



G00002

- 1 -

26 FEB 2003

9904289-7

Process for the hydrogenation of hydroformylation mixtures

The invention relates to a process for the hydrogenation of hydroformylation mixtures which arise in the preparation of higher oxo alcohols by hydroformylation of the corresponding olefins.

Higher alcohols, in particular those having from 6 to 25 carbon atoms, can be prepared, as is known, by catalytic hydroformylation (or oxo reaction) of the olefins having one carbon atom less and subsequent catalytic hydrogenation of the aldehyde- and alcohol-containing reaction mixtures. They are predominantly used as starting materials for preparing plasticizers or detergents.

It is known that, in the catalytic hydroformylation of olefins, reaction mixtures are formed which, apart from the desired products, i.e. aldehydes and the corresponding alcohols, depending on the catalyst and the reaction conditions, can comprise by-products and secondary products, such as unreacted olefins, saturated hydrocarbons formed from the olefins by hydrogenation, water, esters of the desired alcohols (e.g. formates), acetals of the target products aldehyde and alcohol, enol ethers and other by-products or secondary products. Said substances can be subdivided into low-boilers having a boiling point below the boiling point of the aldehyde and high-boilers having a boiling point above the boiling point of the alcohol. In the hydrogenation of the reaction mixtures, from some of the by-products, such as esters and acetals, the alcohols wanted as target product are formed, which improves the yield. In particular it is desired that the formates, which can occur in amounts up to 10% by weight, are hydrogenated under comparatively mild conditions and particularly at low



166166

- 2 -

pressure using commercially conventional catalysts to give the desired alcohol (and methanol as by-product).

The catalytic hydrogenation of reaction mixtures which were prepared by cobalt-catalyzed hydroformylation of olefins having from 2 to 24 carbon atoms is described, for example, in DE 35 42 595. The hydrogenation is carried out in two stages. In the first stage, the hydroformylation mixture is hydrogenated at 150-230°C and a hydrogen pressure of 10-350 bar with 80-95% conversion on a supported SiO_2 catalyst which comprises 5-15% by weight of nickel and 2-20% by weight of molybdenum in the form of molybdenum oxide. In the second stage, the hydrogenation is completed at 150-230°C and 10-350 bar hydrogen pressure on a catalyst whose active mass consists of 55-60% by weight of cobalt, 15-20% by weight of copper, 4-10% by weight of manganese and 2-5% by weight of molybdenum in the form of molybdenum oxide and, if appropriate, up to 10% by weight of activating additives. In the process, the formates and acetals present in the mixture are converted to the corresponding alcohols. However, the process has the disadvantage that the hydrogenation is carried out in two stages and at high pressures - in the example at 250 and 245 bar.

According to US-A 5 399 793, for the hydrogenation of cobalt-depleted reaction mixtures, as arise in the hydroformylation of C_5 - C_{12} olefins, use is made of Ni/Mo catalysts on Al_2O_3 or $\text{Al}_2\text{O}_3\cdot\text{SiO}_2$ as support materials. The total process comprises the following individual steps:

- (a) cobalt-catalyzed hydroformylation
- (b) cobalt depletion of the reaction mixture
- (c) hydrogenation of the crude reaction mixture at elevated temperature and at elevated pressure
- (d) production of alcohols having very low amounts of aldehydes by distillation and

- 3 -

(e) finish-hydrogenation of the alcohols.

The hydrogenation of stages (c) and/or (e) can be carried out using a bimetallic, phosphorus-free Ni/Mo hydrogenation catalyst. This hydrogenation catalyst produces fewer high-boiling by-products than a corresponding phosphorus-containing catalyst. A disadvantage with this process is that to prepare an on-specification alcohol which is suitable for preparing plasticizers, two hydrogenation stages are necessary and that at least in the hydrogenation stage (b) a relatively high pressure of 1000 psig (about 70 bar) is necessary.

The object which underlays the present invention was to hydrogenate reaction mixtures of the hydroformylation of C_5 to C_{24} olefins under comparatively mild conditions and in particular low pressures on conventional catalysts having a high service life in such a manner that the aldehydes and the formates present as by-products are converted into the desired alcohols.

