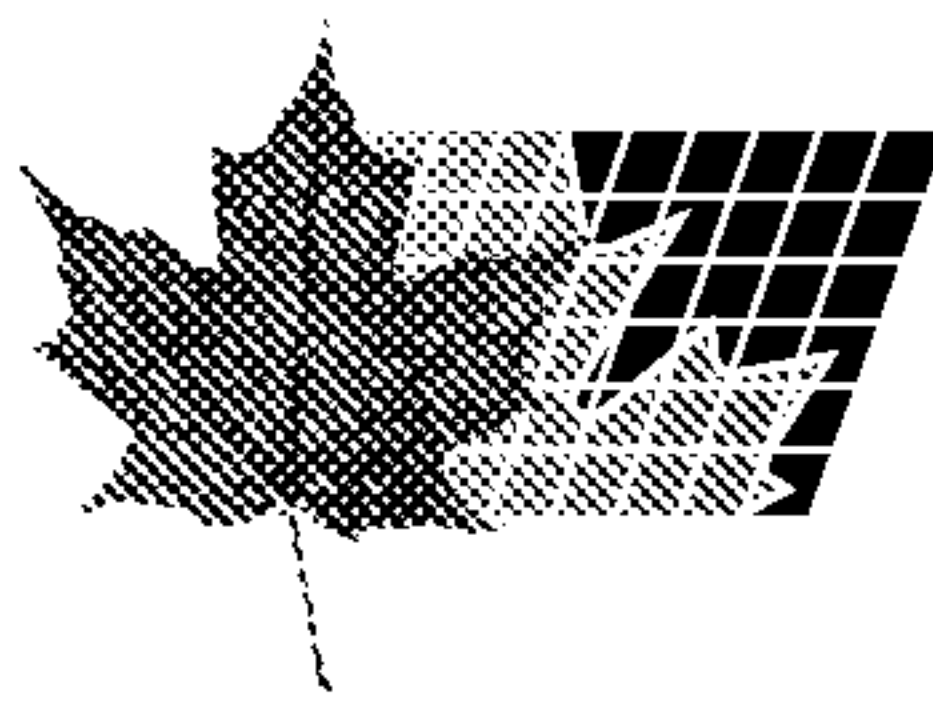




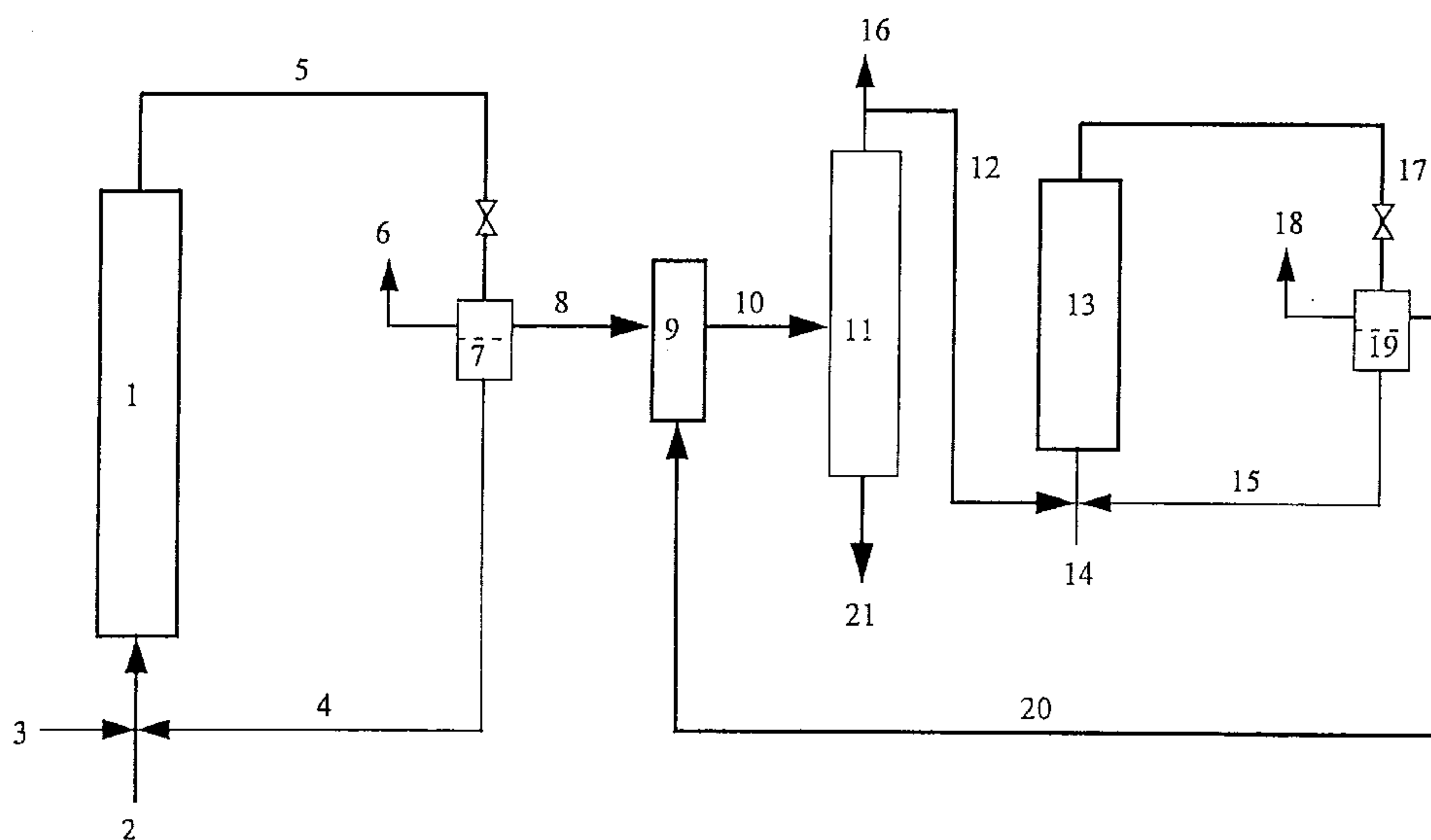
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(54) **PROCEDE DE PREPARATION D'OXO-ALCOOLS SUPERIEURS
PAR HYDROFORMYLATION EN DEUX ETAPES DE
MELANGES D'OLEFINES**

(54) **PROCESS FOR PREPARING HIGHER OXO ALCOHOLS FROM
OLEFIN MIXTURES BY TWO-STAGE
HYDROFORMYLATION**



(57) Disclosed is a process for preparing higher oxo alcohols from isomeric olefin mixtures having from 5 to 24 carbon atoms, which comprises first hydroformylation, selectively hydrogenating the first hydroformylation stage reaction mixture, separating the hydrogenation mixture in a distillation into crude alcohol and low-boilers predominantly consisting of olefins, passing these low-boilers to a second hydroformylation stage, optionally selectively hydrogenating the second hydroformylation stage reaction mixture, optionally separating the hydrogenation mixture in one distillation into crude alcohol and low-boilers, working up the crude alcohol by distillation to pure alcohol and taking off at least some of the low-boilers to discharge saturated hydrocarbons.

