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COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide in the Presence of a Liquid

We, RHEINPREUSSEN AKTIENGESELLSCHAFT FUER BERGBAU UND CHEMIE, of (22a) Homberg, (Niederrhein), Germany, a German Joint Stock Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the catalytic hydrogenation of carbon monoxide in which the catalyst is suspended in a liquid medium.

In the hydrogenation of carbon monoxide, a mixture of carbon monoxide and hydrogen conventionally termed "synthesis gas" is brought into contact with a suitable catalyst and is reacted to form saturated and unsaturated aliphatic hydrocarbons and also oxygen-containing derivatives thereof. This synthesis has become generically known as the Fischer-Tropsch synthesis and the general conditions of pressure, temperature, type and composition of catalyst and of catalyst additives essential for such synthesis are well known and established in the art.

When using a dry catalyst and particularly when using it as a so-called fluid catalyst, i.e. a finely divided catalyst suspended in the synthesis gas within the synthesis reactor, the heat evolved by the exothermic nature of the conversion may cause a runaway reaction leading to difficultly controllable increases in temperatures beyond those desirable for satisfactory yields. For the purpose of providing conditions, for the Fischer-Tropsch type synthesis, which permit of better control, the proposal has been made to suspend finely divided catalyst material in a liquid medium, preferably a hydrocarbon mixture such, for example, as may be obtained from the higher boiling components of the synthesis products. This suspension can then be cooled to remove continuously therefrom excess heat. One of the disadvantages of this proposal, however, is that it permits only a relatively low hourly throughput of synthesis gas. Thus, for example, a catalyst oil suspension (hydrocarbon fraction boiling between about 250° and 300° C.) containing from 10—50% by weight of base metal, such as iron, in the catalyst-oil suspension is only capable of utilising an hourly throughput of synthesis gas of from about 10—100 normal cubic metres per cubic metre of the catalyst-oil suspension. With this relatively low throughput of gas, the reactor is not used to full capacity, as the maximum yield of synthesis products obtained in a twenty-four period is only 400 kilograms per cubic metre of reactor space.

One object of the invention is to provide an improved process for the catalytic hydrogenation of carbon monoxide utilizing a finely divided catalyst in suspension in a liquid.

Another object of the invention is to provide a process for the catalytic hydrogenation of carbon monoxide giving a high yield with the use of a catalyst, preferably an iron catalyst, suspended in a hydrocarbon oil.

It has been found that by maintaining certain critical conditions in a catalytic hydrogenation of carbon monoxide in the presence of oil-suspended catalysts and preferably iron type catalysts, considerable increases in yield per unit of time and volume of reactor can be obtained, while at the same time appreciably increasing the yield of the more valuable or more readily marketable products of the synthesis, both on the basis of volume of synthesis gas put through the reactor as well as per weight unit of catalyst employed.

According to the invention, synthesis gas is continuously passed into a suspen-

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sion of a carbon monoxide hydrogenation catalyst in a hydrocarbon oil having a concentration of the order of magnitude of from 50—500 grams of catalyst-base metal per litre of suspension, the catalyst particle size being of the order of magnitude of from 0.002—1.0 mm., at a rate of gas flow, expressed in N litres (N litre=1 litre at 760 mm. mercury pressure and 0° C.) per hour per litre of catalyst suspension, equivalent to about 10—30 times the percentage content by weight of catalyst base metal in the suspension. The catalyst suspension of the above-given concentration and particle size of catalyst into which the synthesis gas is passed at the above-stated rate of flow is maintained under a gauge pressure of the order of magnitude of from 3—150 atmospheres whereby within these limits the value of the applied pressure is adapted to the rate of flow of the synthesis feed gas in such a manner that the rate of flow of the compressed synthesis feed gas is substantially maintained at a value per hour of an order of magnitude of from 5—100 litres of gas under the applied pressure per litre of catalyst suspension.

When proceeding in accordance with the invention and within the limits stated, an intimate mixture of synthesis gas and catalyst suspension is obtained having a substantially constant volume of about 40—100 per cent greater than the volume of the suspension itself and substantially independent of variations in the rate of flow of synthesis gas provided that this is maintained within the limits specified. Under these conditions, the two phases of oil and gas will form a substantially stable system as a substantially homogeneous mixture as illustrated in Figure 1b of the accompanying drawings. With a lower throughput of gas (Figure 1a) than that provided in accordance with the invention, the individual gas bubbles will move up the liquid column separately and at different speeds. Their speed in this case is governed by such factors as bubble size, differentials between liquid and gas densities, viscosity, and surface tension of the liquid. The system gas-liquid will then contain a maximum of nearly 10% by volume of gas. Upon increasing the gas throughput to a value which equals or exceeds the minimum gas throughput in accordance with the invention, the volume of the system gas-liquid will suddenly expand by at least 40—70% and in many cases by 100% and remain substantially constant even if gas throughput is further increased (Figure 1b). The following observation is then made:— the gas bubbles are all substantially uniform in size, separated only by thin layers or films of liquid and the speed of their vertical movement is only a fraction of the speed of the vertical movement of gas bubbles of equal size in the system illustrated in Figure 1a. The bubbles of the system shown in Figure 1b, however, are at the same time vigorously torn about in a more horizontal direction. In this state of expanded volume in accordance with the invention, 35—50% of the volume of the system gas-liquid consists of gas bubbles. The catalyst suspension, in effect, then floats as a fine dispersion in between the gas bubbles.

