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(54) HYDROGENATION OF CARBON OXIDES

(54) HYDROGENATION D'OXYDES DE CARBONE

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(72) [illegible] (Country):	**LOUIS C. RUBIN** (Not Available) **HENRY G. MCGRATH** (Not Available)
(73) [illegible] (Country):	**THE M. W. KELLOGG COMPANY** (United States)
(71) [illegible] (Country):	
(74) [illegible]	
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This invention relates to an improved method for hydrogenating carbon oxides to produce hydrocarbons and oxygenated organic compounds. Primarily the improved process involves reacting hydrogen and carbon monoxide under highly efficient conditions to produce hydrocarbons and oxygenated organic compounds. The improved process is applicable also in reacting hydrogen with other organic compounds containing the carbonyl group, and herein designated as "carbon oxides", whose reaction with hydrogen is promoted by the catalysts which are effective with carbon monoxide, such as carbon dioxide, ketones, aldehydes, and acyl halides, organic acids and their salts and esters, acid anhydrides, and amines. In the following description of the invention the hydrogenation of carbon oxide will be referred to specifically. It will be understood, however, that the invention is of wider application, including within its scope the hydrogenation of any suitable carbon oxide.

The improved process involves flowing a gaseous mixture comprising hydrogen and the carbon oxide to be hydrogenated upwardly in a reaction zone containing a mass of finely divided metal catalyst for the reaction. The hydrogen and carbon oxide reactant are passed in the gas form through the reaction zone, under conditions effective to react all, or a major proportion, of the carbon oxide reactant, at a charging rate, in relation to the quantity of catalyst in the reaction zone, which is much higher than the charging rates previously employed in similar operations. The gaseous mixture is passed upwardly through the mass of catalyst at a velocity effective to suspend or entrain the catalyst mass in the gas stream. The velocity of the gas stream passing through the reaction zone, however, is preferably sufficiently low to maintain the catalyst mass in a dense, fluidized, pseudo-liquid condition. 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 movement of the catalyst mass as such in the direction of flow of the gas stream. It is preferred, however, to maintain the upward velocity of the gas stream sufficiently high to maintain the fluidized catalyst mass in a highly turbulent condition in which the catlyst particles circulate at a high rate in the pseudo-liquid mass. In this preferred condition of operation a small proportion of catalyst in the fluidized mass may become entrained in the gas stream emerging from the upper surface of the fluidized mass whereby catalyst thus entrained is carried away from the mass.

In the improved process it is preferred to employ the hydrogen and carbon oxide in ratios such that there is a substantial excess of hydrogen. Therefore, the charging rate in the improved process is defined by reference to the rate at which the carbon oxide is charged, in terms of standard cubic feet, in the gas form, of the carbon oxide, per hour per pound of the metal catalyst in the dense pseudo-liquid mass of catalyst in the reaction zone. The improved process is operated at a minimum space velocity equivalent to charging 1.1 standard cubic feet of the carbon oxide reactant, per hour, per pound of the metal catalyst in the dense catalyst phase. A standard cubic foot of the carbon oxide is that quantity of a normally gaseous carbon oxide which would occupy one cubic foot at atmospheric pressure and 60°F, or an equivalent quantity of a normally liquid carbon oxide reactant. When reacting carbon monoxide it is preferred to employ still higher space velocities, as will be described in more detail below.

The catalyst employed in the present invention is a finely divided powder consisting of a metal, or metal oxide, which is, or becomes in the reaction zone, a catalyst for the reaction, or a mixture of such metal and metal oxide catalytic materials. Finely divided metallic iron, or iron oxide, or a mixture of metallic iron and iron oxide, are representative examples of the catalysts employed in this invention. Other metals, and metallic oxides, may be employed which are effective in catalyzing the hydrogenation of carbon monoxide, such as cobalt and nickel, or their oxides. While the catalyst powder consists essentially of such catalytic metals and metallic oxides it may include also a minor amount of promoting ingredients, such as alkalies, alumina, silica, titania, thoria, manganese, oxide, magnesia, etc. In the following description and claims, catalyst powders consisting of a metal and/or a metal oxide and containing at most a minor proportion of promoter are referred to as "finely divided metal catalyst".

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 in an optimum degree of oxidation or carburization. Consequently, the powdered catalyst which is in a substantially completely 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 condition when first contacted with the reactants.

The catalyst is employed in a fine state of sub-division. Preferably the powdered catalyst initially contains no more than a minor proportion by weight of material whose particle size is greater than 250 microns. Preferably also the greater proportion of the catalyst mass comprises material whose particle size is smaller than 100 microns, including at least 25 weight percent of the material in particle sizes smaller than 37 microns. A highly desirable powdered catalyst comprises at least 75 percent by weight of material smaller than 150 microns in particle size, and at least 25 per cent by weight smaller than 37 microns in particle size.

In the preferred form of the invention the powdered catalyst mass is maintained in a reactor substantially larger than the volume occupied by the catalyst mass in the fluidized condition. In this operation all but a minor proportion of the catalyst mass is contained in the dense fluidized pseudo-liquid mass, which may be designated as the dense phase of the catalyst. The dense phase of the catalyst occupies the lower part of the reactor while that part of the reactor above the dense phase is occupied by a mixture of gases and powdered catalyst in which the concentration of catalyst is much lower, and of a different order of magnitude, than the concentration of the catalyst in the dense phase. This diffuse phase may be said to be a disengaging zone in which the solids lifted above the dense phase by the gas stream are disengaged therefrom and returned to the dense phase to the extent that such solids are present in the diffuse phase in excess of the carrying capacity of the gas stream at the superficial velocity of the gas stream. The latter is the velocity at which the gas stream would flow through the reactor in the absence of catalyst. In the dense phase the concentration of the catalyst in the gas stream varies from a maximum near the gas inlet to a minimum in the upper part of this phase. Likewise the concentration of catalyst in the diffuse phase varies from a maximum near the upper surface of the dense phase to a minimum in the upper part of the reactor. Between the dense phase of high average concentration and the diffuse phase of low average concentration there is a relatively narrow zone in which the concentration of solids in the gas stream changes in a short space from the high concentration of the dense phase to the low concentration of the diffuse phase. This zone has the appearance of an interface between two visually distinct phases.

As the improved method of operation ordinarily involves employment of catalyst powders and gas velocities such that a portion of the dense fluidized catalyst mass is carried away by entrainment, it is necessary to provide means in the reactor for separating such entrained catalyst and returning it to the dense phase, or to provide means externally of the reactor to separate entrained catalyst from the gas stream and return it to the reactor, or otherwise to recover catalyst from the product gas stream. When catalyst is permitted to pass out of the reactor in entrainment in the gas stream it is necessary to return such catalyst to the reactor, or replace it with fresh or revivified catalyst, in order to maintain the desired volume of fluidized catalyst in the reaction zone.

The improved method of operation, in which the finely powdered catalyst is employed in a form consisting of the metal catalyst, or its oxide, and containing at most minor proportions of promoting agents, provides very high catalyst concentrations in the reaction zone. The employment of the finely powdered metal catalyst in a fluidized bed with efficient cooling means also is a factor in permitting the use of high catalyst concentrations, since it facilitates the removal of heat from the relatively concentrated reaction zone. The improved operation, employing the finely divided metal catalyst, results in initial catalyst concentrations of at least 30 pounds per cubic foot of the fluidized dense catalyst phase, while the preferred gas velocities result in initial concentrations of 40 to 120, or more pounds per cubic foot of dense phase. It will be understood that these figures refer to the initial average concentration in the dense phase. The accumulation of reaction products on the catalyst particles as the operation proceeds reduces the catalyst density and increases the bulk of the dense fluidized mass.

The temperature employed may approximate those employed with the catalyst in question in fixed catalyst bed operations. With the iron catalyst, temperatures in the range of 350-750°F are employed, while temperatures below 450°F may be employed with the cobalt catalyst. Likewise the pressures employed may approximate those previously employed in fixed bed operations. With the iron catalyst, for example, pressures between atmospheric pressure and the maximum pressure at which condensation is avoided may be employed. It is desirable, however, to employ pressures of at least 80 p.s.i.

In this specification, pressures are expressed as pounds per square inch (gage) and gas volumes as cubic feet measured at 60° F and atmospheric pressure.

The linear velocity of the gas stream passing upwardly through the dense phase is conveniently expressed in terms of the superficial velocity, which is the linear velocity the charge gas stream would assume if passed through the reactor in the absence of catalyst. This is designated either as initial superficial velocity or average superficial velocity, the latter taking into account the shrinkage in volume caused by the reaction. These superficial velocities preferably are in the range of from 0.1 to 10 feet per second, but higher velocities may be used without departing from the scope of this invention.

In a preferred modification of the invention a metallic iron powder, having the preferred distribution of particle sizes and having combined therewith a small amount of promoters such as alkalies and non-reducible oxides, is employed under special conditions of operation to effect rates of conversion not previously attained.

The improved process is carried out at space velocities substantially greater than those previously employed. The reactants are passed into and through the reaction zone at a space velocity equivalent to at least 1.1 standard cubic feet of the carbon oxide per hour per pound of metal catalyst in the dense catalyst phase. In the hydrogenation of carbon monoxide with the iron catalyst it is preferred to operate at a space velocity equivalent to at least 2.2 standard cubic feet of carbon monoxide per hour per pound of iron catalyst in the dense catalyst phase. The charging rate is defined by reference to the carbon monoxide reactant, since the ratio of the hydrogen reactant to the carbon monoxide reactant in the charge gas may vary within wide limits. In the improved process, however, this ratio will be in excess of 1:1 and preferably at least 2:1. At the 1:1 ratio the preferred charging rate of hydrogen and carbon monoxide would, therefore, be at least 4.4 standard cubic feet per hour per pound of iron catalyst in the dense catalyst phase. At the 2:1 ratio this preferred rate would be 6.6 standard cubic feet of hydrogen and carbon monoxide.

The volume of reactants, per hour, per volume of dense catalyst phase depends upon the charge rate and also upon the density of the dense phase, the latter being affected by the condition of the catalyst and the gas velocity. At the preferred gas velocities mentioned above, and when employing the iron catalyst, the minimum space velocity may be defined as 100 volumes of carbon monoxide (measured at standard conditions of temperature and pressure) per hour per volume of the dense catalyst phase.

