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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 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 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 been found that a modification of the extraction process brings about unexpected improvements in synthesis product and catalyst life in an elevated pressure synthesis. This modification is described in the co-pending Application No. 5691/60 (Serial No. 845559), the subject-matter of which has been divided out of the present Application. That co-pending Application claims 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.

When a synthetic diesel oil fraction obtained by the catalytic hydrogenation of carbon monoxide was used as the solvent, it was noticed that the amount of methane formed in the synthesis became higher and that, particularly with sintered catalysts, there was an appreciable decrease in the olefin content of the synthesis products. It was found that this undesirable effect arose from acids present in the solvent.

According to the present invention, in a process for the catalytic hydrogenation of

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carbon monoxide carried out at a pressure greater then 3 atmospheres absolute, preferably between 10 and 60 atmospheres absolute, the catalyst is extracted, without shutting-off the synthesis gas and/or recycle gas, with an oil which has been synthesised by the catalytic hydrogenation of carbon monoxide and which has been treated with an alkaline material before use. The amount of alkaline material may be in excess of, for example from 10 to 50 times, the stoichiometric amount required to neutralise the oil.

Practically any alkaline-reacting material may be used for neutralizing the free acids present. Of particular advantage, however, is the use of the oxides including magnesium oxide, the hydroxides, the carbonates and the bicarbonates of alkali and alkaline earth metals. Ammonia may also be used in certain instances.

The treatment with alkalis is not limited to the use of aqueous solutions. With aqueous solutions however, the extraction oil may be passed upwardly through a suitable column in countercurrent to the aqueous alkali solution, or the extraction oil and aqueous solution may be contacted with each other in another manner, for example, in a vessel provided with a stirrer.

Particularly favourable operation is possible however, if the alkaline compounds are used in solid form. The extraction oil may, for example, be trickled over the solid material packed in a column or tower, or the oil and solid material may be stirred together after which the extraction oil is allowed to settle and is thereafter used.

It is not always necessary to neutralize all of the acids contained in an extraction oil. For example, an oil with a neutralization number of 35 has been used satisfactorily for extraction after treatment with alkali equivalent to only 7 neutralizing, that is, as little as 20% of the acid. The neutralization number is the number of milligrams of potassium hydroxide required to neutralize completely 1 gram of oil. It is generally sufficient to use an oil with a neutralization number of about 3–20 and preferable 5–15.

The catalyst employed in the synthesis may be an iron, cobalt or nickel catalyst, an iron catalyst, particularly a fused or sintered catalyst, being preferred.

The extraction oil 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 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 portions, for example, 10–20% by weight, of compounds boiling above 320°C. and also substantial portions of lower boiling compounds, that is, compounds boiling below 180°C. Although a product with such a wide and hitherto unused boiling range was used for the extraction, it could be 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. and generally used in the art.

The boiling range of the extraction oil is of considerable importance for the effect of the process. Extraction oils 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 for the extraction contained at least 50% and preferably more than 75% by weight of compounds boiling between about 180°C. and 320°C. and preferably between about 200°C. and 260°C. The extraction oil should not have too high a content, preferably less than 10% by weight, of constituents boiling above 320°C. since obstructions in the conveying equipment and line can occur by flocculated soft and hard paraffin, 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 an extraction oil 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 could be obtained with an extraction oil 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 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 packings such as Raschig rings and located downstream of the hot-separator which, in the case of normal condensation, is arranged downstream of the synthesis reactor. The gas should be passed through these tanks in an upward direction. The presence of packing in the tanks and the upward flow of the gas effect a rectification effect which produces an oil suitable for use as an extraction oil. Its content of low boiling and high boiling compounds, that is, compounds boiling outside its range 180°C. to 320°C. is about 20% by weight of each and it is desirable that it should be less. This kind of separation and recovery of extraction oil has been found to be particularly good since the process of the invention requires an extraction oil in which the proportion of compounds boiling below 180°C. and compounds boiling above 320°C. should each not exceed about 10% by weight. An extraction oil of this kind could very simply be recovered in the manner described directly within the condensation system for the synthesis products without additional rectifying equipment. The extraction efficiency obtained when using the extraction oil thus obtained was at least as good as the efficiency obtained when using a Diesel oil fraction obtained by distillation and boiling between 200°C. and 280°C.

