

Preparation of essentially unbranched octenes and dodecenes by oligomerization of unbranched butenes

5 The present invention relates to the oligomerization of 1-butene and/or 2-butene to form essentially linear octenes and dodecenes in the presence of a heterogeneous nickel-containing catalyst, where the concentration of the oligomers formed in the reaction
10 mixture is maintained at at most 25 % by weight.

Olefins having from 2 to 6 carbon atoms and mixtures thereof, in particular olefins having 4 carbon atoms, are available in large quantities both from FCC plants and from steam crackers. The
15 respective C₄ fraction, i.e. the mixture of butenes and butanes, is, after separating off the isobutene, very well suited to the preparation of oligomers, in particular octenes and dodecenes. Both the octenes and dodecenes can, after hydroformylation and subsequent hydrogenation to give the corresponding alcohols, be
20 used, for example, for the preparation of plasticizers.

For use as plasticizer alcohol, the degree of branching plays a decisive role in determining the properties of the plasticizers. The degree of branching is described by the iso index which
25 indicates the mean number of methyl branches in the respective fraction. Thus, for example, n-octenes contribute 0, methylheptenes contribute 1 and dimethylhexenes contribute 2 to the iso index of a fraction. The lower the iso index, the more linear are the molecules in the respective fraction. The higher
30 the linearity, i.e. the lower the iso index, the higher are the yields in the hydroformylation and the better are the properties of the plasticizer prepared therewith.

The oligomerization is carried out on an industrial scale using
35 either homogeneous or heterogeneous catalysts.

The homogeneously catalyzed method is described in detail, for example, by A. Chauvel and G. Lefebvre in Petrochemical Process, Volume 1, Éditions Technip (1989), pp. 183 to 187.
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A disadvantage of the homogeneously catalyzed process is the necessity of separating the catalyst from the reaction mixture. This separation step results in waste streams which, owing to
45 environmental regulations, have to be worked up again. Finally, the homogeneous catalyst cannot be regenerated.

In contrast, these disadvantages do not occur in the heterogeneously catalyzed olefin oligomerization. A heterogeneously catalyzed process operated on an industrial scale is the Octol process of the companies UOP and Hüls AG in which
5 C₃- and C₄-olefins are reacted at from 30 to 250°C and pressures of from 20 to 80 bar over a catalyst comprising, for example, phosphoric acid applied to SiO₂ as support to give higher olefins. This process is described, for example, in Petrochemical Processes loc. cit. and in Hydrocarbon Processing, February 1992,
10 pages 45/46.

Furthermore, it is known from DE-A 43 39 713 that the oligomerization of butene can be carried out advantageously and in a very high selectivity in respect of linear products when
15 particular nickel-containing catalysts are used.

While the homogeneously catalyzed process has the stated disadvantages in respect of catalyst utilization and the
20 heterogeneously catalyzed Octol process leads to few linear products when acid catalysts are used, the process described in DE-A 43 39 713 was still in need of improvement in respect of the catalyst life and the selectivity for octene formation.

25 It is an object of the present invention to find a heterogeneously catalyzed process which makes possible a long catalyst life together with a very good conversion and high selectivity in respect of the formation of oligomers having little branching.

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We have found that this object is achieved by a process for preparing essentially unbranched octenes and dodecenes by oligomerization of hydrocarbon streams which comprise 1-butene and/or 2-butene and butane and are essentially free of isobutene,
35 at from 30 to 280°C and a pressure of from 10 to 300 bar over a nickel-containing heterogeneous catalyst, wherein the butane and unreacted butene separated from the reaction mixture are recirculated to the oligomerization reaction in such amounts that the maximum content of oligomers in the converted reaction
40 mixture does not exceed 25 % by weight, preferably 20 % by weight, at any point in the reactor or, if a reactor cascade is used, at any point of the reactor cascade.

For the purposes of the present application, "oligomers" are
45 dimers, trimers and higher oligomers of 1-butene and/or 2-butene.

