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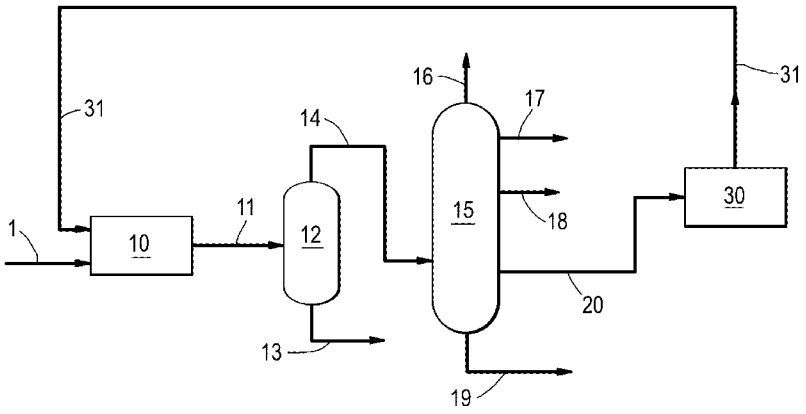
(54) **Title**: PROCESS FOR PREPARING ETHYLENE AND PROPYLENE FROM AN OXYGENATE

Fig.1



(57) **Abstract**: The invention relates to a process for preparing lower olefins from an oxygenate, the process comprising: a) contacting the oxygenate with a molecular sieve- comprising catalyst, at a temperature in the range of from 350 to 1000 °C to obtain an olefinic product stream comprising ethylene, propylene and C4 hydrocarbons; b) subjecting the olefinic product stream to one or more separation steps such that at least ethylene and/or propylene and a fraction comprising C4 hydrocarbons including saturated and mono-unsaturated C4 hydrocarbons, are obtained; c) subjecting the fraction comprising C4 hydrocarbons obtained in step b) to partial dehydrogenation by contacting the fraction with a dehydrogenation catalyst under partial dehydrogenation conditions to obtain a partially dehydrogenated C4 hydrocarbon stream; and d) recycling the partially dehydrogenated C4 hydrocarbon stream to step a).

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PROCESS FOR PREPARING ETHYLENE AND PROPYLENE FROM AN OXYGENATE

Field of the invention

The invention relates to a process for preparing ethylene and propylene from an oxygenate.

Background to the invention

Conventionally, lower olefins such as ethylene and propylene are produced via steam cracking of paraffinic hydrocarbon feedstocks including ethane, propane, naphtha, gasoil and hydrowax. An alternative route to lower olefins is the so-called oxygenate-to-olefin process. In such oxygenate-to-olefin process, an oxygenate such as methanol or dimethylether (DME) is provided to a reaction zone containing a suitable oxygenate conversion catalyst, typically a molecular sieve-comprising catalyst, and converted into ethylene and propylene. In addition to the desired lower olefins, a substantial part of the oxygenate is converted into $C4^+$ olefins and paraffins.

In WO2009/065848 an oxygenate-to-olefin process is disclosed wherein the yield of lower olefins is increased by recycling a fraction comprising $C4^+$ olefins to the reaction zone. At least part of the $C4^+$ olefins in the recycle are converted into the desired lower olefins. A disadvantage of the process of WO2009/065848 is, however, that at least part of the recycle stream needs to be purged in order to avoid undesired accumulation of paraffins in the recycle stream. With the purge, also valuable $C4^+$ olefins will be removed from the process without being

converted into lower olefins. The purged part of the recycle comprising $C4^+$ olefins can be reduced to achieve a higher yield of lower olefins, but then an increasing volume of recycle is needed, which is undesirable from an economic point of view.

In US 7,923,591 a process is disclosed for manufacturing lower olefins from an oxygenate-containing reaction mixture, wherein a product stream comprising C4 and C5 hydrocarbons from the oxygenate conversion step is subjected to extractive distillation to separate saturated butanes from it. The remaining butenes and C5 hydrocarbons are, after solvent stripping, recycled to the oxygenate conversion step to yield lower olefins.

Summary of the invention

It has now been found that by recycling to the oxygenate-to-olefins step a C4 hydrocarbon fraction from the oxygenate-to-olefin effluent after such fraction has been partially dehydrogenated, a comparable or even higher yield of lower olefins can be obtained at an equal volume of the recycle stream, compared to the situation wherein part of the recycle stream is purged.

Accordingly, the invention relates to a process for preparing ethylene and propylene from an oxygenate, the process comprising the following steps:

a) contacting the oxygenate with a molecular sieve-comprising catalyst, at a temperature in the range of from 350 to 1000 °C to obtain an olefinic product stream comprising ethylene, propylene and C4 hydrocarbons;

b) subjecting the olefinic product stream to one or more separation steps such that at least ethylene and/or propylene and a fraction comprising C4 hydrocarbons

including saturated and mono-unsaturated C4 hydrocarbons, are obtained;

c) subjecting the fraction comprising C4 hydrocarbons obtained in step b) to partial dehydrogenation by contacting the fraction with a dehydrogenation catalyst under partial dehydrogenation conditions to obtain a partially dehydrogenated C4 hydrocarbon stream; and

d) recycling the partially dehydrogenated C4 hydrocarbon stream to step a).