The process is not only applicable to a carbon monoxide hydrogenation operation which results in the preferred production of hydrocarbons but also to synthesis processes directed to 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. and preferably about 30–60 mm. 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, preferably, in the reduced form, as, for example, a sintered catalyst. When the catalyst is charged in its reduced form, precautions have to be observed in 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 degrees C. per hour

The synthesis pressure may 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 per 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 are 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 conditions described above, namely a synthesis pressure of 30 atmospheres absolute, a gas load of 750v/v/hr. and a recycle ratio 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 carrying out an extraction, 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% would not be reached under these conditions at a temperature of less than 280°–290°C.

Except where highly active precipitated catalysts are being used, extraction is started fairly early during the initial operation. With a fixed-bed catalyst in particular, extraction of the catalyst is effected at intervals of 4 to 48 hours, preferably at intervals not greater than 24 hours.

Short extraction periods are preferred, namely periods 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 volume of extraction oil charged to the catalyst within 5 minutes should preferably be chosen so that it is 0.01 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 volume of extraction liquid 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 volume of extraction oil corresponding to 0.04 to 0.4 times and preferably to 0.1 to 0.25 times the catalyst volume is 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 above example shows the catalyst being contacted with a relatively large amount of liquid, which quickly removes by extraction the high molecular weight compounds deposited on it. Otherwise these high molecular weight compounds remain there and inhibit the synthesis reaction. The effect of this measure according to the invention is very impressively demonstrated by the increase in the carbon dioxide content of the gas leaving the reactor. This carbon dioxide value is directly connected with the conversion in the synthesis reaction. It shows an increase within 20 to 60 minutes, depending upon the duration of the extraction, after which time the catalyst will reach again its optimum activity.

Furthermore, in the case of 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 extraction oil is controlled in the reactor during or immediately after the extraction. A pressure drop ranges between about 0.2 and 5 atmospheres absolute and preferably 0.4 and 2.5 atmospheres absolute, results in 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 depending upon the mechanical properties of the catalysts and the gas rate, type of gas, recycle ratio and other factors. The figures given above are understood to be in addition to the normal pressure losses observed in the catalyst bed when no extraction being carried out. This "pressure extraction" of the catalyst effects a particularly rapid and substantially complete removal of the high molecular weight products adhering to the surface of the catalyst so that the activity of the catalyst is restored immediately or shortly thereafter.

During the course of extended periods of operation, a very slight decrease in the conversion may occur 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 perferably in succession, for example, of twice the duration and double the quantity of extraction oil. By this measure, a substantially complete regeneration of the catalyst is attained. The small amounts of higher molecular weight products which have accumulated on the catalyst surface in spite of the routine extractions, are completely removed.

It can hardly be avoided that small amounts of 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 oily product. If particular circumstances cause separation, the lower aqueous phase must be removed since it may have an adverse effect on the catalyst activity. The content of water in the extraction oil should not exceed 3% by weight; it is advantageously less than 2% by weight and preferably below 1% by weight.

With highly active precipitated catalysts stationarily arranged in tubes, the extraction has caused difficulties in particular cases. Such highly active precipitated catalysts are carrierless or contain only less than 30 parts of carrier material and preferably less than 15 parts of carrier material based on the iron or other catalyst metal present. These catalysts are substantially more active than sintered or fused catalysts of similar composition. They permit the synthesis to be carried out at temperatures which are too low for fused or sintered catalysts, especially at elevated gas loads such as 500 volumes of gas per volume of catalyst per hour. The operation of the synthesis with extraction, from the beginning of the use of a fresh catalyst, proved impossible to carry out successfully. The increase in activity caused by the extraction resulted in an increase in conversion that failures in the catalyst at the gas inlet side, partially accompanied by increased resistance in the synthesis tubes, followed.

These difficulties can be avoided by operating the highly active precipitated catalysts for an extended period before subjecting them to an extraction.