It has been found that this method makes it possible to carry out the oligomerization of butene at a conversion of over 70 % and at the same time a C₈ selectivity of over 80 %. Apart from the good conversion and selectivity values, adherence to the concentration limit also results in a longer catalyst life since the formation of relatively high-boiling compounds which deposit on the catalyst surface and thus reduce the activity is suppressed.

In general terms, a recirculation (C₄-recycle) is already indicated in the homogeneously catalyzed process and for the Octol process, but to a lesser extent than in the present process and without the advantageous results according to the present invention.

Thus in the Octol process, the unreacted C₃-C₄-hydrocarbons (together with undesired high boilers) are, according to Petrochemical Processes, page 185, recirculated "to serve as diluents and avoid excess conversions that would cause a drop in selectivity". In contrast thereto, high conversions and high selectivities are obtained in the process of the present invention.

It can also be seen from Fig. 1, p. 45, of Hydrocarbon Processing, February 1992, that a C₄-recycle was carried out. However, it is obvious that the recirculation was carried out only to a small extent, i.e. in amounts which must have led to over 25 % by weight of oligomers in the reaction mixture, since the reaction is carried out pseudoisothermally while the relatively large amount of liquid gas to be recirculated according to the present invention allows an industrially simpler pseudoadiabatic procedure.

Suitable catalysts are generally nickel-containing catalysts which are known per se and effect a low degree of branching, as are described, for example, by O'Connor et al. in Catalysis Today, 6, 329 (1990), in particular pages 336-338, and in the literature references cited as prior art in DE-A 4 339 713, so that the references quoted there are expressly incorporated by reference into the present description. In this context, mention may be made, by way of example, of nickel on silicon dioxide, nickel on silicon dioxide/aluminum oxide, nickel on silicon dioxide/aluminum oxide/sheet silicates such as mica and clays, in particular montmorillonites, nickel on zeolite supports such as mordenite, faujasite, zeolite X, zeolite Y, zeolite ZSM-5 or other zeolites of the ZSM type, zeolites having an MCM-41 structure or CZS-1 structure, also nickel on aluminum oxide,

nickel on zirconium oxide which has been treated with acids such as sulfuric acid, phosphoric acid or boric acid, $\text{NiO}_2/\text{ZrO}_2/\text{SO}_4/\text{SiO}_2$, and also nickel on sulfated titanium dioxide as catalysts. The nickel in these catalysts is generally in the form of NiO .

According to a preferred embodiment of the process of the invention, the oligomerization is carried out in the liquid phase using the catalysts described and claimed in DE-A 43 39 713. For this reason, that patent is expressly incorporated by reference into the present description.

The catalytic compositions of the catalysts described there consist essentially, i.e. without taking account of impurities which have been introduced via starting materials or process chemicals during preparation of the catalyst, of nickel oxide, silicon dioxide, titanium dioxide and/or zirconium dioxide and possibly aluminum oxide. These catalysts contain from 10 to 70 % by weight of nickel oxide, from 5 to 30 % by weight of titanium dioxide and/or zirconium dioxide, from 0 to 20 % by weight of aluminum oxide and silicon dioxide as balance to 100 % by weight and are obtainable by precipitation of the catalyst composition at pH 5-9 by addition of an aqueous solution comprising nickel nitrate to an alkali metal silicate solution comprising titanium dioxide and/or zirconium dioxide, filtering, drying and heating at from 350 to 650°C.

The catalysts are preferably arranged in a fixed bed and are therefore preferably used in the form of discrete bodies, e.g. in the form of pellets (5 mm x 5 mm, 5 mm x 3 mm, 3 mm x 3 mm), rings (7 mm x 7 mm x 3 mm, 5 mm x 5 mm x 2 mm, 5 mm x 2 mm x 2 mm) or extrudates (1.5 mm-diameter, 3 mm-diameter, 5 mm-diameter). The sizes stated above are given merely by way of example and do not represent any restriction of the subject matter of the present invention.

Specifically, the process of the present invention is carried out by reacting a hydrocarbon stream comprising 1-butene, 2-butene, butane and at most small amounts of isobutene, preferably in the liquid phase, over the NiO -containing catalysts mentioned as examples.

