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Process for the hydroformylation of olefins

5 The invention relates to a process for preparing aldehydes having 3-26 carbon atoms by reacting olefins having 2-25 carbon atoms with hydrogen and carbon monoxide in the presence of a catalyst in a tube reactor.

10 Aldehydes are used in the synthesis of many organic compounds. Their direct downstream products are alcohols and carboxylic acids which are likewise utilized industrially. Aldol condensation of these aldehydes and subsequent hydrogenation of the condensate gives alcohols having twice the number of carbon atoms as the starting aldehydes. The alcohols prepared from the aldehydes by hydrogenation are used, inter alia, as solvents and as intermediates for the production of plasticizers and detergents.

15 It is known that aldehydes and alcohols can be prepared by reaction of olefins with carbon monoxide and hydrogen (hydroformylation, oxo process). The reaction is catalyzed by hydridometal carbonyls, preferably by those of metals of group VIII of the Periodic Table. Apart from cobalt, which is widely used industrially as catalyst metal, rhodium has acquired increasing importance in recent times. In contrast to cobalt, rhodium allows the reaction to be carried out at low pressures. The hydrogenation of the olefins to form saturated hydrocarbons takes place to a significantly lesser extent when using rhodium catalysts than when using cobalt catalysts.

25 In the hydroformylation process carried out in the industry, the rhodium catalyst is formed during the process from a catalyst precursor, synthesis gas and possibly further ligands. When using modified catalysts, the modifying ligands can be present in excess in the reaction mixture. Ligands which have been found to be particularly useful are tertiary phosphines or phosphites. Their use has made it possible to reduce the reaction pressure to values of significantly less than 300 bar.

35 However, separating off the reaction products and recovering the catalysts homogeneously dissolved in the reaction product are problems in this process. In general, the reaction product is distilled from the reaction mixture. In practice, this route is possible only in the hydroformylation of

lower olefins having up to 5 carbon atoms in the molecule because of the thermal sensitivity of the catalyst or the products formed.

On an industrial scale, C₄- and C₅-aldehydes are prepared by
5 hydroformylation, for example as described in DE 32 34 701 or DE 27 15 685.

In the process described in DE 27 15 685, the catalyst is present in
10 solution in an organic phase comprising product and high boilers (formed from the product). Olefin and synthesis gas are passed into this mixture. The product is carried from the reactor with the synthesis gas or is taken off as liquid. Since the activity of the catalyst slowly decreases, part of it has to be continually bled off together with high boilers and replaced by an
15 equivalent amount of fresh catalyst. Owing to the high price of rhodium, recovery of the rhodium from this bleed stream is absolutely necessary. The work-up process is complex and thus constitutes an encumbrance on the process.

According to DE 32 34 701, this disadvantage is overcome, for example,
20 by the catalyst being dissolved in water. The water solubility of the rhodium catalyst used is achieved by means of trisulphonated triarylphosphines as ligands. Olefin and synthesis gas are passed into the aqueous catalyst phase. The product produced by the reaction forms a second liquid phase. The liquid phases are separated from one another
25 outside the reactor and the catalyst phase which has been separated off is returned to the reactor.

The latter process involving the advantageous separation of catalyst
30 displays lower space-time yields than processes in which a liquid organic phase with a catalyst dissolved therein is present. The reason for this is the different solubility of the olefins. While olefins are readily soluble in an organic solution or may even themselves form the liquid organic phase in which the catalyst is dissolved, olefins are virtually insoluble in aqueous
35 solution. The already low solubility of the olefins in an aqueous solution decreases further with increasing molar mass of the olefins. As a result, higher aldehydes cannot be prepared economically by this process.

- Addition of an organic solvent which is soluble in the aqueous catalyst phase enables the reaction rate of the hydroformylation to be increased. The use of alcohols such as methanol, ethanol or isopropanol as cosolvent increases the reaction rate, but has the disadvantage that rhodium goes over into the product phase (B. Cornils, W.A. Herrmann, Aqueous-Phase Organometallic Catalysis, Wiley-VCH, p. 316-317) and is thus removed from the catalyst circuit. An increase in the reaction rate can be achieved, for example, by addition of ethylene glycol. However, this measure reduces the selectivity of aldehyde formation since acetal derivatives are formed from aldehyde and ethylene glycol (V. S. R. Nair, B.M. Bhanage, R.M. Deshpande, R.V. Chaudhari, Recent Advances in Basic and Applied Aspects of Industrial Catalysis, Studies in Surface Science and Catalysis, Vol. 113, 529-539, 1998 Elsevier Science B.V.).
- EP 0 157 316 describes increasing the reaction rate in the hydroformylation of 1-hexene by addition of solubilizers such as carboxylic acid salts, alkyl polyethylene glycols or quaternary onium compounds. This enabled the productivity to be increased by a factor of 4, depending on the solubilizer. Increasing the reaction rate by addition of polyglycols (e.g. PEG 400) and polyglycol ethers is known. Thus, DE 197 00 805 C1 describes the hydroformylation of propene, 1-butene and 1-pentene, and DE 197 00 804 C1 describes the hydroformylation of higher olefins such as 1-hexene, 4-vinylcyclohexene, 1-octene, 1-decene or 1-dodecene. In both these processes, the use of solubilizers does increase the reaction rate, but the separation of aqueous catalyst phase and organic product phase is made more difficult. This means losses of catalyst which, undesirably, goes over from the aqueous phase into the organic phase and losses of desired products which become soluble in the aqueous phase. If the amount of solubilizer is reduced to minimize these losses, the reaction rate is simultaneously reduced again.
- DE 199 25 384 states that the space-time yield of aldehydes in the hydroformylation of olefins in a multiphase reaction in which a continuous catalyst phase and a further liquid phase are present can be improved if the reaction is carried out not in a stirred reactor but in a flow reactor at a loading factor $B > 0.8$. This process for the hydroformylation of olefins by means of a multiphase reaction has very high loading factors of the tube reactor, i.e. extremely high mixing of the phases. As additives, phase

transfer reagents, surface-active or amphiphilic reagents or surfactants can be added to the catalyst phase, and water is preferred as solvent for the catalyst.

- 5 It is therefore an object of the invention to develop a process for the hydroformylation of olefins which displays high space-time yields and selectivities.

10 It has surprisingly been found that the hydroformylation of olefins in a multiphase reaction can be carried out in high yields and with low formation of by-products if the catalyst phase comprises a solvent mixture.

The present invention accordingly provides a process for the hydroformylation of one or more olefins having from 2 to 25 carbon atoms
15 by means of a multiphase reaction in a tube reactor, wherein

- a) the catalyst is present in the continuous phase,
- b) the continuous phase contains a solvent mixture,
- c) at least one olefin is present in the disperse phase and
- d) the loading factor of the tube reactor is equal to or greater than
20 0.8.

According to the invention, the hydroformylation is carried out in a tube reactor, i.e. a flow tube. The catalyst phase and the disperse phase containing at least one olefin are pumped into the tube reactor. After the
25 reaction, the reaction mixture is separated into a product phase and a catalyst phase, and the catalyst phase is recirculated to the tube reactor. The product phase is removed from the circuit and can, for example, be worked up by distillation to isolate the aldehydes.

30 The invention further provides for the use of the aldehydes prepared in this way. Thus, the aldehydes prepared by the process of the invention can be used for preparing alcohols by hydrogenation, used in aldol condensations or used for preparing carboxylic acids by oxidation.

35 The catalyst solution used in the process of the invention contains a solvent mixture and a catalyst.

As one component of the solvent, it is possible to use protic polar substances, for example water, ethylene glycol, 1,2-propylene glycol, 1,3-propylene glycol, butanediols or glycerol. A preferred solvent component is water.