The volume of dense catalyst phase is that occupied by the catalyst when fluidized in a fresh condition by the charge gas at the reaction velocity. The absolute space velocity of the charge gas is determined by dividing the carbon monoxide space velocity by the volumetric fraction of the charge gas represented by carbon monoxide. Thus when employing a charge gas consisting entirely of hydrogen and carbon monoxide in a 2:1 ratio the above minimum space velocity would be 300 volumes of such a gas per hour per volume of dense catalyst phase. Necessarily, the absolute space velocity of the charge gas is affected by the H_2:CO ratio as well as by the presence of other constituents which are relatively inert under the conditions for reacting carbon monoxide, such as nitrogen and hydrocarbon gases.

The reaction gas mixture may consist entirely of hydrogen and carbon monoxide but may include, in addition, other relatively non-reactive ingredients such as nitrogen and hydrocarbon gases such as methane, ethane and propane.

The operation is carried out with a charge gas containing hydrogen and carbon monoxide in a ratio substantially greater than the ratio in which these compounds are converted to other compounds in the reaction zone. Previous investigators have noted little advantage in the use of H_2:CO ratios greater than 1:1 in connection with iron catalysts. In this improved process it has been discovered, however, that material advantages follow the use of H_2:CO ratios greater than about 1.2:1, preferably greater than about 2:1. The presence of excess hydrogen in the reaction zone favorably affects the quality of the product, improves the selectivity of the reaction, minimizes the formation of carbon and thus facilitates operation at high temperature levels, lessens the formation of carbon dioxide, and minimizes the need for revivification of the catalyst.

In connection with the present invention it has been discovered that the conversion operation carried out in the manner described above can be extended substantially indefinitely without the necessity for catalyst regeneration by careful control of the ratio of hydrogen to carbon monoxide. In the foregoing operation the metal catalyst accumulates carbonaceous deposits including tarry material, waxy materials, hydrocarbon liquids and oxygenated compounds of high molecular weight.

It is found that these deposits continue to accumulate on the catalyst at a rate and to a final percentage which is affected by the temperature and the ratio of hydrogen to carbon monoxide in the charge gas mixture. It has been found, when operating at temperatures effective for a high conversion rate, that the lower the ratio of hydrogen to carbon monoxide in the charge gas mixture the more rapid will be the accumulation of carbonaceous deposits on the catalyst surface and the higher will be the percentage of the catalyst mass represented by carbonaceous deposits when equilibrium conditions are reached. More specifically, it has been found that if the mol ratio of hydrogen to carbon monoxide is maintained greater than 5:1 the accumulation of carbonaceous deposits is stabilized at a relatively low percentage of the total catalyst mass whereby the activity of the catalyst under such stabilized conditions of operation is sufficiently high to continue the operation indefinitely without the necessity for revivification treatment of the catalyst. More specifically, it has been found that the operation can be continued indefinitey without catalyst regeneration if the H_2:CO ratio is maintained greater than 5:1, for example about 10:1, or greater.

Conveniently, the high H_2:CO ratio may be maintained in the charge gas mixture by the combined effect of supplying a fresh feed gas mixture containing hydrogen and carbon monoxide in a relatively high ratio and recycling unconverted gases to form a composite charge gas mixture having the desired ratio of hydrogen to carbon monoxide. It the hydrogenation of carbon monoxide by the manner described above the carbon monoxide content of the charge gas mixture is substantially completely reacted during the passage of the charge gas through the reaction zone. Consequently, the unconverted gas contains hydrogen in an H_2:CO ratio substantially greater than in the charge gas. By recycling such unconverted gas in combination with a fresh feed containing H_2 and CO in a lower ratio than that desired in the charge gas a composite charge gas mixture having the desired ratio may be prepared.

The gases to be recycled may be obtained from the reaction product by a simple preliminary cooling of the product which separates only the more readily separable liquid reaction products, or the recycle gases may be obtained from the product gas after extensive condensation treatment to remove substantially all condensable hydrocarbons and oxygenated compounds. The volumetric ratio of recycle gas to fresh feed gas is preferably between about 0.5:1 and about 5:1, but other ratios may be used if desired. For example, a composite charge gas mixture may be formed by combining a fresh feed mixture having an H_2:CO ratio of about 3:1 with a recycle gas stream containing essentially no carbon monoxide to produce a composite feed containing hydrogen and carbon monoxide in a ratio of about 12:1. The carbon monoxide in this composite feed is substantially completely reacted in passing the mixture through the reaction zone. A portion of the unconverted gases is discarded from the system to prevent the accumulation of inerts, such as nitrogen, and the remainder may be recycled in an amount effective to produce the desired ratio in the composite charge gas.

The principal effect of a high H_2:CO ratio on the reaction product is the substantial elimination of CO_2 as a product. In previous operations employing H_2:CO ratios heretofore considered desirable about 40 per cent of the CO converted appeared in the product as CO_2. In the practice of this invention it has been possible to avoid any production of CO_2 and even effect consumption of CO_2 in the feed gas.

The improved operation is carried out at temperature levels which are relatively high as compared to those which would be permissible in fixed catalyst bed operations under comparable operating conditions. This results from the excellent heat transfer capacity of the fluidized mass of finely divided iron or iron oxide and the effect of excess hydrogen in minimizing carbon formation. It is preferred to operate at whatever temperature level, in the range of 550°F to 750°F, is necessary to effect high or substantially complete conversion of carbon monoxide when treating a gas charge containing more hydrogen than carbon monoxide, at space velocities equivalent to at least 1.8 standard cubic feet of carbon monoxide per hour per pound of iron catalyst in the dense phase.

The invention will be described further by reference to the accompanying drawing which is a view in elevation, partly in section, of a relatively small reactor employed in carrying out the present invention, and by reference to specific examples of operations embodying the present invention and carried out in apparatus exemplified by the drawing.

Referring to the drawing, 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 2.48 inches respectively. Reactor 1 is connected by a 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 catalyst 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 dimensioned 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 vapors 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 1/2 inches in outside diameter, the filter walls being approximately 3/4 of an inch thick.

The greater part of reactor 1 is enclosed in a jacket 15 which extends from a point near the top of reactor 1 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 4.83 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 "Dowtherm". The vapors which are evolved by the heat of reaction are withdrawn at 16, condensed, and returned to the body of temperature control fluid in jacket 15. The condensate returned to jacket 15 may be introduced through line 16, or directly at a low point, adjacent pipe 3, by an inlet means not shown. 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 coils, not shown, are provided in connection with jacket 15 to maintain the temperature control fluid therein at any desired temperature when it is desired to heat the contents of reactor 1.

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 operations carried out in this apparatus the catalyst recovery means, comprising filters 9 and 10, are effective to separate substantially completely entrained catalyst from the outgoing stream of gases and vapors. 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 vapors 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 blow-back gas and dislodged catalyst flows downwardly in the conduit enclosing the filter and into manifold 6, in which the blow-back 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.

The amount of catalyst charged to the reactor initially is regulated, with reference to any preliminary treatment of the catalyst in the reactor and the gas velocity to be employed, whereby the upper level of the dense phase is substantially lower than the top of reactor 1. During the operation the accumulation of deposited reaction products on the catalyst particles may cause an expansion of the dense phase and a rise in the height of the dense phase. In certain of the operations discussed hereinafter the dense phase became extended up into members 5 and 6, and in other operations a portion of the catalyst was withdrawn to control the volume of the dense phase.

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 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. During the reaction the liquid in jacket 15 is maintained at the desired temperature by controlling its pressure. 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. In most of the operations described hereinafter it was preferred to preheat the reaction mixture to temperatures of at least 350° F.

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.

In this apparatus operating runs were made to test the efficacy of the process in the treatment of a gas charge containing hydrogen and carbon monoxide to convert these reactants to hydrocarbons and oxygenated compounds. In each operating run conditions were varied to test the effect of various combinations of operating conditions. The results of each operating run are represented by the results observed during a stabilized period of operation under a given combination of operating conditions. The conditions of operation and the results obtained in these operating runs are described below in the following examples.

In the following more detailed description references to linear velocity in the reactor are based on the cross-sectional area of the straight portion of the reactor, ignoring the effect of the presence of the catalyst. The inlet velocity is calculated from the gas rate entering the bottom of the reactor, with corrections for temperature and pressure existing at the bottom of the reactor. The average superficial linear velocity is calculated from the arithmetic average of the gas rate at the bottom of the reactor and at the top of the reactor. The latter is arrived at by correcting the outlet gas volume for water and hydrocarbons condensed in the receivers, with corrections for pressure and average catalyst temperature. Contact times referred to below are the superficial time, in seconds, that the gas takes in passing through the dense phase of the catalyst bed. It is calculated by dividing the dense bed height by the average superficial velocity.

Example I

The catalyst for use in this operation was prepared from an ammonia synthesis catalyst which had been prepared by fusion of alumina and potassium oxide in molten iron oxide to produce a mixture of iron oxide, alumina and potassium oxide. This material consisted principally of iron oxide and contained 2.9 percent alumina, 1.7 percent potassium oxide and 68.6 percent iron. To prepare this material for use in this improved process 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 potassium oxide content from 1.7 percent to 0.55 percent. The leached material was then dried at 210°F. and reduced in a stream of hydrogen.

In the reduction treatment a heated stream of hydrogen was passed through a granular mass, treated to remove water formed by the reduction reaction, and then recirculated. The temperature was raised gradually and the reduction reaction was initiated at about 700-800°F. The temperature of the catalyst mass was then raised to about 1215°F. in 2 hours while continuing the flow of the hydrogen stream. During the next 4 hours the temperature was raised to approximately 1285°F., during which time the reduction was substantially completed, as evidenced by the practical cessation of water formation.

