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DRAWINGS ATTACHED

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COMPLETE SPECIFICATION

Process for the Hydrogenation of Carbon Monoxide

We, RUHRCHEMIE AKTIENGESELLSCHAFT of Oberhausen-Holten, Germany, and LURGI GESELLSCHAFT FUER WAERMETECHNIK m.b.H. of Frankfurt am Main, Germany, both German Companies 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:—

The invention relates to a process for the hydrogenation of carbon monoxide.

It is known that it is necessary in the synthesis of hydrocarbons by the hydrogenation of carbon monoxide with iron, cobalt or nickel catalysts under atmospheric pressure and at slightly elevated pressures up to about 3 atmospheres, to extract with a solvent the fixed-bed catalysts which are used in tubular or lamellar reactors, at predetermined intervals. This is necessary because of the rapid decrease in catalytic activity caused by the deposition of high boiling hydrocarbons on the catalyst surface. Many methods are known for the removal or extraction of the high boiling hydrocarbons from the catalyst. For example, a portion of the liquid synthesis products obtained in the hydrogenation may be used for the extraction of the catalyst. The moist catalyst thus extracted is dried and used again in the synthesis. Frequent extraction coupled with regeneration by hydrogen or steam is also known. This may be effected with diesel oil, particularly during the starting-up period which allows the use of low synthesis temperatures without decreasing the high $CO+H_2$ conversion.

Further suggestions are mentioned in Kainer's "Die Kohlenwasserstoffsynthese nach Fischer-Tropsch", 1950, pages 93–97. The extraction of catalysts, particularly of cobalt catalysts, effected on a large scale is also described in F. Martin, E. Weingaertner, "Die Fischer-Tropsch-Synthese".

The number of such references in the literature shows that the maintenance of catalytic activity in a process operated at atmospheric or slightly elevated pressures, by extraction with a solvent has been dealt with extensively. In general, however, the opinion has been that extractions of this kind are not necessary in an elevated pressure synthesis because operating above 8 atmospheres as there was no comparable decrease in yield. Indeed better results and a longer catalyst life in elevated pressure synthesis have been obtained in practice by not extracting the catalyst with a solvent.

It has now been found that certain modifications of the extraction process bring about unexpected improvements in synthesis product and catalyst life in an elevated pressure synthesis.

According to the invention, in a process for the catalytic hydrogenation of carbon monoxide carried out at a pressure greater than 8 atmospheres absolute, high molecular weight products of the hydrogenation or synthesis are extracted from the catalyst at intervals with a solvent for the high molecular weight products and without shutting off the synthesis gas and/or recycle gas, the solvent being fed into the synthesis zone in the liquid phase whilst its residence time in that zone is such that it does not undergo degradation or cracking. The synthesis pressure is preferably between 10 and 60 atmospheres absolute. The extraction is carried out in the synthesis reactor, preferably at intervals.

The catalyst may be sintered, fused or precipitated cobalt, nickel or iron catalyst, the preferred catalyst being an iron catalyst in a sintered or fused form.

The duration of each extraction is advantageously less than 60 minutes and preferably less than 30 minutes or even less than 15 minutes. Such short periods of extraction require the use of relatively large flows of the solvent. The surprising and unforseeable effect of this process is that catalysts extracted in this manner permit the synthesis to be carried out at temperatures which are 30–50 deg. C.

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lower than those required by the same catalysts under identical synthesis conditions when no extraction is effected. This considerable decrease in the synthesis temperature is accompanied by a surprising improvement in the synthesis product. In spite of the decrease in the synthesis temperature the catalysts extracted in accordance with the invention can be exposed to high gas loads (high space velocities) and still attain high conversion. The method in accordance with the invention offers advantages not only in the so-called "slurry synthesis", i.e. a carbon monoxide hydrogenation with the catalyst suspended in a liquid, but particularly in a synthesis operation with fixed-bed catalysts where its outstanding efficiency can be very clearly demonstrated.

The method according to the invention is applicable to a carbon monoxide hydrogenation operation carried out for the preferred production of hydrocarbons as well as to synthesis processes with the preferred formation of oxygen-containing compounds or primary aliphatic amines or mixtures of these three components.