The precipitated catalysts are operated in the synthesis unit under the usual conditions, for example, at gas loads of between about 100 and 1000 volumes of gas per volume of catalyst per hour and preferably 250–750 volumes of gas per volume of catalyst per hour and synthesis pressures of between 5 and 50 atmospheres and preferably between 10 and 40 atmospheres. It is possible to work with once-through operation or with recycling using, for example, a recycle ratio of 1 : 1 to 5 : 1. Since the timing of the initial extraction is partially dependent upon the $CO+H_2$ conversion, the $CO+H_2$ conversion should not for this reason be too low, keeping above 60% and preferably above 70%. Highly active precipitated catalysts may, for example, be operated under the conditions mentioned above between about 210°C. and 230°C. without subjecting them to extraction.

If the highly active precipitated catalysts are operated for months and any slight decrease in conversion is compensated by an increase in temperature, the temperature reached after a given operating period depends upon the percentage conversion maintained during this time. If, for example, the $CO+H_2$ conversion is set at 80%, temperatures in the region of 250°C. will be reached after about 4 months. When operating with a conversion of about 70–75%, the same temperatures are reached after 5–6 months. Too long an operating period under the usual synthesis conditions without extraction is not advantageous since the production of methane will reach a level which is undesirable from the economic and technical point of view, for example, 15% of the theoretical yield.

After the said 4 or 5–6 months, the periodic extractions are started. At first, the final reaction temperature is lowered by about 20–30 degrees, in order to avoid any troubles in the synthesis operation. The extraction is then effected in a careful manner. It is preferred to use an extraction time of about 10–20 minutes and a quantity of extraction oil of about 15–20% by volume based on the catalyst contained in the reactor. Naturally, the quantity of extraction oil is dependent upon the type of catalyst and the boiling range of the synthesis products. A catalyst for the production of paraffin wax will require more extraction oil than one which gives a higher yield of gasoline.

The number of extractions is determined by the boiling range of the primary products of the particular catalyst. It was possible, for example, to maintain a constant $CO+H_2$ conversion of above 80% with only one extraction after each 6–7 operating days. In many cases, however, the intervals between the extractions have to be shortened to 48–72 hours and in special cases even to 24 hours.

Under the extraction conditions stated above, the temperature is adjusted so as to obtain the $CO+H_2$ conversion desired which is in general about 60% and preferably above 70%. This operating temperature is maintained until a slight decrease of the conversion occurs. This will not generally occur for several months, for example, 3–6 months, after the beginning of the first extraction. It is preferred not to further increase the reaction temperature at this time but to use somewhat more severe extraction conditions, for example, by reducing the extraction time, increasing the quantity of extraction oil or increasing the number of extractions. It is also possible, however, to combine these measures. The synthesis temperature is not normally raised until all these measures have been applied.

This method of working with highly active precipitated catalysts allows very long operating periods of, for example, 12, 18 or 24 months without the large increase in the production of methane and corresponding decrease in the yield of directly usable compounds, as found in normal operation after 6–8 months.

The temperature at which the extraction oil 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, for example, 30–80°C. or higher. The relatively large amount of liquid charged to the reactor in so short a time should not, however, be allowed to cool the synthesis reactor unduly.

If the extraction oil is derived from the synthesis itself, the pump used for feeding the extraction oil need only overcome the pressure difference between the reactor outlet and inlet. With the previous methods using oil from another source, the feed pump had to force the extraction oil at normal pressure into the synthesis reactor at pressures somewhat higher than the synthesis pressure.

Intervals between the extractions must not be too long. The working method in accordance with the invention offers the possibility of extracting several reactors in succession with only one pump.

The invention provides the possibility of greatly improving the synthesis conditions. Thus, a highly active precipitated catalyst which, after 3½ months operation without having been treated in accordance with the invention, gave a $CO+H_2$ conversion of about 65% (volume of methane: 20% of theoretical yield) at a load of 500 litres of synthesis gas per litre of catalyst per hour and a synthesis temperature of 268°C. Extraction according to the invention at that stage restored the $CO+H_2$ conversion to more than 70% (methane volume: 13–15% of theoretical yield). The temperature was only 245°C. and the load 750 litres of synthesis gas per litre of catalyst per hour. This significant and completely unexpected effect suggests the possibility of increasing the catalyst life to an usual extent and maintaining high gas loads. Total catalyst service times of 1–2 years or more appear to be possible.