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As further solvent components for forming the solvent mixture, it is possible to use polar organic substances, particularly ones which contain at least two oxygen atoms. These are, for example, compounds selected from the group consisting of diols, triols, polyols and their partial and full
10 ethers. A few compounds or compound groups may be listed by way of example: ethylene glycol, ethylene glycol monoethers, ethylene glycol diethers, ethylene glycol ethoxylates, ethers or ethylene glycol ethoxylates, ethylene glycol propoxylates, monoethers and diethers of ethylene glycol propoxylates, propylene glycol propoxylates, their
15 monoethers and diethers, polyols which can be produced by hydrogenation of carbohydrates (e.g. hydrogenated monosaccharides, disaccharides, oligosaccharides), and their partial and full ethers.

A solvent mixture of water and a water-miscible organic solvent containing
20 at least two oxygen atoms can therefore be used as continuous phase in the process of the invention.

The mass ratio of the solvents in the solvent mixture can be varied within a wide range as long as the following conditions are adhered to:

25

The resulting mixture has to form a homogeneous phase. The solubility of the catalyst in this homogeneous solution (phase) has to be sufficient for the desired catalyst concentrations. Furthermore, the solution must not become so viscous that difficulties occur in the reaction and/or in the
30 subsequent phase separation.

Preference is given to using solvent mixtures which have a dielectric constant at 20°C of from 50 to 78. Examples of such solvent mixtures are water/ethylene glycol mixtures as shown in the following table.

% by weight of water	% by weight of ethylene glycol	Dielectric constant
80	20	74.65
70	30	72.19
60	40	69.11
50	50	65.42
0	100	37.89

As hydroformylation catalysts, it is possible to use compounds of metals of transition group VIII of the Periodic Table of the Elements, namely Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt, preferably in the form of complexes. These metal compounds should advantageously be soluble in the catalyst phase but not the product phase under the reaction conditions. If aqueous catalyst solutions are used, this requires water-soluble metal compounds. Preferred catalysts are rhodium or water-soluble rhodium compounds. Suitable rhodium salts are, for example, rhodium(III) sulphate, rhodium(III) nitrate, rhodium(III) carboxylates such as rhodium acetate, rhodium propionate, rhodium butyrate or rhodium 2-ethylhexanoate.

The type of ligands in the metal complexes used as catalyst depends on the metal used and the solvent mixture. These complexes should not lose their catalytic activity even in long-term operation. A prerequisite for this is that the ligands do not change, for example by reaction with the solvent.

As ligands for the abovementioned catalytically active metals, it is possible to use triarylphosphines. Suitable phosphines contain one or two phosphorus atoms and have three aryl radicals per phosphorus atom; the aryl radicals may be identical or different and are each a phenyl, naphthyl, biphenyl, phenylnaphthyl or binaphthyl radical. The aryl radicals may be bound to the phosphorus atom either directly or via a $-(CH_2)_x$ group, where x is an integer from 1 to 4, preferably 1 or 2, particularly preferably 1. For water-soluble catalyst systems, one ligand should contain from 1 to 3 $-(SO_3)M$ groups, where M may be identical or different and are each H, an alkali metal ion such as Na or K, an ammonium ion, a quaternary ammonium ion, a (arithmetically half) alkaline earth metal ion such as Ca, or Mg or a zinc ion.

The $-(SO_3)M$ groups are usually substituents on the aryl radicals and give the triarylphosphines the required water solubility. A preferred sulphonated triarylphosphine having one phosphorus atom is trisodium tri(m-sulphophenyl)phosphine.

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Instead of being substituted by sulphonato units $-(SO_3M)$, the phosphines used can also be substituted by other polar groups such as carboxylato units.

- 10 The solvent mixture can be introduced directly, i.e. without the catalyst, into the hydroformylation or it is possible to carry out a preformation of the catalyst beforehand in the solvent mixture and to use the mixture containing the preformed catalyst. However, if the solvent mixture contains water, the catalyst solution can also be prepared in a comparatively simple
- 15 way by dissolving a water-soluble metal salt and/or the water-soluble ligands in water, forming the complex and subsequently adding the further solvent or solvents to form the solvent mixture.

- The metal salt concentration used in the process of the invention can vary
- 20 over a wide range, with the reaction rate also depending on the metal salt concentration. In general, higher reaction rates are achieved at higher metal salt concentrations, but higher metal salt concentrations incur higher costs. An optimum can therefore be selected depending on the reactivity of the starting material and the other reaction conditions; this optimum can
- 25 readily be determined by means of preliminary experiments. If rhodium is used as active catalyst, the rhodium content of the catalyst phase is usually from 20 ppm to 2000 ppm, preferably from 100 to 1000 ppm. The molar ratio of metal to ligands can be varied in order to achieve the optimum for each individual reaction. This metal/ligand ratio is from 1/5 to
- 30 1/200, in particular from 1/10 to 1/60.

- The pH of the catalyst solution can be optimized for the hydroformylation of each olefin so as to give the best selectivity of aldehyde formation. It is
- 35 from 2 to 8, preferably from 3.0 to 5.5. The pH can be set while the process is running by, for example, addition of sodium hydroxide solution or sulphuric acid.

Starting materials which can be used in the process of the invention are olefinic compounds having 2-25 carbon atoms, preferably 3-12 carbon atoms. The olefinic compounds can contain one or more carbon-carbon double bonds which may each be terminal or internal. Preference is given to olefinic compounds having a terminal carbon-carbon double bond. It is possible to use an olefin of uniform structure, but olefin mixtures can also be used. The mixture can consist of isomeric olefins having the same number of carbon atoms or of olefins having different numbers of carbon atoms or of a mixture containing both isomeric olefins and olefins having a different number of carbon atoms. Furthermore, the olefins or olefin mixtures can contain materials which are inert under the reaction conditions, e.g. aliphatic hydrocarbons. The olefins together with any inert materials present preferably form the disperse phase.

In the process of the invention, it is possible to use olefins from a wide variety of sources. For example, olefins from cracking processes, dehydrogenations or from the Fischer-Tropsch synthesis may be employed. Olefins or olefin mixtures formed by dimerization, oligomerization, codimerization, cooligomerization or metathesis of olefins are likewise suitable starting materials.

The olefins used may be gaseous, liquid or solid (under normal conditions). Solid olefins are used as solutions. Solvents used are inert liquids which are insoluble or only slightly soluble in the catalyst phase. Particular preference is given to solvents which have a boiling point higher than that of the products to be produced, since this makes separation by distillation and recirculation easier.

Preference is given to using α -olefinic compounds in the process of the invention. Examples of suitable α -olefinic compounds are 1-alkenes, alkyl alkenoates, alkenyl alkanoates, alkenyl alkyl ethers and alkenols, e.g. propene, butene, pentene, butadiene, pentadiene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene, 1-dodecene, 1-hexadecene, 2-ethyl-1-hexene, 1,4-hexadiene, 1,7-octadiene, 3-cyclohexyl-1-butene, styrene, 4-vinylcyclohexene, allyl acetate, vinyl formate, vinyl acetate, vinyl propionate, allyl methyl ether, vinyl methyl ether, vinyl ethyl ether, allyl alcohol, 3-phenyl-1-propene, hex-1-en-4-ol, oct-1-en-4-ol, 3-butenyl acetate, allyl propionate, allyl butyrate, n-propyl 7-octenoate, 7-octenoic

acid, 5-hexenamide, 1-methoxy-2,7-octadiene and 3-methoxy-1,7-octadiene. Particularly suitable olefins are propene, 1-butene or industrially available olefin mixtures containing essentially 1-butene, 2-butene and i-butene, and/or 1-pentene.

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The products of the hydroformylation of olefins are aldehydes having one more carbon atom and possibly the corresponding alcohols which have been formed by hydrogenation during the process of the invention. The aldehydes prepared by the process of the invention can, however, also be
10 hydrogenated to form the corresponding saturated alcohols which can be used as solvents and for producing detergents or plasticizers.