Modern synthesis reactors for fixed-bed catalysts consist chiefly of smooth tubes of a diameter of from 20 to 100 mm., particularly about 30-60 m., and an overall length of more than 5 metres and particularly from 10 to 25 metres. These tubes are charged with the catalyst produced in the conventional manner, the catalyst being either in the unreduced or, which is particularly favourable, in the reduced form, as, for example, a sintered catalyst. When the catalyst is charged into the reactor in the reduced form, special precautions have to be observed during the charging operation, for example, the catalyst has to be charged under a protective atmosphere of carbon dioxide or nitrogen or it has to be impregnated with paraffin wax.

Such a modern synthesis reactor is started up by relatively rapidly increasing the temperature to 150°C. Following this rapid increase, the rate of temperature increase is slowed down as, for example, to 1–2 deg. C. per hour.

The synthesis pressure may preferably range between about 10 and 60 atmospheres absolute, for example, 30 atmospheres absolute. The gas load may be 750 litres of gas per litre of catalyst per hour and the recycle ratio may be 2.5 : 1 (2.5 volumes of recycle gas to 1 volume of fresh gas).

The recycling of exit gas is of advantage in many cases. The process of the invention is, however, not limited to gas recycling. Suitable synthesis gases include all gases containing carbon monoxide and hydrogen and produced by conventional gas production methods. The ratio of CO to H_2 in the synthesis gas may vary between about 2 : 1 and 1 : 10 by volume. The content of $CO+H_2$ in the synthesis gases may vary between about 30% and 100% by volume. A typical gas may contain 28% CO, 50% H_2 by volume the remainder being methane, carbon dioxide and nitrogen.

Under the specific conditions described above, namely, a synthesis pressure of 30 atmospheres absolute, a gas load of 750 v/v/hr. and a recycle ration of 2.5 : 1, the synthesis gas being the typical gas referred to, the first $CO+H_2$ conversion will be observed at temperatures in the region of 190°C.

If, under these conditions, the synthesis reaction were to be continued in the conventional manner, that is an increase in temperature at a more or less uniform rate were to be effected without solvent extraction of the catalyst, then the further increase in $CO+H_2$ conversion would be relatively slow. For example, in the case of sintered catalysts, a final conversion of about 70% $CO+H_2$ would not be reached under these conditions at a temperature of less than 280°–290°C.

The extraction in accordance with the invention is generally applied early during the initial operation. A periodic extraction of the catalyst is effected at intervals of 4 to 48 hours and preferably at intervals of 4–24 hours. As hereinbefore stated, short extraction periods are preferred, namely, an extraction period of less than 60 minutes and preferably less than 30 minutes. It is particularly expedient in many cases to use an extraction period of less than 15 minutes. The quantity of solvent to be charged to the catalyst within 5 minutes should preferably be chosen so that it is 0.04 to 0.4 times and preferably 0.1 to 0.25 times that of the catalyst volume; these figures apply to reactors having an overall length of about 10 metres. For reactors with overall lengths of about 20 metres, it is preferred to charge the catalyst within 10 minutes with a quantity of solvent which amounts to 0.04–0.4 times and preferably to 0.1–0.25 times the catalyst volume. For reactors with an overall length of about 5 metres, the quantities of solvent corresponding to 0.04 to 0.4 times and preferably to 0.1 to 0.25 times the catalyst volume are preferably charged to the catalyst within as little as 3 minutes. For reactors with overall lengths ranging between these sizes, there apply corresponding intermediate values.

The $CO+H_2$ conversion reached under the above-mentioned conditions is, for example, 70% at a temperature of 245°C.

The example shows the catalyst being contacted within a very short time with a relatively large amount of liquid, which quickly extracts the high molecular weight compounds deposited on it. Otherwise these high molecular weight compounds remain there and inhibit the synthesis reaction. The effect of the extraction is very impressively demonstrated by the increase in the carbon dioxide content of the gas leaving the reactor. This carbon dioxide value is directly related to the conversion in the synthesis reaction. It shows an increase within 20 to 60 minutes, depending upon the duration of the extraction, after which the catalyst will again reach its optimum activity.

It has furthermore been found that in a synthesis with a fixed-bed catalyst, the results are improved if the pressure drop caused by the extraction, that is by the short-time supply of relatively large quantities of solvent, is controlled in the reactor during or immediately after the extraction. A pressure drop between about 0.2 and 5 atmospheres absolute and preferably 0.4 and 2.5 atmospheres absolute results in decreased methane production and increased catalyst activity and life. As is known, reactors having an overall length of between about 10 and 20 metres and containing the catalyst in a stationary form as, for example, a catalyst in the form of spheres or small cylinders, have a resistance or pressure drop of the order of 1–10, generally about 2–5, atmospheres absolute, depending upon the mechanical properties of the catalysts and the gas rate, type of gas, recycle ratio and other factors. The figures given for the pressure drop caused by the extraction are to be understood as being in addition to the normal pressure drops observed in the catalyst bed when no extraction is being carried out. This "pressure extraction" of the catalyst effects a particularly rapid and substantially complete removal of the polymerized products adhering to the surface of the catalyst so that maximum activity of the catalyst is restored immediately or shortly thereafter.

