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COMPLETE SPECIFICATION.

Process for the Catalytic Conversion of Carbon Monoxide into higher Hydrocarbons by means of Hydrogen.

We, RUHRCHEMIE AKTIENGESELLSCHAFT, of Oberhausen-Holten, Germany, a Company organised and existing under the laws of the German State, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement :—

It has been found that when carbon monoxide is catalytically converted into higher hydrocarbons by the use of hydrogen, all the catalysts employed lose their efficiency after a relatively short period. An attempt has been made to compensate the reduction in yield by raising the temperature. Such an increase of temperature is, however, possible only within narrow limits, and therefore revivification is possible for a short time only. Finally, a further rise in temperature is impossible by reason of too large a formation of methane which then sets in. The catalyst must therefore after a relatively short period of use be replaced by a fresh charge of catalyst. A catalyst thus spent cannot readily be revivified.

It has been found that the life of catalysts can be considerably lengthened if those substances which settle in the catalyst and exhaust it, such as paraffins having a high melting point, are removed at short intervals from the catalyst before the substances in question affect the catalytic strength to any appreciable extent.

It has long been known in connection with the synthesis of hydrocarbons, that the effective life of a catalyst is longer according as the reaction temperature can be maintained low. Nevertheless, it has not been possible to ensure longer effective periods than for example one to two months. Even in these periods it has not been possible to maintain maximum yields continuously, and after the expiry of one to two months it has been necessary to treat the catalyst again outside the synthesis furnace. No method is known for permanently securing the desired yields at low reaction temperatures. The present invention indicates a method of securing this result.

The prejudicial effect of the non-volatile reaction products which settle in the catalysts is already apparent after a few days. According to the invention, therefore, these substances are removed from the catalyst at short intervals whereby the oridinal catalytic efficiency is restored without the necessity for raising the reaction temperature. If for example with cobalt catalysts the non-volatile reaction products are continuously removed from the catalyst in sufficient measure at regular intervals, the effective life of the same catalysts is increased many times, the catalytic efficiency remaining unvaryingly high, without the necessity for considerably increasing the reaction temperature beyond that originally effective. In this way it is furthermore possible to maintain the reaction temperature so low that no harmful quantities of those different by-products which are produced only at high temperature, and which cannot be removed at all from the catalyst within the synthesis furnace, settle in the catalyst.

If, generally, instructions are given to work at a constant temperature such instructions are to be understood to mean that a small increase of temperature is not excluded so long as no injurious effect results. If the synthesis is at first carried out at a temperature of 185° C., a rise of temperature to about 190° C. would not be excluded.

The non-volatile reaction products can be removed for example by dissolving out these substances by means of solvents or mixtures of solvents in known manner, for example with benzine, alcohols or

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Price 4s 3d

suitable fractions of the oils produced during the synthesis itself. In carrying out the invention in practice, it is particularly advantageous to effect this extraction in the synthesis furnace itself, without any necessity for the catalyst to be removed from it, according to the present custom.

Furthermore, it has been found that the non-volatile reaction products can be removed from the catalyst very simply by treating the catalyst with hydrogen, or gases or vapours such as steam, that contain or yield hydrogen, which vapours or gases can be used singly or in admixture. Of particular importance in this connection is the further observed fact that this treatment can be carried out successfully at low synthesis temperatures such as 180° to 200° C. For this reason the treatment of the catalyst with hydrogen can according to the invention be likewise carried out in the synthesis furnace itself even when these furnaces are operated with water under pressure or with circulating oil as heat regulating agent which admits of no appreciably higher working temperatures. It has been found particularly effective first of all to extract the catalyst with a solvent and then to treat it with hydrogen in the manner hereinbefore described.

The intervals at which the revivification is effected may vary within limits. If, for example, after each revivification a small drop in catalytic efficiency (of for example 5%) is permitted, it is sufficient for the revivification to take place at intervals of a few days, such as once a week. The deciding factor is that the restoration of the initial activity is obtained by the removal of non-volatile substances but not by correspondingly increasing the reaction temperature. The shorter the intervals between the revivifying operations, the smaller becomes the drop in yield in the intervals. For example, the revivification may be carried out every second or third day or every day, or it may be effected several times daily, in which case the yield remains in practice unvaryingly high and uniform.