The process of the invention is not limited to a carbon monoxide hydrogenation with fixed-bed catalysts. It is also applicable to a method in which a catalyst suspended in a liquid is used. This method of carrying out the synthesis is variously termed "wet synthesis", "slurry synthesis", "jiggling-bed synthesis" or "liquid phase synthesis". Extensive studies showed that, in a wet synthesis, the suspending oil originally used is discharged with the reaction products within a relatively short time and that thereafter an equilibrium exists between chiefly high molecular weight products and relatively small amounts of low boiling products. Owing to the preponderant presence of high molecular weight compounds, the solvent effect on the high molecular weight compounds present on the catalyst surface is relatively poor. The continuous or intermittent supply of extraction oil causes a considerable decrease in the percentage of high molecular weight compounds in the liquid phase and a simultaneous increase in the proportion of low boiling compounds, for example, in the fraction boiling between about 320°C. and

380°C. and preferably in the fraction boiling between 180°C. and 320°C. The result is that the liquid phase continuously dissolves the high molecular weight compounds present on the catalyst and continuously regenerates its activity. Thereby, as with the fixed-bed catalysts, a high activity is maintained at surprisingly low temperatures giving a high $CO+H_2$ conversion with low methane production with a high gas load. In contrast to the synthesis with fixed-bed catalysts, it is possible in the synthesis effected in a liquid medium to carry out the extraction continuously that is, to bring about the same effect by the continuous supply of small amounts of extraction oil as that obtained by intermittently feeding larger amounts. In this continuous operation the volume of extraction oil changed per hour is 0.1–100%, advantageously 0.5–25% and preferably 0.5–10% of the volume of the reaction space. The extraction oil is preferably introduced at the bottom of the reactor.

Of decisive importance for proportioning the extraction oil is the fact that the proportion of higher molecular weight compounds boiling above 320°C. in the liquid phase should be below 50% and preferably below 25% and most favourably below 10%. It is preferred for the proper adjustment of the ratio of compounds boiling below 320°C. to compounds boiling above 320°C., to distil several samples and to adjust the quantity of extraction oil per unit of time in accordance with the result.

A special embodiment has been found to be particularly suitable for the synthesis with iron catalysts suspended in liquids. This embodiment involves batchwise or preferably continuous feeding into the reactor of amounts between 0.04 and 4 times the volume of catalyst of low boiling compounds having a boiling range of about 180°–320°C., preferably hydrocarbons. The amounts should be such that the portion of high molecular weight hydrocarbons boiling above 320°C. does not account for more than 50% by volume and preferably less than 25% by volume of the suspending liquid. It is known to effect the hydrogenation of carbon monoxide with catalysts suspended in liquids in such a manner that although a relatively low boiling fraction of, for example the diesel oil boiling range is generally used as the liquid medium in the initial operation of such catalysts, this liquid medium is enriched more or less rapidly during the course of the synthesis with high boiling products boiling above 320°C. Thus after a more or less long operating period, the liquid medium contains almost only high boiling hydrocarbons and small portions of oxygenated compounds with small amounts of low boiling hydro-carbons dissolved therein. These amounts are dependent upon the particular synthesis pressure and the synthesis temperature.

High concentrations of high molecular weight hydrocarbons in the suspending liquid in a liquid-phase synthesis limit the gas load and the percentage conversion. If care is now taken by the method of the invention that the content of high molecular weight hydrocarbons does not exceed a certain maximum, then a considerable increase in conversion follows. It is possible in many cases to increase at the same time the gas load and/or to decrease the reaction temperature.

The liquid phase or wet synthesis itself is effected under the conditions usual for a wet synthesis, that is, at synthesis pressures of between about 5 and 50 atmospheres and preferably 10 and 30 atmospheres. The gas load may range between 100 and about 600 volumes of gas per volume of catalyst per hour.

Recycling of synthesis gas to the usual extent as, for example, 1 volume of recycle gas per volume of fresh gas or 2 volumes of recycle gas per volume of fresh gas is possible without difficulty. The ratio of carbon monoxide to hydrogen in the synthesis gas may be varied within wide limits. It is possible, for example, favourably to process gases rich in carbon monoxide having a $CO : H_2$ volume ratio of 1.5 : 1, but also hydrogen-rich gases containing CO and $H_2$ in a volume ratio of 1 : 2 may be charged.

