PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Process for the Production of Oxygenated Hydrocarbon Compounds and the Oxygenated Hydrocarbon Compounds so Produced

We, NAAMLOOZE VENNOOTSCHAP DE BATAAFSCHE PETROLEUM MAATSCHAPPIJ, of 30, Carel van Bylandtlaan, The Hague, The Netherlands, a Netherlands Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of oxygenated hydrocarbon compounds by reacting hydrocarbon compounds having at least one olefinic bond with a gas containing carbon monoxide and hydrogen, which process is generally known as the Oxo-process.

The reaction is usually carried out in the presence of a cobalt catalyst, which may be suspended in the olefinic hydrocarbon compounds or in another suitable liquid material, particularly when gaseous hydrocarbons are used as the initial material.

By this process a product is obtained which generally consists mainly of aldehydes, besides alcohol, and condensation products, usually designated as "thick oil". The product also contains various other substances, among which are soluble cobalt compounds, such as cobalt carbonyls and hydrocarbonyls, complex products containing cobalt, cobalt enolates and alcoholates.

These cobalt compounds have to be decomposed before the product can be subjected to a further treatment to convert the aldehydes into alcohols by reduction with hydrogen.

The aldehydic product containing the cobalt resulting from the decomposition treatment may be subjected to the hydrogenation treatment.

In general the cobalt is used on a carrier, such as kieselguhr.

When working with a finely divided cobalt catalyst on kieselguhr a few per cent. by weight of catalyst is generally added to the initial material. In the vessels in which the reactions are carried out and which have a much larger diameter than the pipes of the apparatus, a larger local concentration of catalyst may develop due to settling. The amount of catalyst in the reaction vessel is dependent on various factors such as fineness of the particles, the amount of gas used, which causes mixing of the reactants, and the throughput.

The catalyst has to be separated from the final products and may then be returned to the process.

Since the carrier disintegrates during the process it is necessary to remove continuously or intermittently some of the finest particles, which make the separation of the catalyst from organic compounds difficult, due to clogging of filters or otherwise.

Cobalt is also removed with the carrier, which cobalt has to be recovered and again deposited onto carrier material.

Also some fresh cobalt catalyst has to be added to compensate for small losses.

It was hitherto the common practice to introduce this additional amount of catalyst to the first stage of the process.

According to the present invention, in the production of oxygenated hydrocarbon compounds by reacting in a first stage hydrocarbon compounds having at least one olefinic bond with a gas containing carbon monoxide and hydrogen in the presence of a suspended finely divided cobalt catalyst and by converting the resulting aldehydes into alcohols in a second stage, fresh catalyst is introduced into the second stage of the process and catalyst, after use in the second stage, is recycled to the first stage.

When carrying out the process in accordance with the present invention, the proportion of the used catalyst to be

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removed from the system may be removed after the first or second stage. The quantity of used catalyst removed may amount to a few per cent. of the total amount of catalyst which is circulated, for example, the amount removed may be between 2 and 10 per cent.

The fresh catalyst has better hydrogenating properties than the catalyst which comes from the first stage. Moreover it is possible by introducing the catalyst into the second stage to regulate separately the amount of catalyst in this stage. In case the hydrogenation reaction does not proceed sufficiently rapidly, it can be accelerated by increasing the amount of fresh catalyst which is added. The process according to the present invention thus has the advantage of permitting better operating conditions to be maintained in the second stage.

A further advantage is that the catalyst coming from the second stage and which is recycled to the first stage, in which the olefinic feed is converted into an aldehydic product, has a lesser tendency to promote the production of thick oil, by which larger yields of valuable aldehydic products are obtained.

The invention will be further illustrated with reference to the accompanying drawing, which shows diagrammatically the flow of the reactants in the production of alcohols having from 7 to 9 carbon atoms in the molecule from an olefinic feed stock having from 6 to 8 carbon atoms in the molecule.

This feed stock is obtained by fractionation of the olefinic product from a paraffin-wax cracking process and may contain, for example, 87% by weight olefines. It is fed through line 1 and combined with recycled hydrocarbons coming through line 2 in the ratio of 3:1 and pumped to preheater 3. Catalyst consisting of a 25% by weight suspension of used cobalt on kieselguhr catalyst in thick oil is supplied through line 4.

Fresh water gas is introduced through line 5 under a pressure of 200 atmospheres in an amount of 0.5 cubic metres per kilogram of fresh olefinic feed together with 0.75 cubic metres of recycle gas, supplied through line 6 (gas volumes being given at normal temperature and pressure).

The mixture of olefinic feed, catalyst and gas passes through the preheater 3 and is then introduced into the reaction vessel 7 in which an aldehydic product is formed.

This product is cooled in a heat exchanger 22. The gases are separated in separator 23 and returned to the reaction space 7 through line 8 by means of booster compressor 9. The liquid products are partially released from pressure and after separation of gases (not shown) subjected to a treatment in vessel 10 with hydrogen, introduced through line 11 at an elevated temperature in order to decompose cobalt carbonyl and other compounds. The resulting product is then, after separation from gases in vessel 12, introduced into the hydrogenation vessel 13, where it is treated with hydrogen supplied through line 14.

Fresh catalyst is added to the feed through line 15 in an amount of 1.3% by weight calculated on the feed.

The reaction product is cooled in heat exchanger 16. The gases are separated in vessel 17 and recycled, if desired, partly through line 18. Then the pressure on the liquid product which contains the catalyst in suspension is released, whereupon the catalyst is separated by filtration in filter 19. The filter cake contains about 50% by weight of solids; 91 per cent of this filter cake is made up into a pumpable paste with thick oil in vessel 21 and is recycled to the first stage of the process, whereas 9 per cent is rejected through line 20.

When working in this manner the final product yields amount to 0.937 ton of alcohols having from 7 to 9 carbon atoms in the molecule per ton olefinic feed.

What we claim is:—

1. A process for the production of oxygenated hydrocarbon compounds by reacting in a first stage hydrocarbon compounds having at least one olefinic bond with a gas containing carbon monoxide and hydrogen in the presence of a suspended finely divided cobalt catalyst and by converting into alcohols in a second stage the aldehydes obtained in the first stage, in which fresh catalyst is added in the second stage of the process and catalyst, after use in the second stage, is recycled to the first stage.

2. A process according to claim 1, in which a proportion of used catalyst is removed after the second stage.

3. A process according to claim 1, in which a proportion of used catalyst is removed after the first stage.

4. A process according to claims 1 to 3, in which the quantity of used catalyst which is removed amounts to 2—10% of the total amount employed and this amount is replaced by fresh catalyst which is introduced in the second stage.

5. A process for the production of oxygenated hydrocarbon compounds substantially as hereinbefore described with reference to the specific example.

6. Oxygenated hydrocarbon compounds whenever prepared by the process claimed in any one of the preceding claims.

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1 SHEET

This drawing is a reproduction of the Original on a reduced scale.