The reduced catalyst was ground in an atmosphere of CO_2, first in a hand grinder and then in a ball mill, to produce a powder having the following screen and Roller analyses:

<u>Roller Analysis</u>

Particle Size		
0-10 Microns	11.0	%
10-20	16.4	"
20-40	20.6	"
40-60	32.2	"
60+	19.8	"

Screen Analysis

U.S. Standard Sieve		
+40 mesh	Trace	
40- 60	Trace	
60- 80	0.5	%
80-100	0.5	"
100-120	Trace	
120-140	Trace	
140-200	13.5	"
200-Pan	84.5	"

11,316 grams of 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 CO_2 and a small stream of 1 or 2 cu. ft. of CO_2 per hour was passed upwardly through reactor 1 to prevent packing of the catalyst. After the catalyst was charged to reactor 1 the CO_2 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 reactor was then heated externally while hydrogen was passed upwardly through the reactor at this rate. When a temperature of 530°F, was reached the hydrogen stream was replaced by a stream of synthesis gas consisting essentially of H_2 and CO in the ratio of about 2:1. The synthesis gas was passed upwardly through reactor 1 at the rate of 32-46 cu. ft. per hour. At the same time the outlet pressure on the reactor was increased to 15 pounds. After 3 hours at this condition the flow rate was raised to 60 ,cu. Fft. per hour and the pressure was raised to 30 pounds. After 5 hours longer the flow rate was raised to 90 cu. ft. per hour and the pressure was raised to 60 pounds. After 5 hours of operation at the last-mentioned condition the flow rate was increased to 120 cu. ft. per hour and the pressure was raised to 100 pounds. At that condition the desired conversion of H_2 and CO to hydrocarbons was soon achieved and subsequently the pressure was reduced to 80 pounds to control the rate of reaction.

Because of the extreme rapidity of the strongly exothermic reaction between H_2 and CO relative to the rate of mixing at the rather low linear velocities employed, the initial period of operation may be considered as a catalyst activation conditioning, or induction period. During the first several days of operation temperature conditions were observed to be somewhat different from those observed subsequently. Following this preliminary conditioning period, the activity and composition of the catalyst became more or less stabilized, the rate of change being largely a function of operating conditions.

This operation was continued for a total run length of 812 hours, at which time the operation was terminated voluntarily to free the apparatus for another operation. During the operating run various combinations of operating conditions were tested. The results observed in periods of stabilized operation are set forth in Table I.

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TABLE I

		A	B	C	D	E
	Operating Conditions					
	Reactor Temp. - Ave. - °F.					
1	12 ft. above pipe 3	535	528	524	531	
2	10.5 ft. above pipe 3	550	545	538	549	543
3	8.5 " " " "	562	556	562	581	558
4	6.5 " " " "	566	578	572	587	594
5	4.5 " " " "	587	598	628	614	620
6	2.5 " " " "	584	592	606	588	580
7	1.5 " " " "	561	572	612	579	546
8	0.5 " " " "	479	364	372	403	484
9	Feed Gas Temp. - °F.	438	441	425	435	436
10	Reactor Outlet Pr. - PSI	98	80	81	80	81
	Gas Throughputs - SCF/Hr.					
11	Gas Entering Catalyst Bed	132.2	146.4	133.7	162.7	215.1
12	Gas Leaving Catalyst Bed	70.7	82.7	73.0	87.8	107.5
13	Blow Back to Filter	29.7	33.4	17.9	25.0	24.2
	Analysis - Gas Entering Bed					
14	% Hydrogen	62.7	62.5	63.9	63.8	63.1
15	% Carbon Monoxide	32.8	33.0	30.4	31.2	33.2
16	% Carbon Dioxide	1.7	1.6	1.6	2.1	1.4
17	% Hydrocarbons and Inerts	2.8	2.9	4.1	2.9	2.3
18	H_2:CO - Gas Entering Bed	1.91	1.89	2.10	2.04	1.90
19	Inlet Velocity - Ft./Sec.	0.42	0.49	0.43	0.54	0.76
20	CO/Hr./Lb.Fe. - S.C.F.	1.8	2.1	1.8	2.2	3.7
	Yields (based on fresh feed)					
21	Vol. % Contraction	45.1	41.9	44.1	44.5	48.9
22	C_3's - c.c./cu. meter					32
23	C_4's " " "					8
24	C_5's " " "					6
25	Light Naphtha " " "	11			20	15
26	Heavy Oil " " "	54	48	41	42	42
27	Tot. Liq. Hydrocarbons " " "					103
28	Water " " "	50	40	69	64	58
29	Tot. Liq. Hydrocarbons - Gals./Day/Lb. Fe					0.21
30	Oxygenated Comp'ds in Water - cc/cu.meter	7	5	7	8	7
31	% H_2 Disappearance	47.7	48.2	52.0	51.7	55.5
32	% CO	100.0	100.0	100.0	100.0	100.0
33	H_2: CO Reaction Ratio	0.91	0.91	1.09	1.05	1.05
	CO Distribution					
34	% to CO_2					39.0
35	% to CH_4					12.2
36	% to C_2's					6.8
37	% to C_3's and heavier					38.6
38	% to Oxygenated Comp'ds					3.4
39	% to C_5's and heavier					26.3

F	G	H	J	K	L	M	N
	540	540	543	580	649	611	600
531	532	545	535	572	649	599	596
552	546	559	547	570	650	615	609
587	549	567	554	568	651	614	610
613	581	582	566	572	664	622	617
562	565	585	569	569	661	620	618
538	548	588	572	570	662	622	619
512	519	587	571	569	644	616	616
444	449	499	507	568	616	544	505
81	80	81	149	52	49	80	80
250.1	293.3	311	406.4	291. 7	204.8	292.7	194.8
120.9	168.5	155.5	186.2	214. 0	96.9	153.5	94.8
25.1	31.7	31.2	18.4	22.5	22.8	26.6	17.9
62.6	62.4	62.9	61.6	62.9	62.1	62.6	54.7
33.7	34.4	31.5	31.2	29.6	32.6	31.0	38.8
0.7	1.1	1.8	2.7	2.5	1.8	1.2	0.9
3.0	2.1	3.8	4.5	5.0	3.5	5.2	5.6
1.86	1.81	2.00	1.97	2.12	1.91	2.02	1.41
0.90	1.06	1.21	0.96	1.45	1.05	1.18	0.81
4.5	5.3	5.2	6.7	4.6	3.6	4.8	4.0
50.7	41.2	50.0	52.8	24.6	51.3	46.1	49.8
35	23	34					44
5	14	12					13
6	2	11					11
20	19	23	13		19	26	27
50	42	47	62	13	19	20	49
116	100	127					144
62	42	67	79	21	74	70	59
0.28	0.28	0.38					0.27
7	55	6	10	2	5	5	3
56.8	44.8	53.8	62.0	30.7	63.5	57.3	65.9
100.0	85.6	100.0	100.0	57.9	1000	98.8	100.0
1.05	.95	1.10	1.22	1.12	1.21	1.17	0.93
34.2	37.9	30.4					37.3
9.2	10.1	10.8					10.4
8.0	8.4	9.3					8.3
44.0	42.6	47.1					42.7
4.6	3.0	2.4					1.3
31.7	29.4	33.0					28.3

		A	B	C	D	E
	Heavy Oil Inspections					
40	Gravity - °A.P.I.	54.6	52.1	51.5	51.9	51.8
	ASTM Distillation - °F.					
41	I.B.P.	150	185	136	166	121
42	5%	183	227	183	202	178
43	10%	221	243	210	221	196
44	30%	298	302	273	280	264
45	50%	390	385	337	346	333
46	70%	524	497	442	457	445
47	90%	702	722	646	698	644
48	95%	722	crkd.	735	crkd.	738
49	E.B.P.	747	at 92.5	755	at 93.5	crkd.
50	% Mono-olefins	34.9	59.5		69.3	64.8
	Absorber Naphtha Inspections					
51	Gravity -° A.P.I.	84.1			80.8	80.3
	ASTM Distillation - °F.					
52	I.B.P.	82			80	85
53	5%	94			93	98
54	10%	98			98	102
55	30%	109			114	115
56	50%	123			134	131
57	70%	145			172	156
58	90%	212			234	219
59	95%	254			265	251
60	E.B.P.	297			306	292
61	Reid Vapor Pressure - PSI	15.5			16.4	15.0
62	% Mono-olefins	39.6			65.9	70.2
63	Hours on Condition	18	12	12	18.3	24
64	Total Operating Hours	46	58	130	148.3	214

TABLE I

	G	H	J	K	L	M	N
53.4	50.0	55.2	56.9	45.8	35.8	52.2	52.9
132	164	180	134	171	208	144	140
179	206	190	180	233	261	188	180
197	228	206	196	257	283	210	206
264	291	264	256	325	350	273	264
331	371	332	324	420	439	337	338
445	479	430	433	580	569	439	442
670	696	682	665	737	744	679	646
crkd.	crkd.	crkd.	crkd.	crkd.	crkd.	crkd.	732
at 94.5	at 95%						crkd.
	66.1	75.7	70.7	61.2	55.6	66.9	55.2
83.2	81.5	82.2	80.6		77.8	79.4	82.0
80	83	83	87		84	83	83
86	96	94	104		99	98	95
89	100	97	110		105	102	98
97	111	107	128		125	116	108
112	123	120	143		148	132	120
132	144	140	158		176	156	139
198	201	180	189		206	197	187
250	246	194	204		221	216	208
307	300	219	234		244	258	230
20.2	16.5	15.6	13.6		13.6	15.2	14.9
78.8	80.6	74.1	70.3		76.6	73.0	72.4
17	12	72	30	24	24	42	36
231	266.5	454.5	497	608	662	737	787

The data in Table I are arranged to present the results observed in 13 periods of stabilized operation during this operating run. Before and after each of these periods of stabilized operation there were short periods of operation in which operating conditions were being changed. Results observed during these periods of unsettled operation are not presented, as they would be without significance. In effect, therefore, each of the periods of operation for which data are presented in Table I represents an independent run whose results are comparable with the results of the other runs, except for changes in the condition of the catalyst. The superficial contact times employed in these periods ranged from 35 to 95 seconds. The data in line 20 are based on the total quantity of iron in the catalyst initially charged to the reactor. The effective charge rates would, therefore, be somewhat higher than the figures given in line 20, since some of the catalyst would be retained on the sloping surfaces of the apparatus at 4 and 6 and out of effective contact with the stream of reactants. Likewise some of the catalyst forms a permanent mat on the filter surface. At the beginning of the operation of Table I the seration of the catalyst bed resulted in an average density of the pseudo-liquid fluidized dense phase of over 100 pounds per cubic foot and the upper level of the dense phase was approximately 10 feet above pipe 3. However, accumulations of carbonaceous deposit on the catalyst particles, which doubled the weight of the catalyst mass and reduced the density of the catalyst particles, reduced the density of the fluid bed whereby the upper level of the dense phase rose substantially higher than 10 feet above pipe 3 to levels in manifold 6. The density of the dense phase was reduced also by the subsequent increases in the inlet velocity of the gas stream. The combination of these effects reduced the density of the dense phase to about 40 pounds per cubic foot and increased the volume about four-fold.

