of a mixture of particles varying in size from 40 to 400 microns (average diameter), although particles of larger or smaller diameter may be present.

The operation is initiated by charging to the reactor a quantity of freshly prepared, unreduced contact material equivalent to the quantity of reduced contact material which it is desired to maintain in the reaction zone during the conversion operation. The passage of a fluidizing gas through the reactor may be initiated during the addition of the unreduced contact material to the reactor or all of the contact material may be charged to the reactor prior to the passage of gas therethrough.

In its simplest form, the reducing gas consists of gaseous hydrogen. However, other reducing gases such as carbon monoxide, methane, ethanol, methanol or formaldehyde may be employed and the gas stream may include other ingredients in amounts which do not interfere with the reducing action. Such reducing gas will be referred to hereafter simply as hydrogen.

The fluidization of the unreduced contact material may be brought about initially by the passage of the stream of hydrogen through the reactor at the temperature desired for effecting reduction. It is preferred, however, to pass a stream of inert gas through the reactor initially to fluidize the contact material and purge the reactor of oxidizing gases. Thereafter, the introduction of a fluidizing stream of hydrogen, at the reducing temperature, is initiated. Alternatively, the passage of the hydrogen stream may be initiated at a low temperature, after which the temperature of the hydrogen stream is gradually raised to the necessary reducing temperature.

It is necessary ordinarily to contact the hydrogen and the unreduced catalyst at a reducing temperature which is substantially higher than the temperature to be employed in the hydrogenation of the carbon oxide. For example, the contact material comprising metallic cobalt as the hydrogenating metal may be contacted with the reactants comprising hydrogen and carbon monoxide in the temperature range of 350° F.—450° F., whereas the preliminary reduction of the cobalt to the metallic form requires the use of temperatures in the range of 550° F.—850° F.

The reduction treatment is continued, by the passage of the hydrogen gas through the reaction zone at the velocity effective to produce the desired fluidized condition of the finely divided contact material, until reduction is substantially complete. This is indicated ordinarily by the substantial absence of water in the gas stream emerging from the reactor. Thereafter, the stream of hydrogen is replaced by a stream of reaction gas comprising hydrogen and a carbon oxide. This stream may include vapours of normally liquid reactants but is designated hereafter simply as a gas.

The stream of reaction gas, such as a mixture of hydrogen and carbon monoxide or carbon dioxide, is passed through the reaction zone at a velocity effective to maintain the dense fluidized condition of the reduced contact material and at a somewhat lower temperature than the temperature of the reducing step. It is preferable, however, that the reaction gas mixture be brought into contact with the freshly reduced catalyst at a temperature of at least 350° F. If a lower temperature contact of the reaction gas and the freshly reduced catalyst occurs, it is desirable to limit the time of such contact by rapidly raising the temperature to a level of 350° F. or higher. It is preferable in any case to maintain the reaction temperature at least that high since the hydrogenation of the carbon oxides proceeds most rapidly at temperatures above 350° F.

Under these conditions, the reaction gas stream may be passed through the reaction zone in contact with the fluidized mass of catalyst under conditions effective to convert a large proportion of the gas stream to the desired product in operating runs of long duration. The quantity of contact material remains in a substantially dry, powdery, fluidizable condition. The quantity of wax and carbonaceous materials which accumulates on the catalyst surface does not become sufficiently great to interfere with the fluidizing qualities of the contact material. There occurs, however, a gradual loss of catalytic activity during operating runs of long duration as a result of oxidation of the hydrogenating metal, formation of carbon soot, or coke, and the accumulation of miscellaneous products such as waxes, resins, and oils. It is desirable, therefore, to subject the partially deactivated catalytic contact material periodically to a reducing treatment similar in character to the treatment originally applied to the freshly prepared contact material. After such regeneration treatment, the passage of the reaction gas mixture through the reaction zone may be resumed.

Treating the partially deactiviated contact material with hydrogen in this manner reduces the partially oxidized hydrogenating metal to the more active metallic state. Furthermore, this treatment also appears to eliminate at least a part of the wax from the contact surface, either by direct vaporization and/or by conversion of the wax to lower boiling hydrocarbons which are vaporized. The hydrogen treatment may also effect a partial removal of other carbonaceous deposits, which appear to be tarry in character, but the removal of this material by the hydrogen treatment is less effective with certain catalysts than the removal of the wax. It may be desirable, therefore, to subject the partially deactivated catalyst to a preliminary oxidation treatment to burn carbon and non-volatile carbon containing compounds from the catalyst. Thereafter the oxidized contact material is subjected to the hydrogen treatment in the manner described above. In the case of iron contact materials the invention does not include passing the contact material after contact with hydrogen and carbon oxide mixture to a separate oxidizing zone.

The preliminary hydrogen treatment of the catalyst, the revivification of the catalyst by hydrogen treatment, and the oxidation treatment, may be carried out in the same vessel in which the synthesis reaction is carried out, or separate vessels may be employed subject to the above proviso with respect to iron contact materials. The latter method is advantageous when it is desired to operate a single reaction vessel continuously without interrupting the synthesis reaction in order to revivify the contact material. If separate vessels are employed for the revivification treatments a small portion of the contact material in the reaction vessel may be transferred continuously to a revivification vessel while the contact material drawn from the reaction vessel is replaced by contact material continuously supplied thereto from the revivification vessel. Alternatively the revivification treatment may be carried out intermittently by withdrawing a portion of the contact material from the reactor, passing it to the regenerator, revivifying it therein, and returning the revivified contact material to the reactor.

The invention in various modifications will be described further by reference to the accompanying drawings in which Fig. I is a view in elevation, partly in section, of a relatively small reactor suitable for carrying out the invention, and in which Fig. II is a diagrammatic view in elevation of an arrangement of apparatus adapted for carrying out the new process in a continuous manner with separate reducing and oxidizing chambers. The invention will also be described in more detail by reference to specific examples of the improved process, which were carried out in the reactor shown in Fig. I. It will be evident, however, that the arrangements of equipment indicated in the drawings merely illustrate certain modifications of the invention, which is capable of other modifications as will be evident to those skilled in the art.

In such further description pressures are expressed pounds per square inch (gauge) and volumes of gas as cubic feet measured at 70° F. and atmospheric pressure.

Referring to Fig. I reactor 1 consists of a length of extra heavy 2-inch steel pipe which is 153 inches long and has inside and outside diameters of 1.94 inches and 2.38 inches respectively. Reactor 1 is connected, by conical section 2, to an inlet pipe 3 made of extra heavy half-inch steel pipe having an inside diameter of 0.55 inches. Reactor 1 is connected at the top, by means of conical section 4, with an enlarged conduit 5 comprising a length of 6-inch extra heavy steel pipe having an inside diameter of 5.76 inches. Conical section 4 and conduit 5 constitute an enlarged extension of reactor 2 which facilitates disengagement of catalysts from the gas stream after passage of the latter through the dense catalyst phase.

Conduit 5 is connected by means of manifold 6 with conduits 7 and 8 which comprise other sections of extra heavy 6-inch steel pipe. Conduits 7 and 8 contain filters 9 and 10 which are constructed of porous material which is permeable to the gas and vapors emerging from the reaction zone but impermeable to the catalyst particles carried by entrainment in the gas stream. Filters 9 and 10 are cylindrical in shape and closed at the bottom ends. They are dimensiond in relation to conduits 7 and 8 to provide a substantial annular space between the filter and the inner wall of the enclosing conduit for the passage of gases and vapours and entrained catalyst upwardly about the outer surface of the filter. The upper ends of filters 9 and 10 are mounted in closure means 11 and 12 in a manner whereby the gases and vapors must pass through either filter 9 or filter 10 to reach exit pipes 13 and 14. Each of filters 9 and 10 is approximately 36 inches long and 4.5 inches in outside diameter, the filter walls being approximately 0.75 inch thick.