If the removal of the non-volatile reaction products from the catalyst is carried out at sufficiently short intervals, the fluctuations in operation of the furnace are so slight that automatically operating parts may be employed for converting the synthesis gas, and the gases or vapours used for blowing off.

One particular advantage of employing the process according to the invention is that the yield of liquid products is on an average higher than it is possible to secure by any other known method with the same catalyst. Furthermore it has been found that this process provides means for substantially raising the yield of the desired higher molecular fractions of the reaction products as compared with the synthesis processes which proceed without short-interval revivification but with a continued rise of temperature.

The invention is illustrated by means of the following examples:—

EXAMPLE 1.

A catalyst of cobalt, thorium and kieselguhr is caused to act at about 185°—190° C. with a mixture of gases consisting of 28—29% carbon monoxide, 56—60% hydrogen, the remainder consisting of carbon dioxide and nitrogen. Every 24 hours hydrogen at 180°—185° C. is passed for one hour through the catalyst in the same quantity hourly as previously was the synthesis gas. The high molecular paraffin hydrocarbons contained in the catalyst and formed during synthesis are thus withdrawn partly as solid paraffin or high-boiling oils, and partly as methane or other gaseous hydrocarbons. Directly after the treatment with hydrogen a mixture of gases is again passed over the catalyst and this again gives 100—110 gm. of liquid products per cubic metre of the gas mixture. In this way it is possible to continue for many months without the necessity for fresh catalyst. In case part of the higher molecular hydrocarbons to be removed are to be withdrawn from the catalyst as far as possible unchanged, the catalyst is first treated with steam and only then with hydrogen.

EXAMPLE 2.

To obtain conversion of a considerable part of the carbon monoxide into paraffins having a high melting point, a mixture of carbon monoxide and hydrogen is passed over an alkaline iron catalyst at a temperature of from 225° to 250° C. At intervals of four days, the temperature of the catalyst is lowered to about 110° C. Thereupon the paraffins, which melt at a high temperature, are dissolved out from the catalyst within the synthesis furnace with a benzene fraction boiling at between 130 and 140° C. When the dissolving operation is finished, hydrogen is passed through the catalyst, while at the same time the temperature is again brought to the point required for synthesis with the iron catalyst. Shortly before this temperature is reached, a gas mixture is again passed over the catalyst and the synthesis is continued until the next revivification (after about four days). The extract is separated by distillation into solvent on the one hand and high boiling paraffins on the other.

Further, it has been found that for the regeneration of catalysts containing particularly nickel and cobalt, those gases are advantageously employed which are not only free from carbon monoxide but also from carbon dioxide as the catalyst also in this spent condition effects conversion of the oxides of carbon with the hydrogen into methane, which conversion in turn leads to a useless consumption of hydrogen. Furthermore it has been found particularly advantageous to carry out the regeneration under pressure, preferably at pressures of from 50 to 150 atmospheres.

For the revivification of the catalysts, hydrogen or a gas free from oxides of carbon and containing hydrogen is passed continuously through the synthesis furnace during the whole regeneration operation, according to the directions hereinbefore set forth for carrying out the process of the invention, the condensible and easily absorbed constituents being removed from the issuing gases by cooling and treatment with active carbon, and the residual gas leaving the adsorption plant being discarded. If for example for the revivification of the catalysts a gas is employed which contains 25% of nitrogen and 75% of hydrogen and is free from impurities, that is to say for example a synthetic ammonia gas, the final gas which leaves the adsorption plant contains for example in addition to nitrogen and 20% of methane, 45% of hydrogen, so that only about one third of the hydrogen introduced into the synthesis furnace is consumed for the regeneration of the catalyst.

Hitherto this residual gas has not been used over again for the regeneration of the catalysts, on the assumption that the gases thus produced, for example methane, would interfere with the further regeneration of the catalysts.

It has furthermore been found that a considerable economy in hydrogen can be effected if the greater part of the final gases still containing hydrogen be returned to circulate in the synthesis furnace to be regenerated and only a correspondingly smaller quantity of fresh hydrogen introduced hourly into the synthesis furnace during the regeneration process.

