

Energy-efficient process for removing butenes from C4-hydrocarbon streams and subsequent n/iso separation

5 The present invention relates to a process for separation of butenes from C4-hydrocarbon streams containing not only the butenes but also butanes by extractive distillation with a suitable solvent. The process according to the invention features heat integration with which the heat of the solvent is utilized for heating and/or at least partially evaporating different streams.

10 The separation of butane-butene mixtures by extractive distillation is known per se. This employs an aprotic solvent (for example N-methyl-2-pyrrolidone (NMP) or acetonitrile (ACN)) to increase the relative volatility of the alkanes compared to the alkenes. In one extractive distillation column, the absorber, the butenes are preferably dissolved in the solvent and the butanes are separated as tops product. The laden solvent is subsequently freed of the butenes in a stripping column, the desorber, at elevated temperature and/or reduced pressure, and said butenes are obtained in
15 enriched form as tops product. The solvent freed of butenes is then recycled to the extractive distillation.

Heat integration is of great importance to the economy of the process due to the high solvent to feed ratio. Hot solvent is obtained at the bottom of the desorber and the energy content thereof
20 may be utilized in various ways. US 2014/0124358 A1 presents a process for selective extraction of olefins which is said to solve the problem of heat integration. This document proposes utilizing the energy content of the hot solvent for heating a sidestream from the desorber, for heating the bottoms product of the absorber which is passed to the desorber, for heating one or more
25 sidestreams of the absorber and for preheating the feed stream.

However, the solution proposed in the prior art can solve the problem of ideally full recovery of the energy streams present in the system only incompletely or via relatively complex constructions.

30 It is accordingly the object of the present invention to provide a process where an improved, ideally maximum possible, energy recovery is achieved and this is done in a way with less plant engineering complexity.

This object is achievable by the embodiment of the process proposed in claim 1. Preferred
35 embodiments are specified in the dependent claims. The process according to the invention is a process for separating butenes from a C4-hydrocarbon stream which contains at least butenes and the butanes n-butane and isobutane by extractive distillation with a solvent, wherein the process comprises the steps of:

- a. at least partially evaporating the liquid C4-hydrocarbon stream in a feed evaporator, supplying the gaseous C4-hydrocarbon stream and supplying the liquid solvent, preferably NMP, above the C4-hydrocarbon stream to an absorber in which the C4-hydrocarbon stream and the solvent are contacted with one another to transfer predominantly butenes from the C4-hydrocarbon stream to the solvent, wherein the thus-laden solvent, preferably NMP, is collected in a liquid collector of the absorber, passed through an absorber evaporator and then passed into the bottom of the absorber below the liquid collector to outgas predominantly butanes from the laden solvent, preferably NMP, wherein the laden solvent, preferably NMP, is subsequently passed to a desorber as bottoms stream and wherein a stream enriched in butanes relative to the employed C4-hydrocarbon stream is obtained at the top of the absorber;
- b. supplying the laden solvent, preferably NMP, to the desorber, the bottom of which is at an elevated temperature and preferably a lower pressure relative to the bottom of the absorber and in which the butenes are separated from the solvent, preferably NMP, to obtain at the top of the desorber a stream enriched in butenes, wherein a solvent, preferably NMP, at least partially freed of butenes is collected in a liquid collector of the desorber, passed through a desorber evaporator and then passed into the bottom of the desorber below the liquid collector to outgas any butenes remaining in the solvent and wherein the solvent is subsequently recycled to the absorber as bottoms stream;
- c. supplying the stream enriched in butanes to an n/iso splitter in which n-butane and isobutane are separated from one another to obtain a stream enriched in isobutanes at the top of the n/iso splitter and a stream enriched in n-butanenes at the bottom of the n/iso splitter;
- wherein the heat of the solvent withdrawn as a bottoms stream of the desorber is used for heat integration by employing the heat of the solvent in at least one respective heat exchanger for preheating the laden solvent passed to the desorber, for evaporation in the absorber evaporator and for evaporation of the liquid C4-hydrocarbon stream and wherein the stream enriched in butenes is withdrawn at the top of the desorber and subjected to a condensation, wherein the heat of condensation is at least partially used for heating the n/iso splitter.

One advantage of the present process is the relatively simple construction of the heat integration which nevertheless allows efficient energy recovery. The simplest embodiment of the present invention further does not mandate additional side evaporators which entail additional plant engineering complexity and thus higher costs. The present case also allows the heat of condensation formed in the condensation of the stream enriched in butenes and optionally the heat of hydrogenation of an upstream hydrogenation step or one or two downstream hydrogenation steps to be utilized for an n/iso separation of the butanes using an n/iso splitter with the result that

less external energy, if any, need be supplied for such a step. Quantities of waste heat generated in the process according to the invention or other additional integrated processes would also be usable for heating the n/iso splitter.