The greater part of reactor 1 is enclosed in a jacket 15 which extends from a point near the top of the reactor to a point sufficiently low to enclose the 3-inch length of conical section 2 and approximately 5 inches of pipe 3. Jacket 15 comprises a length of extra heavy 4-inch steel pipe having an inside diameter of 3.83 inches. The ends of jacket 15 are formed by closing the ends of the 4-inch pipe in any suitable manner, as shown. Access to the interior of jacket 15 is provided by an opening 16 in the top thereof through a 2-inch steel pipe. Jacket 15 is adapted to contain a body of liquid for temperature control purposes, such as water, or a mixture of diphenyl and diphenyl ether. The vapours which are evolved by the heat of reaction are withdrawn at 16, condensed, and returned through 16 to the body of temperature control fluid in jacket 15. The temperature control fluid in jacket 15 is maintained under a pressure at which the liquid boils at the temperature desired in jacket 15. Heating means, not shown, are provided in connection with jacket 15 to heat the temperature control fluid therein to any desired temperature.

In order to show all the essential parts of the reactor and associated catalyst separation means on a single sheet a large proportion of the apparatus has been eliminated by the breaks at 17 and 18. For a clear understanding of the relative proportions of the apparatus reference may be had to the over-all length of the apparatus, from the bottom of jacket 15 to exit pipes 13 and 14, which is 224 inches. In each of breaks 17 and 18 the portion of the apparatus eliminated is identical with that portion shown immediately above and below each break.

In the operations carried out in the apparatus of the drawing the catalyst recovery means comprising filters 9 and 10 is effective to separate substantially completely entrained catalyst from the outgoing stream of gases and vapours. The disengagement of solids from the gas stream is promoted by the lowered velocity of the gas stream in conduit 5 and remaining solids are separated on the outer surfaces of filters 9 and 10. The latter are employed alternatively during the operation so that the stream of gases and vapours and entrained solids passes from conduit 5 through either the left or right branches of manifold 6 into conduit 7 or conduit 8. During the alternate periods the filter which is not in use is subjected to a back pressure of gas which is introduced at a rate sufficient to dislodge catalyst which has accumulated on the outer surface of the filter during the active period. Such "blowback" gas and dislodged catalyst flow downwardly in the conduit enclosing the filter and into manifold 6 in which the "blowback" gas is combined with the reaction mixture flowing upwardly from conduit 5. The greater part of the catalyst thus dislodged settles downwardly into the reactor and is thus returned for further use.

In the operation of the apparatus of the drawing the desired quantity of powdered catalyst is introduced directly into the reactor through a suitable connection, not shown, in conduit 5. After any desired preliminary activation treatment the temperature of the fluid in jacket 15 is adjusted, by the heating means mentioned above and by the pressure control means, to the temperature desired to be maintained in jacket 15 during the reaction. After the catalyst mass has reached the reaction temperature the introduction of the reaction mixture through pipe 3 is initiated. The reaction mixture may be preheated approximately to the reaction temperature prior to its introduction through pipe 3 or the reactants may be heated to the reaction temperature through the passage thereof through that portion of pipe 3 which is enclosed by jacket 15 and by contact with the hot catalyst. It will be understood, furthermore, that the enclosure of pipe 3 in jacket 15 is not necessary to the invention and that the reactants may be heated to the reaction temperature solely by contact with the hot catalyst.

Pipe 3 is dimensioned with respect to reactor 1 and the desired superficial velocity whereby the velocity of the gases passing through pipe 3 is sufficiently high to prevent the passage of solids downwardly into pipe 3 against the incoming gas stream. A ball check valve, not shown, is provided in pipe 3 to prevent solids from passing downwardly out of the reactor when the gas stream is not being introduced into pipe 3.

The following examples illustrate the manner in which the invention may be carried out.

EXAMPLE I.

A catalyst was prepared in accordance with the following procedure:

A cobalt nitrate solution was prepared by dissolving 10,000 grams of cobalt nitrate hexahydrate in 50 litres of water. A sodium carbonate solution was prepared by dissolving 6,100 grams of sodium carbonate monohydrate in 50 litres of water. With both solutions at the boiling point the cobalt nitrate solution was added with stirring to the sodium carbonate solution. After thorough stirring 4,000 grams of dried "Super-Filtrol" (Registered Trade Mark) preheated to 180—200° F. were added with vigorous stirring. The slurry thus obtained was filtered and the filter cake was reslurried in 30 gallons of softened water. After standing for several hours the slurry thus obtained was heated to boiling with vigorous stirring, after which the slurry was filtered again. During this operation the filter cake was washed with 300 gallons of hot softened water. The filter cake thus obtained had a water content of approximately 70 weight per cent. This material was partially dried at room temperature to a water content of approximately 57% and was then extruded through a 0.375 inch diameter orifice. The extruded material was heated overnight in an oven at 420° F. The material thus obtained was in the form of hard lumps and had a water content of approximately 7.6 weight per cent. This material was then ground in a Braun disc mill and screened to collect material passing through a 40 mesh sieve. Material which did not pass the sieve was recycled to reduce the batch to a size smaller than 40 mesh.

The following is a screen analysis of this powder:

Size Range	Weight Per Cent
40+ (Mesh)	Trace
40/60	5.0
60/80	6.9
80/100	4.0
100/120	1.0
120/140	9.4
140/200	12.9
200/pan	60.8

6.3 pounds of this material were charged to reactor 1. The reactor was flushed out with nitrogen by the passage of that gas therethrough for a few minutes. Thereafter passage of hydrogen into the reactor through pipe 3 was started. Jacket 15 was then filled with a mixture of diphenyl and diphenyl ether, a temperature control fluid. Passage of hydrogen through the reactor was continued under conditions effective to reduce the catalyst until the formation of water substantially ceased. These conditions are indicated in the following table:

Catalyst Temperatures at Various Distances in Feet Above Pipe 3. – °F.

Time	12	10.5	8.5	6.5	4.5	2.5	1.5	0.5	Cu. Ft. H_2 per Hour
Start	286	305	320	346	358	340	333	290	—
1 hour	312	416	447	460	474	475	476	464	28
2	490	558	563	566	570	564	560	544	28
3	525	602	624	632	635	620	606	574	40
4	660	695	704	700	692	654	630	597	41
5	686	700	708	706	692	636	620	594	38
6	678	700	710	708	700	656	636	600	39
7	646	694	700	700	698	666	640	586	30
8	442	496	588	606	620	620	620	592	37
9	670	706	712	714	718	708	702	672	38
10	522	546	684	696	706	686	676	618	37
11	686	724	728	728	730	720	708	666	37
12	528	645	680	700	720	710	690	590	24
13	630	714	722	730	734	726	712	574	10
14	534	620	694	716	730	710	672	526	10
15	714	738	738	738	742	732	721	554	11
16	568	684	704	714	725	714	690	530	10
17	540	624	700	720	726	710	664	490	11
18	634	720	724	732	734	724	702	502	11
19	536	650	700	716	729	718	686	481	11
20	614	662	708	726	728	701	665	468	11
21	698	734	740	739	740	734	720	503	11
22	572	690	706	717	728	715	686	478	11
23	700	678	708	725	727	695	665	453	11
24	673	735	735	739	741	731	705	488	11
25	635	714	724	730	737	726	703	490	11
26	563	682	705	717	728	720	685	480	10
27	600	684	706	708	712	688	664	556	23
28	610	704	714	720	730	718	704	576	24

Thereafter, the hydrogen flow rate was lowered to 5 cubic feet per hour and the temperature was lowered to 300° F. The composition of the catalyst thus prepared was one part by weight of cobalt to two parts of "Super Filtrol."