Abstract of the Disclosure

Disclosed is a process for preparing higher oxo alcohols from isomeric olefin mixtures having from 5 to 24 carbon atoms, which comprises first hydroformylation, selectively hydrogenating the first hydroformylation stage reaction mixture, separating the hydrogenation mixture in a distillation into crude alcohol and low-boilers predominantly consisting of olefins, passing these low-boilers to a second hydroformylation stage, optionally selectively hydrogenating the second hydroformylation stage reaction mixture, optionally separating the hydrogenation mixture in one distillation into crude alcohol and low-boilers, working up the crude alcohol by distillation to pure alcohol and taking off at least some of the low-boilers to discharge saturated hydrocarbons.

PROCESS FOR PREPARING HIGHER OXO ALCOHOLS FROM OLEFIN
MIXTURES BY TWO-STAGE HYDROFORMYLATION

Field of the Invention

The invention relates to a process for preparing higher oxo alcohols by two-stage hydroformylation of olefin mixtures, which process includes selective hydrogenation of the hydroformylation mixtures.

Prior Art

10 It is known that higher alcohols, in particular those having from 6 to 25 carbon atoms, can be prepared 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 the preparation of plasticizers or detergents.

20 The type of catalyst system and the optimum reaction conditions for the hydroformylation are dependent on the reactivity of the olefin used. The dependence of the reactivity of olefins on their structure is described, for example, by J. Falbe, New Syntheses with Carbon Monoxide, Springer-Verlag, Berlin, Heidelberg, New York, 1980, pages 95 ff. The varying reactivity, especially of the isomeric octanes, is likewise known (B. L. Haymore, A. van Hasselt, R. Beck, Annals of the New York Acad. Sci., 415 (1983), pages 159-175).

Industrial olefin mixtures which are used as starting materials for the oxo synthesis comprise olefin

isomers of the most varied structures having differing degrees of branching, differing position of the double bond in the molecule and, in some cases even differing carbon numbers. This applies especially to olefin mixtures which have been produced by dimerization, trimerization or further oligomerization of C_2 - C_5 olefins or other easily accessible higher olefins or by cooligomerization of these olefins. As examples of typical isomeric olefin mixtures which can be reacted by rhodium-catalyzed, or preferably by cobalt-

10 catalyzed, hydroformylation to give the corresponding aldehyde mixtures and alcohol mixtures, tripropenes and tetrapropenes and dibutenes, tributenes and tetrabutenes may be mentioned.

The rate of the hydroformylation reaction decreases with increasing carbon number and with the degree of branching. The reaction rate of linear olefins can be greater by a factor of 5 to 10 than that of the branched isomers. The position of the double bond in the olefin molecule also influences the reactivity. Olefins having a terminal double bond react markedly more rapidly than isomers having the

20 double bond in the interior of the molecule. Because of the differing reactivity of the olefin isomers, relatively long reaction times are required if it is desired to achieve the most substantial possible conversion of the olefins. However, as a result, the product yield is decreased due to unwanted side reactions and secondary reactions. The same occurs if attempts are made to shorten the reaction times by higher reaction temperatures. Especially because of the varying reactivity of the isomers, it is difficult to achieve high

conversion rates and simultaneously high selectivities in the hydroformylation of olefin mixtures. This applies in particular to single-stage hydroformylations.

According to German Patent Publication (DE)

32 32 557 A1, alcohols are prepared by a two-stage hydroformylation of monoolefins having from 3 to 20 carbon atoms. In the first reaction stage, the olefins are converted to the aldehyde, using a cobalt catalyst, with degrees of conversion of from 50 to 90%, whereby the formation of alcohols is suppressed. The cobalt catalyst is then removed from the reaction mixture and this reaction mixture is hydroformylated in a second stage using a cobalt organophosphine complex as catalyst. At the same time, the aldehyde formed in the first stage is hydrogenated to the alcohol. A disadvantage in this process is that, particularly in the second hydroformylation stage, a considerable part of the olefins is hydrogenated instead of being hydroformylated.

Summary of the Invention

An object of the invention is to provide a process for preparing higher oxo alcohols from the corresponding olefin mixtures, at high conversion rates with high selectivities and, in addition, at high space-time yields.

The invention therefore provides a process for preparing higher oxo alcohols from isomeric olefin mixtures having from 5 to 24 carbon atoms by two-stage hydroformylation in the presence of a cobalt catalyst or rhodium catalyst at elevated temperature and at elevated pressure.

The process comprises:

(A) first hydroformylation stage of the isomeric olefin mixture in the presence of a cobalt or rhodium catalyst at an elevated temperature and an elevated pressure;

(B) first selective hydrogenation of a reaction mixture of the first hydroformylation stage;

(C) separation of a reaction mixture of the first selective hydrogenation by distillation into crude alcohol and low-boilers consisting essentially of unreacted olefin mixtures;

10 (D) second hydroformylation stage of the low-boilers separated from the first selective hydrogenation reaction mixture in the presence of a cobalt or rhodium catalyst at an elevated temperature and an elevated pressure;

(E) optionally, second selective hydrogenation of a reaction mixture of the second hydroformylation stage;

(F) optionally, separation of a reaction mixture of the second selective hydrogenation by distillation into crude alcohol and low-boilers;

20 (G) distillation of the crude alcohol to obtain pure alcohol; and

(H) discharge of at least a part of the low-boilers to remove saturated hydrocarbons.

Preferably, expanded reaction mixtures from both hydroformylation stages are freed from the hydroformylation catalyst prior to the selective hydrogenations.

Brief Description of the Drawings

Figure 1 is a block diagram showing a first particularly preferred embodiment of the process of the

present invention; and

Figure 2 is a block diagram showing a second particularly preferred embodiment of the process of the present invention.

Description of Preferred Embodiments of the Invention

The process according to the invention can be carried out batchwise or, preferably, continuously. Various process variants are possible for the continuous procedure.

10 In Figure 1, as an example, a block diagram of a plant is shown in which the first particularly preferred embodiment of the process can be carried out continuously in a closed reaction system. This variant of the process lacks the optional second selective hydrogenation (E) and the optional second separation (F). Initially, the olefin mixture 2, synthesis gas (carbon monoxide and hydrogen) 3 and catalyst 4 are introduced into the first hydroformylation reactor 1. The hydroformylation mixture 5 is expanded, the expansion gas 6 (unconsumed synthesis gas) is taken off and the expanded hydroformylation mixture 5 is freed from catalyst 4 in the
20 first catalyst removal stage 7. The catalyst, optionally after supplementation by fresh catalyst, is recirculated to the first hydroformylation reactor 1. The catalyst-freed hydroformylation mixture 8 is passed into the selective hydrogenation stage 9 in which the aldehydes and by-products present in the mixture, such as acetals of the aldehydes and esters of the alcohols, in particular their formates, are hydrogenated to the alcohols. The low-boilers 12 are removed from the hydrogenation mixture 10 in the distillation 11. The

low-boilers predominantly consist of unreached isomeric olefins and most of them are conducted into the second hydroformylation reactor 13, into which synthesis gas 14 and catalyst 15 are also introduced. A part of the low-boilers 12 is discharged as residual low-boilers 16. The second hydroformylation mixture 17 from the second hydroformylation reactor 13 is in turn expanded and expansion gas 18 is taken off. The expanded second hydroformylation mixture 17 is freed from catalyst 15 in the second catalyst separation stage 19.

