PATENT SPECIFICATION

669,382

Date of Application and filing Complete Specification Sept. 11, 1945.
Nos. 23377/45 and 23378/45.
Application made in United States of America on Aug. 23, 1944.
Application made in United States of America on Aug. 23, 1944.
(Under Section 91, sub-sections (2) and (4) of the Patents and Designs Acts, 1907 to 1946, a single Complete Specification was left in respect of these Applications and of Application Nos. 23376/45 and 23379/45 and was laid open to inspection on Feb. 24, 1946).
Complete Specification Published April 2, 1952.

Index at acceptance.—**Classes 1(i),** F3b1; **and 2(iii),** B1g, C3ax.

COMPLETE SPECIFICATION

Improvements in or relating to the Hydrogenation of Carbon Oxides

We, THE M. W. KELLOGG COMPANY, a corporation organized under the laws of the State of Delware, United States of America, of Foot of Danforth Avenue, Jersey City, State of New Jersey, United States of America, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to an improved method for reacting hydrogen and a carbon oxide to produce normally liquid hydrocorbons in which a fluidized metallic catalyst comprising cobalt supported upon a bentonite type of support is employed.

According to the present invention there is provided a process for the hydrogenation of a carbon oxide to produce normally liquid hydrocarbons which comprises continuously flowing gaseous mixture comprising hydrogen and a carbon oxide upwardly in a reaction zone at a velocity effective to suspend in the gaseous mixture a finely-divided contact material comprising either a freshly reduced or used cobalt catalyst supported on a bentonite type support at the reaction temperature, the process being characterised further by the fact that the resulting mixture of contact material, hydrogen and carbon oxide is maintained at an equilibrium temperature not lower than 350° F. at substantially all times and any time of contact of catalyst, hydrogen and carbon oxide at temperatures lower than 350° F. does not exceed a period of time in which less than an amount equivalent to 15 parts by weight of carbon oxide is in contact with one part by weight of reduced metal catalyst whereby the excessive formation of solid products such as wax is prevented and said contact mass is continuously maintained in a fluidized condition, said reaction mixture being cooled to maintain the reaction temperature at the desired temperature level, and said gaseous mixture being withdrawn from the reaction zone to recover normally liquid reaction products therefrom.

The product produced by the process of the invention is a highly saturated liquid hydrocarbon which is a desirable ingredient of Diesel fuel. The simultaneous production of wax-like products is largely eliminated by our avoidance of contact between the carbon oxide, hydrogen and contact material at temperatures lower than 350° F. for a period of time longer than that indicated above. In prior processes the catalyst was held at temperatures below this temperature for longer periods of time.

In carrying out the process in accordance with the invention the gas mixture, comprising hydrogen and carbon monoxide in suitable proportions, is passed upwardly in a reaction zone through a mass of finely divided contact material comprising a reduced, preferably freshly reduced, metal hydrogenating cobalt catalyst which has been used or produced under conditions which do not build up waxy deposits on the surface thereof, or one which has been revivified by hydrogen treatment to restore it substantially to its original fresh condition.

The hydrogenating catalyst is employed in the metallic form with a bentonite type of support and may or may not be associated with promoters, such as magnesia, thoria, alumina, silica, titania or manganese oxide. The cobalt catalyst is associated with a bentonite support, in the ratio of one part by weight of cobalt to two parts by weight of the support. Preferably also promoters such as the metal oxides listed above are incorporated in small proportions. The catalyst may be combined with the supporting material and promoters in any suitable manner, and the final product is then converted to a state of fine sub-division. Preferably the powdered catalyst employed in the improved process consists principally of a mixture of particles varying in size from 40 to 400 microns (average diameter). However, particles of larger or smaller diameter may be present.