In the process according to the invention, the recycled C4 hydrocarbon fraction is partially dehydrogenated to avoid further build-up of saturated hydrocarbons in the recycle stream. Thus, there might be no need to purge part of the recycle stream and the loss of valuable mono-unsaturated C4 hydrocarbons with such purge can be avoided.

In order to favour the desired dehydrogenation of saturated hydrocarbons into mono-unsaturated C4 hydrocarbons over the undesired formation of di-olefins, it is preferred that the ratio of saturated C4 hydrocarbons to mono-unsaturated hydrocarbons in the recycled C4 hydrocarbon fraction has at least a certain value before it is subjected to partial dehydrogenation. This may for example be achieved by recycling the C4 hydrocarbon fraction in the start-up phase of the process directly to oxygenate conversion step a), i.e. without subjecting the fraction to partial dehydrogenation, until a certain value of the ratio of saturated C4 hydrocarbons to mono-unsaturated hydrocarbons in the recycled C4 hydrocarbon fraction is obtained. Once such ratio is obtained, the recycled fraction is subjected to partial dehydrogenation

step c). Alternatively, the C4 hydrocarbon fraction may be recycled after subjection to partial dehydrogenation already in the start-up phase, but under application of much milder dehydrogenation conditions. Alternatively or additionally, a high ratio of saturated to mono-unsaturated C4 hydrocarbons may be achieved in a start-up phase by combining an external stream comprising saturated and mono-unsaturated C4 hydrocarbons with a relatively high ratio of saturated to mono-unsaturated C4 hydrocarbons with the C4 hydrocarbon fraction to form a combined C4 hydrocarbon stream that is subjected to partial dehydrogenation.

A further advantage of the process according to the invention is that no dedicated separation step for separating by-products formed in the dehydrogenation step is needed. The partially dehydrogenated stream may be directly recycled to the oxygenate-to-olefin step. The most important by-product, hydrogen, may be separated from the olefin products in a separation section that is used for separating the desired olefin products from the effluent obtained in the oxygenate-to-olefin step. Other byproducts, such as for example butadiene, will be partly converted in the oxygenate-to-olefin step into conversion products such as cyclic and aromatic components that can be separated from the desired product in the separation section.

The process according to the invention may be advantageously combined with a process for steam cracking a paraffinic feedstock, such as for example naphtha. In steam cracking of such paraffinic feedstock, a product stream comprising ethylene, propylene and C4 hydrocarbons including saturated and unsaturated C4 hydrocarbons is obtained. By adding a fraction comprising C4 hydrocarbons that is separated from such steam cracker product stream to

the fraction comprising C4 hydrocarbons that is recycled to the oxygenate conversion step, the selectivity of the dehydrogenation step towards mono-olefins and the olefins yield of the process is advantageously increased. A further advantage of adding a C4 fraction of a steam cracker is that more hydrogen is produced in the partial dehydrogenation step. Such hydrogen may advantageously be used for hydrogenation of a stream obtained in the combined oxygenate conversion and steam cracking process according to the invention, for example for hydrotreatment of pyrolysis gas, hydrogenation of acetylene to ethylene, or hydrogenation of butadiene. Alternatively, the steam cracker step may be further integrated in the process according to the invention by using a combined separation section for the effluents of oxygenate-to-olefin step a) and the steam cracker step. Thus, a fraction comprising C4 hydrocarbons is obtained that comprises C4 hydrocarbons both from oxygenate conversion and from steam cracking of paraffins. This C4 hydrocarbon fraction is then partially dehydrogenated, preferably after removal of butadiene by means of partial hydrogenation, and recycled to oxygenate-to-olefin step a).

Brief description of the drawings

In Figure 1 is schematically shown a process according to the invention comprising an oxygenate conversion step.

In Figure 2 is schematically shown an embodiment of the invention wherein a steam cracking step is integrated in the process according to the invention.

Detailed description of the invention

In the process according to the invention, an oxygenate is first converted into lower olefins by contacting the oxygenate with a molecular sieve-comprising

catalyst at a temperature in the range of from 350 to 1000 °C (oxygenate conversion step a)). Besides lower olefins, i.e. ethylene and propylene, C4 olefinic and paraffinic hydrocarbons and, in a lesser amount $C5^+$ olefinic and paraffinic hydrocarbons are formed as by-product. Thus, an olefinic product stream comprising ethylene, propylene, C4 hydrocarbons and higher hydrocarbons is obtained in step a). Typically, $C4^+$ paraffins such as isobutane, n-butane, n-pentane, iso-pentane, and C4+ olefins such as isobutene, n-butenes, n-pentenes, iso-pentenes and C5+ naphtenes such as cyclopentane and cyclopentene will be present in the olefinic product stream. Small amounts of dienes like butadienes may be present in the olefinic product stream.