The hydroformylation agent used in the process of the invention is a mixture of hydrogen and carbon monoxide (synthesis gas) or a mixture of
15 hydrogen, carbon monoxide and further materials which are inert under the reaction conditions. Preference is given to using synthesis gas containing 50% by volume of H_2 and 50% by volume of CO.

When using liquid olefins or solid olefins in solution, it is useful to use the
20 hydroformylation agent in excess so that as complete as possible a conversion is achieved. This reduces the costs of the work-up. When using gaseous olefins, it can, in contrast, be useful to use a deficiency of the hydroformylation reagent since the excess gaseous olefin separates from the liquid product phase and can be returned to the process.

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The molar ratio of olefin to hydrogen and of olefin to carbon monoxide can in each case be greater than, smaller than or equal to 1.

When using a gaseous olefin, the process of the invention is initially a two-
30 phase reaction, but a liquid product phase forms during the reaction and a three-phase system thus results. When using a liquid olefin, an at least three-phase system is present from the beginning.

The tube reactor used in the process of the invention can contain packing
35 or internal fittings. For the purposes of the present invention, examples of packing are: Raschig rings, saddles, Pall rings, tellerettes, wire mesh rings or woven wire mesh. Examples of internal fittings are filter plates, baffles, column trays, perforated plates or other mixing devices. However, for the

purposes of the present invention, internal fittings can also comprise a plurality of narrow, parallel tubes to form a multitube reactor. Particular preference is given to structured mixer packings or demister packings.

- 5 In the process of the invention, it is also of critical importance to adhere to or exceed a minimum cross-sectional throughput or loading factor B of the tube reactor. In upflow operation of the reactor (flow direction from the bottom to the top), the flooding point should be exceeded. The reactor is thus operated above the point at which bubble columns are usually
10 operated. In downflow operation (flow direction from the top to the bottom), the cross-sectional throughput must be set so that the reactor is completely flooded. Thus, the process is operated above the point at which it would still be possible to speak of a trickle bed.
- 15 To fix the minimum necessary loading of the reactor more precisely, the loading factor B of the tube reactor is calculated as a dimensionless pressure drop

$$B = PD/PS$$

- 20 where PD [Pa/m] is a pressure drop per unit length over the reactor under operating conditions and PS [Pa/m] is a mathematical parameter having the dimensions of a pressure per unit length, defined as the ratio of mass flow M [kg/s] of all components in the reactor to the volume flow V [m³/s] of
25 all components under operating conditions, multiplied by $g = 9.81 \text{ m/s}^2$, i.e. $PS = (M/V) g$. To put it in concrete terms, PS would be the static pressure per meter of a multiphase mixture in an upright tube if all phases were to flow at the same velocity. PS is a purely mathematical parameter which is derived from the mass flows fed to the reactor and is independent of the
30 flow direction in the reactor, the flow velocity of all phases or the flooding state of the reactor.

- The pressure drop PD [Pa/m] is used as a mathematical parameter to fix the process conditions and can be calculated by established methods for
35 single-phase or multiphase flows. Appropriate methods of calculating the pressure drop PD in tubes, internal fittings or packed beds, etc., may be found, for example, in the VDI-Wärmeatlas, 7th augmented edition, VDI-Verlag GmbH, Düsseldorf 1994, sections La1 to Lgb7, and also in the

standard work by Heinz Brauer, Grundlagen der Einphasen- und Mehrphasenströmungen, Verlag Sauerländer, Aarau and Frankfurt am Main, 1971.

- 5 The pressure drop PD in the case of single-phase flow through an empty tube is given by

$$PD = C_w \rho w^2 / D$$

- 10 where

ρ [kg/m³]: density of the flowing medium under operating conditions,

w [m/s]: flow velocity = volume of flow/cross-sectional area.

D [m]: tube diameter

- 15 C_w [-]: resistance coefficient of the tube through which flow occurs

- In the case of flow through packing, beds or internal fittings, the velocity w is to be replaced by the effective velocity (w/ψ) and the tube diameter D is to be replaced by the hydraulic channel diameter d_H of the packing or internal fittings, so that:
- 20

$$PD = C_w \rho / 2 (w/\psi)^2 1/d_H$$

- 25 where

d_H [m]: hydraulic channel diameter

ψ [-]: empty tube fraction

C_w [-]: resistance coefficient of the apparatus with filling through which flow occurs.

- 30

The packing-related data d_H and ψ are frequently part of the delivery specifications for packing. For a series of packings, data are given in the abovementioned VDI-Wärmeatlas.

- 35 The empty tube fraction ψ can also be determined experimentally by, for example, measuring the capacity of the reactor before and after filling with the packing. The hydraulic channel diameter can in turn be calculated, if it is not known, from the specific surface area F [m²/m³] of the packing or

internal fittings (generally known or able to be determined experimentally) using the simple relationship

$$d_H = 4\psi/F.$$

5

The resistance coefficient of tubes, internal fittings and packing is generally described as a function of the Reynolds number Re which gives information about the flow state under the chosen conditions. In the case of packing, internal fittings, etc., the following relationship can almost
10 always be employed:

$$C_w = K_1/Re^n + K_2/Re^m$$

15

where frequently employed exponents are $n = 1$, $m = 0$ (method of S. Ergun, Chem. Engng. Progr. 48, (1948), 89) or $n = 1$, $m = 0.1$ (method of Brauer et al.). K_1 , K_2 are packing-related constants which are known from supply data or from the literature (examples may be found in the VDI-Wärmeatlas and in Brauer et al.). However, they can also be determined experimentally by passing a liquid through the tube reactor containing
20 packing at various velocities and determining C_w as a function of Re from the known data and the measured pressure drop.

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Finally the dimensionless Reynolds number Re is defined as $Re = w(p/\eta)D$ for empty tubes or $Re = (w/\psi)(\rho/\eta)d_H$ for tubes containing internal fittings or packing. In each case, η [Pa·s] is the viscosity and ρ [kg/m³] is the density of the flowing medium.

30

In the case of two-phase flows (here gas-liquid for synthesis gas/catalyst solution), the pressure drop increases overproportionally. Usually, using the Lockhart-Martinelli method (in Brauer et al.), the pressure drop of the two-phase flow P_g is expressed in relation to the pressure drop of one of the two phases, for example to the pressure drop of the pure flowing liquid phase P_l , and expressed in relation to the ratio of the pressure drop of the two phases P_l and P_g regarded as flowing alone.

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To calculate pressure drops in two-phase flow, use is frequently made of the dimensionless pressures $\phi^2 = P_g/P_l$ and $X^2 = P_l/P_g$. The further

relationship $\phi^2 = \text{function}(X^2)$ has frequently been examined. Examples may be found in the following literature references:

- 5 Y. Sato, T. Hirose, F. Takahashi, M. Toda: "Pressure Loss and Liquid Hold Up in Packed Bed Reactor with Cocurrent Gas-Liquid Down Flow", J. Chem. Eng. Of Japan, Vol. 6 (No. 2), 1973, 147-152;
- D. Sweeney: "A Correlation for Pressure Drop in Two-Phase Concurrent Flow in Packed Beds", AIChE Journal, Vol. 13, 7/1967, 663-669;
- 10 V. W. Weekman, J. E. Myers: "Fluid-Flow Characteristics of Cocurrent Gas-Liquid Flow in Packed Beds", AIChE Journal, Vol. 10 (No. 6), 11/1964, 951-957;
- R. P. Larkins, R. P. White, D. W. Jeffrey: "Two-Phase Cocurrent Flow in Packed Beds", AIChE Journal, Vol. 7 (No. 2), 6/1961, 231-239 or
- 15 N. Midoux, M. Favier, J.-C. Charpentier: "Flow Pattern, Pressure Loss and Liquid Holdup Data in Gas-Liquid Down-flow Packed Beds with Foaming and Nonfoaming Liquids"; J. Chem. Eng. Of Japan, Vol. 9 (No. 5), 1976, 350-356.