The effect produced by this condition on the hydrogenation of carbon monoxide is quite surprising. Its most conspicuous feature is that, starting with low gas throughputs, the conversion of CO is only moderate at first, until the critical minimum gas throughput is reached or exceeded, at which point the conversion will suddenly rise to nearly 100% and will remain substantially at this level although the other conditions remain constant and even though gas throughput is further increased to a multiple of its original value. It is to be noted that the state or physical characteristics of the expanded volume gas-liquid suspension are distinctly different from those of a froth state. In the former the shape of the gas bubbles is still almost spherical, resulting in an irregular thickness of the liquid layers or films between the gas bubbles, and the two phases gas-liquid are in relative movement to each other. In a froth, on the other hand, the gas bubbles are forced into polyhedrons and are separated by liquid layers or films of substantially uniform thickness which move together with the gas bubbles in the same direction.

If gas throughput is increased in excess of the limits stipulated in the invention, the system gas-liquid suspension is gradually destroyed as a growing number of gas bubbles will coalesce and rapidly break through to the top (bubbling) (Figure 1c), resulting in stratification of gas and liquid. Gas conversion will then suddenly fall.

While the invention insures substantially complete conversion of gas within the ranges of synthesis pressure and catalyst concentration set forth, the use of the higher range of catalyst concentrations which is coupled, according to the invention, with increased gas throughput and increased synthesis pressure, will allow an appreciable increase in the time unit yield per cubic metre of reactor space, which yield may be as high as 4000 kg. of synthesis products in twenty-four hours.

The benefits obtained on the basis of prolonged activity of catalyst and high yields per unit base metal in the catalyst is, for example, demonstrated by the fact that one ton of iron in the catalyst will yield an average of 700 tons of synthesis products during the whole period of catalyst service, of about 90 days.

Though attempts have been made at various times to check the formation of methane in the hydrogenation of carbon monoxide, such as by using constant low synthesis temperatures, no carbon monoxide hydrogenation process has hitherto been known which successfully solves this problem. Previously known methods of synthesis and particularly those conducted under conditions seeking relatively high outputs, produce methane in considerable quantities. This, however, is not the case in the process of the present invention in which no appreciable formation of methane takes place. This effect is new and unexpected inasmuch as the many unsuccessful attempts made to control the undesirably high formation of methane in the synthesis process, have led to the general assumption that the formation of large amounts of methane is an unavoidable evil.

One of the advantages of the process of the invention is that it permits the utilization of higher synthesis temperatures than are normally possible within the limits required for relatively high output yields. Ordinarily, temperatures above approximately 250° C. favour the production of methane and the separation of carbon, thereby resulting in poorer yields, and it is necessary that, in order to maintain a fair equilibrium in favour of the higher molecular hydrocarbons or hydrocarbon derivatives, fairly low temperatures be ordinarily used.

When proceeding in accordance with the invention, however, the reaction temperature may be generally kept from 10° C. to 70° C. higher than is normally considered a safe upper limit for substantially complete gas conversion with a minimum of undesirable by-products. The upper limit of the temperature is governed by the requirement that the particular hydrocarbon or oil used for the suspension is not deleteriously affected by cracking, and ordinarily a temperature of 360° C. constitutes the limit beyond which danger of cracking may be present. For best results, we find it of advantage to use average synthesis temperatures between 200° C. and 360° C. and preferably between 220° C. and 320° C. It is thus possible, by utilizing higher synthesis temperatures, to take advantage of higher reaction velocities and thereby to promote the formation of predominantly low molecular, largely unsaturated and more highly isomerized hydrocarbons without excessive formation of methane or appreciable deposition of carbon whereby practically the entire yield is obtained in the form of desirable products. Thus the ultimate output of synthesis products per unit volume of synthesis gas used is still further increased.

The accompanying drawings show, in cross-section, a reactor suitable for use in the process of the invention, the only difference between Figures 1a, 1b and 1c being the differences in the two phase liquid-gas system hereinbefore referred to, with Figure 1a showing less than the critical limitations for gas throughput in accordance with the invention, Figure 1c an excess of those critical limitations, and Figure 1b an illustration of the two phase systems when operating within these limitations. The reactor as shown comprises the outer cylindrical wall 1 enclosing the reaction zone which is charged with the catalyst suspension. Gas inlet duct 2 is provided at the bottom of the reactor and passes the synthesis gas to and through a distributor 3 which is preferably formed as a porous filter of, for example, ceramic material. The reactor carries the exit gas duct 7 in cover 6 and is further provided with a withdrawal duct 5. A suitable conventional arrangement for maintaining the temperature (not shown) may be provided by a double jacket through which a suitable heat exchange liquid is passed which, as is well understood in the art, may serve either as a heating medium or as a cooling medium in accordance with the particular conditions required in the reactor at any given time. When the synthesis gas is introduced into the reactor through duct 2, it will be distributed and dispersed into the liquid by way of the porous bed or filter member 3. The dotted line 4 indicates the normal liquid level of the catalyst suspension before gas is introduced into the reactor. Line 8 indicates the level of the suspension-gas phases when operating under one set of conditions within the critical limits of the invention. The large bubbles indicating a breakdown of the homogeneous gas-suspension phase are shown as such in Figure 1c. Suitable means (not shown) for maintaining the synthesis pressure will also be included.

The synthesis gas usable in accordance with the invention is the conventional gas mixture generally applicable to the synthesis of hydrocarbon products in accordance with a carbon monoxide hydrogenation procedure of the Fischer-Tropsch type. Such synthesis gas may include a gas product obtained, for example, by a typical water-gas reaction or may have been generated in any other suitable manner well known in the art for this type of reaction. The oil used for the suspension of the catalyst is preferably a hydrocarbon oil of a boiling range which, under the conditions of temperature and pressure at which the particular carbon monoxide hydrogenation is to proceed, will not appreciably volatilize. Thus, for example, it is preferred to use a hydrocarbon fraction having an initial boiling point somewhat higher than the highest reaction temperature that is to be used in the synthesis. Within the general scope of invention, hydrocarbon fractions boiling between 250° C. and 360° C. are normally satisfactory. Within the preferred embodiment of the invention, however, it has been found to be of advantage to use, for the suspension of the catalyst, an oil product obtained in the synthesis itself and having the requisite boiling range.