10 This catalyst, again optionally after supplementation, is recirculated to the second hydroformylation reactor 13, and, as catalyst-depleted second hydroformylation mixture 20, is transferred to the selective hydrogenation 9. There, it is selectively hydrogenated together with the catalyst-freed hydroformylation mixture 8 from the first hydroformylation reactor 1. the crude alcohol 21 taken off from the distillation 11 is worked up to be purified in a further distillation which is not shown.

20 The block diagram of an alternative second continuous process variant for carrying out the process in a closed reaction system according to a particularly preferred embodiment of the invention is shown in Figure 2. This variant includes the second selective hydrogenation (E) and the second separation (F). The olefin mixture 2, synthesis gas 3 and catalyst 4 are introduced into the first hydroformylation reactor 1. The hydroformylation mixture 5 is expanded, the expansion gas 6 is taken off and the expanded hydroformylation mixture is freed from catalyst 4 in the first

catalyst removal stage 7. The catalyst, optionally after supplementation by fresh catalyst, is recirculated to the first hydroformylation reactor 1. The catalyst-freed hydroformylation mixture 8 is passed into the first selective hydrogenation stage 9, in which the aldehydes and the acetals and esters present as by-products, in particular the formates of the alcohols are hydrogenated to the alcohols. The low-boilers 12 are separated off from the first hydrogenation mixture 10 in the first distillation stage 11. The low-boilers predominantly consist of unreacted isomeric olefins and are passed to the second hydroformylation reactor 13, into which synthesis gas 14 and catalyst 15 are also introduced. The hydroformylation mixture 17 from the second hydroformylation reactor 13 is in turn expanded, and expansion gas 18 is taken off. The expanded hydroformylation mixture 17 is freed from catalyst 15 in the second catalyst removal stage 19. This catalyst in turn, optionally after supplementation by fresh catalyst, is recirculated to the second hydroformylation reactor 13, and as catalyst-depleted hydroformylation mixture 20, is passed into a second comparatively small selective hydrogenation stage 22. The second hydrogenation mixture 23 is fractionated in the second, comparatively small distillation stage 24 into paraffin-rich low-boilers 16, which are taken off, and crude alcohol 25 which is passed to the first distillation stage 11 and is there distilled together with the first hydrogenation mixture 10. The crude alcohol 21 is in turn worked up to pure alcohol in a further distillation which is not shown.

An essential difference between the two process procedures is that according to Figure 1 only one selective hydrogenation 9 is provided in which the two catalyst-depleted hydroformylation mixtures 8 and 20 are hydrogenated, and only one distillation stage 11 in which the hydrogenation mixture 10 is separated, whereas according to Figure 2 the second hydroformylation mixture 20 is hydrogenated in a second selective hydrogenation 22 and the hydrogenation mixture is separated in a second distillation stage 24. The variant according to Figure 2 has higher capital costs because additional, but comparatively small apparatus is required. In compensation, the olefin is more substantially utilized, since the low-boilers 16 according to Figure 2 are smaller in quantity than the low-boilers 16 according to Figure 1 and are in addition substantially free of olefins, whereas the low-boilers 16 according to Figure 1 still comprise considerable amounts of olefins.

Hydroformylation

The starting materials for the hydroformylation are generally but not exclusively mixtures of monoolefins having from 5 to 24 carbon atoms and a terminal or middle-position C-C double bond, 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, 1-heptene, 2- or 3-methyl-1-hexene, 1-octene, the isomeric C₈ olefin mixture (dibutene) produced in the dimerization of butenes, 1-heptene, 1-nonene, 2- or 3-methyl-1-octene, the isomeric C₉ olefin mixture (tripropene) produced in the trimerization of

1-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 cooligomerization of olefins having different carbon numbers (preferably 2 to 4), optionally after separating off by distillation into fractions of identical or similar carbon numbers. Preferred starting material are C₈, C₉, C₁₂ or C₁₆ olefin mixtures.

The invention does not lie in the type or the conditions of the hydroformylation in the two stages. The olefins are rather hydroformylated in a manner generally well known per se. Rhodium catalysts or more preferably in both stages cobalt catalysts are therefore employed, with or without complex-stabilizing additions, such as organic phosphines or phosphites. The temperatures and the pressures can vary within broad ranges, depending on catalyst and olefin mixture. The temperatures may generally be 100-200°C and the pressures may generally be 10-45 MPa (100-450 atm.). Since the more reactive olefins react preferentially in the first stage, in the second hydroformylation stage, more energetic reaction conditions with respect to temperature, amount of catalyst etc. may preferably be established. For a given olefin mixture, the optimum conditions for the two hydroformylation stages may be established without difficulty by experiment. A description of the hydroformylation of

olefins is given, for example, in J. Falbe, New Syntheses with Carbon Monoxide, Springer-Verlag, Heidelberg-New York, 1980, pages 99 ff., and in Kirk-Othmer, Encyclopedia of Chemical Technology, Volume 17, 4th edition, John Wiley & Sons, pages 902-919 (1996).

Generally, the hydroformylation is carried out in the first stage in such a manner that from 50 to 90%, preferably from 60 to 85%, of the fed olefin mixture is reacted. Obviously, the hydroformylation reactors and the other apparatuses must be designed accordingly.

The degree of conversion of the olefins in the first hydroformylation stage is restricted to the desired value by altering the hydroformylation reaction conditions appropriately. By selecting lower reaction temperatures and/or catalyst concentrations and shorter residence times, the olefin conversion rate in the reactor can be decreased. The degree of conversion of the olefins in the first reactor is determined on the basis of the amount and composition of the fresh olefin mixture 2 and of the amount and composition of the hydroformylation mixture 5. The overall degree of conversion is determined on the basis of the amount and composition of the fresh olefin mixture 2 and of the amount and composition of the discharged low-boilers (16 according to both the figures). To determine the olefin contents in the various mass streams, gas-chromatographic analysis can be employed.

Catalyst removal

The hydroformylation reaction mixtures are as

mentioned above, preferably firstly freed from catalyst, in a manner known per se. If a cobalt catalyst is used, this can be achieved by pressure reduction, separating off an aqueous catalyst phase, oxidizing with air or oxygen cobalt carbonyl compounds remaining in the hydroformylation mixture and extracting the resulting cobalt compounds with water or aqueous acid. Decobalting 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
10 served as hydroformylation catalyst, it can be removed from the hydroformylation mixture as distillation residue by means of thin-film evaporation.