The extraction can be effected with the conventional solvents used in this type of synthesis carried out at atmospheric pressure. Use is preferably made of liquids obtained in the carbon monoxide hydrogenation itself and containing not less than 50% by weight of compounds boiling above 180°C. as, for example between about 180°C. and 320°C. and preferably between about 200°C. and 260°C.

The solvent is, for example, withdrawn from the so-called intermediate separator, an air-cooled separator generally provided downstream of what is known as the hot-separator of the synthesis unit. The location of this intermediate separator is, for example, upstream of the heat exchangers and the condensation unit proper, that is, upstream of the position where separation of the liquid synthesis products by water cooling is effected. Naturally, the product withdrawn from this intermediate separator does not exclusively comprise the usual boiling range of a diesel oil fraction but contains also considerable proportions, for example, 10–20% by weight of compounds boiling above 320°C. and also substantial proportions of lower boiling compounds, that is, compounds boiling below 180°C. Although a product with such a wide boiling range is used for the extraction, it is observed that the effect of the extraction is surprisingly even more favourable in many cases than that obtained when using the diesel oil fraction boiling between about 180°C. and 320°C. such as is generally used in the art.

The boiling range of the solvent is of considerable importance for the effect of the process. Solvents consisting of low molecular weight hydrocarbons, that is, such as those of the gasoline fraction, are not very suitable. Good results were found to be obtained when the oils used as solvents, preferably products obtained in the carbon monoxide hydrogenation itself, include by weight at least 50% and preferably more than 75% of fractions boiling between about 180°C. and 320°C. and preferably between about 200°C. and 260°C. The presence of oxygen-containing and/or nitrogen-containing compounds in all fractions, even to the extent of more than 10% by weight, is not detrimental to the process of the invention. It is unfavourable, however, if the solvent has too high a content of constituents boiling above 320°C. since obstructions in the conveying equipment and line can occur by flocculated soft and hard paraffin wax, especially at fluctuating temperatures, and cause breakdowns. Moreover, the extraction efficiency is more or less reduced thereby.

It has been found, for example, that only a poor extraction efficiency is obtained with a solvent which is derived from the cold-separator of a synthesis unit and therefore represents a synthesis product which, after extensive separation of the high molecular weight hydrocarbons and the hydrocarbons boiling in the diesel oil range, includes products of the gasoline fraction. A product of this kind had, for example, the following composition:—

Boiling up to 180°C.	64%	by weight
180°–320°C.	30%	,,
320°–460°C.	5%	,,

In contrast to this, good results can be obtained with a solvent derived from the intermediate separator of the synthesis unit and having about the following boiling range:—

Up to 180°C.	18%	by weight
180°–320°C.	57%	,,
320°–460°C.	23%	,,
above 460°C.	2%	,,

Even better extraction efficiency can be obtained with the use of a product derived directly downstream of the intermediate separator. One example of such a product had the following composition:—

Up to 180°C.	12%	by weight
180°–320°C.	80%	,,
320°–460°C.	8%	,,
above 460°C.	—	

In the hydrogenation of carbon monoxide, the synthesis products which may consist of hydrocarbons mixed, as the case may be, with oxygen-containing organic compounds are preferably withdrawn in one or several series-connected tanks filled with suitable packing such as Raschig rings and located downstream of the hot-separator. Usually the hot-separator is immediately downstream of the synthesis reactor. The gas is passed through these tanks in an upward direction and leaves them at the top. The presence of packing in the tanks and the upward flow of the gas, effect a rectification which produces an oil suitable for use as a solvent. Its content of low boiling and high-boiling compounds, that is, compounds boiling outside the range 180°C. to 320°C. is about 20% of each and it is desirable that it should be less. This kind of separation and recovery of solvent has been found to be particularly applicable since the process of the invention requires a solvent in which the proportion of compounds boiling below 180°C. and compounds boiling above 320°C. is less than 10% each. A solvent of this kind can very simply be recovered in the manner described directly from the condensation system for the synthesis products without additional rectifying equipment. The extraction efficiency obtained when using this solvent was at least as good as that with a diesel oil fraction boiling between 200°C. and 280°C.

