(19) DANMARK

(10) **DK/EP 3683200 T3**

(12) Oversættelse af europæisk patentskrift

Patent- og Varemærkestyrelsen

(51) Int.Cl.: ***C 07 C 1/20 (2006.01)*** ***C 07 C 4/06 (2006.01)*** ***C 07 C 7/00 (2006.01)*** ***C 07 C 7/09 (2006.01)*** ***C 07 C 11/02 (2006.01)*** ***C 07 C 11/06 (2006.01)*** ***C 10 G 3/00 (2006.01)***

(45) Oversættelsen bekendtgjort den: **2025-02-17**

(80) Dato for Den Europæiske Patentmyndigheds bekendtgørelse om meddelelse af patentet: **2024-11-27**

(86) Europæisk ansøgning nr.: **19020033.7**

(86) Europæisk indleveringsdag: **2019-01-18**

(87) Den europæiske ansøgnings publiceringsdag: **2020-07-22**

(84) Designerede stater: **AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**

(73) Patenthaver: **L'AIR LIQUIDE, SOCIÉTÉ ANONYME POUR L'ÉTUDE ET L'EXPLOITATION DES PROCÉDÉS GEORGES CLAUDE, 75 Quai d'Orsay, 75007 Paris, Frankrig**

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(54) Benævnelse: **FREMGANGSMÅDE TIL FREMSTILLING AF OLEFINER AF METHANOL OG/ELLER DIMETHYLETHER**

(56) Fremdragne publikationer:
WO-A1-2012/016786
DE-A1- 102013 101 575
DE-A1- 102014 118 967

Process for producing olefins from methanol and/or dimethyl ether

Field of the invention

The invention relates to a process for preparing olefins from oxygenates, comprising the following steps:
(i) heterogeneously catalysed conversion of the oxygenates in an oxygenate-to-olefin reactor under oxygenate conversion conditions to give a product stream containing water, hydrocarbons and at least one oxygenate,
(ii) quenching the product stream in at least one quench stage to obtain a gaseous stream G comprising hydrocarbons and olefins, a liquid aqueous stream W consisting predominantly of water and oxygenates, and a liquid stream O consisting predominantly of hydrocarbons and comprising olefins,
(iii) separating stream G and/or stream O into a C4- stream consisting predominantly of hydrocarbons having four or fewer carbon atoms and comprising olefins, and a C4+ stream consisting predominantly of hydrocarbons having four or more carbon atoms and comprising olefins.

The invention also further encompasses the use of a corresponding plant in the process according to the invention.

Prior art

Short-chain olefins, for example propylene (propene), are among the most important commodities in the chemical industry. The reason for this is that, proceeding from these unsaturated compounds with a short chain length, it is possible to form molecules having a long-chain carbon skeleton and additional functionalizations.

The main source of short-chain olefins in the past was steamcracking, i.e. thermal cracking in mineral oil processing. In the past few years, however, further processes for preparing short-chain olefins have been developed. One reason for this is

rising demand that can no longer be covered by the available sources; secondly, the increasing scarcity of fossil raw materials is requiring the use of different starting materials.

The MTP (methanol-to-propylene) or else MTO (methanol-to-olefin) processes for preparing propylene and other short-chain olefins proceed from methanol as starting material. Reference is also made in this connection in generalized form to oxygenate-to-olefin (OTO) processes since oxygen-containing organic components such as methanol or dimethyl ether (DME) are also referred to as oxygenates. In these heterogeneously catalysed processes, there is accordingly, for example, at first partial formation of the dimethyl ether intermediate from methanol, and subsequently of a mixture of ethylene and propylene and hydrocarbons having a higher molar mass, including olefins, from a mixture of methanol and dimethyl ether. Moreover, water is present in the product stream, which firstly originates from the process steam which is optionally supplied to the MTO reactor for modulation of reaction and secondly from the water of reaction produced in the MTP reactor.

The subsequent purification is intended firstly to remove unwanted by-products and unconverted reactants, and to prepare the individual hydrocarbon fractions with maximum purity. Typically, for this purpose, a quench system is employed in the first step. Quenching is understood to mean an abrupt or shock cooling which is usually brought about by direct heat exchange with a fluid quench medium. If a liquid such as water or methanol is used for the purpose, there is additionally a certain cleaning effect in relation to the remaining gas phase.

One example of the purification that follows an OTO reaction can be found in DE 10 2014 112 792 A1, which describes how, in a first step, a heterogeneously catalysed conversion of at least one oxygenate to a product stream comprising C2 olefins, C3 olefins, C4 olefins, C5/6 hydrocarbon compounds and C7+ hydrocarbon compounds and, in a second step, a removal of a

propylene stream consisting to an extent of at least 95% by weight of C3 olefins is generated.

The further purification steps that are described in DE 10 2014 112 792 A1 are in accordance with the concept customary in the art. The quenching can already result in a coarse separation of the fractions depending on their chain length of the resultant olefins owing to the partial condensation, such that a liquid C4+ fraction can be removed from the quench. The C4- fraction removed in gaseous form is subsequently fed into a compression stage. The C4- fraction coming from the compression is then sent to a separation apparatus in which C3- hydrocarbons are separated from the C4+ hydrocarbons. In subsequent purifying steps, the C3 fraction is separated from the C2- fraction in a further separating unit, which has to be effected under pressure owing to the low boiling points of the two fractions. Overall, the purification of the product stream is complicated since the aim is a high purity of the products. This is true of MTP plants having typical production capacities of about 470 kta of propylene, but becomes even more crucial if the plant capacity is lower (100 kta or 200 kta of propylene). This means that small plants are currently uneconomic.

For optimization of the propylene yield, it is possible to at least partly return olefin-containing streams to the reaction section from the purification region. The production of very specific recycle streams such as C2, C4 and C5/C6 olefins entails multiple separation steps according to the prior art. There is no recycling of the C7+ olefins to date. By contrast, DE 10 2014 112 792 A1 teaches that at least 10% by weight of the propylene stream is additionally also returned to the heterogeneously catalysed reaction from the purification. However, the recycling of propylene is problematic since propylene is specifically the desired product of value and hence the overall yield of the process is possibly lowered.

However, the optimized adjustment of the various recycle streams is also very complex irrespective of the question of propylene

recycling since the composition of the individual streams and the process conditions in combination with the catalyst performance and distribution in the reactor have to be taken into account. Moreover, every further recycle conduit and the associated control demands lead to higher capital costs.