Suitable C_4 -hydrocarbon streams are, for example, mixtures having the following composition:

butane:	from 10 to 90 % by weight
butene:	from 10 to 90 % by weight

where the butene fraction can have the following composition:

- 1-butene: from 1 to 50 % by weight
cis 2-butene: from 1 to 50 % by weight
trans-2-butene: from 1 to 99 % by weight
5 isobutene: 1 - 5 % by weight

A particularly preferred starting material is raffinate II, i.e. a butene-containing C₄-hydrocarbon mixture as is obtained from the C₄-fraction of crackers after separating off more highly
10 unsaturated hydrocarbons such as diolefins, in particular 1,3-butadiene, or acetylene and subsequently separating off the isobutene present therein. A typical composition of a raffinate II is, for example:

- 15 i-, n-butane: 26 % by weight
i-butene: 1 % by weight
1-butene: 26 % by weight
trans-2-butene: 31 % by weight
cis-2-butene: 16 % by weight

20 The C₄-hydrocarbon streams can be freed, for example, of butadiene, sulfur-containing and oxygen-containing compounds such as alcohols, aldehydes, ketones or ethers in a manner known per se from DE-A-39 14 817 by selective hydrogenation or adsorption
25 on molecular sieves.

The oligomerization reaction generally takes place at from 30 to 280°C, preferably from 30 to 140°C and in particular from 40 to 130°C, and a pressure of generally from 10 to 300 bar, preferably
30 from 15 to 100 bar and in particular from 20 to 70 bar. The pressure is advantageously selected so that the starting hydrocarbon mixture is liquid or in a supercritical state at the temperature employed. The reactor is generally a cylindrical reactor which is charged with the catalyst and through which the
35 liquid reaction mixture flows, for example, from the top downward. The oligomerization process of the present invention can be carried out in a single reactor to the desired final conversion of the butenes; the oligomerization catalyst can be arranged in a single fixed bed or a plurality of fixed beds in
40 the reactor. As an alternative, the process of the present invention can be carried out using a reactor cascade comprising a plurality of, preferably two, reactors connected in series, where the butene in the reaction mixture is only partly converted during passage through the reactor or reactors preceding the last
45 reactor or reactors of the cascade and the desired final conversion is achieved only on passing the reaction mixture through the last reactor of the cascade. In the individual

reactors of the reactor cascade, the oligomerization catalyst can be arranged in a single catalyst fixed bed or in a plurality of catalyst fixed beds. Furthermore, different pressure and/or temperature conditions within the abovementioned pressure and temperature ranges can be set in the individual reactors of the reactor cascade. It is also possible to use different oligomerization catalysts in the individual reactors of the cascade, although the use of the same catalyst in all reactors of the cascade is preferred. When using a single oligomerization reactor or when using a reactor cascade in whose reactors the same oligomerization catalyst is used, reference will hereinafter be made to a single-stage reaction zone, while if different oligomerization catalysts are employed in the individual reactors of the cascade, it will hereinafter be referred to as a multistage reaction zone.

If a single oligomerization reactor is used, the recirculated C₄-hydrocarbon mixture depleted in butenes and comprising predominantly butanes is advantageously mixed into the hydrocarbon feed mixture before the latter enters the reactor, but it is also possible to introduce the hydrocarbon feed mixture and the recirculated C₄-hydrocarbon mixture into the oligomerization reactor via separate lines. If the catalyst is arranged in the oligomerization reactor in a plurality of fixed beds, the recirculated hydrocarbon stream can be divided and introduced into the reactor at a plurality of points, e.g. before the first fixed bed in the flow direction of the reaction mixture and/or between the individual catalyst fixed beds. An analogous situation applies when using a reactor cascade, where the recirculated hydrocarbon stream can either be fed in full to the first reactor of the cascade or be distributed among the individual reactors of the cascade via a plurality of feed lines, as described for the case of an individual reactor. After leaving the single-stage or multistage reaction zone, the oligomers formed are separated in a manner known per se from the unreacted C₄-hydrocarbons and all or most of these C₄-hydrocarbons are recirculated, in each case in such an amount that the content of oligomers in the converted reaction mixture does not exceed 25 % by weight, preferably 20 % by weight, at any point in the reactor or, if a reactor cascade is used, at any point of the reactor cascade. Expressed in other words, the recirculation of the C₄-hydrocarbon mixture is to be controlled such that the oligomer content of the converted reaction mixture does not exceed 25 % by weight, preferably 20 % by weight, at any point in the reactor, or if a reactor cascade is used, at any point of the reactor cascade and the oligomer content of the converted reaction mixture on leaving the reactor or, if a reactor cascade is used,