It appeared during the course of extended periods of operation that, in certain circumstances, a very slight decrease in the conversion occurs after a certain time and may become more pronounced upon continuing the operation. It has been found advantageous in this case, as soon as the decrease in conversion becomes perceptible, to effect one or several extractions preferably in succession, for example, of twice the duration and correspondingly, double the quantity of solvent. By this measure, a substantially complete regeneration of the catalyst is attained. The small amounts of high molecular weight products which have accumulated on the catalyst surface in spite of the routine extractions of the invention, are completely removed.

It can hardly be avoided that small amounts of the water produced in the synthesis remain in the product and are condensed, for example, in the intermediate separator. This quantity is generally not sufficiently large to separate so it remains dissolved in the solvent. If particular circumstances cause separation, the lower, acqueous phase must be removed since it may have an adverse effect on the catalyst activity. The content of water in the solvent should not exceed 3% by weight. It is advantageously below 2% and preferably below 1% by weight.

The temperature at which the solvent is charged to the catalyst is of no practical importance with regard to the extraction efficiency. It may be at room temperature, but, in general, it should be somewhat warmer, say 30°–80°C. or higher. Care should only be taken that the relatively large amount of liquid charged to the reactor in so short a time does not cool the synthesis reactor unduly.

The method in accordance with the invention offers the advantage that if products from the synthesis itself are used as solvent, the pump used for feeding the solvent need only overcome the pressure difference between the reactor outlet and inlet. With the previous working methods and particularly when using oil from another source as solvent, the feed pump had to force the solvent at normal pressure into the reactor at pressures somewhat higher than the synthesis pressure.

It is not necessary to discontinue the synthesis operation during the extraction. The quantity provided of extraction oil is pumped over the catalyst within the time provided while the synthesis is proceeding.

It is not desirable for the intervals between extractions to be too long. In the process according to the invention, several reactors can be extracted in succession with only one pump.

The process in accordance with the invention is also applicable to a carbon monoxide hydrogenation operated with a fluidized catalyst bed or a moving bed catalyst. As is known, one difficulty of these two types of synthesis consists in that the dust-like catalyst frequently has the tendency to cake or agglomerate with the smaller amounts of paraffin wax whose formation is almost unavoidable. This may cause more or less pronounced collapsing of the fluidized bed and disturb the synthesis operation. When using the process of the invention in these types of synthesis it is advantageous to effect purification of the catalyst surface by spraying the solvent. Thereby, small residues of high molecular weight compounds are removed from the catalyst surface in the single operation so that the deposition of paraffin wax which results in the troublesome caking mentioned above, no longer occurs.

It is possible to work in a similar manner to that described for fixed-bed catalysts in the liquid phase synthesis.

Two methods of carrying out the process of the invention are diagrammatically illustrated by way of example in the accompanying drawings, in which

Figure 1 illustrates the process when carried out with a fixed-bed catalyst, and

Figure 2, illustrates the process when carried out as a liquid-phase synthesis, that is to say, with the catalyst suspended in a liquid.

In Figure 1, fresh synthesis gas enters through line 4 and is fed by a pump 5 through line 7 into line 9 in which it is mixed with recycle gas which is fed through line 8 by a pump 6, the mixture of fresh synthesis gas and recycle gas passing from line 9 into a reactor 10 containing a fixed-bed catalyst (not shown). The synthesis products leave the reactor 10 through line 11 and pass into a hot separator 12 surrounded by a steam jacket 13 into which steam is fed at a pressure of 2.3 atmospheres. High boiling products condense in the separator 12 and are removed through line 20. The uncondensed material passes through line 14 into a warm separator 15 packed with Raschig rings, in which separator intermediate boiling products are condensed, the intermediate boiling products being drawn off at 21. The products still in the gaseous phase pass through line 16 into a condenser 17 and a cold separator 18 from which low boiling products are drawn off at 22. Gas leaves the cold separator 18 through line 19, part being withdrawn from the system through line 26 and part being recycled by the pump 6 through line 8.

A part of the intermediate product condensed in the warm separator 15 is drawn through line 23 by a pump 24 to be passed through line 25 at intervals into the reactor 10, as the solvent to extract the catalyst.