During the whole operation of Table I the flow of the reaction mixture out of the reactor was alternated between filter 9 and filter 10 every 15 minutes, and the off-stream filter was blown back with feed gas at the rate necessary to clear the filter of adhering the catalyst.

During the run of Table I the reaction products were recovered for the most part by cooling the reaction mixture to room temperature, or lower, to obtain a condensate, and then passing the remaining gas through an adsorbent. The condensate comprised both heavy oil and water product fractions. The heavy oil fraction contained a small quantity of oxygenated compounds and the water product fraction contained substantial amounts of oxygenated compounds. The adsorbed product was recovered by steam distillation, which produced a light naphtha fraction condensate water and a gas fraction. The condensate water contained additional oxygenated compounds. The gas fraction was almost entirely hydrocarbons having 3, 4 or 5 carbon atoms per molecule. The yields of the various fractions were determined by measurement of the condensed product and by absorption and combustion analyses of the gas from the condenser.

After period L, hydrogen at a rate of 15 cu. ft. per hour was substituted for synthesis gas. Simultaneously the pressure was reduced to one atmosphere and the temperature to 500° F. The hydrogen was kept in for nine hours, after which synthesis was resumed.

Immediately following period M and after 737 hours of operation, there occurred a brief period of operation at relatively high temperature. Following this high temperature operation, the catalyst was subjected to a revivification treatment with hydrogen. In this treatment, the unit pressure was reduced to 30 pounds per square inch and one hour later the synthesis gas was replaced with hydrogen at about 25 cubic feet per hour and the temperature was reduced to about 500° F. After 4 hours, the temperature was raised to about 615° F. over a period of 3 hours. The pressure was maintained at 30 pounds per square inch for 6 hours of the hydrogen treatment and then raised to 80 pounds per square inch for the remaining 3 hours.

Operating period N, which immediately followed the revivification treatment, may be referred to for an example of the results obtained during this operating run. In this period of 36 hours the "Dowtherm A" in jacket 15 was maintained under a pressure of 20 pounds per square inch to produce a temperature in jacket 15 of 580° F. During this operation the height of the dense bed was approximately 15.4 feet above pipe 3, whereby the upper level of the dense bed was located in manifold 6. The catalyst density in the dense phase was approximately 44 pounds per cubic foot whereby the space velocity was approximately 160 volumes of feed gas per hour per volume of dense phase. The quality of the liquid products obtained is indicated in Table I. The gas fraction obtained from the adsorber comprised about 75 percent olefins. The gas from the condenser contained no carbon monoxide not attributable to the blow-back gas. This indicated complete conversion of carbon monoxide in the reactor to hydrocarbons, oxygenated compounds and carbon dioxide. The amounts of these products detected in the reaction product mixture accounted for 99 percent of the carbon monoxide charged to the reactor.

For an example of the quality of the product made during the operating run of Table I, reference can be had to determinations made on the product obtained in period H. These determinations were made on a specimen prepared by blending the light naphtha and condensed oil, debutanizing the blend, and distilling it to 300° F. end point. At the same time a diesel oil boiling between 338° and 650° F. was obtained. The raw gasoline thus obtained was 65.1 percent of the total of the light naphtha and condensed oil. The diesel oil fraction accounted for 31.5 percent, and the remaining 3.4 percent was material boiling above 650° F. The raw gasoline fraction had an aniline point of 88° F., a gravity of 73.1 API and a Reid vapor pressure of 8.5 pounds per square inch. The diesel oil fraction had an ASTM pour point of -15° F. and a diesel index of 61.5.

The octane number determinations on the raw gasoline are given in the first column of the following table.

	Raw Gasoline	100% Pentane Recovery	Total Product
Octane No. (ASTM)	69	71	74
Octane No. (ASTM) + 3 cc. TEL	79	80	82
Octane No. (CFR-R)	77	80	84
Octane No. (CFR-R) + 3 cc. TEL	91	92	94

In the foregoing table the octane numbers given under the heading "100% Pentane Recovery" are based on blending, with the raw gasoline, all the pentane-pantene fraction not recovered in the condensate oil or in the light naphtha. The octane numbers under the column headed "Total Product" are based on 100% pentane recovery, the addition of the polymer product obtained by polymerizing the propylene and butylene portion of the product, and the addition of a sufficient proportion of the butane product to produce a gasoline having a Reid vapor pressure of 10 pounds per square inch.

A concentrate of low molecular weight oxygenated chemicals was obtained by careful distillation of a blend of several aqueous fractions produced at 80 pounds per square inch. Originally, the water layer contained approximately 8 percent oxygenated compounds. The distillation was conducted in a batch column equivalent to about 10 theoretical plates. Before commencing the distillation, a small amount of caustic was added to the still pot to neutralize the organic acids present. Formaldehyde and acetaldehyde were present in the original water solution, but the amounts were very small and not determined. The concentrate of oxygenated compounds from the primary distillation was subsequently refractionated for identification purposes. Five principal cuts were obtained which were predominantly acetone, methylethyl ketone, ethanol, n-propanol, and n-butanol, results for which appear below.

Blend Number	Vapor Temp.-°F.	Principal Constituent	Water Content of Cut- Wt.%	Yield on Concen~~trate~~trate Vol.%
I	131-132	Acetone	0.5	18
II	162-163	Methyl ethyl ketone	7.6	7
III	171-175	Ethanol	7.6	30
IV	187-190	n-Propanol	27.7	15
V	198-200	n-Butanol	-	5

As the distillation progressed to a vapor temperature above 192° F., a condensate consisting of two phases appeared. The upper and lower phases were principally n-butanol and water, respectively.

Example II

The catalyst for use in this operation was prepared from the same source material as the catalyst in Example I, and by the same general procedure. In this case, however, the catalyst was leached sufficiently to reduce the potassium oxide content from 1.7 to 0.41 percent. The leached granular material was dried at 200° F, overnight and then reduced in a stream of hydrogen in the general manner described in Example I. Reduction of the catalyst was initiated at about 700° F. thereafter and the temperature of the catalyst mass was raised to about 1350° F. in 4 hours, while continuing the flow of the hydrogen stream. This condition was maintained for 2 hours longer, during which time the reduction was substantially completed. 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 CO_2. The catalyst powder had the following screen and roller analyses:

Roller Analysis

Particle Size	
0-10 Microns	17 %
10-20	19.5 "
20-40	24 "
40-60	32 "
60+	7.5 "

Screen Analysis

U.S. Standard 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 "

9,080 grams of this catalyst were then charged into reactor 1 by the procedure described in Example I. After starting the passage of hydrogen through the reactor at the rate of 15-20 cubic feet 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. The hydrogen flow rate was then increased to 50 cubic feet per hour and the temperature was then raised to 500° F. Then the hydrogen stream was replaced with a stream of synthesis gas consisting essentially of H_2 and CO in the ratio of 2:1. The synthesis gas was passed upwardly through the reactor at the rate of 140 cubic feet per hour. After one hour the temperature was raised to 550° F. and the flow rate was increased to 200 cubic feet per hour. After 5 hours longer the temperature was raised to 620° F. and after 3 hours operation at 620° F. the flow rate was increased to 325 cubic feet per hour. At that point conversion of the H_2 and CO to hydrocarbons started, and the temperature was reduced to 600° F. Operation at these conditions was continued for 35 hours longer, at which time the pressure was raised to 100 pounds.

This operation was continued for a total run length of 1166 hours, after which the operation was terminated voluntarily to free the apparatus for another operation. During this period the superficial gas contact times were varied between 14 and 35 seconds. The results observed in periods of stabilized operation are set forth in Table II.

TABLE II

			A	B	C	D	E
	Operating Conditions						
	Reactor Temp. - Ave. - °F.						
1	12 ft. above pipe 3		540	549	548	562	583
2	10.5 ft. above pipe 3		541	548	548	561	576
3	8.5 " " " "		546	553	555	567	575
4	6.5 " " " "		550	559	561	576	578
5	4.5 " " " "		560	575	582	584	587
6	2.5 " " " "		571	594	608	607	588
7	1.5 " " " "		576	598	614	609	586
8	0.5 " " " "		573	582	592	593	580
9	Feed Gas. Temp. - °F.		450	370	403	512	501
10	Reactor Outlet Pressure -PSI		102	148	150	246	250
	Gas Throughputs - SCF/Hr.						
11	Fresh Feed		220.6	276.2	402.4	404.0	329.4
12	Gas Entering Catalyst Bed		310.2	401.1	402.4	629.9	670.3
13	Gas Leaving Catalyst Bed		165.1	209.7	176.3	343.2	448.4
14	Net Product Gas		93.3	87.0	176.3	141.7	109.5
15	Blow Back to Filter		9.0	18.6	23.6	31.6	31.1
16	Recycled Gas:Fresh Feed		.3	.5	0	.5	1.0
	Analysis - Gas Entering Bed						
17	% Hydrogen		60.6	56.5	59.7	58.1	55.2
18	% Carbon Monoxide		24.1	24.1	35.0	22.7	18.7
19	% Carbon Dioxide		7.4	9.3	1.1	9.0	13.1
20	% Hydrocarbons		7.8	10.1	4.2	10.2	13.0
21	H_2:CO - Gas Entering Bed		2.5	2.3	1.7	2.6	2.9
	Fresh Feed						
22	Total H_2 and CO - %		95.1	95.3	94.7	94.3	94.3
23	H_2: CO Ratio		1.9	1.8	1.7	1.9	1.8
24	Fresh Feed/Hr./Lb.Fe - SCF		11.9	14.9	21.6	21.7	18.6
25	Total Gas/Hr./Lb.Fe - SCF		16.7	21.6	21.6	33.9	37.9
26	CO/Hr./Lb.Fe - SCF		4.0	5.2	7.6	7.7	7.1
	Yields (Based on Fresh Feed)						
27	Vol. % Contraction		57.7	68.6	56.2	65.0	66.8
28	C_3's	c.c. cu. motor	30	26	33	35	36
29	C_4's	" " "	4	11	8	16	18
30	C_5's	" " "	39	16	14	18	12
31	Light Naphtha	" " "	29	35	23	35	3
32	Heavy Oil	" " "	462	61	64	53	68
33	Tot. Liq. Hydrocarbons	" " "	137	149	142	157	137
34	Oxygenated Comp'ds	" " "	14	14	13	17	18
35	Total Liquid	" " "	151	163	155	174	155
36	Water Produced	" " "	98	126	75	119	136