on leaving the reactor cascade is advantageously not less than 10 % by weight. To achieve such an oligomer content in the converted reaction mixture, the weight ratio of recirculation stream to fresh hydrocarbon feed stream is generally set at from 0.5 to 10, preferably from 1 to 7, in particular from 1 to 4, based on the steady state of the reaction system.

At the lower end, there is no limit as such for the oligomer content in the reaction mixture, although the process becomes uneconomical when a very low oligomer content is chosen, because the recycle stream becomes excessively large. For this reason, the oligomer content in the converted reaction mixture is generally kept above a lower limit of 10 % by weight before it is worked up.

For the purposes of the present invention an adiabatic reaction procedure is, in contrast to an isothermal reaction procedure in which the heat produced in an exothermic reaction is removed by cooling by means of cooling or thermostating devices such as thermostatted baths, cooling jackets or heat exchangers and the temperature in the reactor is thus kept constant, i.e. isothermal, a mode of operation in which the heat liberated in an exothermic reaction is taken up by the reaction mixture in the reactor and no cooling by means of cooling devices is employed. It is obvious that a purely adiabatic reaction procedure in the theoretical academic sense of the term "adiabatic" could be achieved in industry only with an uneconomically high outlay since a part, even if a negligibly small part, of the heat liberated in the exothermic reaction is virtually unavoidably taken up by the reactor body and given off into the environment by means of heat conduction and heat radiation. In the industrial sense, therefore, an adiabatic reaction procedure or mode of operation is a reaction procedure or mode of operation in which, apart from the part of the heat of reaction given off to the environment by means of natural heat conduction and heat radiation from the reactor, the total heat of reaction is taken up by the reaction mixture and removed from the reactor together with this reaction mixture. The term "pseudoadiabatic" reaction procedure is therefore also used in the industrial sense as a synonym for an adiabatic reaction procedure. An adiabatic reaction procedure as employed in the present invention thus corresponds to an adiabatic reaction procedure in the above-described industrial sense. In contrast to this adiabatic reaction procedure, an isothermal reaction procedure involves, in the industrial sense, the removal of the heat of reaction from the reactor by means of cooling or thermostating devices to an extent specifically forced above that resulting from natural heat

conduction or heat radiation, with the heat of reaction generally first being taken up by a heat-transfer medium, the coolant, before it is given off to the environment or, for example when using heat exchangers, utilized for heating materials or for
5 energy recovery. Of course, an isothermal reaction procedure differs in the industrial sense from an isothermal reaction procedure in the theoretical academic sense since a part, even if a negligably small part, of the heat of reaction is virtually unavoidably carried out with the heated reaction mixture, for
10 which reason the term "pseudoisothermal" reaction procedure is synonymously employed in an industrial sense for the isothermal reaction procedure.

Since the exothermic reaction in the case of the present
15 oligomerization process takes place only by contact of the butenes with the oligomerization catalyst and heat is therefore liberated only in the region of the catalyst bed, the reaction temperature in the catalyst bed and thus also the temperature in the reactor can in principle be controlled by the introduction of
20 the reactants. The more butene reacted over the catalyst, the more the temperature increases in the catalyst bed, i.e. the higher the reaction temperature becomes. Since no heat is removed via cooling devices in such an adiabatic mode of operation, the heat of reaction produced in the oligomerization is removed
25 virtually only by the reaction mixture flowing through the catalyst bed. In such a mode of operation without additional measures when using the hydrocarbon feed mixture to be used according to the present invention, the throughput and thus the conversion per unit time, based on one volume unit of the
30 oligomerization catalyst used, would be greatly limited since increasing the conversion would cause a great increase in the reaction temperature, which would result in increased formation of by-products and in the worst case could lead to an uncontrolled runaway reaction resulting in polymerization of the
35 butenes and overheating and irreversible damage to the catalyst.