5 The heat integration removes heat from the solvent. The reason for this is not only that other streams or columns are to be heated therewith but rather primarily the cooling of the solvent for the absorption. The absorption of the butenes (here: step a) is usually carried out at a lower temperature than the desorption (here: step b). If in the course of the heat integration sufficient heat is withdrawn from the solvent, i.e. it has a suitable temperature, the solvent may be passed
10 directly into the absorber. However, it is also conceivable that despite the heat integration present the solvent does not yet have the correct temperature. In such a case the solvent may be passed through a residual cooler to be cooled to a suitable temperature after the heat integration and before entry into the absorber.

15 Heat is a process parameter. The heat supplied or removed corresponds to the change in internal energy minus the work done. The terms heat, heat transport and heat integration used in the present invention are in every instance based on this definition.

The present process relates to the separation of butenes from butene-containing C4-hydrocarbon streams. These streams contain not only the butenes but also alkanes (n-butanes and isobutanes).
20 In the context of the present invention - unless something else is being described - the term butanes is to be understood as meaning both n-butane and isobutane. In the present process the at least partial separation of the butenes is to be followed by a separation of the alkanes into n-butane and isobutane to obtain both n-butane and isobutane in the highest possible purity. To this
25 end an n/iso separation in an n/iso splitter is provided according to the invention. A hydrogenation of the residual butenes in the streams may be performed before or after this separation of the butanes. The process according to the invention may therefore employ any C4-hydrocarbon streams which contain at least butenes and butanes provided that the amounts in which the butenes and/or butanes are present allow economic performance of the process. In a preferred
30 embodiment of the present invention the employed C4-hydrocarbon stream consists essentially, i.e. to an extent of more than 98% by weight, preferably to an extent of more than 99% by weight, of butanes and butenes. The corresponding streams may also contain impurities or other hydrocarbons, such as 1,3-butadiene or C5-hydrocarbons, in small amounts.

35 In the process according to the invention step a employs a liquid solvent which dissolves primarily the butenes of the employed gaseous C4-hydrocarbon stream. Suitable solvents are aprotic solvents, for example N-methyl-2-pyrrolidone (NMP). The process according to the invention is preferably performed with NMP as the solvent. In a further preferred embodiment of the present

invention the solvent contains water, in particular in the range from 1% to 10% by weight, preferably from 4% to 9% by weight, in each case based on the total amount of solvent.

Absorbers that may be employed include in particular random-packed columns which comprise at least two random-packing beds. Such columns are known in principle to those skilled in the art. Preferably arranged above the first random-packing bed is a backwashing zone comprising a plurality of theoretical trays to hold back the solvent entrained in the gas phase. Above the backwashing zone is the top of the absorber where a stream enriched in butanes relative to the employed C4-hydrocarbon stream is obtained. The liquid collector according to the invention would be arranged below the last random-packing bed, the bottom of the absorber being arranged below said collector. The precise construction of the absorber depends on various parameters and is variable in certain aspects.

The liquid solvent is supplied to the absorber spatially above the inlet for the C4-hydrocarbon stream. In a preferred embodiment the solvent is supplied to the absorber above the first random-packing bed and the C4-hydrocarbon stream is added to the absorber in one or more random-packing beds below the first random-packing bed. In the absorber the liquid solvent will trickle downwards and is brought into contact with the (ascending) vaporous C4-hydrocarbon stream to transfer a portion of the C4-hydrocarbon stream containing predominantly butenes to the solvent to form a laden solvent. In step a the C4-hydrocarbon stream and the solvent are brought into contact with one another in particular in countercurrent. In a preferred embodiment of the present invention the portion of the C4-hydrocarbon stream transferred to the solvent comprises at least 70% by weight, particularly preferably at least 80% by weight, of butenes based on the composition of the portion of the C4-hydrocarbon stream transferred to the solvent. This has the result that in particular at least 80%, particularly preferably at least 90%, of the butenes present in the employed C4-hydrocarbon stream are transferred to the solvent.

The laden solvent flows downwards in the absorber and is collected in a suitable liquid collector, in particular a chimney tray. The temperature of the laden solvent obtained in the liquid collector is preferably between 40°C and 90°C, particularly preferably between 45°C and 65°C. The laden solvent is withdrawn from the liquid collector, passed through an absorber evaporator and then passed into the bottom of the absorber below the liquid collector to outgas predominantly butanes from the laden solvent. The absorber evaporator is preferably a once-through evaporator where the laden solvent is passed through the evaporator only once. This allows achievement of the lowest possible temperatures, thus making it possible to prevent fouling. The driving temperature difference is additionally increased, thus allowing even more efficient energy utilization of the NMP stream. The absorber evaporator may also be configured as a multi-stage apparatus i.e. a plurality of heat exchangers/a plurality of evaporators belonging to the absorber evaporator may be present.

The solvent laden predominantly with butenes then remains in the bottom and is withdrawn therefrom and passed to the desorber as bottoms stream. The temperature in the bottoms stream of the absorber, which is fed to the desorber, is here preferably between 70°C and 130°C, particularly preferably between 85°C and 120°C.

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A stream enriched in butanes relative to the employed C4-hydrocarbon stream is obtained at the top of the absorber. This stream enriched in butanes may additionally contain water originating from the solvent. This water may be separated in a subsequent step. The stream enriched in butanes is withdrawn at the top of the absorber and subjected to a single-or multi-stage
10 condensation to condense out a water-containing stream and a butane-containing product stream. These two streams may be separated from one another in a suitable apparatus, for example a spider. The water-containing stream separated from the butane-containing product stream may be passed to the absorber or to the desorber and/or partially discharged from the process depending on its composition.