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F	G	H	J	K	L	M	N	P	Q	R	S
585	577	538	523	500	506	539	557	576	555	530	530
580	574	543	526	510	528	547	562	577	563	543	543
581	576	560	542	536	556	574	587	593	584	575	570
585	583	569	554	546	568	593	608	608	608	591	587
594	590	579	561	558	587	611	618	618	618	610	605
596	589	579	558	565	604	612	614	618	608	621	617
594	587	577	554	556	606	606	612	620	607	623	619
591	576	573	544	539	587	583	598	610	578	617	615
508	526	508	507	545	459	381	463	575	481	552	546
245	151	150	248	250	152	251	249	249	249	250	255
351.6	281.5	277.3	304.8	220.3	380.7	425.6	3322.3	467.3	285.7	207.0	210.7
656.7	404.9	403.9	636.7	636.0	380.7	687.3	866.6	901.3	585.2	424.0	410.7
407.5	230.6	216.5	400.0	476.0	202.7	579.4	650.5	627.5	418.3	275.1	269.9
104.4	100.8	90.1	86.6	60.4	202.7	133.2	106.2	193.5	109.8	58.9	70.0
28.6	23.7	16.0	10.4	10.9	15.8	14.9	15.2	17.0	12.8	19.2	5.5
.8	.4	.4	.9	11.8	0	1.0	1.6	.9	1.0	1.0	.9
54.1	59.0	59.5	56.2	50.4	68.3	52.3	38.5	50.3	46.8	49.1	54.1
21.0	25.1	23.6	19.8	14.9	25.3	19.0	19.6	24.2	26.9	18.3	16.5
11.9	7.6	6.8	11.2	13.7	2.9	12.5	22.1	11.9	14.8	12.4	8.3
13.0	8.3	10.1	12.8	21.0	3.5	16.2	19.8	13.6	11.5	20.2	21.1
2.6	2.3	2.5	2.8	3.4	2.7	2.8	2.0	2.1	1.7	2.7	3.3
95.4	94.7	95.0	95.3	94.9	93.6	95.9	93.9	94.1	95.4	93.9	91.9
1.7	1.8	1.9	1.9	2.0	2.7	1.8	1.3	1.5	1.3	1.9	2.1
19.9	16.3	16.3	18.4	13.6	33.1	39.0	32.6	51.3	33.6	27.2	27.7
37.1	23.4	23.8	38.3	39.2	33.1	79.5	87.4	99.0	68.8	55.8	54.0
7.8	5.8	5.6	7.6	5.9	8.4	15.1	17.2	24.0	8.8	10.2	8.9
70.2	64.2	67.5	71.6	72.6	46.7	68.0	67.0	58.6	61.6	71.6	66.8
38	36	34	32	38	30	43	35	34	42	33	35
19	13	13	16	18	12	16	13	22	20	12	10
21	15	20	13	11	8	5	20	10	14	22	15
37	33	29	28	33	23	15	34	25	28	18	26
45	40	52	56	36	27	58	39	33	38	54	28
160	137	148	143	135	100	137	141	124	142	139	113
16	12	14	18	20	11	15	11	13	13	14	14
176	149	162	163	155	111	152	162	137	155	153	127
119	99	110	126	125	76	116	80	66	58	114	118

TABLE II -

		A	B	C	D	E	F
	% H_2 Disappearance	64.4	78.5	62.2	72.5	73.4	81.1
38	% CO	100	100	100	100	100	100
39	H_2:CO Reaction Ratio	1.24	1.42	1.06	1.35	1.31	1.41
	CO Distribution						
40	% to CO_2	27.1	24.9	32.1	19.3	20.3	21.3
41	% to CH_4	10.8	11.1	8.7	9.5	9.8	10.3
42	% to C_2's	6.6	4.7	6.6	8.5	9.2	8.3
43	% to C_3's and heavier	51.6	55.6	49.1	58.1	55.4	55.9
44	% to Oxygenated Comp'ds	3.9	3.7	3.5	4.6	5.3	4.2
45	% to C_5's and heavier	42.0	44.8	37.7	42.6	37.5	39.5
46	% to H_2O	44.8	49.1	35.5	59.5	57.5	55.8
	Heavy Oil Inspections						
47	Gravity - °A.P.I.	53.5	55.5	57.2	58.0	57.9	57.9
	ASTM Distillation - °F.						
48	I.B.P.	131	114	106	110	105	105
49	5%	187	158	152	145	144	144
50	10%	209	182	164	167	164	164
51	30%	272	248	226	235	234	234
52	50%	335	306	284	293	299	299
53	70%	430	392	380	390	393	393
54	90%	610	548	564	586	581	581
55	95%	706	630	655	crkd	702	702
56	E.B.P.	718	698	658	—	crkd	crkd
57	% Mono-olefine	75.8	76.0	76.9	76.0 (76600)	73.5	73.5 ?
	Absorber Naphtha Inspections						
58	Gravity - °A.P.I.	76.9	79.6	82.0	78.7	70.4	76.6
	ASTM Distillation - °F.						
59	I.B.P.	89	87	82	86	114	86
60	5%	109	100	92	98	144	104
61	10%	116	105	94	108	156	110
62	30%	136	118	103	124	179	130
63	50%	156	133	115	142	202	152
64	70%	181	156	136	169	227	184
65	90%	219	202	188	218	255	242
66	95%	235	228	225	241	265	264
67	E.B.P.	258	256	252	280	316	292
68	Reid Vapor Pressure - PSI	12.6	15.6	17.6	13.2	6.6	12.9
69	% Mono-olefins	77.0	78.1	78.8	75.4	64.0	75.6
70	Hours On Condition	43	48	44	46	24	48
71	Total Operating Hours	100	152	196	242	266	314

UED

	H	J	K	L	M	N	P	Q	R	S
71.1	74.8	78.8	85.6	48.4	78.0	84.2	71.6	77.1	84.3	78.3
100	100	99.6	100	95.0	100	95.4	92.5	93.2	100	100
1.30	1.43	1.60	1.67	1.38	1.37	1.13	1.13	1.12	1.59	1.25
22.9	23.9	21.7	19.8	23.0	27.3	34.2	33.0	31.8	21.5	18.9
10.2	5.7	4.9	9.6	15.2	10.5	9.0	10.6	11.2	11.8	15.6
9.1	8.7	8.4	10.6	11.3	9.1	8.4	8.8	9.0	9.3	10.5
54.4	57.7	59.7	53.7	46.8	50.3	45.6	43.9	44.9	53.9	50.7
3.4	4.0	5.6	6.3	3.7	2.8	2.8	3.7	3.1	4.3	4.3
38.3	42.8	48.7	34.9	29.8	32.1	32.8	26.8	28.4	38.6	33.5
53.5	51.4	54.8	58.0	63.6	44.9	32.0	33.4	36.8	65.8	60.3
55.3	56.9	56.4	58.1	59.9	63.6	57.2	54.6	54.8	63.1	59.2
116	116	117	118	113	94	107	112	114	97	108
174	-	164	163	-	119	140	176	154	128	152
194	195	191	183	-	135	159	194	184	141	172
259	253	265	263	229	188	239	268	266	191	231
318	315	332	336	283	250	305	335	330	248	297
418	408	534	441	359	330	400	440	434	334	366
619	580	648	707	513	506	608	666	712-crkd	529	539
700	688	crkd	crkd	633	618	726	crkd		667	659
crkd	702			640	628	crkd			crkd	676
71.9	64.6	65.9	64.2	59.8	65.1	68.9	69.0	67.5	63.4	50.1
79.4	(81.0)	79.8	78.9	80.2	80.8	76.3	75.4	76.9	74.7	78.8
87	82	89	92	89	94	90	94	92	93	90
97	95	101	104	101	105	104	112	107	106	102
101	98	107	111	105	108	110	118	113	113	107
113	110	121	126	117	117	129	135	128	138	121
134	122	136	145	132	127	153	156	146	173	138
165	145	159	171	160	145	171	183	175	223	166
228	203	207	215	221	197	253	238	240	275	230
238	244	243	241	255	243	291	276	284	311	276
290	274	274	278	284	280	325	334	338	357	334
15.0	16.8	13.7	13.0	13.8	13.8	12.4	10.1	13.1	11.8	14.4
77.2	73.8	72.3	70.4	66.9	(74)	72.8	72.2	63.4	68.3	64.5
68	48	72	60	52	34	48	24	24	18	51
382	447	519	579	679	726	828	940	988	1062	1114

The data in Table II are arranged to present the results observed in 17 periods of stabilized operation during the operating run. Throughout this operating run the fresh feed to the operation contained hydrogen and CO in ratios varying from 1.3:1 to 2.7:1. In most of the periods of stabilized operation presented in Table II sufficient unconverted gas was recycled to increase the H_2:CO ratio in the gas entering the catalyst bed substantially above the corresponding figure in the fresh feed. In the recycling operations the H_2:CO ratio in gas entering the catalyst bed varied from 1.7:1 to 3.4:1. In most cases no unconverted CO was observed in the product mixture when operating even at relatively high space velocities. For example, at a charge rate as high as 15.1 cubic feet of carbon monoxide per hour per pound of iron complete disappearance of the CO was observed. At the maximum charging rate employed, 24.0 cubic feet of CO per hour per pound of iron, only 68 percent of the CO charged to the reactor was observed in the product mixture. This occurred in period P, during which time the total gas charge entering the bed was introduced at the rate of 99.0 cubic feet per hour per pound of iron. This corresponded to a space velocity of 1,915 volumes of gas entering the catalyst bed per hour per cubic foot of dense catalyst phase.