The diphenyl and diphenyl ether mixture was then removed from jacket 15 and replaced with water at a temperature equivalent to a catalyst temperature of 300° F. The introduction of feed gas, consisting essentially of two parts of hydrogen and one part of carbon monoxide, was then initiated at a space velocity of 333 standard volumes per hour per volume of dense catalyst phase. The temperature was raised rapidly during two hours to 360° F. and thereafter was raised to 400° F. in a space of 14 hours. The operation was continued thereafter under various experimental conditions for 1,115 hours, at the end of which time the unit was shut down arbitrarily and the catalyst withdrawn for examination. During this time the average temperature in the reaction zone varied from a minimum of 380° F. to a maximum of 460° F. and the pressure varied from atmospheric to 50 pounds. The feed gas consisted substantially of hydrogen and carbon monoxide in ratios of 2:1 to 3:1 throughout this period and it was charged to the reactor at space velocities varying from 175 to 1200 standard volumes per hour per volume of dense catalyst phase.

Throughout this period the contact material was observed to remain in the desired dense fluidized pseudo-liquid condition whereby uniform temperature conditions throughout the dense phase were observed. There was no deposition of material on the surfaces of the contact material which interfered in any way with the fluidizable character of that material. At the end of this operation the accumulation of deposits on the contact material was found to amount to less than 1 weight per cent of the contact material. Such deposits consisted of waxy oil and carbon. In spite of such deposits, however, the contact material remained perfectly dry and non-adherent throughout the operation.

For a specific example of the conditions and product obtained during this operation reference is made to a 24 hour period occurring after 531 hours of operation. During this operation the average temperature in the reactor varied from approximately 450° F., at a point 6 inches above pipe 3, to 433° F. at a point 6.5 feet above pipe 3. During this operation the feed gas, containing 30.0% of carbon-monoxide, 61.7% of hydrogen, and small amounts of carbon dioxide, methane and nitrogen was introduced through pipe 3 at a pressure of 47 pounds per square inch (gauge). This produced a pressure of 45 pounds at the outlet. Under these conditions the dense bed had a depth of approximately 5.5 feet, corresponding to a density therein of 49 pounds cubic foot. The inlet superficial velocity was 0.75 feet per second. The feed gas was charged at the range of 1170 cubic feet (measured at standard conditions of temperature and pressure) per hour per cubic foot of dense phase. This corresponded to 5.0 litres of gas per hour per gram cobalt. The gas was charged at room temperature and was preheated to the reaction temperature during the passage thereof through pipe 3 and by contact with the contact mass. 40% of the carbon monoxide charged during this period was reacted, of which 11.4% was converted to hydrocarbons of lower molecular weight than propylene and 27.0% was converted to a liquid product composed of hydrocarbons of three or more carbon atoms per molecule. The material that condensed from the reactants at room temperature and operating pressure had an initial boiling point of 194° F. and an end point of 657° F. The olefin content of this hydrocarbon liquid was 2.3%.

EXAMPLE II.

A catalyst for promoting the reaction of carbon monoxide with hydrogen was prepared as follows: 10,000 grams of cobalt nitrate, $Co(NO_3)_2.6H_2O$, and 1910 grams of magnesium nitrate, $Mg(NO_3)_2.6H_2O$, were dissolved in 50 litres of treated water. 6100 grams of sodium carbonate, $Na_2CO_3.H_2O$, were dissolved in 50 litres of treated water. Both solutions were heated to the boiling point and the nitrate solution was then added to the carbonate solution with continuous stirring. After the resulting mixture had been stirred thoroughly 4,000 grams of "Super-Filtrol" which had previously been dried at 900° F. for 1.5 hours were added at a temperature of 210° F. to the solution with vigorous stirring. After thorough stirring the resulting mixture was then filtered under a pressure of 30 pounds per square inch. The filter cake was washed in the filter with 160 gallons of softened water at 180° F. The washed filter cake was dried overnight at room temperature by means of a blower. The partially dried material was dried further at 210° F. to a moisture content of about 54% and was then extruded through 0.375 inch dies. The extruded material was then dried overnight at 210° F. to obtain a product having a moisture content of about 16%. This material was then ground to produce a granular mass finer than 6 mesh but coarser than 20 mesh. The granular material thus produced was reduced in an oven by means of a circulating stream of hydrogen from which water and carbon dioxide were removed continuously. The temperature of the mass of catalyst during this operation was raised to a final temperature of 700° F., during which time the production of water ceased. The reduced catalyst was then ground in an atmosphere of carbon dioxide to a powder of the desired size. The following is a screen analysis of this powder:

Size Range	Weight Per Cent
40 + (Mesh)	0.0
40/60	45.2
60/80	22.8
80/100	6.7
100/120	4.8
120/140	4.3
140/200	5.7
200/pan	10.5

This catalyst had the approximate composition of 1 part by weight cobalt to 0.15 part magnesium oxide to 2.0 parts "Super-Filtrol."

Reactor 1 was purged by means of carbon dioxide and, while a small stream of carbon dioxide was passed through reactor 1, 9 pounds of the catalyst prepared as described above were introduced while maintained in an atmosphere of carbon dioxide. The catalyst mass was then heated to approximately 300° F. by heating the water bath in jacket 15. At that point a small stream of hydrogen was substituted for the carbon dioxide as the aerating medium. Heating was continued to a temperature of approximately 360° F. at which point the flow of the reaction gas, consisting essentially of hydrogen and carbon monoxide in the ratio of approximately 2:1, was initiated. The reaction temperature was then raised during a period of 11 hours to 400° F.

This operation was continued for 516 hours during which time the gas was passed through the reactor at varying experimental conditions. The reaction temperature varied from 369° F. to 426° F. The pressure varied from 1 atmosphere to 45 pounds per square inch (gauge). The feed gas, which consisted for the most part of hydrogen and carbon monoxide in ratios of 2:1 to 3:1, was charged to the reactor at space velocities of 250 to 880 volumes of gas (measured at standard conditions of temperature and pressure) per volume of dense catalyst phase per hour. Throughout this operation the catalytic contact mass exhibited the desired dense fluidized pseudo-liquid condition whereby uniform temperature conditions were maintained.

For a specific example of the operating conditions for production rate in this operation reference is made to a 12 hour period occurring after 147 hours of operation. In this period the feed gas consisted of 65.5% of hydrogen, 29.7% of carbon monoxide and 4.8% of inerts. This gas was charged through pipe 3 at a temperature of 217° F., at the rate of 118.5 standard cubic feet per hour under a pressure equivalent to an outlet pressure of 44 pounds per square inch. This produced a superficial inlet velocity of 0.62 feet per second. The resulting dense fluidized mass of contact material rose to a height of 8.6 feet in the reactor, corresponding to a density of 46 pounds per cubic foot. The space velocity was, therefore, 685 standard cubic feet per hour per cubic foot of fluidized contact mass. This corresponded to 2.54 standard litres of gas per hour per gram of cobalt. During this period the average temperature in the reactor varied from a maximum of 413° F. at a point 2.5 feet above pipe 3 to a minimum 386° F. at a point 6 inches above pipe 3. The average temperature in the dense phase during this period was 402° F. This resulted in the reaction of 63.4% of the carbon monoxide charged to the operation. Of this 5.1% was converted to hydrocarbons having molecular weights lower than that of propylene and 57.9% was converted to a liquid hydrocarbon product comprising hydrocarbons of 3 or more carbon atoms per molecule. The yield of this latter product was equivalent to 149 cc/m^3 of synthesis gas. The fraction of this oil which condensed substantially at room temperature contained 6.9 mol per cent olefins.