In Figure 2, fresh synthesis gas enters through line 30 and is passed by a pump 31 through lines 32 and 33 into a synthesis reactor 34 in which the catalyst is suspended in a liquid medium. Recycle gas is mixed with fresh gas in the line 33, the recycle gas being fed through line 35 by a pump 36.

A part of the liquid in the reactor 34 passes through a filter 52 and a line 53 into a hot separator 54 in which high boiling products are condensed and removed through line 55 whilst uncondensed material passes out through line 56.

The remainder of the synthesis products are withdrawn in gaseous form from the reactor 34 through line 37 and are passed into a warm separator 38 packed with Raschig rings. A part of the intermediate boiling product which condenses in separator 38 is removed through line 39 while another part is passed at intervals through line 40, pump 41 and line 42 back into the reactor as the solvent to extract the catalyst.

Uncondensed gas leaves the warm separator 38 through line 43 and passes into a condenser 44 and then through line 45 into a cold separator 46 from which the low boiling synthesis products are removed through line 47. Uncondensed gas leaves the cold separator through line 48, part being drawn through line 49 by the pump 36 for recycling, the remainder passing out through the line 50.

The reactants fed into the synthesis reactor may comprise carbon monoxide and water vapour or steam. In this case, the steam reacts with part of the carbon monoxide, with the aid of the catalyst present, to produce carbon dioxide and hydrogen and it is the constituents of the gas mixture so produced which are the starters for the synthesis reaction proper.

The process of the invention is illustrated by the following examples.

Example 1

100 parts of iron and 25 parts of copper, both in powder form and in the highest oxidation state, were intimately mixed with 10 parts of ZnO on a rotating plate and then mixed with crushed potassium carbonate in a ball mill and thoroughly stirred. The mixture contained 4 parts of K_2O in the form of potassium carbonate per 100 parts of iron. Water was slowly added by spraying and a spherical product obtained which, by means of a vibrator, was scived to a particle size of between 2 and 3.5 mm. Oversize particles were crushed and recycled; undersize particles were returned to the rotating plate.

The sieved particles were dried for 24 hours at 120°C. which practically completely removed the water.

Following this, the particles were sintered for 30 minutes at 1150°C. This was followed by a reduction at 350°C. effected for 4 hours with a H_2/N_2 mixture at a flow velocity of 1.5 metres/second measured linear and cold. The reduction value or the percentage of free iron (based on total iron) in the catalyst was thereafter about 95%.

8 litres of this catalyst were placed in a vertical reaction tube of 32 mm. inside diameter and 10 metres length. A synthesis gas including by volume about 27% of carbon monoxide, 54% of hydrogen, the remainder being methane, carbon dioxide and nitrogen, was charged at a rate of 500 volumes of gas per volume of catalyst per hour. The synthesis pressure was 30 atmospheres absolute. Part of the tail gas was recycled to give a recycle ratio of 2.5 : 1.

The catalyst was taken into operation in a careful manner. The $CO+H_2$ conversion was about 50% after 170 hours and about 60% after 250 hours. At 265°C., 70% conversion was attained. The production of methane was 18% by volume of theoretical yield, and the consumption ratio, that is, the ratio in which the carbon monoxide and hydrogen combined, was 1.45.

After about 1000 hours, a gas having carbon monoxide : hydrogen in a ratio of 1 : 3 by volume was used instead of the gas mentioned above. During this stage of the run, the reaction temperature was increased by 2 deg. C. The $CO+H_2$ conversion was about 68%, the volume of methane produced was 20–21% of the theoretical yield and the consumption ratio was about 2.0.

After 2000 hours, the catalyst was extracted at atmospheric pressure first using diesel oil as solvent at about 200°C. and then a gasoline fraction at about 120°C. After having taken the catalyst again into operation, a $CO+H_2$ conversion of 68% was reached at a temperature of only 230°C. However, within 6 days an increase in temperature by 35 deg. C. had to be effected to maintain the conversion at this level. No intermediate extractions had been effected.

After 2300 hours, the catalyst was again extracted at atmospheric pressure in the manner described above and thereafter again taken into operation under the previous conditions at 230°C. In addition, the catalyst was continuously sprayed with diesel oil at a rate of 100 c.c of diesel oil per hour. In spite of this measure, a continuous increase in temperature had to be effected in order to keep the CO conversion at the initially observed level of about 70%. Also in this case, the final temperature was about 265°C.