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The butane-containing product stream thus obtained from the condensation may still contain small amounts of water, in particular in an amount of up to 1500 ppmw, based on the total composition of the butane-containing product stream. In addition, the butane-containing product stream obtained from the condensation may further contain residual butenes, wherein the streams contain typically
20 less than 20% by weight, preferably less than 15% by weight, particularly preferably less than 5% by weight, of butenes based on the total composition of the butane-containing product stream.

Depending on the requirements for the obtained butane-containing product stream it may be necessary for the butane-containing product stream to be subjected to a drying following the
25 condensation, preferably in a drying column, to separate the water still present. The butane-containing product stream preferably contains a maximum amount of water of 50 ppmw, preferably of 25 ppmw, after the drying. The water obtained during the drying may be recycled to the condensation in the absorber.

30 According to the invention the stream enriched in butanes or, if a condensation is carried out, the butane-containing product stream is passed to an n/iso splitter in which n-butane and isobutane are separated from one another. An n/iso splitter is in particular a suitable distillation column. An isobutane-enriched stream is obtained at the top of the n/iso splitter and an n-butane-enriched stream is obtained at the bottom of the n/iso splitter. The n/iso splitter according to the invention is
35 an apparatus suitable for separating the n-butenes from the isobutenes, in particular a distillation column. The temperature in the bottom of the n/iso splitter is preferably 50°C to 70°C, particularly preferably 55°C to 65°C. The pressure in the n/iso splitter is preferably 4 to 10 bar absolute, particularly preferably 5 to 7 bar absolute. The exact configuration and the operation of a corresponding n/iso splitter/a corresponding distillation column is known to those skilled in the art.

The stream enriched in isobutanes obtained at the top of the n/iso splitter consists predominantly of isobutane. The isobutane-enriched stream preferably consists of isobutane to an extent of 98% by weight, more preferably 99% by weight, particularly preferably 99.5% by weight. The stream
5 enriched in n-butanes obtained at the bottom of the n/iso splitter consists predominantly of n-butane. The n-butane-enriched stream preferably consists of n-butane to an extent of 98% by weight, more preferably 99% by weight, particularly preferably 99.5% by weight.

The energy necessary for heating the n/iso splitter and thus for achieving separation of the butanes
10 is at least partially obtained from the heat of condensation formed during condensation of the stream enriched in butenes withdrawn at the top of the desorber. The heat of condensation is thus at least partially utilized. The corresponding condenser for condensation of the stream enriched in butenes withdrawn at the top of the desorber may be a heat exchanger known to those skilled in the art. It is also conceivable for the condenser of the desorber to be in the form of a kettle.
15 Depending on the availability of internal streams it is also possible for the condenser to be configured as a multi-stage apparatus, wherein heat integration is only effected with the condensation in the first stage and an external cooling medium is used in the second stage.

It is mentioned hereinabove that the stream enriched in butanes or, if a condensation is carried out,
20 the butane-containing product stream already consists predominantly of n- and isobutanes. Butenes not transferred into the solvent during the extraction may also still be present in these streams. If it is sought to obtain olefin-free n-butane/isobutane streams by way of the n/iso separation, the stream enriched in butanes withdrawn at the top of the absorber or, if a condensation is carried out, the butane-containing product stream may be subjected to a
25 hydrogenation before entry into the n/iso splitter to convert any remaining butenes into butanes. Such a residual olefin hydrogenation is generally familiar to those skilled in the art and shall not be described in detail here.

In a particularly preferred embodiment at least a portion of the heat of reaction formed during the
30 hydrogenation upstream of the n/iso splitter is used for heating the n/iso splitter. This makes it possible to save at least a portion of the otherwise necessary external energy for heating the n/iso splitter.

It is also alternatively possible for such a hydrogenation to be arranged not upstream of the n/iso
35 splitter but only downstream thereof. Any remaining 1-butenes and isobutenes are typically obtained at the top of the n/iso splitter and would then be present in the isobutane-enriched stream. The 2-butenes end up in the bottoms and are present in the n-butane-enriched stream. In a preferred embodiment of the present invention one of the isobutane-enriched stream and the stream enriched in n-butenes or both streams is/are subjected to a hydrogenation to convert any

remaining butenes into butanes. It is thus also possible to hydrogenate only one stream obtained from the n/iso splitter while the other stream is not hydrogenated.

5 In a particularly preferred embodiment of the present invention at least a portion of the heat of reaction formed during the hydrogenation of one of the two streams or at least a portion of the heat of reaction formed during the two hydrogenations of the two streams is used for heating the n/iso splitter. This makes it possible to save an additional amount of the otherwise necessary external energy for heating the n/iso splitter. In some cases additional external energy is no longer required. Appropriate heat integration of the heat of reaction formed could also be provided by an internal hot
10 water circuit for example. Such plant engineering steps are familiar per se to those skilled in the art.