After 516 hours of this operation the composition of the gas stream was changed from the mixture consisting essentially of hydrogen and carbon monoxide to substantially pure hydrogen. The temperature of the catalyst mass also was raised gradually to a maximum of about 850° F. The time of this treatment, the temperatures existing in the catalyst zone during the treatment and the rate of flow of the hydrogen stream are shown in the following table:

Catalyst Temperatures at Various Distances in Feet Above Pipe 3. – °F.

Time	12	10.5	8.5	6.5	4.5	2.5	1.5	0.5	Cu. Ft. Hydrogen per Hour
Start	246	259	451	482	489	481	448	304	18
60 Min.	425	446	486	517	536	506	476	377	18
120 ,,	582	636	658	676	689	665	640	563	41
180 ,,	736	752	760	787	814	804	782	734	38
240 ,,	792	806	818	838	850	838	826	780	40
300 ,,	684	688	674	700	700	680	656	620	36

Following the revivification treatment the compositon of the gas stream was again changed to that of a mixture of hydrogen and carbon monoxide and the catalytic reaction was resumed. The improvement in the activity of the catalyst is indicated by a comparison of results obtained before and after this treatment. For this purpose reference may be had to an 18-hour period occurring after 496 hours of operation and a 6-hour period occurring after 47 hours of operation following the revivification treatment. Operating data for these periods are given in the following table:

	Before Rereduction	After Rereduction
Feed Gas		
Hydrogen —%	33.7	34.8
Carbon Monoxide —%	17.1	18.2
Inerts —%	49.2	47.0
Feed Gas Temperature—°F.	389	388
Average Catalyst Temperature—°F.	438	396
Outlet Pressure—lbs. per sq. in.	45	45
Cu. ft. CO and H_2 per lb. Co	38.2	31.9
Vol. CO and H_2 per vol. dense phase per hr.	635	600
CO reacted—cu. ft. per hr.	9.3	13.5
CO converted to oil—%	37.2	55.1

The improvement in catalyst activity which was effected by rereducing the catalyst in the reactor in a fluidized condition is shown by the increased rate of conversion of the carbon monoxide indicated in the foregoing table as having been achieved after rereduction. The operating temperature employed in the period after rereduction was substantially lower than that employed previously and yet the rate of conversion of carbon monoxide was approximately 50% greater. After the rereduction treatment this operating run was continued to a total run length of approximately 650 hours at varying experimental conditions. Throughout this period of the operating run the contact mass exhibited the desired dense fluidized psuedo-liquid condition. After the run was terminated, voluntarily, examination of the catalyst showed it to be a finely divided, non-adherent, easily fluidizable material.

Example III.

The catalyst for use in this operation was prepared by suitable treatment of a mixture of iron oxide and alumina and potassium oxide, previously prepared, by fusion of the alumina and potassium oxide in molten iron oxide, for use in catalyzing ammonia synthesis. This material consisted principally of iron oxides and contained 0.7% of alumina, 1.7% of potassium oxide, 0.2% of silica, 0.8% of titania and 96% of iron oxides. It was first ground to a 6—20 mesh size and then subjected to leaching with water to remove potassium oxide. This treatment reduced the content of potassium oxide from 1.7% to 0.4—0.5%. The treated granular material was dried at 200° F. overnight and then reduced in a stream of hydrogen.

In the reduction treatment a heated stream of hydrogen was passed through the granular mass, treated by heat exchange with tap water to remove most of the water formed by the reduction reaction, and then recirculated. Reduction was initiated at about 700° F. The temperature of the catalyst mass was then raised to about 1350° F. in four hours, while continuing the flow of the hydrogen stream. This condition was maintained for two hours longer, during which time the reduction was substantially completed, as evidenced by the practical cessation of water formation. The reduced mass was then cooled to room temperature in the hydrogen atmosphere.

The reduced catalyst was then ground, first in a hand mill and then in a ball mill, to the desired degree of fineness. Throughout this period the catalyst was not permitted to come in contact with air, the grinding operations being conducted in an atmosphere of carbon dioxide. The catalyst powder had the following Screen and Roller analyses:

Roller Analysis

Particle Size in Microns	
0—10	17 %
10—20	19.5%
20—40	24 %
40—60	32 %
60+	7.5%

Screen Analysis

U.S. Std. Sieve	
+40 mesh	Trace
40—60	Trace
60—80	Trace
80—100	Trace
100—120	Trace
120—140	Trace
140—200	5 %
200—Pan	93.5%

9080 grams of the catalyst thus prepared were charged into reactor 1 through an inlet (not shown) in section 5. During this operation the catalyst was maintained in the atmosphere of carbon dioxide and a small stream of 1 or 2 cu. ft. per hour of carbon dioxide was passed upwardly through reactor 1 to prevent packing of the catalyst. After the catalyst was charged to the reactor the carbon dioxide stream was replaced with a stream of hydrogen which was passed upwardly through reactor 1 at the rate of 15 to 20 cu. ft. per hour. The outlet pressure on the reactor was then raised to 80 pounds and the temperature in the reactor was raised to approximately 450° F. by means of the heating coils around jacket 15. At that point the hydrogen flow rate was increased to 50 cu. ft. per hour and the temperature was then raised to 500° F. At that point the hydrogen stream was replaced with a stream of synthesis gas consisting essentially of hydrogen and carbon monoxide in the ratio of 2:1. The synthesis gas was passed upwardly through reactor 1 at the rate of 140 cu. ft. per hour. The conversion of H_2 and CO to hydrocarbons was apparently initiated almost as soon as the synthesis gas was passed over the catalyst. After 1 hour at this condition the temperature was raised to 550° F. and flow rate was increased to 200 cu. ft. per hour. After 5 hours longer the temperature was raised to 620° F. After 3 hours operation at 620° F. the flow rate was increased to 325 cu. ft. per hour. At that point the reaction of the hydrogen and carbon monoxide to hydrocarbons and oxygenated compounds became more vigorous and the temperature was reduced to 600° F. This operation was continued at those conditions for 35 hours longer at which time the pressure was raised to 100 pounds.

This operation was continued for 382 hours, during which time the gas was passed through the reactor at varying experimental conditions. The average temperature in the reactor varied from 557° F. to 588° F. The pressure varied from 102 to 250 pounds per square inch gauge. In the fresh feed the ratio of hydrogen to carbon monoxide varied between 1.8:1 and 1.9:1. During certain periods of this part of the operating run varying amounts of the product mixture, after removal of liquids, were recycled to the reaction to increase the hydrogen to carbon monoxide ratio. By this means charge gases containing hydrogen to carbon monoxide ratios up to 2.9:1 were prepared by recycling. In terms of carbon monoxide in the total gas charged to the reactor the rate of feed varied from 4.3 to 9.1 cubic feet of carbon monoxide per pound of iron per hour. Under these varying conditions complete or substantially complete conversion of carbon monoxide was attained.