Patent publication DE 102013101575 A1 describes a process for preparing olefins from oxygenates, comprising the following steps:
(i) heterogeneously catalysed conversion of at least one oxygenate to an overall stream containing liquid and gaseous organic compounds and water, and
(ii) separation of the overall stream in a first separation apparatus into a fraction containing the gaseous organic compounds in the overall stream to an extent of at least 90% by volume, a fraction containing the liquid organic compounds in the overall stream to an extent of at least 90% by weight, and a fraction containing the water in the overall stream to an extent of at least 90% by weight.

International patent publication WO 2012/016786 A1 discloses a process for converting an alcohol mixture (A) containing about 20% by weight to 100% isobutanol in order to prepare essentially propylene, comprising: a) introducing a stream into a reactor (A), which the mixture (A), mixed with a stream (D I), which olefins having 4 carbon atoms or more (C4+ olefins), optionally water, optionally inert, b) contacting of the stream with a catalyst (AI) at a temperature above 500°C in reactor (A) under conditions that are effective for dehydration of at least a portion of the isobutanol and possibly other alcohols and for cracking, c) recovering an outflow from reactor (A), comprising: ethylene, propylene, water, any unconverted alcohols from mixture (A), various hydrocarbons, and the optional inert component from step a), d) fractionating the outflow from step c) in order to produce at least one ethylene stream, a propylene stream stream, a fraction consisting essentially of hydrocarbons having 4 or more carbon atoms, water and the optional inert component from step a), wherein, optionally, ethylene is wholly

or partly recycled at the inlet of reactor (A), where the fraction consisting essentially of hydrocarbons having 4 carbon atoms or more is optionally recycled at the inlet of reactor (A).

A disadvantage is that the two latter patent publications do not offer specific and convincing solutions for improved and value-increasing utilization of a C4+ stream obtained in the process.

Description of the invention

The problem addressed by the present invention is therefore that of providing a novel concept for the recycle streams, by means of which considerable capital cost savings can be achieved without impairing the propylene yield. This problem is solved by a process having the features of Claim 1, and by a use having the features of Claim 10. Further, especially advantageous, configurations can be found in the respective dependent claims.

Process according to the invention:

Process for preparing olefins from oxygenates, comprising the following steps:

(i) heterogeneously catalysed conversion of the oxygenates in an oxygenate-to-olefin reactor under oxygenate conversion conditions to give a product stream containing water, hydrocarbons and at least one oxygenate,

(ii) quenching the product stream in at least one quench stage to obtain a gaseous stream G comprising hydrocarbons and olefins, a liquid aqueous stream W consisting predominantly of water and oxygenates, and a liquid stream O consisting predominantly of hydrocarbons and comprising olefins,

(iii) separating stream G and/or stream O into a C4- stream consisting predominantly of hydrocarbons having four or fewer carbon atoms and comprising olefins, and a C4+ stream consisting predominantly of hydrocarbons having four or more carbon atoms and comprising olefins,

characterized in that the C4+ stream obtained in step (iii) is returned directly to step (i) and/or guided into a gasoline fraction.

The introducing of the C4+ stream obtained in step (iii) into a gasoline fraction can preferably be effected by introducing into a gasoline stabilizer column, which serves to separate volatile constituents from the gasoline fraction by distillation or rectification in order, for example, to improve the storability of the gasoline fraction.

The oxygenate conversion conditions required for the conversion of oxygenates to olefin products are known to the person skilled in the art from the prior art, for example the publications discussed by way of introduction. These are those physicochemical conditions under which a measurable conversion, preferably one of industrial relevance, of oxygenates to olefins is achieved. Necessary adjustments to these conditions to the respective operational requirements will be made on the basis of routine experiments. Any specific reaction conditions disclosed may serve here as a guide, but they should not be regarded as limiting in relation to the scope of the invention.

Thermal separation processes for the purposes of the invention are all separation processes based on the establishment of a thermodynamic phase equilibrium. Preference is given to distillation or rectification. In principle, however, the use of other thermal separation processes is also conceivable, for example of extraction or extractive distillation.

A purification step in connection with the present invention should in principle be considered to mean all process steps that make use of a thermal separation process; preference is given to using distillation or rectification.

Fluid connection between two regions or plant components shall be understood to mean any kind of connection that enables flow of a fluid, for example a reaction product or a hydrocarbon

fraction, from one to the other of the two regions, regardless of any intermediately connected regions, components or required conveying means.

A means is understood to mean something that enables or is helpful in the achievement of a goal. In particular, means of performing a particular process step are understood to mean all those physical articles that would be considered by a person skilled in the art in order to be able to perform this process step. For example, the person skilled in the art will consider means of introducing or discharging a stream of matter to be all transporting and conveying apparatuses, i.e., for example pipelines, pumps, compressors, valves, which seem necessary or sensible for performance of this process step on the basis of his knowledge of the art.

Oxygenates are understood in principle to mean all oxygen-containing hydrocarbon compounds that can be converted under oxygenate conversion conditions to olefins, especially to short-chain olefins such as propylene, and further hydrocarbon products.

Short-chain olefins in the context of the present invention are especially understood to mean the olefins that are in gaseous form under ambient conditions, for example ethylene, propylene and the isomeric butenes 1-butene, cis-2-butene, trans-2-butene, isobutene.

Higher hydrocarbons in the context of the present invention are especially understood to mean those hydrocarbons that are in liquid form under ambient conditions.

Hydrocarbon fractions are identified using the following nomenclature, "Cn fraction" refers to a hydrocarbon fraction containing predominantly hydrocarbons of carbon chain length n, i.e. having n carbon atoms. "Cn- fraction" refers to a hydrocarbon fraction containing predominantly hydrocarbons of carbon chain length n and having shorter carbon chain lengths.

"Cn+ fraction" refers to a hydrocarbon fraction containing predominantly hydrocarbons of carbon chain length n and having longer carbon chain lengths. Owing to the physical separation processes used, for example distillation, the separation in terms of carbon chain length should not be considered to mean that hydrocarbons having another chain length are rigorously excluded. For instance, a Cn- fraction, according to the process conditions of the separation process, will always contain small amounts of hydrocarbons having a carbon number greater than n.

The solid, liquid and gaseous/vaporous states of matter mentioned should always be considered in relation to the local physical conditions that exist in the respective process step or in the respective plant component, unless stated otherwise. In the context of the present application, the gaseous and vaporous states of matter should be considered to be synonymous.