The catalyst used in the process of the invention may be any suitable catalyst conventionally employed for carbon monoxide hydrogenation in accordance with the Fischer-Tropsch type synthesis. Such catalysts contain, as is known, metals of the 8th group of the periodic system, such as iron, nickel, cobalt or ruthenium. In accordance with the preferred embodiment, however, it is preferred to use an iron catalyst. Iron type catalysts, as is well known, may for example, be obtained from ferric oxides obtained or processed from other types of iron compounds, such as iron salts, under particularly careful manufacturing conditions in accordance with well known practice. Such iron type catalysts obtained from ferric oxides are of exceptionally high activity. As is well known, the catalytic material is generally first introduced into the reaction zone in the form of the metal oxide or other reducible metal compound and is then subjected to a reducing reaction. This may be done either in the dry state, or preferably, by suspending the oxide or other reducible catalyst material in the oil to be used as a carrier and subjecting the material therein to a reducing reaction, for example, to the action of a synthesis gas whereby the catalytic material is converted into its active form. Active ferric oxide catalyst materials have the advantage that the active catalytic material obtained therefrom will catalyze carbon monoxide hydrogenation to hydrocarbons even at comparatively low temperatures. However, in order to produce low boiling synthesis products that are rich in olefines and isohydrocarbons, the process in accordance with the invention may utilize higher temperatures in the range 280° to 320° C. Catalysts which are particularly suitable for use in the synthesis at such increased temperatures by reason of their relatively low sensitivity to such temperatures are, for example, represented by the following industrial materials: hammer scales, residues of ferric oxide derived from the alkaline disintegration of bauxite, iron powder and iron filings. Natural iron compounds, i.e., compounds of mineral origin that may be used for catalytic purposes in accordance with the invention, may also include magnetic iron ore, red (oligiste) iron ore, brown iron ore (limonite), needle iron ore, goethite, ruby iron mica, bog-ore iron spar and materials of a similar type.

To the extent that the catalysts employed for the synthesis in liquid medium in accordance with the invention are completely free from activators or almost wholly consist of metals of the 8th group of the periodic system or their compounds, it is desirable to add suitable activating substances conventionally known and used for synthesis of the Fischer-Tropsch type. When employing iron catalysts, the quantity of activator or activators, other than an alkali-metal compound or compounds, should not exceed 1% by weight of the iron contained in the catalyst. Copper, for example, is such an activating additive. Cobalt or nickel catalysts may be activated by addition of thorium, magnesium or copper or their compounds in quantities of not more than a few per cent of the catalyst basic metal contained in the catalyst. For a further increase in activity, alkali compounds may be added to the catalysts, governed by the desired quality of the synthesis products.

A preferred method for the conversion proceeding in accordance with the invention, of the forenamed oxidic catalyst materials, particularly iron oxide catalyst material, into their active form, comprises treating the material in particle form (preferably ball mill ground) in the hydrogenation reactor in the presence of oil and preferably as a suspension in the oil, at temperatures about

10°—50° C. in excess of those applied in the subsequent synthesis, with carbon monoxide or gases containing carbon monoxide as the chief constituent, under gauge pressures of 1—10 atmospheres and preferably at 2 atmospheres gauge pressure at an hourly rate of gas flow within the reactor of more than 100 Ncbm of gas per cubic metre of catalyst suspension. With this kind of treatment, high activity and a fine, uniform dispersion of the catalyst owing to particle bursting is attained. If iron catalysts of low temperature sensitivity are used, it is not necessary to increase the conversion temperature above the temperature of the subsequent synthesis in the designated degree. In consequence of the higher reaction temperature of these particular iron catalysts the conversion with carbon monoxide can already be operated at the same temperature as those of the reaction.

In another method for the conversion of oxidic catalyst material into its active form, a dry process may be used. In this case the particled material, preferably ball mill ground material, in dry form is subjected to a suitable reducing agent. This may be effected in a reactor type chamber, it being desirable, however, in this case to use a synthesis type gas mixture rather than carbon monoxide or hydrogen alone. In contrast to the treatment in the presence of an oil medium, in which positive pressures are used, ordinary atmospheric pressure is preferable, higher pressures being detrimental to the activation reaction. Rates of gas flow in the reactor down to about 50 Ncbm for each cbm catalyst volume are useful. By reason, however, of the shortened reaction period required for activation and the relatively high activity of the catalyst, it is desirable to treat the dry catalyst material to be activated with a gas mixture at a rate of flow preferably in excess of 600 litres per litre of catalyst material per hour of flow at temperatures between 230° and 500° C. and in the case of oxidic iron catalysts preferably between 300° and 350° C. and at normal atmospheric pressure or even reduced pressure. In some cases slightly increased pressure may be used. Pressures, however, of the order of magnitude prescribed for the activation in the presence of oil as hereinbefore described, are to be avoided. It is further possible to conduct this type of dry catalyst material activation with the recycling of exit gases or at least a portion thereof in volume proportion of one part fresh gas for each one to thirty parts of exit gas, with or without removal of carbon dioxide from the gas mixture. After the activation, the activated catalyst material obtained in this manner is then ground with oil or otherwise dispersed in the oil and is then ready for use in accordance with the invention. When using the dry material activation method, the catalyst material of the oxidic type need not necessarily be present in finely subdivided form. It is possible to effect the activation with materials present in relatively large pieces. In fact, it is easier in many cases to grind or otherwise subdivide the reduced oxidic catalyst material as compared with the non-reduced oxidic material. It is furthermore possible in accordance with conventional and well-known practice to obtain oxidic catalyst material, such as oxidic iron catalyst material, by suitable precipitation in the form of a very fine powder up to a finely granular material, without the necessity of grinding larger pieces. In this case, the reduced or activated catalytic material is obtained in dry form in sufficiently subdivided particles to be relatively easily dispersed in the oil in accordance with the invention.