If the preferred cobalt catalysts are used, the first hydroformylation stage reaction mixtures freed from catalyst comprise, depending on the degree of conversion, generally 8-45% by weight, usually 15-35% by weight of low-boilers having a lower boiling point than the aldehydes, principally olefins, in addition the corresponding saturated hydrocarbons and water and methanol; in addition 30-80% by
20 weight of aldehydes, 5-30% by weight of alcohols, up to 10% by weight of formates of the alcohols and 0.5-5% by weight of high-boilers having a higher boiling point than the alcohols.

The second hydroformylation stage reaction mixtures contain, generally 10-40% by weight, usually 15-30% by weight, of low-boilers, including less olefins and more saturated hydrocarbons and water and methanol, in addition 30-70% by weight of aldehydes, 5-40% by weight of alcohols, up to 10% by weight of formates of these alcohols and 3-12% by weight of

high-boilers having a higher boiling point than the alcohols.

If rhodium catalysts were used, the reaction mixtures comprise considerably less paraffins and formates.

Selective hydrogenation

10 The selective hydrogenation of the reaction mixtures from both hydroformylation stages, preferably freed from catalyst, is an essential feature of the process according to the invention. As a result, the aldehydes and certain accompanying substances, including acetals of the aldehydes and esters of the alcohols and of these, in particular, the formates, are hydrogenated to the desired alcohols. In the course of this selective hydrogenation, the unreacted olefins are not hydrogenated or are virtually not hydrogenated, so that high yields based on the olefin mixtures used are achieved. Less than 5% (based on the olefins) of the olefins used are lost due to hydrogenation to the saturated hydrocarbons.

20 Selective hydrogenation of hydroformylation mixtures may preferably be conducted by contacting the mixtures with hydrogen at elevated temperature and at elevated pressure in the presence of a supported catalyst which comprises, as active components, copper, nickel and chromium, supported on a supporting material.

Preferred catalysts of this type are supported catalysts which comprise, as active components, copper and nickel at concentrations in each case of from 0.3 to 15% by weight, chromium at a concentration of from 0.05 to 3.5% by weight and an alkali metal component at a concentration of

from 0.01 to 1.6% by weight, preferably of 0.02-1.2% by weight, in each case based on the supported catalyst. Another preferred supported catalyst comprises copper, nickel and chromium in the above-specified amounts, but no alkali metal component. Suitable support substances are, in particular, silicon dioxide and aluminum oxide. The amounts specified are based on the catalyst which is prepared as described below prior to reduction.

10 In the hydrogenation, the aldehydes in the reaction mixtures of both hydroformylation stages are in each case hydrogenated to the corresponding alcohols in only one hydrogenation stage step with conversion rates greater than 98% at a selectivity of greater than 99%. The esters and acetals are likewise converted into the desired alcohols. The starting olefins present in the mixture remain surprisingly by far for the most part unchanged, although the preferred supported catalysts, under comparable conditions, also hydrogenate virtually quantitatively the olefinic double bond in 2-ethylhex-2-enal (EP 0 326 674 A2). The hydrogenation can
20 be carried out in the lower-pressure region of below 30 bar and at high space-time yields.

These catalyst components can be distributed homogeneously in the pores of a support material or enriched in its edge zones. In the former case, an aqueous solution is made up which comprises the components in the form of metal salts and whose volume expediently roughly corresponds to 0.8 times the pore volume of the support material. As copper salts, nickel salts and chromium salts as catalyst precursor,

use is advantageously made of those which are converted on heating into oxides, such as nitrates and acetates. If the catalyst is to contain an alkali metal component, this can be introduced together with chromium in the form of alkali metal chromate or alkali metal dichromate, in particular as sodium chromate or sodium dichromate. The metal salt concentration in the solution depends on the desired concentration of the respective component in the finished catalyst. The metal salt solution is then sprayed onto the non-preheated support material, situated in a coating drum, and penetrates into the pores thereof. The catalyst is then dried.

If it is desired to have a catalyst with components which are enriched in the edge zones of a porous or a more or less pore-free support material, the metal salt solution can be sprayed onto the preheated support material and the support material can be further heated during the spraying, so that the water evaporates and the catalyst components are fixed essentially on the surface of the support material.

After the catalyst components are applied, the catalysts of both the types are calcined, i.e. depending on the catalyst precursor used, heated to temperatures of 200-400°C, as a result of which the catalyst precursors are converted into the oxidic state. The catalyst is then reduced with hydrogen at said hydrogenation temperatures. The reduction can be performed just after the catalyst is prepared or expediently not until in the hydrogenation reactor.

The catalysts are preferably used in a form in which they offer a low resistance to flow, e.g. in the form of

granules, pellets or shaped bodies such as tablets, cylinders or rings. They are expediently activated prior to use by heating in a hydrogen stream, e.g. at said hydrogenation temperatures, if they have not been reduced in the reactor.

The hydrogenation can be carried out continuously or batchwise and either in the gas phase or in the liquid phase. Hydrogenation in the liquid phase is preferred, since the gas-phase process requires a higher energy consumption, because of the necessary circulation of large gas volumes. In addition there is the fact that evaporating aldehydes having an increasing carbon number requires more energy, and, in addition, the starting material loading in the reduction gas decreases, so that a gas-phase process in the case of aldehydes having a carbon number greater than about 8 makes it scarcely possible still to carry out the overall process economically.

Various process variants can be selected for the liquid-phase hydrogenation. It can be carried out adiabatically or virtually isothermally, i.e. having a temperature rise of $<10^{\circ}\text{C}$, in a single stage or two stages. In the latter case, both reactors, preferably tube reactors, can be operated adiabatically or virtually isothermally or one can be operated adiabatically and the other virtually isothermally. In addition, it is possible to hydrogenate the hydroformylation mixtures in a straight pass or with product recycling. The reactors can be operated as concurrent flow reactors with a trickle bed (trickle flow) or preferably with high liquid flow rates (pulse flow). In the interest of a

high space-time yield, the reactors are preferably operated with high liquid flow rates of 5-100 m³, in particular 15-50 m³ per m² of cross section of the empty reactor and hour. If a reactor is operated isothermally and in a straight pass, the liquid hourly space velocity (LHSV) values can be between 0.1 and 10 h⁻¹, preferably between 0.5 and 5 h⁻¹.

The liquid-phase hydrogenation is generally carried out at an overall pressure of from 5 to 30 bar, in particular between 15 and 25 bar. The gas-phase hydrogenation can also
10 be carried out at lower pressures, say at 2-20 bar, with correspondingly greater gas volumes. The reaction temperatures, in the case of hydrogenations in the liquid or gas phase, are generally between 120 and 220°C, in particular between 140 and 180°C.