The batchwise or continuous feeding of the extraction oil may be started as early as at the beginning of the synthesis. It is also possible to start the feeding at any other time thereafter. The quantity to be applied naturally depends on whether the particular wet synthesis is effected with the preferred production of low molecular or high molecular weight compounds. In the former case, considerably less extraction oil will be required.

From the catalyst composition and its mode of preparation, and the other operating conditions, it is possible to predict the approximate boiling range of the products formed during the wet synthesis and consequently the proportion of hydrocarbons boiling above 320°C. formed. Since the synthesis is generally started with a hydrocarbon fraction boiling between 180°C and 320°C. as the suspending liquid it is possible on the basis of the estimated content of products boiling above 320°C. to calculate the quantity of extraction oil to be fed batchwise, for example, at intervals of 6, 12 or 24 hours, or continuously. These results are periodically checked by taking samples of the suspending liquid.

If the wet synthesis is operated with catalysts for which the proportion of products boiling above 320°C. is not known, the quantity of extraction oil must be determined by initially taking samples at shorter intervals.

The processing of the liquid product leaving the reactor is effected in the manner usual for liquid-phase synthesis operations. It is advantageous in many cases to recover directly an extraction oil which meets all requirements by partial condensation in the required temperature range.

The feeding of the extraction oil in a liquid-phase synthesis as well as the introduction of the synthesis gas is effected in the bottom part of the reactor either through a nozzle or through an immersion pipe. It is advantageous to introduce the two media commonly, for example, through concentric tubes, nozzles or similar devices.

It is true that it has been suggested continuously to add low boiling hydrocarbons in a liquid-phase synthesis. This serves the purpose of removing some of the heat of reaction by evaporation. This, however, is not the process of the invention. The continuous addition of low boiling hydrocarbons such as hexane, heptane, octane or the like, or of appropriate mixtures does not have the effect of the measures of the invention because by far the greater part of the said hydrocarbons evaporates immediately on feeding into the synthesis reactor and the balance, due to its low boiling range, is in any case unsuitable for the extraction of high molecular weight compounds.

The process of the invention is also applicable to a carbon monoxide hydrogenation carried out with a fluidized catalyst bed or with a moving bed of 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 to agglomerate with the small amounts of paraffin wax whose formation is almost unavoidable. This may cause 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 spray the catalyst with the extraction oil. Thereby, small residues of high molecular weight compounds are removed from the catalyst surface and the troublesome caking mentioned above, no longer occurs.

The reactants fed into the reactor may consist of or comprise carbon monoxide and steam instead of carbon monoxide and hydrogen. In this case, the steam reacts with part of the carbon monoxide, with the aid of the synthesis catalyst, to produce carbon dioxide and hydrogen and it is the constituents of the gases so produced which then react in the synthesis reaction proper.

One method of carrying out the process of the invention is diagrammatically illustrated by way of example in the accompanying drawing.

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 stream jacket 13 into which steam is fed at a pressure of 2.5 atmospheres. High boiling products condense in the separator 12 and are removed through line 20. The uncondensed material passes through line 14 into and upwardly through 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 passed through line 27 into a neutralization chamber 28, containing potassium hydroxide in solid form, through a line 29 into a reservoir 30. The liquid in reservoir 30 is drawn by a pump 31 and passed through line 32 into the reactor 10 in order to extract the catalyst.

The process of the invention is illustrated in the following example.

### *Example.*

100 parts of iron and 10 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 sieved to a grain 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 into a vertical synthesis tube of 10 metres length and 32 mm. inside diameter. The catalyst was operated with a synthesis gas which had a $CO : H_2$ volume ratio of 1 : 2 and a $CO+H_2$ content of 85%. The synthesis pressure was 30 atmospheres absolute, the gas load or space velocity was 1000 litres of gas per litre of catalyst per hour, and the recycle ratio was 2 : 1.

From the beginning of the synthesis, periodic extractions were effected at intervals of 6 hours, each extraction lasting 5 minutes and being carried out with 2 litres of Diesel oil.

Under these conditions, a $CO+H_2$ conversion of 70–75% was obtained at a temperature of 256°C. The volume of methane produced was between 14% and 16% of the theoretical yield and the consumption ratio, that is, the ratio in which the carbon monoxide and hydrogen combined, was about 1.45.