During the operating run of Table II the quantity of iron catalyst in the reactor was reduced periodically during the operation in order to obtain samples for analysis, and in order to reduce the volume of the catalyst mass in the reactor. The accumulation of carbonaceous deposits on the catalyst particles increased the volume of the catalyst in the reactor as the operation proceeded so that the upper level of the dense phase rose to over 14 feet above pipe 3 to a level in manifold 6. In order to maintain all of the dense phase in reactor 1 proper, and in order to permit operation at relatively high space velocities, the quantity of iron catalyst in the reactor was progressively reduced whereby the amount of iron catalyst in the dense phase decreased from about 16 pounds in period A to about 5 pounds in period ⑤. ? The catalyst density decreased from an initial figure of over 80 pounds per cubic foot to about 40 pounds in period P. The density also was affected by changes in the velocity of the gases passing through the reactor.

During the operation of Table II the flow of the reaction mixture out of the reactor was alternated between filter 9 and filter 10 every 15 minutes, and the off-stream filter was blown back with feed gas at the rates indicated in Table II.

The reaction products were recovered during the operation of Table II by cooling the reaction mixture to room temperature, or lower, to obtain a condensate and then passing the remaining gas through an adsorbent. Heavy oil and water product fractions were obtained from the condensate. The heavy oil fraction contained, in addition, oxygenated compounds such as butyl, amyl, hexyl and heptyl alcohols. The water product fraction contained substantial amounts of oxygenated compounds such as ethyl, propyl and butyl alcohol, acetone and methyl ethyl ketone. The adsorbed product was recovered by steam distillation, which produced a light naphtha fraction condensate water and a gas fraction. The condensate water yielded additional oxygenated compounds. The gas fraction was almost entirely hydrocarbons having 3, 4 or 5 carbon atoms per molecule. The amounts of other compounds in the reaction product mixture was determined by absorption, combustion and mass spectrometry.

Forty-one hours after synthesis gas was introduced to the system hydrogen was added for a short period of time to dilute the synthesis gas and improve the general operation. Just before the addition of hydrogen the maximum temperature in the catalyst bed was on the order of 690° F. After period G of the operation of Table II the feed to the operation was changed to substantially pure hydrogen. At the same time the "Dowtherm" was removed from jacket 13 and the reaction chamber was heated by means of the external heating coils to a higher temperature to effect reduction of the catalyst by means of the hydrogen. In this operation the hydrogen was passed through the reactor at flow rates varying from 18 to 37 cubic feet per hour and the temperature of the catalyst was raised in about 6 hours to an average temperature of approximately 930° F. This condition was maintained, with a maximum catalyst temperature of 972° F., for approximately 10 hours, after which time the temperature of the catalyst was reduced in 7 more hours to approximately 430° F. The temperature was subsequently raised to about 500-

550° F. and maintained for a short time.

The pressure during the hydrogen treatment was held at atmospheric for 27 hours with hydrogen once through, then it was raised to 150 pounds per square inch and then hydrogen recirculation was started. The following hydrogen rates entering the reactor were used:

Pressure	Hydrogen	Rate
1 Atmosphere	Once-through	9-37 Std.cu.ft./hr.
150 #/sq.in.	Once-through	20-65 Std.cu.ft./hr.
150 #/sq.in.	Recycling	60-500 Std.cu.ft./hr.

The total length of hydrogen treatment was 40 hours. Thereafter, the feed to the reactor was changed to the synthesis gas mixture and the conversion reaction was resumed. Prior to this reduction treatment of the catalyst the 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 the treatment 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.

After this reduction treatment of the catalyst and after a short period of variable conditions period H of the operating run was started. The improvement in activity of the catalyst following the reduction treatment is shown by a comparison of the data of periods G and H, which show that a lower temperature after reduction provided the same rate of conversion of carbon monoxide as was reached previously at a higher temperature. These data show also an improved yield of oil and reduced production of hydrocarbon gases.

Most of the operating periods of the operating run of Table II involved recycling of unconverted gas at ratios of recycled gas to fresh feed varying from .3:1.0 to 1.8:1.0. The recycling operations ordinarily involved relatively high H_2:CO ratios in the gas entering the catalyst bed. However, the data indicate that, other conditions being equal, and at the same H_2:CO ratio, the operating runs under rdcycling conditions produced substantially more oil per unit quantity of fresh feed.

One of the beneficial effects of recycling lies in the great improvement in the selectivity of the synthesis reaction. This point is clearly demonstrated by comparison of periods selected after 828 and 1114 hours of operation. Recycling was employed in each case; however, in the former period the H_2:CO ratio entering the reactors was 2.0 and in the latter case, 3.3. A few salient features of each of these tests are listed below:

Test Designation	N	S
Hours on Operation	828	1114
Pressure - #/sc.in.	-----250	--------
Fresh Feed/Hr./Lb.Fe	32.6	27.2
H_2:CO - Gas Entering Bed	2.0	3.3
CO Distribution		
% to CO_2	34.2	18.9
% to CH_4 & C_2's	18.4	26.1
Total	51.6	45.0

Thus the conversion to carbon dioxide, methane, ethylene, and ethane was materially lower at Condition S than at Condition N.

Varying amounts of hydrocarbons and oxygenated chemicals were recycled with the fresh feed to the synthesis reactor. The recycle stream was taken after the product gas had passed through the secondary receiver which was ordinarily maintained, during the recycling tests, at approximately 40° F. and reaction pressure. During some of these operations the recycle gas was passed through the charcoal adsorber and stripped of the oxygenated compounds present and of all but the very lightest hydrocarbons. In other operations the stream was not adsorbed and contained light oxygenated materials and hydrocarbons, predominantly olefins, through C_{10}. The recycle stream was taken just after the secondary receiver and after passing through or by-passing the adsorbers the pressure was released and the gas fed to the suction of the synthesis compressor. When the recycle was passing through the adsorber the product gas was merely vented to the atmosphere after metering and sampling whereas during a number of the operations where the recycle was not adsorbed the adsorber was on the product stream. When Conditions A? B, D, F, G, H, J, P and Q were obtained the recycle gas was taken after passage over activated carbon, and when Conditions K and S were obtained the recycle was passed over activated carbon for the greater part of the tests.

At the beginning of the operating run of Table II the reactor was filled with catalyst to a catalyst bed height of about 10 feet above pipe 3. At an average superficial velocity of about 0.76 feet per second the dense phase had, in the lower portion thereof, a density of about 83 pounds per cubic foot.

As the operation proceeded the iron become partially oxidized and the catalyst also accumulated carbon and deposits of oil and wax. After 586 hours operation a sample of the catalyst was withdrawn and aerated with inert gas at 1.2 feet per second. The catalyst density was 45.0 pounds per cubic foot. A similar test at 1166 hours indicated a density of 41.5 pounds per cubic foot. Changes in the composition of the catalyst during the run are indicated below in the table headed "Catalyst Composition".

CATALYST COMPOSITION

Total Hours On Stream	0	245	383	383	445	586	940	1114	1166
Hours After H_2 Treat.	-	-	-	0	62	203	560	728	780
Catalyst Analysis									
Carbon - Wt. %	0	12.4	12.4	13.4	15.1	13.6	18.3	20.9	23.2
Oil + Wax	0	4.1	5.8	0.1	1.8	8.0	18.9	18.6	15.6
Fe	93	63.8	63.7	79.1	67.1	59.8	47.4	45.0	46.5
Al_2O_3	4								
K_2O	0.5								
Iron Distribution									
Oil, Wax and C Free									
Fe	89.1	37.2							46.0
Fe Oxides	5.0	57.1							37.0
Lbs. C/100 Lbs. Fe	0	19.4	19.5	16.9	22.5	22.7	38.6	46.5	50.0
Lbs. Cat/100 Lbs. Fe	107	157	157	126	149	167	211	222	215

The effect of the intermediate hydrogenation treatment of the catalyst is indicated in the two columns at 383 hours on stream. The specific effect of this treatment on the various ingredients of the catalyst has been indicated above. The overall effect can be seen in the foregoing table in the reduction of the weight of catalyst per 100 pounds of iron from 157 to 126.

Oxygenated chemicals were recovered from synthol oil produced at 250 pounds per square inch by means of the following procedure. The oil product was first caustic-washed to remove organic acids and subsequently treated with a solvent to obtain the remaining oxychemicals. The condensed oil fraction subjected to the extraction step was found to contain 6.25 weight percent of oxygenated chemicals. Since a small amount of carbonyl compounds aldehydes and ketones - was produced, this extract material was hydrogenated and then redistilled. The distillation indicated a distribution of alcohols in the hydrogenated extract from the oil shown below.

Ethyl Alcohol - %	8
Propyl Alcohol - %	9
Butyl Alcohol - %	13
Amyl Alcohol - %	22
Hexyl Alcohol - %	22
Heptyl Alcohol - %	13
Higher Alcohols - %	13

The alcohols produced in this operation were principally straight chain.

A breakdown of the principal acid-free oxychemicals from this operation, including those chemicals recovered in the water product, is presented in the following tabulation:

Acetone	8.6 Vol. %
Methyl ethyl ketone	5.7
Ethyl alcohol	46.9
Propyl alcohol	26.8
Butyl alcohol	8.3
Amyl alcohol	1.4
Hexyl alcohol	1.4
Heptyl & higher alcohols	0.9
	100.0

A small amount of carbonyl compounds recovered with the synthol oil has not been included.

EXAMPLE III

This was a stabilized period of operation in a relatively long operating run carried out in the reactor whose construction and operation are similar to that shown in the drawing and described in Example I. The catalyst, employed in a finely divided condition, consisted principally of iron and contained 0.70 weight per cent K_2O. The average operating temperature in the reactor during this operating period was $551^{o}F$. The fresh feed to the operation was 90 per cent H_2 and CO, the remainder being CO_2, N_2 and hydrocarbon gases. In the fresh feed the H_2:CO ratio was 2:1. The fresh feed was charged to the operation at the rate of 3.8 standard cubic feet per hour per pound of the original reduced catalyst present in the reactor. The tail gas from the operation was recycled to the reaction zone in a ratio of recycled gas to fresh feed of 5.2:1. During the operation all, or nearly all, the CO was converted to products other than CO_2. Consequently, the H_2:CO ratio in the total charge gas was 5:1 to 10:1.