After 2500 hours, another extraction of the catalyst was effected in the same manner as at the 2000th hour. Thereafter, the catalyst was again taken into operation at 230°C. under the previous conditions except that a gas having $CO : H_2$ volume ratio of 1 : 2 was now used as at the beginning of the run. Moreover, periodic extractions were effected at intervals of 12 hours, each extraction lasting 5 minutes and being carried out with 1.5 litres of diesel oil (boiling between 200°C. and 260°C.) without shutting down the synthesis operation. Under these conditions, a $CO+H_2$ conversion of about 72% was obtained at 230°C. while the volume of methane decreased to 14% of the theoretical yield. The consumption ratio remained between 1.5 and 1.6.

After 2800 hours the gas load was increased to 750 litres of fresh gas per litre of catalyst per hour. The synthesis pressure remained at 30 atmospheres absolute. The reaction temperature was increased to 245°C. The recycle ratio was 2 : 1.

Under these conditions, a constant $CO+H_2$ conversion of 71% was maintained up to the 3500th hour. The volume of methane produced was about 16% of theoretical yield and the consumption ratio was about 1.4.

During this time, periodic extractions were effected at intervals of 8 hours, each extraction lasting 10 minutes and being carried out with 1000 cc. of diesel oil.

Upon the termination of this step of the run, the operation was continued under the previous conditions except that the extractions effected at the same intervals were now carried out with a product derived from the synthesis itself. For example, between the 3700th and 3800th hour there was used a synthesis product which showed that no separation of wax at room temperature and included 18% by weight of constituents boiling up to 180°C. During this period of 100 hours, no change of the synthesis results with regard to conversion, production of methane, consumption ratio and temperature range occurred.

Following this, the extractions were effected with a synthesis product which, in contrast to that mentioned in the preceding paragraph, contained about 30% of constituents boiling below 180°C. In this case the $CO+H_2$ conversion decreased from about 71% to 65% while maintaining the previous extraction conditions.

After this step of the run, a diesel oil fraction boiling between 200°C. and 260°C. was again used for the extraction. The $CO+H_2$ conversion did not change and remained between 70% and 71% and the volume of methane produced remained between 14% and 16% of the theoretical yield.

After a total of 4000 hours of operation, the run was terminated because of a breakdown and the catalyst was extracted in the reactor at normal pressure in the manner described for the first extraction.

Thereafter, the catalyst was started up again at a gas load of 1000 litres per litre of catalyst per hour, a recycle ratio of 2 : 1 and a pressure of 30 atmospheres using a synthesis gas having a $CO : H_2$ volume ratio of 1 : 2. From the beginning of actual synthesis, periodic extractions were effected at intervals of 8 hours, each extraction lasting 13 minutes and being effected with 2.5 litres of diesel oil.

Under these conditions, a $CO+H_2$ conversion of about 64% was obtained at 255°C. The volume of methane produced was 14% of the theoretical and the consumption ratio was about 1.38.

When the extractions were effected at intervals of 6 hours with the individual extractions lasting 6 minutes and each being carried out with 1.3 litres of diesel oil, an increase in $CO+H_2$ conversion to about 71% was reached while maintaining the previous synthesis temperature. The volume of methane produced was between 15% and 16% of the theoretical, the consumption ratio being 1.4. The run was operated under these conditions up to the 7000th hour without any change of the temperature range and the synthesis results. Thereafter, it was discontinued in order to have the synthesis tube available for a new experiment.

Example 2

A catalyst mass was precipitated by adding a sufficient quantity of a boiling solution of the nitrates of iron and copper in a ratio of 100 Fe : 5 Cu to a boiling soda solution to obtain a pH value of 7. This catalyst mass was then washed with hot distilled water to a residual alkali content of about 0.3% calculated as weight percentage of K_2O based on the weight of iron present. This washed mass was suspended in distilled water at room temperature and mixed with a solution of potassium waterglass (potassium silicate) containing sufficient silicic acid as to give 25 parts of SiO_2 per 100 parts of Fe. Sufficient nitric acid was then added to give, after filtration, a residual alkali content of 5% calculated as above. The mass was superficially dried, shaped in suitable equipment into small cylinders of 3.5 mm. diameter and subsequently dried for 24 hours at 105°C. After this about 8% water remained.