Reference herein to an oxygenate is to a compound comprising at least one alkyl group that is covalently linked to an oxygen atom. Preferably, at least one alkyl group has up to five carbon atoms, more preferably up to four, even more preferably one or two carbon atoms, most preferably at least one alkyl group is methyl. Mono-alcohols and dialkylethers are particularly suitable oxygenates. Methanol and dimethylether or mixtures thereof are examples of particularly preferred oxygenates.

The oxygenate conversion in step a) is carried out by contacting the oxygenate with a molecular sieve-comprising catalyst at a temperature in the range of from 350 to 1000 °C, preferably of from 350 to 750 °C, more preferably of from 450 to 700 °C, even more preferably of from 500 to 650 °C. The conversion may be carried out at any suitable pressure, preferably at a pressure in the range of from 1 bar to 50 bar (absolute), more preferably of from 1 bar to 15 bar (absolute). A pressure in the range of from 1.5 to 4.0 bar (absolute) is particularly preferred.

Any molecular sieve comprising catalyst known to be suitable for the conversion of oxygenates, in particular alkanols and dialkylethers, into lower olefins may be used. Preferably the catalyst comprises a molecular sieve having a 8-, 10- or 12-ring structure and an average pore size in the range of from 3 Å to 15 Å. Examples of suitable molecular sieves are silicoaluminophosphates (SAPOs), aluminophosphates (AlPO), metal-substituted aluminophosphates or metal-substituted silicoaluminophosphates. Preferred SAPOs include SAPO-5, -8, -11, -17, -18, -20, -31, -34, -35, -36, -37, -40, -41, -42, -44, -47 and -56. SAPO-17, -18, -34, -35, and -44 are particularly preferred.

A particular suitable class of molecular sieves are zeolites. In particular in case not only oxygenates but also C4+ olefins or compounds that form C4+ olefins under the reaction conditions prevailing in oxygenate conversion step a) are supplied to step a), e.g. a tertiary alcohol such as tertiary butanol or a tertiary alkylether such as methyl tertiary butylether, a zeolite-comprising catalyst is preferred as molecular-sieve comprising catalyst, more preferably a catalyst comprising a zeolite with a 10-membered ring structure. Zeolite-comprising catalysts are known for their ability to convert higher olefins to lower olefins, in particular C4+ olefins to ethylene and/or propylene. Suitable zeolite-comprising catalysts include those containing a zeolite of the ZSM group, in particular of the MFI type, such as ZSM-5, the MTT type, such as ZSM-23, the TON type, such as ZSM-22, the MEL type, such as ZSM-11, the FER type. Other suitable zeolites are for example zeolites of the STF-type, such as SSZ-35, the SFF type, such as SSZ-44 and the EU-2 type, such as ZSM-48. Preferably, the

catalyst comprises at least one zeolite selected from MFI, MEL, TON and MTT type zeolites, more preferably at least one of ZSM-5, ZSM-11, ZSM-22 and ZSM-23 zeolites.

The zeolite in the oxygenate conversion catalyst is preferably predominantly in the hydrogen form. Preferably at least 50 wt%, more preferably at least 90 wt%, even more preferably at least 95 wt%, still more preferably at least 100 wt% of the zeolite is in the hydrogen form.

The molecular sieve-comprising catalyst may further comprise a binder material such as for example silica, alumina, silica-alumina, titania, or zirconia, a matrix material such as for example a clay, and/or a filler.

In step a), not only lower olefins and $C4^+$ hydrocarbons, but also water is formed. Water is typically separated from the olefinic product stream by means known in the art, for example by cooling the effluent of step a) in a quench water tower.

In step b) of the process according to the invention, the olefinic product stream is subjected to one or more separation steps such that at least ethylene and/or propylene and a fraction comprising C4 hydrocarbons including saturated and unsaturated C4 hydrocarbons, are obtained. Such separation in different fractions is done by means known in the art. Typically, the stream is fractionated in at least a fraction mainly comprising propylene and a fraction comprising C4 hydrocarbons. Usually, a fraction comprising mainly ethylene is first separated from the olefinic product stream in a de-ethaniser and a fraction mainly comprising propylene is then separated from the bottoms of the de-ethaniser in a de-propaniser. Instead of fractionating the olefinic product stream into separate ethylene and propylene

fractions, a fraction comprising both ethylene and propylene may be obtained by directly supplying the olefinic product stream to a de-propaniser. The bottoms of the de-propaniser contain $C4^+$ hydrocarbons. Preferably, the bottoms of the de-propaniser is further separated into a fraction mainly comprising C4 hydrocarbons and a fraction comprising $C5^+$ hydrocarbons. The fraction comprising C4 hydrocarbons comprises saturated and unsaturated C4 hydrocarbons.

The fraction comprising C4 hydrocarbons, preferably the entire fraction comprising C4 hydrocarbons, is in step c) subjected to partial dehydrogenation by contacting the fraction with a dehydrogenation catalyst under partial dehydrogenation conditions to obtain a partially dehydrogenated C4 hydrocarbon stream. The partially dehydrogenated C4 hydrocarbon stream is, in step d), recycled to oxygenate conversion step a). The partially dehydrogenated C4 hydrocarbon stream is preferably heated prior to being recycled in order to bring it to the temperature at which oxygenate conversion in step a) is carried out.