In connection with the present invention, separating of a stream of matter should be considered to mean division of the stream into at least two substreams. Unless stated otherwise, it can be assumed that the physical composition of the substreams corresponds to that of the starting stream, except in the cases in which it is immediately apparent to the person skilled in the art that there must inevitably be a change in the physical composition of the substreams owing to the separation conditions.

A gasoline fraction is understood to mean a substance mixture which is in liquid form under ambient conditions and consists predominantly, preferably substantially completely, of higher hydrocarbons, and may be suitable for use as a gasoline fuel.

The predominant portion of a fraction, of a stream of matter etc. is understood to mean a proportion quantitatively greater that all other proportions each considered alone. Especially in the case of binary mixtures or in the case of separation of a fraction into two parts, this is understood to mean a proportion

of more than 50% by weight, unless stated otherwise in the specific case.

The statement that a stream of matter consists predominantly of one component or group of components shall be understood to mean that the molar proportion (mole fraction) or proportion by mass (mass fraction) of this component or group of components is quantitatively greater than all other proportions of other components or groups of components each considered alone in the stream of matter. Especially in the case of binary mixtures, this is understood to mean a proportion of more than 50%. Unless stated otherwise in the specific case, the basis here is the proportion by mass (mass fraction).

According to the invention, in a first process step (i), a heterogeneously catalysed conversion of the oxygenates is effected to give a product stream containing water, hydrocarbons and at least one oxygenate. Subsequently, in a second step (ii), this product stream is quenched in at least one quench stage to obtain a gaseous stream G comprising hydrocarbons and olefins, a liquid aqueous stream W consisting predominantly of water and oxygenates, and a liquid stream O consisting predominantly of hydrocarbons. Stream G and stream O are then separated collectively or separately in a third step (iii) into a C4- stream consisting predominantly of hydrocarbons having four or fewer carbon atoms and a C4+ stream consisting predominantly of hydrocarbons having four or more carbon atoms. It is also possible that solely stream G or stream O is subjected to this separation.

It is crucial that the C4+ stream obtained in the third step (iii) is ultimately returned as recycle stream directly to step (i) and/or guided into a gasoline fraction.

Process step (iii) can be employed for any kind of oxygenate-to-olefin plant (OTO plant) and is independent of the design and conception of the upstream reaction section, the heat of reaction recovery section, the cooling and water separation

section (quench system) and the compression section. What is instead crucial is that the direct recycling of the C4+ stream obtained as debutanizer bottom product, especially of the predominant portion, i.e. preferably more than 50% by weight, more preferably more than 75% by weight, of the debutanizer bottom product, and/or the direct branching-off into the gasoline fraction can significantly improve the removal of heavy hydrocarbons. By comparison, in the conventional process, this stream is processed a further column (dehexanizer) to produce a C5/C6 recycle stream in the top of the column and a C5+ gasoline product from the bottom. A portion of the top product is processed further in a gasoline stabilizer column which produces a bottom product stream which is used to adjust the boiling range of the gasoline.

In this connection, studies have shown that the recycling of heavy hydrocarbons containing C7+ hydrocarbons does not have an adverse effect on the propylene yield provided that a small amount of heavy hydrocarbons is removed from the circulating hydrocarbon stream as a purge stream, which is preferably effected continuously or periodically. Instead, the recycling of the C7+ hydrocarbons into the reactor still leads to a rise in the propylene yield.

Preferably, in the inventive process, the majority of the C4+ stream is directly evaporated and returned to the OTO reactor. Only a liquid fraction that remained in the evaporation and a relatively small proportion of the debutanizer bottom stream stream amounting to preferably less than 25% by weight, more preferably less than 10% by weight, of the overall stream as the sum total of the recycle stream and the gasoline fraction hydrocarbon stream is sent to a gasoline stabilizer column. Thus, there is no need for a column to separate off the C6+ fraction with the appropriate heat exchangers and pumps. The evaporation of the recycle stream can favourably be configured as a partial evaporation with a blowdown, which is transferred to the gasoline stabilizer column or forms a constituent of the latter. It is optionally possible to use a stripper that

separates the evaporated fraction from the liquid fraction in order to prevent the enrichment of unwanted heavy hydrocarbons.

A further advantage of the process according to the invention is that the unwanted heavy hydrocarbons that are obtained in the quench step by condensation are not conducted through further columns but conducted directly to the gasoline fraction. This reduces the load on columns present (the debutanizer in particular) and hence the energy expenditure, the column size required and the tendency to soiling on the trays. It may even be the case that columns are dispensed with.

One aspect of the invention is thus to simplify the purifying section according to the prior art without suffering propylene losses that are caused by the generation of a heavier recycle stream according to the prior art. Surprisingly, the composition of the recycle streams obtained by the process according to the invention is helpful to the process and allows an increase in olefin production in the OTO reactor. The direct recycling of the majority of the debutanizer bottom product and/or the direct feeding thereof into the gasoline fraction therefore achieves savings in the capital costs and operating costs without impairing the propylene yield.

Since the hydrocarbon recycling plays a major role in respect of the propylene yield of the OTO plant, both the total flow rate and the composition are carefully controlled by open-loop or closed-loop control. For example, the MTP process can be designed for any ratio of hydrocarbon recycling to reactor feeding of methanol of 0.75 to 1.5. The division of the various streams can be adjusted over the lifetime of the catalyst in order to maximize the streams that are most advantageous in respect of the propylene yield.

Further preferred configurations of the invention

It has also been found to be favourable when a further liquid stream S consisting predominantly of hydrocarbons having four

or more carbon atoms is obtained during the quench (step (ii)), such that very heavy hydrocarbon fractions can be removed at this early stage.

It is particularly favourable when stream S is combined with the C4+ stream and/or at least a portion of stream S is guided into the gasoline fraction. This means that stream S likewise becomes part of the gasoline product of value.

In respect of the quench system, this means that the cooled OTO reactor wastewater is guided into the quench system, where the reactor wastewater is cooled further and the majority of the water is condensed and separated from the hydrocarbon product. The uncondensed hydrocarbons leave the pre-quench and quench columns provided with preference as overhead vapour. Depending on the configuration of the quench system and the catalyst operation, a small stream of liquid hydrocarbons may be produced in the quench system. These are passed onward to the downstream purification section. The majority of the quench water is circulated in the quench water circuit.