The solvent withdrawn at the bottom of the absorber and laden predominantly with butenes is supplied to the desorber. To this end the laden solvent may be passed to the desorber using a pump for example. Relative to the bottom of the absorber the bottom of the desorber is at an
15 elevated temperature and preferably a lower pressure. The temperature in the bottom of the desorber is preferably between 120°C and 200°C, more preferably between 130°C and 195°C. The head pressure in the desorber may be between 1 and 6 bar absolute, preferably between 2 and 5 bar absolute. The elevated temperature and the preferably lower pressure relative to the absorber has the result that the butenes and optionally any butanes still present are at least
20 partially removed from the solvent. In a preferred embodiment the solvent at least partially freed of butenes contains up to 5000 ppmw of butenes, particularly preferably 100 to 900 ppmw of butenes. The solvent at least partially freed of butenes flows downwards in the desorber and is collected in the liquid collector of the desorber. From there the solvent at least partially freed of butenes is passed through a desorber evaporator and then passed into the bottom of the desorber below the
25 liquid collector, in particular a chimney tray, to outgas any butenes remaining in the solvent. The desorber evaporator is preferably a once-through evaporator where the solvent at least partially freed of butenes is passed through the evaporator only once. This allows achievement of the lowest possible temperatures, thus making it possible to prevent fouling. The desorber evaporator may also be configured as a multi-stage apparatus, i.e. a plurality of heat exchangers belonging to
30 the desorber evaporator may be present. The solvent freed of butenes then remains in the bottom and is withdrawn therefrom, passed to the absorber as bottoms stream and reused there as solvent for the absorption of butenes.

Before being passed to the absorber the solvent freed of butenes may be partially or completely
35 subjected to a regeneration to remove impurities, for example the abovementioned by-products present in the employed C4-hydrocarbon stream and/or formed from the butenes at the temperatures in the desorber such as oligomeric or polymeric compounds, from the solvent, preferably the NMP. The regeneration is preferably performed such that the solvent freed of butenes is passed into a container and evaporated at a pressure of less than 500 mbar absolute,

more preferably of less than 200 mbar absolute and a temperature between 100°C and 150°C. The container may have a column connected to it. Heavy boilers in particular are separated by the regeneration. If only a portion of the solvent freed of butenes is subjected to a regeneration the regenerated portion of the solvent is subsequently combined with the unregenerated solvent and recycled to the absorber.

Especially a stream enriched in butenes relative to the employed C4-hydrocarbon stream is then obtained at the top of the desorber. This stream enriched in butenes may additionally contain water originating from the solvent. This water may be separated in a subsequent step. The stream enriched in butenes is withdrawn at the top of the desorber and subjected to a single-or multi-stage condensation to condense out a water-containing stream which may contain not only water but also residues of organics as well as a butene-containing product stream. These two streams may be separated from one another in a suitable apparatus, for example a spider. The water-containing stream separated from the butene-containing product stream may then be recycled to the desorber. Discharging the entirety or portions of the water-containing stream to remove the organics is also possible.

In a preferred embodiment of the present invention the condensation of the stream enriched in butenes withdrawn at the top of the desorber is configured as a two-stage condensation, wherein in a first stage a water-containing stream is condensed out and then recycled to the desorber and in the second stage the butene-containing product stream is condensed out. However, it may also be the case that water remaining is also condensed out in the second stage. This residual water may be separated from the butene-containing product stream via a suitable apparatus, for example a spider.

The butene-containing product stream obtained from the condensation preferably contains less than 20% by weight, more preferably less than 16% by weight, of butanes based on the total composition of the butene-containing product stream. By contrast, the butene-containing product stream obtained from the condensation preferably has a butene content of at least 70% by weight, more preferably of at least 75% by weight, particularly preferably of at least 86% by weight, based on the total composition of the butene-containing product stream.

A characterizing feature of the present invention is the heat integration using the heat of the solvent on the way from the desorber back to the absorber. The heat of the solvent, preferably of the NMP, withdrawn as a bottoms stream of the desorber is according to the invention used for heat integration by employing the heat of the solvent in at least one respective heat exchanger for preheating the laden solvent passed to the desorber, for evaporation in the absorber evaporator and for evaporation of the liquid C4-hydrocarbon stream.

In a preferred embodiment of the present invention the preheating of the laden solvent passed to the desorber is performed in two stages, wherein a first heat transfer to the laden solvent passed to the desorber is effected in a heat exchanger, preferably a tube bundle heat exchanger, and a second heat transfer to the laden solvent passed to the desorber is effected in a kettle evaporator.

5 Such an embodiment has the advantage that in the abovementioned preferred embodiment the heat transferred to the laden solvent in both stages, i.e. in the heat exchanger and in the kettle evaporator, originates from the solvent withdrawn as the bottoms stream of the desorber as heat transfer medium. The use of a kettle evaporator would also have the advantage that it would allow there to be a lower supply pressure in the conduit to the desorber. A high supply pressure is

10 normally necessary to prevent evaporation in the pipe conduit that could lead to problems including bursting of the pipe conduit. A further advantage is that the thermal load is limited, thus ensuring that the temperature difference is/remains sufficiently large for heat transfer.