The gaseous mixture is passed upwardly through the mass of powdered contact material at a velocity effective to suspend the mass in the gas stream. The gas stream is passed through the reaction zone at a velocity sufficiently low to maintain the contact mass in a dense, fluidized, pseudo-liquid condition. In this condition the contact mass may be said to be suspended in the gas stream, but not entrained therein in the sense that there is movement of the contact mass as such in the direction of flow of the gas stream. It is preferred to flow the gas stream through the mass at a velocity sufficiently high to maintain the fluidized contact mass in a highly turbulent condition in which the particles of contact material circulate at a high rate in the pseudo-liquid mass. In this preferred condition of operation a small proportion of contact material in the fluidized mass may become entrained in the gas stream emerging from the upper surface of the mass whereby it is carried away from the mass.

The gas mixture is introduced into the reactor, in which the contact mass is located, through an inlet in the bottom thereof whereby the gas stream passes upwardly through the contact mass to be maintained in a fluidized condition. The cross-sectional area of the inlet is substantially less than the corresponding dimension of the space in the chamber occupied by the contact mass. In that manner the gas stream may be passed into the reactor through the inlet at a high velocity whereby solids do not pass downwardly out of the reactor through the gas inlet. For convenience the velocity of the gas stream in the chamber or reactor is given in terms of the theoretical velocity of the gas stream through an empty chamber, referred to hereafter as the superficial velocity.

If the catalyst chamber or reactor is somewhat larger than the volume occupied by the fluidized mass, the catalyst in the reactor appears to be distributed in two visually distinct phases. The first of these is the relatively dense, pseudo-liquid mass of fluidized catalyst, previously described, which occupies the lower portion of the reactor and comprises all but a minor proportion of the catalyst in the reactor. This phase is designated as the dense phase. The second phase, which occupies the upper part of the reactor, is a diffused phase in which the concentration of contact material is far less, and of a different order of magnitude from the average concentration in the dense phase. The diffuse phase may be said to be a disengaging zone in which the solid particles lifted above the dense phase by the gas stream are disengaged therefrom to the extent that such solid particles are present in excess of the carrying capacity of the gas stream at the minimum velocity reached by the gas stream in the reactor. Between the dense phase of high concentration and the diffuse phase of low concentration there is a relatively narrow zone in which the concentration of solids 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.

The invention may be operated with contact material having relatively large particle size such that substantially no part of the contact material is carried by entrainment in the gas stream at the superficial velocity. The preferred method of operation involves ordinarily the use of contact material and operating conditions such that a portion of the contact material is carried by entrainment in the gas stream at the superficial velocity. This results from the fact that finely divided contact materials present a greater ratio of surface to volume and afford the maximum efficiency of heat transfer between particles and the further fact that sufficient mixing of a catalyst mass of substantial cross-sectional area ordinarily requires the use of superficial velocities which entrain a portion of the finely divided contact material in the gas stream. In this preferred method of operation mere settling is not sufficient to disengage all the catalyst from the gas stream emerging from the dense phase of the catalyst mass. Hence it is necessary to provide means in cooperation with the reactor to separate entrained catalyst from the gas stream. The catalyst charged to the reactor may comprise fresh contact material or catalyst previously carried out of the reactor by entrainment.

The gas stream is withdrawn from the top of the reactor through an exit which is ordinarily of substantially smaller cross-sectional area than the reactor. This provides a high velocity outlet for the gases which is surrounded by an area in which the gas velocity accelerates. The nearer this zone of accelerating gas velocity is to the dense phase, the greater is the concentration of solids in the gas stream entering the zone and the greater is the quantity of solids carried out of the reactor in the exit stream. The quantity approaches the carrying capacity of the high velocity exit gas stream when it is desired to maintain the upper level of the dense phase in the vicinity of the zone of accelerating velocity.

In the preferred method of operation the reactor is made sufficiently larger than the required volume of dense fluidized catalyst mass to provide a relatively large diffuse phase in which substantial disengagement of catalyst from the gas stream occurs by mere settling.

The quantity of contact material required in the reactor may be charged to the latter prior to the passage of a gas stream therethrough. Alternatively the highly turbulent dense pseudo-liquid phase may be established by flowing a gas stream through the empty reactor and charging finely divided contact material into the reactor at a rate greater than the carrying capacity of the gas stream at its superficial velocity. As a result of such excess loading the desired volume of dense phase is built up in the reactor.