After 382 hours of operation the composition of the feed was changed to substantially pure hydrogen. At the same time the temperature-control mixture of (diphenyl and diphenyl ether) was removed from jacket 15 and the reaction chamber was heated to the temperature desired for rereduction of the catalyst by the use of the heating coils previously described. Rereduction of the catalyst mass was carried out at temperatures and hydrogen flow rates indicated in the following table:

Catalyst Temperatures at Various Distances in Feet Above Pipe 3.—°F.

Time	12	10.5	8.5	6.5	4.5	2.5	1.5	0.5	Cu. Ft. H_2 per Hour
Start	670	684	689	689	693	681	667	596	29.40
1 hr.	762	767	768	796	800	800	799	794	37.30
2 hrs.	837	852	868	880	888	888	886	878	34.20
3 hrs.	900	918	930	942	946	940	940	927	25.85
4 hrs.	921	935	945	955	959	953	953	944	23.75
5 hrs.	940	950	960	968	972	964	966	954	21.25
6 hrs.	928	938	944	947	950	944	942	932	22.50
7 hrs.	922	930	935	938	942	933	932	922	28.60
8 hrs.	923	933	939	942	944	936	936	924	27.70
9 hrs.	926	935	944	948	950	942	939	928	18.00
10 hrs.	925	938	943	947	948	940	940	928	22.00
11 hrs.	926	936	943	948	952	943	940	928	21.02
12 hrs.	930	940	949	952	956	947	944	932	21.48
13 hrs.	934	946	951	956	958	951	947	935	25.54
14 hrs.	850	851	848	844	841	829	826	815	20.09
15 hrs.	727	723	711	700	693	683	677	671	20.74
16 hrs.	694	692	682	674	668	656	652	648	22.93
17 hrs.	664	660	658	651	648	637	634	628	14.31
18 hrs.	643	638	629	613	600	563	540	525	26.50

Prior to the rereduction treatment, the catalytic contact mass contained 0.195 pounds of carbon, 0.268 pounds of oxygen and 0.091 pounds of oil and wax per pound of iron. After rereduction, the contact mass contained 0.170 pounds of carbon, 0.070 pounds of oxygen and 0.001 pounds of oil and wax per pound of iron.

The improvement in the activity of the catalyst mass brought about by the foregoing rereduction treatment is indicated by a comparison of results obtained before and after this treatment. For this purpose reference may be had to a 68-hour period of operation immediately preceding the rereduction treatment and a 48-hour period starting 17 hours after rereduction. Operating data for these periods are given in the following table:

	Before Rereduction	After Rereduction
Operating Conditions		
Temperature—°F.	582	565
Pressure—lbs. per sq. in.	150	
Recycle Ratio—Total Feed/Fresh	1.4	
Space Velocity—CF/Hr./lb. Fe	19	
H_2:CO Inlet Gas	2.35	2.52
H_2:CO Fresh Feed	1.83	1.91
CO Conversion—%	96	
Yields		
Total Oil + Oxygenated Compounds— c.c. per cu. meter	195	195
H O—c.c. per cu. meter	99	110
CO Distribution—%		
CO conv. to oil + Oxygenated Compounds	63.0	65.1
CO ,, ,, Ethane and lighter compounds	16.9	13.1
CO ,, ,, CO_2	20.1	21.8

The improvement in activity of the catalyst brought about by the rereduction treatment is indicated by the lower temperature necessary after rereduction to reach the same rate of conversion of carbon monoxide as was reached previously at a higher temperature, and improved yield of oil and lowered production of hydrocarbon gases. Oil is defined as hydrocarbons of molecular weight at least as great as propylene.

After rereduction the operation was continued for a total run length of 1166 hours. During this part of the operating run operating conditions were again varied experimentally as in the part of the operating run preceding rereduction. The run was terminated voluntarily to free the apparatus for another operation. Throughout this long operating run the contact mass remained in a relatively dry, finely divided, fluidizable condition.

In the foregoing detailed description of the invention reference has been made to operations of the type exemplified by Figure 1 in which reduction and rereduction of the catalyst are carried out in the reactor in the absence of feed gas. The invention includes in its scope the operation of the reactor in a continuous manner with continuous or intermittent removal of a part of the catalyst from the reactor for transfer to separate revivification means. This modification of the invention is illustrated by Figure 2, which is a diagrammatic view in elevation of an apparatus adapted to maintain the reactor in continuous operation. The apparatus of Figure 2 comprises a reactor 20, a reducing chamber 21 and an oxidizing chamber 22, suitably connected for carrying out the invention. It should be noted, however, that the oxidizing chamber 22 is not used in the case of an iron contact material.

Reactor 20 is adapted to contain a mass of finely divided catalyst to be maintained in a fluidized condition with the upper level, or interface, at about the point indicated by numeral 23. Reactor 20 also is provided with a suitable cooling means 24 for removing the heat of reaction, to maintain the catalyst mass at the desired temperature level. Cooling means 24 suitably comprises a plurality of tubes, containing a vaporizable liquid, and connected to a common header which is maintained at the pressure necessary to cause the liquid in the tubes to boil at the temperature necessary to provide the desired rate of heat exchange with the catalyst mass. Instead of the specific temperature control means shown in connection with reactor 20 any suitable temperature control means may be employed which does not interfere with the maintenance of the catalyst mass in the desired fluidized, pseudo-liquid condition.

The reaction mixture, such as a mixture of hydrogen and carbon monoxide, is introduced into the system of Figure 2 through line 25, which is provided with a suitable compression means 26. Line 25 connects with the bottom of reactor 20 and has a cross sectional area substantially lower than that of the reactor whereby the introduction of the reaction mixture into reactor 20 at the desired superficial velocity requires a gas velocity in line 25 sufficiently high to prevent the passage of catalyst downwardly out of reactor 20 into line 25.

After passage through the dense turbulent mass of fluidized catalyst in reactor 20 the reaction mixture passes upwardly through the upper part of the reactor in which there occurs a substantial disengagement of catalyst carried by the gas stream. To assist such disengagement suitable means such as cyclone separators may be installed in the upper part of reactor 20 or may be suitably connected with outlet line 27.

In order to maintain the catalyst mass in reactor 20 at a high level of activity a part of such catalyst mass is removed from the reactor, revivified and returned thereto. Preferably a part of the catalyst mass is withdrawn continuously and replaced continuously in order to maintain in reactor 20 a constant quantity of catalyst of unvarying activity. For this purpose there is maintained in reducing chamber 21 a fluidized mass of catalyst undergoing reduction. This fluidized mass may be smaller than the mass of catalyst maintained in reactor 20 and the catalyst density in the dense phase of reducing chamber 21 may be the same or different from the catalyst density in reactor 20. Throughout the discussion of Figure 2, reactor 21 will be referred to as a reducing chamber. It should be borne in mind, however, that catalyst deactivation may occur by other means than by oxidation of the catalyst. As a matter of fact, certain catalysts exhibit optimum activity after some degree of oxidation has taken place. Hydrogen treatment may be required even though the principal reaction occurring in reactor 21 may not be reduction but rather the removal of oil, wax, etc. Therefore, depending on the nature of the energy change involved in reactor 21, temperature control means to provide heating or cooling to maintain the catalyst mass at the desired temperature level are employed. The mass of catalyst in chamber 21 is maintained in a fluidizable condition by the passage therethrough of a reducing gas stream. The reducing gas stream, which may be pure hydrogen, is introduced through line 29 which connects with the bottom of chamber 21 and which is provided with a suitable compression means 30. The reducing gases after a passage through the fluidized mass of catalyst in chamber 21, pass upwardly through any suitable catalyst disengaging means and are withdrawn from chamber 21 through line 31. Means are provided for connecting reactor 20 with reducing chamber 21 to effect the continuous transfer of catalyst between these chambers.