This object was surprisingly achieved by a process for the hydrogenation of reaction mixtures from the hydroformylation of C_5 to C_{24} olefins using hydrogen on fixed catalysts at elevated temperature, in which process the aldehydes, alcohols, formates and low-boilers are evaporated from the reaction mixture and are passed in the vapor state over a support-free Cu/Cr catalyst. Advantageously, entrained droplets of high-boilers are separated off from the evaporated aldehydes, alcohols, formates and low-boilers upstream of the hydrogenation.

The process according to the invention offers a number of advantages. The high-boilers entrained as droplets remaining in the evaporator and also advantageously separated off from the evaporated aldehydes, alcohols, formates and low-boilers are not co-hydrogenated, and

- 4 -

do not therefore burden the hydrogenation stage. They can, for example, be worked up by cleavage or cracking to give materials of value. The aldehydes are hydrogenated to the corresponding alcohols at conversion rates over 98% in a selectivity of above 99% in only one hydrogenation stage. The esters present, in particular the formates, are likewise hydrogenated to the desired alcohols. The hydrogenation can be performed in the low-pressure range of below 25 bar. A desired side effect is that the starting olefins present in the reaction mixture are predominantly not hydrogenated, which enables them to be recirculated to the hydroformylation reaction.

The figure shows a block diagram of a plant in which the process according to the invention can be carried out continuously with recirculation as cycle gas of the hydrogenation hydrogen. The hydroformylation mixture is introduced as starting material **1** into the evaporator **2**, through which heated hydrogen **3** passes cocurrently. The hydrogen stream **4** loaded with aldehydes, alcohols, formates and low-boilers is conducted through the demister **5**, and the high-boilers separated off there and those remaining in the evaporator **2** are taken off continuously or batchwise as high-boiler fraction **6**. The hydrogen stream **7** which is freed from high-boilers and loaded with aldehydes, alcohols, formates and low-boilers is passed into the hydrogenation reactor **8**, from which exits the hydrogenation mixture **9** which is cooled in the cooler **10**. In the product receiver **11**, the hydrogenation mixture separates into hydrogenation product **12** and cycle gas **13**, from which a portion is taken off as exhaust gas **14**, in order to keep the inert gas level to an acceptable height. The hydrogen consumed is replaced by fresh hydrogen **15**.

The starting materials for the hydroformylation are monoolefins having from 5 to 24 carbon atoms and a

- 5 -

terminal or middle-position C-C double bond or mixtures of such monoolefins, such as 1- or 2-pentene, 2-methyl-1-butene, 1-, 2- or 3-hexene, the isomeric C₆ olefin mixture (dipropene) produced in the dimerization of propene, 3-methyl-1-hexene, 1-octene, the isomeric C₈ olefin mixture (dibutene) produced in the dimerization of butenes, 1-nonene, 2-, 3- or 4-methyl-1-octene, the isomeric C₉ olefin mixture (tripropene) produced in the trimerization of propene, 1-, 2- or 3-decene, 2-ethyl-1-octene, 1-dodecene, the isomeric C₁₂ olefin mixture (tetrapropene or tributene) produced in the tetramerization of propene or the trimerization of butenes, 1-tetradecene, 1- or 2-hexadecene, C₁₆ olefin mixtures (tetrabutene) produced in the tetramerization of butenes, and olefin mixtures prepared by co-oligomerization of olefins having different carbon numbers (preferably 2 to 4), if appropriate after separating off by distillation into fractions of identical or similar carbon number. Preferably, mixtures are hydrogenated which are produced in the hydroformylation of C₈, C₉, C₁₂ or C₁₆ olefin mixtures.

The olefins are hydroformylated in a conventional manner and then give the starting materials for the hydrogenation process according to the invention. Rhodium catalysts, or preferably cobalt catalysts, are therefore employed, with or without complex-stabilizing additives, such as organic phosphines or phosphites. The temperatures and the pressures can vary, depending on catalyst and olefin, in broad ranges. A description of the hydroformylation of olefins is found, for example, in J. Falbe, New Syntheses with Carbon Monoxide, Springer-Verlag, Heidelberg-New York, 1980, pages 99ff., and in Kirk-Othmer, Encyclopedia of Chemical Technology, volume 17, 4th edition, John Wiley & Sons, pages 909-919 (1996).

The hydroformylation reaction mixtures are expediently firstly freed from the catalyst. If a cobalt catalyst

- 6 -

was used, this can be achieved by pressure relief, separating off the aqueous catalyst phase, oxidation of the cobalt carbonyl compounds remaining in the hydroformylation mixture with air or oxygen and scrubbing out the resulting cobalt compounds with water or aqueous acid. Cobalt-depletion processes are well known, see, for example, J. Falbe, loc. cit., 164, 165 (BASF process); Kirk-Othmer, loc. cit. and EP-0 850 905 A1.

