Energy-efficient method for oligomerizing olefins

The invention provides a process for oligomerization of C2- to C8-olefins in at least two reaction stages, each comprising at least one reactor and at least one distillation column, and a subsequent separation stage comprising at least one distillation column, wherein reaction heat and/or the condensation energy are made useful using a heat transfer medium.

Oligomerization is generally understood as meaning the reaction of unsaturated hydrocarbons with themselves to form correspondingly longer-chain hydrocarbons, so-called oligomers. For instance, an olefin having six carbon atoms (hexene) can be formed by oligomerization of two olefins having three carbon atoms (propene). The oligomerization of two molecules with one another is also referred to as dimerization.

The resulting oligomers are intermediates that are used, for example, for producing aldehydes, carboxylic acids and alcohols. The oligomerization of olefins is carried out on a large industrial scale either in the homogeneous phase using a dissolved catalyst, heterogeneously over a solid catalyst or with a biphasic catalyst system.

Processes for oligomerization of olefins are well known in the prior art and are used on a large industrial scale. The production quantities amount to several thousand kilotons per year in Germany alone. To ensure the highest possible conversions and, as far as possible, continuous operation of oligomerization processes, industrial plants usually comprise not just one but two or more serially connected reaction stages, each comprising at least one reactor. As a result, the oligomerization process can be kept in operation even in the case of failure of one reaction stage.

The reaction stage further comprises at least one distillation column to separate the oligomers formed from the olefins employed. The input olefin-containing stream is removed overhead as distillate and the oligomer depleted in input olefins is discharged via the column bottom. When separating the resulting oligomers after the reaction industrial plants require the supply of large amounts of energy, for example in the form of heating steam for heating the distillation columns. In addition to the high costs of providing the heating steam this process mode results in high CO_2 emissions. Furthermore problems may also be faced when the conversion of the reaction is to be increased. To achieve the increase in conversion and sustainable utilization of the feed stream the stream depleted of the oligomers and withdrawn at the top of the distillation column may be at least partially recycled to the first reaction stage. However, after the reaction this stream must be processed in the column again, thus leading to an additional use of energy in the form of heating steam.

It was the object of the present invention to provide a process for oligomerization of olefins which does not have the aforementioned problems. The process should be operable in a more cost- and CO_2-efficient

manner and also be operable in a more resource-saving manner with potential measures for the increase in conversion.

The object was achieved by the process according to the invention for oligomerization of C2- to C8-olefins according to Claim 1. Preferred embodiments are specified in the dependent claims.

The process according to the invention is a process for oligomerization of C2- to C8-olefins in at least two reaction stages R1 and RL, each comprising at least one reactor and at least one distillation column, and a separation stage A1 which follows RL and comprises at least one distillation column DKA1, wherein

an input mixture which contains at least the C2- to C8-olefins as reactant olefins is subjected to an oligomerization using a heterogeneous catalyst in the at least one reactor of the first reaction stage R1 and the reaction mixture obtained from the at least one reactor is distilled in the at least one distillation column DKR1 of the first reaction stage R1 to obtain a residual stream RS1 containing at least unconverted reactant olefins and an oligomerizate O1 containing at least the oligomers formed,

RS1 is at least partially passed to a reactor of a subsequent reaction stage;

a residual stream from a preceding reaction stage is subjected to an oligomerization using a heterogeneous catalyst in the at least one reactor of the last reaction stage RL and the reaction mixture obtained from the at least one reactor is distilled in the at least one distillation column DKRL of the last reaction stage RL to obtain a residual stream RSL containing at least unconverted reactant olefins and an oligomerizate OL containing at least the oligomers formed;

OL is at least partially passed to the distillation column DKA1 of the subsequent separation stage A1 and distilled therein to obtain a dimer stream D1 composed to an extent of at least 90% by weight of dimers of the employed reactant olefins and a bottoms stream S1 containing at least trimers and higher oligomers of the employed reactant olefins;

the dimer stream D1 obtained at the top of DKA1 is condensed and then partially recycled to DKA1 as reflux and partially discharged from the process,

the energy generated during condensation of the dimer stream D1 and the heat energy generated in the at least one reactor of the first reaction stage R1 are at least partially transferred to a liquid or gaseous heat transfer medium W1 to form a heated heat transfer medium W1.1; and

energy from the heated heat transfer medium W1.1 is transferred to a further liquid or gaseous heat transfer medium W2 to form a heated heat transfer medium W2.1 which is initially compressed and/or

heated and by means of which a steam stream used to heat at least the distillation columns DKA1 and DKR1 is then produced using a single- or multi-stage compression.

In the context of the present invention the term “reaction stage” means a plant section which in each case comprises at least one reactor and at least one distillation column. A reaction stage may therefore comprise one or more reactor(s) and one or more distillation column(s) following the reactor(s). In a preferred embodiment only one distillation column following the reactor(s) is present per reaction stage. It is further preferable when a reaction stage has at least 2 reactors, particularly preferably precisely 2 reactors, arranged in it. The reactors may be connected in parallel or in series.

In the distillation columns of the respective reaction stages the produced oligomers are separated from the residual output stream from the reactor which comprises, for example, alkanes and unconverted olefins. The oligomers are higher boiling than the unconverted olefins and other substances present in the output stream from the reactor and are therefore enriched in the bottom of the distillation column while the lower boiling unconverted olefins and analogous alkanes optionally present in the input stream are removed from the distillation column overhead and enriched in the distillate.

The advantage of the process according to the invention is that the use of the heat transfer media according to Claim 1 or according to the preferred embodiments makes it possible to save considerable amounts of energy to be supplied externally, mainly in the form of heating steam. This allows the process to be operated in a more cost-effective and CO_2-saving manner.

The input mixture for the process according to the invention contains at least the C2- to C8-olefins, preferably C3- to C6-olefins, more preferably C3- to C5-olefins, particularly preferably C4-olefins and their analogous alkanes. Suitable olefins include α-olefins, n-olefins and cycloalkenes, preferably n-olefins. In a preferred embodiment, the olefin is n-butene.

The olefins are typically used as reactants not in pure form but in industrially available mixtures. The term “input mixture” additionally used in this invention is therefore to be understood as meaning that it relates to any type of mixtures which contain the relevant olefins to be oligomerized in an amount that allows the oligomerization to be performed economically. The input mixtures used in accordance with the invention preferably contain practically no further unsaturated compounds and polyunsaturated compounds such as dienes or acetylene derivatives. It is preferable to employ input mixtures containing less than 5% by weight, in particular less than 2% by weight, of branched olefins based on the olefin proportion.

Propylene is produced industrially by the cracking of naphtha and is a basic chemical that is readily available. C5-olefins are present in light petroleum fractions from refineries or crackers. Industrial mixtures containing linear C4-olefins are light petroleum fractions from refineries, C4-fractions from FC crackers or steam crackers, mixtures from Fischer-Tropsch syntheses, mixtures from the

dehydrogenation of butanes and mixtures formed by metathesis or from other industrial processes. Mixtures of linear butenes suitable for the process according to the invention are obtainable from the C4-fraction of a steam cracker for example. Butadiene is removed in the first step. This is accomplished either by extraction (extractive distillation) of the butadiene or by selective hydrogenation thereof. In both cases a virtually butadiene-free C4-cut is obtained, so-called raffinate I. In the second step, isobutene is removed from the C_4 stream, for example by production of MTBE by reaction with methanol. The now isobutene-free and butadiene-free C4 cut, referred to as raffinate II, comprises the linear butenes and any butanes. If this then also undergoes removal of at least a portion of the 1-butene present, so-called raffinate III is obtained.

In a preferred embodiment, C4-olefin-containing streams are supplied as the input mixture in the process according to the invention. Suitable C4-olefin mixtures are in particular raffinate I, raffinate II and raffinate III.