After sieving to a particle size of between 1.5 and 4 mm. this catalyst was reduced for 60 minutes at 230°C. with a mixture consisting of 75% H_2 and 25% N_2 by volume using a flow velocity of about 1.5 metres/second. The percentage of free iron (based on total iron) in the catalyst was then 26%. 8 litres of the reduced catalyst were carefully charged into a synthesis tube of 10 metres length and 32 mm. inside diameter under a protective atmosphere of carbon dioxide and the catalyst was taken into operation with a synthesis gas containing 85% by volume of carbon monoxide and hydrogen in a ratio 1 : 1.7. The synthesis pressure was 25 atmospheres absolute, the recycle ratio was

2.5 : 1 and the gas load was 500 litres of gas per litre of catalyst per hour.

After careful starting-up for a period of about 120 hours, a $CO+H_2$ conversion of 72% was obtained at a temperature of 220°C. The volume of methane produced at this time was about 5% of theoretical yield and the consumption ratio was about 1.5.

Under these conditions, the catalyst was operated for 2½ months. Thereafter, a gradual increase in temperature became necessary in order to compensate for a slow decrease in activity. After a total of 8000 hours on stream, the final temperature was 264°C., the $CO+H_2$ conversion was about 68% and the volume of methane produced had increased to 30% of the theoretical.

After this time, the catalyst was extracted at atmospheric pressure under the conditions used at the 2000th hour in Example 1 and thereafter taken again into operation under the previous conditions. From this time, diesel oil in amount of 1.3 litres was charged in the space of 6 minutes to the catalyst every four hours. After starting-up in a careful manner, a $CO+H_2$ conversion of 70–71% was obtained at a reaction temperature of 230°C. Thus, the reaction temperature was now 40 deg. C. lower than the temperature after an operating time of 8000 hours. The volume of methane which was at that time 30% of the theoretical decreased to 12–14%, and the consumption ratio had increased from 1.4 to 1.5. These results were ascertained in the 8300th hour of operation.

It was found that the number of extractions could be reduced from 6 to 3 per day without encountering a change in the synthesis results. However, a temporary extension of the interval between two successive extractions from 8 to 24 hours resulted in a decrease in conversion to 66%. Thereafter, the operation was continued with 3 extractions per day.

After 8700 hours on stream, the number of extractions was decreased to 2 per day, each extraction being carried out with 1.3 litres of diesel oil which was charged in 5 minutes. The synthesis results remained practically constant.

After an operating period of 9600 hours, a product derived from the synthesis operation itself was used as solvent instead of the diesel oil used so far. This product contained about 10% by weight of constituents boiling below 180°C. and about 10% by weight of constituents boiling above 320°C. The extraction times and intervals remained unchanged, namely 5 minutes and 12 hours respectively, and so did the percentage conversion. The volume of methane produced was about 10–12% of the theoretical. Under these conditions, the run was continued for months without the necessity of any increase in temperature or other change in the synthesis conditions.

For comparison, the following figures may be given: When conducting the synthesis in known manner without solvent extraction of the catalyst, a reaction temperature of 230°C. was reached after 3500 hours. The $CO+H_2$ conversion was 71% and the volume of methane produced was 14–15% of the theoretical. During the following weeks, a gradual increase in temperature had to be effected so that 240°C. was reached after a total of 2500 operating hours. At that time, the $CO+H_2$ conversion was unchanged at about 70%. The volume of methane produced had, however, increased to 20% of the theoretical.

Thus, within a period of time of 2100 hours, corresponding to 3 months, an increase in temperature of 10 deg. C. was required in normal synthesis operation without solvent extraction of the catalyst while the volume of methane produced increased from about 14% to 20% of the theoretical. In contrast to this, an increase in temperature was not required for a period of 3 months upon operating in accordance with the invention with a catalyst which immediately beforehand had been used for 11 months in normal synthesis operation without extraction. The reaction temperature could be kept unchanged at a level of 230°C. The volume of methane produced remained likewise unchanged at a level of 12% of the theoretical and was thus surprisingly lower than at the time when the corresponding formation of methane was determined at 230°C. in normal operation. The boiling ranges of the gaseous and liquid products after about 3500, 5600 and 9900 hours, respectively, indicated compositions by weight as follows:—

		3500 *hrs.*	5600 *hrs.*	9900 *hrs.*
C_2-C_4	..	16%	23%	18.5%
C_5–C_{10}	..	40%	46%	37.5%
C_{11}–C_{18}	..	24%	18%	22.5%
above C_{18}	..	20%	13%	21.5%

The olefin content of the several fractions was as follows:—

C_2-C_4	..	50%	45%	58%
C_5–C_{10}	..	60%	57%	65%
C_{11}–C_{18}	..	45%	42%	59%
above C_{18}	..	—	—	—

WHAT WE CLAIM IS:—

1. A process for the catalytic hydrogenation of carbon monoxide carried out at a pressure greater than 8 atmospheres absolute, in which high molecular weight products of the hydrogenation or synthesis are extracted from the catalyst at intervals by means of a solvent for the high molecular weight products and without shutting off the synthesis gas and/or recycle gas, the solvent being fed into the synthesis zone in the liquid phase whilst its residence time in that zone is such that it does not undergo degradation or cracking.