Whereas, for example, in the previous method 100 cubic metres of a synthetic ammonia gas containing 25% of nitrogen and 75% of hydrogen passed through the furnace continuously per hour, during the regeneration of a synthesis furnace which takes about 8 hours, about 80% of the final gas leaving the adsorption plant can be returned by means of a blower to the synthesis furnace, so that each hour only about 20 cubic metres of fresh gas containing hydrogen requires to be passed into the synthesis furnace. By returning the final gases the hydrogen therein is very thoroughly utilized, so that according to the process the part of the final gas which is not returned to the synthesis furnace contains for example in addition to 50% of methane and 25% of nitrogen only 25% of hydrogen and thus according to the process 60 to 70% of the hydrogen hitherto effectively introduced is saved in the regeneration of the catalysts.

A process for the industrial manufacture of formaldehyde has before been proposed according to which gases containing hydrogen and carbon monoxide, such as water gas and blast furnace gas, purified beforehand, are subjected under normal pressure and at a temperature between 130 and 200° C. to the action of a catalyst comprising one or more of the reduced metals nickel, iron, cobalt, copper, platinum or palladium, or the oxides of the said metals, the catalyst being regenerated by the passing through it of a current of nitrogen or oxide of nitrogen, the duration of flow of the reaction gas and the regenerating gas being respectively 90 seconds and 30 seconds in the preferred instance.

It has also been proposed to reactivate catalysts employed in the synthesis of methanol or other oxygenated organic compounds from mixtures of carbon monoxide and hydrogen by subjecting the catalytic masses to the action of hydrogen or of a gas mixture rich in hydrogen at temperatures not substantially exceeding those employed in the catalytic reaction, the catalysts so reactivated regaining a very substantial amount of their catalytic power and in some cases being found superior to the original condition.

According to the process of the invention the catalysts by the aid of which higher hydrocarbons are produced from mixtures of carbon and hydrogen are relieved of the non-volatile reaction products that are produced during synthesis and that settle therein, by reactivation at short intervals in such manner that their efficiency is not permitted to become impaired and without the reaction temperature being substantially increased beyond the initial temperature.

We are aware of Specification No. 457,934, which describes and claims in the manufacture and production of normally solid hydrocarbons of the paraffin series by the thermal conversion of carbon monoxide and hydrogen in the presence of a solid catalyst and under a pressure varying from atmospheric pressure to

50 atmospheres, the step of continuously passing the said catalyst through the reaction space, then freeing it outside this space at least partly from solid paraffin hydrocarbons deposited thereon, and subsequently supplying it again to the reaction space, and we make no claim thereto.

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

1. A process for the catalytic conversion of carbon monoxide by means of hydrogen or gases containing hydrogen into higher hydrocarbons, by the use of cobalt, nickel, and iron catalysts, which may contain activators such as magnesium and thorium, characterised in that the non-volatile reaction products which are produced during synthesis and which settle in the catalyst are removed from the catalyst by the action of hydrogen or gases or vapours such as steam containing or yielding hydrogen or by the use of solvents, the revivification being effected at such short intervals that the efficiency of the catalyst is not permitted to be impaired appreciably and without the reaction temperature rising substantially above the initial temperature.

2. A process according to claim 1, wherein the treatment of the catalyst is carried out in the synthesis furnace.

3. A process according to claims 1 and 2, characterised in that the revivification of the catalyst is effected by passing over hydrogen, gases or vapours which contain hydrogen or gases or vapours from which hydrogen is split off, which gases or vapours have been previously freed from oxides of carbon or contain no appreciable quantity of these gases.

4. A process according to claims 1, 2 and 3, characterised in that the revivification of the catalysts is carried out under increased pressure.

5. A process according to claims 1, 2, 3 and 4, characterised in that the greater part of the gases used for regeneration and freed of the condensible and readily adsorbed reaction products are returned into circulation in the synthesis furnace during the regeneration, and only small quantities of fresh hydrogen or gases containing hydrogen are introduced into the synthesis furnace.

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EDWARD EVANS & CO.,
40—43, Chancery Lane, London, W.C.2,
Agents for the Applicants.

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