Under these conditions of operation the total liquid hydrocarbon production (including oil-soluble organic compounds) equalled 104 c.c. per cubic meter of fresh feed gas. This product was obtained by condensation at ice-water temperature and 250 pounds per square inch. This product had an A.P.I. gravity of 65.1 and contained 69.8 mol per cent mono-olefins. At the same time the production of water (including water-soluble organic compounds) equalled 198 c.c. per cubic meter of fresh feed gas. The size of the water production indicated clearly that the oxygen eliminated from the system, in forms other than organic compounds, was being eliminated largely as H_2O, rather than CO_2.

This was a period of a relatively long operating run carried out in a reactor generally similar to the reactor employed in Example III and under generally similar conditions. The finely divided iron catalyst contained, per part of iron, 0.01 part Al_2O_3, 0.011 part TiO_2, 0.008 part SiO_2, and 0.014 part K_2O. In this operating period the temperature varied from 610°F near the inlet to 597°F near the outlet, and a pressure of 250 pounds was maintained on the reactor. Fresh feed was charged to the operation at the rate of 45.3 cubic feet per hour per pound of iron in the catalyst in the reactor. Tail gas was recycled to the operation in a ratio of recycled gas to fresh feed of 2.8:1. The fresh feed gas contained 75.2 mol per cent H_2 and 18.8 per cent CO, the remainder being CO_2 and hydrocarbon gases. The total gas charge, including fresh feed and recycled gas, contained 75.1 mol per cent H_2 and 11.4 mol per cent CO, the remainder being CO_2 and light hydrocarbon gases. Under these conditions 74.7 per cent of the CO was reacted, including 2.3 per cent converted to CO_2. This operation produced total liquid hydrocarbons to the extent of 63 c.c. per cubic meter of fresh feed gas and 21 c.c. of oxygenated compounds per cubic meter of fresh feed gas.

The selectivity of the operation was excellent when these conditions were employed, e.g., 66.5 per cent of the carbon monoxide which reacted was converted to oil (propylene and higher hydrocarbons) and oxygenated chemicals, and only 3.3. per cent of the reacted carbon monoxide was converted to carbon dioxide. In spite of the greater hydrogenating activity of the catalyst as a result of the relatively high concentration of hydrogen in the reaction zone the C_2 fraction contained 44 per cent ethylene, the C_3 fraction 86 per cent propylene, and the C_4 fraction 84 per cent butylenes. The oil which was condensed from the reactor effluent at ice-water temperature and operating pressure contained nearly 30 per cent oxygenated chemicals, largely alcohols and acids.

BLANKET CASE

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for hydrogenating carbon oxides which comprises continuously flowing a gaseous mixture comprising hydrogen and a carbon oxide in a mol ratio of at least 1.2:1 and greater than the mol ratio in which the reactants are converted to other compounds upwardly in a reaction zone through a mass consisting essentially of a finely divided iron catalyst to suspend the catalyst mass in said stream, passing said stream through said mass at a velocity sufficiently low to maintain the mass in a dense fluidized pseudo-liquid condition but sufficiently high to produce rapid circulation of the catalyst particles in the mass, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of said carbon oxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, maintaining a temperature between about 450°F. and about 750°F., a pressure of at least 80 lbs. per square inch gage and a sufficient contact time to convert at least a major proportion of the carbon monoxide at the operating conditions employed, and withdrawing said gaseous mixture from the reaction zone after passage thereof through the dense catalyst mass and recovering reaction products therefrom.

2. A process for hydrogenating carbon monoxide which comprises continuously flowing a gaseous mixture comprising hydrogen and carbon monoxide upwardly in a reaction zone through a mass consisting essentially of a finely divided iron catalyst to suspend the catalyst mass in said stream,

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passing said stream through said mass at a velocity sufficiently low to maintain the mass in a dense fluidized pseudo-liquid condition but sufficiently high to produce rapid circulation of the catalyst particles in the mass, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, charging hydrogen and carbon monoxide in said gaseous mixture to said reaction zone in an H_2:CO ratio substantially greater than 2:1 and the ratio in which these reactants are converted to other compounds in the reaction zone, maintaining at a temperature between about 450°F. and about 750°F., a pressure of at least 80 lbs. per square inch gage and a sufficient contact time to convert at least a major proportion of the carbon monoxide at the operating conditions employed, and withdrawing said gaseous mixture from the reaction zone after passage thereof through the dense catalyst mass and recovering reaction products therefrom.

3. A process for hydrogenating carbon monoxide which comprises continuously flowing a gaseous mixture comprising hydrogen and carbon monoxide upwardly in a reaction zone through a mass consisting essentially of a finely divided iron catalyst to suspend the catalyst mass in said stream, passing said stream through said mass at a velocity sufficiently low to maintain the mass in a dense fluidized pseudo-liquid condition but sufficiently high to produce rapid circulation of the catalyst particles in the mass, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, charging

to the process a fresh feed mixture comprising hydrogen and carbon monoxide in an H_2:CO ratio substantially greater than 2:1 and the ratio in which these reactants are converted to other compounds in the reaction zone, maintaining at a temperature between about 450°F. and about 750°F., a pressure of at least 80 lbs. per square inch gage and a sufficient contact time to convert at least a major proportion of the carbon monoxide at the operating conditions employed, withdrawing said gaseous mixture from the reaction zone after passage thereof through the dense catalyst mass, treating the withdrawn gaseous mixture to separate reaction products and a recycle mixture comprising a substantial proportion of hydrogen in an H_2:CO ratio substantially greater than the corresponding ratio in said fresh feed mixture, and combining said recycle mixture with said fresh feed mixture to form said first-mentioned gaseous mixture.

4. A process for hydrogenating carbon monoxide which comprises continuously flowing a gaseous mixture comprising hydrogen and carbon monoxide upwardly in a mol ratio of at least 1.2:1 and greater than the mol ratio in which the reactants are converted to other compounds in a reaction zone through a mass consisting essentially of a finely divided iron catalyst to suspend the catalyst mass in said stream, passing said stream through said mass at a velocity sufficiently low to maintain the mass in a dense fluidized pseudo-liquid condition but sufficiently high to produce rapid circulation of the catalyst particles in the mass, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 2.2 standard cubic feet of carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, maintaining a temperature

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between about 450°F. and about 750°F., a pressure of at least 80 lbs. per square inch gage and a sufficient contact time to convert at least a major proportion of the carbon monoxide at the operating conditions employed, and withdrawing said gaseous mixture from the reaction zone after passage thereof through the dense catalyst mass and recovering reaction products therefrom.

5. A process for hydrogenating carbon monoxide which comprises continuously flowing a gaseous mixture comprising hydrogen and carbon monoxide upwardly in a mol ratio of at least 1.2:1 and greater than the mol ratio in which the reactants are converted to other compounds in a reaction zone through a mass consisting essentially of a finely divided iron catalyst to suspend the catalyst mass in said stream, passing said stream through said mass at a velocity sufficiently low to maintain the mass in a dense fluidized pseudo-liquid condition but sufficiently high to produce rapid circulation of the catalyst particles in the mass, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, cooling at least a portion of the dense mass of catalyst to maintain the mass temperature at a desired reaction temperature level, maintaining a temperature between about 450°F. and about 750°F., a pressure of at least 80 lbs. per square inch gage and a sufficient contact time to convert at least a major proportion of the carbon monoxide at the operating conditions employed, and withdrawing said gaseous mixture from the reaction zone after passage thereof through the dense catalyst mass and recovering reaction products therefrom.

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6. A process for hydrogenating carbon monoxide which comprises continuously flowing a gaseous mixture comprising hydrogen and carbon monoxide upwardly in a mol ratio of at least 1.2:1 and greater than the mol ratio in which the reactants are converted to other compounds in a vertically elongated reaction zone through a mass consisting essentially of a finely divided iron catalyst to suspend the catalyst mass in said stream in the reaction zone, passing said stream through said mass at a velocity sufficiently low to maintain the mass in a dense fluidized pseudo-liquid condition but sufficiently high to produce rapid circulation of the catalyst particles in the mass, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, subjecting the dense fluidized mass of iron catalyst along the length of the elongated reaction zone to indirect heat exchange with a cooling fluid to remove the exothermic heat of reaction from the reaction zone, maintaining at a temperature between about 450°F. and about 750°F., a pressure of at least 80lbs. per square inch gage and a sufficient contact time to convert at least a major proportion of the carbon monoxide at the operating conditions employed, and withdrawing said gaseous mixture from the reaction zone after passage thereof through the dense catalyst mass and recovering reaction products therefrom.

7. A process for hydrogenating carbon monoxide which comprises continuously flowing a gaseous mixture comprising hydrogen and carbon monoxide upwardly in a reaction zone through a mass consisting essentially of a finely divided

iron catalyst to suspend the catalyst mass in said stream, passing said stream through said mass at a velocity sufficiently low to maintain the mass in a dense fluidized pseudo-liquid condition but sufficiently high to produce rapid circulation of the catalyst particles in the mass, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, charging hydrogen and carbon monoxide in said gaseous mixture to said reaction zone in an H_2:CO ratio substantially greater than 1:1 and greater than the ratio in which these reactants are converted to other compounds, maintaining a temperature between about 450°F. and about 750°F., a pressure of at least 80 pounds per square inch gage and a sufficient contact time to convert at least a major proportion of the carbon monoxide at the operating conditions employed, withdrawing said gaseous mixture from the reaction zone after passage thereof through the dense catalyst mass and after substantially complete conversion of carbon monoxide to other compounds, treating the withdrawn gaseous mixture to separate reaction products therefrom and reincorporating at least a portion of the remainder including unreacted hydrogen in said first-mentioned gaseous mixture prior to introduction thereof into the reaction zone.

8. A process for hydrogenating carbon monoxide which comprises continuously flowing a gaseous mixture comprising hydrogen and carbon monoxide upwardly in a reaction zone through a mass consisting essentially of a finely divided iron catalyst to suspend the catalyst mass in said stream, passing said stream through said mass at a velocity sufficiently low to maintain the mass in a dense fluidized

pseudo-liquid condition but sufficiently high to produce rapid circulation of the catalyst particles in the mass, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, charging to the process a fresh feed mixture comprising hydrogen and carbon monoxide in an H_2:CO ratio not substantially less than 2:1 and greater than the ratio in which these reactants are converted to other compounds, combining said fresh feed mixture with recycle gas to form said first-mentioned gaseous mixture, maintaining at a temperature between about 450°F. and about 750°F., a pressure of at least 80 lbs. per square inch gage and a sufficient contact time to convert at least a major proportion of the carbon monoxide at the operating conditions employed, withdrawing said gaseous mixture from the reaction zone after passage thereof through the dense catalyst mass, treating the withdrawn gaseous mixture to separate reaction products and a recycle gas comprising hydrogen in an H_2:CO ratio substantially greater than 2:1, and recycling said last-mentioned gas as described.