According to the invention the solvent, preferably NMP, at least partially freed of butenes is

15 collected in a liquid collector of the desorber and passed through a desorber evaporator to allow outgassing of any butenes remaining in the solvent. The heat for evaporation in the desorber evaporator may be introduced in a heat exchanger by heat transfer from a suitable heat transfer medium. The heat transfer medium may be in particular heating steam employed in the form of medium pressure or high pressure steam. A preferred heating steam is medium pressure steam

20 having a temperature of 150°C to 270°C, preferably of 160°C to 250°C. The medium pressure steam preferably has a pressure of 15 to 30 bar absolute particularly preferably of 17 to 25 bar absolute. Also employable as heating steam is steam having a pressure of > 30 bar absolute. Such heating steam may also be referred to as high pressure steam.

25 The heating steam used for evaporation may undergo at least partial condensation in the heat exchanger, thus generating a hot condensate at a pressure of 10 to 20 bar absolute, preferably 12 to 17 bar absolute, and a temperature of 150°C to 210°C, preferably 160°C to 200°C. Preferably arranged downstream of the heat exchanger is a condensate container in which the hot condensate may be separated from the steam. The hot condensate may additionally be used for

30 heating the n/iso splitter. The pressure in the condensate container is preferably lower than in the heat exchanger on the heating steam side. The lower pressure may result in a portion of the hot condensate evaporating, as a result of which the combined steam, i.e. the uncondensed proportion of the heating steam and the hot condensate evaporated in the condensate container by decompression, is obtained as low pressure steam in the condensate container. In the present

35 case the low pressure steam preferably has a pressure of more than 0 bar and less than 10 bar absolute. The temperature of the low pressure steam is preferably 100°C to 180°C.

The low pressure steam obtained there still contains energy but this is not utilized in any known process. This is not advantageous from an energetic or economic standpoint, however. However,

this energy can be utilized in a preferred embodiment of the present invention. To this end, the heating steam used for evaporation in the desorber evaporator may be provided using a, preferably controllable, steam ejector (thermocompressor). The thermocompressor is then supplied both with the employed heating steam, originating from an appropriate steam network for example, here especially the preferably employed medium pressure steam, and also with the low pressure steam from the condensate container, thus forming a mixed steam which is accordingly the heat transfer medium for the desorber evaporator. In this embodiment the mixed steam is accordingly the heating steam. Such a steam ejector is configured such that it is operated with motive steam and by means of negative pressure (back pressure in the steam ejector) can aspirate suction steam from a container to then form the mixed steam employed as the heat transfer medium. The motive steam is in the present case the heating steam/the medium pressure steam, with which the low pressure steam is aspirated from the condensate container as suction steam and mixed with the motive steam.

The advantage of such an embodiment is obvious. The energy of the low pressure steam obtained in the condensate container may be utilized, thus saving energy and costs. Such a procedure can also be advantageous for another reason. The employed steam ejector may be controllable such that the amounts of medium pressure and low pressure steam can be adjusted, for example according to particular process parameters. The amount of suction steam is adjusted via the amount of motive steam. The amounts of low pressure and medium pressure steam may be adjusted for example according to the temperature in the desorber.

In a further preferred embodiment the desorber comprises a side evaporator. In such a case the heat transfer medium used for the side evaporator may be the mixed steam from the steam ejector while the desorber evaporator employs medium pressure steam as heating steam. The hot condensate from the desorber evaporator and the side evaporator are then passed to a condensate container according to the above embodiments. The low pressure steam obtained there is then used in the steam ejector, whose mixing steam is employed in the side evaporator. The advantage of this variant is that the hot condensate obtained can be further decompressed to be able to provide a greater amount of low pressure steam.

The presently described process may be employed in integrated chemical systems which comprise in particular an oligomerization and optionally a hydroformylation. It is possible for the separation of butenes by the process according to the invention to be employed at various points in the integrated plant. It is also possible for the separation of butenes according to the invention to be present at various points within an integrated chemical plant. For example the process described here may be employed at the beginning of such an integrated system. The employed C4-hydrocarbon stream may then be in particular a crack C4, a raffinate 1, a raffinate 2 or a mixture thereof. If crack C4 and/or raffinate 2 are employed the separation process according to the

invention may have arranged upstream of it a crack C4 hydrogenation in which butadiene is selectively hydrogenated or a butadiene separation in which butadiene is extractively removed with a solvent such as NMP or nitriles to reduce the content of butadiene. It is possible to arrange a hydroisomerization downstream of an extractive butadiene separation and upstream of the separation according to the invention to facilitate the separation task in the process according to the invention since this converts 1-butene into 2-butene which is more readily absorbed by the solvent.