The resultant water can be utilized for thermal integration at various points in the process. After the final cooling, the water is then returned to the quench. A portion of the quench water preferably leaves this circuit and is guided into the methanol recovery column for purification and recovery of unconverted oxygenates. A portion of the water purified in the methanol recovery column can also be used as feed for the process steam generation, which gives rise to a process steam cycle. The process steam is favourably produced in such a way that no catalyst poisons, for example sodium, remain in the stream sent to the MTP reactor.

The excess of cleaned water (water of reaction) leaves the system for downstream internal use or further processing and external use. Possible external uses of the water of reaction include: cooling water replenishment, recycling for synthesis gas

production, further purification for use as replacement boiler feed water or irrigation water.

A by-product of the MTP reaction is organic acids. If required, a pH-regulating chemical can be added to the quench water in order to control the pH and thus minimize the tendency to corrosion. The methanol recovery column receives additional streams from the purification containing mainly oxygenates and water. These include streams from the extraction that are used for removal of oxygenates from various product streams.

A supplementary or alternative configuration of the invention envisages that stream G and/or stream O is sent to a preferably multistage compression step and a liquid stream K consisting predominantly of hydrocarbons having 4 or more carbon atoms is obtained from this compression step, preferably after the first stage. In this way, it is possible to reduce the load on the downstream stages for purification of long-chain hydrocarbons, such that less soiling per unit time collects in these units that are preferably configured as rectification columns.

For this removal of a stream K, it is particularly advantageous when stream K is mixed into stream S and/or the C4+ stream and/or at least a portion of stream K is guided directly into the gasoline fraction. Optional stabilization of the gasoline fraction by means of an appropriate stabilizer column ensures here that the gasoline product can be stored in an atmospheric tank, which means that both stream S and stream K can be used in a yield-enhancing manner.

It is additionally advantageous when a further liquid phase L is obtained in the compression step and introduced into step (iii). This liquid phase, particularly in the case of removal of a stream S in the quench and K in the compression, already has comparatively high purity based on long-chain hydrocarbons having at least five carbon atoms.

A particularly favourable configuration of the compression is one in which the hydrocarbon vapour product from the quench system is compressed in multiple, preferably in at least three, most preferably in four, stages. After each compression stage, the compressed gas is cooled down and partly condensed. The compressed vaporous and liquid hydrocarbons are sent to the purification plant. The liquid water is returned to the quench system. The separation of water and liquid hydrocarbons can be effected either individually after each compression stage, in which case condensed water streams are produced between the compressor stages, and/or in a common step after the streams from all stages have been mixed.

In order to avoid deposits in the compressor, it may additionally be advantageous to wash the compressor continuously or intermittently. For this purpose, it is possible to use an internal stream having a suitable composition, for example the gasoline fraction obtained. Additional measures may be taken to remove oxygen compounds from the hydrocarbon streams. These include scrubbing of the vapour with water and/or extraction in the liquid with water. The oxygen-rich water is returned to the methanol recovery for separation.

In a further configuration of the invention, the C4+ stream is at least partly evaporated and the resultant vaporous stream D is returned to step (i). As a result, less energy has to be supplied in the separation of the C4- fraction from the C4+ stream. This further reduces the load on the subsequent separation (debutanizer).

If a partial evaporation is envisaged downstream of the compression, this also leaves a liquid stream F which is preferably mixed at least partly with stream S and/or stream K and/or the C4+ stream and/or at least a portion is guided directly into the gasoline fraction. Thus, the comparatively long-chain hydrocarbons are utilized in a value-conserving manner here too.

According to the cooling power downstream of the compressor and the product demands in respect of the C4-containing product, the vapour stream from the compression can also be fed directly to step (iii) for further separation of the C4 fraction.

Preferably, step (iii) is followed by at least one further purification step in which the C4- stream is separated into a C3 stream consisting predominantly of hydrocarbons having three carbon atoms and comprising propylene and into a C2- stream consisting predominantly of hydrocarbons having not more than two carbon atoms and comprising ethene.

It is possible here for the vaporous top product and optionally the hydrocarbon vapour from the compressor to be sent to a downstream purification stage (depropanizer). C3- hydrocarbons are separated therein from C4+ hydrocarbons. In addition, residual amounts of DME and other oxygenates are removed from the hydrocarbons by addition of pure methanol (e.g. grade AA methanol) as washing agent. Detailed options for the extractive distillation are disclosed in DE 10 2004 052 658.

The bottom product from the depropanizer, the C4 stream, is cooled and guided into a C4- extraction section. Absorber methanol and absorbed DME are extracted here from the cooled C4 stream. This is preferably effected in multiple steps, with provision firstly of a mixer-settler combination in which the methanol and a portion of the DME are removed. The water-oxygenate mixture is then sent to the methanol recovery section for separation.

The C4 stream is evaporated and returned to the OTO reactor as return stream. If required, a further removal of oxygenates from the C4 stream or a substream thereof with a C4 extractor may be provided. The water-oxygenate mixture is likewise sent to the methanol recovery section for separation. The top product from the extractor containing the C4 hydrocarbon fraction that has been freed of methanol and DME is combined with the propane from other separation steps and is a product of value (LPG product).

Alternatively, further C4 and C3 product streams may be obtained. An alternative for oxygenate removal is likewise taught in DE 10 2004 052 658.

The top product from the depropanizer, the C3- stream, is free of or has a very low level of DME or other oxygenate components. The vapour phase from the depropanizer is to optionally dried and then sent to a downstream column (deethanizer).

The depropanizer, but in any case after step (iii), is typically followed downstream by a further purification step in which a C3 stream consisting predominantly, preferably to an extent of at least 70% by weight, most preferably to an extent of at least 90% by weight, of hydrocarbons having three carbon atoms and a C2- stream consisting predominantly, preferably to an extent of at least 70% by weight, most preferably to an extent of at least 90% by weight, of hydrocarbons having not more than two carbon atoms are separated from one another. Preferably, the C3 hydrocarbon fraction from the depropanizer is cooled here and partly condensed before being sent to this separation stage (deethanizer). In this column, the C3 hydrocarbon fraction is divided into a C2- stream which is obtained overhead and a C3 stream which is withdrawn at the bottom.