The use of C4-olefin mixtures as the input stream results in the following particularly preferred process: Process for oligomerization of butenes in at least two reaction stages R1 and RL, each comprising at least one reactor and at least one distillation column, and a separation stage A1 which follows RL and comprises at least one distillation column DKA1, wherein

an input mixture which contains at least butenes as reactant olefins is subjected to an oligomerization using a heterogeneous catalyst in the at least one reactor of the first reaction stage R1 and the reaction mixture obtained from the at least one reactor is distilled in the at least one distillation column of the first reaction stage R1 to obtain a residual stream RS1 containing at least unconverted butenes and an oligomerizate O1 containing at least the oligomers formed,

RS1 is at least partially passed to a reactor of a subsequent reaction stage;

a residual stream from a preceding reaction stage is subjected to an oligomerization using a heterogeneous catalyst in the at least one reactor of the last reaction stage RL and the reaction mixture obtained from the at least one reactor is distilled in the at least one distillation column of the last reaction stage RL to obtain a residual stream RSL containing at least unconverted butenes and an oligomerizate OL containing at least the oligomers formed;

OL is at least partially passed to the distillation column DKA1 of the subsequent separation stage A1 and distilled therein to obtain a dimer stream D1 composed to an extent of at least 90% by weight of C8-oligomers and a bottoms stream S1 containing at least C12-oligomers and higher oligomers of the employed butenes;

the dimer stream D1 obtained at the top of DKA1 is condensed and then partially recycled to DKA1 as reflux and partially discharged from the process,

the energy generated during condensation of the dimer stream D1 and the heat energy generated in the at least one reactor of the first reaction stage R1 are at least partially transferred to a heat transfer medium W1 to form a heated heat transfer medium W1.1; and

energy from the heated heat transfer medium W1.1 is transferred to a further heat transfer medium W2 to form a heated heat transfer medium W2.1 which is initially compressed and/or heated and by means of which a steam stream used to heat at least the distillation columns DKA1 and DKR1 is subsequently produced using a single- or multi-stage compression.

The process according to the invention comprises at least two reaction stages R1 and RL. The reaction stage R1 is the first reaction stage and RL refers to the last reaction stage. In a preferred embodiment of the present invention at least one further reaction stage, likewise comprising at least one reactor and at least one distillation column, is present between the reaction stage R1 and the reaction stage RL. In a further-preferred embodiment of the present invention at least two further reaction stages, each comprising at least one reactor and at least one distillation column, are present between the reaction stage R1 and the reaction stage RL. In a particularly preferred embodiment the process for oligomerization comprises at most five reaction stages; i.e. at least three further reaction stages, each comprising at least one reactor and at least one distillation column, are present between the reaction stage R1 and the reaction stage RL. It is possible in all cases for one of the reaction stages to comprise two or more reactors while a preceding or subsequent reaction stage comprises only one reactor.

Accordingly, the process according to the invention may be performed in at least one further reaction stage R2, wherein the reaction stage R2 comprises at least one reactor and at least one distillation column DKR2. It is preferable when the steam stream used for heating the distillation columns DKA1 and DKR1 is also used for heating the distillation column DKR2. This would make it possible to obviate the need to use any additional energy source to be obtained externally.

In the aforementioned case DKR2 would afford a residual stream RS2 containing at least the unconverted reactant olefins and afford an oligomerizate O2 containing at least the oligomers formed. RS2 may then be recycled at least partially to the subsequent reaction stage and optionally at least partially to the at least one reactor of the at least one reaction stage R2. The oligomerizate O2 may be passed to the distillation column DKRL of the last reaction stage RL and/or to the distillation column DKA1 of the subsequent separation stage A1; preferably, the oligomerizate is passed to the distillation column DKRL of the last reaction stage RL.

A further reaction stage R3 may also be present in addition to the reaction stage R2. In this case the process according to the invention is performed in at least one further reaction stage R3, wherein the reaction stage R3 comprises at least one reactor and at least one distillation column DKR3. It is preferable when the steam stream used for heating the distillation columns DKA1, DKR1 and DKR2 is also used for heating the distillation column DKR3. This would make it possible to obviate the need to use any additional energy source to be obtained externally.

In the aforementioned case DKR3 would afford a residual stream RS3 containing at least the unconverted reactant olefins and afford an oligomerizate O3 containing at least the oligomers formed. RS3 may then be recycled at least partially to the subsequent reaction stage and optionally to the at least one reactor of the at least one reaction stage R3. The oligomerizate O3 may be passed to the distillation column DKRL of the last reaction stage RL and/or to the distillation column DKA1 of the subsequent separation stage A1.

The oligomerization of olefins is an exothermic reaction, i.e. a reaction which liberates heat. The heat liberated during the oligomerization of butenes is formed predominantly during isomerization of 1-butene to cis- or trans-2-butene. The reactor(s) in the respective reaction stages of the process according to the invention may be operated isothermally or adiabatically, preferably isothermally. In a preferred embodiment only the reactor(s) of the last reaction stage is/are operated adiabatically while all other reactors of the preceding reaction stage(s) are operated isothermally, especially actively cooled. A cooling medium known to those skilled in the art, for example cooling water, may be employed. In the context of the present invention isothermally means that the temperature increase in the reactor despite cooling does not exceed 10 K. This corresponds to an isothermal operating mode of the reactors. Based on a cooling power of 100% for the reactor(s) in the first reaction stage, the cooling power in the reactor(s) of the subsequent reaction stages is less than 100% but, except in the last reaction stage, not 0%.

According to the invention the input mixture which contains at least the employed olefins is subjected to an oligomerization using a heterogeneous catalyst in the at least one reactor of the first reaction stage R1.

The at least one reactor in the first reaction stage R1 employed may be all reactors known to those skilled in the art which are suitable for the oligomerization, for example tubular reactors, fixed bed reactors, tube bundle reactors, settler-riser reactors or slurry reactors. Preference is given to tubular reactors and/or tube bundle reactors. If the reaction stage has two or more reactors the reactors may be identical or different to one another. The reactors in a reaction stage may also vary in their construction or their configuration. For example the first reactor in a reaction stage may have a larger volume than the subsequent reactor in the same reaction stage. It is likewise possible for the reactors in the individual reaction stages to be identical or different to one another. Here too it is possible for the reactors in the

individual reaction stages to differ in their construction or their configuration. The reactor in the first reaction stage may have a larger volume than one or all reactors in the subsequent reaction stages for example.

It is preferable according to the invention when the reaction stage R1 comprises at least one further reactor which is connected to the first reactor in parallel or in series, preferably is present connected in series. The output from the first reactor preferably passes into the second reactor without preceding separation of the oligomers. It is therefore preferable when the first reactor does not perform complete conversion of the reactant olefins. The reaction heat from the second reactor formed during the oligomerization is preferably likewise transferred to the heat transfer medium W1.

The reactor(s) of the reaction stage R1 each contain a heterogeneous catalyst for performing the oligomerization. Any catalyst suitable for the oligomerization may in principle be employed. Appropriate catalysts are known to those skilled in the art from the literature. The employed catalyst is especially in the form of a granulate, an extrudate or in tablet form.

The heterogeneous catalyst in the at least one reactor R1 preferably comprises a nickel compound, preferably nickel oxide, on an aluminosilicate support material. It is further preferable, however, when, based on the total composition of the oligomerization catalyst, the heterogeneous catalyst contains less than 0.5% by weight, more preferably less than 0.1% by weight, particularly preferably less than 0.01% by weight, of titanium dioxide and/or zirconium dioxide. The support material may be an amorphous, mesoporous aluminosilicate, a crystalline, microporous aluminosilicate or an aluminosilicate having amorphous and crystalline phases. In the context of the present invention “amorphous” is to be understood as meaning the property of a solid which results from the fact that, in contrast to crystalline solids, the solid has no crystal structure, i.e. no long-range order.

The heterogeneous catalyst preferably has a composition of 15% to 40% by weight, preferably 15% to 30% by weight, of NiO, 5% to 30% by weight of Al_2O_3, 55% to 80% by weight of SiO_2 and 0.01% to 2.5% by weight, preferably 0.05% to 2% by weight, of an alkali metal oxide, preferably sodium oxide. The figures are based on a total composition of 100% by weight. The oligomerization catalyst is preferably substantially free from titanium dioxide and zirconium dioxide; in particular, the oligomerization catalyst contains less than 0.5% by weight, preferably less than 0.1% by weight, particularly preferably less than 0.01% by weight, of titanium dioxide and zirconium dioxide in its total composition.