The freshly reduced metallic hydrogenating catalyst is maintained at a high level of activity throughout the operation. This results in greatly restricting the accumulation of waxy deposits on the particles of contact material, whereby long operating runs are made possible, and in the production of a highly saturated liquid product containing little or no wax. The freshly reduced metallic hydrogenating catalyst is maintained at a high level of activity by avoiding contact of the catalyst with the reactants for any substantial length of time under reaction conditions which build up deposits, such as wax, on the particles of contact material. The temperature at which the reactants and contact material are contacted is not permitted to fall below 350° F., other than as specified herein at any point in the reactor. This control of the temperature level is facilitated in the improved process by the employment of the contact material in the fluidized form described above. It is a characteristic of such a fluidized mass of contact material that all parts thereof are maintained substantially at a uniform temperature as a result of the high rate of heat exchange between the rapidly circulating particles.

The highly uniform temperature conditions which exist in a fluidized mass of contact material of the character described above make possible the use of the hydrogenating catalyst at its highest level of activity. This characteristic of the fluidized mass of contact material permits the withdrawal of heat therefrom at whatever rate is necessary to abstract the heat of reaction. The high rate of circulation of the particles of the contact mass serves to promote rapid and efficient heat exchange between that part of the fluidized mass which is subject to cooling means and the remainder thereof and also serves to prevent the occurrence of local zones of overheating.

The catalyst is maintained at all times at its maximum level of activity and the reactants are passed at all times through the reaction zone at a temperature which produces hydrocarbons at a high rate. Furthermore, the temperature control provided by the fluidized contact mass permits the passage of the reactants through the reaction zone at a space velocity far in excess of the space velocity permissible in previous commercial operations. For example it is permissible and even desirable to pass the reactants through a fluidized mass of contact material comprising cobalt on bentonite as the catalyst at a space velocity equivalent to 2 or more litres (measured at standard conditions of pressure and temperature) of hydrogen and carbon monoxide in the 2:1 ratio per hour per gram of cobalt. In this operation this rate is equivalent to about 500 standard volumes per hour per volume of catalyst dense phase. It is preferable furthermore that the contact material and reactants shall not be contacted at a temperature lower than 350° F. However, it is permissible to contact the reactants and fluidized catalyst mass for a short time initially at a temperature lower than 350° F., but the quantity of reactants passed through the contact mass at such conditions should be less than an amount equivalent to 15 parts by weight of carbon monoxide per part by weight of reduced metal catalyst. Preferably the contact mass is heated to a temperature of 350° F. or higher prior to contact thereof with the reactants. This is accomplished by means of a stream of inert gas. Conveniently the contact mass may be brought to this condition by carrying out the reduction of the metal hydrogenating catalyst to the metallic condition just prior to initiating the passage of reactants through the reaction zone. In this manner the reduction step may be employed for preheating the catalyst mass. The reaction mixture need not be preheated under such circumstances since the hot contact mass serves to preheat the reactants initially and thereafter the heat of reaction is more than sufficient to maintain the reactants at the reaction temperature.

The invention will now be described with reference to the accompanying drawing which is a view in elevation, partly in section, of a relatively small reactor employed in connection with the improved process, and by reference to specific examples of operations embodying the present invention and carried out in the apparatus of 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 inch 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 comprises 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 vapours 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 vapours and entrained catalyst upwardly about the outer surface of the filter. The upper ends of filters 9 and 10 are mounted in closure means 11 and 12 in a manner whereby the gases and vapours 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 4½ inches in outside diameter, the filter walls being approximately ¾ 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 the reactor to a point sufficiently low to enclose the 3 inch length of conical section 2 and approximately 5 inches of pipe 3. Jacket 15 comprises a length of extra heavy 4-inch steel pipe having an inside diameter of 3.83 inches. The ends of jacket 15 are formed by closing the ends of the 4-inch pipe in any suitable manner, as shown. Access to the interior to jacket 15 is provided by an opening 16 in the top thereof through a 2-inch steel pipe. Jacket 15 is adapted to contain a body of liquid for temperature control purposes, such as water, or a mixture of diphenyl and diphenyl ether. The vapours which are evolved by the heat of reaction are withdrawn at 16, condensed, and returned through 16 to the body of temperature control fluid in jacket 15. The temperature control fluid in jacket 15 is maintained under a pressure at which the liquid boils at the temperature desired in jacket 15. Heating means, not shown, are provided in connection with jacket 15 to heat the temperature control fluid therein to any desired temperature.