It has now been found that the abovementioned measure of recirculating the unreacted C₄-hydrocarbons separated from the
40 oligomeric product to the oligomerization reactor or, if applicable, to the reactor cascade used for oligomerization enables the reaction temperature in the catalyst bed to be held within the desired temperature range even at a high butene conversion and enables a high selectivity in respect of the desired oligomerization products to be achieved. Since the stream
45 of unreacted C₄-hydrocarbons recirculated to the oligomerization reaction has a lower content of reactive butenes and a higher content of butanes which are inert under the reaction conditions

than the fresh hydrocarbon feed stream fed to the oligomerization reactor, the recycle stream mixed into the feed stream dilutes it with inert butanes which make an additional contribution to removal of the heat of reaction from the catalyst bed. Thus, the
5 oligomerization can be carried out in the oligomerization reactor under adiabatic conditions, i.e. without use of cooling devices in the reactor as are required in the case of an isothermal mode of operation, by removal of the heat of reaction with the reaction mixture.

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A particular aspect of the reaction procedure of the present invention is thus that the process can be carried out pseudoadiabatically, since the change in temperature in the reactor can be controlled as desired via the dilution of the
15 butene with the recirculated hydrocarbon stream and by the selection of the amount and temperature of this stream. The recirculated hydrocarbon stream can, before being mixed into the fresh hydrocarbon feed stream or, in the case of direct introduction into the oligomerization reactor, before it is
20 introduced, have been cooled to a relatively low temperature, which effects an additional improvement in the removal of the heat of reaction. The pseudoadiabatic mode of operation also encompasses a process configuration of the process of the present invention in which the conversion of the butenes into oligomers
25 is distributed over a reactor cascade comprising two or more, preferably two oligomerization reactors and the partially converted reaction mixture is, after leaving one reactor and before entering the following reactor in the cascade, cooled by means of conventional cooling devices such as cooling jackets or
30 heat exchangers. Compared to an isothermally operated process, the adiabatic method of operation leads to a considerable reduction in the costs for apparatus.

35 The recirculation of the unreacted butenes with the recycle stream to the oligomerization reactor achieves high utilization in the oligomerization of the butenes fed to the oligomerization reactor together with the hydrocarbon feed stream. Furthermore, the pseudoadiabatic mode of operation makes possible a high
40 butene conversion together with a high selectivity.

The oligomers are separated in a manner known per se by fractional distillation, especially into the desired octene and dodecene fractions which serve as starting materials for the
45 hydroformylation for the preparation of the plasticizer alcohols nonanol and tridecanol. Owing to the low degree of branching of

the starting oligomers, the higher alcohols prepared therefrom have excellent properties for the preparation of plasticizers.

The following examples illustrate the process of the present invention.

Examples

10 Examples 1 to 4

The experiments were carried out continuously in an isothermal reactor (length about 1.5 m, diameter 30 mm) at 20 bar and 80°C. The feedstock used was a raffinate II having the following composition:

i-butane: 3 % by weight
n-butane: 15 % by weight
i-butene: 2 % by weight
20 1-butene: 30 % by weight
trans-2-butene: 32 % by weight
cis-2-butene: 18 % by weight

25 The catalyst used was a material which had been produced as described in DE-A 43 39 713 and converted into 5 mm x 5 mm pellets. Composition in % by weight of the active components: 50 % by weight of NiO, 12.5 % by weight of TiO₂, 33.5 % by weight of SiO₂, 4 % by weight of Al₂O₃.