Separation of the hydrogenation mixtures by distillation

After the hydrogenation, the reaction mixtures are worked up by distillation in manner known per se. Low-boilers are removed as overhead product, which low-boilers
predominantly comprise olefins and in addition saturated
20 hydrocarbons. According to Figure 1, the low-boilers from both hydroformylation stages are starting material for the second hydroformylation stage. In this process variant, however, some of these low-boilers are discharged, so that the concentration of the inert saturated hydrocarbons produced by hydrogenation of the olefins in the hydroformylation stages is kept to an acceptable level of at most 60%. In the process variant according to Figure 2, all of the low-boilers from the first distillation stage are passed to the second

hydroformylation stage, and the saturated hydrocarbons are discharged as a comparatively small low-boiler fraction of the second distillation.

The hydrogenation mixtures are generally distilled at reduced pressure, e.g. at an absolute pressure of 400-900 mbar. The crude alcohol which is produced as bottom product in the distillation can be worked up to pure alcohol in a conventional manner by distillation.

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

Example 1 (Comparison example)

Nonanols by single-stage hydroformylation of di-n-butene

In a 5 l high-pressure autoclave which was equipped with an agitator and electrical heating, 2000 g of di-n-butene (composition in Table 1, column 2) were hydroformylated in the presence of a cobalt catalyst at 185°C and a synthesis gas pressure kept constant at 280 bar. The synthesis gas comprised 50% by volume of CO and 50% by volume of H₂.

20 To prepare the cobalt hydridocarbonyls, e.g. HCo(CO)₄, serving as catalyst, as catalyst precursor, use was made of an aqueous cobalt acetate solution containing 1% by weight of Co. The cobalt acetate solution was treated with synthesis gas, with stirring for 7 h at 170°C and 280 bar. After cooling to room temperature and expansion, the cobalt carbonyls formed were transferred to the organic phase by extraction with di-n-butene. After removing the aqueous phase the di-n-butene loaded with cobalt carbonyls having a content

of 0.021% by weight of Co (calculated as metal) was hydroformylated under the abovementioned reaction conditions for 3 hours.

After cooling to room temperature, the reaction mixture was emptied, depressurized, from the autoclave and free from cobalt catalyst by treatment with 5% strength acetic acid and air at 80°C. 2487 g of decobalted hydroformylation mixture were obtained, which were analyzed by gas chromatography. The results are listed in Table 2, column 2.

10 According to these, a di-n-butene conversion rate of 92.3% was achieved at a selectivity of product of value of 87.9%, equivalent to a yield of product of value of 81.1%, based on di-n-butene used. Products of value were considered to be C₉ aldehydes, C₉ alcohols and (iso)nonyl formates.

Example 2

Nonanols by two-stage hydroformylation - 1st stage

20 In a 5 l high-pressure autoclave which was equipped with an agitator and electrical heating, 2000 g of di-n-butene (composition in Table 1, column 2) were hydroformylated in the presence of a cobalt catalyst at 170°C and a synthesis gas pressure kept constant at 280 bar. The synthesis gas again comprised 50% by volume of CO and 50% by volume of H₂.

The cobalt catalyst was prepared as in Example 1 and transferred to the di-n-butene. The concentration of the catalyst was 0.019% by weight of Co, based on the di-n-butene. The di-n-butene loaded with cobalt carbonyls was hydroformylated under the abovementioned reaction conditions for 2 hours. The hydroformylation mixture was freed from

cobalt catalyst as in Example 1.

This hydroformylation solution was repeated three times under the same conditions. The hydroformylation mixtures were combined after removal of the cobalt catalyst. This produced 9412 g of reaction mixture which had the composition specified in Table 2, column 3, according to GC analysis. A di-n-butene conversion rate of 67.6% was then achieved at a selectivity for product of value of 94.5%, equivalent to a yield of product of value of 63.9% based on di-n-butene used. Products of value were again considered to be C₉ aldehydes, C₉ alcohols and (iso)nonyl formates.

Example 3

Nonanols by two-stage hydroformylation - 2nd stage

7500 g of the reaction mixture from Example 2 were selectively hydrogenated with retention of the olefins to give the product of value C₉ alcohol. The hydrogenation was carried out batchwise in the liquid phase in a 20 l autoclave at 175°C and 20 bar H₂ pressure in the presence of a supported catalyst containing 12.1% by weight of Cu, 3.0% by weight of Ni and 2.5% by weight of Cr on aluminum oxide as support material. The unreacted olefins were then distilled off as low-boilers from the products of value and the high-boilers from the hydrogenation mixture.

The low-boiler fraction, according to GC analysis, comprised, in addition to 98.5% by weight of hydrocarbons of which 87.9% by weight were C₈ olefins, around 1.5% by weight of methanol which had been formed by hydrogenation of (iso)nonyl formates. The distribution of isomers in the C₈

isomer mixture is listed in Table 1, column 3. In comparison with the fresh di-n-butene containing 23% by weight of dimethylhexenes, this C₈ isomeric mixture containing 44% by weight of dimethylhexenes comprised considerably greater amounts of these less reactive C₈ isomers.

2000 g of this C₈ olefin isomer mixture enriched with dimethylhexenes and comprising 10.6% by weight of C₈ paraffins were hydroformylated in a 5 l autoclave in the presence of a cobalt catalyst in the manner described in Example 1 at 185°C and a synthesis gas pressure of 280 bar. Again a synthesis gas containing 50% by volume of CO and 50% by volume of H₂ was used. At a cobalt content of 0.031% by weight, based on the C₈ olefin mixture, this mixture was hydroformylated for 3 hours at a synthesis gas pressure which was kept constant.

The hydroformylation mixture was expanded and freed from cobalt catalyst as described in Example 1. This produced 2438 g of a decobalted hydroformylation mixture whose composition according to GC analysis is given in Table 2, column 4. According to this, a C₈ olefin conversion rate of 91.3% was achieved at a selectivity for product of value of 83.0%, equivalent to a yield of product of value of 75.8%, based on di-n-butene used. Products of value were considered to be C₉ aldehydes, C₉ alcohols and (iso)nonyl formates.

If Example 2, as first hydroformylation stage, and Example 3, as second hydroformylation stage, of the process according to the invention are combined, after both stages, an overall olefin conversion rate of 97.1% was achieved, at a

selectivity for product of value of 91.5%, equivalent to a total yield of product of value of 88.8%, based on olefin mixture used.

In comparison with the single-stage hydroformylation according to Example 1, there is therefore an increase in the yield of product of value by around 8 percentage points.