An oligomerization catalyst may be produced by the known processes of impregnation, wherein the support material is treated with a solution of a transition metal compound, especially a nickel compound, and then calcined, or coprecipitation, wherein the entire catalyst composition is precipitated from a single, usually aqueous, solution. The oligomerization catalyst may also be produced by other processes familiar

to those skilled in the art. Production may also comprise carrying out a hydrothermal treatment wherein the still-moist catalyst is held at elevated temperature before the catalyst is subjected to drying.

The oligomerization may be performed in one or all reactor(s) of the last reaction stage RL at a temperature in the range from 50°C to 200°C, by preference 60°C to 180°C, preferably in the range from 60°C to 130°C. The pressure may be from 10 to 70 bar, preferably 20 to 55 bar, in each of the reaction stages present. In a preferred embodiment of the present invention the oligomerization is performed in the liquid phase in each reaction stage. If the oligomerization is to be carried out in the liquid phase, the parameters pressure and temperature must be chosen therefor such that the input mixture (the employed olefins or olefin mixtures) is in the liquid phase.

The oligomerization in the at least one reactor of the reaction stage R1 forms a reaction mixture which is withdrawn from the at least one reactor. The reaction mixture obtained from the at least one reactor is distilled in the at least one distillation column DKR1 of the first reaction stage R1, thus affording a residual stream RS1 which contains at least unconverted olefins and an oligomerizate O1 which contains at least the oligomers formed. The distillation accordingly separates at least a portion of the oligomers formed from the unconverted olefins. The energy required for the separation of the reaction mixture is especially introduced via at least one reboiler.

According to the invention the term “reboilers” refers to evaporators that heat the bottom of the distillation column. Such a reboiler is typically disposed outside the respective distillation column. Since reboilers transfer energy, in particular heat, from one stream to another, they are heat transferrers. The stream to be evaporated is withdrawn at the bottom of the distillation column via a takeoff and supplied to the reboiler. The evaporated stream, with or without a residual proportion of liquid, is returned back to the respective distillation column in the region of the bottom via at least one feed.

Suitable evaporators that can be used as reboilers are, for example, natural circulation evaporators, forced circulation evaporators, forced circulation flash evaporators, kettle evaporators, falling-film evaporators or thin-film evaporators. Heat exchangers for the evaporator that are typically used in the case of natural circulation evaporators and forced circulation evaporators are a shell-and-tube or plate apparatus. As well as those mentioned, it is alternatively possible to use any other design of evaporator which is known to those skilled in the art and is suitable for use in a distillation column.

According to the invention it is preferable when the reaction mixture is preheated before it is introduced to the distillation column DKR1. This has the advantage that it is not necessary to introduce the total energy via the at least one reboiler. The preheating also makes it possible to increase the capacity because the hydraulic load in the distillation column is reduced.

The preheating of the reaction mixture is preferably carried out in a heat exchanger. The preheating may be performed with heat exchangers known to those skilled in the art. Suitable evaporators that can be used as heat exchangers are, for example, natural circulation evaporators, forced circulation evaporators, forced circulation flash evaporators, kettle evaporators, falling-film evaporators or thin-film evaporators. As well as those mentioned, it is alternatively possible to use any other design of evaporator which is known to those skilled in the art and is suitable for use for the desired preheating.

The at least one distillation column DKR1 used for the distillation of the reaction mixture may be any desired distillation columns known to those skilled in the art. It is preferable when the distillation column of the first reaction stage R1 contains internals. Suitable internals are for example trays, unstructured packings (random packings) or structured packings. Trays used are typically bubble-cap trays, sieve trays, valve trays having fixed or movable valves, tunnel-cap trays or slotted trays. Unstructured packings are generally beds of random packings. Random packings used are typically Raschig rings, Pall rings, Berl saddles, Super-Rings/Super-Rings Plus or Intalox® saddles. Structured packings are sold for example under the Mellapak® trade name by Sulzer. In addition to the internals mentioned, further suitable internals are known to those skilled in the art and may likewise be used.

Preferred internals have a low specific pressure drop per theoretical plate. Structured packings and random packings have, for example, a significantly lower pressure drop per theoretical plate than trays. This has the advantage that the pressure drop in the distillation column of the first reaction stage R1 remains as low as possible.

In a particularly preferred embodiment of the present invention the distillation column of the first reaction stage R1 comprises a multiplicity of trays, preferably between 5 and 100 trays, more preferably between 10 and 50 trays.

The conditions of the distillation, i.e. temperature and pressure for example, are usually determined by the construction (column height, number of trays, type of trays/packing, spacings etc.). The separation properties of the distillation may also be controlled during operation via the temperature distribution and/or the heat supply into the column and the reflux in the distillate. The separation property may also be adjusted within a certain range by changing the pressure. The precise settings therefore cannot be defined superordinately to and independently of the construction of the distillation column. This is known to those skilled in the art. In a preferred embodiment the pressure during the distillation is in the range from 1 to 6 bar absolute, especially preferably in the range from 2 to 5 bar absolute. The temperature at the top of the distillation column is moreover preferably in the range from 15°C to 60°C, particularly preferably in the range from 25°C to 50°C.

The distillation of the reaction mixture affords a residual stream RS1 containing at least unconverted olefins and an oligomerizate O1 containing at least the oligomers formed. The residual stream RS1 will

generally be obtained at the top of the distillation column DKR1. The oligomerizate O1 is then obtained at the bottom of the distillation column DKR1.

The residual stream RS1 is at least partially passed to a reactor of a subsequent reaction stage. The subsequent reaction stage may be the reaction stage RL. There are then altogether only two reaction stages. However, the subsequent reaction stage may also be a reaction stage present between the reaction stage R1 and the reaction stage RL. In this case there are at least three reaction stages. Also possible are embodiments where more than two reaction stages are present between the reaction stage R1 and the reaction stage RL. It is preferable according to the invention when at least one further reaction stage comprising at least one reactor and at least one distillation column is present between the reaction stage R1 and the reaction stage RL.

It is further preferable when the residual stream RS1 is at least partially recycled to the at least one reactor of the reaction stage R1. This reflux of the residual stream makes it possible to dilute the input mixture.

In a preferred embodiment of the present invention the residual stream RS1 is divided into at least two substreams RS1a and RS1b. The substream RS1b can then be recycled to the reactor of the first reaction stage R1. It is further preferable when the substream RS1a is compressed to form a stream VR1 which is compressed relative to the residual stream RS1 and energy from the compressed stream VR1 is used to preheat the reaction mixture upstream of DKR1 and/or to preheat the input mixture upstream of the oligomerization. The preheating may thus also be effected using thermal integration measures, here vapour compression, thus obviating the need to supply external energy in the form of heating steam. Only electrical energy for the compression need be employed here.

The compression of the substream RS1a may be carried out in any desired manner known to those skilled in the art. For example, the compression can thus be performed mechanically and in a single- or multi-stage compression. In this context the term “single-stage” means that compression from one pressure level to another is carried out. The term “multi-stage” means that compression to a pressure level X and then from X to the pressure level Y is carried out first. A multi-stage compression may employ two or more compressors of the same type or compressors of different types. A multi-stage compression may be carried out with one or more compressors. The use of a single-stage compression or a multi-stage compression depends on the compression ratio and hence on the pressure to which the substream RS1a is to be compressed.

A suitable compressor in the process according to the invention, especially for compression of the substream RS1a, is any compressor known to those skilled in the art, preferably mechanical compressors, with which gas streams can also be compressed. Suitable compressors include, for

example, single-stage or multi-stage geared turbocompressors, piston compressors, screw compressors, centrifugal compressors or axial compressors.

It has already been mentioned that in a preferred embodiment the process comprises at least a second reaction stage R2, wherein the at least one reactor affords a reaction mixture that is separated in the distillation column DKR2. It is particularly preferable when energy from the compressed stream VR1 is also used for preheating the reaction mixture upstream of DKR2.

After preheating, the substream RS1a may be at least partially condensed and subsequently at least partially passed to the at least one reactor of the second reaction stage R2 as input mixture.