It is a well-known phenomenon that carbon monoxide hydrogenation synthesis requires progressively increasing temperatures commensurate with the progressive exhaustion of the catalyst in substantially continuous operations. Ordinarily these increased temperatures are necessary for increased reactivity or rather to compensate for lost activity of the catalyst due to its partial exhaustion. On the other hand, the increased temperatures give rise to the formation of undesirable by-products. When proceeding in accordance with the present invention, however, the increased temperatures do not give rise to such formation of undesirable by-products to any appreciable extent. It is thus possible to raise the temperature gradually within the reactor and still not materially interfere with the synthesis or its yields and actually to compensate thereby for any losses that a partially exhausted catalyst may entail. It is thus possible in accordance with the invention substantially to maintain the beneficial results and yields even after a considerable time of operation and even though a portion of the catalyst may be exhausted. On the other hand, the possibility of raising the temperature without interfering with the reaction mechanism or equilibrium in favour of undesirable by-products, permits the maintaining of a temperature range about 10°—50° C. in excess of that at which the synthesis was commenced and at which activation of oxidic catalyst materials can be successfully effected. It is in this manner possible to add, once the temperature of synthesis is at the desired level at which oxidic catalyst material can be converted to activated catalyst, in a continuous or periodic operation, finely divided catalyst material in its oxidic form and preferably such catalyst material already suspended in an oil of the type within the reactor at the time of the addition of the catalyst suspension. Such addition should preferably be made from the gas entry side of the reactor and may be either continuously or periodically effected with a corresponding continuous or periodic removal of used catalyst suspension from the gas exit side of the reactor. In this manner, a continuous synthesis operation is possible substantially unlimited in time, and constancy in output can be achieved. Instead of non-activated, i.e. oxidic catalyst material, activated or spent and regenerated catalyst material may be used.

When proceeding in accordance with the invention in its application to a reactor in which a predetermined alkali or range of alkali content is to be maintained, and utilizing in the preferred embodiment of the invention substantially continuous operation including the continuous addition or periodic addition of catalyst material with commensurate removal of spent suspension, it is desirable for best results substantially to maintain the alkali metal content constant within the reactor. This may be accomplished by adding to the catalyst material to be freshly introduced or adding together with such material a somewhat higher alkali metal content than is ordinarily contained in the catalyst material within the reactor at that time. This will make up for the loss in alkali metal which occurs when removing suspension from the reactor and aids in keeping substantially constant the percentage of hydrocarbons in excess of C_3 in the total yield. The predetermined range of alkali metal content lies between 0.1% and 10% calculated as and based on the weight of catalyst base metal in the applied catalyst. Suitable alkali metal compounds are the oxides, hydroxides, carbonates, hydrocarbonates, phosphates, silicates and borates of sodium and potassium, furthermore their formates, acetates or the salts of higher organic acids, such as soaps. The quantity of the alkali metal compounds to be introduced with fresh catalyst suspension must be sufficient to replace the loss in alkali metal, which loss occurs through removal of catalyst suspension from the reactor. If the formation of a larger quantity of higher boiling synthesis products is desired, which formation can be obtained by increasing the alkali metal content of the catalyst suspension, a correspondingly large amount of alkali metal compounds are introduced.

Within a further embodiment of the invention, it is found possible so to adjust the conditions that the process may be adapted to any particular synthesis mixture whether the mixture be, on the one hand, rich in hydrogen, or, on the other hand, rich in carbon monoxide. When utilizing a gas mixture, rich in hydrogen with an iron catalyst in the synthesis, the water produced in the reaction enters with part of the carbon monoxide into an equilibrium reaction in accordance with the equation:—

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

This results in the removal of part of the carbon monoxide from the synthesis gas, thus withdrawing it from the hydrocarbon synthesis and so causing lower yields of synthesis products. It has been found that it is possible within the process conditions of the invention as hereinbefore given, substantially to eliminate this disadvantage and to effectuate, even with gases rich in hydrogen, a practically complete utilization of the carbon monoxide with a maximum yield of synthesis products per cubic metre of synthesis gas used. This result is obtained by effecting a reduced gas-catalyst contact period which may be obtained by so adjusting the rate of flow of the synthesis gas through the suspensions within the specified range that the suspensions remain in individual contact therewith for only a relatively short period of time. The synthesis gas, however, is then repeatedly contacted with the catalyst suspension whereby each individual contact is at a relatively high velocity or rate of feed through the suspension within the general rate of gas flow limitations herein specified in accordance with the invention. Thus, for example, gases rich in hydrogen (e.g. 2 vols. H_2:1 vol. CO) are run at a velocity or rate of flow through the suspension up to fifteen times as high as that employed for gases rich in carbon monoxide (e.g. 1 vol. H_2:2 vols. CO). This increased rate of flow applies to each individual contacting, and the gases, having passed the suspension at that rate of flow, are then recontacted with catalyst suspension for a sufficient number of times within the limits of rate of flow of fresh synthesis gas in accordance with the invention until substantially all of the carbon monoxide is effectively utilized. This repeated contacting may be done by either recycling the emergent gases in each case through the same suspension at the higher rate of flow mentioned or by passing these gases into and through successive stages of a multiple stage synthesis unit. When recycling part or all of the exit gases in accordance with this procedure, it has been found to be of advantage to add a certain amount of fresh synthesis gas to the mixture. Depending upon conditions affecting the conversion ratio $H_2:CO$ such as pressure, temperature, nature of catalyst and rate of fresh gas feed, it has been found to be of advantage to have the recycle ratio for exit gas to fresh feed gas from about 2 to 5 times as high as the volume ratio $H_2:CO$ in the fresh feed gas.