30 The following results were obtained (on reaching a steady state):

	Example	1 (Comparison)	2	3	4
35	Throughput kg _{RaffII} /(l _{cat} ·h))	0.75	0.75	0.5	0.375
	C ₄ -Recycle/Raff.II (wt./wt.)	0	1	1.5	2
	[C ₈ ⁺]Reactor outlet (% by wt.)	42.6	24.3	22.3	20.0
40	C ₄ -Conversion based on the butenes present in the Raff.II (% by wt)	52.0	59.2	67.9	73.1
	Selectivity (% by wt))				
	C ₈	76.9	81.7	81.5	81.4
45	C ₁₂	18.4	14.8	14.9	15.1
	C ₁₆ ⁺	4.7	3.5	3.6	3.5
	C ₈ -Iso-Index	0.97	0.95	0.94	0.93

Example 5

The experiments were carried out continuously in a reactor cascade comprising two adiabatically operated reactors with intermediate cooling (length 2 x about 4 m, diameter 80 cm) at 30 bar. The feedstock used was a raffinate II having the following composition:

10	i-butane:	2 % by weight
	n-butane:	10 % by weight
	i-butene:	2 % by weight
	1-butene:	32 % by weight
	trans-2-butene:	37 % by weight
15	cis-2-butene:	17 % by weight

The catalyst used was a material which had been produced as described in DE-A 43 39 713 and converted into 5 mm x 5 mm pellets. Composition in % by weight of the active components:

20 50 % by weight of NiO, 12.5 % by weight of TiO₂, 33.5 % by weight of SiO₂, 4 % by weight of Al₂O₃.

The following results were obtained (on reaching a steady state):

25	Throughput (kg _{RaffII} /(l _{Kat} ·h))	0.375
	C ₄ -Recycle/Raffinate II (wt/wt)	3
	Inlet temperature, 1st reactor (°C)	38
	Outlet temperature, 1st reactor (°C)	67
	Inlet temperature, 2nd reactor (°C)	60
30	Outlet temperature, 2nd reactor (°C)	75
	[C ₈ ⁺] _{Reactor outlet} (% by wt)	18.3
	C ₄ -Conversion based on the butenes present in the raffinate II (% by weight)	83.1
	C ₈ -Selectivity (% by weight)	83.3
35	C ₈ -Iso index	1.00

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We claim:

- 5 1. A process for preparing essentially unbranched octenes and dodecenenes by oligomerization of hydrocarbon streams which comprise 1-butene and/or 2-butene and butane and are essentially free of isobutene, at from 30 to 280°C and a pressure of from 10 to 300 bar over a nickel-containing heterogeneous catalyst, wherein the butane and unreacted butene separated from the reaction mixture are recirculated to the oligomerization reaction in such amounts that the maximum content of oligomers in the converted reaction mixture does not exceed 25 % by weight at any point in the reactor or, if a reactor cascade is used, at any point of the reactor cascade.
- 10 2. A process as claimed in claim 1, wherein the oligomerization is carried out in the liquid phase.
- 15 3. A process as claimed in claim 1, wherein the content of oligomers in the converted reaction mixture does not exceed 25 % by weight at any point in the reactor or, if a reactor cascade is used, at any point of the reactor cascade and the oligomer content of the converted reaction mixture on leaving the reactor or, if a reactor cascade is used, on leaving the reactor cascade is not less than 10 % by weight.
- 20 4. A process as claimed in claim 1, wherein the amount and temperature of the return stream are selected so that the heat of the reaction is taken up and the oligomerization is carried out adiabatically or essentially adiabatically.
- 25 5. A process as claimed in claim 1, wherein the oligomerization is carried out over a fixed-bed catalyst consisting essentially of NiO, SiO₂, TiO₂ and/or ZrO₂ and, if desired, Al₂O₃.
- 30 6. A process as claimed in claim 1, wherein the oligomerization is carried out over a fixed-bed catalyst consisting essentially of from 10 to 70 % by weight of NiO, from 5 to 30% by weight of TiO₂ and/or ZrO₂, of from 0 to 20 % by weight of Al₂O₃ and of SiO₂ as the balance to 100 % by weight.
- 35 7. A process as claimed in claim 1, wherein the oligomerization is carried out in a reactor cascade.
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- 45