It is an advantage of the process according to the invention that the partially dehydrogenated C4 hydrocarbon stream may be directly recycled to step a), i.e. without any further separation or conversion steps, since the most important byproduct formed in the dehydrogenation step, i.e. hydrogen, will act as an inert in oxygenate conversion step a). Hydrogen may be separated from the olefinic product stream obtained in the one or more separation steps of step b). Alternatively, a light fraction obtained in one of the separation steps of step b), e.g. a fraction comprising $C2^-$ hydrocarbons and hydrogen, may be used to

hydrogenate, in a so-called front-end hydrogenation unit, unsaturated compounds, such as acetylene, methylacetylene, or propadiene, produced in the process. Preferably, the entire partially dehydrogenated C4 hydrocarbon stream is recycled to step a), i.e. without separating a purge stream from the partially dehydrogenated C4 hydrocarbon stream.

In dehydrogenation step c), not only saturated C4 hydrocarbons will be dehydrogenated to C4 mono-olefins, i.e. butenes, but also C4 mono-olefins will be dehydrogenated to C4 di-olefins, i.e. butadiene. The presence of butadiene in oxygenate conversion step a) will, however, result in coke formation and is thus not desired. Since alkane dehydrogenation is favoured at a lower olefin partial pressure, the weight ratio of saturated to mono-unsaturated C4 hydrocarbons in the stream that is contacted with the dehydrogenation catalyst, is preferably at least 0.1, more preferably at least 0.25, in order to increase the selectivity of dehydrogenation of alkanes compared to the selectivity of dehydrogenation of mono-olefins into di-olefins. A very high concentration of saturated C4 hydrocarbons in the stream contacted with the dehydrogenation catalyst will, however, also result in a relatively high concentration of saturated C4 hydrocarbons in the partially dehydrogenated C4 hydrocarbon stream that is recycled to step a). In step a) such butanes act as inerts and therefore decrease the costs efficiency of this step. Therefore, the weight ratio of saturated to mono-unsaturated C4 hydrocarbons in the stream that is contacted with the dehydrogenation catalyst is preferably at most 4, more preferably at most 3. A weight ratio of saturated to mono-unsaturated C4 hydrocarbons in the stream that is

contacted with the dehydrogenation catalyst in the range of from 0.4 to 2.5 is particularly preferred.

In order to achieve that the weight ratio of saturated to mono-unsaturated C4 hydrocarbons in the stream that is subjected to partial dehydrogenation catalyst in step c) is at least 0.1 or even higher, it is preferred that during start-up of the process of the invention, the C4 hydrocarbon fraction obtained in step b) is directly recycled to oxygenate conversion step a), i.e. without subjecting the fraction to partial dehydrogenation, until sufficient saturated C4 hydrocarbons have built-up in the C4 hydrocarbon fraction. Once the desired ratio of saturated to mono-unsaturated C4 hydrocarbons in the fraction comprising C4 hydrocarbons is achieved, the fraction is subjected to partial dehydrogenation step c). Alternatively or additionally, an external stream comprising saturated and mono-unsaturated C4 hydrocarbons, preferably in a weight ratio of at least 0.1, more preferably at least 0.25, may be combined during the start-up of the process with the C4 hydrocarbon fraction to form a combined C4 hydrocarbon stream that is subjected to partial dehydrogenation.

The dehydrogenation catalyst may be any suitable dehydrogenation catalyst known in the art. Such catalysts are for example known from C.H. Bartholomew and R.J. Farrauto, *Fundamentals of Industrial Catalytic Processes*, 2nd ed., John Wiley & Sons, Inc., 2006, p. 533-542. Dehydrogenation catalysts are known to be able both to dehydrogenate alkanes into olefins and to convert saturated hydrocarbons into aromatic compounds, also referred to as catalytic reforming. In the process according to the invention, catalytic reforming in step c) is undesired.

Therefore, the dehydrogenation catalyst preferably has a relatively low reforming activity.

The dehydrogenation catalyst preferably comprises a Group VIII metal, more preferably Pt, Pd, Ni or Cu or is a chromia-based catalyst.

The partial dehydrogenation conditions may be any suitable partial dehydrogenation conditions known in the art. Suitable dehydrogenation conditions are for example disclosed in C.H. Bartholomew and R.J. Farrauto, *Fundamentals of Industrial Catalytic Processes*, 2nd ed., John Wiley & Sons, Inc., 2006, p. 533-542. Preferably, the dehydrogenation conditions comprise a temperature in the range of from 350 to 750 °C, more preferably in the range of from 450 to 700 °C, even more preferably in the range of from 500 to 650 °C. The partial dehydrogenation is preferably conducted at low pressures, more preferably at a total reaction pressure in the range of from 0.01 to 10 bar (absolute), more preferably of from 0.1 to 5 bar (absolute). Steam or other inert diluent gases such as nitrogen, helium, carbon dioxide, or argon may be used to reduce the partial pressure of the hydrocarbons present and of the hydrogen formed during partial dehydrogenation.