The pressure in the recycle system of the deethanizer must be adjusted to the available cooling medium in the liquefier and compressed in the upstream compressor. One option is to operate the debutanizer, depropanizer and deethanizer at about 20 bara (bar, absolute) and to use a supply medium significantly colder than propylene coolant (< -40°C) in the deethanizer condenser. A second option is to operate the depropanizer and deethanizer or the deethanizer only at a pressure that permits the use of propylene coolant in the deethanizer condenser. A third option is to operate all columns at about 20 bara and to use just one compressor for the top stream from the deethanizer in order to use propylene coolant as operating medium in the deethanizer condenser.

A small amount of carbon dioxide (CO2) is present as an unwanted secondary component in the top product from the deethanizer. In order to eliminate these CO2 components, the stream drawn off at the top of the column is guided into a CO2 scrubber. Removal of CO2 from the C2 stream can be accomplished using two or more alkali circuits. Normally, a final scrubbing zone with demineralized water prevents the breakthrough of alkali. The gas exiting from the CO2 scrubber can then be utilized as C2 recycle stream.

The bottom product from the deethanizer is sent to a C3 splitter in order to separate the propylene product from the propane by-product in the desired purity. Depending on the exact specifications for use of the monomeric propylene, for example for preparation of polypropylene, additional purification steps will follow.

Ethylene can additionally be removed at various positions, for example as uncondensable liquid from the deethanizer condenser. When CO_2 has to be removed from this stream, the light components can be collected by partial condensation of the recycle stream and purging of the uncondensable substances. The ethylene is purified by a removal of water and CO_2 for avoidance of ice and hydrate formation. Subsequently, the stream is sent to a demethanizer. The top product from the demethanizer can be used as fuel gas, while the bottom product from the demethanizer is passed onward into a C_2 splitter in which ethylene is separated off in a quality suitable for polymer production. The ethane separated off here can likewise be used as fuel gas.

In order to prevent polymerization, an inhibitor can be added to the condensers and reboilers of at least one separation column, especially the debutanizer, dehexanizer and any gasoline stabilizer column present.

The invention additionally also encompasses the use of a plant for performing the process according to the invention. Such a use has the features of Claim 10.

In detail, such a plant for preparation of olefins from oxygenates comprises a reactor for heterogeneously catalysed conversion of the oxygenates to a product stream containing water, hydrocarbons and at least one oxygenate, at least one quench stage for quenching the product stream to obtain a gaseous stream G comprising hydrocarbons and olefins, a liquid aqueous stream W consisting predominantly of water and oxygenates, and a liquid stream O consisting predominantly of hydrocarbons and comprising olefins, further comprising a separation apparatus for separating stream O consisting predominantly of hydrocarbons into a C4- stream consisting predominantly of hydrocarbons having four or fewer carbon atoms and a C4+ stream consisting predominantly of hydrocarbons having four or more carbon atoms. The plant according to the invention is characterized by at least one recycle conduit with which at least a portion of the C4+ stream is returned to the reactor and/or a conduit by which at least a portion of the C4+ stream is guided into a gasoline fraction.

Such a plant has distinctly lower capital and operating costs since it is possible to dispense with at least one separation apparatus compared to corresponding plants according to the prior art.

Further, particular configurations can be inferred from the corresponding dependent claims. Their properties and advantages have already been mentioned in the description of corresponding process configurations.

Working examples

Further features, advantages and possible applications of the invention are apparent from the description of a working example which follows and the drawings.

The figures show:

Fig. 1 a schematic diagram of a process/plant according to prior art,
Fig. 2 a schematic diagram of a process/plant according to the invention.

Figure 1 shows, as a special case of an OTO plant, the construction of an MTP plant as known from the prior art. The OTO reactor 100 in which the formation of olefins from oxygenates, for example methanol and/or dimethyl ether (DME), proceeds is charged via a fresh feed conduit (not shown) with oxygenates and water vapour as diluent; in addition, recycle streams are also returned to the reactor via conduits 103 and 131. Via conduit 111, the product stream from the reactor 100 is introduced into the quench system 110. A phase contained essentially water is removed from the quench system 110 via conduit 114 and introduced into a methanol recovery unit 130. The gaseous phase removed in the quench system 110 enters a compressor 120 via conduit 112. Via conduit 113, a liquid phase consisting essentially of hydrocarbons is additionally fed from the quench system 110 into the compressor 120.

From the compressor 120, a liquid stream is conducted via a conduit 121 into a separation apparatus 140. In this separation apparatus 140, the C3- fraction is separated from the C4 fraction, which is why it is also referred to as depropanizer. The separation apparatus 140 is preferably configured as a separation column. The rectification in the separation apparatus 140 is preferably effected as an extractive distillation, and it is therefore possible to supply an extractant, for example methanol, via conduit 147 if desired.

The top product drawn off overhead, containing the C3- fraction, is fed via conduit 142 to a dryer 145, from which it goes on to enter a further separation apparatus 150 via conduit 146. A direct connection of separation apparatus 140 to separation apparatus 150 is also possible. In this separation apparatus 150, the C3 fraction is separated from the C2- fraction, which

is why the separation apparatus 150 is also referred to as deethanizer.

Via conduit 151, the top product from the separation apparatus 150 enters a separation apparatus 160, preferably in the form of a scrubber. When it is in the form of a scrubber, a scrubbing agent, for example scrubbing water, is introduced via conduit 161 and drawn off again via conduit 162. The C2- stream present is drawn off overhead by conduit 163 and can be sent via conduit 164 to a recycle stream in conduit 103 that leads back into the reactor 100 and/or discharged from the system via conduit 165 and sent, for example, to a fuel gas utilization or to a further separation apparatus for purification of the products present in order to obtain, for example, ethylene present as pure product.

The bottom product from the separation apparatus 150 is fed via conduit 152 to a separation apparatus 153 that separates propane from propylene. In this so-called C3 splitter, propane is drawn off from the system via conduit 154, and this can find use as fuel gas, for example. The propylene target product is drawn off via conduit 155, and this can optionally, depending on quality demands, be sent to a further purifying apparatus 156, from which it is then discharged via conduit 157. The purification apparatus 156 may be filled, for example, with a sorbent selected for oxygenates, such that oxygenates can be removed down to small traces from the propylene product stream according to the specification.

A liquid phase is drawn off from the compressor via conduit 122, and this is sent to a separation apparatus 170 in which the C4- fraction and the oxygenates are separated from the C4+ fraction. This separation apparatus 170 is also referred to as debutanizer. Via conduit 171, the C4- fraction and the oxygenate-containing top product from the separation apparatus 170 enter the separation apparatus 140.