It has also sometimes been found to be advantageous to add a suitable additive affecting the surface tension of the oil in the catalyst suspension. This additive may be one of the surface tension reducing type or of the surface tension increasing type. Suitable surface tension modifying agents useful in accordance with the invention are, for example, the fatty acid salts of alkali metals and of aluminium, preferably sodium or aluminium stearate, palmitate or oleate. Also useful in this direction are, for example, pyridine, higher boiling esters, preferably those of inorganic acids such as phosphoric acid esters.

When using multiple stage synthesis, the process involves a passage of the catalyst suspension from stage to stage to meet in each stage fresh synthesis gas.

In the process of the invention, between 180 grams and 195 grams of hydrocarbons are formed from a normal cubic metre of applied $CO+H_2$. The properties of the hydrocarbons formed vary within wide limits and depend on the catalyst and operating conditions. For example, products can be produced which consist predominantly of C_3—C_8 olefines with a considerable percentage of iso-hydrocarbons, or hydrocarbons predominantly solid at normal temperature both with a high and low degree of branching and both with a high and low olefine content.

In the process according to the invention, carbon dioxide is produced in large quantities as a by-product in the synthesis. It is expedient to re-use the carbon dioxide in the gas generating process in order to reduce the carbon dioxide to carbon monoxide. This improvement is of particular importance for the production of synthesis gases in which the CO content is to exceed the H_2 content.

EXAMPLE 1.

In a vertical reaction tube 20 cm. in diameter, provided with a jacket 700 cm. in length through which a heat transfer medium can be passed, 10—15 Ncbm per hour of a gas of the composition 3 vols. CO:2 vols. H_2 are passed through a suspension of a catalyst containing 10 Kilograms of iron, 40 grams of copper and 100 grams of K_2CO_3 with a particle size of 0.05 mm. in 90 Kilograms of synthesis oil of the 300°—320° C. distillation range, for 20 hours, at 230° C. and under a gas pressure of 12 atmospheres gauge.

Towards the end of this period, a vivid synthesis of hydrocarbons sets in. While the use of synthesis gas of similar composition is continued, conditions are adapted to synthesis operation by reducing the temperature to 258° C., increasing the gas pressure to 25 atmospheres gauge and raising gas throughput to 25 Ncbm of fresh gas per hour. The catalyst-oil suspension will then form, together with the gas bubbles rising at a comparatively slow rate, a stable three-phase system, the volume of which is about 60% greater than that of the suspension alone. Under these conditions, 96%—97% of the carbon monoxide is converted. 183 g. of synthesis products are formed from a normal cubic metre of carbon monoxide and hydrogen introduced.

Synthesis products include:—

	Percentage by weight
Methane + ethane	3
C_3+C_4 hydrocarbon	21
Liquid hydrocarbons up to 180° C.	55
Liquid hydrocarbons 180°—320° C.	17
Hydrocarbons boiling above 320° C.	4

The octane number of the 20° C.—150° C. fraction is 72 (motor method).

80% of the C_3+C_4 hydrocarbons are unsaturated. The olefine content of the liquid products amounts to 78%—82%, the alcohol content being 2%.

If, on the other hand, considerably less than 10 Ncbm. of synthesis gas are introduced instead of 25 Ncbm per hour, the other operating conditions remaining unchanged, the three-phase system of catalyst-oil-gas breaks down, being reduced to the two-phase system of catalyst-oil the volume of which is only a few per cent greater than that of the suspension itself before the introduction of gas. Together with the decrease in volume, the conversion of carbon monoxide drops below 70% and at the same time, the percentage of C_1+C_2 hydrocarbons in the total products rises to 7%.

Example 2.

Ferric oxide produced by precipitation from nitrate of iron (III) with subsequent washing and rapid drying, containing 0.5% of copper and 0.8% of K_2CO_3, is crushed to a particle size of less than 0.05 mm. in the presence of three times its weight of synthesis oil. This catalyst-oil suspension is mixed in a tall reaction cylinder at 280° C. with a quantity of synthesis oil of the 300°—340° C. distillation range so as to yield a suspension containing 20% by weight of iron. At the temperature of 280° C. this suspension is treated for 16 hours with 100—200 Ncbm of carbon monoxide per hour per cbm of suspension under a pressure of 3 atmospheres. After this activation, 300 normal cubic metres per hour of synthesis gas containing 38% of carbon monoxide and 50% of hydrogen are passed through 1 cbm of suspension at an initial temperature of 250° C. while the gas is kept under a pressure of 20 atmospheres. Part of the exit gas is, without expansion and after removal of the reaction products which are separated at 30°—50° C., again passed through the reactor together with fresh synthesis gas in the ratio of 3 volumes of recycle gas per volume of fresh feed gas. 92% of the carbon monoxide and 87% of the hydrogen are converted. One normal cubic metre of applied $CO+H_2$ will yield 172 grams of products of the following compositions:—6% of C_1-C_2 hydrocarbons; 74% of C_3+C_4 and gasoline hydrocarbons with a distillation end point of 200° C; and 17% of hydrocarbons boiling above 200° C. The gasoline and C_3+C_4 hydrocarbons contain between 76% and 84% of olefines.