If a rhodium compound served as hydroformylation catalyst, it can be separated off from the hydroformylation mixture as distillation residue by means of thin-film evaporation.

The hydroformylation reaction mixtures expediently freed from catalyst generally comprise 3-40% by weight, usually 5-30% by weight, of low-boilers, in addition 30-90% by weight of aldehydes, 5-60% by weight of alcohols, up to 10% of formates of these alcohols and from 5 to 15% by weight of high-boilers. However, it may be stressed that the process according to the invention can also be carried out using hydroformylation mixtures whose composition does not correspond to these specifications in this and/or that relationship.

The aldehydes, alcohols, formates and low-boilers are then evaporated from the generally undistilled hydroformylation reaction mixture, which if appropriate is freed from catalyst. The low-boilers particularly include unreacted olefins and the corresponding saturated hydrocarbons formed during the hydroformylation and water. The content of low-boilers in the reaction mixture varies within the limits mentioned above, depending on the starting olefin, the reaction conditions and the degree of conversion of the hydroformylation. The high-boilers which according to the invention are not to pass to the hydrogenation

- 7 -

catalyst comprise, inter alia, aldolization and/or condensation products of the resulting aldehydes and also acetals and enol ethers and boil, as higher-molecular-weight substances, considerably higher than the alcohols, aldehydes, formates and low-boilers.

The conditions under which aldehydes, alcohols, formates and low-boilers are separated from the high-boilers are considerably dependent on the carbon number of the starting olefins. The reaction mixture is expediently separated under the same conditions with respect to temperature and pressure under which the subsequent hydrogenation is carried out. The pressure is accordingly generally below 25 bar. It is expediently from 1 to 25 bar, and in particular from 15 to 20 bar. In the case of reaction mixtures from the hydroformylation of olefins having from 6 to 12 carbon atoms (for example octenes which were obtained by dimerizing butenes), temperatures of, for example, from 150 to 250°C, advantageously from 160 to 220°C, can be employed. For other hydroformylation mixtures, the optimum temperature conditions for separating off the high-boilers can be determined without difficulty by preliminary experiments.

To separate the hydroformylation mixtures, use is made of conventional apparatuses, e.g. thin-film evaporators or falling-film evaporators. In an advantageous embodiment, the mixture is added to a hydrogen stream of appropriate temperature. Independently of the evaporation method selected, it is advantageous to free the vapor stream from high-boiler droplets, since in this manner the service life of the catalyst is increased. Use is made of conventional demisters, in which the velocity of the vapor stream is decreased, the vapor stream is exposed to the action of centrifugal forces or the droplets are separated off by impact, e.g. on baffles or screens.

- 8 -

If the hydroformylation mixture was evaporated by introduction into a heated hydrogen stream, the hydrogen/vapor mixture is conducted over the catalyst. Otherwise, hydrogen is added to the vapor mixture. The hydrogen is expediently employed in a considerable stoichiometric excess. Advantageously, a hydrogen:starting material mass ratio of from 3.5:1 to 0.7:1, in particular from 3:1 to 1.1 [sic], is employed. The unconsumed hydrogen can be recirculated.

The catalyst is a support-free Cu/Cr catalyst. It is expediently employed as a fixed-bed catalyst and generally comprises from 25 to 40% by weight of copper and from 18 to 30% by weight of chromium. The catalyst can comprise up to 20% by weight of basic substances, such as alkali metal oxides or alkaline earth metal oxides or alkali metal hydroxides or alkaline earth metal hydroxides, and other, inert or property-modifying substances in the same amounts, for example graphite. "Support-free" means the absence of support material which has been sprayed or impregnated with a solution of the active components or onto which the active components have been adhesively applied in another manner. The initially oxidic catalyst is expediently reduced by passing over hydrogen at elevated temperature, e.g. the hydrogenation temperature, and then develops its optimum activity. The specified percentages by weight relate to the oxidic, unreduced form of the catalyst. Suitable catalysts are, for example, the catalyst E406TU from Mallinckrodt, Erie, Pennsylvania, USA and the catalyst G99B from Süd-Chemie AG, 80333 Munich. The catalysts are expediently used in a form which offers a low resistance to flow, e.g. in the form of granules, pellets or shaped bodies such as tablets, cylinders, rod extrudates or rings. Temperatures at the catalyst and the pressure advantageously correspond, as mentioned, to the conditions under which the aldehydes,

- 9 -

alcohols, formates and low-boilers are evaporated from the hydroformylation mixture.