Via conduit 172, the bottom product from the separation apparatus 170 is introduced into a further separation apparatus 173, from which the C7+ fraction is separated from the C6 fraction, which is why the separation apparatus 173 is also referred to as dehexanizer. The bottom product is drawn off via conduit 174, 175. Via conduit 176, 177 and 178, a recycle stream can be sent to a conduit 101, which leads via conduits 102 and 103 back to the reactor 100.

Moreover, a conduit 179 may be branched off from conduit 176, and this leads into a separation apparatus 180 (gasoline stabilizer column). The gasoline obtained here is discharged as product of value via conduit 181 and conduit 175. The C4 hydrocarbons removed overhead are fed via conduit 182 to conduits 177 and 178, such that they ultimately open into the recycle stream in conduits 102, 103.

The bottom product from the separation apparatus 140 is drawn off via conduit 148 and thus enters a mixer-settler combination 190. Hydrocarbons are drawn off therefrom via conduit 191 and can be returned wholly or partly via conduits 101, 102, 103 to the reactor 100. Alternatively or additionally, it is possible to send the hydrocarbons via conduit 192 to a separation apparatus 193 which is preferably configured as an extraction. The top product from the separation apparatus 193 is discharged as fuel gas via conduit 194.

From the methanol-dimethyl ether recovery 130, an oxygenate recycle stream is firstly returned via conduit 131 to the reactor 100. Via conduits 132 and 133, it is optionally possible to feed methanol- and/or dimethyl ether-laden water into the mixer-settler unit 190, from which it can then also be fed via conduit 195 back to conduits 197 and 196.

Via conduits 132, 134, the water can be conducted as extractant into the separation apparatus 193 if it is configured as an extraction, from which it can then also be fed via conduit 197

back to conduit 196. The water can ultimately be discharged from the system via conduit 135.

Fig. 2 shows a plant configured in accordance with the invention for performance of the process according to the invention. The complex of reactor 200 and quench system 210 here corresponds essentially to the description elucidated in connection with Fig. 1.

According to the invention, in Fig. 2, a liquid, hydrocarbon-containing second stream is fed directly to the gasoline stabilizer column 280 via conduits 300, 301 and 302. The gaseous quench stream 212 is additionally likewise fed to the compression 220, as is a first liquid stream 213, which corresponds to the procedure in the plant according to prior art, Fig. 1.

In a departure from the procedure shown in Fig. 1, it is optionally possible to branch off a further stream 303 from the compression 220, which is conducted here into the conduits 300, 301 and 302 and hence likewise enters the gasoline stabilizer column 280. It is equally possible also to conduct this stream into the gasoline stabilizer column 280 by means of a separate conduit (not shown).

In addition, the bottom product is drawn off from the separation apparatus 270 via conduit 304, and this is conducted either wholly or partly via conduit 305 into the gasoline stabilizer column 280 and/or at least partly enters an optional additional evaporation 310 via conduit 306. In this specific configuration with additional evaporation, vaporous or gaseous fractions are produced and combined with the recycling conduits 321, 322 via conduit 311. The liquid fraction from the evaporation 310 is introduced into the conduit 301, 302 via conduit 312 and thus likewise enters the gasoline stabilizer column 280. Separate mixing with other streams, for example with that guided into conduit 305, or separate introduction into the gasoline stabilizer column 280 is likewise possible.

By virtue of the process regime according to the invention, the separation apparatus 173 with the accompanying conduits 174 to 178 is dispensed with entirely. The recycle conduits 320, 321 and 322 thus conduct streams with a somewhat different composition.

List of reference numerals

100	OTO reactor
101-103	conduit
110	quench system
111-114	conduit
120	compressor
121-123	conduit
130	methanol-DME recovery
131-135	conduit
140	separation apparatus
142	conduit
150	separation apparatus
151, 152	conduit
153	separation apparatus
154, 155	conduit
156	purification stage
157	conduit
160	separation apparatus
161-165	conduit
170	separation apparatus
171, 172	conduit
173	separation apparatus
174-179	conduit
180	separation apparatus (gasoline stabilizer column)
181, 182	conduit
190	mixer-settler combination
191,192	conduit
193	separation apparatus
194-197	conduit
200	reactor
210	quench system
211-214	conduit
220	compressor
221-223	conduit
230	methanol-DME recovery
231-235	conduit

240	separation apparatus
242	conduit
250	separation apparatus
251, 252	conduit
253	separation apparatus
254, 255	conduit
256	purification stage
257	conduit
260	separation apparatus
261-265	conduit
270	separation apparatus
271	conduit
280	separation apparatus (gasoline stabilizer column)
281, 282	conduit
290	mixer-settler combination
291, 292	conduit
293	separation apparatus
294-297	conduit
300-306	conduit
310	evaporator
311, 312	conduit
320-323	conduit

Patentkrav

1. Fremgangsmåde til fremstilling af olefiner af methanol og/eller dimethylether (DME), der omfatter følgende trin:
(I) heterogent katalyseret omdannelse af methanol og/eller dimethylether som oxygenater i en oxygenat-til-olefin-reaktor under oxygenat-omdannelsesbetingelser til en produktstrøm, der indeholder vand, kulbrinter og mindst én oxygenat,
(ii) quenching af produktstrømmen i mindst ét quench-trin, hvorved der opnås en strøm G, der omfatter gasformige kulbrinter og olefiner, en flydende vandig strøm W, der overvejende består af vand og oxygenater, og en flydende strøm O, der overvejende består af kulbrinter og omfatter olefiner,
(iii) opdeling af strømmen G og/eller strømmen O i en strøm C4-, der overvejende består af kulbrinter med fire eller færre kulstofatomer og omfatter olefiner, og en strøm C4+, der overvejende består af kulbrinter med fire eller flere kulstofatomer og omfatter olefiner,
kendetegnet ved, at strømmen C4+, der opnås i trin (iii), direkte via en benzinstabiliseringskolonne føres tilbage til trin (i) og/eller ledes til en benzinfraktion.

2. Fremgangsmåde ifølge krav 1, kendetegnet ved, at der i trin (ii) opnås en yderligere flydende strøm S, der overvejende består af kulbrinter med fire eller flere kulstofatomer.