The transfer of catalyst between reactor 20 and chamber 21 may be effected by separating catalyst from the gas stream leaving reactor 20 through line 27 and from the gas stream leaving chamber 21 through line 31. The catalyst separated from the reaction mixture may then be passed to chamber 21 by any suitable means and the reduced catalyst separated from the reducing gases may be transferred to reactor 20 by the same or different means. It is preferred however, to withdraw catalyst for transfer from the reactor to the reducing chamber, or *vice versa*, directly from the fluidized mass in the chamber. Thus a part of the catalyst circulating in reactor 20 may be deflected out of the path of the reaction gases in reactor 20 by the provision of suitable baffling means 32. Means 32 may comprise a vertical standpipe, or a vertical partition extending across a segment of reactor 20 extending upwardly to a height below the upper level of the dense catalyst phase.

The catalyst thus deflected from the path of the reaction gases by baffle means 32 flows downwardly through the passageway provided by means 32 and is withdrawn from the bottom thereof by means of standpipe 33 which connects at its lower end with line 29. The column of catalyst passing into standpipe 33 is kept in a fluidized condition and is stripped of reaction gases by the introduction of a suitable fluidizing and stripping gas at 34. This gas may be a reducing gas or an inert gas such as steam, carbon dioxide, or methane.

The introduction of catalyst from standpipe 33 into line 29 is regulated by valve 35 in pipe 33. If the pressure in line 29 is higher than that in reactor 20 this differential may be overcome by maintaining the column of catalyst in and above standpipe 33 at a length and at a density whereby the pressure of this column at valve 33 is effective to overcome the pressure of line 29.

The catalyst emerging from standpipe 33 is picked up by the stream of reducing gas flowing through line 29 and carried in suspension therein into chamber 21, wherein the reducing gas and the suspended catalyst are heated, by contact with the hot catalyst undergoing reducing treatment, to the temperature level necessary for effective reduction. The size of the mass of catalyst undergoing reducing treatment in relation to the rate of transfer of catalyst to and from chamber 21 is regulated to provide a residence time of catalyst in chamber 21 effective to reduce the catalyst to the degree necessary to restore activity.

The reduced catalyst preferably is withdrawn from chamber 21 in a manner similar to the withdrawal of catalyst from reactor 20. For this purpose baffle means 36, similar to means 32, may be provided in chamber 21 to provide a space for the collection of catalyst deflected from the path of flow of the reducing gases in chamber 21. A standpipe 37 may be provided to connect such collecting space with line 25. As in connection with standpipe 33, a valve 38 is provided to control the flow of catalyst through standpipe 37 and an aerating gas is introduced at 39 to strip reducing gases from the catalyst and maintain the catalyst in standpipe 37 in a fluidized condition at the desired density.

The reduced catalyst is picked up by the stream of reactants flowing through line 25 and carried thereby in suspension into reactor 20. In reactor 20 the reduced catalyst and the reaction mixture are brought to the desired temperature level by contact with the fluidized catalyst mass, in which the catalyst particles are circulating at a high rate.

In order to conserve hydrogen it may be desired to recirculate the greater part of the reducing gas through chamber 21. For this purpose line 40 may be provided to connect line 31 with line 29. For recirculating a part of the outgoing gases through chamber 21, line 40 may be provided with suitable compression means 41. This exemplifies the problem of disengaging catalyst from the stream of reducing gas, since the greater part of the catalyst thus carried out of chamber 21 is returned through line 29.

That portion of the reducing gas stream passing through line 31 which is necessary to replace with fresh reducing gas to maintain the reducing power of the gas stream at an effective level may be passed to any suitable catalyst disengaging means. Advantageously however, this gas stream may be combined with the reaction gas mixture in order to effect disengagement of the catalyst in the same catalyst disengaging means as are employed in connection with the reaction gases. For this purpose line 42 may be provided to connect line 31 with line 25. Preferably however, the reducing gas stream from line 31 is introduced into reactor 20 at a point above the dense phase, as by means of line 43. Lines 31, 40, 42 and 43 are suitably provided with valves as shown to regulate the distribution of the gas stream from chamber 21 in the desired manner. If either of lines 42 and 43 is used it is desirable to operate chamber 21 at a pressure higher than the pressure of reactor 20.

As an alternative method of transferring reduced catalyst from chamber 21 to reactor 20, the catalyst may be permitted to pass overhead through line 31 in the stream of reducing gases, at a rate whereby the gas stream passing through line 42 or line 43 carries a sufficient quantity of catalyst to effect the replacement of reduced catalyst in reactor 20 at the desired rate. Necessarily the concentration of catalyst in the gas stream passing through line 40 will be substantially the same as that in the gas streams in lines 42 and 43, but this presents no difficulty since the velocity of the gas in line 40 is sufficient to carry the catalyst entrained therein without difficulty.

As has been pointed out previously the reduction of used catalyst, as in chamber 21, substantially removes accumulations of wax, oil, and carbon from the catalyst but does not effect a substantial reduction in the carbon content of certain catalysts. It may be necessary therefore, to subject all, or part, or the catalyst undergoing reduction treatment to a preliminary oxidation treatment to reduce the carbon content of the catalyst to the desired level. For this purpose an oxidizing chamber 22, similar in construction and operation to reducing chamber 21, may be provided. However, as already pointed out, this is not used in the case of an iron contact material. Chamber 22 may be approximately the same size as chamber 21, or may be considerably smaller if it is desired to remove carbon from only a part of the catalyst to be reduced in chamber 21.

The transfer of catalyst to and from oxidizing chamber 22 may be carried on intermittently or continuously, but in either case it is desirable to maintain in chamber 22 a substantial body of catalyst which is kept in a fluidized condition by the passage of a stream of oxidizing gas, such as air, or steam, through line 44 which is provided with pressure means 45. If steam is employed in this step provision may be required to supply heat to maintain reactor 22 at the desired temperature. To effect the transfer of catalyst from reactor 20 to chamber 22, baffle means 46, similar in construction and operation to baffle means 32, may be provided. Similarly a standpipe 47 may be provided for transferring catalyst from the passageway provided by means 46 to line 44. A valve 48 is provided in standpipe 47 to regulate the rate of transfer of catalyst from reactor 20 to line 44. Stripping and aeration of the catalyst passing downwardly through standpipe 47 are provided for by the introduction of a suitable gas stream at 49.

Preferably oxidizing chamber 22 is operated continuously whereby catalyst is transferred continuously between chamber 22 and reactor 20. The residence time of the catalyst in chamber 22 is regulated to effect an average removal of carbon from the catalyst which is sufficient to maintain the average carbon content of the catalyst in reactor 20 below the desired maximum.

In an alternative method of operation the transfer of catalyst from reactor 20 to chamber 22 may be carried on, without withdrawing catalyst from chamber 22, until the quantity of catalyst in chamber 22 reaches a desired figure. Thereafter this quantity of catalyst may be maintained in chamber 22, without additions to or withdrawals therefrom, until the oxidizing treatment has substantially completely removed carbon from all catalyst contained in chamber 22. Thereafter the completely reduced catalyst may be withdrawn completely from chamber 22, during a period in which no additions of catalyst are made to chamber 22, or, during the period of removal of catalyst, after complete reduction, the catalyst may be replaced by a continuous introduction of catalyst from reactor 20, through line 44. Operation of chamber 22 on such intermittent basis, whereby the extent of removal of carbon from the catalyst is relatively great, may be found to be advantageous since it requires transfer of the smallest quantity of catalyst to and from chamber 22.

