

## Method for preventing three-phase separation of butenes from C4 hydrocarbon streams

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.

- 5 The process according to the invention features heat integration with which the heat of the solvent is utilized for heating different streams.

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  
10 relative volatility of the alkanes. 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 said butenes are obtained in enriched form as tops product. The solvent freed of butenes is then recycled to the extractive distillation.

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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 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  
20 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 sidestreams of the absorber and for preheating the feed stream.

In the separation of butene-butane mixtures both energy recovery and prevention of a three-phase  
25 system in the absorber are important features. A butane-enriched stream passes overhead in the absorber. To prevent portions of the solvent also passing overhead, the solvent must be backwashed. To this end, a certain amount of reflux which may contain a high proportion of n-butane is passed into a backwashing zone in the upper portion of the absorber. However, high n-butane contents render the occurrence of a second liquid phase in the absorber more likely which  
30 not only impedes the separation task of the absorber but can also lead to foaming problems (Ross-type foaming). It must also be considered that, depending on the integration of the butene-butane separation in an integrated chemical system, a higher n-butane content may be present in the feed stream to the butane-butene separation. However, high n-butane contents in the feed stream shift the equilibrium position of the n-butane in the solvent which then in turn increases the likelihood of  
35 a second liquid phase occurring.

It is accordingly an object of the present invention to provide a process where the occurrence of a second liquid phase and thus the likelihood of foam formation can be reduced. It is a further object

of the present invention to achieve an increase in the separation efficiency of the butane-butene separation and optimal energy utilization.

5 This object is achievable by the embodiment of the process proposed in claim 1. Preferred 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 butanes by extractive distillation with a solvent, wherein the process comprises the steps of:

- 10 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 to a liquid distributor above the C4-hydrocarbon stream to an absorber which comprises more than two random-packing beds and 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, wherein the laden solvent 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 at least partially condensed and a portion of the condensate is returned to the top of the absorber as reflux;  
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- b. supplying the laden solvent, preferably NMP, to the desorber, which is at an elevated temperature and preferably a lower pressure relative to 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 and to obtain at the bottom of the desorber the solvent, preferably NMP, at least partially  
25 freed of butenes, wherein the 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, preferably NMP, is subsequently recycled to the absorber as bottoms stream;

30 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

35 at least a portion of a liquid phase is withdrawn at the liquid distributor above the first or second random-packing bed and separated into a heavy liquid phase and a light liquid phase in a decanter, of which the heavy liquid phase is returned to the absorber and/or the reflux in the absorber is

withdrawn from the absorber via a runoff cup, mixed with the liquid solvent in a static mixer and then, with the liquid solvent, supplied to the liquid distributor above the first random-packing bed.

- One advantage of the present process is the relatively simple apparatus setup by means of which the occurrence of a second liquid phase and/or the risk of foam formation can be prevented. This has the result of improving the separation efficiency of the process and achieving energetic optimization of the process. The process according to the invention is additionally characterized by efficient energy recovery by heat integration with the hot solvent.
- 10 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
- 15 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.
- 20 The present process relates to the separation of butenes from butene-containing C4-hydrocarbon streams. These streams usually contain not only the butenes but also alkanes (n-butane, isobutane). 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. The process according to the invention may therefore employ any C4-hydrocarbon streams which contain at least butenes
- 25 and butanes provided that the amounts in which the butenes and/or butanes are present allow economic performance of the process. In a preferred 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
- 30 or C5-hydrocarbons, in small amounts.

- In the extraction process according to the invention a liquid solvent is employed 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
- 35 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-packing beds 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. Arranged above each of the random-packing beds is a liquid distributor by means of which the liquid is distributed. 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 a liquid distributor into the absorber spatially above the inlet for the C4-hydrocarbon stream. In a preferred embodiment the solvent is supplied to a liquid distributor above the first or second random-packing bed and the C4-hydrocarbon stream is added to the absorber in one or more random-packing beds below the first or second 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. In a further 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.

In step a the C4-hydrocarbon stream and the solvent are brought into contact with one another in particular in countercurrent. The temperature at the bottom of the absorber is preferably between 40°C and 70°C, particularly preferably between 45°C and 65°C. The head pressure in the absorber may be between 3 and 7 bar absolute, preferably between 4 and 6.5 bar absolute.

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.

5 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 on 120°C.

10 In particular a stream enriched in butanes relative to the employed C4-hydrocarbon stream is then obtained at the top of the absorber. This stream is at least partially, preferably completely, condensed in a suitable apparatus, for example a condenser, to obtain a condensate. At least a portion of the condensate is then passed to the absorber as reflux. The reflux is preferably supplied above the backwashing zone of the absorber, from where the reflux passes into the liquid distributor above the first random-packing bed (below the backwashing zone). The liquid solvent  
15 may be continuously supplied to the liquid distributor above the first random-packing bed. At this point or else in the random-packing beds arranged therebelow, the butane proportions in the reflux may result in the occurrence of a second liquid phase which then leads to undesired foam formation.

20 The present invention begins at this point. The liquid phase which comprises the liquid solvent and the reflux to the absorber/the liquid running back from the backwashing zone may be withdrawn at the liquid distributor above the first random-packing bed and passed to a decanter where a separation into a heavy liquid phase comprising primarily NMP and a light liquid phase comprising primarily butanes from the reflux is carried out. The heavy liquid phase is then passed back to the  
25 absorber, in particular the liquid distributor in the absorber. The light liquid phase may be discharged from the process, passed to the desorber or subjected to a further separation. This optional single- or multi-stage separation is carried out before entry into the desorber. One option is that the light liquid phase is heated and passed to a flash vessel where a liquid phase comprising the liquid solvent and a gaseous phase comprising butanes are obtained. Only the liquid phase is  
30 then passed to the desorber. The gaseous phase is withdrawn from the flash vessel, condensed, and may then be discharged from the process, for example also together with the butane-containing product stream.