3. Fremgangsmåde ifølge krav 2, kendetegnet ved, at strømmen S føres sammen med strømmen C4+, og/eller at i det mindste en del af strømmen S ledes ind i benzinfraktionen.

4. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at strømmen G og/eller strømmen O tilføres et fortrinsvis flertrins kompressionstrin, og at der fra dette kompressionstrin, fortrinsvis efter det første trin, opnås en flydende strøm K, der overvejende består af kulbrinter med 4 eller flere kulstofatomer.

5. Fremgangsmåde ifølge krav 4, kendetegnet ved, at strømmen K iblandes strømmen S og/eller strømmen C4+, og/eller at i det mindste en del af strømmen K ledes direkte ind i benzinfraktionen.

6. Fremgangsmåde ifølge krav 4, kendetegnet ved, at der i kompressionstrinnet opnås en yderligere flydende fase L, der indføres i trin (iii).

7. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at strømmen C4+ i det mindste delvist fordamper, og den opståede dampformige strøm D føres tilbage i trin (i).

8. Fremgangsmåde ifølge krav 7, kendetegnet ved, at der ved den delvise fordampning også opnås en strøm F, som forbliver i den flydende tilstand, og som i det mindste delvist iblandes strømmen S og/eller strømmen K og/eller strømmen C4+, og/eller i det mindste en del ledes direkte ind i benzinfraktionen.

9. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at der efter trin (iii) følger mindst ét yderligere oprensningstrin, i hvilket strømmen C4- opdeles i en strøm C3, der overvejende består af kulbrinter med tre kulstofatomer og omfatter propylen, og i en strøm C2-, der overvejende består af kulbrinter med højst to kulstofatomer og omfatter ethylen.

10. Anvendelse af et anlæg, der omfatter:
- en reaktor til heterogent katalyseret omdannelse af methanol og/eller dimethylether (DME) som oxygenater til en produktstrøm, der indeholder vand, kulbrinter og mindst én oxygenat,
- mindst ét quench-trin til quenching af produktstrømmen, hvorved der opnås en strøm G, der omfatter gasformige kulbrinter og olefiner, en flydende vandig strøm W, der overvejende består af vand og oxygenater, og en flydende strøm O, der overvejende består af kulbrinter og omfatter olefiner,
- en adskillelsesanordning til opdeling af strømmen O, der overvejende består af kulbrinter, i en strøm C4-, der

overvejende består af kulbrinter med fire eller færre kulstofatomer, og en strøm C4+, der overvejende består af kulbrinter med fire eller flere kulstofatomer,

- kendetegnet ved en benzinstabiliseringskolonne og mindst én returledning, med hvilken i det mindste en del af strømmen C4+ føres tilbage fra benzinstabiliseringskolonnen til reaktoren, og/eller en ledning, gennem hvilken i det mindste en del af strømmen C4+ ledes fra benzinstabiliseringskolonnen til en benzinfraktion, i en fremgangsmåde til fremstilling af lavere olefiner ifølge krav 1.

11. Anvendelse af et anlæg ifølge krav 10 til fremstilling af lavere olefiner af oxygenater, hvor quench-trinnet omfatter en yderligere ledning, med hvilken en yderligere flydende strøm S, der overvejende består af kulbrinter med fire eller flere kulstofatomer, udledes fra quench-trinnet.

12. Anvendelse af et anlæg ifølge krav 11 til fremstilling af lavere olefiner af oxygenater, hvor den yderligere ledning er udformet på en sådan måde, at strømmen S føres sammen med strømmen C4+, og/eller i det mindste en del af strømmen S ledes ind benzinfraktionen.

13. Anvendelse af et anlæg ifølge krav 10 eller 11 til fremstilling af lavere olefiner af oxygenater, der omfatter midler, der gør det muligt, at strømmen G og/eller strømmen O tilføres et fortrinsvis flertrins kompressionsttrin, og at der fra dette kompressionstrin, fortrinsvis efter det første trin, opnås en strøm K, der overvejende består af kulbrinter med 4 eller flere kulstofatomer.

14. Anvendelse af et anlæg ifølge krav 13 til fremstilling af lavere olefiner af oxygenater, der omfatter midler, der gør det muligt, at strømmen K iblandes strømmen S og/eller strømmen C4+, og/eller i det mindste en del af strømmen K ledes direkte ind benzinfraktionen.

15. Anvendelse af et anlæg ifølge krav 13 til fremstilling af lavere olefiner af oxygenater, der omfatter midler, der gør det muligt, at der i kompressionstrinnet opnås en yderligere flydende fase L, der ledes ind i adskillelsesanordningen.

16. Anvendelse af et anlæg ifølge et af kravene 10 til 15 til fremstilling af lavere olefiner af oxygenater, der omfatter midler, der gør det muligt, at strømmen C4+ i det mindste delvist fordamper, og den opståede dampformige strøm D føres tilbage i trin (i).

17. Anvendelse af et anlæg ifølge krav 16 til fremstilling af lavere olefiner af oxygenater, der omfatter midler, der gør det muligt, at strømmen F, der ved den delvise fordampning forbliver i den flydende tilstand, i det mindste delvist iblandes strømmen S og/eller strømmen K og/eller strømmen C4+, og/eller i det mindste en del ledes direkte ind benzinfraktionen.

18. Anvendelse af et anlæg ifølge et af kravene 10 til 17 til fremstilling af lavere olefiner af oxygenater, hvor adskillelsesanordningen er i en fluidforbindelse med en yderligere oprensningsanordning, hvor denne omfatter midler, der gør det muligt, at strømmen C4- opdeles i en strøm C3, der overvejende består af kulbrinter med tre kulstofatomer og omfatter propylen, og i en strøm C2-, der overvejende består af kulbrinter med højst to kulstofatomer og omfatter ethylen.