For effecting the transfer of oxidized catalyst from chamber 22, baffle means 50, similar in construction and operation to baffle means 32, 36 and 46, may be provided. Similarly standpipe 51 may be provided to transfer oxidized catalyst from chamber 22 to line 29 whereby the oxidized catalyst passes to reducing chamber 21, alone or in mixture with other catalyst introduced into line 29 through standpipe 33. Standpipe 51 is provided with a valve 52 and stripping and aerating gas at 53. The gas introduced at 53 should be substantially inert, such as nitrogen or carbon dioxide.

The oxidizing gas passes upwardly in chamber 22 through the fluidized mass of catalyst undergoing oxidation and is withdrawn therefrom through line 54. If desired, a portion of the gas stream, and accompanying suspended catalyst, passing through line 54 may be recycled for reuse through line 55, which is provided with compression means 56 and connects with line 44. By this means the gas recycled through line 55 forms part of the gas stream flowing through chamber 22. The recirculation of gas through line 55 permits greater utilization of oxygen, assists in aeration and assists in temperature control in chamber 22 by reducing the concentration of oxygen in the oxidizing gas. To assist in temperature control, the gas passing through line 55 may be substantially cooled at 57. By this means it may be possible to remove substantially all the heat of oxidation generated in chamber 22. However, in place of such cooling means, or in addition thereto, indirect heat exchange similar to that employed in reactor 20 may be employed in chamber 22.

Utilization of gas recirculation for temperature control also may be applied to chamber 21 by cooling means 58 in line 40.

The gas withdrawn through line 54 from the system preferably is passed through suitable catalyst disengaging means, such as cyclone separators, magnetic separators and Cottrell precipitators. Catalyst thus disengaged from the exit gas may be returned directly to chamber 22 or may be passed to reducing chamber 21.

Reducing chamber 21 and oxidizing chamber 22 are shown as interconnected with a single, relatively large, reactor 20. It will be understood however, that a single reducing and oxidizing system involving one reducing chamber and one oxidizing chamber, may be interconnected with a plurality of reactors for continuous or intermittent, transfer of catalyst. In such an operation the reducing and oxidizing chambers may exchange catalyst continuously with each of a plurality of reactors. Or, the withdrawal and replacement of catalyst may be carried out intermittently with respect to each reactor while operating the oxidizing and reducing chambers in a continuous manner.

In the system shown in Figure 2, the reaction conditions may vary within relatively wide limits. In reactor 20 temperatures in the range of 350° F. to 750° F. may be maintained, while passing the reaction mixture therethrough at a velocity equivalent to an inlet superficial velocity of 0.1 to 10 feet per second. In chamber 21 the temperature may be in the range of 350° F. to 2000° F. and the inlet superficial velocity may vary within the range of 0.1 to 10 feet per second. In oxidizing chamber 22 the temperature should be sufficiently high to sustain combustion but below the temperature which would cause any detrimental structural change in the catalyst. In general the temperature employed will be within the range of 900° F. to 2000° F. The inlet superficial velocity employed in chamber 22 may be 0.1 to 10 feet per second. The introduction of aerating and stripping gases into the various standpipes will be governed by the results desired to be accomplished in such standpipes. In general however such gases are introduced at rates equivalent to superficial velocities somewhat lower than those employed in the chamber with which such standpipes are connected, particularly where it is desired to pass catalyst from a zone of low pressure to a zone of higher pressure.

In the foregoing description of Figure 2, the function of reducing chamber 21 is described as the treatment of catalyst which has been employed in reactor 20. It will be understood however, that when initiating the operation the freshly prepared catalyst may be given a preliminary reducing treatment in chamber 21, while in the fluidized condition.

The reducing gas preferably includes hydrogen and may also include other inert gases, such as nitrogen and methane. The presence of these inert gases may be beneficial in vaporizing and removing deposits of oil and wax from the catalyst surface. The principal requirement of this gas stream is that it shall be free of reactants, such as carbon monoxide, to the extent that such reactants do not interfere with the desired action of the gas stream in revivifying the catalyst. The oxidizing gas likewise includes oxygen or steam and may also include relatively inert gases, such as nitrogen.

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 a carbon oxide by contacting a gaseous reaction mixture comprising hydrogen and a carbon oxide with a finely divided contact material comprising a catalytic hydrogenating metal, which comprises passing a stream of a reducing gas upwardly through a mass of said finely divided contact material containing said catalytic hydrogenating metal in an oxidized condition, in the case of an iron contact material, said oxidized condition having been obtained other than by passing the contact material after its contact with the hydrogen and carbon oxide mixture to a separate oxidizing zone where it is oxidized, flowing said stream of reducing gas through said mass at a velocity effective to suspend said mass in said stream in a dense fluidized pseudo-liquid condition, permitting a sufficient time of contact at a temperature level effective to cause substantial reduction of the oxidized hydrogenating metal, and thereafter contacting the finely divided contact material thus subjected to reducing treatment with an upwardly flowing stream of

said reaction mixture comprising hydrogen and a carbon oxide under conditions effective to suspend a mass of said finely divided contact material in said stream of reactants in a dense fluidized pseudo-liquid condition at a temperature level effective to produce the desired catalytic reaction.

2. A process according to claim 1, in which the upward passage of the reaction mixture through said contact material is periodically discontinued when said contact material is to be reduced by said treatment with a reducing gas.

3. A process for hydrogenating a carbon oxide by contacting a gaseous reaction mixture comprising hydrogen and a carbon oxide with a finely divided contact material comprising a catalytic hydrogenating metal, which comprises passing a stream of a reducing gas upwardly in a reducing zone through a mass of said finely divided contact material containing said catalytic hydrogenating metal in an oxidized condition, in the case of an iron contact material, said oxidized condition having been obtained other than by passing the contact material after its contact with the hydrogen and carbon oxide mixture to a separate oxidizing zone where it is oxidized, flowing said stream of reducing gas through said mass in said reducing zone at a velocity effective to suspend said mass in said stream in a dense fluidized pseudo-liquid condition, permitting a sufficient time of contact at a temperature level effective to cause substantial reduction of the oxidized hydrogenating metal, transferring the finely divided contact material from said reducing zone to a reaction zone, passing a stream of said reaction mixture comprising hydrogen and a carbon oxide upwardly through said reaction zone to suspend a mass of said finely divided contact material in said zone in a dense fluidized pseudo-liquid condition, and maintaining the temperature in said reaction zone at a level effective to produce the desired catalytic reaction.

4. A process according to claim 3, which includes continuously transferring a portion of the catalyst comprising said first-mentioned fluidized mass of contact material from said reaction zone to said reducing zone, and continuously transferring from said reducing zone to said reaction zone a balancing quantity of finely divided contact material.

5. A process according to any of claims 1 to 4, in which the temperature of contact of said reducing gas stream with said fluidized mass is maintained at a level substantialy higher than the said catalytic reaction temperature level.