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

In the operations carried out in the apparatus of the drawing the catalyst recovery means, comprising filters 9 and 10, are effective to separate substantially completely entrained catalyst from the outgoing stream of gases and vapours. The disengagement of solids from the gas stream is promoted by the lowered velocity of the gas stream in conduit 5 and remaining solids are separated on the outer surfaces of filters 9 and 10. The latter are employed alternatively during the operation so that the stream of gases and vapours and entrained solids passes from conduit 5 through either the left or right branches of manifold 6 into conduit 7 or conduit 8. During the alternate periods the filter which is not in use is subjected to a back pressure of inert gas which is introduced at a rate sufficent 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.

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

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

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

EXAMPLE I.

A catalyst for promoting the reaction of carbon monoxide with hydrogen was prepared as follows: 10000 grams of cobalt nitrate, $Co(NO_3)_2.6H_2O$, and 1910 grams of magnesium nitrate, $Mg(NO_3)_2.6H_2O$ were dissolved in 50 litres of softened water. 6100 grams of sodium carbonate, $Na_2CO_3.H_2O$ were dissolved in 50 litres of softened water. Both solutions were heated to the boiling point and the nitrate solution was then added to the carbonate solution with continuous stirring. After the resulting mixture had been stirred thoroughly 4000 grams of the acid-activated bentonite clay known under the Registered Trade Mark "Superfiltrol" (previously dried at 900° F. for 1.5 hours) at a temperature of 210° F. were added to the solution with vigorous stirring. After thorough stirring the resulting mixture was then filtered under a pressure of 30 pounds per square inch. The filter cake was washed in the filter with 160 gallons of softened water at 180° F. The washed filter cake was dried overnight at room temperature by means of a blower. The partially dried material was dried at 210° F. to a moisture content of about 54% and was then extruded through 0.375 inch dies. The extruded material was then dried overnight at 210° F. to obtain a product having a moisture content of about 16%. This material was then ground to produce a granular mass finer than 6 mesh but coarser than 20 mesh. The granular material thus produced was reduced in an oven by means of a circulating stream of hydrogen from which water and carbon dioxide were removed constantly. The temperature of the mass of catalyst during this operation was raised to a final temperature of 700° F. during which time the production of water ceased. The reduced catalyst was then ground in an atmosphere of carbon dioxide to a powder of the desired size. The following is a screen analysis of this powder.

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

This catalyst had the following approximate composition in parts by weight:—

1.0 of Co:0.15 of MgO.2.0 of Superfiltrol.

Reactor 1 was purged by means of carbon dioxide and while a small stream of carbon dioxide was passed through the reactor 9 pounds of the catalyst prepared as shown were introduced while maintained in an atmosphere of carbon dioxide. The catalyst mass was then heated to approximately 400° F. by heating the water bath in jacket 15. During this time the catalyst was aerated with small streams of carbon dioxide until the temperature reached 300° F. Then hydrogen was used as the aerating medium until the admission of feed gas. When the catalyst temperature reached approximately 360° F. the stream of hydrogen was stopped and the passage of feed gas through the reactor was initiated. The reaction temperature was raised during a period of 11 hours to 400° F. This operation was continued for approximately 650 hours during which time the gas was passed through the reactor at varying experimental conditions. The reaction temperature varied from 380° F. to 425° F. The pressure varied from atmospheric to 50 pounds (gauge) per square inch. The feed gas, which consisted substantially entirely of hydrogen and carbon monoxide in ratios of 2:1 to 3:1 was charged to the reactor at space velocities of 330 to 875 volumes of gas (measured at standard conditions of temperature and pressure) per volume of dense catalyst phase per hour. A high rate of conversion to liquid hydrocarbon products was maintained throughout the operation, which was terminated arbitrarily in order to examine the catalyst. After 516 hours of this operation the catalyst was revivified by treatment with a stream of hydrogen at 700—850° F. for 6 hours. The function of this regeneration treatment appeared to be the reduction of oxides formed on the catalyst surface during the operation rather than the removal of waxy deposits. At no time during the operation was there absorbed any accumulation of deposits on the contact material which interfered with the fluidized condition of the catalyst and the final examination of the catalyst after the termination of the operation showed it to be a finely divided non-adherent, easily fluidizable material. The liquid product obtained throughout this operation was highly paraffinic in character but the production of wax was very small. For an example of the character of the product obtained in this operation reference may be had to the results obtained during a 22 hour period after 71 hours of operation. In this period a gas consisting essentially of hydrogen and carbon monoxide in a 2.6:1 ratio was reacted at 405° F. An exit pressure of 25 pounds per square inch was maintained on the reactor and the feed gas was passed through the reactor at a space velocity of 476 volumes per hour per volume of fluidized catalyst. This corresponds to a superficial inlet velocity of 0.64 feet per second. The dense phase rose to a level of 9.4 feet above pipe 73. During this period a contraction of 67.5% was observed and a liquid product consisting of propane and heavier hydrocarbons was obtained at the rate of 147 cc. per cubic metre of feed gas.