2. A process according to claim 1, in which the synthesis pressure is between 10 and 60 atmospheres absolute.

3. A process according to claim 1 or claim 2, in which the catalyst is an iron catalyst in a sintered or fused form.

4. A process according to any one of the

preceding claims, in which the extraction is effected at intervals of not more than 48 hours.

5. A process according to any one of the preceding claims, in which the duration of each extraction is less than 60 minutes.

6. A process according to any one of the preceding claims, in which the duration of each extraction is less than 15 minutes.

7. A process according to any one of the preceding claims, in which the catalyst is present as a fixed-bed.

8. A process according to claim 7, in which with a reactor having an overall length of about 10 metres, the quantity of the solvent which is passed over the catalyst in 5 minutes is from 0.04 to 0.4 times the volume of the catalyst.

9. A process according to claim 7, in which with a reactor having an overall length of about 20 metres, the quantity of solvent which is passed over the catalyst in 10 minutes is from 0.04 to 0.4 times the volume of the catalyst.

10. A process according to claim 7, in which with a reactor having an overall length of about 5 metres, the quantity of solvent which is passed over the catalyst in 3 minutes is from 0.04 to 0.4 times the volume of the catalyst.

11. A process according to any one of claims 7 to 10, in which the solvent is charged at such a rate that a pressure drop, across the fixed-bed catalyst, of between 0.2 and 5 atmospheres absolute is present during or immediately after extraction, in addition to the pressure drop observed in the synthesis operation when no extraction is taking place.

12. A process according to any one of the preceding claims, in which the solvent consists of hydrocarbons and/or other liquids obtained by the hydrogenation of carbon monoxide, the solvent including more than 75% by weight of compounds boiling between 180°C. and 320°C.

13. A process according to claim 12, in which more than 75% by weight of the compounds boil between 200°C. and 260°C.

14. A process according to any one of the claims 1 to 6, in which a fluidized or moving bed catalyst is used, the extraction of the catalyst being effected by spraying it with the solvent.

15. A process substantially as hereinbefore described with reference to Example 1 or Example 2.

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845559 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

FIG.1.

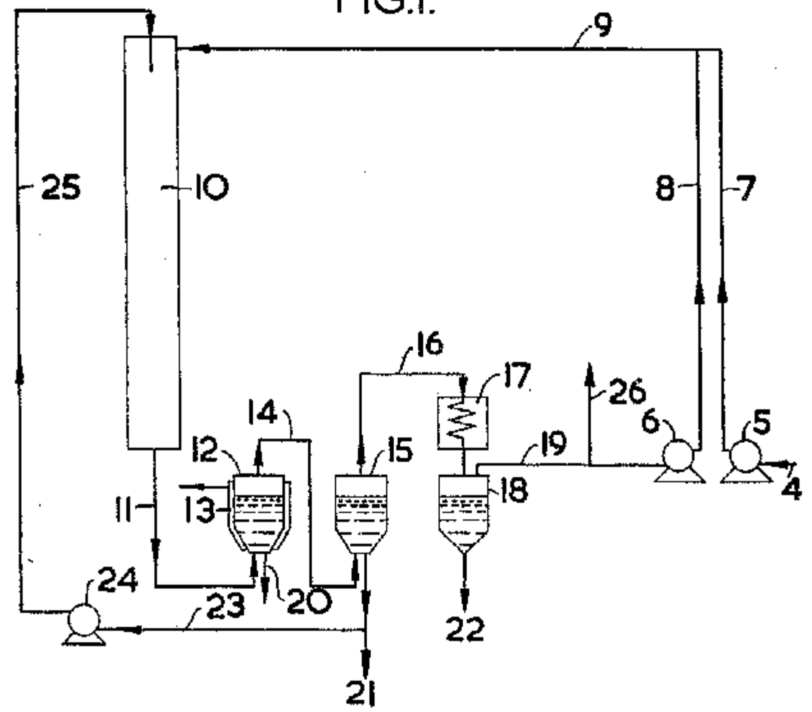

FIG.2.