The oligomerizate O1 contains the oligomers formed. In a preferred embodiment the oligomerizate O1 is at least partially, preferably completely, passed to the distillation column of the last reaction stage RL. All oligomerizates may be collected there and subsequently passed together to the separation stage A1. Residues of unreacted olefins may also be separated there.

Irrespective of how many reaction stages are present the residual stream from the previous reaction stage is passed to the last reaction stage RL. This may be at least a portion of the residual stream RS1 from the first reaction stage R1 but could also be a different residual stream provided at least one further reaction stage is present between R1 and RL. Thus, a residual stream from a preceding reaction stage is passed to the at least one reactor of the last reaction stage RL. This residual stream may be the residual stream RS1 if no further reaction stage is present between the two reaction stages R1 and RL. If at least one reaction stage is present between the reaction stage R1 and the reaction stage RL the residual stream from one of these reaction stages, the penultimate reaction stage, is passed to the last reaction stage RL.

According to the invention the supplied residual stream is subjected to an oligomerization using a heterogeneous catalyst in the at least one reactor of the last reaction stage RL.

The at least one reactor in the first reaction stage RL employed may be all reactors known to those skilled in the art and suitable for the oligomerization, for example tubular reactors, fixed bed reactors, tube bundle reactors, settler-riser reactors or slurry reactors. Preference is given to tubular reactors and/or tube bundle reactors. If the reaction stage has two or more reactors the reactors may be identical or different to one another. The reactors in a reaction stage may also vary in their construction or their configuration. For example the first reactor in a reaction stage may have a larger volume than the subsequent reactor in the same reaction stage. It is likewise possible for the reactors in the individual reaction stages to be identical or different to one another. Here too it is possible for the reactors in the individual reaction stages to differ in their construction or their configuration. The reactor in the first

reaction stage may have a larger volume than one or all reactors in the subsequent reaction stages for example.

It is preferable according to the invention when the reaction stage R1 comprises at least one further reactor which is connected to the first reactor in parallel or in series, preferably is present connected in series. The output from the first reactor preferably passes into the second reactor without preceding separation of the oligomers. It is therefore preferable when the first reactor does not perform complete conversion of the reactant olefins. The reaction heat generated in this further reactor can also be integrated via a heat transfer medium, as has already been described for the first reactor.

The reactor(s) of the reaction stage RL each contain a heterogeneous catalyst for performing the oligomerization. Any catalyst suitable for the oligomerization may in principle be employed. Appropriate catalysts are known to those skilled in the art from the literature. The employed catalyst is especially in the form of a granulate, an extrudate or in tablet form.

The heterogeneous catalyst in the at least one reactor of the reaction stage RL preferably comprises a nickel compound, preferably nickel oxide, on an aluminosilicate support material. It is further preferable, however, when, based on the total composition of the oligomerization catalyst, the heterogeneous catalyst contains less than 0.5% by weight, more preferably less than 0.1% by weight, particularly preferably less than 0.01% by weight, of titanium dioxide and/or zirconium dioxide. The support material may be an amorphous, mesoporous aluminosilicate, a crystalline, microporous aluminosilicate or an aluminosilicate having amorphous and crystalline phases. In the context of the present invention “amorphous” is to be understood as meaning the property of a solid which results from the fact that, in contrast to crystalline solids, the solid has no crystal structure, i.e. no long-range order.

The heterogeneous catalyst in the at least one reactor of the reaction stage RL preferably has a composition of 15% to 40% by weight, preferably 15% to 30% by weight, of NiO, 5% to 30% by weight of Al_2O_3, 55% to 80% by weight of SiO_2 and 0.01% to 2.5% by weight, preferably 0.05% to 2% by weight, of an alkali metal oxide, preferably sodium oxide. The figures are based on a total composition of 100% by weight. The oligomerization catalyst is preferably substantially free from titanium dioxide and zirconium dioxide; in particular, the oligomerization catalyst contains less than 0.5% by weight, preferably less than 0.1% by weight, particularly preferably less than 0.01% by weight, of titanium dioxide and zirconium dioxide in its total composition.

An oligomerization catalyst may be produced by the known processes of impregnation, wherein the support material is treated with a solution of a transition metal compound, especially a nickel compound, and then calcined, or coprecipitation, wherein the entire catalyst composition is precipitated from a single, usually aqueous, solution. The oligomerization catalyst may also be produced by other processes familiar

to those skilled in the art. Production may also comprise carrying out a hydrothermal treatment wherein the still-moist catalyst is held at elevated temperature before the catalyst is subjected to drying.

The oligomerization is performed in the reactor(s) of the last reaction stage by preference at a temperature in the range from 50°C to 200°C, preferably 60°C to 180°C, more preferably in the range from 60°C to 130°C. The pressure may be in the range from 10 to 70 bar, preferably from 20 to 55 bar. In a preferred embodiment of the present invention the oligomerization is performed in the liquid phase in each reaction stage. If the oligomerization is to be carried out in the liquid phase, the parameters pressure and temperature must be chosen therefor such that the input mixture (the employed olefins or olefin mixtures) is in the liquid phase.

The oligomerization in the at least one reactor of the reaction stage RL forms a reaction mixture which is withdrawn from the at least one reactor. The reaction mixture obtained from the at least one reactor is distilled in the at least one distillation column DKRL of the last reaction stage RL, thus affording a residual stream RSL which contains at least unconverted olefins and an oligomerizate OL which contains at least the oligomers formed. The distillation accordingly separates at least a portion of the oligomers formed from the unconverted olefins. In addition to the reaction mixture the oligomerizates from the preceding reaction stages, for example the oligomerizate O1, may also be worked up in the distillation column DKRL. The energy required for the separation of the reaction mixture is especially introduced via at least one reboiler.

According to the invention the term “reboilers” refers to evaporators that heat the bottom of the distillation column. Such a reboiler is typically disposed outside the respective distillation column. Since reboilers transfer energy, in particular heat, from one stream to another, they are heat transferrers. The stream to be evaporated is withdrawn at the bottom of the distillation column via a takeoff and supplied to the reboiler. The evaporated stream, with or without a residual proportion of liquid, is returned back to the respective distillation column in the region of the bottom via at least one feed.

Suitable evaporators that can be used as reboilers are, for example, natural circulation evaporators, forced circulation evaporators, forced circulation flash evaporators, kettle evaporators, falling-film evaporators or thin-film evaporators. Heat exchangers for the evaporator that are typically used in the case of natural circulation evaporators and forced circulation evaporators are a shell-and-tube or plate apparatus. As well as those mentioned, it is alternatively possible to use any other design of evaporator which is known to those skilled in the art and is suitable for use in a distillation column.

According to the invention it is preferable when the reaction mixture is preheated before it is introduced to the distillation column DKRL. This has the advantage that it is not necessary to introduce the total energy via the at least one reboiler. The preheating also makes it possible to increase the capacity because the hydraulic load in the distillation column is reduced.

The preheating of the reaction mixture is preferably carried out in a heat exchanger. The preheating may be performed with heat exchangers known to those skilled in the art. Suitable evaporators that can be used as heat exchangers are, for example, natural circulation evaporators, forced circulation evaporators, forced circulation flash evaporators, kettle evaporators, falling-film evaporators or thin-film evaporators. As well as those mentioned, it is alternatively possible to use any other design of evaporator which is known to those skilled in the art and is suitable for use for the desired preheating.

The at least one distillation column DKRL used for the distillation of the reaction mixture from the reactor of the last reaction stage RL may be any desired distillation columns known to those skilled in the art. It is preferable when the distillation column DKRL of the last reaction stage RL contains internals. Suitable internals are for example trays, unstructured packings (random packings) or structured packings. Trays used are typically bubble-cap trays, sieve trays, valve trays having fixed or movable valves, tunnel-cap trays or slotted trays. Unstructured packings are generally beds of random packings. Random packings used are typically Raschig rings, Pall rings, Berl saddles, Super-Rings/Super-Rings Plus or Intalox® saddles. Structured packings are sold for example under the Mellapak® trade name by Sulzer. In addition to the internals mentioned, further suitable internals are known to those skilled in the art and may likewise be used.

Preferred internals have a low specific pressure drop per theoretical plate. Structured packings and random packings have, for example, a significantly lower pressure drop per theoretical plate than trays. This has the advantage that the pressure drop in the distillation column of the first reaction stage RL remains as low as possible.