- 20 The relationship proposed by Midoux, which has been checked for many gas-liquid systems, is frequently utilized for the calculation. For example:

$$\Phi^2 = 1 + 1/X + 1.14X^{0.54}$$

- 25 This so-called Lockart-Martinelli relationship is depicted in graphical form in many works; detailed discussions of it may be found in many textbooks on process engineering and publications, for example in Brauer et al.

- 30 The pressure drop of the two-phase flow P_{g1} is then derived from the experimentally determined pressure drop, or the pressure drop estimated as described above, of the pure flowing liquid phase P_l using

$$P_{g1} = \phi^2 P_l$$

- 35 In the present case of the preparation of aldehydes by hydroformylation of olefins, the calculation of the pressure drop is even more complex. Apart from the synthesis gas phase and a liquid catalyst phase, it is also necessary to take into account the presence of an organic liquid phase.

This problem can be solved by determining a further dimensionless pressure $\varphi_{org}^2 = P_{gII}/P_{Ig}$, so that the pressure drop is determined as follows:

$$P_{gII} = \varphi^2 \varphi_{org}^2 P_I$$

- 5 In general, expressed as a function of the reactor length L [m]

$$PD = P_{gI}/L \text{ or } PD = P_{gII}/L.$$

The pressure drop of a multiphase flow can thus be calculated by customary methods of chemical engineering. The same applies to the
10 previously defined dimensionless pressure drop B , i.e. the loading factor of the multiphase reactor.

The magnitude of the dimensionless loading factor B is a necessary
15 fundamental condition in the process of the invention; B should be greater than or equal to 0.8, preferably greater than or equal to 0.9 or particularly preferably greater than or equal to 1. In the region where B is greater than or equal to 0.8, a reactor operated from the top downwards begins to flood. It may be expressly pointed out that when these conditions are adhered to, the advantages of the process of the invention are achieved even when
20 the reactor is operated from the bottom upwards or in another direction.

Higher cross-sectional loadings of the reactor ($B \gg 1$), recognizable by the increasing differential pressure over the reactor, are possible at any time and even desirable as long as the increasing space-time yields justify
25 the similarly increasing energy consumption. An upper limit is therefore imposed only by practical considerations such as energy consumption or difficulty of separating the phases after the reaction is complete.

It can thus be seen that, apart from the volume flow of the individual
30 phases or the empty tube velocities $w = V(\pi D^2/4)$ derived therefrom, the physical dimensions of the reactor (length L , diameter D) and, in particular, the data for the packing used (hydraulic diameter d_H , empty tube fraction ψ) play an important role. With the aid of these parameters, the process can be matched without difficulty to a wide variety of requirements; it is
35 only important to adhere to the condition $B \geq 0.8$, preferably $B \geq 0.9$ and particularly preferably $B \geq 1$.

In the case of a slow reaction, one will, for example, select a small hydraulic diameter of the packing or select a large specific surface area of the packing, so that the required conditions for B are achieved even at small flow velocities. In this way, sufficient residence times over the length
5 of a sensibly dimensioned industrial reactor are obtained. In the case of very fast reactions, a converse procedure is advisable.

A further criterion in carrying out the process of the invention is the ratio of the mass flow of the liquid, catalyst-containing phase M_1 to the mass-flow
10 of the disperse phase or phases M_2 . In the present case of the hydroformylation, the mass flow of the catalyst phase M_1 is significantly greater than the mass flow of the disperse phases, i.e. the organic olefin phase M_{2a} and the synthesis gas phase M_{2b} . In the process of the invention, the mass ratio M_1/M_2 of the continuous phase (M_1) to the
15 disperse phases (M_2) can be greater than 2; it is preferred that $M_1/M_2 > 10$. Flow ratios of $M_1/M_2 > 100$ are quite possible and frequently even advantageous. Under the condition $M_1/M_2 > 2$, the catalyst phase is the continuous phase, while the disperse phases are divided into fine bubbles or fine droplets. In the process of the invention, it is possible for at least
20 one starting material (olefin) to be dispersed by means of the energy introduced into the tube reactor by the continuous phase (catalyst). This leads to dispersion of at least one starting material as bubbles or droplets within the continuous catalyst phase.

25 This, too, can be estimated by means of customary engineering methods. Suitable methods employ relationships involving dimensionless parameters, for example

$$d_s/d_H = k Re_{g1(gll)}^m We_{g1(gll)}^n$$

30

where

d_s : diameter of the droplets or bubbles obtained by the Sauter method (described in Brauer et al.),

d_H : hydraulic diameter of the packing,

$Re_{g1(gll)}$: Reynolds number of the multiphase flow = $w_{g1(gll)} (\rho/\eta_l) (d_H/\Psi)$,

$We_{g1(gll)}$: Weber number of the multiphase flow = $w_{g1(gll)}^2 (\rho/\sigma_{g1}) (d_H/\Psi)^2$,

k,m,n: empirical constants (known or determined by experiment),

w: empty tube velocity [m/s] = $V/(\pi D^2/4)$,

V: volume flow under operating conditions [m³/s],

ρ : density under operating conditions [kg/m³],

η : viscosity under operating conditions [Pa·s] and

γ : interfacial tension under operating conditions [N/m]

and the indices l (liquid phase), g (gas phase), gl (gas/liquid two-phase flow) and gll (gas/liquid/liquid three-phase flow).

In the case of structured packings such as Sulzer SMV or narrow tubes as internal fittings, it seems plausible that a calculated bubble or droplet diameter d_s greater than the channel diameter is not sensible. However, this does not apply to permeable packings and packing elements such as wire mesh rings or woven wire mesh (known as demister packings or droplet precipitators). In the process of the invention, it is possible to use calculated droplet diameters which are at least equal to or smaller than the hydraulic channel diameter:

$$d_s/d_H \leq 1, \text{ preferably } < 0.9.$$

The calculated droplet diameter finally allows a mass transfer area to be calculated in accordance with

$$A_s = 6\phi_g d_s [m^2/m^3].$$

For the phase fraction ϕ_g of the disperse phase (in the case of hydroformylation, synthesis gas and/or organic phase are/is dispersed), the ratio of the empty tube velocities of the phases can be used:

$$\phi_g \sim w_g/w_{gl}.$$

The residence time τ of the phases flowing through the reactor can be calculated approximately as $\tau \sim L/w_g$. The residence time τ in the process of the invention is generally much less than one hour and can be in the minute range or even lower. Nevertheless, this completely unusual method of operation (high catalyst throughput in the reactor, comparatively low proportion of starting material in the reaction composition, and as a result a very short residence time) achieves surprisingly high space-time

yields. Alternatively, at the same space-time yields it is possible to work at significantly lower temperatures than is customary, since the increase in the reaction rate, which can, for example, result in minimization of secondary reactions and thus improve selectivity, makes this economically
5 feasible.

The process of the invention can be matched very flexibly to a wide variety of requirements. For specific requirements, the following embodiments of the process of the invention are possible:

10

If the application requires a very long mixing zone or calming zones are required, for example for decreasing mass flows, a cascaded arrangement of tube reactors having internal fittings or packing can be employed.

15 A cascaded arrangement of tube reactors or the alternative arrangement of packed and empty tube sections is advisable if a particularly low pressure drop is desired.

20 Furthermore, parallel arrangement of tube reactors or the use of a multitube reactor, in which the tubes can assume the function of internal fittings, can be used. In addition, reactors having multiple introduction of gas along the length of the reactor can be provided if the gas consumption is so high that unfavourable phase ratios of gas to liquid result from combining the two phases upstream of the reactor.

25

The particular conditions of the process of the invention allow further embodiments of the process. Thus, the high circulation of the catalyst phase or the continuous phase which is necessary can be additionally exploited for the operation of a jet nozzle which is located as a liquid jet
30 gas compressor upstream of the actual tube reactor. This can be used for thorough premixing of the two phases and for compression of the gas phase, which makes it possible to operate at higher admission pressures in the reactor. This is a possibility when using gaseous olefins. Finally, if, rather than compressing the gas, the suction is exploited, circulation of gas
35 with simultaneous premixing of the phases becomes possible. The energy introduced into the tube reactor by the catalyst-containing continuous phase can thus be used for dispersing the starting material phase or at least one starting material.