Preferably, the stream subjected to partial dehydrogenation in step c) comprises less than 5 wt% hydrocarbons with more than 4 carbon atoms, more preferably less than 1 wt%. $C5^+$ hydrocarbons typically comprise cyclic hydrocarbons that easily dehydrogenate to form for example cyclopentadiene, a compound that will contribute to undesired coke formation in oxygenate conversion step a).

Preferably, the hydrogenation conditions are such that in the range of from 1 to 20 wt% of the saturated hydrocarbons in the stream subjected to partial

dehydrogenation in step c) is dehydrogenated into mono-unsaturated C4 hydrocarbons.

The dehydrogenation conditions may comprises any suitable weight hourly space velocity (WHSV), preferably a WHSV in the range of from 0.01 to 20 h^{-1}, more preferably of from 0.1 to 15 h^{-1}, even more preferably of from 0.2 to 10 h^{-1}.

The partial dehydrogenation step may be carried out in any suitable reactor configuration known in the art, for example an adiabatic fixed bed, an isothermal fixed bed, a moving bed or a fluidised bed configuration, preferably an adiabatic or isothermal fixed bed configuration.

In the process according to the invention, an external stream comprising saturated and unsaturated C4 hydrocarbons may be added to the hydrocarbons that are recycled to step a). Such external stream may be added prior to or after such recycled hydrocarbons are subjected to partial dehydrogenation, i.e. to the fraction comprising C4 hydrocarbons obtained in step b) or to the partially dehydrogenated C4 hydrocarbon stream that is recycled to step a). In case the external stream is combined with the fraction comprising C4 hydrocarbons to form a combined C4 hydrocarbon stream and the combined C4 hydrocarbon stream is subjected to partial dehydrogenation in step c), such combined stream preferably has a weight ratio of saturated to mono-unsaturated C4 hydrocarbons of at least 0.1, more preferably at least 0.1, even more preferably in the range of from 0.4 to 2.5.

Preferably, the external stream is a C4 hydrocarbon fraction obtained from a process for cracking a paraffinic feedstock such as for example butane, naphtha or gasoil into ethylene and propylene or a C4 hydrocarbon fraction

from an effluent of a fluid catalytic cracking unit. Optionally, the external stream is subjected to partial hydrogenation or other butadiene removal step in order to remove at least part of any butadiene or other di-olefins present before being combined with the fraction comprising C4 hydrocarbons or with the partially dehydrogenated C4 hydrocarbon stream.

An advantage of adding such external stream to the recycle is that additional olefins may be produced from the C4 hydrocarbons present in the external stream. Moreover, additional hydrogen is produced in the partial dehydrogenation step from the saturated C4 hydrocarbons present in the external stream.

In case the external stream comprises a weight ratio of saturated to mono-unsaturated C4 hydrocarbons that is higher than such ratio in the fraction comprising C4 hydrocarbons, the external stream is preferably added to the fraction comprising C4 hydrocarbons obtained in step b) to form a combined stream C4 hydrocarbon stream that is subjected to partial dehydrogenation in step c). Such combined stream then has a relatively high butane concentration, which advantageously improves the selectivity of the dehydrogenation reaction towards mono-olefins.

In case the external stream has a ratio of saturated to mono-unsaturated C4 hydrocarbons that is lower than such ratio in the fraction comprising C4 hydrocarbons that is subjected to partial dehydrogenation in step c), it is preferred to add such external stream to the partially dehydrogenated stream that is recycled to step a) or to supply such external stream directly to oxygenate conversion step a).

In order to avoid undesired build-up of saturated C4 hydrocarbons in the recycle, it is preferred that the amount of saturated C4 hydrocarbons in the external stream does not exceed the amount of C4 saturated hydrocarbons that is dehydrogenated in step c). Therefore, the weight ratio of saturated to mono-unsaturated C4 hydrocarbons in the external stream is preferably at most 0.4, more preferably at most 0.25.

In case the external stream has an amount of saturated C4 hydrocarbons that exceeds the amount of C4 saturated hydrocarbons that is dehydrogenated in step c), it is preferred to purge part of the recycle stream, preferably to purge part of the recycle stream before such stream is subjected to partial dehydrogenation in step c).

In another embodiment of the process according to the invention, steam cracking of a paraffinic feedstock to produce ethylene and propylene is integrated in the process. The process then comprises an oxygenate conversion step (step a)) to produce ethylene and propylene from an oxygenate and a steam cracking step (step e)) to produce ethylene and propylene from a paraffinic feedstock. In a combined separation section comprising one or more combined separation steps, combined effluent from oxygenate conversion step a) and from steam cracking step e) is separated into ethylene and/or propylene and a fraction comprising C4 hydrocarbons including saturated and unsaturated C4 hydrocarbons as described hereinabove for step b). In steps c) and d) of the process according to the invention, the C4 fraction thus obtained is partially dehydrogenated and recycled to oxygenate conversion step a) as described hereinabove. Preferably, the C4 fraction thus obtained is, prior to partial dehydrogenation in step c),

subjected to partial hydrogenation or extractive distillation in order to remove at least part of any butadiene present. Butadiene is typically formed in steam cracking step e) and, to a lesser extent, in oxygenate conversion step a).