Table 1**Distribution of the C₈ isomers in the feed olefin mixture**

1	2	3
C ₈ isomers	di-n-butene starting material Examples 1 and 2 (% by weight)	C ₈ olefin mixture starting material Example 3 (% by weight)
Dimethylhexenes	23	44
3-Methylheptenes	62	51
n-Octenes	15	5

Table 2**Composition of hydroformylation mixtures**

1	2	3	4
Composition according to GC analysis	Example 1 (% by weight)	Example 2 (% by weight)	Example 3 (% by weight)
C ₈ olefins	6.2	27.4	7.0
C ₈ paraffins	3.3	2.4	4.5
Isononanal	55.1	48.7	51.2
Esters/isononyl formates	4.5	2.0	8.8
Isononanol	23.9	18.5	18.8
Residue	7.0	1.0	9.8

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for preparing a higher oxo alcohol from an isomeric C_5-C_{24} olefin mixture which process comprises:

(A) first hydroformylation stage of the isomeric olefin mixture in the presence of a cobalt or rhodium catalyst at an elevated temperature and an elevated pressure;

(B) first selective hydrogenation of a reaction mixture of the first hydroformylation stage;

(C) separation of a reaction mixture of the first selective hydrogenation by distillation into crude alcohol and low-boilers consisting essentially of unreacted olefin mixtures;

(D) second hydroformylation stage of the low-boilers separated from the first selective hydrogenation reaction mixture in the presence of a cobalt or rhodium catalyst at an elevated temperature and an elevated pressure;

(E) optionally, second selective hydrogenation of a reaction mixture of the second hydroformylation stage;

(F) optionally, separation of a reaction mixture of the second selective hydrogenation by distillation into crude alcohol and low-boilers;

(G) distillation of the crude alcohol to obtain pure alcohol; and

(H) discharge of at least a part of the low-boilers to remove saturated hydrocarbons.

2. The process as claimed in claim 1, wherein the reaction mixture of the first hydroformylation stage is expanded and freed from the cobalt or rhodium catalyst prior to the first selective hydrogenation; and the reaction mixture of the second hydroformylation stage is expanded and freed from the cobalt or rhodium catalyst prior to the second selective hydrogenation, when the second selective hydrogenation is conducted.

3. The process as claimed in claim 1 or 2, wherein C_8 , C_9 , C_{12} or C_{16} isomeric olefin mixture is used as the starting isomeric olefin mixture.

4. The process as claimed in one of claims 1 to 3, wherein the cobalt catalyst is employed in both the first and second hydroformylation stages.

5. The process as claimed in one of claims 1 to 4, which lacks the second selective hydrogenation (E) and the separation (F).

6. The process as claimed in claim 5, wherein a part of the low-boilers separated by the distillation of the separation step (c) is taken off to discharge paraffins.

7. The process as claimed in one of claims 1 to 4, which comprises the second selective hydrogenation (E) and the second separation (F).

8. The process as claimed in claim 7, wherein the low-boilers separated by distillation of the separation step (F) are taken off to discharge paraffins.

9. The process as claimed in one of claims 1 to 8, wherein the selective hydrogenations are conducted at elevated temperature and at elevated pressure on a supported catalyst which comprises, as active components, copper, nickel and chromium.

10. The process as claimed in claim 9, wherein the supported catalyst comprises, as active components, copper and nickel at concentrations in each case of from 0.3 to 15% by weight and chromium at a concentration of from 0.05 to 3.5% by weight and also comprises an alkali metal component at a concentration of from 0.01 to 1.6% by weight, each based on the support catalyst.

11. The process as claimed in claim 10, wherein the concentration of the alkali metal component is from 0.2 to 1.2% by weight.

12. The process as claimed in claim 9, wherein the supported catalyst comprises, as active components, copper and nickel at concentrations in each case of from 0.3 to 15% by weight and chromium at a concentration of from 0.05 to 3.5% by weight, each based on the supported catalyst.

13. The process as claimed in one of claims 9 to 12, wherein the catalyst is supported on a catalyst support material which is silicon dioxide or aluminum oxide.

14. The process as claimed in one of claims 1 to 13, wherein the selective hydrogenation is carried out continuously or batchwise in a liquid phase.

15. The process as claimed in claim 14, wherein the hydrogenation is carried out in the liquid phase under an overall pressure of from 5 to 30 bar.

16. The process as claimed in claim 15, wherein the overall pressure is from 15 to 25 bar.

17. The process as claimed in one of claims 1 to 16, wherein the selective hydrogenation is carried out at a temperature of 120 to 220°C.

18. The process as claimed in claim 17, wherein the temperature is from 140 to 180°C.

19. The process as claimed in one of claims 1 to 18, wherein the selective hydrogenation is carried out in the liquid phase and at a liquid flow rate of 5-100 m³ per m² of cross section of a reactor and hour.

20. The process as claimed in claim 19, wherein the liquid flow rate is 15-50 m³ per m² of cross section of a reactor and hour.

21. A process for preparing a higher C₆-C₂₅ oxo alcohol from a C₅-C₂₄ isomeric olefin mixture in a closed reaction system, which comprises:

(A) first hydroformylation stage of the isomeric olefin mixture with carbon monoxide and hydrogen in the presence of a cobalt or rhodium catalyst at an elevated temperature and an elevated pressure in such a manner that 50 to 90% of the olefin is reacted, to form a catalyst containing first hydroformylation stage reaction mixture;

(I-a) removal of the cobalt or rhodium catalyst from the catalyst containing first hydroformylation stage reaction mixture, to obtain a catalyst-freed first hydroformylation stage reaction mixture which consists essentially of 30-80% by weight of C₆-C₂₅ aldehydes, 5-30% by weight of C₆-C₂₅ alcohols, up to 10% by weight of formates of the C₆-C₂₅ alcohols, 0.5-5% by weight of high-boilers having a boiling point higher than the C₆-C₂₅ alcohols and 8-45% by weight of low-boilers having a boiling point lower than the C₆-C₂₅ aldehydes, wherein the low-boilers consist essentially of unreacted C₅-C₂₄ olefins and their corresponding saturated hydrocarbons;

(B) first selective hydrogenation of the catalyst-freed first hydroformylation stage reaction mixture, by

contacting the reaction mixture with hydrogen in the presence of a supported catalyst comprising, as active components, copper, nickel and chromium at a temperature of 120-220°C at an elevated pressure of no more than 30 bar, thereby hydrogenating the aldehydes and the formates to the corresponding alcohols while hydrogenating only less than 5% (based on the unreacted C_5-C_{24} olefins) of the unreacted C_5-C_{24} olefins, to obtain a first selective hydrogenation mixture;

(C) separation of the first selective hydrogenation mixture by distillation into crude C_6-C_{25} oxo alcohol and the low-boilers

(D) second hydroformylation stage of the low-boilers separated in the step (C) with carbon monoxide and hydrogen in the presence of a cobalt or rhodium catalyst at an elevated temperature and an elevated pressure, to form a catalyst-containing second hydroformylation stage reaction mixture;

(I-b) removal of the cobalt or rhodium catalyst from the catalyst-containing second hydroformylation stage reaction mixture, to obtain a catalyst-depleted second hydroformylation stage reaction mixture consisting essentially of 30-70% by weight of C_6-C_{25} aldehydes, 5-40% by weight of C_6-C_{25} alcohols, up to 10% by weight of formates of the C_6-C_{25} alcohols, 3-12% by weight of high-boilers having a boiling point higher than the C_6-C_{25} alcohols and 10-40% by weight of low-boilers having a boiling point lower than the C_6-C_{25} aldehydes, where the low-boilers consist essentially of

the unreacted C_5-C_{24} olefins in amounts less than the catalyst-freed first hydroformylation stage reaction mixture and their corresponding saturated hydrocarbons in amounts higher than the catalyst-freed first hydroformylation stage reaction mixture;