If the separation process is employed at the beginning of the integrated system the obtained product stream may be supplied to an MTBE synthesis which may then preferably be followed successively by a 1-butene separation, an oligomerization and one or more hydroformylations of the purified oligomers. A hydroformylation may be carried out not only with the product stream from the oligomerization, thus making it possible to produce for example INA (isononanol) from di-n-butenes after subsequent hydrogenation or ITDA (isotridecanal) from tributenes, but also with the unconverted butenes of the oligomerization, thus making it possible to produce 2-PH (2-propylheptanol) after subsequent aldol condensation followed by hydrogenation. The unconverted butenes from the oligomerization could optionally also be used to operate a further oligomerization instead of a hydroformylation. The conditions of the individual process steps are familiar to those skilled in the art. The individual process steps may comprise further steps, such as for example the separation of the products or the workup of the resulting stream, but these are not explicitly mentioned here. However, the separation process according to the invention may also be introduced at any other point of such an integrated system.

In one embodiment of the present invention the C4 hydrocarbon stream employed in the separation process according to the invention is withdrawn from an MTBE synthesis after separation of MTBE and the butene-containing product stream is subsequently supplied to a 1-butene separation, after which an oligomerization and one or more hydroformylations for subsequent production of 2-PH, ITDA and/or INA are successively carried out. The individual process steps may comprise further steps, such as for example the separation of the products or the workup of the resulting stream, but these are not explicitly mentioned here.

In a further embodiment of the present invention the C4-hydrocarbon stream employed in the separation process according to the invention is withdrawn from a 1-butene separation and the butene-containing product stream is subsequently supplied to an oligomerization, after which one or more hydroformylations for subsequent production of 2-PH, ITDA and/or INA are carried out. The individual process steps may comprise further steps, such as for example the separation of the products or the workup of the resulting stream, but these are not explicitly mentioned here.

In a further embodiment of the present invention the C4-hydrocarbon stream employed in the separation process according to the invention is withdrawn from an oligomerization and the butene-containing product stream is subsequently supplied to a hydroformylation for subsequent production of 2-PH. The individual process steps may comprise further steps, such as for example the separation of the products or the workup of the resulting stream, but these are not explicitly mentioned here.

In a further embodiment of the present invention the separation process according to the invention is employed at the end of the integrated system. In that case the employed C4-hydrocarbon stream is withdrawn from a 2-PH production downstream of the hydroformylation. The butene-containing product stream then obtained from the separation process according to the invention may in this case be recycled and employed at a suitable point in the integrated system, for example for 1-butene separation, for oligomerization or one or more hydroformylations. This makes it possible to enhance the efficiency of the overall integrated system since even after passing through the last process step in the integrated system up to 20% by weight of butenes may still be present.

Independently of the point in the integrated system where the separation process according to the invention is arranged, the butane-containing product stream may be supplied for example to an adiabatic oligomerization, a hydrogenation of the butenes still present or an n/iso splitting of the butanes where n-butane and isobutane are separated from one another. The n/iso splitting may also be carried out after an adiabatic oligomerization. Another possibility would be inclusion of the butane-containing product stream upstream of the oligomerization in an above-described integrated system composed of MTBE synthesis, 1-butene separation, oligomerization and a hydroformylation.

In a particularly preferred embodiment of the present invention the energy required for n/iso splitting may be effected at least partially by heat integration with the first stage of a two-stage condensation at the top of the desorber. This has the advantage that the energy obtained in the condensation is utilized and not simply released to the environment as in the prior art.

The present invention is hereinbelow elucidated with reference to figures. The figures are for illustration but are not to be understood as limiting.

Fig. 1 shows the basic configuration of the present invention. The liquid C4-hydrocarbon stream is evaporated via a heat exchanger (4) and passed into the absorber (1). The solvent is - where necessary - brought to the desired temperature via a residual cooler (3) and likewise passed into the absorber, wherein the inlet is spatially above the inlet for the C4 hydrocarbon stream, in the present case above the first random-packing bed. Obtained at the top of the absorber (1) is the stream enriched in butanes which is passed to the n/iso splitter (20). A preceding condensation is

possible (not shown). The n/iso splitter is heated using the heat of condensation from the condenser (21) which may also be a two-stage condenser. The laden solvent is collected in the bottom of the absorber (1) as indicated by the chimney tray in the figure. There, at least a portion of the laden solvent is withdrawn and passed to the bottom of the absorber (2) via an absorber evaporator (5). The laden solvent is withdrawn from the bottom of the absorber (1) and using a pump (9) passed via the heat exchanger (6) for preheating of the laden solvent to the desorber (2) where the butenes present in the solvent are separated from the solvent. The stream enriched in butenes is obtained at the top of the desorber. This stream is sent to a condensation in the condenser (21) and passed to a phase separator (18). The aqueous phase is passed to the desorber. The butene-containing product stream is discharged. Only a possible recycle stream is indicated. The solvent at least partially freed of butenes is collected in the bottom of the desorber (2) as indicated by the chimney tray in the figure. There, at least a portion of the laden solvent is withdrawn and passed to the bottom of the desorber via a desorber evaporator (7). The solvent freed of butenes is then withdrawn from the bottom of the desorber (2) and using a pump (8) recycled to the absorber via the heat exchanger (6) for preheating the laden solvent, the absorber evaporator (5), the heat exchanger (4) for evaporating the C4-hydrocarbon stream and the residual cooler (3).