From the 700th hour, the catalyst was extracted with a diesel oil obtained in the synthesis itself and containing about 9% by weight of constituents boiling above 320°C. and 8% by weight of constituents boiling below 180°C. Under these conditions, the catalyst was operated for months at unchanged temperature and with practically constant synthesis results.

After a total operating period of 4 months, the extraction oil derived from the synthesis operation and having a neutralization number of about 35 was treated with alkali. This was done in such a manner as to treat a quantity of extraction oil for about 10 minutes in a vessel provided with a stirrer with 20 times its chemical equivalent of solid KOH or $K_2CO_3$. Thereafter, the mixture was allowed to settle and the top layer of clear liquid was used for the extraction. After the alkali treatment, the neutralization number of its oil was 7.

It was possible in this manner to reduce the volume of methane produced from its former value of 16% to about 9–10% of the theoretical yield. At the same time, the volume content of olefins in the normally gaseous hydrocarbons increased by about 15–20% and in the gasoline fraction boiling between 30°C. and 180°C. by about 5–8% by weight.

After a further 2 months, the alkali treatment of the extraction oil derived from the synthesis operation was effected with an aqueous solution containing 30 grams of sodium carbonate per litre which trickled down through a column packed with Raschig rings. The extraction oil leaving the column had a neutralization number of 15. When this product was used as the extraction oil, practically the same results were obtained as with its extraction oil treated with solid alkali compounds.

In two further experiments, the treatment with alkali was effected at 50°C. for it had previously been carried out at room temperature. By so increasing the temperature it was possible in the first case to cut the stirring or contact time by one half and still reach the same neutralization number, whilst in the second or countercurrent process, the neutralization number could be reduced from 15 to about 9–10.

WHAT WE CLAIM IS:—

1. A process for the catalytic hydrogenation of carbon monoxide carried out at a pressure greater than 3 atmospheres, which includes extracting the catalyst, without shutting-off the synthesis gas and/or recycle gas, with an oil which has been synthesised by the catalytic hydrogenation of carbon monoxide and which has been treated with alkaline material prior to use.

2. A process according to claim 1, in which the alkaline material is used in an amount in excess of the stoichrometric amount required to neutralise the oil.

3. A process according to any one of the preceding claims, in which the alkaline material used is in the solid state.

4. A process according to any one of the preceding claims, in which the residual neutralization number of the extraction oil is between 5 and 15.

5. A process according to any one of the preceding claims, in which the catalyst is an iron catalyst in a fused or sintered form.

6. A process according to any one of the preceding claims, in which the catalyst is extracted at intervals of not more than 48 hours.

7. A process according to any one of claims 1 to 4, in which a highly active precipitated catalyst is used, the catalyst being operated for a period of several months before the first extraction.

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

9. A process according to claim 8, in which the duration of each extraction is less than 15 minutes.

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

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

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

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

14. A process according to any one of claims 10 to 13, in which the extraction oil is charged at such a rate that a pressure drop, across the fixed-bed catalyst, of between 0.4 and 2.5 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.

15. A process according to any one of claims 1 to 5, in which the catalyst is suspended in a liquid medium.

16. A process according to claim 15, in which the extraction oil is introduced, continuously or batchwise, at a rate of 0.5 to 25% by volume of the reaction space per hour.

17. A process according to any one of the preceding claims, in which the extraction oil contains more than 75% of compounds boiling between 200°C. and 260°C.

18. A process according to claim 15 or claim 16, in which the extraction oil contains not more than 20% by volume of compounds boiling above 320°C. and is fed into the reaction space at a rate such that the content of higher molecular weight hydrocarbons boiling above 320°C. in the liquid in the reaction space is not more than 25% by volume.

19. A process according to any one of the preceding claims, in which the synthesis pressure is in the range 10 to 60 atmospheres absolute.

20. A process for the catalytic hydrogenation of carbon monoxide, substantially as hereinbefore described in the Example.