The optimum temperature in the catalyst bed is expediently determined for a given hydroformylation mixture by preliminary experiments. In the hydroformylation mixtures which were obtained by hydroformylation of olefins having from 6 to 12 carbon atoms, it is, as mentioned, from 150 to 250°C, advantageously from 160 to 220°C. It is expedient that the temperature of the cycle gas comprising the evaporated portion of the hydroformylation mixture at the inlet of the hydrogenation reactor is at least as high as at the outlet of the demister. Advantageously, it is therefore provided that the cycle gas in this process section can be heated, expediently can be indirectly heated, and can be thermostated.

The hydrogenation proceeds exothermically. The reaction can be conducted adiabatically with temperature increase. Alternatively, it is also possible to arrange the hydrogenation essentially isothermically, i.e. to permit a temperature rise of only up to 10°C from the reactor inlet to the exit of the hydrogenation mixture. In the latter case, the temperature is expediently controlled by feeding cold hydrogen.

The process according to the invention permits high throughputs. The liquid hourly space velocity (LHSV) of the catalyst is given as the hourly volumetric flow of the still liquid starting material divided by the catalyst volume. It depends, inter alia, on the temperature selected and is generally between 0.07 h⁻¹ and 0.40 h⁻¹, in particular between 0.12 h⁻¹ and 0.25 h⁻¹. The residence time of the gas phase in the catalyst zone essentially depends on the GHSV (gas hourly space velocity), the temperature selected and the pressure and can be, for example, between 3 and 30 seconds.

- 10 -

The hydrogenation mixture can, after separating off excess hydrogen, be fractionated into its constituents by fractional condensation or by complete condensation and distillation. The non-hydrogenated olefins can be recovered from the low-boiler fraction, advantageously by distillation, and recirculated into the hydroformylation. Alternatively, the olefins, together with the saturated hydrocarbons formed from them in the hydroformylation or the hydrogenation can be used as raw material for crackers or for heating purposes. This is the case especially if the hydroformylation was operated with high conversion of the starting olefins. The alcohols are produced in a purity of > 99%, determined by gas-chromatographic analysis. The residue can be combined with the high-boilers, which remained in the evaporation of the aldehydes, alcohols, formates and low-boilers, and can be worked up together with them to materials of value. For example, by cracking, olefins can be produced which in turn can be hydroformylated.

The examples below are to explain the invention further, but not to restrict its field of application which is given by the patent claims.

Example 1

As starting material **1**, hydroformylated di-n-butene was fed by a metering pump into the evaporator **2** of a gas-phase hydrogenation apparatus according to the figure, into a hydrogen stream **3** heated to 200°C. The hydrogen stream **4** which leaves the evaporator and is loaded with aldehydes, alcohols, formates and low-boilers and comprises high-boiler droplets was passed through the demister **5** and, after separating off high-boilers, was passed as material stream **7** to the top of the hydrogenation reactor **8**. The high-boilers **6** remaining in the evaporator and separated off in the demister **5** were taken off every 12 h.

- 11 -

The reactor was a steel tube of 38 mm open width, in which 800 ml (= 1200 g) of the catalyst E406TU from Mallinckrodt had been arranged, fixed, in the form of pellets. The catalyst in its oxidic unreduced form comprised

42% by weight of CuO, equivalent to 33.55% by weight of Cu

40% by weight of Cr₂O₃ equivalent to 27.37% by weight of Cr

8% by weight of BaO and

10% by weight of graphite.

The catalyst was reduced by 2500 l(S.T.P.)/h of nitrogen firstly being passed, at 150°C and 1 bar, over 800 ml of catalyst. A maximum of 5% of the nitrogen was replaced by hydrogen and the gas stream was controlled in such a manner that the temperature rise remained below 10°C. After 2 h in each case, the volumetric concentration of the hydrogen was increased by 5%. After reduction had finally been carried out using pure hydrogen, the temperature was elevated to 160°C. After a further 2 h in each case, the temperature was increased each time by 10°C. After a temperature of 190°C had been reached, the hydrogen pressure was elevated stepwise to 15 bar under strict temperature control and the catalyst was kept under these conditions for 12 h.