In order to maintain an average gas conversion of at least 90%, the catalyst is, after about 500 hours of operation, gradually removed from the reactor and replaced by corresponding quantities of fresh or regenerated catalyst at such a rate that the average residence time of the catalyst in the reactor is about 900 hours. Renewal of the fluid medium proceeds at about the same rate as that of the catalyst. The catalyst removed from the reactor is separated from the oil and may be re-used in the synthesis after simple regeneration, e.g. by extraction.

The decrease in the alkali metal content in the reactor, which occurs upon removal of part of the suspension, is compensated for by providing the catalyst to be freshly introduced with an alkali metal content which is correspondingly higher.

Example 3.

Active ferric oxide nearly roentgen-amorphous is produced by precipitation from a solution of nitrate of iron (III), containing 5—10% of Fe, with sodium carbonate, caustic soda or ammonia with subsequent thorough washing and rapid drying. If the natural copper content should be lower, such a quantity of nitrate of copper is added to the catalyst prior to the precipitation so as to obtain a final copper content of about 0.5—1% of the iron. Before drying 0.5% by weight of K_2CO_3 (in relation to Fe) is added to the ferric oxide. The dry catalyst is mixed with synthesis oil of the 290°—330° C. distillation range in the weight ratio of 1:3 and crushed to a particle size of less than 0.01 mm.

This concentrated catalyst-oil suspension is mixed in a reaction cylinder of 12 metres height with synthetic oil, preheated to 280° C., of the 240°—330° C. distillation range in a ratio to obtain a suspension containing about 10% of iron.

Under a gauge pressure of 10—15 atmospheres, this suspension is immediately treated with 150 Ncbm of synthesis gas per hour per cubic metre of catalyst-oil suspension at 270°—275° C. The synthesis gas contains about 35% of CO and 55% of H_2 the remainder consisting of CO_2 and N_2. At the end of 5 to 10 hours, as soon as 96—98% of the CO is consumed, the temperature is reduced to 255° C. the throughput per hour of synthesis gas is increased to 220 Ncbm per cubic metre of reactor, and part of the exit gas, mixed with the fresh synthesis gas, is passed again over the catalyst in the ratio of 3.5 volumes of recycle gas per volume of fresh feed gas, without previous expansion. Before reintroducing the exit gas into the synthesis process, the gas is freed from the synthesis hydrocarbons carried with it and separated at normal temperature, and from the synthesis water.

The average service life of the catalyst until the output drops to 90% of the initial value is 800—1200 hours approximately. Within this period, the catalyst is gradually replaced by fresh or regenerated catalyst without any interruption in operation, to maintain the output of the synthesis apparatus at a constant level. The average synthesis temperature is 275° C.

The following results are obtained:—

Hydrocarbons:— 174 grams per Ncbm of applied $CO+H_2$

Composition:—	C_1+C_2	3.5%
	C_3+C_4	16%, olefine content 74%
	C_5-C_9	61%, olefine content 77%
	C_{10}+higher	19.5%

In addition 2.7% of water-soluble alcohols are produced.

300—350 tons of C_3 and higher hydrocarbons are produced per ton of iron. One cubic metre of reactor will yield 800 kg. of C_3 and higher hydrocarbons in 24 hours.

By the use of a catalyst alkalized with 1—3% of K_2CO_3, while the high molecular paraffin hydrocarbons accumulating in the reactor are quickly removed, e.g., by filtration of part of the suspension to be carried out continuously or at brief intervals, a synthesis product is formed which predominantly consists of hydrocarbons solid at normal temperature with a yield of 170—178 grams per Ncbm. 70% of this product has a distillation end point above 320° C., while the C_1+C_2 hydrocarbons drop below 2%.

The yield of the high molecular hydrocarbons boiling above 320° C. can be increased to 150 grams per Ncbm of $CO+H_2$ and more by the continuous feeding into the reactor of corresponding quantities of lower molecular hydrocarbons boiling below 320° C., these hydrocarbons being subject to molecular enlargement during synthesis. For this purpose, paraffin hydrocarbons can be used as well as olefines.

EXAMPLE 4.

A ferruginous residue from the conventional alkaline disintegration of bauxite, containing about 60% of Fe_2O_3, is freed from the main part of its Na_2CO_3+NaOH content, amounting to about 5—6%, by washing with a little hot water and is mixed with about 2% by weight of K_2CO_3 in relation to the Fe content. After drying, the catalyst is crushed in the presence of oil. Operation can be started with CO at about 2 atmospheres gauge pressure or with synthesis gas containing CO and H_2 at 10 atmospheres gauge pressure, as has been described in Examples 2 and 3.

In a suspension of the catalyst in a synthetically produced hydrocarbon oil of the 290°—330° C. distillation range containing 50 grams of Fe per litre, 140 Ncbm of synthesis gas are converted per hour per cubic metre of fluid medium under the following conditions:— Gas pressure —15 atmospheres gauge pressure; temperature —255°—310° C.; synthesis gas containing 54% of CO and 35% of H_2; one single passage of gas. At a CO conversion of initially 96%, and finally 88%, one Ncbm of applied $CO+H_2$ will yield, on the average, the following products:—

Total hydrocarbons:—	182 grams
including C_1+C_2 hydrocarbons	16 grams
liquid gas C_3+C_4	31 grams with 85% olefines
gasoline (15°—200° C.)	95 grams with 83% olefines
gas oil (200°—320° C.)	28 grams with 76% olefines
hydrocarbons above 320° C.	7 grams
water-soluble alcohols	5 grams

Without regeneration, catalyst life is 600—700 service hours which is equal to an output of 250—280 tons of products (C_3 hydrocarbons and higher hydrocarbons up to and including solid paraffins) per ton of iron contained in the catalyst.

EXAMPLE 5.