The heat removal in the case of strongly exothermic reactions such as the hydroformylation of olefins is also not critical in the process of the invention. The high throughput of the catalyst circuit acts as heat transfer medium so that, even in the case of adiabatic operation of the reactor, only small temperature differences arise and a homogeneous temperature distribution in the reactor without temperature peaks results. The heat generated can then conveniently be removed or exploited for energy recovery by means of any conventional heat exchanger located in the external catalyst circuit. To improve removal of heat, it can sometimes be useful to run the catalyst circuit at a higher circulation rate (i.e. at a higher B value) than is technically necessary, since the catalyst circuit enables a smaller temperature gradient over the reactor to be set.

Compared with the prior art, the process of the invention offers considerable advantages, for example:

- High space-time yields can be achieved at comparatively low temperatures.
- The formation of by-products is extremely low; values of 1-2% by weight and below are possible.
- The process is gentle on the catalyst and it suffers from very little deactivation; continuous discharge is eliminated.

In the present case of the preparation of aldehydes by hydroformylation of olefins using the process of the invention, there are further advantages:

- Owing to the higher reaction rate, this process can also be utilized economically for the hydroformylation of higher olefins having more than 6 carbon atoms.
- In the case of gaseous olefins, the proportion of starting material remaining after partial conversion can be recycled by simple recirculation by means of a jet nozzle.

In the process of the invention, the catalyst phase is the continuous phase; a mass ratio of catalyst phase to the disperse phase or phases, i.e. the olefinic phase(s), at the reactor inlet in the range from 5000/1 to 4/1, preferably in the range from 2000/1 to 50/1, is advantageous. The mass

ratio of catalyst phase to the hydroformylation agent (generally synthesis gas) is from 4/1 to 10,000/1, preferably from 200/1 to 4000/1.

5 The reactants can be preheated, i.e. in the region of the reaction temperature, before being introduced or can be fed in cold. Owing to the high phase ratio of the catalyst phase, preheating can also be carried out by means of the process heat.

10 The process of the invention for the hydroformylation of olefins is preferably carried out in a temperature range from 20°C to 250°C, particularly preferably in the range from 90°C to 150°C. Here, the total pressure is from 10 bar to 300 bar, preferably from 20 bar to 150 bar.

15 The phases can flow through the tube reactor in cocurrent from the top to the bottom or vice versa. For safety reasons, preference is given to feeding the phases in from the top.

20 The heat of reaction can be removed via various heat exchangers. The heat exchangers do not have to be in the vicinity of the reaction space, but can also, if desired, be located outside the reactor. The individual heat flows are dependent on the specific heat of reaction and on the desired temperatures in the reactor and in the work-up equipment.

25 The heat of reaction which has been removed can thus be utilized very simply, e.g. in the process itself, for heating a distillation apparatus or for generating steam.

30 When gaseous olefins are used or in the case of incomplete conversion, the mixture leaving the reactor can be degassed in a gas-liquid separation vessel. The gas-liquid separation can be carried out at the same pressure as prevails at the reactor outlet. This is particularly advantageous when at least part of the gas released is recirculated to the reactor. Otherwise, degassing can be carried out at lower pressure (down to 1 bar).

35 The gas stream which has been separated off can be completely or partly recirculated to the reactor.

This recirculation can be achieved in a known manner, e.g. by means of a jet nozzle or mixing nozzle which is located in the catalyst circuit upstream of the reactor, or by means of a circulating gas compressor. For energy considerations, preference is given to using a jet nozzle or mixing nozzle
5 which is located in the catalyst circuit upstream of the reactor.

The remaining, or if desired the total, amount of gas can be passed to a waste gas utilization system either after cooling or without cooling. When using a cooler, the gas condensate obtained in the cooler can be
10 conveyed via a line to the gas-liquid separation vessel.

The degassed liquid mixture is mechanically separated in a liquid-liquid separation vessel into catalyst phase and product phase. This can be carried out in settling vessels of various construction types or in
15 centrifuges. For cost reasons, preference is given to settling vessels.

Although the residence times in the separation apparatus are not critical per se, they are advantageously kept short. This has the following advantages: the separation apparatus is small and its capital cost is
20 correspondingly low. When residence times are short, virtually no secondary reactions occur in the separation vessel. For the separation of the phases to occur quickly, the density difference between the two phases has to be sufficiently large and their viscosities have to be low. All three parameters are a function of the temperature and can easily be
25 determined by initial experiments.

In addition, the density and viscosity of the catalyst solution can be varied by choice of the solvent and the catalyst concentration. A further possibility is to alter the density and viscosity of the product phase by addition of a
30 solvent.

Phase separation can be carried out in a wide temperature range. Here, the separation temperature can also be higher than the temperature of the reaction product at the outlet from the reactor. However, for energy
35 reasons, it is disadvantageous to employ a higher temperature than the liquid temperature in the gas separator. The lowest possible temperature may be regarded as the pour point of one of the two liquid phases.

However, in order to achieve short separation times, excessively low temperatures are not chosen, as mentioned above.

5 The product stream can be fractionated by known methods, e.g. by distillation.

10 The catalyst solution which has been separated off is, if desired after bleeding off a small proportion and replacing it by fresh catalyst solution, returned to the reactor.

The following examples illustrate the invention without restricting its scope, which is defined in the claims.

15 Hydroformylation of propene:

Example 1 (Comparative example, batch reaction)

20 290.3 g of TPPTS ligand (triphenylphosphinetrisulphonate) in the form of its sodium salt, 31.8 g of propene and part of 291 g of a solvent consisting of 20% by weight of ethylene glycol and 80% by weight of water were placed at 120°C in a stirring autoclave and 50 bar of synthesis gas were injected. The hydroformylation reaction was started by addition of 0.531 g of rhodium acetate dissolved in the remainder of the solvent. After complete conversion, which could be detected by means of the synthesis gas absorption curve, a liquid sample was taken from the reaction mixture.

25

Example	1
Substance	Proportion in % by weight
Propene	0.64
i-Butyraldehyde	5.90
n-Butyraldehyde	75.76
n-Butanol	1.69
i-Propyl-1,3-dioxolane	0.74
n-Propyl-1,3-dioxolane	7.33
High boilers	7.94

All continuous hydroformylation experiments (even those using a starting material other than propene) were carried out in an experimental apparatus as shown schematically in Fig. 1. Unless a different reactor is specified in the description of the example, use was made of a reactor
5 having a length of 3 m and a diameter of 17.3 mm (volume: 705 ml) and containing static mixing elements from Sulzer having a hydraulic diameter of 2 mm. The aqueous catalyst is circulated by means of a pump 1. Olefin (propene) 3 and synthesis gas 4 are mixed into the catalyst solution. The multiphase mixture 5 obtained in this way is pumped via the mixing nozzle
10 11 through the tube reactor 6 which is provided with static mixing elements. At this point, the intimate mixing of the phases, which is a function of the Reynolds number for given mixing elements, is of particular importance. The resulting mixture 7, comprising product, unreacted starting material and the catalyst, is degassed in the vessel 8. Most of the
15 gas 9, comprising olefin (propene), synthesis gas and accumulated inerts is fed back to the reactor 6 via a gas return line 10 with the aid of a mixing nozzle 11. A small part of the gas stream 9 is bled off via a line 12. By means of appropriate coolant 13 and recirculation of the supercritical propene, the bleed stream 14 is reduced to accumulated inerts and small
20 amounts of unreacted synthesis gas.

As a result of this arrangement, the conversion of olefin (propene) is virtually unaffected by the discharge of inerts.