Another option is that the liquid phase is withdrawn at the liquid distributor above the second  
35 random-packing bed and passed to a decanter. The first random-packing bed is "sacrificed" here, i.e. the occurrence of a third phase is permitted in the first or above the first random-packing bed. Only afterwards is this prevented by the appropriate measure, i.e. passage through the decanter. The liquid phase withdrawn above the second random-packing bed comprises the mixture originating from the first random-packing bed.

The formation of the second liquid phase and the associated foam formation may also be reduced or prevented in another manner in accordance with the invention. According to the invention, the reflux to the absorber may be withdrawn from the absorber, preferably completely, via a runoff cup.

5 Here, the reflux does not come into contact with the liquid solvent in the liquid distributor. Instead the reflux is mixed with the liquid solvent in a static mixer and then passed, with the liquid solvent, to the absorber, in particular to the liquid distributor above the first random-packing bed of the absorber. The use of such a static mixer leads to a low propensity for foam formation inter alia on account of the low concentration differences between the reflux and the NMP in the absorber. A

10 further advantage is that any foam formation then occurs outside the absorber where it can be better handled. The static mixer may be arranged both upstream and downstream of the residual cooler for the recycled NMP.

The two methods described here, i.e. the preceding mixing with the solvent and passage through a

15 decanter, may also be combined with one another.

The 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 condensation to condense out a water-

20 containing stream, which also contains butanes, 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. In the context of the present invention the reflux to the absorber is thus to be

25 understood as meaning a portion of the butane-containing product stream.

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

30 from the condensation may further contain residual butenes, wherein the streams contain typically 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

35 necessary for the butane-containing product stream to be subjected to a drying following the 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.

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 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 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 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 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 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 water 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 to the absorber and the hot condensate which is obtained in the desorber evaporator. 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. 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 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  
 5 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  
 10 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.

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 200°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 pressure in the condensate container is  
 20 preferably lower than in the heat exchanger. 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 case the low pressure steam preferably has a pressure of more than 0 bar and less than 10 bar  
 25 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  
 30 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  
 35 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.

5 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  
10 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  
15 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.

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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  
25 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  
30 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  
35 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 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 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 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.

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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.

15 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.

20 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 to a liquid distributor (not shown). From there the liquid phase is withdrawn and passed to the decanter (31). The light liquid phase is returned to the desorber (here together with the laden solvent) and the heavy liquid phase is returned to the absorber (1) via a pump (32). Obtained at the top of the absorber (1) is the stream enriched in butanes which is withdrawn. A possible condensation is not shown here - only the reflux is shown. 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 (1) 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 may be subjected to a single- or multi-stage condensation which is not shown in the figure. 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 (2) 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 an embodiment which is largely identical to the embodiment shown in Fig 1. The difference is that the liquid phase is withdrawn from the liquid distributor (not shown) above the second random-packing bed and passed to the decanter (31).

Fig. 3 shows a preferred embodiment of the present invention where the light liquid phase is initially heated in a suitable heating apparatus (33) and subsequently supplied to a flash vessel (34). The gaseous phase is discharged but the different options are not shown. The liquid phase is passed from the flash vessel (34) to the desorber (2), here together with the laden solvent.

Fig. 4 shows the further embodiment according to the invention. The reflux is withdrawn via a runoff cup and via a pump (35) passed to a static mixer (36) arranged downstream of the residual cooler (3) where the reflux is mixed with the liquid solvent and then, together with the liquid solvent, passed to the absorber (1). Alternatively, the static mixer (36) may already be arranged upstream of the residual cooler (3), i.e. directly downstream of the heat exchanger (4).

## Claims

1. Process for separating butenes from a C4-hydrocarbon stream which contains at least butenes and butanes 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 to a liquid distributor above the C4-hydrocarbon stream to an absorber which comprises more than two random-packing beds and 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, wherein the laden solvent 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 and at least partially condensed and a portion of the condensate is returned to the top of the absorber as reflux;
  - b. supplying the supplying the laden solvent, preferably NMP, to the desorber, which is at an elevated temperature and preferably a lower pressure relative to 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 and to obtain at the bottom of the desorber the solvent at least partially freed of butenes, preferably NMP, wherein the solvent at least partially freed of butenes, preferably NMP, 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, preferably NMP, is subsequently recycled to the absorber as bottoms stream;

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

at least a portion of a liquid phase is withdrawn at the liquid distributor above the first or second random-packing bed and separated into a heavy liquid phase and a light

liquid phase in a decanter, of which the heavy liquid phase is returned to the absorber and/or the reflux in the absorber is withdrawn from the absorber via a runoff cup, mixed with the liquid solvent in a static mixer and then, with the liquid solvent, supplied to the liquid distributor above the first random-packing bed.

- 5 2. Process according to Claim 1 or 2, 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.
- 15 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 water and butene-containing product stream are condensed out and separated from one another and the water is recycled to the absorber.
- 20 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.
- 25 7. Process according to any of the preceding claims, wherein the heavy liquid phase is passed from the decanter to the absorber using a pump.
8. Process according to any of the preceding claims, wherein the light liquid phase obtained at the decanter is passed to the desorber.
- 30 9. Process according to Claim 8, wherein the light liquid phase is first heated and passed to a flash vessel where a liquid phase and a gas phase are obtained, of which the liquid phase is passed to the desorber.
- 35 10. Process according to Claim 9, wherein the gaseous phase from the flash vessel is condensed and discharged from the process.
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 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 medium pressure steam and the low pressure steam obtained in the condensate container.