A catalyst produced by rapid thermal decomposition of ferric nitrate which contains 0.5% of copper and 0.5% of K_2O in relation to the iron content is ground in a ball mill with three times its weight of hydrocarbon oil produced during the synthesis and having a boiling range 280°—320° C. and is introduced into a reactor preheated to 280° C. in which there is already a like amount in weight of the same synthesis oil. The whole suspension contains approximately 20—22 per cent by weight of iron. A quantity of sodium stearate equal to 2 per cent by weight of the iron content is added to this suspension. Instead of sodium stearate, other salts of fatty acids of the alkali metals or of aluminium, pyridine or organic esters of phosphoric acid may be used, generally in amounts between 0.1% and 4% by weight of iron in the catalyst.

From the bottom of the reaction chamber, synthesis gas (i.e. fresh gas) with a content of approximately 38 per cent by volume of hydrogen and 55 per cent by volume of carbon monoxide is passed through the suspension in a state of fine distribution under a pressure of 20 atmospheres with a space velocity of 400 (i.e. 400 normal cubic metres of synthesis gas per cubic metre of suspension per hour). After 2—3 hours 96%—98% of the carbon monoxide is converted. Thereupon the synthesis temperature is lowered within 24 hours from 280° C. to 260° C. or 265° C. Over 400 working hours an average of 93 per cent of the carbon monoxide is converted and over 700 hours an average of 90% CO is converted. Each normal cubic metre of the applied synthesis gas yields in the beginning an average of 182 grams, and over the whole working period an average of 174 grams, of hydrocarbon products with more than two carbon atoms per molecule with a content of oxygen-containing organic compounds of about 4 per cent. 65 per cent of the synthesis products consists of the hydrocarbon fraction boiling within the range 20°—150° C., 17 per cent consists of higher boiling hydrocarbon oils and 16 per cent consists of C_3— and C_4 hydrocarbons. The proportion of olefines in the entire synthesis products amounts to nearly 82 per cent.

In the course of 700 working hours, the synthesis temperature is gradually increased to 295° C. During the whole period of operation, nearly 2000 Kilograms of synthesis products are produced by 1 Kilogram of iron in the catalyst. The average output of hydrocarbons with three and more carbon atoms per molecule amounts to 1530 kilograms daily per cubic metre of catalyst suspension.

Similar results are obtained by employing other suitable catalysts conventionally employed for carbon monoxide hydrogenation, for example, nickel, cobalt or ruthenium catalysts. The methods for the preparation and activation of such catalysts are much the same as the methods given for the preparation and activation of oxidic iron catalysts.

What we claim is:—

1. A process for the hydrogenation of carbon monoxide which comprises passing a synthesis gas containing carbon monoxide and hydrogen through a carbon monoxide hydrogenation catalyst in suspension in a hydrocarbon oil, the suspension containing 50—500 grams of catalyst-base metal per litre, the catalyst being of a particle size of 0.002—1 mm., the flow rate of fresh synthesis gas expressed in normal litres per hour per litre of suspension being 10—30 times the percentage content by weight of the catalyst-base metal in the suspension, at a pressure within the range 3—150 atmospheres, the pressure being adapted to the said flow rate of the synthesis gas in such manner that the flow rate of the synthesis gas, measured under that pressure, is within the range 5—100 litres per hour per litre of catalyst suspension, whereby the mixture of gas and catalyst suspension attains a constant volume about 40% to 100% greater than the volume of the suspension itself.

2. A process according to claim 1, in which the catalyst-base metal is a metal of the 8th group of the periodic system.

3. A process according to claim 2, in which the catalyst-base metal is iron.

4. A process according to any of the preceding claims in which the hydrocarbon oil is one which will not crack under the process conditions.

5. A process according to any of the preceding claims, in which the boiling range of the hydrocarbon oil lies within the range 250° C.—360° C.

6. A process according to any of the preceding claims, in which an agent for modifying the surface tension of the oil is added to the oil.

7. A process according to any of the preceding claims, in which the temperature lies within the range 200° C.—360° C.

8. A process according to claim 7, in which the temperature lies within the range 220° C.—320° C.

9. A process according to any of the preceding claims, in which the catalyst contains one or more of the metals copper, thorium and magnesium or their compounds as activators.

10. A process according to claims 3 and 9, in which the activator or activators constitute not more than 1% by weight of the iron.

11. A process according to any of the preceding claims, in which the catalyst contains one or more alkali metal compounds.

12. A process according to claim 11, in which the alkali metal content, calculated as K_2O, of the catalyst is in the range 0.1%—10% by weight of the catalyst-base metal.

13. A process according to any of the preceding claims, in which the spent catalyst is intermittently or continuously replaced with active catalyst.

14. A process according to claim 13,

in which the active catalyst contains a higher alkali metal content than the spent catalyst removed.

15. A process according to any of the preceding claims, in which, with an iron catalyst and a synthesis gas containing more hydrogen than carbon monoxide, the synthesis gas is repeatedly passed through the catalyst suspension at an increased flow rate up to fifteen times greater than the flow rate used with a synthesis gas rich in carbon monoxide.

16. A process according to claim 15, in which the gas is passed through the catalyst suspension in the several stages of a multi-stage unit.

17. A process according to claim 16, in which the recycled gas is admixed with fresh gas mixture at each passage through the catalyst suspension.

18. A process according to claim 17, in which the ratio of recycled gas to fresh gas mixture is 2—5 times the volume ratio of hydrogen to carbon monoxide in the fresh gas mixture.

19. A process employing an iron catalyst according to any of the preceding claims, in which the iron catalyst is prepared from iron filings, iron powder, hammer slag, ferric oxide derived from the alkaline disintegration of bauxite, magnetite, red oligiste iron ore, needle iron ore, ruby iron mica, goethite, limonite, bogore or iron spar.