(E) second selective hydrogenation of the catalyst-depleted second hydroformylation stage reaction mixture, by contacting the reaction mixture with hydrogen in the presence of a supported catalyst comprising, as active components, copper, nickel and chromium at a temperature of 120-220°C at an elevated pressure of no more than 30 bar, thereby hydrogenating the aldehydes and the formates to their corresponding alcohols while hydrogenating only less than 5% (based on the unreacted C_5-C_{24} olefins) of the unreacted C_5-C_{24} olefins, to obtain a second selective hydrogenation mixture;

(F) separation of the second selective hydrogenation mixture by distillation into crude higher C_6-C_{25} oxo alcohol and the low-boilers which are rich in the saturated hydrocarbons, and recirculation of the separated crude higher C_6-C_{25} oxo alcohol to the separation stage (C);

(G) distillation of the crude higher C_6-C_{25} oxo alcohol obtained by the step (C) to obtain the desired higher C_6-C_{25} oxo alcohol in a substantially pure form; and

(H) discharge of at least a part of the low-boilers separated by the step (F) to remove the saturated hydrocarbons out of the closed reaction system.

22. A process for preparing a higher C_6-C_{25} oxo alcohol from a C_5-C_{24} isomeric olefin mixture in a closed reaction system, which comprises:

(A) first hydroformylation stage of the isomeric olefin mixture with carbon monoxide and hydrogen in the presence of a cobalt or rhodium catalyst at an elevated temperature and an elevated pressure in such a manner that 50 to 90% of the olefin is reacted, to form a catalyst containing first hydroformylation stage reaction mixture;

(I-a) removal of the cobalt or rhodium catalyst from the catalyst containing first hydroformylation stage reaction mixture, to obtain a catalyst-freed first hydroformylation stage reaction mixture which consists essentially of 30-80% by weight of C_6-C_{25} aldehydes, 5-30% by weight of C_6-C_{25} alcohols, up to 10% by weight of formates of the C_6-C_{25} alcohols, 0.5-5% by weight of high-boilers having a boiling point higher than the C_6-C_{25} alcohols and 8-45% by weight of low-boilers having a boiling point lower than the C_6-C_{25} aldehydes, wherein the low-boilers consist essentially of unreacted C_5-C_{24} olefins and their corresponding saturated hydrocarbons;

(B) first selective hydrogenation of the catalyst-freed first hydroformylation stage reaction mixture, by contacting the reaction mixture with hydrogen in the presence of a supported catalyst comprising, as active components, copper, nickel and chromium at a temperature of 120-220°C at an elevated pressure of no more than 30 bar, thereby

hydrogenating the aldehydes and the formates to the corresponding alcohols while hydrogenating only less than 5% (based on the unreacted C_5-C_{24} olefins) of the unreacted C_5-C_{24} olefins, to obtain a first selective hydrogenation mixture;

(C) separation of the first selective hydrogenation mixture by distillation into crude C_6-C_{25} oxo alcohol and the low-boilers

(D) second hydroformylation stage of the low-boilers separated in the step (C) with carbon monoxide and hydrogen in the presence of a cobalt or rhodium catalyst at an elevated temperature and an elevated pressure, to form a catalyst-containing second hydroformylation stage reaction mixture;

(I-b) removal of the cobalt or rhodium catalyst from the catalyst-containing second hydroformylation stage reaction mixture, to obtain a catalyst-depleted second hydroformylation stage reaction mixture consisting essentially of 30-70% by weight of C_6-C_{25} aldehydes, 5-40% by weight of C_6-C_{25} alcohols, up to 10% by weight of formates of the C_6-C_{25} alcohols, 3-12% by weight of high-boilers having a boiling point higher than the C_6-C_{25} alcohols and 10-40% by weight of low-boilers having a boiling point lower than the C_6-C_{25} aldehydes, where the low-boilers consist essentially of the unreacted C_5-C_{24} olefins in amounts less than the catalyst-freed first hydroformylation stage reaction mixture and their corresponding saturated hydrocarbons in amounts higher than the catalyst-freed first hydroformylation stage reaction

mixture;

(G) distillation of the crude higher C_6-C_{25} oxo alcohol obtained by the step (C) to obtain the desired higher C_6-C_{25} oxo alcohol in substantially pure form; and

(H) discharge a part of the low-boilers separated by the step (c) to remove the saturated hydrocarbons out of the closed reaction system,

wherein the catalyst-depleted second hydroformylation stage reaction mixture obtained by the step (I-b) is recirculated into the first selected hydrogenation (B).

23. The process of claim 21, wherein the supported catalyst employed in the second selective hydrogenation (E) comprises 0.3 to 15% by weight of copper, 0.3 to 15% by weight of nickel, 0.05 to 3.5% by weight of chromium and no or 0.01 to 1.6% by weight of an alkali metal component, each based on the supported catalyst and also comprises silicon dioxide or aluminum oxide as a supporting material.

24. The process of claim 21 or 23, wherein the second selective hydrogenation (E) is carried out in a liquid phase at an overall pressure of from 5 to 30 bar.

25. The process of claims 21, 22, 23 or 24, wherein the supported catalyst employed in the first selective hydrogenation (E) comprises 0.3 to 15% by weight of copper, 0.3 to 15% by weight of nickel, 0.05 to 3.5% by weight of chromium and no or 0.01 to 1.6% by weight of an alkali metal

component, each based on the supported catalyst and also comprises silicon dioxide or aluminum oxide as a supporting material.

26. The process of any one of claims 21 to 25, wherein the cobalt or rhodium catalyst removed by the step (I-a) is recirculated to the first hydroformylation stage (A); and the cobalt or rhodium catalyst removed by the step (I-b) is recirculated into the second hydroformylation stage (D).