25 The liquid stream 15 obtained after degassing in the vessel 8 is conveyed to a phase separation vessel 16. Here, the aqueous catalyst phase 2 is separated off and returned to the circuit. The heat of reaction can be elegantly removed by means of an external heat exchanger 17.

30 **Examples 2 to 5 (comparative examples, continuous process without solvent mixture)**

These examples represent comparative experiments in the continuous apparatus described in order to demonstrate the advantages of the
35 present invention in terms of space-time yield compared with a purely aqueous solvent. For these examples, the line 10 for recirculation of the gas was closed. Water was used as solvent for the catalyst. 400 kg/h of catalyst flowed through the 705 ml reactor at a temperature of 120°C. The reaction pressure was 50 bar. The concentration of rhodium was 800 ppm

- based on the solvent phase. As ligand, TSTPP was used in the form of its sodium salt (NaTSTPP); the P/Rh ratio was 60. Example 3 was carried out under the reaction conditions of Example 2, except that the reaction temperature was 130°C. Experiment 4 was carried out under the reaction conditions of Example 2, except that the reaction pressure was 70 bar. Example 5 was carried out under the reaction conditions of Example 2, except that 300 kg/h of catalyst were passed through the reactor. The molar flows of starting materials fed in and of the products are shown in the table in mol/h.

10

Example	2	3	4	5
STY [te/(m ³ h)]	0.98	1.39	1.23	0.71
Starting material				
CO	22.79	16.99	28.24	12.73
H ₂	21.28	15.87	26.38	11.89
N ₂	0.12	0.09	0.15	0.07
Propene	51.49	35.57	31.13	33.45
Propane	0.17	0.12	0.10	0.11
Product				
CO	2.15	2.09	2.08	2.11
H ₂	0.89	0.93	0.98	0.97
Propene	3.35	6.73	3.04	4.00
i-Butanal	0.24	0.51	0.53	0.20
n-Butanal	5.46	11.03	9.82	4.66
i-Butanol	<0.01	<0.01	<0.01	<0.01
n-Butanol	0.07	0.07	0.07	0.07
2-Ethylhexanal	0.09	0.03	0.08	0.02
2-Ethylhexenal	0.26	0.19	0.18	0.09
Off-gas				
CO	9.50	3.06	13.23	6.81
H ₂	8.45	1.46	9.97	3.59
N ₂	0.29	0.10	0.09	0.16
Propene	37.37	13.56	17.72	36.93
Propane	0.17	0.10	0.17	0.09
i-Butanal	0.08	0.08	0.03	0.01
n-Butanal	4.59	3.13	2.72	2.56

Examples 6 to 11 (according to the invention)

These examples describe the use according to the invention of solvent mixtures in the continuous apparatus described, using a solvent mixture of water/ethylene glycol as an example. The measured data make clear the increased space-time yields. Here, there was no appreciable formation of dioxolanes, in contrast to stirred systems. Example 6 was carried out under the reaction conditions of Example 5, except that a mixture of water and ethylene glycol (20% by weight) was used as solvent; in Example 7, the concentration of ethylene glycol was increased to 40% by weight. Example 8 was carried out under the reaction conditions of Example 7, except that 400 kg/h of catalyst were passed through the reactor and the reaction temperature was 130°C. Example 9 was carried out under the reaction conditions of Example 8, except that the reaction temperature was 120°C and the reaction pressure was 70 bar. Example 10 was carried out under the reaction conditions of Example 9, except that the reaction temperature was 90°C. This experiment demonstrates that it is possible to carry out the hydroformylation of propene in a multiphase system at high space-time yields even at low temperatures. Example 11 was carried out under the reaction conditions of Experiment 10, except that the reaction pressure was 50 bar and the rhodium concentration was 200 ppm, based on the solvent. This experiment demonstrates that it is possible to carry out the hydroformylation of propene in a multiphase system at high space-time yields even when using low rhodium concentrations. The molar flows of starting materials fed in and of the products are shown in the table in mol/h.

Example	6	7	8	9	10	11
STY[te/m ³ /h]	1.3	1.7	3.8	2.3	0.3	0.5
Starting material						
CO	23.31	23.28	53.28	45.72	22.96	23.23
H ₂	21.40	21.57	49.16	42.38	21.70	21.33
N ₂	0.12	0.11	0.25	0.20	0.12	0.09
Propene	49.88	35.20	59.35	42.89	38.04	35.59
Propane	0.12	0.08	0.12	0.09	0.08	0.07
Product						
CO	2.25	8.55	2.05	2.50	0.61	0.29
H ₂	0.83	1.51	0.41	1.02	0.16	0.10
Propene	4.37	5.38	6.33	4.14	0.51	0.18
i-Butanal	0.55	1.20	3.47	2.13	0.06	0.03
n-Butanal	9.34	17.25	36.99	21.60	0.96	0.52
i-Butanol	0.00	0.00	0.03	0.02	0.00	0.00
n-Butanol	0.06	0.15	0.48	0.23	0.01	0.00
i-Propyl-dioxolane	<0.01	0.02	0.04	0.03	<0.01	<0.01
n-Propyl-dioxolane	0.05	0.21	0.46	0.37	0.13	0.12
2-Ethyl-hexanal	0.20	0.21	0.46	0.39	0.08	0.05
2-Ethyl-hexenal	0.41	0.50	0.60	0.58	0.10	0.17
Off-gas						
CO	9.09	3.15	5.79	16.42	18.42	18.37
H ₂	5.05	1.20	1.85	11.61	14.90	14.29
N ₂	0.22	0.09	0.33	0.25	0.13	0.12
Propene	30.09	6.31	9.21	13.04	35.28	34.04
Propane	0.18	0.06	0.17	0.20	0.10	0.10
i-Butanal	0.09	0.04	0.01	0.26	0.13	0.20
n-Butanal	3.43	0.36	1.35	1.87	1.61	2.95

Selective hydroformylation of 1-butene

A further application of the process of the invention is the selective hydroformylation of 1-butene from a raffinate I mixture. This mixture
5 comprises C₄-olefins and C₄-paraffins and contains 26-29% by weight of 1-butene. The catalyst solvent selected was a mixture of water and ethylene glycol (50/50% by weight).

Example 12 (comparative example, batch process)

10

This example represents a comparative experiment in a stirring autoclave in order to demonstrate the advantages of the present invention in terms of product quality compared with conventional stirred reactors. 29.81 g of NaTSTPP, 86.2 g of 1-butene, 13.5 g of isobutane and 67.7 g of a solvent
15 consisting of 30% by weight of ethylene glycol and 70% by weight of water were placed at 105°C in a stirring autoclave and 30 bar of synthesis gas was injected. The hydroformylation reaction was started by addition of 2.09 g of a rhodium acetate solution containing 3.7% of Rh (in 30% by weight of ethylene glycol and 70% by weight of water). After complete
20 conversion, which could be detected by means of the synthesis gas absorption curve, a liquid sample was taken from the reaction mixture. For the following listing, isobutane which served as internal standard was disregarded in the calculation.

Example	12
Substance	Proportion in % by weight
1-Butene	6.1
2-Methylbutanal	1.19
Pentanal	77.4
i-Propyl-1,3-dioxolane	0.13
n-Propyl-1,3-dioxolane	11.9
Remainder	3.28

The continuous hydroformylation of 1-butene in Examples 13 to 26 was carried out in the same way as the hydroformylation of propene except that the gas return line 10 was closed.