In a particularly preferred embodiment of the present invention the distillation column DKRL comprises a multiplicity of trays, preferably between 5 and 100 trays, more preferably between 10 and 50 trays.

The conditions of the distillation, i.e. temperature and pressure for example, are usually determined by the construction (column height, number of trays, type of trays/packing, spacings etc.). The separation properties of the distillation may also be controlled during operation via the temperature distribution and/or the heat supply into the column and the reflux in the distillate. The separation property may also be adjusted within a certain range by changing the pressure. The precise settings therefore cannot be defined superordinately to and independently of the construction of the distillation column. This is known to those skilled in the art. The pressure during the distillation is preferably in the range from 1 to 6 bar absolute, preferably in the range from 2 to 5 bar absolute.

The distillation of the reaction mixture and the optionally present oligomerizates from preceding stages affords a residual stream RSL containing at least unconverted olefins and an oligomerizate OL containing at least the oligomers formed. The residual stream RSL will generally be obtained at the top of the

distillation column DKRL. The oligomerizate OL is then obtained at the bottom of the distillation column DKRL.

The residual stream RL may be at least partially recycled to one or more reactors of the same reaction stage or the preceding reaction stage(s). It is also possible to withdraw at least a substream as a purge to prevent enrichment of inert alkanes or enrichment of impurities. If at least a substream is withdrawn and thus discharged from the process as a purge this substream may be used as a synthesis raw material for further processes (for example hydroformylation, carbon source for arcs in acetylene production), as combustion gas or, after full hydrogenation to the alkanes, as propellant gas, as cooking gas or the like.

The oligomerizate OL contains the oligomers formed. The oligomers formed generally include at least dimers, trimers and tetramers. However, higher oligomers may likewise be present in the oligomerizate in very small quantities. The obtained oligomerizate is therefore passed to a further workup in the separation stage A1 to separate the dimers, trimers and tetramers from one another.

The oligomerizate OL is thus at least partially passed to the distillation column DKA1 of the separation stage A1 and distilled therein to obtain a dimer stream D1 which is composed, based on the total weight of the dimer stream D1, to an extent of at least 90% by weight, preferably to an extent of at least 95% by weight, particularly preferably to an extent of at least 99% by weight, of dimers of the employed olefins and a bottoms stream S1 containing at least trimers and higher oligomers of the employed olefins. It is preferable when the oligomerizate OL is entirely passed to the distillation column DKA1 of the separation stage A1.

The bottoms stream S1, which contains at least trimers and higher oligomers of the employed reactant olefins, may be resolved in one or more subsequent distillation steps into the further oligomers which are subsequently converted to value products such as aldehydes or alcohols. The oligomers from the dimer stream D1 may then each be supplied to a further processing, for example a hydroformylation, an alkoxycarbonylation or a hydrogenation. The dimers of butenes, C8-olefins, may be converted to an isononanal mixture by hydroformylation. This isononanal mixture provides either the corresponding carboxylic acids by oxidation or a C9-alcohol mixture by hydrogenation. The C9-carboxylic acids may be used for producing lubricants or siccatives. The C9-alcohol mixture is a precursor for the production of plasticizers, especially of diisononyl phthalates (DINP), DINCH (1,2-diisononylcyclohexanedicarboxylate) or DINCD (1,4-diisononylcyclohexanedicarboxylate).

The energy required for separating the oligomerizate OL in the distillation column DKA1 is especially introduced via at least one reboiler. According to the invention the term “reboilers” refers to evaporators that heat the bottom of the distillation column. Such a reboiler is typically disposed outside the respective distillation column. Since reboilers transfer energy, in particular heat, from one stream to another, they are heat transferrers. The stream to be evaporated is withdrawn at the bottom of the distillation column via a takeoff and supplied to the reboiler. The evaporated stream, with or without a residual proportion of

liquid, is returned back to the respective distillation column in the region of the bottom via at least one feed.

Suitable evaporators that can be used as reboilers are, for example, natural circulation evaporators, forced circulation evaporators, forced circulation flash evaporators, kettle evaporators, falling-film evaporators or thin-film evaporators. Heat exchangers for the evaporator that are typically used in the case of natural circulation evaporators and forced circulation evaporators are a shell-and-tube or plate apparatus. As well as those mentioned, it is alternatively possible to use any other design of evaporator which is known to those skilled in the art and is suitable for use in a distillation column.

The at least one distillation column DKA1 used for the distillation of the oligomerizate OL may be any desired distillation columns known to those skilled in the art. It is preferable when the distillation column DKA1 of the separation stage A1 contains internals. Suitable internals are for example trays, unstructured packings (random packings) or structured packings. Trays used are typically bubble-cap trays, sieve trays, valve trays having fixed or movable valves, tunnel-cap trays or slotted trays. Unstructured packings are generally beds of random packings. Random packings used are typically Raschig rings, Pall rings, Berl saddles, Super-Rings/Super-Rings Plus or Intalox® saddles. Structured packings are sold for example under the Mellapak® trade name by Sulzer. In addition to the internals mentioned, further suitable internals are known to those skilled in the art and may likewise be used.

Preferred internals have a low specific pressure drop per theoretical plate. Structured packings and random packings have, for example, a significantly lower pressure drop per theoretical plate than trays. This has the advantage that the pressure drop in the distillation column of the first reaction stage RL remains as low as possible.

In a particularly preferred embodiment of the present invention the distillation column DKA1 comprises a multiplicity of trays, preferably between 5 and 100 trays, further preferably between 10 and 50 trays.

The conditions of the distillation, i.e. temperature and pressure for example, are usually determined by the construction (column height, number of trays, type of trays/packing, spacings etc.). The separation properties of the distillation may also be controlled during operation via the temperature distribution and/or the heat supply into the column and the reflux in the distillate. The separation property may also be adjusted within a certain range by changing the pressure. The precise settings therefore cannot be defined superordinately to and independently of the construction of the distillation column. This is known to those skilled in the art.

The dimer stream D1 obtained at the top of DKA1 is condensed and then partially recycled to DKA1 as reflux and partially discharged from the process. The energy generated during condensation of the dimer

stream D1 and the heat energy generated in the at least one reactor of the first reaction stage R1 are at least partially transferred to a heat transfer medium W1 to form a heated heat transfer medium W1.1.

The condensation of the dimer stream D1 may be carried out in any condenser known to those skilled in the art and configured as a heat exchanger to allow transfer of the condensation heat energy to the liquid or gaseous heat transfer medium W1. Possible heat exchangers that may be employed include for example natural circulation evaporators, forced circulation evaporators, forced circulation flash evaporators, kettle evaporators, falling-film evaporators or thin-film evaporators. In a preferred embodiment the heat exchanger used is a kettle evaporator in whose tubes the dimer stream D1 is condensed and in whose shell space the heat transfer medium is heated.

The heat transfer medium W1 utilized in the process according to the invention may be any working medium familiar to those skilled in the art. The heat transfer medium W1 is preferably selected from the group consisting of water; alcohols; alcohol-water mixtures; salt-water solutions; ammonia; mineral oils, for example diesel oils; thermal oils, for example silicone oils; biological oils, for example limonene; and aromatic or aliphatic hydrocarbons, for example dibenzyltoluene. It is preferable to employ water, methanol, ethanol, propanol, n-pentane, n-butane, n-hexane, n-propane or ammonia as the heat transfer medium W1. It is particularly preferable to use water as the heat transfer medium W1.

If the heat transfer medium W1 is employed in the liquid phase, i.e. a liquid heat transfer medium W1, and is supplied with energy, preferably heat, the heat transfer medium W1 undergoes at least partial evaporation to obtain an at least partially gaseous heat transfer medium W1.1. If the heat transfer medium W1 is employed in the gaseous phase, i.e. a gaseous heat transfer medium W1, and is supplied with energy, preferably heat, this likewise affords a gaseous heat transfer medium W1.1.

In a preferred embodiment of the present invention the separation stage A1 comprises at least one further distillation column DKA2 for distillation of the bottoms stream S1 which separates trimers from the higher oligomers. The trimers would be obtained as a stream at the top of the distillation column DKA2. The higher oligomers are accordingly obtained in the bottom of DKA2.