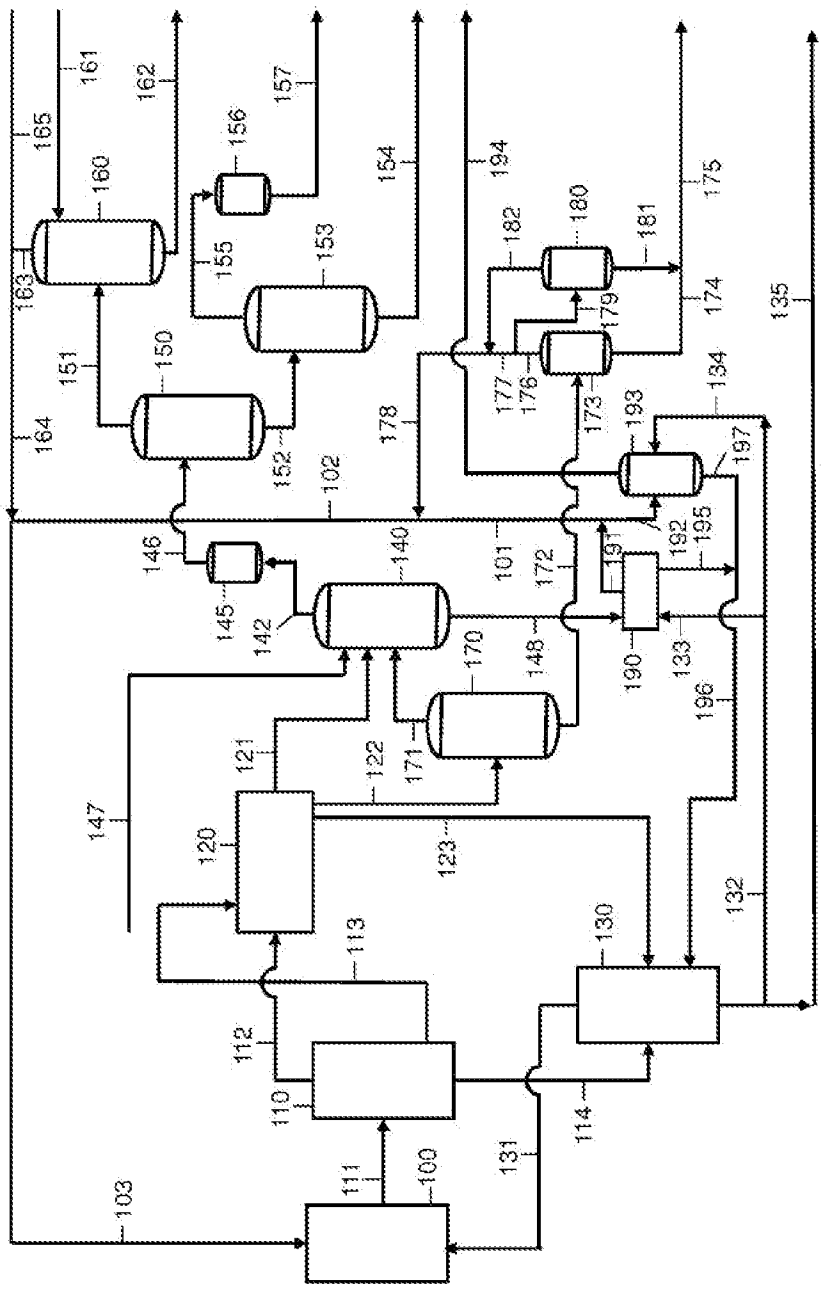
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Fig. 1

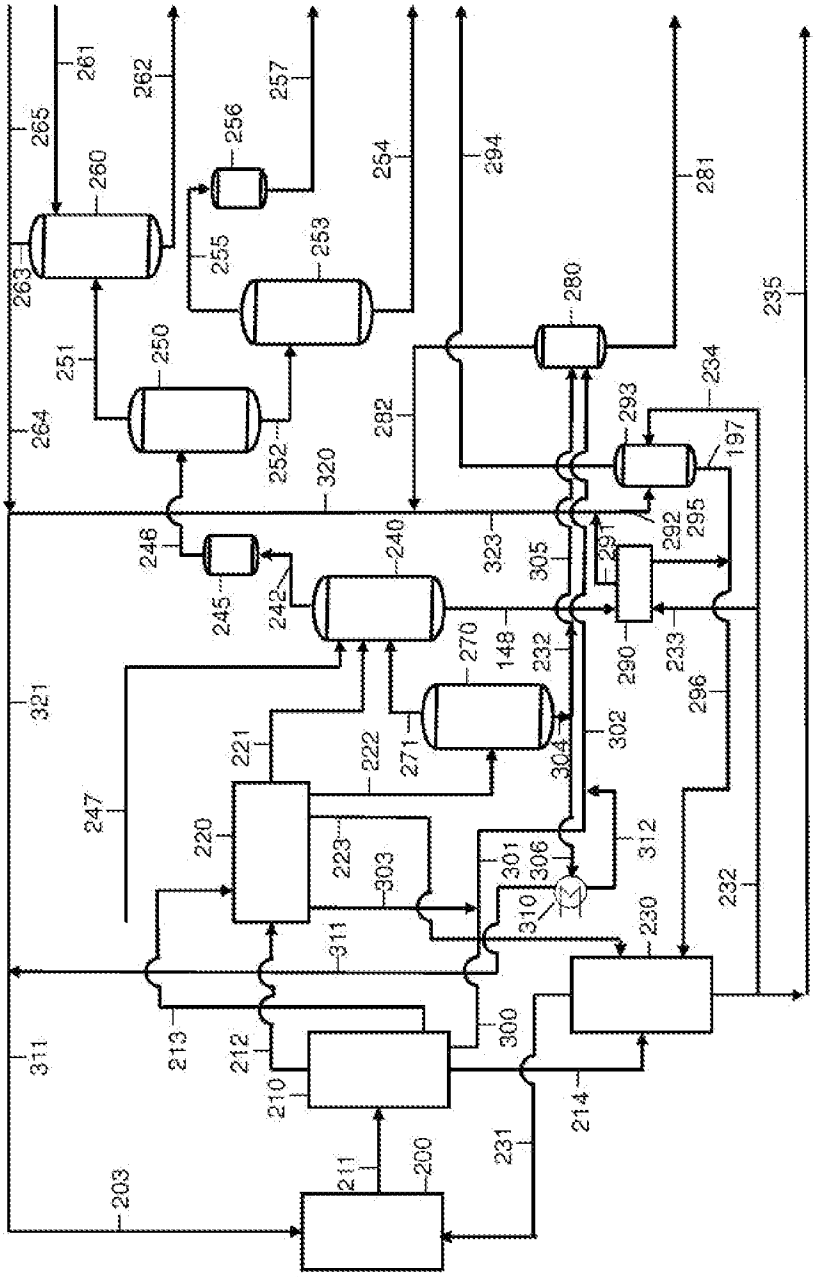
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Fig. 2