Conditions in partial dehydrogenation step c) are preferably chosen such that the amount of saturated C4 hydrocarbons formed in oxygenate conversion step a) and, if applicable, formed in steam cracking step e) and/or added with the external stream, is balanced by the partial dehydrogenation of saturated C4 hydrocarbons in dehydrogenation step c). Thus, there is no further build-up of saturated C4 hydrocarbons in the recycle stream, even not in the preferred situation that no purge of recycled hydrocarbons is applied. In case the amount of saturated C4 hydrocarbons formed in oxygenate conversion step a) and, if applicable, formed in steam cracking step e) and/or added with the external stream, exceeds the amount of C4 saturated hydrocarbons that is dehydrogenated in step c), it is preferred to purge part of the recycle stream, preferably to purge part of the recycle stream before such stream is subjected to partial dehydrogenation in step c).

Detailed description of the drawings

In Figure 1 is shown an embodiment of the invention wherein the C4 hydrocarbon fraction of an oxygenate conversion process is partially dehydrogenated and then recycled to the oxygenate conversion process.

In the process as shown in Figure 1, methanol is fed via line 1 to oxygenate conversion reaction zone 10 comprising an oxygenate conversion catalyst. In reaction zone 10, methanol is converted into olefins and water. Effluent from reaction zone 10 is supplied via line 11 to

water quench tower 12 to be separated into water and an olefinic product stream. Water is withdrawn from tower 12 via line 13 and the olefinic product stream is supplied via line 14 to a compression section (not shown), a caustic treatment (not shown) and then to fractionation section 15. Fractionation section 15 comprises a de-ethaniser, a de-propaniser and a de-butaniser (not shown). The olefinic product stream is first fractionated by means of the de-ethaniser and de-propaniser into an ethylene-rich stream, a propylene-rich stream, a $C4^+$ hydrocarbon fraction and a lighter stream comprising light by-products such as methane and carbon oxides. The $C4^+$ hydrocarbon fraction is further fractionated in the de-butaniser into a C4 hydrocarbon fraction comprising isobutene and a fraction rich in $C5^+$ hydrocarbons. The lighter stream, the ethylene-rich stream, the propylene-rich stream and the fraction rich in $C5^+$ hydrocarbons are withdrawn from fractionation section 15 via lines 16, 17, 18 and 19, respectively. The fraction comprising C4 hydrocarbons is fed via line 20 to partial dehydrogenation unit 30 comprising a dehydrogenation catalyst. A partially dehydrogenated C4 hydrocarbon stream is obtained in unit 30 and recycled via line 31 to oxygenate conversion reaction zone 10.

In Figure 2 is shown an embodiment of the invention wherein the effluents of a steam cracking process and of an oxygenate conversion process are combined to be separated in a combined separation section and wherein the C4 hydrocarbon fraction obtained in the combined separation section is partially dehydrogenated and then recycled to the oxygenate conversion process. Corresponding reference numbers have the same meaning as in Figure 1.

In the process as shown in Figure 2, naphtha and steam are fed via lines 41 and 42, respectively, to steam cracking zone 40. Cracker effluent is withdrawn from cracking zone 40 and supplied via line 43 to quench tower 12 wherein both the combined effluents from zones 40 and 10 are quenched to separate water from an olefinic product stream. The combined olefinic product stream is supplied via line 14 and via a compression section and a caustic treatment (both not shown) to fractionation section 15. The fraction comprising C4 hydrocarbons thus obtained is first hydrotreated to remove butadiene (not shown) and then fed via line 20 to partial dehydrogenation unit 30 comprising a dehydrogenation catalyst. A partially dehydrogenated C4 hydrocarbon stream is obtained in unit 30 and recycled via line 31 to oxygenate conversion reaction zone 10.

In case the amount of saturated C4 hydrocarbons formed in oxygenate conversion zone 10 and cracking zone 40 exceeds the amount of saturated C4 hydrocarbons that is dehydrogenated in zone 30 at a dehydrogenation percentage of at most 20%, part of the fraction comprising C4 hydrocarbons in line 20 is preferably purged (purge not shown).

C L A I M S

1. A process for preparing ethylene and propylene from an oxygenate, the process comprising the following steps:
   a) contacting the oxygenate with a molecular sieve-comprising catalyst, at a temperature in the range of from 350 to 1000 °C to obtain an olefinic product stream comprising ethylene, propylene and C4 hydrocarbons;
   b) subjecting the olefinic product stream to one or more separation steps such that at least ethylene and/or propylene and a fraction comprising C4 hydrocarbons including saturated and mono-unsaturated C4 hydrocarbons, are obtained;
   c) subjecting the fraction comprising C4 hydrocarbons obtained in step b) to partial dehydrogenation by contacting the fraction with a dehydrogenation catalyst under partial dehydrogenation conditions to obtain a partially dehydrogenated C4 hydrocarbon stream; and
   d) recycling the partially dehydrogenated C4 hydrocarbon stream to step a).