The at least one distillation column DKA2 used for the distillation of the bottoms stream S1 may be any desired distillation columns known to those skilled in the art. It is preferable when the distillation column DKA2 of the separation stage A1 contains internals. Suitable internals are for example trays, unstructured packings (random packings) or structured packings. Trays used are typically bubble-cap trays, sieve trays, valve trays having fixed or movable valves, tunnel-cap trays or slotted trays. Unstructured packings are generally beds of random packings. Random packings used are typically Raschig rings, Pall rings, Berl saddles, Super-Rings/Super-Rings Plus or Intalox® saddles. Structured packings are sold for example under the Mellapak® trade name by Sulzer. In addition to the internals mentioned, further suitable internals are known to those skilled in the art and may likewise be used.

Preferred internals have a low specific pressure drop per theoretical plate. Structured packings and random packings have, for example, a significantly lower pressure drop per theoretical plate than trays. This has the advantage that the pressure drop in the distillation column of the first reaction stage RL remains as low as possible.

In a particularly preferred embodiment of the present invention the distillation column DKA2 comprises a multiplicity of internals, preferably between 5 and 80 separation stages, more preferably between 10 and 40 separation stages.

The conditions of the distillation, i.e. temperature and pressure for example, are usually determined by the construction (column height, number of trays, type of trays/packing, spacings etc.). The separation properties of the distillation may also be controlled during operation via the temperature distribution and/or the heat supply into the column and the reflux in the distillate. The separation property may also be adjusted within a certain range by changing the pressure. The precise settings therefore cannot be defined superordinately to and independently of the construction of the distillation column. This is known to those skilled in the art. The pressure during the distillation is preferably a vacuum, more preferably in the range from 100 to 800 mbar, more preferably in the range from 200 to 700 mbar, particularly preferably 300 to 500 mbar.

The tops stream obtained in DKA2 is preferably condensed and then preferably partially recycled to DKA2 as reflux and partially discharged from the process. In addition, the energy generated during condensation of the tops stream from DKA2 will be particularly preferably at least partially transferred to a heat transfer medium W1.

The energy from the heated heat transfer medium W1.1 is then transferred to a further heat transfer medium W2 to form a heated heat transfer medium W2.1 which is initially compressed and/or heated and by means of which a steam stream used to heat at least the distillation columns DKA1 and DKR1 is subsequently produced using a single- or multi-stage compression.

Energy, especially heat energy, is thus initially transferred from the heat transfer medium W1.1 to the heat transfer medium W2. The heat transfer medium W2 utilized in the process according to the invention may be any working medium familiar to those skilled in the art. The heat transfer medium W2 is preferably selected from the group consisting of water; alcohols; alcohol-water mixtures; salt-water solutions; ammonia; mineral oils, for example diesel oils; thermal oils, for example silicone oils; biological oils, for example limonene; and aromatic or aliphatic hydrocarbons, for example dibenzyltoluene. It is preferable to employ water, methanol, ethanol, propanol, n-pentane, n-butane, n-hexane, n-propane or ammonia as the heat transfer medium W2. It is particularly preferable to use water and/or methanol as the heat transfer medium W2.

If the heat transfer medium W2 is employed in the liquid phase, i.e. a liquid heat transfer medium W2, and is supplied with energy, preferably heat, the heat transfer medium W2 undergoes at least partial evaporation to obtain an at least partially gaseous heat transfer medium W2.1. If the heat transfer medium W2 is employed in the gaseous phase, i.e. a gaseous heat transfer medium W2, and is supplied with energy, preferably heat, this likewise affords a gaseous heat transfer medium W2.1.

The transfer of energy from W1.1 to W2 may be performed by processes known to those skilled in the art or with heat exchangers known to those skilled in the art, for example the aforementioned evaporators. Suitable evaporators that can be used as heat exchangers are, for example, natural circulation evaporators, forced circulation evaporators, forced circulation flash evaporators, kettle evaporators, falling-film evaporators or thin-film evaporators. As well as those mentioned it is alternatively possible to use any other design of evaporator which is known to those skilled in the art provided the desired energy transfer is thereby ensured.

The heat transfer media W1 and W2 may in principle be identical or different to one another. This means that it is possible in principle for the heat transfer medium W1 and the heat transfer medium to be the same liquid or the same gas. It is similarly possible for the two heat transfer media W1 and W2 to be different. Both process variants are described below.

According to the invention the heated heat transfer medium W2.1 is initially compressed and/or heated to allow subsequent production of a steam stream using a single- or multi-stage compression. Heating may be effected for example by means of the evaporators already described. Compression may be carried out in any desired manner known to those skilled in the art, as has already been described previously.
In a particularly preferred embodiment of the present invention the heat transfer medium W2 employed is methanol. Through energy transfer from the heated heat transfer medium W1.1 the methanol is brought to a higher pressure and/or a higher temperature (and referred to as W2.1) and subsequently subjected to single- or multi-stage, preferably multi-stage, compression. The subsequent compression forms the compressed heat transfer medium W2.2, in this case methanol.

The compression of methanol as W2.1 can be for example performed mechanically and in single-stage or multi-stage fashion. In this context the term “single-stage” means that compression from one pressure level to another is carried out. The term “multi-stage” means that compression to a pressure level X and then from X to the pressure level Y is carried out first. A multi-stage compression may employ two or more compressors of the same type or compressors of different types. A multi-stage compression may be carried out with one or more compressors. The use of single-stage compression or multistage compression depends on the compression ratio and hence on the pressure to which the heat transfer medium W2.1 is to be compressed.

In the present case the methanol as W2.1 is subjected to a single- or multi-stage compression to give W2.2 at a pressure in the range from 3 to 30 bar, by preference 5 to 20 bar, preferably 7 to 15 bar.

A suitable compressor in the process according to the invention, especially for compression of methanol as the heat transfer medium W2.1, is any compressor known to those skilled in the art, preferably mechanical compressors, that may be used to compress gas streams. Suitable compressors include, for example, single-stage or multi-stage geared turbocompressors, piston compressors, screw compressors, centrifugal compressors or axial compressors.

In a likewise particularly preferred embodiment of the present invention the heat transfer medium W2 employed is water under a light vacuum in the range between 300 and 800 mbar. The energy transfer from the heated heat transfer medium W1.1 at least partially evaporates the water (and is referred to as W2.1). The partially evaporated water as W2.1 is preferably brought, i.e. compressed, to a higher pressure via a single- or multi-stage, preferably multi-stage, blower and is obtained as slack steam. The described compression forms the compressed heat transfer medium W2.2, in this case slack steam. The slack steam generated is preferably used for heating or preheating the feed streams to the distillation columns.

Irrespective of the heat transfer medium used as heat transfer medium W2 a heated heat transfer medium W2.1 is in any case produced and compressed to obtain compressed heat transfer medium W2.2. In a further-preferred embodiment of the present invention energy is subsequently transferred from the compressed heat transfer medium W2.2 to a further heat transfer medium W3, preferably water, to form a heated heat transfer medium W3.1 which is subjected to a single- or multi-stage, preferably multi-stage, compression and is then used as a steam stream to heat at least the distillation columns DKA1 and DKR1, preferably all of the distillation columns present in the reaction stages and all of the distillation columns present in the separation stage. Furthermore the steam stream produced by the thermal integration described according to the invention may additionally also be used to heat the distillation column DKA2 if this distillation column is present.

The heat transfer medium W3, preferably the water, is subjected to a single- or multi-stage, preferably multi-stage compression. This single- or multi-stage compression brings the heat transfer medium W3 to a pressure in the range from 5 to 40 bar, preferably 10 to 30 bar, preferably 12 to 25 bar, and is in the form of a vapour in this range. If a multi-stage compression is carried out, water condensate is preferably injected between the compressor stages to prevent overheating during compression.

The heat transfer media W1, W2 and W3 are all used for transferring energy, especially energy in the form of heat. Due to the respective energy transfer the temperature and/or the pressure will decrease, thus leading to at least partial condensation. The heat transfer media W1, W2 and W3 preferably form a

dedicated circuit, i.e. the heat transfer media are recycled after energy transfer in order to be able to recover energy again.