5 **Example 13:**

10 This example describes the use according to the invention of a solvent mixture of 50% by weight of water and 50% by weight of ethylene glycol in the continuous apparatus described. The measured data make clear the significantly reduced formation of dioxolanes compared with stirred systems. 400 kg/h of catalyst were passed through the 3 m long reactor at a temperature of 115°C. In addition, 600 standard l/h of synthesis gas and 3 kg/h of raffinate I were fed in. The reaction pressure was 50 bar. The following data were determined:

15

Example	13
1-Butene, % by weight in feed	27.00
C (1-butene)	64.68%
STY [te/m ³ /h]	0.74
Product:	
i-Butane	1.39
n-Butane	5.77
Cyclobutane	0.04
trans-Butene	5.93
1-Butene	5.07
Isobutene	21.77
cis-Butene	4.14
Neopentane	0.04
1,3-Butadiene	0.00
2-Methylbutanal	1.88
3-Methylbutanal	5.28
n-Pentanal	42.58
2-Methylbutanol	0.12
Methylpropyldioxolane	0.09
1-Pentanol	0.41
2-n-Butyl-1,3-dioxolane	0.25
Ethylene glycol	0.03

Example 14:

This example was carried out under the reaction conditions of Example 13,
5 except that 200 kg/h of catalyst were passed through the reactor.

Example	14
1-Butene, % by weight in feed	27.30
C (1-butene)	59.46%
STY [te/m ³ /h]	0.69
Product:	
i-Butane	3.10
n-Butane	9.71
Cyclobutane	0.06
trans-Butene	8.55
1-Butene	9.50
Isobutene	35.98
cis-Butene	5.60
Neopentane	0.06
1,3-Butadiene	0.00
2-Methylbutanal	1.03
3-Methylbutanal	2.25
n-Pentanal	22.07
2-Methylbutanol	<0.01
Methylpropyldioxolane	<0.01
1-Pentanol	0.22
2-n-Butyl-1,3-dioxolane	0.23
Ethylene glycol	<0.01

Example 15:

This example was carried out under the reaction conditions of Example 13, except that 100 kg/h of catalyst were passed through the reactor and the reaction temperature was 85°C.

Example	15
1-Butene, % by weight in feed	28.90
C (1-butene)	17.09%
STY [te/m ³ /h]	0.21
Product:	
i-Butane	1.98
n-Butane	10.50
Cyclobutane	0.07
trans-Butene	9.89
1-Butene	22.17
Isobutene	37.42
cis-Butene	6.19
Neopentane	0.09
1,3-Butadiene	0.11
2-Methylbutanal	0.29
3-Methylbutanal	0.48
n-Pentanal	9.61
2-Methylbutanol	0.03
Methylproyldioxolane	0.03
1-Pentanol	0.23
2-n-Butyl-1,3-dioxolane	0.19
Ethylene glycol	<0.01

Example 16:

10

This example was carried out under the reaction conditions of Example 13, except that 250 kg/h of catalyst were passed through the reactor and the reaction temperature was 85°C.

Example	16
1-Butene, % by weight in feed	28.90
C (1-butene)	20.98%
STY [te/(m ³ h)]	0.26
Product:	
i-Butane	1.88
n-Butane	8.53
Cyclobutane	0.06
trans-Butene	8.88
1-Butene	17.07
Isobutene	28.61
cis-Butene	5.48
Neopentane	0.09
1,3-Butadiene	0.00
2-Methylbutanal	0.77
3-Methylbutanal	0.68
n-Pentanal	27.55
2-Methylbutanol	0.05
Methylpropyldioxolane	0.01
1-Pentanol	0.11
2-n-Butyl-1,3-dioxolane	0.04
Ethylene glycol	<0.01

Example 17:

- 5 This example was carried out under the reaction conditions of Example 13, except that the reaction temperature was 90°C.

Example	17
1-Butene, % by weight in feed	28.90
C (1-butene)	27.11%
STY [te/(m ³ h)]	0.33
Product:	
i-Butane	2.19
n-Butane	8.97
Cyclobutane	0.06
trans-Butene	8.94
1-Butene	17.11
Isobutene	32.67
cis-Butene	5.53
Neopentane	0.07
1,3-Butadiene	0.00
2-Methylbutanal	0.76
3-Methylbutanal	0.57
n-Pentanal	22.99
2-Methylbutanol	0.05
Methylpropyldioxolane	0.00
1-Pentanol	0.07
2-n-Butyl-1,3-dioxolane	0.03
Ethylene glycol	<0.01

Example 18:

- 5 This example was carried out under the reaction conditions of Example 13, except that the reaction temperature was 70°C.

Example	18
1-Butene, % by weight in feed	27.00
C (1-butene)	9.39%
STY [te/(m ³ h)]	0.11
Product:	
i-Butane	2.51
n-Butane	10.96
Cyclobutane	0.06

Example	18
trans-Butene	9.80
1-Butene	23.13
Isobutene	39.01
cis-Butene	6.38
Neopentane	0.06
1,3-Butadiene	0.17
2-Methylbutanal	0.24
3-Methylbutanal	0.63
n-Pentanal	4.79
2-Methylbutanol	0.02
Methylpropyldioxolane	0.08
1-Pentanol	0.3
2-n-Butyl-1,3-dioxolane	0.31
Ethylene glycol	<0.01

Example 19:

This example was carried out under the reaction conditions of Example 13,
5 except that the reaction temperature was 80°C.

Example	19
1-Butene, % by weight in feed	27.00
C (1-butene)	19.71%
STY [te/(m ³ h)]	0.23
Product:	
i-Butane	2.01
n-Butane	10.91
Cyclobutane	0.08
trans-Butene	11.71
1-Butene	18.23
Isobutene	28.57
cis-Butene	8.01
Neopentane	0.12
1,3-Butadiene	0.15
2-Methylbutanal	0.67
3-Methylbutanal	0.41

Example	19
n-Pentanal	17.79
2-Methylbutanol	0.04
Methylpropyldioxolane	0.04
1-Pentanol	0.25
2-n-Butyl-1,3-dioxolane	0.02
Ethylene glycol	<0.01

Example 20:

- 5 This example was carried out under the reaction conditions of Example 13, except that the reaction temperature was 85°C.

Example	20
1-Butene, % by weight in feed	27.00
C (1-butene)	24.23%
STY [te/(m ³ h)]	0.28
Product:	
i-Butane	1.68
n-Butane	9.18
Cyclobutane	0.06
trans-Butene	9.01
1-Butene	16.27
Isobutene	31.89
cis-Butene	6.34
Neopentane	0.07
1,3-Butadiene	0.09
2-Methylbutanal	0.78
3-Methylbutanal	0.47
n-Pentanal	19.07
2-Methylbutanol	0.06
Methylpropyldioxolane	0
1-Pentanol	0.15
2-n-Butyl-1,3-dioxolane	0.03
Ethylene glycol	<0.01

Example 21:

This example was carried out under the reaction conditions of Example 13, except that the reaction temperature was 95°C.

5

Example	21
1-Butene, % by weight in feed	27.00
C (1-butene)	32.66%
STY [te/(m ³ h)]	0.38
Product:	
i-Butane	1.90
n-Butane	9.81
Cyclobutane	0.07
trans-Butene	10.01
1-Butene	14.99
Isobutene	31.62
cis-Butene	7.04
Neopentane	0.08
1,3-Butadiene	0.07
2-Methylbutanal	0.82
3-Methylbutanal	0.75
n-Pentanal	22.39
2-Methylbutanol	0.05
Methylpropyldioxolane	0.01
1-Pentanol	0.09
2-n-Butyl-1,3-dioxolane	0.02
Ethylene glycol	<0.01

Example 22:

This example was carried out under the reaction conditions of Example 13, except that the reaction temperature was 105°C.

10

Example	22
1-Butene, % by weight in feed	27.00
C (1-butene)	44.34%
STY [te/(m ³ h)]	0.51

Example	22
Product:	
i-Butane	2.09
n-Butane	9.47
Cyclobutane	0.06
trans-Butene	8.97
1-Butene	12.56
Isobutene	34.63
cis-Butene	6.24
Neopentane	0.06
1,3-Butadiene	0.05
2-Methylbutanal	0.85
3-Methylbutanal	1.08
n-Pentanal	21.35
2-Methylbutanol	0.05
Methylpropyldioxolane	0.00
1-Pentanol	0.12
2-n-Butyl-1,3-dioxolane	0.04
Ethylene glycol	<0.01

Example 23:

5 This example was carried out under the reaction conditions of Example 13, except that the reaction temperature was 115°C.