2. A process according to claim 1, the process further comprising:
   e) steam cracking a paraffinic feedstock under cracking conditions in a cracking zone to obtain a cracker effluent comprising ethylene, propylene and C4 hydrocarbons including saturated and unsaturated C4 hydrocarbons,

wherein step b) comprises subjecting the cracker effluent and the olefinic product stream obtained in step a) to one or more combined separation steps to obtain at least ethylene and/or propylene and the fraction comprising C4 hydrocarbons including saturated and unsaturated C4 hydrocarbons.

3. A process according to claim 1 or 2, wherein an external stream comprising saturated and unsaturated C4 hydrocarbons is combined with the fraction comprising C4 hydrocarbons to form a combined C4 hydrocarbon stream that is subjected to partial dehydrogenation in step c).

4. A process according to claim 1 or 2, wherein an external stream comprising saturated and unsaturated C4 hydrocarbons is combined with the partially dehydrogenated C4 hydrocarbon stream that is recycled to step a).

5. A process according to claim 3 or 4, wherein the external stream is a fraction comprising C4 hydrocarbons including saturated and unsaturated C4 hydrocarbons obtained from an effluent of a steam cracker unit.

6. A process according to any one of the preceding claims, wherein the fraction comprising C4 hydrocarbons or the combined C4 hydrocarbon stream that is subjected to partial dehydrogenation has a weight ratio of saturated C4 hydrocarbons to mono-unsaturated C4 hydrocarbons in the range of from 0.4 to 2.5.

7. A process according to any one of the preceding claims, wherein in step c) in the range of from 1 to 20 wt% of the

saturated C4 hydrocarbons in the fraction comprising C4 hydrocarbons or in the combined C4 hydrocarbon stream is dehydrogenated into mono-unsaturated C4 hydrocarbons.

8. A process according to any one of the preceding claims, wherein the partially dehydrogenated C4 hydrocarbon stream is directly recycled to step a).

9. A process according to any one of the preceding claims, wherein in step d) the entire partially dehydrogenated C4 hydrocarbon stream is recycled to step a).

10. A process according to any one of the preceding claims, wherein the fraction comprising C4 hydrocarbons and/or the combined C4 hydrocarbon stream comprises less than 5 wt% hydrocarbons with more than 4 carbon atoms.

11. A process according to any one of the preceding claims, wherein the dehydrogenation catalyst comprises a Group VIII metal, preferably Pt, Pd, Ni or Cu or is a chromia-based catalyst.

12. A process according to any one of the preceding claims, wherein the dehydrogenating conditions comprise a temperature in the range of from 350 to 750 °C.

13. A process according to any one of the preceding claims, wherein the molecular sieve-containing catalyst is a zeolite-comprising catalyst.

14. A process according to claim 13, wherein the zeolite-comprising catalyst comprises at least one of ZSM-5, ZSM-11, ZSM-22 and ZSM-23 zeolites.

15. A process according to any one of the preceding claims, where the oxygenate is methanol, dimethylether, or a mixture thereof.