20. A process according to any of the preceding claims, in which the catalyst-base metal, in the form of its oxide or other reducible compound, is ground and before use in the hydrogenation of carbon monoxide, is subjected, in the presence of the hydrocarbon oil to treatment with a reducing gas consisting largely or wholly of carbon monoxide at a temperature 10°—50° C. higher than the temperature in the subsequent carbon monoxide hydrogenation, and at an absolute pressure of 2—11 atmospheres, preferably 3 atmospheres, the rate of gas flow being in excess of 100 volumes of gas per volume of catalyst and oil per hour.

21. A process for the hydrogenation of carbon monoxide, substantially as hereinbefore described with reference to any of the Examples.

22. A process for the hydrogenation of carbon monoxide, substantially as hereinbefore described.

23. Hydrocarbons and oxygen-containing organic compounds whenever produced by the process claimed in any preceding claim.

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707,987 **COMPLETE SPECIFICATION**
1 SHEET
This drawing is a reproduction of the Original on a reduced scale.

FIG. 1a

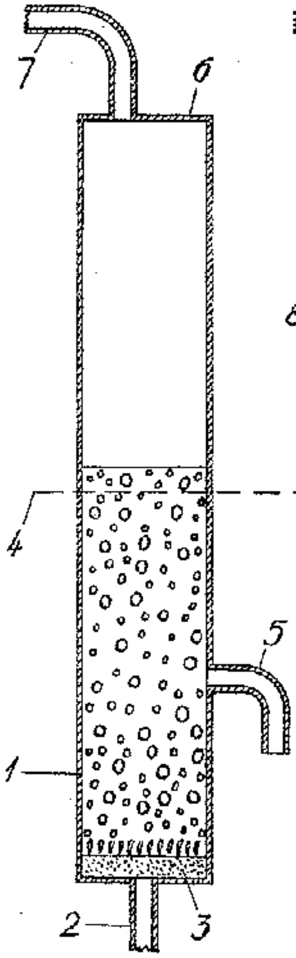


FIG. 1b

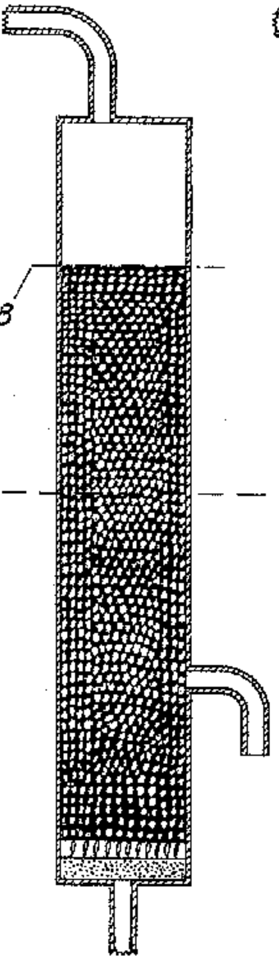
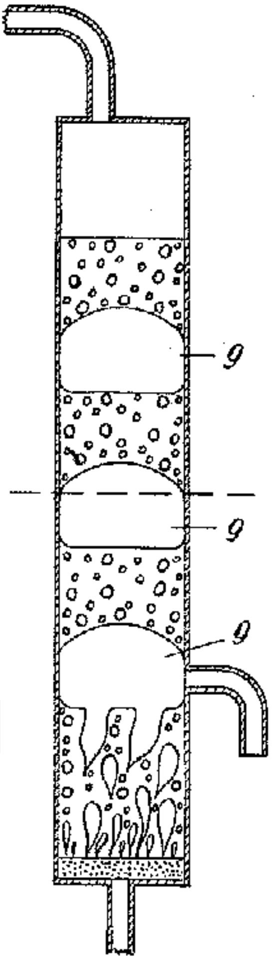


FIG. 1c



PATENT SPECIFICATION

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Index at acceptance:—**Classes 1(1),** F3B(1: 2X); **and 2(3),** B1G.

COMPLETE SPECIFICATION

Process for the Catalytic Hydrogenation of Carbon Monoxide in the Presence of a Liquid

ERRATUM

SPECIFICATION No. 707,987

Page 1, line 2, *for* " Beigbau " *read* " Bergbau "

THE PATENT OFFICE,
13*th October*, 1955.

Tropsch synthesis and the general conditions of pressure, temperature, type and composition of catalyst and of catalyst additives essential for such synthesis are well known and established in the art.

When using a dry catalyst and particularly when using it as a so-called fluid catalyst, i.e. a finely divided catalyst suspended in the synthesis gas within the synthesis reactor, the heat evolved by the exothermic nature of the conversion may cause a runaway reaction leading to difficultly controllable increases in temperatures beyond those desirable for satisfactory yields. For the purpose of providing conditions, for the Fischer-Tropsch type synthesis, which permit of better control, the proposal has been made to suspend finely divided catalyst material in a liquid medium, preferably a hydrocarbon mixture such, for example, as may be obtained from the higher boiling components of the synthesis products. This suspension can

[*Price*

lytic hydrogenation of carbon monoxide utilizing a finely divided catalyst in suspension in a liquid.

Another object of the invention is to provide a process for the catalytic hydrogenation of carbon monoxide giving a high yield with the use of a catalyst, preferably an iron catalyst, suspended in a hydrocarbon oil.

It has been found that by maintaining certain critical conditions in a catalytic hydrogenation of carbon monoxide in the presence of oil-suspended catalysts and preferably iron type catalysts, considerable increases in yield per unit of time and volume of reactor can be obtained, while at the same time appreciably increasing the yield of the more valuable or more readily marketable products of the synthesis, both on the basis of volume of synthesis gas put through the reactor as well as per weight unit of catalyst employed.

According to the invention, synthesis gas is continuously passed into a suspen-