Example	23
1-Butene, % by weight in feed	28.10
C (1-butene)	66.66%
STY [te/(m ³ h)]	0.80
Product:	
i-Butane	1.71
n-Butane	7.77
Cyclobutane	0.05
trans-Butene	7.37
1-Butene	6.19
Isobutene	26.46
cis-Butene	4.87

Example	23
Neopentane	0.03
1,3-Butadiene	0.00
2-Methylbutanal	1.8
3-Methylbutanal	4.65
n-Pentanal	36.17
2-Methylbutanol	0.09
Methylpropyldioxolane	0.1
1-Pentanol	0.41
2-n-Butyl-1,3-dioxolane	0.47
Ethylene glycol	<0.01

Example 24:

This example was carried out under the reaction conditions of Example 13, except that the reaction pressure was 33 bar.

Example	24
1-Butene, % by weight in feed	28.30
C (1-butene)	52.86%
STY [te/(m ³ h)]	0.64
Product:	
i-Butane	2.63
n-Butane	10.63
Cyclobutane	0.06
trans-Butene	10.22
1-Butene	12.20
Isobutene	35.78
cis-Butene	7.45
Neopentane	0.03
1,3-Butadiene	0.01
2-Methylbutanal	0.48
3-Methylbutanal	1.3
n-Pentanal	17.64
2-Methylbutanol	0.04
Methylpropyldioxolane	<0.01
1-Pentanol	0.14
2-n-Butyl-1,3-dioxolane	0.15

Example	24
Ethylene glycol	<0.01

Example 25:

5 This example was carried out under the reaction conditions of Example 13, except that the reaction pressure was 43 bar.

Example	25
1-Butene, % by weight in feed	28.30
C (1-butene)	58.59%
STY [te/(m ³ h)]	0.71
Product:	
i-Butane	1.67
n-Butane	8.02
Cyclobutane	0.05
trans-Butene	8.37
1-Butene	7.90
Isobutene	24.87
cis-Butene	6.20
Neopentane	0.04
1,3-Butadiene	0.01
2-Methylbutanal	1.29
3-Methylbutanal	5.18
n-Pentanal	30.29
2-Methylbutanol	0.04
Methylpropyldioxolane	0.47
1-Pentanol	0.79
2-n-Butyl-1,3-dioxolane	1.48
Ethylene glycol	<0.01

Example 26:

10 This example was carried out under the reaction conditions of Example 13, except that the reactor length was 1 m.

Example	26
1-Butene, % by weight in feed	27.60
C (1-butene)	62.22%
STY [te/(m ³ h)]	0.73
Product:	
i-Butane	2.11
n-Butane	8.16
Cyclobutane	0.06
trans-Butene	8.50
1-Butene	7.14
Isobutene	25.78
cis-Butene	5.50
Neopentane	0.05
1,3-Butadiene	0.01
2-Methylbutanal	1.64
3-Methylbutanal	4.57
n-Pentanal	33.65
2-Methylbutanol	0.07
Methylpropyldioxolane	0.09
1-Pentanol	0.41
2-n-Butyl-1,3-dioxolane	0.34
Ethylene glycol	<0.01

Example 27:

- 5 This example was carried out under the reaction conditions of Example 13, except that the reactor length was 2 m (with the same internal fittings and diameter).

Example	27
1-Butene, % by weight in feed	27.60
C (1-butene)	62.53%
STY [te/(m ³ h)]	0.73
Product:	
i-Butane	1.38
n-Butane	6.41

Example	27
Cyclobutane	0.04
trans-Butene	7.16
1-Butene	6.02
Isobutene	22.28
cis-Butene	5.35
Neopentane	0.05
1,3-Butadiene	0.01
2-Methylbutanal	1.34
3-Methylbutanal	3.36
n-Pentanal	36.93
2-Methylbutanol	0.04
Methylpropyldioxolane	<0.03
1-Pentanol	0.61
2-n-Butyl-1,3-dioxolane	0.43
Ethylene glycol	<0.01

Hydroformylation of 1-decene

In Examples 28 and 29, 400 kg/h of catalyst solution were passed through the reactor of the experimental apparatus. The reaction temperature was 125°C and the reaction pressure was 70 bar. The concentration of the rhodium was 800 ppm, based on the catalyst phase. As ligand, use was made of TSTPP in the form of its sodium salt.

10 Example 28 (comparative example, continuous process without solvent mixture)

Water was used as solvent for the catalyst. The pH was 4.5. The P/Rh ratio in the catalyst was 5. The molar flows of starting materials fed in and of the products are shown in the table in mol/h.

Example	28
STY [te/(m ³ h)]	0.05
B	13.96
Starting material	
CO	11.38
H ₂	10.52
N ₂	0.05
1-Decene	7.12
Product	
1-Decene	6.67
Undecanal	0.34
2-Methyldecenal	0.11
Off-gas	
CO	10.36
H ₂	9.89
N ₂	0.05

Example 29 (according to the invention)

- 5 The example describes the use according to the invention of a solvent mixture of 50% by weight of water and 50% by weight of ethylene glycol for the hydroformylation of 1-decene, in order to demonstrate the superiority of the present invention in terms of the space-time yield over the solvent water.

10

The solvent used for the catalyst was a mixture of water and ethylene glycol (1:1). The pH was 7.3. The P/Rh ratio in the catalyst was 60. The molar flows of starting materials fed in and of the products are shown in the table in mol/h.

Example	29
STY [te/(m ³ h)]	0.08
B	12.94
Starting material	
CO	13.86
H ₂	12.86
N ₂	0.06
1-Decene	7.33
Product	
1-Decene	6.65
Undecanal	0.61
2-Methyldecanal	0.04
Off-gas	
CO	12.92
H ₂	12.27
N ₂	0.07



Claims:

1. Process for the hydroformylation of one or more olefins each having from 2 to 25 carbon atoms by means of a multiphase reaction in a tube reactor, characterized in that
 - a) the catalyst is present in the continuous phase,
 - b) the continuous phase contains a solvent mixture,
 - c) at least one olefin is present in the disperse phase and
 - d) the loading factor of the tube reactor is equal to or greater than 0.8.
2. Process according to Claim 1, characterized in that the solvent mixture has a dielectric constant of from 50 to 78.
3. Process according to Claim 1 or 2, characterized in that the solvent mixture comprises water and a water-miscible organic solvent containing at least two oxygen atoms.
4. Process according to any of Claims 1 to 3, characterized in that the catalyst contains a metal of transition group VIII of the Periodic Table of the Elements.
5. Process according to any of Claims 1 to 4, characterized in that the catalyst contains rhodium.
6. Process according to any of Claims 1 to 5, characterized in that water-soluble rhodium compounds are used as catalyst.
7. Process according to any of Claims 1 to 6, characterized in that the loading factor B is greater than or equal to 0.9.
8. Process according to any of Claims 1 to 6, characterized in that the loading factor B is greater than or equal to 1.0.
9. Process according to any of Claims 1 to 8, characterized in that the mass ratio of the continuous phase to the disperse phase or phases is greater than 2.



10. Process according to any of Claims 1 to 9, characterized in that the continuous phase drives a jet nozzle upstream of the tube reactor.
- 5 11. Process according to any of Claims 1 to 10, characterized in that at least one starting material is dispersed by means of the energy introduced into the tube reactor by the continuous phase.
12. Use of aldehydes prepared according to any of Claims 1 to 11 for preparing alcohols.
- 10 13. Use of aldehydes prepared according to any of Claims 1 to 11 in aldol condensations.
- 15 14. Use of aldehydes prepared according to any of Claims 1 to 11 for preparing carboxylic acids.