Fig.1

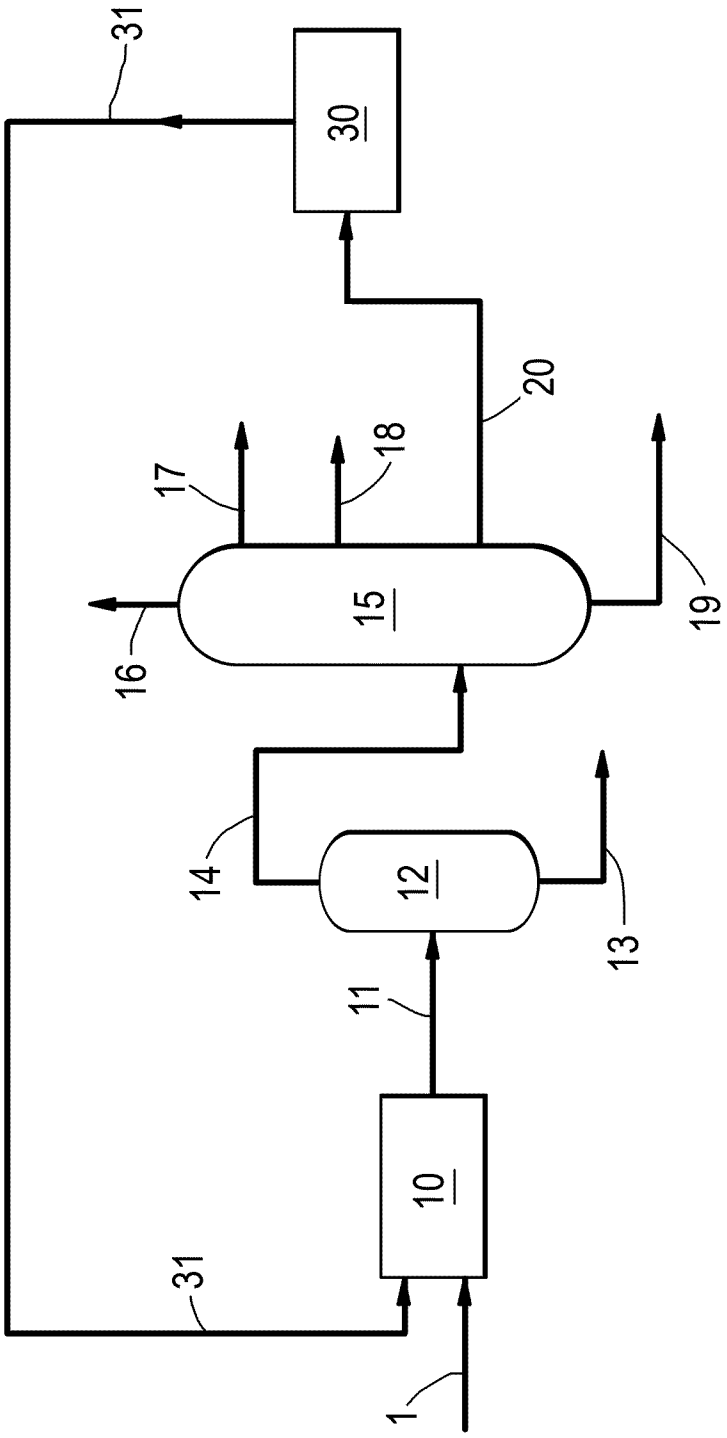
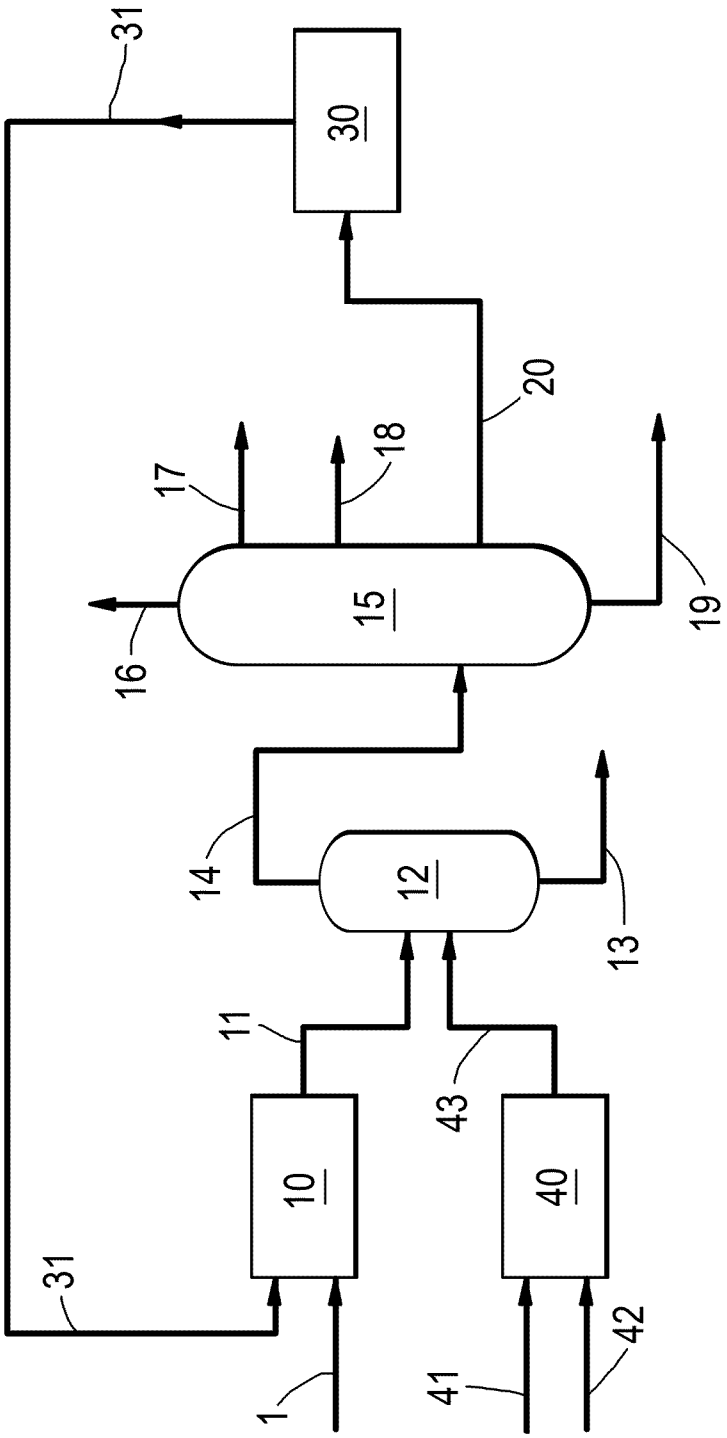


Fig.2



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/078006

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C1/20 C07C11/04 C07C11/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2010/298619 A1 (CHEWTER LESLIE ANDREW [NL] ET AL) 25 November 2010 (2010-11-25) claims 1-15; figures 1-3; examples 1-6	1-15
A	WO 03/020667 A1 (EXXONMOBIL CHEM PATENTS INC [US]) 13 March 2003 (2003-03-13) claims 1-19; figures 1-5; examples 1,2	1-15

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents :

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
17 January 2014	04/02/2014

Name and mailing address of the ISA/	Authorized officer
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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/078006

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