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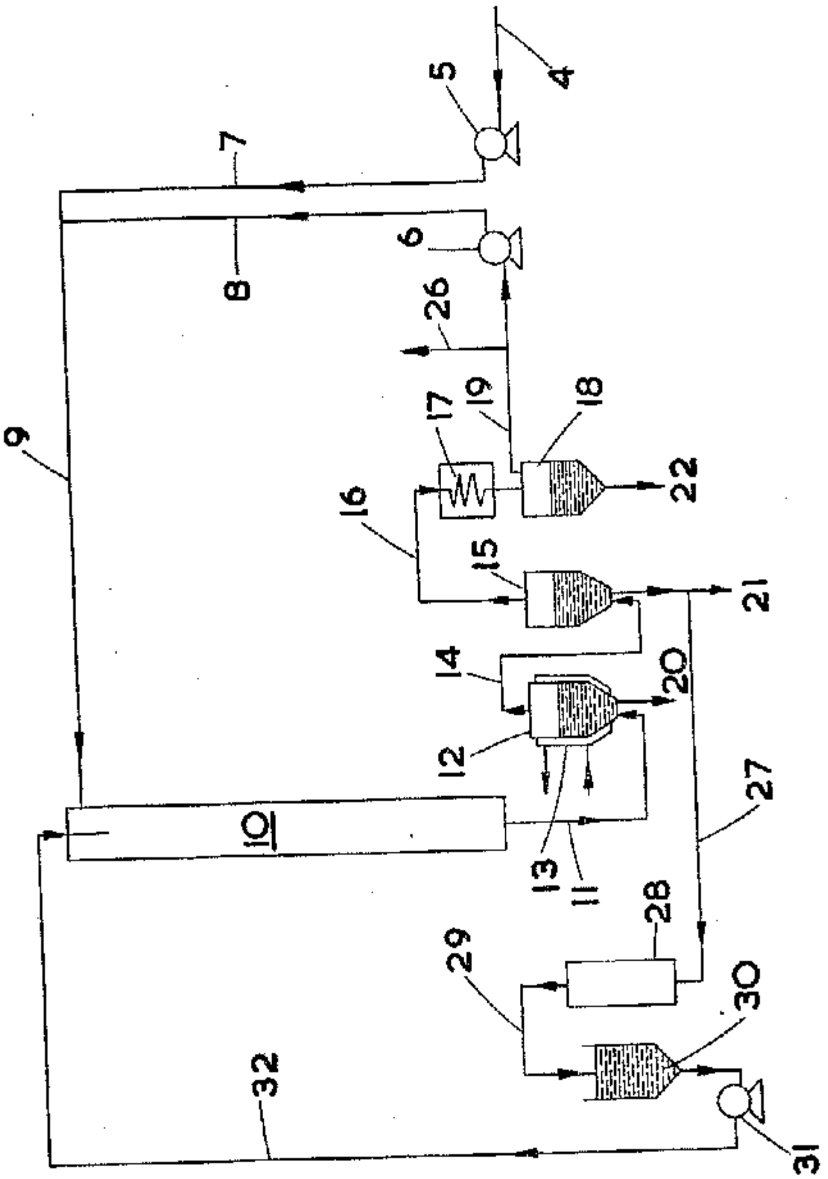
845558 COMPLETE SPECIFICATION
1 SHEET *This drawing is a reproduction of the Original on a reduced scale*



# PATENT SPECIFICATION

DRAWINGS ATTACHED

# 845,558

*Date of Application and filing Complete Specification Oct. 15, 1956.*
*No. 31369/56.*
*Application made in Germany on Oct. 15, 1955.*
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*Complete Specification Published Aug. 24, 1960.*

Index at Acceptance:—Class 2(3), B1G.

## ERRATA

## SPECIFICATION NO. 845,558

Page 5, line 16, *after* "degrees" *insert* "C"

Page 5, line 103, *for* "usual" *read* "unusual"

THE PATENT OFFICE,
*10th November, 1960*

DS 82174/1(10/8485 200 10/6

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 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

a solvent.

It has been found that a modification of the extraction process brings about unexpected improvements in synthesis product and catalyst life in an elevated pressure synthesis. This modification is described in the co-pending Application No. 5691/60 (Serial No. 845559), the subject-matter of which has been divided out of the present Application. That co-pending Application claims 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.

When a synthetic diesel oil fraction obtained by the catalytic hydrogenation of carbon monoxide was used as the solvent, it was noticed that the amount of methane formed in the synthesis became higher and that, particularly with sintered catalysts, there was an appreciable decrease in the olefin content of the synthesis products. It was found that this undesirable effect arose from acids present in the solvent.

According to the present invention, in a process for the catalytic hydrogenation of