6. A process according to any of claims 1 to 5, in which the contact material, prior to reduction by the reducing gas, is removed from contact with the stream of reaction mixture, and treated by passing a stream of an oxidizing gas upwardly through a mass of the contact material thus removed from contact with said reaction mixture at a velocity effective to suspend said mass in said stream of oxidizing gas in a dense fluidized pseudo-liquid condition, the temperature of contact of said oxidizing gas with said last-mentioned fluidized mass being maintained at a level effective to oxidize carbonaceous material deposited on said contact material by said catalytic reaction.

7. A process according to any of claims 1 to 6, in which said contact material contains cobalt or iron.

8. A process according to any of claims 1 to 7, in which said reducing gas is hydrogen.

9. A process for hydrogenating a carbon oxide substantially as hereinbefore described.

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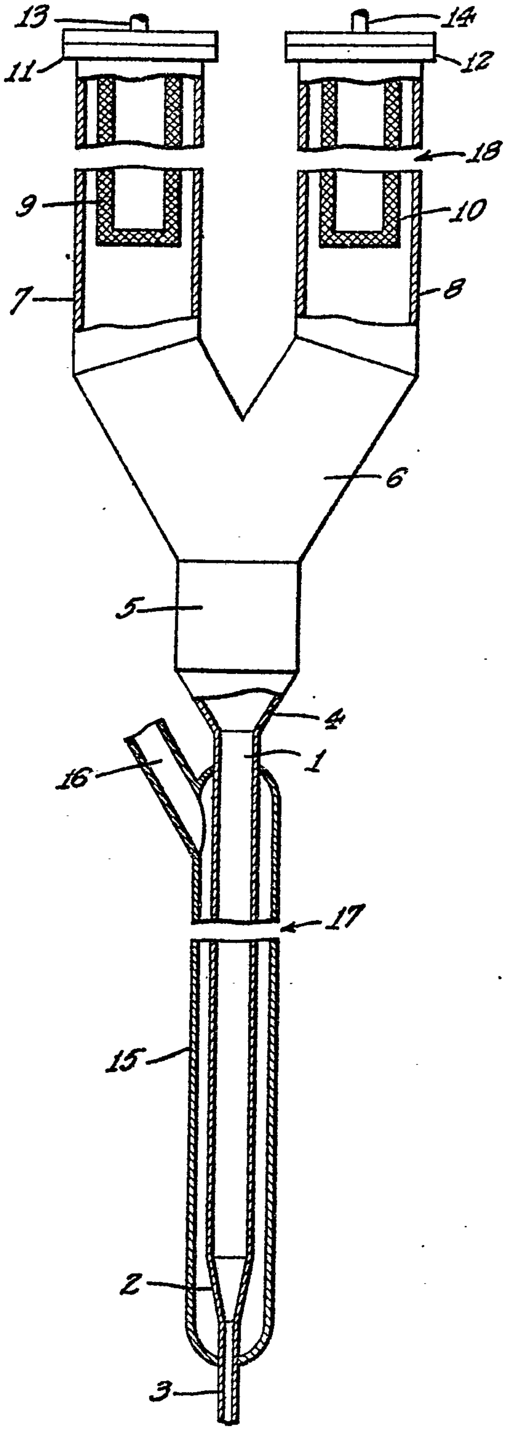
Fig.1.

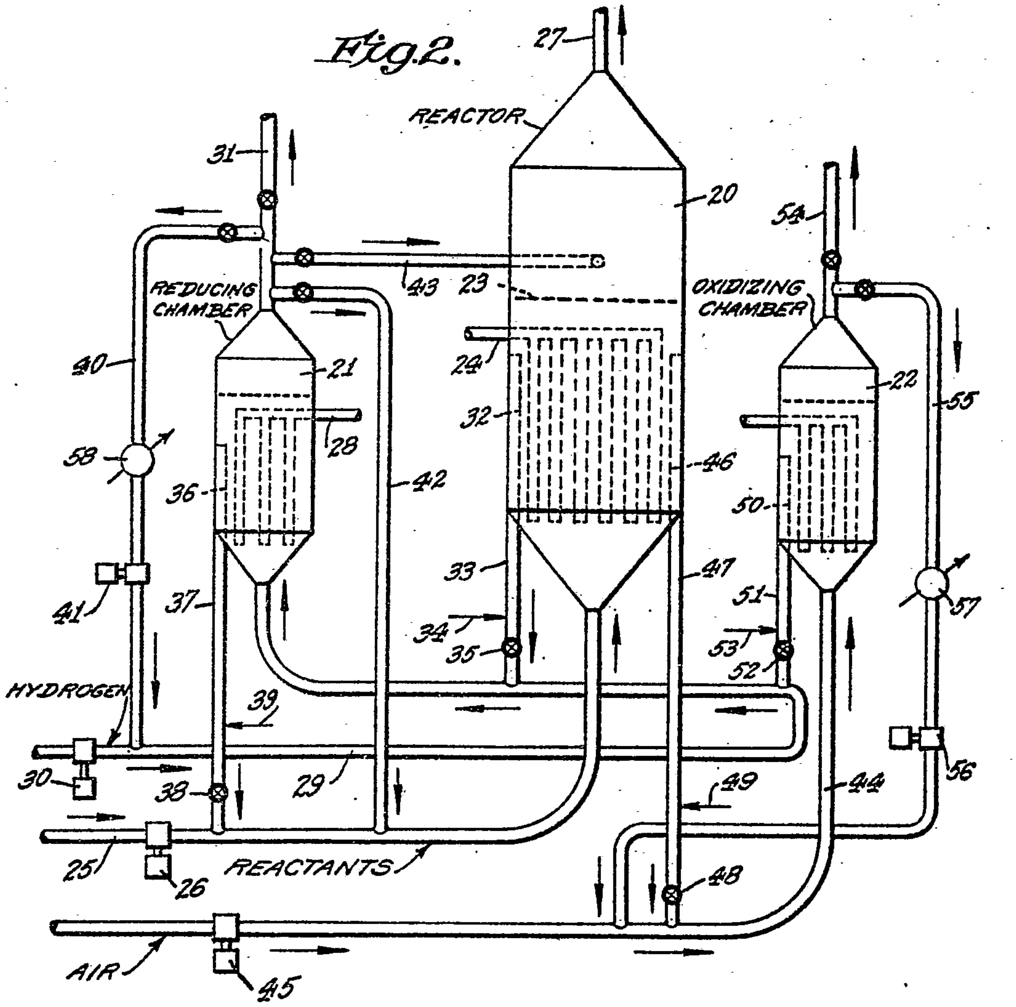


624,869 AMENDED SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale.*

SHEETS 1 & 2

Fig. 2.



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2 SHEETS

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SHEETS 1 & 2

Fig. 1.

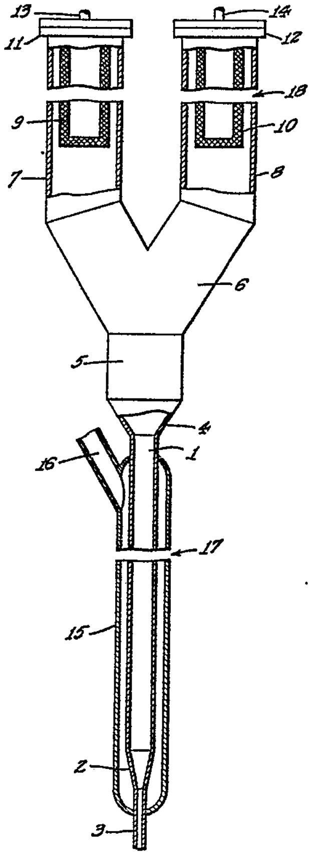

Fig. 2.