The liquid condensate obtained in this operation, boiling between 134° F. and 574° F., and including all the higher boiling products contained but 0.8 mol per cent. of olefins. No wax formation was detected.

Example II.

A catalyst was prepared in accordance with the following procedure:—

A cobalt nitrate solution was prepared by dissolving 10000 grams of the hexahydrate in 50 litres of water. A sodium carbonate solution was prepared by dissolving 6100 grams of $Na_2CO_3.H_2O$ in 50 litres of water. With both solutions at the boiling point the cobalt nitrate solution was added with stirring to the sodium carbonate solution. After thorough stirring 4000 grams of dried "Superfiltrol" preheated to 180—200° F. were added with vigorous stirring. The slurry thus obtained was filtered and the filter cake was reslurried in 30 gallons of softened water. After standing for several hours the slurry thus obtained was heated to boiling with vigorous stirring, after which the slurry was filtered again. During this operation the filter cake was washed with 300 gallons of hot softened water. The filter cake thus obtained had a water content of approximately 70 weight per cent. This material was partially dried at room temperature to a water content of approximately 57% and was then extruded through a 0.375 inch diameter orifice. The extruded material was heated overnight in an oven at 420° F. The material thus obtained was in the form of hard lumps and had a water content of approximately 7.6 weight per cent. This material was then ground in a Braun disc mill and screened to collect material passing through a 40 mesh sieve. Material which did not pass the sieve was recycled to reduce the batch to a size smaller than 40 mesh.

The following is a screen analysis of this powder:—

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

6.3 pounds of this material was charged to reactor 1, this amount being chosen to produce 5.8 pounds of catalyst in the reactor after reduction. The unit was flushed out with nitrogen and then hydrogen was passed in through pipe 3. Jacket 15 was filled with a suitable temperature control fluid such as diphenyl-diphenyl ether mixture and by heating this fluid in the manner described above the temperature of the catalyst mass was gradually raised. After the temperature of the catalyst was raised to 400° F. the rate of introduction of hydrogen was increased to 40 cubic feet per hour and the temperature was raised, while operating at that velocity, to 700° F. This operation was continued until the formation of water ceased, after which the hydrogen flow rate was lowered to 5 cu. feet per hour and the temperature was lowered to 300° F. The catalyst composition in parts by weight was 1 of Co:2 of "Superfiltrol". The diphenyl-diphenyl ether mixture was removed from jacket 15 and replaced with water at a pressure sufficient to produce a boiling temperature of 300° F. (i.e. about 53 lbs. per square inch gauge). The introduction of feed gas consisting approximately of two parts of hydrogen and one part of carbon monoxide was then initiated at a space velocity of 333 standard volumes of gas per hour per volume of dense catalyst phase, and the temperature was raised rapidly to the desired reaction temperature range. The time during which the temperature was raised from the initial temperature of 300° F. to 360° F. was only two hours. During this two hour period 4.3 pounds of carbon monoxide per pound of cobalt were present. Thereafter the temperature was raised to 400° F. in a space of 14 hours.