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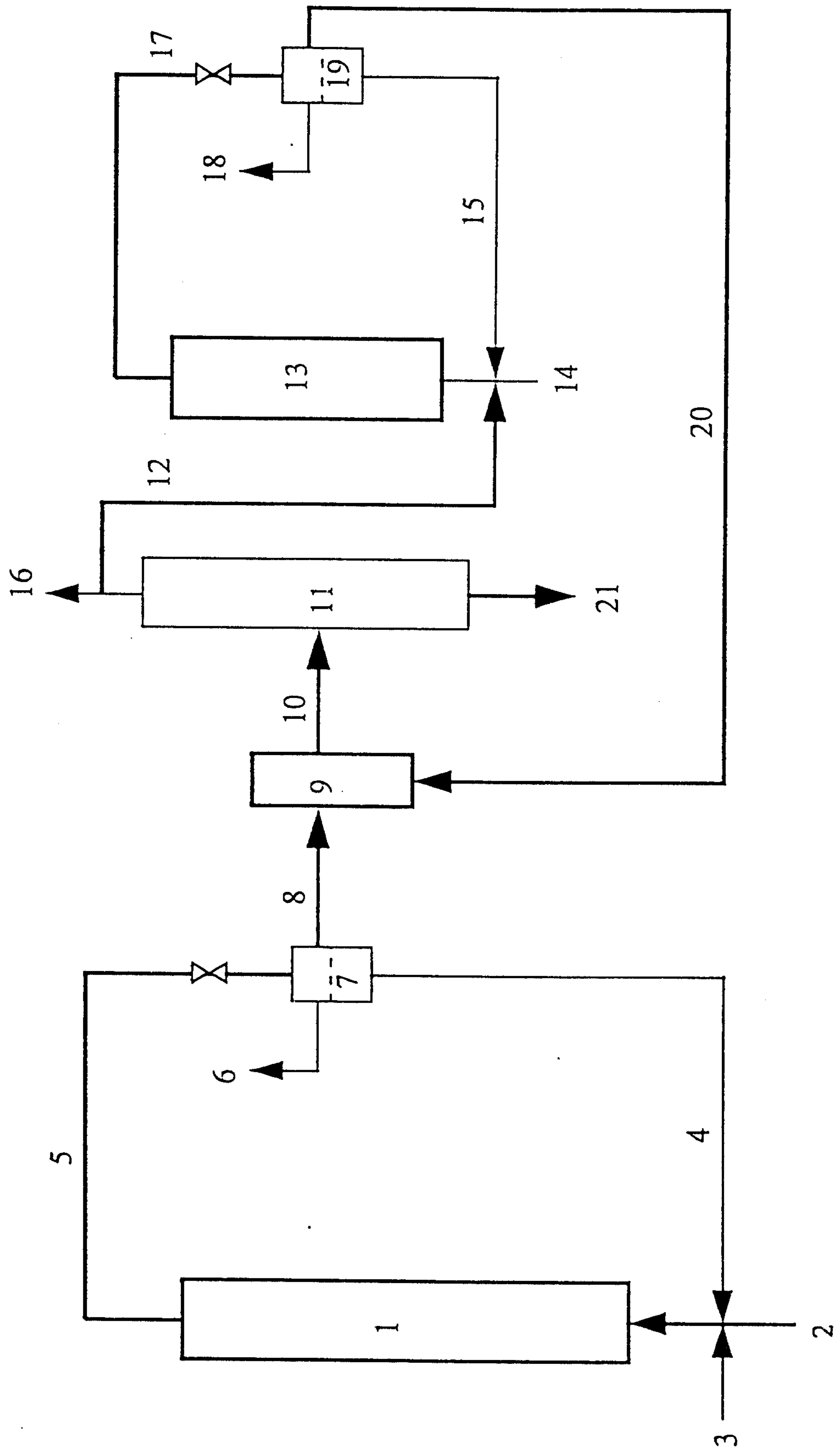
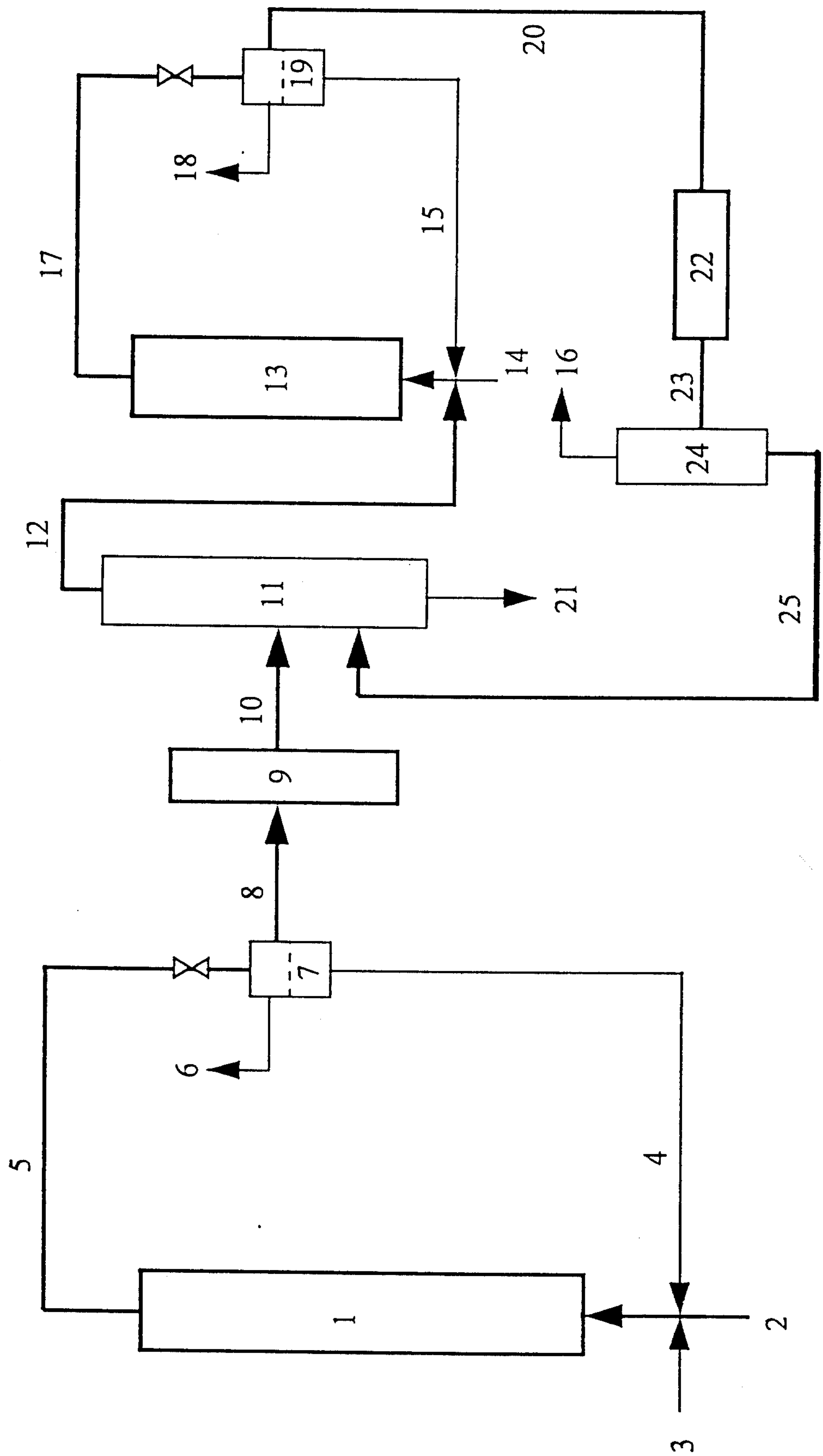


Fig. 1

Fig. 2