9. A process for hydrogenating carbon monoxide which comprises continuously flowing a gaseous mixture comprising hydrogen and carbon monoxide upwardly in a reaction zone through a mass consisting essentially of a finely divided iron catalyst to suspend the catalyst mass in said stream, passing said stream through said mass at a velocity sufficiently low to maintain the mass in a dense fluidized pseudo-liquid condition but sufficiently high to produce rapid circulation of the catalyst particles in the mass, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 2.2 standard cubic feet

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of carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, charging to the process a fresh feed mixture comprising hydrogen and carbon monoxide in an H_2:CO ratio not substantially less than 2:1 and greater than the ratio in which these reactants are converted to other compounds, combining said fresh feed mixture with recycle gas to form said first-mentioned gaseous mixture, maintaining at a temperature between about 450°F., and about 750°F., a pressure of at least 80 lbs. per square inch gage and a sufficient contact time to convert at least a major proportion of the carbon monoxide at the operating conditions employed, withdrawing said gaseous mixture from the reaction zone after passage thereof through the dense catalyst mass, treating the withdrawn gaseous mixture to separate reaction products and a recycle gas comprising hydrogen in an H_2:CO ratio substantially greater than 2:1, and recycling said last-mentioned gas as described.

10. In the hydrogenation of carbon oxides wherein a gaseous mixture of hydrogen and a carbon oxide reactant is passed through a reaction zone in contact with a finely divided metal catalyst suspended therein, the improvement which comprises minimizing catalyst deactivation by limiting the mol percentage of said carbon oxide reactant in the gas mixture passing through said zone for a major proportion of the time of operation to an amount equivalent to a mol ratio of hydrogen to said carbon oxide reactant greater than 5:1 and greater than the mol ratio in which these reactants are converted to other compounds, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of said carbon oxide per hour per pound of metal catalyst in the dense fluidized mass of

catalyst, and maintaining a temperature between about 350°F. and about 750°F. and a pressure of at least 80 pounds per square inch gage.

11. In the hydrogenation of carbon oxides wherein a gaseous mixture of hydrogen and a carbon oxide reactant is passed through a reaction zone in contact with a finely divided metal catalyst suspended therein, the improvement which comprises minimizing catalyst deactivation by limiting the mol percentage of said carbon oxide reactant in the gas mixture passing through said zone for a major proportion of the time of operation to an amount equivalent to a mol ratio of hydrogen to said carbon oxide reactant about 10:1, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of said carbon oxide per hour per pound of metal catalyst in the dense fluidized mass of catalyst, and maintaining a temperature between about 350°F. and about 750°F. and a pressure of at least 80 pounds per square inch gage.

12. In the hydrogenation of carbon oxides wherein a gaseous mixture of hydrogen and a carbon oxide reactant is passed upwardly through a reaction zone containing finely divided metal catalyst to suspend the catalyst mass in said stream in a dense fluidized pseudo-liquid condition, the improvement which comprises minimizing catalyst deactivation by limiting the mol percentage of said carbon oxide reactant in the gas mixture passing through said zone for a major proportion of the time of operation to an amount equivalent to a mol ratio of hydrogen to said carbon oxide reactant greater than 5:1 and greater than the mol ratio in which these reactants are converted to other compounds, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of said carbon oxide per hour per pound of metal catalyst in the

dense fluidized mass of catalyst, and maintaining a temperature between about 350°F. and about 750°F. and a pressure of at least 80 pounds per square inch gage.

13. In the hydrogenation of carbon oxides wherein a gaseous mixture of hydrogen and a carbon oxide reactant is passed upwardly through a reaction zone containing finely divided iron catalyst to suspend the catalyst mass in said stream in a dense fluidized pseudo-liquid condition, the improvement which comprises minimizing catalyst deactivation by limiting the mol percentage of said carbon oxide reactant in the gas mixture passing through said zone for a major proportion of the time of operation to an amount equivalent to a mol ratio of hydrogen to said carbon oxide reactant greater than 5:1 and greater than the mol ratio in which these reactants are converted to other compounds, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of said carbon oxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, and maintaining a temperature between about 350°F. and about 750°F. and a pressure of at least 80 pounds per square inch gage.

14. In the hydrogenation of carbon monoxide wherein a gaseous mixture of hydrogen and carbon monoxide is passed upwardly through a reaction zone containing finely divided metal catalyst to suspend the catalyst mass in said stream in a dense fluidized pseudo-liquid condition, the improvement which comprises minimizing catalyst deactivation by maintaining the mol ratio of hydrogen to carbon monoxide in the gas mixture passing through said zone for a major proportion of the time of operation greater than 5:1 and greater than the mol ratio in which these reactants are converted to

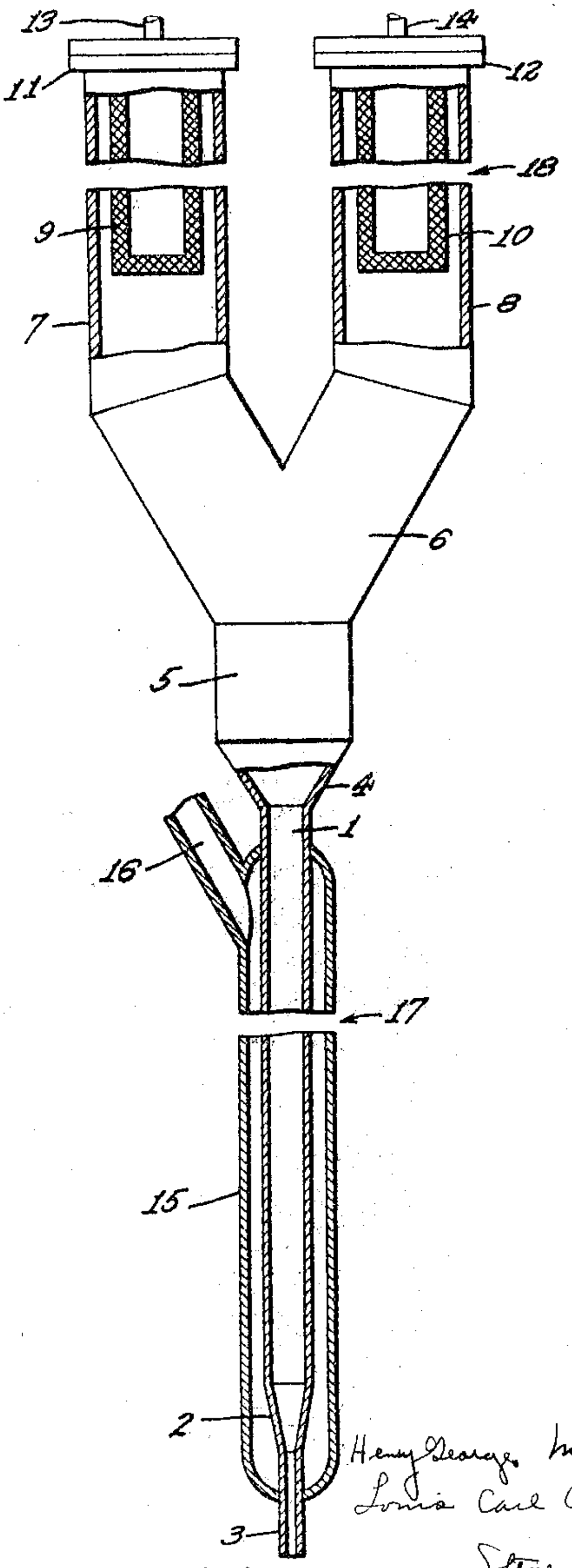
other compounds, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of said carbon monoxide per hour per pound of metal catalyst in the dense fluidized mass of catalyst, and maintaining a temperature between about 350°F. and about 750°F. and a pressure of at least 80 pounds per square inch gage.

15. In the hydrogenation of carbon monoxide wherein a gaseous mixture of hydrogen and carbon monoxide is passed upwardly through a reaction zone containing finely divided iron catalyst to suspend the catalyst mass in said stream in a dense fluidized pseudo-liquid condition at temperatures in the range of 450-750°F., the improvement which comprises maintaining a pressure of at least 80 lbs. per square inch gage and a H_2:CO ratio of at least 1:1 in the fresh feed to the operation, passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of said carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst, separating unconverted gases and recycling unconverted gases for passage through the reaction zone in admixture with the fresh feed, and maintaining the H_2:CO ratio of the fresh feed greater than the ratio in which these reactants are converted to other compounds to maintain the H_2:CO ratio in the composite feed for a major proportion of the time of operation greater than 5:1.

16. In the hydrogenation of carbon monoxide wherein a gaseous mixture of hydrogen and carbon monoxide is passed upwardly through a reaction zone containing finely divided iron catalyst to suspend the catalyst mass in said stream in a dense fluidized pseudo-liquid condition at temperatures in the range of 450-750°F., the improvement which comprises minimizing catalyst deactivation by maintaining the H_2:CO

ratio in the gas mixture passing through said zone for a major proportion of the time of operation greater than 5:1 and greater than the mol ratio in which these reactants are converted to other compounds, and passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of said carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst.

17. In the hydrogenation of carbon monoxide wherein a gaseous mixture of hydrogen and carbon monoxide is passed upwardly through a reaction zone containing finely divided iron catalyst to suspend the catalyst mass in said stream in a dense fluidized pseudo-liquid condition at temperatures in the range of 450-750°F., the improvement which comprises minimizing catalyst deactivation by maintaining the H_2:CO ratio in the gas mixture passing through said zone for a major proportion of the time of operation about 10:1 and passing the gaseous mixture through said catalyst mass at a feed rate equivalent to at least 1.1 standard cubic feet of said carbon monoxide per hour per pound of iron catalyst in the dense fluidized mass of catalyst.



Henry George Mc Grath
Louis Carl Rubin

INVENTORS

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

New York, New York, July 19 1947

Stevens, Langner, Parry + Rollinson

ATTORNEYS