The operation thereafter was continued under various experimental conditions for 1115 hours at the end of which time the unit was shut down voluntarily and the catalyst withdrawn for examination. During this time the temperature of the reaction zone varied from a minimum of 380° F. to a maximum of 460° F. and the pressure varied from atmospheric to 50 pounds per square inch (gauge). The feed gas consisted substantially of hydrogen and carbon monoxide in ratios of 2:1 to 3:1 throughout this period and it was charged to the reactor at space velocities varying from 175 to 1200 volumes (measured at standard conditions of temperature and pressure) per voulme of the dense catalyst phase per hour. Throughout this period the conversion rate was maintained at a high level to form a liquid product which was highly paraffinic but on the other hand substantially free from wax. During the period, however, the accumulation of deposits on the surfaces of the contact material was infinitesimal compared to the accumulation of wax which would have been formed on a comparable catalyst in a fixed bed operation. The finely divided contact material remained perfectly dry and non-adherent throughout the operation and the fluidized condition of the contact material was maintained without difficulty.

The results obtained during one period in the above operation may be referred to to illustrate the character of the product obtained. In this period, of 66 hours duration, after 423 hours of operation, a gas consisting essentially of hydrogen and carbon monoxide in the 2:1 ratio was passed through the reactor at a space velocity of 800—1200 volumes per volume of dense catalyst phase per hour. This corresponded to superficial inlet velocities of 0.43—0.73 feet per second. The dense phase rose to a level of 5.1—5.8 feet above pipe 73. The reaction was maintained at an average temperature of 430° F. and an exit pressure of 45 pounds per square inch (gauge) was maintained on the reactor. Under these conditions a contraction of 41% was observed. A liquid yield (including propane and heavier hydrocarbons) of 76 cc. per cubic metre of charge gas was obtained. This included 33 cc. per cubic metre of normally liquid hydrocarbons boiling up to 300° F. and 24 cc. per cubic metre of hydrocarbons boiling above 300° F. This high boiling product constituted an excellent diesel fuel. The diesel oil product boiled between 330° F. and 668° F. It had an API gravity of 54.8 and an aniline point of 186° F., a pour point of 30° F. and a diesel index of 102. The diesel oil contained 2% of olefins and 1.7 weight per cent. of wax of a melting point of 124° F. The gasoline fraction contained 11% of olefins and had an octane number of 42.7 A.S.T.M. This was raised to 67.5 by the addition of 3 cc. of tetra-ethyl lead per gallon.

The results obtained in this example differ substantially from the results obtained in previous fixed bed operations, in the production of a highly saturated liquid product while at the same time substantially suppressing the formation of wax.

In each of the foregoing examples the accumulation of material on the surface of the contact throughout the operation was less than one weight per cent. of the contact material. This included a waxy oil and carbon.

The results obtained in the foregoing examples are different from results obtained in previous operations principally in the formation of a highly paraffinic liquid product while substantially avoiding the formation of wax. It may be postulated that when the freshly reduced catalyst is in its initial state of activity the formation of wax occurs only at temperatures substantially below 350° F. It may be that the freshly reduced catalyst has too high a capacity for adsorbing hydrogen at temperatures above 350° F. to permit the formation of wax. Thus by initiating the operation at such high temperatures the formation of wax is substantially inhibited from the beginning and the capacity of the catalyst for adsorbing hydrogen is not reduced by the accumulation of wax thereon. At the same time the high activity of the catalyst for hydrogenation results in the formation of a highly saturated liquid product. It will be understood, however, that the foregoing is offered merely as a possible explanation and that the invention is not limited by such theoretical considerations.

The present invention provides a process in which the catalyst is maintained at a high level of activity during operating periods of long duration. This results in the formation of a maximum yield of liquid product and a minimum production of solid products such as wax. Such a liquid product contains a fraction which is a highly valuable diesel fuel because of its substantially completely paraffinic character, because it is composed substantially entirely of straight chain hydrocarbons, and because of the relatively low pour point resulting from the small amount of wax contained therein.