Fig. 2 shows a further preferred embodiment of the present invention where a steam ejector (12) is present at the desorber evaporator (7). This steam ejector is supplied with the regular heating steam, i.e. for example the medium pressure steam from the steam network and the low pressure steam obtained in the condensate container (11), thus forming a mixed steam which is then used as heating steam for the desorber evaporator (7). The mode of operation of a steam ejector is elucidated in the description of Fig. 7. Everything else corresponds to what has been previously specified in connection with Fig. 1.

Fig. 3 shows a preferred embodiment of the present invention where the preheating of the laden solvent passed to the desorber (2) is performed in two stages. The first heat transfer is carried out in the heat exchanger (6) and the second heat transfer is subsequently carried out in the kettle evaporator (10). The mode of operation of a kettle evaporator is elucidated in the description of Fig. 6. Everything else corresponds to what has been previously specified in connection with Fig. 2.

Fig. 4 shows a preferred embodiment of the present invention where a hydrogenation is present in a hydrogenation unit (22). The arrangement of the hydrogenation is a variable, as a result of which the various possibilities have been shown with dashed lines. The hydrogenation may be carried out either before entry into the n/iso splitter or after the n/iso splitter. After the n/iso splitter the hydrogenation may be carried out on the tops stream and/or on the bottoms stream. Everything else corresponds to what has been previously specified in connection with Fig. 1.

Fig. 5 shows a preferred embodiment of the present invention where the heat of the hot condensate which is likewise obtained in the condensate container (11) is additionally used for heating the n/iso splitter (20) via the heat exchanger (23). Everything else corresponds to what has been previously specified in connection with Fig. 2.

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Figure 6 shows the schematic construction of a kettle evaporator (10). The liquid feed is passed into the evaporator via the feed port (101) on the shell side. The liquid feed is partially evaporated in the kettle evaporator and passed into the desorber via the gas port (103) on the shell side. The proportion of the feed that is not evaporated passes over a weir and into the desorber (2) as liquid product via the product port (102) on the shell side. On the tube side the hot bottoms product of the desorber (2) is used as heating medium which is passed through the tubes via the entry port (104) and exits again at the exit port (105).

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Figure 7 shows the schematic construction of a steam ejector (12). Here, the motive steam (121) is the heating steam, in particular the medium pressure steam from the steam network. The suction steam (123) is the low pressure steam from the condensate container. The two are mixed via the control unit (124) and via the exit passed to the desorber evaporator (7) as mixed steam (122). The amount of motive steam and suction steam can be adjusted via the control unit, thus making it possible to influence the pressure and temperature of the mixed steam and thus the possible heating output.

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Examples

Example 1 - embodiment according to figure 1

The butane-butene separation shown in figure 1 was simulated with Aspen Plus v10. A modified NRTL parameter set was used to describe interactions between the components. In the simulation 19 t/h of a hydrocarbon-containing feed were passed into a butane/butene separation (according to figure 1). Said feed contains altogether 45% by weight of butanes (35% by weight n-butane and 10% by weight isobutane), 30% by weight of isobutene and 25% by weight of n-butene.

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Altogether 7 t/h of butane-containing tops product are withdrawn at the absorber. The butane-containing tops product of the absorber consists of 70% by weight of n-butane, 27% by weight of isobutane and 3% by weight of butenes. The solvent laden with the butene-containing product stream are withdrawn at the bottom. The butene-containing product stream contains 14% by weight of n-butane, 47% by weight of isobutene and 39% by weight of n-butene. The established solvent/feed ratio of 13 accordingly allows a butene yield of 98% to be achieved. The large excess of solvent is then also used for the heat integration.

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Only at the desorber (2) is energy introduced from outside the plant, namely via the heating steam for the desorber evaporator (7). 6.9 MW are transferred at the desorber evaporator (7). Otherwise, heat integration with the solvent is performed throughout this example, with the result that no further external energy is required. The hot bottoms product of the desorber (2) is passed through the heat exchanger for preheating (6) of the desorber. 8.4 MW are transferred here. After preheating of the desorber (6) the solvent is passed to the bottom of the absorber (1) where 7.8 MW are transferred via the heat exchanger (5) there. A further 1.8 MW are transferred from the solvent to the feed via the heat exchanger (4) for feed evaporation to evaporate the C4-feed stream. In a residual cooler (3) the solvent is brought to the optimum extraction temperature with cooling water. For this example a temperature of 40°C was assumed. A further 2.5 MW must therefore be removed from the solvent to achieve this temperature. This interconnection allows the external heat input to be reduced and the internal heat to be optimally utilized. In fact if at least one of the heat exchangers (4), (5) and (6) were not to be present, the untransferred energy would have to be removed in the residual cooler (3) and thus destroyed. In addition, the then untransferred energy would have to be supplied externally. This process mode altogether requires only 6.9 MW of external energy.

In addition, the n/iso splitter is heated with the heat of condensation. This allows 3.5 MW from the condensation to be utilized for the separation in the n/iso splitter. If, in addition, a hydrogenation is also present a further 0.7 MW from the hydrogenation may be utilized for the separation in the n/iso splitter.