During recycling of the heat transfer media these heat transfer media may be used to heat the heat transfer medium in the circuit prior to compression. For example after energy transfer, the heat transfer medium W2.2 could transfer in addition energy to W2.1 prior to compression. Known heat exchangers may be used to this end.

The present invention is described with reference to the drawings described below. The drawings are merely examples of suitable embodiments which do not limit the subject matter of the invention.

Fig. 1 shows a noninventive configuration of the oligomerization with subsequent separation of the oligomers. The input mixture is initially passed to the first reaction stage (R1) where the oligomerization is carried out in the reactor (1) and the subsequent separation of the reaction mixture is carried out in the distillation column DKR1 (2). The residual stream obtained at the top of the distillation column DKR1 (2) is at least partially condensed in a condenser (3) and then in each case partially returned to the reactor (1) and passed to the next reaction stage (RX). In this example RX would be RL in the context of the present invention. The oligomerizate O1 is passed to the distillation column DKRX (6). The energy for the separation in the distillation column DKR1 (2) is introduced via a reboiler (4). The residual stream passed to the next reaction stage RX is converted in the reactor (5). The reaction mixture obtained is separated in the distillation column DKRX (6). In this example DKRX would correspond to DKRL. The residual stream obtained at the top of the distillation column DKRX (6) is at least partially condensed in a condenser (7) and then at least partially returned to the reactor (5). The energy for the separation in the distillation column DKRX (6) is introduced via a bottoms evaporator (8). The oligomerizate OL obtained in the bottoms is passed to the separation stage A1 where the separation of the oligomers is carried out in the distillation column DKA1 (9). The dimer stream D1 is obtained at the column top and is at least partially condensed in a heat exchanger (10). The energy for the separation in the distillation column DKA1 (9) is introduced via a reboiler (11).

Fig. 2 likewise shows a noninventive configuration of the oligomerisation. In addition to the process mode shown in Fig. 1 this configuration includes an additional vapour compression where the residual stream obtained at the top of the distillation column DKR1 (2) is compressed in a compressor (13) and then used to heat the reaction mixture in a preheater (14). In the recycling from the preheater (14) a further preheater (12) effects preheating of the stream upstream of the compressor (13).

Fig. 3 likewise shows a noninventive configuration of the oligomerisation. In addition to the process mode shown in Fig. 2 the residual stream compressed in the compressor (13) is used for heating the reaction mixture of the reaction stage RX in a preheater (15).

Fig. 4 shows an inventive configuration of the oligomerization. In addition to the process mode shown in Fig. 1 this configuration comprises a thermal integration according to the present invention. The condensation heat from the distillation column DKA1 (9) is removed via the heat exchanger (10) and the reaction heat from the reactor (1) is removed using a heat transfer medium A via the heat exchanger (16). Using the heat transfer medium A heated in this way a further heat transfer medium B is heated in an evaporator (17) and subjected to a multi-stage compression in a compressor (19). The compressed heat transfer medium B is then used to heat another heat transfer medium C, for example water, in an evaporator (20). A flash vessel (23) where the gas phase obtained there is passed between the compressor stages of the compressor (19) may be interposed in the recycling of the heat transfer medium B. The liquid output from the flash vessel (23) may be employed in a heat exchanger (18) for preheating the heat transfer medium B prior to compression. The heat transfer medium C is likewise subjected to a multi-stage compression in a compressor (21) and then used to heat the bottoms evaporators (4 and 11). A flash vessel (22) where the gas phase obtained there is passed between the compressor stages of the compressor (21) may be interposed in the recycling of the heat transfer medium C downstream of the reboilers. The liquid output from the flash vessel (22) is recycled to the evaporator (20).

Fig. 5 likewise shows an inventive configuration of the oligomerization. In contrast to the process mode shown in Fig. 4 there are only two heat transfer media. The heat transfer medium B is heated in the evaporator (17) and then subjected to a compression in the compressor (19) which in the present case is preferably a blower. The compressed heat transfer medium is passed to a flash vessel (24). The gas phase obtained there is passed to a further compressor (21), subjected to multi-stage compression and is then used to heat the bottoms evaporators (4 and 11). The liquid phase from the flash vessel is at least partially recycled to the evaporator (17) using a pump (25) but may also be passed between the compressor stages of the compressor (17) or downstream of the compressor (21).

Fig. 6 likewise shows an inventive configuration of the oligomerization. In addition to the process mode shown in Fig. 5 this configuration comprises two additional preheaters (26 and 27). These preheaters (26, 27) are operated directly with the gas phase from the flash vessel (24) as an energy source.

The examples which follow are intended to illustrate the invention without restricting its scope of application resulting from the description and the claims.

Examples

All of the following examples were simulated with Aspen Plus V.10. The kinetic model and the material data were validated using operational data. All examples were simulated with the same boundary conditions. A feed of 40 t/h was simulated to have a butene content of 70 wt% (25 wt% 1-butene, 30 wt% trans-butene and 15 wt% cis-butene). The proportion of n/i-butane was simulated as 30 wt%, assuming

3% of isobutane in the feed. The feed temperatures to the reaction stages were kept constant at 95°C in all cases.

Example 1 (noninventive)

A configuration as shown in Fig. 1 was used for the simulation. The fresh feed is mixed with a recyclate stream of 19 t/h and brought to the feed temperature of 95°C with a heat exchanger. The feed is passed through a reaction stage R1 at 25 bar abs (tubular reactor (1) with catalyst). The reactor (1) is cooled to remove the reaction heat. A total of 4.2 MW must be removed. After the first reaction stage the reaction mixture is subjected to a distillative separation. The distillation column (2) is operated at a column top pressure of 4.3 bar abs. The distillation column (2) preferably has a separation sharpness of less than 1 percent heavy boilers in the distillate in order not to inhibit the reaction too excessively. This results in a tops temperature of 45°C. 13 trays are simulated. To achieve the purity a reflux of 16 t/h and a heating power of 5.1 MW are required, the latter being introduced via 20 bar steam (obtained from an external source). A condensation heat of 5.3 MW is generated and is removed via an air cooler or an apparatus (3) operated with recycled cooling water.

A portion of the liquid distillate is returned to the first reaction stage (19 t/h), the other portion of 20 t/h (having a weight fraction of n/i-butane of 60%) is passed to a further, final reaction stage RL. This stream is in turn mixed with a recyclate stream of 15 t/h and brought to a feed temperature of 95°C. A reactor (5) identical to the reactor (1) of the first stage R1 is used. Here too, the reaction heat is removed via a process water circuit operated in co-current. 1 MW must be removed. The reaction mixture is likewise sent for distillative separation here. The distillation column (6) has a total of 28 trays. In the distillate from the second column a C8-content of less than 0.1 wt% is specified. This requires a reflux of 2 t/h and a heating power of 2 MW, the latter in turn being introduced via external heating steam. 3 MW must be removed via the condenser (10). The column (9) is likewise operated at 4.3 abs. This results in a column top temperature of 44°C. The distillate stream is in turn divided. A portion of 15 t/h is returned to the reaction stage and the other portion of 14.5 t/h comprising 82 wt% of n/i-butane may be passed to another process unit or to a tank farm. A conversion of 90% is achievable.

The oligomers C8/C12/C16+ are obtained in the bottom of the distillation column (6) and are subjected to a further separation in the separation unit A1. In the distillation column (9) the C8-isomers (preferably 1-octene and 2-methylheptene) are separated from the longer-chain oligomers under vacuum at a column top pressure of 350 mbar. To obtain a purity of preferably greater than 99% a reflux of 14 t/h must be established. A column top temperature of 86°C is established. A total of 1.4 MW of heating power is required (external steam) and 3 MW of condensation heat must be removed.

A total of 11.3 MW of condensation heat and 5.2 MW of reaction heat are removed from the system (16.5 MW in total). The system must be supplied with a total of 8.5 MW of heating power.