The foregoing examples indicate satisfactory operating conditions. In general it may be said that any pressure from atmospheric to any feasible superatmospheric pressure may be employed. The temperatures should be maintained above 350° F. and temperatures in the range of 390° to 450° F. are highly satisfactory to effect substantial conversion at high space velocities. At temperatures of 350 to 450° F. space velocities of 50 to 2000 standard volumes of reactants per hour per volume of fluidized dense phase are satisfactory; higher velocities being in general associated with higher temperatures. For catalysts comprising about one-third by weight of hydrogenating metal the above range corresponds to about 0.2 to 10 standard litres per hour per gram of hydrogenating metal.

In Patent Specification No. 568,913, which although of prior date to the present application was not published until after the priority date of the present application, claims a continuous process for carrying out chemical reactions in the vapour phase, wherein the gaseous or vaporised reactants are discharged into an elongated vertical reaction zone of substantially uniform cross-section, the temperature within such zone being maintained within a desired range by the maintenance therein of a body of powdered material, which may be either catalytic or inert, the velocity of the gases being regulated so as to maintain substantially the same body of powdered material in the reaction zone in a dense phase suspension of powder in gas with the flow characteristics of a fluid, a powder disengaging zone being provided above such reaction zone in which the velocity of the gas is reduced to permit substantially complete disengagement of the powdered material therefrom, the disengaged material gravitating into such reaction zone. According to that specification the temperature of the incoming gas and the powdered material is adjusted so that the gas is maintained substantially uniform at optimum temperatures, and powdered material separated from the reaction products is returned to the reaction zone. That patent also provides that a sufficient amount of catalyst is present in the reaction zone to absorb excess heat and thereby temper said reaction.

In Patent Specification No. 647,155 which was not published at the date of the present application but which is of prior effective date, there is claimed a process of obtaining synthesis products consisting chiefly of hydrocarbons and oxygenated compounds by reaction of carbon monoxide and hydrogen wherein a gas mixture comprising carbon monoxide and hydrogen is contacted with synthesis catalyst under synthesis conditions, which comprises employing synthesis catalyst in finely divided form, maintaining said synthesis catalyst in suspended dense phase liquid-like condition in the synthesis zone by introducing the carbon monoxide - hydrogen mixture at the base of said zone and passing gases upwardly therein at a low velocity, separating unreacted gases and reaction products from said suspended catalyst and removing unreacted gases and light normally gaseous products from the heavier reaction products. In starting up the system described therein, the catalyst is heated from the exterior by steam to a temperature of, for example, 380° F. The make gas stream is introduced at the base of the reactor so that it will have a vertical velocity of 1 foot per second and the powdered catalyst is dispersed or suspended in this up-flowing gas until the reactor is filled with a dense phase of suspende catalyst. After a preliminary soaking period the synthesis reaction is initiated and as soon as there is a rise in the reactor the steam is replaced by water. The temperature of this water is controlled by maintaining a regulated pressure on the steam which is produced by its vaporization. Means are provided whereby any accumulated waxy oils may be withdrawn from the reactor.

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

1. A process for the hydrogenation of a carbon oxide to produce normally liquid hydrocarbons which comprises continuously flowing a gaseous mixture comprising hydrogen and a carbon oxide upwardly in a reaction zone at a velocity effective to suspend in the gaseous mixture a finely-divide contact material comprising either a freshly reduced or used cobalt catalyst supported on a bentonite type support at the reaction temperature, the process being characterised further by the fact that the resulting mixture of contact material, hydrogen and carbon oxide is maintained at an equilibrium temperature not lower than 350° F. at substantially all times and any time of contact of catalyst, hydrogen and carbon oxide at temperatures lower than 350° F. does not exceed a period of time in which less than an amount of equivalent to 15 parts by weight of carbon oxide is in contact with one part by weight of reduced metal catalyst whereby the excessive formation of solid products such as wax is prevented and said contact mass is continuously maintained in a fluidized condition, said reaction mixture being cooled to maintain the reaction temperature at the desired temperature level, and said gaseous mixture being withdrawn from the reaction zone to recover normally liquid reaction products therefrom.