Claims

1. Process for separating butenes from a C4-hydrocarbon stream which contains at least butenes and the butanes n-butane and isobutane by extractive distillation with a solvent,
 - 5 wherein the process comprises the steps of:
 - a. at least partially evaporating the liquid C4-hydrocarbon stream in a feed evaporator, supplying the gaseous C4-hydrocarbon stream and supplying the liquid solvent above the C4-hydrocarbon stream to an absorber in which the C4-hydrocarbon stream and the solvent are contacted with one another to transfer predominantly butenes from the C4-hydrocarbon stream to the solvent, wherein the thus-laden solvent is collected in a liquid collector of the absorber, passed through an absorber evaporator and then passed into the bottom of the absorber below the liquid collector to outgas predominantly butanes from the laden solvent and wherein the laden solvent is
 - 10 subsequently passed to a desorber as bottoms stream and wherein a stream enriched in butanes relative to the employed C4-hydrocarbon stream is obtained at the top of the absorber;
 - b. supplying the laden solvent to the desorber, the bottom of which is at an elevated temperature and preferably a lower pressure relative to the bottom of the absorber and in which the butenes are separated from the solvent to obtain at the top of the desorber a stream enriched in butenes, wherein a solvent, at least partially freed of butenes is collected in a liquid collector of the desorber, passed through a desorber evaporator and then passed into the bottom of the desorber below the liquid collector
 - 15 to outgas any butenes remaining in the solvent and wherein the solvent is subsequently recycled to the absorber as bottoms stream;
 - c. supplying the stream enriched in butanes to an n/iso splitter in which n-butane and isobutane are separated from one another to obtain a stream enriched in isobutane at the top of the n/iso splitter and a stream enriched in n-butane at the bottom of the n/iso splitter;
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 - characterized in that the heat of the solvent withdrawn as a bottoms stream of the desorber is used for heat integration by employing the heat of the solvent in at least one respective heat exchanger for preheating the laden solvent passed to the desorber, for evaporation in the absorber evaporator and for evaporation of the liquid C4-hydrocarbon stream and in that
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the stream enriched in butenes is withdrawn at the top of the desorber and subjected to a condensation, wherein the heat of condensation is at least partially used for heating the n/iso splitter.

- 5 2. Process according to Claim 1, wherein the employed solvent is NMP.
3. Process according to Claim 1 or 2, wherein the solvent/the NMP contains water and the water content is between 1% and 10% by weight, preferably between 4% and 9% by weight.
- 10 4. Process according to any of the preceding claims, wherein the stream enriched in butenes obtained at the top of the desorber additionally contains water originating from the solvent.
5. Process according to Claim 5, wherein the stream enriched in butenes is withdrawn at the top of the desorber and subjected to a condensation, wherein a water-containing stream and a butene-containing product stream are condensed out and separated from one another.
- 15 6. Process according to Claim 6, wherein the butene-containing product stream obtained from the condensation has a butene content of at least 70% by weight, preferably at least 75% by weight, particularly preferably at least 86% by weight, based on the total composition of the butene-containing product stream.
- 20 7. Process according to any of the preceding claims, wherein the stream enriched in butanes withdrawn at the top of the absorber is subjected to a hydrogenation before entry into the n/iso splitter to convert any remaining butenes into butanes.
- 25 8. Process according to Claim 7, wherein at least a portion of the heat of reaction formed during the hydrogenation is used for heating the n/iso splitter.
9. Process according to any of Claims 1 to 6, wherein the stream enriched in isobutane obtained at the top of the n/iso splitter and/or the stream enriched in n-butane obtained at the bottom of the n/iso splitter are/is subjected to a hydrogenation to convert any remaining butenes into butanes.
- 30 10. Process according to Claim 9, wherein at least a portion of the heat of reaction formed during the hydrogenation or at least a portion of the heat of reaction formed during the two hydrogenations is used for heating the n/iso splitter.
- 35 11. Process according to any of the preceding claims, wherein the preheating of the laden solvent passed to the desorber is performed in two stages, wherein a first heat transfer to the

solvent is effected in a heat exchanger and a second heat transfer to the solvent is effected in a kettle evaporator.

- 5 12. Process according to any of the preceding claims, wherein the heat for evaporation in the desorber evaporator may be introduced in a heat exchanger by heat transfer with a suitable heat transfer medium, in particular heating steam.
- 10 13. Process according to any of the preceding claims, wherein the employed heating steam undergoes at least partial condensation in the heat exchanger, thus generating a hot condensate at a pressure of 10 to 20 bar absolute, preferably 12 to 17 bar absolute, and a temperature of 150°C to 200°C, preferably 160°C to 190°C, which is passed to a condensate container.
- 15 14. Process according to Claim 13, wherein the pressure in the condensate container is lower than in the heating steam side of the heat exchanger, thus causing a portion of the heating condensate to be re-evaporated, as a result of which the combined steam is obtained as low pressure steam.
- 20 15. Process according to any of the preceding claims, wherein the heating steam for the desorber evaporator is provided using a steam ejector supplied with high pressure or medium pressure steam and the low pressure steam obtained in the condensate container.