Example 2 (noninventive):

A configuration as shown in Fig. 2 was used for the simulation. The foregoing from example 1 also applies here. A vapour compression where the condensation heat is at least partially utilized via the compressor (13) and the heat exchangers (12, 14) is additionally present. In this example the feed preheater (14) introduces 1.75 MW into the system. An electrical power of 200 kW is required to bring the vapour stream to the required temperature level. Excessive energy input via the feed evaporator results in a shift in the temperature profile. Heavy boilers are forced upwards. More reflux is required. The total heating power increases to 5.75 MW. However, the external heating demand is reduced to 4 MW at the first distillation column. The total external heating power is thus reduced from 7.2 MW.

Example 3 (noninventive):

A configuration as shown in Fig. 3 was used for the simulation. The foregoing from examples 1 and 2 also applies here. In addition to the feed preheater (14), the feed preheater (15) of the last stage is also operated via the vapour compression. This introduces a further 1.2 MW into the system. The heating power for the last stage altogether increases to 2.4 MW but the external heating power falls to 1.2 MW. To achieve this an electrical power of 350 kW must be introduced via the compressor. The total external heating power is 6.4 MW.

Example 4 (inventive):

A configuration as shown in Fig. 4 was used for the simulation. The foregoing relating to the reaction stages and the separation stage from example 1 also applies here. The condensation heat from the vacuum distillation and the reaction heat from the first stage is at least partially transferred to a hot water circuit via heat exchangers (10, 16). The heat from the hot water circuit is then used to evaporate a heat transfer medium, in this case methanol at 2.0 bar abs., in the evaporator (17). Methanol is subjected to a multi-stage compression (19) to 10 bar abs. This requires an electrical power of 1.2 MW. The condensation of the methanol causes water to be evaporated at 3 bar abs. in the evaporator (20). The steam is subjected to a multi-stage compression (21) to 20 bar abs. The compression to 20 bar abs. requires an electrical power of 1.6 MW. The steam is needed to heat the reboilers (4, 8, 11). A total of 8.5 MW of external heating power are substituted by 2.8 MW of electrical power. No external heating medium (steam) is required.

Example 5 (inventive):

A configuration as shown in Fig. 5 was used for the simulation. The foregoing relating to the reaction stages and the separation stage from example 1 and also the foregoing from example 4 apply here too.

The configuration is identical to example 4. In this case water is employed as the heat transfer medium instead of methanol. Water is evaporated under a light vacuum (550 mbar) and compressed to 3 bar abs. in the compressor (19). This procedure requires more electrical power. A total of 3.1 MW of electrical power is required to substitute 8.5 MW of external heating power (steam).

Example 6 (inventive):

A configuration as shown in Fig. 5 was used for the simulation. The foregoing relating to the reaction stages and the separation stage from example 1 and also the foregoing from example 5 apply here too. The optimization of example 5 is shown. The concept of the feed evaporators (26, 27) is taken up again here (cf. examples 2 and 3). In this example the feed preheaters (26, 27) are operated with the 3 bar abs. steam produced, with the result that the amount that must be brought to the highest pressure level is reduced. The electrical power is reduced to 2.2 MW.

An overview of the results of examples 1 to 6 is found in table 1:

Table 1: Comparison of the energy values for all examples

Example	1	2	3	4	5	6
Heating steam external / MW	8.5	7.2	6.4	0	0	0
Electrical power / MW	0	0.2	0.35	2.8	3.1	2.2
Removed, unutilized energy / MW	16.5	15	13.9	10.8	11.1	10.2

Claims

1. Process for oligomerization of C2- to C8-olefins in at least two reaction stages R1 and RL, each comprising at least one reactor and at least one distillation column, and a separation stage A1 which follows RL and comprises at least one distillation column DKA1, wherein

an input mixture which contains at least the C2- to C8-olefins as reactant olefins is subjected to an oligomerization using a heterogeneous catalyst in the at least one reactor of the first reaction stage R1 and the reaction mixture obtained from the at least one reactor is distilled in the at least one distillation column DKR1 of the first reaction stage R1 to obtain a residual stream RS1 containing at least unconverted reactant olefins and an oligomerizate O1 containing at least the oligomers formed,

RS1 is at least partially passed to a reactor of a subsequent reaction stage;

a residual stream from a preceding reaction stage is subjected to an oligomerization using a heterogeneous catalyst in the at least one reactor of the last reaction stage RL and the reaction mixture obtained from the at least one reactor is distilled in the at least one distillation column DKRL of the last reaction stage RL to obtain a residual stream RSL containing at least unconverted reactant olefins and an oligomerizate OL containing at least the oligomers formed;

OL is at least partially passed to the distillation column DKA1 of the subsequent separation stage A1 and distilled therein to obtain a dimer stream D1 composed to an extent of at least 90% by weight of dimers of the employed reactant olefins and a bottoms stream S1 containing at least trimers and higher oligomers of the employed reactant olefins;

the dimer stream D1 obtained at the top of DKA1 is condensed and then partially recycled to DKA1 as reflux and partially discharged from the process,

the energy generated during condensation of the dimer stream D1 and the heat energy generated in the at least one reactor of the first reaction stage R1 are at least partially transferred to a liquid or gaseous heat transfer medium W1 to form a heated heat transfer medium W1.1; and

energy from the heated heat transfer medium W1.1 is transferred to a further liquid or gaseous heat transfer medium W2 to form a heated heat transfer medium W2.1 which is initially compressed and/or heated and by means of which a steam stream used to heat at least the distillation columns DKA1 and DKR1 is then produced using a single- or multi-stage compression.

2. Process according to Claim 1, wherein RS1 is at least partially recycled to the at least one reactor of the reaction stage R1.

3. Process according to Claim 1 or 2, wherein at least one further reaction stage comprising at least one reactor and at least one distillation column is present between the reaction stage R1 and the reaction stage RL.

4. Process according to any of the preceding claims, wherein the reaction stage R1 comprises at least one further reactor R1.2 which is connected to the reactor R1.1 in parallel or in series, preferably is present connected in series.

5. Process according to Claim 4, wherein the energy generated at the reactor 2.1 is also at least partially transferred to the heat transfer medium W1.

6. Process according to any of the preceding claims, wherein the process is performed in at least one further reaction stage R2, wherein reaction stage R2 comprises at least one reactor R2.1 and at least one distillation column DKR2.

7. Process according to any of the preceding claims, wherein the steam stream produced is also used for heating the distillation column DKR2.

8. Process according to any of the preceding claims, wherein the heat transfer medium W1 is selected from the group consisting of water; alcohols, alcohol-water solutions; salt-water solutions; mineral oils, for example diesel oils; thermal oils, for example silicone oils; biological oils, for example limonene; and aromatic hydrocarbons, for example dibenzyltoluene.

9. Process according to any of the preceding claims, wherein the heat transfer medium W2 is selected from the group consisting of water; alcohols, alcohol-water solutions; salt-water solutions; mineral oils, for example diesel oils; thermal oils, for example silicone oils; biological oils, for example limonene; and aromatic hydrocarbons, for example dibenzyltoluene.

10. Process according to any of the preceding claims, wherein the heated heat transfer medium W2.1 is compressed to obtain compressed heat transfer medium W2.2.

11. Process according to Claim 10, wherein energy is transferred from the compressed heat transfer medium W2.2 to a further heat transfer medium W3 to form a heated heat transfer medium W3.1 which is subjected to single- or multi-stage, preferably multi-stage, compression and is subsequently used as a steam stream for heating all of the distillation columns present in the reaction stages and all of the distillation columns present in the separation stage.

12. Process according to Claim 11, wherein the heat transfer medium W3.1 is brought to a pressure in the range from 5 to 40 bar, preferably 10 to 30 bar, preferably 12 to 25 bar, by way of the single- or multi-stage compression.

13. Process according to any of the preceding claims, wherein the reaction mixture is preheated before it is introduced to the distillation column DKR1.

14. Process for oligomerization according to any of the preceding claims, wherein the reactors of the individual reaction stages employ an oligomerization catalyst which comprises a nickel compound on an aluminosilicate support material and which preferably contains less than 0.5% by weight of titanium dioxide and zirconium dioxide in its overall composition.

15. Process for oligomerization according to any of the preceding claims, wherein the process is a process for oligomerization of C3- to C6-olefins, preferably of C3- to C5-olefins, particularly preferably of C4-olefins.