2. A process according to claim 1 in which a space velocity of 200 to 2000 standard volumes of reactants per hour per volume of fluidized dense phase of catalyst is maintained.

3. A process according to either of claims 1 or 2 in which reduction of the metal hydrogenating catalyst to the metallic condition is effected in the reactor employed just prior to initiating the passage of the reactants through the reaction zone.

4. A process according to any of claims 1 to 3 in which the catalyst mass is heated prior to contact thereof with the mixture of hydrogen and carbon monoxide to a temperature not lower than 350° F.

5. A process according to any of claims 1 to 4 in which the freshly reduced catalyst is maintained in contact with the mixture of hydrogen and carbon monoxide at a temperature of 390—450° F.

6. A process according to any of the preceding claims in which the catalyst support consists essentially of an acid treated bentonite clay.

7. A process according to any of the preceding claims in which the reaction is carried out by passing the reacting gases upwardly through a **Y**-shaped reactor the arms of the **Y** containing filters permeable by the gases and vapours emerging from the reaction zone but impermeable to catalyst particles.

8. A process according to any of the preceding claims in which the internal volume of the reactor is made sufficiently large to provide a relatively large diffuse phase in which substantial disengagement of catalyst from the gas stream occurs by settling.

9. A process for the hydrogenation of a carbon oxide substantially as hereinbefore described with reference to either of the Examples.

10. Normally liquid hydrocarbons whenever produced by the process or processes particularly described and ascertained.

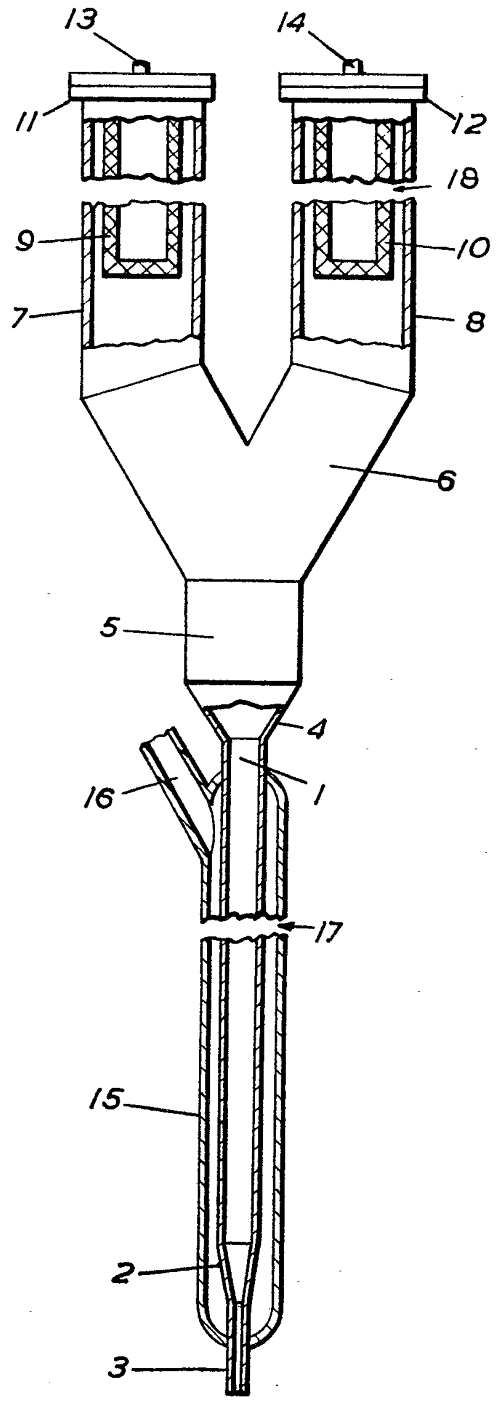
Dated the 11th day of September, 1945.

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

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1952.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

669,382 COMPLETE SPECIFICATION 1 SHEET

This Drawing is a reproduction of the Original on a reduced scale



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