The hydrogenation mixture was cooled in the cooler **10**. The condensed hydrogenation product **12** was taken off from the receiver **11**, the cycle gas **13** recirculated to the evaporator and some of the cycle gas was taken off as exhaust gas **14**. Consumed hydrogen was replaced by fresh hydrogen **15**.

The process was carried out under the following conditions:

- 12 -

Starting material fed	160 g/h
Fresh hydrogen fed	62 l(S.T.P.)/h
Cycle hydrogen gas	2500 l(S.T.P.)/h
Exhaust gas	50 l(S.T.P.)/h
High-boilers	3 g/h
Temperature downstream of the evaporator	180 °C
Temperature at the hydrogenation reactor inlet	185 °C
Temperature in the hydrogenation reactor	185 °C
Pressure in the system	16 bar
Hydrogenation product approximately	158 g/h

GC analyses of the starting material and of the hydrogenation product gave the following values:

Substance	Starting material (% by weight)	Product (% by weight)
Isononanal	39.4	0.2
Isononanol	41.8	87.9
Isononyl formate	4.2	< 0.1
High-boilers	5.9	2.2

After operation for one week, a steady state was reached and the product composition remained the same for a period of more than 6 months.

Example 2

If the same experiment was carried out without a demister under otherwise identical conditions, as soon as after 6 weeks a markedly impaired hydrogenation performance was observed, recognizable by a higher content of isononyl formates.

Claims:

- 13 -

1. A process for the hydrogenation of reaction mixtures from the hydroformylation of C_5 to C_{24} olefins, comprising:

evaporating the aldehydes, alcohols, formates and low-boilers from a reaction mixture obtained from the hydroformylation of C_5 to C_{24} olefins to produce a vapor; and
reacting the vapor with hydrogen in the presence of a support-free Cu/Cr catalyst.

2. The process of Claim 1, wherein the process is carried out continuously.

3. The process of Claim 1, wherein, using a demister, entrained droplets of high-boilers are separated off from the evaporated aldehydes, alcohols, formates and low-boilers upstream of the hydrogenation.

4. The process of Claim 3, wherein the high-boilers produced in the demister and in the evaporator are worked up to materials of value.

5. The process of Claim 3, wherein the cycle gas, after leaving the demister and upstream of entry into the hydrogenation reactor, is heated and thermostated.

6. The process of Claim 3, wherein the temperature of the cycle gas at the inlet of the hydrogenation reactor is at least as high as at the outlet of the demister.

- 14 -

7. The process of Claim 1, wherein the catalyst comprises from 25 to 40% by weight of Cu and from 18 to 30% by weight of Cr, based on the oxidic form of the catalyst.

8. The process of Claim 7, wherein the catalyst comprises up to 20% by weight of a basic substance.

9. The process of Claim 8, wherein the catalyst comprises up to 20% by weight of an inert or property-modifying substance.

10. The process of Claim 1, wherein the hydrogenation is carried out on a fixed-bed catalyst.

11. The process of Claim 1, wherein the hydrogenation is conducted at from 150 to 250°C.

12. The process of Claim 1, wherein the hydrogenation is conducted from 160 to 220°C.

13. The process of Claim 1, wherein the hydrogenation is conducted adiabatically.

14. The process of Claim 1, wherein the hydrogenation is essentially conducted isothermically, by controlling the temperature by feeding cold gas.

- 15 -

15. The process of Claim 1, wherein the hydrogenation is conducted at a pressure of from 1 to 25 bar.

16. The process of Claim 1, wherein the hydrogenation is conducted at a pressure of from 15 to 20 bar.

17. The process of Claim 1, wherein the liquid hourly space velocity of the catalyst is between 0.07 h^{-1} and 0.40 h^{-1} .

18. The process of Claim 1, wherein the liquid hourly space velocity of the catalyst is between 0.12 h^{-1} and 0.25 h^{-1} .

19. The process of Claim 1, wherein the hydrogenation is conducted at a hydrogen:starting material mass ratio of from 35:1 to 07:1.

20. The process of Claim 1, wherein the hydrogenation is conducted at a hydrogen:starting material mass ratio of from 3:1 to 1:1.

21. The process of Claim 1, wherein the hydroformylation reaction mixture is obtained by cobalt-catalyst hydroformylation.

22. The process of Claim 21, wherein the hydroformylation reaction mixture is undistilled.